SYNTHESIS AND CHARACTERISATION OF METAL-ORGANIC FRAMEWORKS BASED HYDROGEN STORAGE MATERIALS

Ph.D. Thesis

By DHARMENDRA KUMAR PANCHARIYA



DISCIPLINE OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE DECEMBER 2019

SYNTHESIS AND CHARACTERISATION OF METAL-ORGANIC FRAMEWORKS BASED HYDROGEN STORAGE MATERIALS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

by **DHARMENDRA KUMAR PANCHARIYA**



DISCIPLINE OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE DECEMBER 2019



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled SYNTHESIS AND CHARACTERISATION OF METAL-ORGANIC FRAMEWORKS BASED HYDROGEN STORAGE MATERIALS in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF MECHANICAL ENGINEERING, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from December 2014 to December 2019 under the supervision of Dr. Sanjay Kumar Singh, Associate Professor,Indian Institute of Technology Indore and Dr. E. Anil Kumar, Associate Professor,Indian Institute of Technology Tirupati.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

> Signature of the student with date (Dharmendra Kumar Panchariya)

This is to certify that the above statement made by the candidate is correct to the best of my/our

knowledge. May 28, 2020 Signature of Thesis Supervisor #1 (Dr. SANJAY KUMAR SINGH)

Quan (br. C. And (Paper)

Signature of Thesis Supervisor #2 (Dr. E. ANIL KUMAR)

Dharmendra Kumar Panchariya has successfully given his/her Ph.D. Oral Examination held on May 28, 2020.

2122 - Sale 10

Signature of Chairperson (OEB) Date:May 28, 2020

Signature of PSPC Member #1 Date:May 28, 2020

SSL

Signature of Head of Discipline Date: May 28, 2020

Signature of External Examiner Date: May 28, 2020

Signature of PSPC Member #2 Date: May 28, 2020 Signature(s) of Thesis Supervisor(s) Date:May 28, 2020

Signature of Convener, DPGC Date:May 28, 2020

Date:May 28,

ACKNOWLEDGEMENTS

First and foremost, I am grateful to my thesis supervisors *Dr. E. Anil Kumar* and *Dr. Sanjay Kumar Singh*, for their unfailing support and guidance throughout this journey. This thesis would not have been possible without their invaluable advice, suggestion, motivation, and encouragement.

I am also deeply indebted to my PSPC committee members, *Dr. I. A. Palani* and *Dr. Biswarup Pathak*, for providing me their valuable comments and innovative suggestions from time to time during the course of my work.

I owe my gratitude to *The Director, Indian Institute of Technology Indore,* for establishing state-of-the-art facilities at the institute and enabling a very friendly environment for research scholars like me.

I am also very grateful to *The Dean of Academic Affairs, The Dean of Research and Development,* and *The Dean of Student Affairs, IIT Indore,* to furnish the best academic program, research center and student life, which no doubt will have positive effect on our future.

My sincere thanks are due to *Head and DPGC Convener of Discipline of Mechanical Engineering*, for providing a good infrastructure with a wellequipped research lab in the institute.

I am grateful to *Dr. Abhishek Srivastava*, *Dr. Santosh Kumar Vishvakarma*, *Dr. Yuvraj Kumar Madhukar*, *Dr. Subbareddy Daggumati*, *Dr. Vinod Kumar* and *Dr. Ajay Kumar Kushwaha* for their motivation, invaluable suggestions and sharing their scholarly learning and rich experience with me.

I express a very special thanks to the *Sophisticated Instrumentation Center (SIC), IIT Indore* for providing me with the required. I acknowledge services providing by the *Sophisticated Instruments Facility (SIF), IISc Bangalore, Sophisticated Analytical Instrument Facility (SAIF), IIT Bombay, Materials Research Centre (MRC), MNIT Jaipur* and *Department of Mechanical Engineering, IIT Tirupati,* which helped me greatly in my work.

I am also very thankful for the help I required from the various technical staff members of the SIC, IIT Indore; Mr. Kinny Pandey, Mr. Nitin Upadhyay,

Mr. Ghanshyam A. Bhavsar, Dr. Ravinder and *Ms. Sarita Batra*. Without their timely helped and cooperation I could not have completed my work.

I also wish to thank all the staff members of the *Discipline of Mechanical Engineering and Chemistry* for their excellent service and, my special thanks to *Mr. Arun Kumar Bhagwaniya* and *Mr. Ashwin Wagh*, a member of Heat Transfer Laboratory for their generous help during my research work.

Besides, I would like to thank *Mr. Anand Petare* DGM (Workshop) and all the staff members at the Workshop, IIT Indore especially to *Mr. Rishiraj Chauhan, Mr. Satish Kaushal, Mr. Pawan Chauhan, Mr. Deepak Dhepte, Mr. Umakant Sharma* and *Mr. B. Vishwakarma* for their help in various aspects of experimentation.

Also, I would like to thank *Dr. Anjali Bandiwadekar* Deputy Librarian, the Center Library, IIT Indore and the following library team; *Mr. Rajesh Kumar*, *Mr. Lala Ram Ahirwar*, *Mr. Satish Bisen*, *Mr. Kapil Gupta*, *Mr. Sunil Kapoor*, *Mr. Ranjeet*, *Mrs. Kriti Jain*, *Ms. Kajal*, *Mr. Manglesh* and *Mr. Mohanlal* for their unstinting support and helping me using the library facilities.

I owe my special thanks to *Dr. Lakshmi Iyengar*, visiting faculty, School of Humanities and Social Science, IIT Indore, for fine tuning the language of my work.

My special thanks to *Prof. Pratibha Sharma*, IIT Bombay, *Dr. Pratibha Sharma*, DAVV Indore, and *Dr. Mrigendra Dubey*, IIT Indore, for providing the extended research facilities.

I am also thankful to *Nishant Enterprises*, *Katni, India*, for providing me required material-rice husk ash (RHA).

I greatly acknowledge the financial support provided by the *Ministry of Human Resource Development, India,* and *IIT Indore,* during my research journey.

I wish to express my gratitude to the group member of Heat Transfer and Organometallics and Nanotech Catalysis; *Dr. Vinod Kumar Sharma, Dr. Yogesh Madaria, Dr. Vinod Kumar Singh, Dr. Rakesh Sharma, Dr. Rohit Kumar Rai, Dr. Deepika Tyagi, Dr. Kavita Gupta, Dr. Ambikesh Dhar Dwivedi, Ms. Chinky* Binnani, Mr. Debasish Panda, Mr. Dhanajay Mishra, Mr. Soumyadip Patra, Mr. Mahendra Awasthi, Mr. Vinod Sahu, Mr. Ankit Kumar, Ms. Bhanu Priya, Ms. Vaishnavi and Mr. Sanjeev for their invaluable advice, helpful suggestions and discussions. My special thanks to Dr. Rohit Kumar Rai for giving me his precious time and valuable advice on the objective of my research work. I also express my thanks to M.Sc. and B. Tech. students of the lab for helping me with my lab work.

I am especially grateful to Dr. Harimohan Kushwaha, Dr. Sambhaji Kadam, Dr. Robin Singh Bhadoriya, Dr. Balmukund Dhakar, Dr. Yogesh Singh, Dr. Rajan Lanjekar, Dr. Gaurav Bajpai, Mr. Vikas Yadav, Dr. Ankur Saxena, Dr. Naresh Raghuwanshi, Dr. Sandeep Gupta, Dr. Tameshwar Nath Tiwari, Dr. Bhushan S. Prouhit, Dr. Harish Kumar Kotapally, Dr. Jayant Kumar and Dr. Sonam Mandani, for their immense support, and encouragement during my Ph.D.

The following friends have stood by me at all times; *Mr. Avadhesh* Sharma, Mr. Saurabh Yadav, Mr. Vishal Sharma, Mr. Vishal Nirgude, Mr. Gurjeet Singh, Mr. Vasudev Chaudhari, Mr. Sidharth Jain, Mr. Rajendra Rajpoot, Mr. Prateek Bhojane, Mr. Sourabh Jain, Mr. Vijay Choyal, Mr. Pushpanjay Singh, Mr. Rohit Kothari, Mr. Akash Sharma and Mr. Anuj Kumar, without their help and support I could not have ventured on this great task.

Last but not the least, I am greatly indebted to my parents (*Shri Param Sukh Ji* and *Smt. Madhu Devi*), brothers (*Mr. Bhanu Prakash* and *Mr. Narendra*), sisters (*Ms. Nirmala*, *Ms. Aarti* and *Ms. Deepika*) and the other members of my family for their immense moral support and encouragement. And finally, a special thanks goes to my life partner *Ms. Madhu*, stood by me to see my Ph.D. through.

I express my sincere thanks to all those who directly or indirectly have contributed, helped, and supported me.

Dharemendra Kumar Panchariya 117 Indore

Dedicated

70

Thesis Supervisors

"The mediocre teacher tells. The good teacher explains. The superior teacher demonstrates. The great teacher inspires."

-William Arthur Ward

List of Publications

List of Journal Publications based on Ph.D. Thesis:

- Dharmendra K. Panchariya, Sanjay K. Singh, and E. Anil Kumar "Inducing in situ hydrothermal carbonization of glucose to synthesize carbon MIL-101 hybrid composites for improved hydrogen uptake" *Energy & Fuels*, 2019, 33, 10123-10132. (DOI:10.1021/acs.energyfuels.9b01809) (Impact Factor: 3.021)
- Dharmendra K. Panchariya, Sanjay K. Singh, and E. Anil Kumar "Lithiumdoped silica-rich MIL-101(Cr) for enhanced hydrogen uptake" *Chemistry: An Asian Journal*, 2019, 14, 3728-3735. (DOI:10.1002/asia.201900833) (Impact Factor: 3.698)
- Dharmendra K. Panchariya, Rohit K. Rai, Sanjay K. Singh, and E. Anil Kumar "Silica-rich MIL-101(Cr) for enhanced hydrogen uptake" *Journal of Porous Materials*, 2019, 26, 1137-1147. (DOI:10.1007/s10934-018-0710-4) (Impact Factor: 1.947)
- Dharmendra K. Panchariya, Rohit K. Rai, E. Anil Kumar, and Sanjay K. Singh "Core-shell zeolitic imidazolate frameworks for enhanced hydrogen storage" ACS Omega, 2018, 3, 167-175. (DOI:10.1021/acsomega.7b01693) (Impact Factor: 2.584)

List of Conference Proceedings based on Ph.D. Thesis:

 Dharmendra K. Panchariya, Rohit K. Rai, Sanjay K. Singh, and E. Anil Kumar "Synthesis and characterization of MIL-101 incorporated with Darco type activated charcoal" *Materials Today: Proceedings*, 2017, 4, 388-394. (DOI:10.1016/j.matpr.2017.01.037)

List of International Conferences based on Ph.D. Thesis:

1. **Dharmendra K. Panchariya**, Rohit K. Rai, Sanjay K. Singh, and E. Anil Kumar "Synthesis and characterization of MIL-101 incorporated with Darco type activated charcoal" 5th International Conference of Materials Processing and Characterization (ICMPC 2016), 12-13 March 2016, Hyderabad, India.

ABSTRACT

Hydrogen gas is one of the most prominent and efficient energy carriers for several energy conversion and storage applications. To explore hydrogenbased economy with full potential, efficient hydrogen storage materials need to be developed. The recent improvement in the development of metal-organic frameworks (MOFs) structure (mono-bi metallic, hybrid composite and core-shell structure) attracts wide attention for solid-state hydrogen storage and its application. Hence in this thesis, MOF structures such as core-shell ZIFs structure (ZIF-8@ZIF-67 and ZIF-67@ZIF-8), hybrid MOFs composite (carbon-MIL-101, RHA-MIL-101, and AC-MIL-101) and alkali metal doped hybrid MOFs composites are synthesised and their H₂ gas sorption properties are investigated.



Fig. 1 Schematic representation for enhanced hydrogen uptake of core-shell zeolitic imidazolate frameworks

In this direction, core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 based zeolitic imidazole frameworks are synthesised by solvothermal method using seed-mediated methodology. TEM-EDXS line scan, elemental mapping, XPS, and ICP-AES analysis were probed to confirm the formation of core-shell structure with the controlled Co:Zn elemental composition of ~0.50 for both the

core-shell ZIF frameworks. The synthesised core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks exhibited enhanced H₂ (2.03 wt% and 1.69 wt%) storage properties at 77 K and 1 bar, which is *ca.* 41% and 18%, respectively higher than the parent ZIF-8. Notably, remarkably enhanced H₂ storage properties shown by both the core-shell ZIFs over the bimetallic Co/Zn-ZIF and the physical mixture of ZIF-8 and ZIF-67, clearly evidenced the unique structural properties (confinement of porosity) and elemental heterogeneity due to the core-shell morphology of the outperforming core-shell ZIFs. Along with the remarkably enhanced H₂ storage capacities exhibited by the core-shell ZIFs, they also displayed improved CO₂ capture behavior. Hence, we demonstrated here that the controlled structural features endorsed by rationally designed porous materials might find high potential for H₂ storage applications.



Fig. 2 Schematic representation for improved hydrogen uptake of carbon-MIL-101 hybrid composites

For development of hybrid MOFs composite structure, a sustainable methodology was explored to synthesise carbon-MIL-101 hybrid composites by advantageously inducing *in situ* hydrothermal carbonization (HTC) of glucose during the synthesis of MIL-101. By tuning the content of glucose, carbon-MIL-101 hybrid composites with varying carbon content were synthesised. The HTC of glucose and incorporation of carbon in MIL-101 was confirmed by probing ¹³C NMR, TEM, XPS and Raman investigations. The microporosity of composites can be fine-tuned by optimizing the carbon loading. Consequently, the carbon-MIL-101 hybrid composites with optimized pore size, high pore volume, and surface area conferred enhanced H₂ uptake properties (by *ca.* 11% as compared to MIL-101) at 77 K and 1 bar. The noteworthy enhancement in H₂ uptake for the synthesised carbon-MIL-101 hybrid composites endorsed the potential of the studied methodology to design hybrid MOF composites with tuned porosity for the H₂ storage application.



Improved low pressure H₂ uptake over silica rich MOF composite

Fig. 3 Schematic representation for enhanced hydrogen uptake of silica-rich MIL-101(Cr)

Another hybrid composite of MIL-101 with silica-rich rice husk ash (RHA) was synthesised to explore such materials for improved low-pressure hydrogen storage applications, compared to the well-explored carbon-based composites of MIL-101. RHA-MIL-101 was prepared by in situ incorporation of RHA in MIL-101 during the synthesis, under hydrothermal conditions. The incorporation of RHA in MIL-101 was confirmed by PXRD, FTIR, TGA, SEM, EDXS, and N₂ adsorption and desorption isotherms studies. The as-synthesised RHA-MIL-101 composite displayed enhanced BET surface area (8.6% compared to bare MIL-101), whereas AC-MIL-101 showed an enhancement of 12.7% in BET surface area compared to the bare MIL-101. Hydrogen uptake properties of these materials were evaluated at 77 K and 1 bar. Despite that RHA-MIL-101 exhibited lower surface area as compared to AC-MIL-101, the hydrogen uptake capacities of RHA-MIL-101 reached an enhanced value of 1.54 wt%, which is higher than the bare MIL-101 (1.40 wt%) and AC-MIL-101 (1.48 wt%) by 9.1% and 5.7%, respectively, and is comparable with most of the reported carbon incorporated MOFs. The observed improved hydrogen uptake properties were attributed to the bifunctional properties of the synthesised RHA-MIL-101, abundance of silanol bonds of RHA (which shows high affinity towards H_2 molecules) and tuned porous properties of RHA-MIL-101.



Fig. 4 Schematic representation for enhanced hydrogen uptake of lithium-doped silica-rich MIL-101(Cr)

In continuation to the previous research work, a simple methodology to enhance the hydrogen uptake properties of RHA incorporated MIL-101 (RHA- MIL-101) by controlled doping of Li⁺ ions were also explored. Hydrogen gas uptake of Li-doped RHA-MIL-101 was found to be significantly higher (up to 72%) compared to the undoped RHA-MIL-101, where the content of Li⁺ ions doping greatly influenced the hydrogen uptake properties. We attributed the observed enhancement in hydrogen gas uptake of Li-doped RHA-MIL-101 to the favorable Li⁺ ion to H₂ interactions and the co-operative effect of silanol bonds of silica-rich rice-husk ash incorporated in MIL-101.

The obtained results implied that the developed MOFs structures have the potential for enhanced hydrogen gas storage, and various adsorption based applications.

Keywords: Core-shell frameworks, ZIF-8, ZIF-67, MIL-101, carbon-MIL-101 hybrid composite, HTC of glucose, Hydrothermal condition, Silica-rich composite, Rice husk ash, Lithium, Adsorption, Hydrogen storage, CO₂ capture

TABLE OF CONTENTS

Abstract		
List of Figures x		xiii
List of Tables		xix
Nomenclature x		xxi
Acronyms xx		xxiii
Chapter	1 Introduction	1
1.1	An overview on hydrogen as an energy carrier	1
1.2	Hydrogen storage technology	3
1.2.1	Compressed hydrogen storage	4
1.2.2	Liquid hydrogen storage	4
1.2.3	Solid-state hydrogen storage	4
1.3	Metal-organic frameworks as physisorption material	6
1.4	Development of MOFs for gas storage application	7
1.4.1	Zeolitic imidazolate frameworks (ZIFs)	8
1.4.2	Materials of Institute Lavoisier (MIL)	10
1.5	Metal-organic frameworks for hydrogen storage	11
1.5.1	Low temperature (cryogenic) hydrogen storage in MOFs	12
1.5.2	Ambient temperature hydrogen storage in MOFs	14
1.6	Instruments for material characterisation	16
1.6.1	Powder X-ray diffraction	16
1.6.2	Thermogravimetric analysis	16
1.6.3	Fourier transform infrared spectroscopy	16
1.6.4	Raman spectroscopy	17
1.6.5	Elemental analysis	17
1.6.6	Inductively coupled plasma atomic emission spectroscopy	17
1.6.7	X-Ray photoelectron spectroscopy	17
1.6.8	Scanning electron microscope	18
1.6.9	Transmission electron microscope	18
1.6.10	¹³ C Solid-state single pulse nuclear magnetic resonance	18

spectroscopy

1.6.11	Nitrogen sorption isotherms 1		
1.6.12	Hydrogen sorption measurements		
1.7	Fundamentals of adsorption mechanism		
1.8	Adsorption equilibrium isotherm		
1.9	Adsorption equilibrium isotherm models	21	
1.9.1	Two parameter isotherm models		
1.9.1.1	Langmuir isotherm model		
1.9.1.2	Freundlich isotherm model		
1.9.2	Three parameter isotherm models	22	
1.9.2.1	Toth isotherm model		
1.9.2.2	Sips isotherm model	23	
1.9.2.3	Multilayer physisorption isotherms	23	
1.10	Adsorption thermodynamics 2		
1.10.1	Isosteric heat of adsorption		
1.11	Validation of adsorption isotherm equation		
1.11.1	Normalize standard deviation		
1.11.2	Average relative error		
1.12	Motivation for the present research work		
1.13	Objectives and scope of the present research work		
1.14	Structure of the present thesis	28	
1.15	References	29	
Chapter	2 Core-Shell Zeolitic Imidazolate Frameworks:	37	
	Synthesis, Characterisation and Hydrogen Storage		
2.1	Introduction	37	
2.2	Experimental section	40	
2.2.1	Chemicals and reagents	40	
2.2.2	Preparation of core-shell ZIF-8@ZIF-67 framework	40	
2.2.3	Preparation of core-shell ZIF-67@ZIF-8 framework	41	
2.2.4	Preparation of ZIF-67 framework	41	
2.2.5	Preparation of physical mixture of ZIF-8+ZIF-67	42	

frameworks

2.2.6	Issues and challenges encountered while conducting	42
	experimental work	
2.3	Material characterisation	42
2.3.1	Evaluation of H ₂ storage and CO ₂ capture performance	44
2.3.2	Adsorption equilibrium isotherm model	
2.4	Results and discussion	
2.4.1	Synthesis and morphology characteristics of core-shell ZIFs	44
2.4.2	H ₂ storage properties	51
2.4.3	CO ₂ capture properties	56
2.5	Conclusions	59
2.6	References	59
Chapter	3 Inducing in situ Hydrothermal Carbonization of	69
	Glucose to Synthesise carbon-MIL-101 Hybrid	
	Composites: Synthesis, Characterisation and	
	Hydrogen Storage	
3.1	Introduction	69
3.2	Experimental section	71
3.2.1	Materials and reagents	71
3.2.2	Synthesis of MIL-101	71
3.2.3	Hydrothermal carbonization (HTC) of glucose	72
3.2.4	Synthesis of carbon-MIL-101 hybrid composites	72
3.3	Material characterisation and evaluation of H ₂ uptake	73
	performance	
3.3.1	Sips adsorption equilibrium isotherm models	75
3.4	Results and discussion	75
3.5	Conclusion	90
3.6	References	91
Chapter	4 Silica-rich MIL-101(Cr): Synthesis, Characterisation	99
and Hydrogen Storage		
4.1	Introduction	99

4.2	Experimental details 101			
4.2.1	Reagents and materials			
4.2.2	Preparation of MIL-101 adsorbent			
4.2.3	Pre-treatment of rice husk ash and activated charcoal			
4.2.4	Preparation of RHA-MIL-101 and AC-MIL-101 hybrid	102		
	composites			
4.2.5	Preparation of physical mixture of AC and RHA with MIL-	103		
	101 adsorbent			
4.3	Instruments for physical characterisation	104		
4.3.1	Hydrogen adsorption measurement	105		
4.3.1.1	Low pressure hydrogen adsorption measurements	105		
4.3.2	Adsorption equilibrium isotherm models	105		
4.4	Results and discussion	105		
4.5	Conclusions	117		
4.6	References	117		
Chapter	5 Lithium-doped Silica-rich MIL-101(Cr): Synthesis,	125		
	Characterisation and Hydrogen Storage			
5.1	Introduction	125		
5.1 5.2	Introduction Experimental section	125 129		
5.1 5.2 5.2.1	Introduction Experimental section Materials	125 129 129		
5.1 5.2 5.2.1 5.2.2	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101	125 129 129 129		
 5.1 5.2 5.2.1 5.2.2 5.3 	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments	125 129 129 129 129 130		
5.1 5.2 5.2.1 5.2.2 5.3 5.3.1	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements	125 129 129 129 130 131		
 5.1 5.2 5.2.1 5.2.2 5.3 5.3.1 5.3.2 	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements Adsorption equilibrium isotherm model	125 129 129 129 130 131 131		
 5.1 5.2 5.2.1 5.2.2 5.3 5.3.1 5.3.2 5.3.3 	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements Adsorption equilibrium isotherm model Isosteric heat of adsorption	125 129 129 129 130 131 131 131		
 5.1 5.2 5.2.1 5.2.2 5.3 5.3.1 5.3.2 5.3.3 5.4 	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements Adsorption equilibrium isotherm model Isosteric heat of adsorption Results and discussion	125 129 129 130 131 131 131 132		
5.1 5.2 5.2.1 5.2.2 5.3 5.3.1 5.3.2 5.3.3 5.4 5.5	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements Adsorption equilibrium isotherm model Isosteric heat of adsorption Results and discussion Conclusions	125 129 129 130 131 131 131 132 144		
5.1 5.2 5.2.1 5.2.2 5.3 5.3.1 5.3.2 5.3.3 5.4 5.5 5.6	Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements Adsorption equilibrium isotherm model Isosteric heat of adsorption Results and discussion Conclusions	125 129 129 130 131 131 131 132 144 144		
 5.1 5.2 5.2.1 5.2.2 5.3 5.3.1 5.3.2 5.3.3 5.4 5.5 5.6 Chapter 	 Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements Adsorption equilibrium isotherm model Isosteric heat of adsorption Results and discussion Conclusions References 6 Conclusions and Future Scope 	 125 129 129 129 130 131 131 132 144 144 153 		
 5.1 5.2 5.2.1 5.2.2 5.3 5.3.1 5.3.2 5.3.3 5.4 5.5 5.6 Chapter 6.1 	 Introduction Experimental section Materials Synthesis of Li-doped RHA-MIL-101 General methods and instruments Hydrogen adsorption measurements Adsorption equilibrium isotherm model Isosteric heat of adsorption Results and discussion Conclusions References 6 Conclusions and Future Scope Conclusion drawn from the present studies 	125 129 129 130 131 131 131 132 144 144 153 153		

6.3	Limitations of the present work	157
6.4	Scope for future Work	157
Appendix A- Table A1		159
Appendix B- Uncertainty and Error of Experiment		165
Appendix C- Permission licences		169

LIST OF FIGURES

Figure 1	Schematic representation for enhanced hydrogen uptake of	i
	core-shell zeolitic imidazolate frameworks	
Figure 2	Schematic representation for improved hydrogen uptake of	ii
	carbon-MIL-101 hybrid composites	
Figure 3	Schematic representation for enhanced hydrogen uptake of	iii
	silica-rich MIL-101(Cr)	
Figure 4	Schematic representation for enhanced hydrogen uptake of	iv
	lithium-doped silica-rich MIL-101(Cr)	
Figure 1.1	Steps to use hydrogen as an energy carrier	1
Figure 1.2	Hydrogen storage technologies	3
Figure 1.3	Potential application of MOFs structure	7
Figure 1.4	Developmental phases of MOFs for gas storage application	8
Figure 1.5	Presents the ZIF-8 and ZIF-67 crystals, each row has the nets	9
	(blue line and black dot drawings) shown stacked on top of the	
	tiles representing the subdivision of space (variously colored	
	polyhedral shapes) in the net labeled with the three-letter net	
	symbol, followed by the single crystal XRD structures of ZIFs	
	corresponding to each of the nets. The largest cage in each ZIF	
	is shown with ZnN_4 tetrahedra in blue and CoN_4 in pink. The	
	yellow ball is placed in the structure for clarity and to indicate	
	space in the cage. H atoms have been omitted [IM and IM-type	
	links are shown in ball-and stick representation (C, black; N,	
	green; O, red; Cl, pink)]. Reproduced from ref. [25] with the	
	permission of The American Association for the Advancement	
	of Science	
-		

Figure 1.6(A and B) Ball-and-stick view and free dimensions (Å) of the11pentagonal and hexagonal windows, (C and D) Ball-and-stickview of the two cages, chromium octahedra, oxygen, fluorineand carbon atoms are in green, red, red and blue, respectively.

Reproduced from ref. [26] with the permission of The American Association for the Advancement of Science

Figure 1.7 Adsorption isotherms, q = f(P) at T 20 Figure 2.1 (a) Synthetic scheme of preparation of core-shell ZIF-8@ZIF-45 67 and ZIF-67@ZIF-8, (b) UV-visible spectra and (c) PXRD patterns of ZIF-8, ZIF-67, ZIF-8@ZIF-67, ZIF-8+ZIF-67 and ZIF-67@ZIF-8 Figure 2.2 Photographs of the synthesised core-shell ZIF-8@ZIF-67 and 46 ZIF-67@ZIF-8, along with the parent ZIF-8 and ZIF-67 frameworks Figure 2.3 47 (a,e) SEM images (inset TEM images) (b,f) line scanning, (cd, g-h) elemental mapping of (a-d) ZIF-8@ZIF-67 and (e-h) ZIF-67@ZIF-8 frameworks 48 Figure 2.4 EDXS plots of (a) ZIF-8@ZIF-67 and (b) ZIF-67@ZIF-8 Figure 2.5 49 (a,d) Wide scan XPS and (b,c,e,f) respective high resolution XPS spectra showing Zn 2p and Co 2p core bands, of ZIF-8, ZIF-67, ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks Figure 2.6 (a) FTIR spectra, (b) TGA profiles, of the core-shell ZIF-49 8@ZIF-67 and ZIF-67@ZIF-8, along with the parent ZIF-8 and ZIF-67 Figure 2.7 51 (a) N_2 sorption and (b) DFT pore size distribution of ZIF-8, ZIF-67, ZIF-8@ZIF-67, ZIF-67@ZIF-8 and ZIF-8+ZIF-67 physical mixture frameworks Figure 2.8 (a) H_2 storage isotherm at 77 K with Langmuir model, (b) 53 enlarged view of H₂ storage isotherm in the pressure range of 0.80-1.0 bar, (c) comparative H_2 storage, and (d) H_2 storage isotherm at 77 K and 298 K Figure 2.9 (a) PXRD patterns of ZIF-8@ZIF-67-B and ZIF-67@ZIF-8-B 54 (before) and ZIF8@ZIF-67-A and ZIF-67@ZIF-8-A (after) gas adsorption (b) H₂ storage isotherm at 77 K with Freundlich

model

- **Figure 2.10** (a) CO₂ capture isotherms at 298 K, 1 bar (b) enlarged view of 57 CO₂ uptake in the pressure range of 0.02-0.15 bar
- **Figure 2.11** Comparative CO_2 capture isotherms at 298 K, 1 bar 57
- Figure 3.1 (a) FTIR spectra, (b) TGA curve, (c) PXRD pattern and (d) 78
 Raman spectra of carbon-MIL-101 hybrid composites, MIL-101, carbon (HTC of glucose), glucose and the physical mixture of MIL-101 and carbon (HTC of glucose)
- Figure 3.2 (a-f) SEM images of MIL-101, carbon-MIL-101 hybrid 79 composites, and carbon sphere (HTC of glucose-C100)
- **Figure 3.3** (a-c) Schematic representation of the morphology evolution 80 and (d–f) SEM images of the physical mixture of MIL-101 and carbon sphere (HTC of glucose-C100)
- Figure 3.4 (a) N₂ sorption, (b) micropore size distribution by DA method, 81 and (c,d) DFT pore size distribution of incremental and cumulative pore volume of carbon-MIL-101 hybrid composites, MIL-101 and the physical mixture of MIL-101 and HTC of glucose (C100)
- **Figure 3.5** (a,b) Low-pressure ranges (up to 10^{-3} and 10^{-4}) profile for N₂ 82 sorption isotherms of various adsorbents
- Figure 3.6(a) ¹³C solid-state NMR and (b-e) high-resolution XPS spectra83of C 1s and Cr 2p for C100-MIL-101 composite and MIL-101
- Figure 3.7 (a) Wide scan XPS spectra and (b-c) high-resolution XPS 84 spectra showing O 1s for MIL-101 and C100-MIL-101 hybrid composite
- **Figure 3.8** (a,c) SEM images and (b,d) TEM images (inset HR-TEM) of 85 (a,b) MIL-101 and (c,d) C100-MIL-101 composite
- **Figure 3.9** (a) Low-pressure hydrogen uptake (at 77 K), (b) Correlation of 86 hydrogen uptake isotherm with Sips isotherm model, and (c) comparative hydrogen uptakes with BET surface area for carbon-MIL-101 hybrid composites, MIL-101, carbon (HTC of glucose) and the physical mixture of MIL-101 and carbon

Figure 3.10N2 sorption analysis of physical mixture C100+MIL-10188

103

Synthetic scheme of hybrid composite MIL-101

Figure 4.1

- **Figure 4.2** (a) PXRD patterns and (b) FTIR vibration bands of MIL-101, 106 RHA-MIL-101 and AC-MIL-101 (*inset* shows the enlarged view of FTIR vibration bands of RHA-MIL-101 in the range of 800-1200 cm⁻¹)
- Figure 4.3 (a-d) SEM images and (*inset*) particle size distribution of (a-b) 107
 RHA-MIL-101, (c) MIL-101, (d) AC-MIL-101, (e) physical mixture of RHA+MIL-101, (f) physical mixture of AC+MIL-101, (g) pure AC and (h) pure RHA
- Figure 4.4 (a-c) Elemental mapping, showing carbon (C), chromium (Cr) 108 and silica (Si), and (d-f) EDXS analysis of (a,d) MIL-101, (b,e) AC-MIL-101 and (c,f) RHA-MIL-101
- Figure 4.5 (a) N₂ isotherms, (b) Enlarge view of N₂ isotherms (P/P₀=0.1 110 to 0.9) (c) Pore size distribution and (d) TGA curve of prepared MIL-101, RHA-MIL-101, AC-MIL-101 and pure AC, RHA
- Figure 4.6(a) N2 adsorption desorption isotherms and (b) NLDFT pore112size distribution of AC+MIL-101 and RHA+MIL-101
- Figure 4.7 (a) Low pressure hydrogen uptake isotherms and (b) 113 comparative hydrogen uptakes for MIL-101, RHA-MIL-101 and AC-MIL-101 at 77 K, (c) Correlation of hydrogen uptake isotherm for RHA-MIL-101 with two parameter (Langmuir and Freundlich) and three parameter (Toth and Sips) nonlinear isotherm model
- Figure 4.8 Plausible weak interactions of silanol bonds with hydrogen 115 molecules contributing in the observed improved H₂ uptake properties of RHA-MIL-101
- Figure 4.9 Correlation of hydrogen uptake for MIL-101 and AC-MIL-101 116 with two (Langmuir and Freundlich) and three parameter (Toth and Sips) non-linear isotherm model

- Figure 5.1 Photographs of undoped RHA-MIL-101 and Li-doped RHA- 133 MIL-101
- **Figure 5.2** (a) PXRD and (b) FTIR of RHA-MIL-101 and *x*Li-RHA-MIL- 133 101
- Figure 5.3 FESEM images of (a-b) RHA-MIL-101, (c) 0.06Li-RHA-133 MIL-101, (d) 0.3Li-RHA-MIL-101, (e) 0.6Li-RHA-MIL-101 and (f) 6.0Li-RHA-MIL-101
- **Figure 5.4** TGA of RHA-MIL-101 and *x*Li-RHA-MIL-101 134
- **Figure 5.5** (a) N₂ sorption isotherms, (b) NLDFT incremental pore size 135 distribution for RHA-MIL-101 and *x*Li-RHA-MIL-101
- Figure 5.6 (a) N_2 sorption isotherms and (b) low pressure range (P/P₀ \leq 137 0.01) profile for N_2 adsorption isotherms of RHA-MIL-101 and 0.06Li-RHA-MIL-101
- **Figure 5.7** (a) low-pressure hydrogen sorption isotherms at 77 K, and (b) 138 correlation between surface area, total pore volume and hydrogen capacities for RHA-MIL-101 and *x*Li-RHA-MIL-101
- Figure 5.8 (a-b) High-pressure hydrogen adsorption profiles at 298 K for 140 undoped RHA-MIL-101 and 0.06Li-RHA-MIL-101 (c) Sips non-linear isotherm model of hydrogen uptake for undoped RHA-MIL-101 and *x*Li-RHA-MIL-101 (d) Isosteric heat of adsorption (at 77 K and 298 K) (Q_{st}) for undoped RHA-MIL-101 and 0.06Li-RHA-MIL-101
- **Figure 5.9** Comparative hydrogen adsorption profile for RHA-MIL-101 141 and *x*Li-RHA-MIL-101
- Figure 6.1 Comparative chart of hydrogen uptake from the present 156 research work

LIST OF TABLES

Table 1.1	DOE technical targets for onboard hydrogen storage for light-			
	duty vehicles			
Table 1.2	Comparison of different hydrogen storage methods			
Table 1.3	High-pressure hydrogen uptake performance at 77 K for			
	selected porous MOFs			
Table 1.4	4 High-pressure hydrogen uptake performance at 298 K for			
	selected porous MOFs			
Table 2.1	Molar ratio of Co^{2+}/Zn^{2+} , Core Size (nm), Shell thickness (nm)	47		
	of the ZIF-8@ZIF-67 and ZIF-67@ZIF-8			
Table 2.2	Surface area, pore volume, pore size and H ₂ storage properties	51		
	of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks			
	along with ZIF-8, ZIF-67 and ZIF-8+ZIF-67 physical mixture			
Table 2.3	Comparative surface area, pore volume and H_2 storage	55		
	properties of several monometallic and bimetallic MOF			
	materials			
Table 2.4	Isotherm constants for the Langmuir and Freundlich model of	56		
	ZIF-8, ZIF-8@ZIF-67, ZIF-67@ZIF-8, physical mixture ZIF-			
	8+ZIF-67 and ZIF-67 H_2 storage at 77 K and 1 bar			
Table 2.5	Surface area, pore volume, pore size and CO ₂ capture properties	57		
	of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks			
Table 2.6	Isotherm constants for the Freundlich model of ZIF-8, ZIF-	58		
	8@ZIF-67, ZIF-67@ZIF-8 and ZIF-67 CO_2 capture at 298 K			
	and 1 bar			
Table 2.7	Comparative surface area, pore volume, CO ₂ capture properties	58		
	of several monometallic and bimetallic MOF materials			
Table 3.1	Elemental analysis (%), O/C, H/C ratio of carbon-MIL-101	77		
	hybrid composite and HTC of glucose (C100)	<i></i>		
Table 3.2	Surface area, pore volume and H ₂ storage properties of carbon-	81		
	MIL-101 hybrid composites, MIL-101, HTC of glucose (C100)			

and the physical mixture of MIL-101 and carbon

- **Table 3.3** Comparative charts for the surface area, pore volume, and H289uptake data for selected MOFs at 77 K and 1 bar
- **Table 3.4**Isotherm constants for the three-parameter Sips isotherm90models of carbon-MIL-101 hybrid composites and MIL-101
- Table 4.1Quantitative analysis of EDXS data for MIL-101, RHA-MIL-109101 and AC-MIL-101
- Table 4.2 N₂ adsorption and desorption properties, and low-pressure 110 hydrogen uptake isotherms of MIL-101, RHA-MIL-101, AC-MIL-101 and pure AC, RHA at 77 K
- **Table 4.3** Comparative charts for the surface area, pore volume and H_2 114uptake data for selected MOFs at 77 K and 1 bar
- Table 4.4Isotherm constants for the two (Langmuir and Freundlich) and 116three (Toth and Sips) parameter isotherm models of MIL-101,RHA-MIL-101 and AC-MIL-101
- Table 5.1N2 and H2 low-pressure adsorption measurements of undoped136RHA-MIL-101 and xLi-RHA-MIL-101
- **Table 5.2** Correlation of H2 adsorption and pore volume in undoped 137RHA-MIL-101 and xLi-RHA-MIL-101
- **Table 5.3** Isotherm constants for the three-parameter Sips isotherm 141models of RHA-MIL-101 and xLi-RHA-MIL-101
- **Table 5.4** Comparison of surface area, pore volume and H_2 uptake data 143for selected Li⁺-doped MOFs at 77 K and 1 bar
- **Table A1** Comparison of surface areas of reported MIL-101(Cr) 159according to additive, time, temperature (synthesis and
activation) and purification steps

NOMENCLATURE

Amount of adsorbate adsorbed on adsorbent, wt%

I e	Equilibrium pressure, bar
am	Langmuir isotherm equation parameter, wt%
b	Langmuir isotherm equation parameter, bar ⁻¹
k	Freundlich isotherm equation parameter, bar ⁻¹
n	Freundlich isotherm equation parameter
k _t	Toth isotherm equation parameter
at	Toth isotherm equation parameter, bar ⁻¹
t	Toth isotherm equation parameter
ks	Sips isotherm equation parameter, bar ⁻¹
ts	Sips isotherm equation parameter

- a_s Sips isotherm equation parameter, bar⁻¹
- N Avogadro constant, 6.022x10²³ mol⁻¹

Equilibrium pressure bar

- A_m Effective cross-sectional area of the N₂, 0.162 nm²
- M_v Volume occupied by 1 mole of the adsorbate gas at STP, 22414 cm³
- V_m Volume of monolayer adsorbed gas, cm³ g⁻¹
- P Partial vapor pressure of adsorbate, bar
- P₀ Saturated vapor pressure of the adsorbed gas, bar
- V Volume of gas adsorbed per gram adsorbent at STP, $cm^3 g^{-1}$
- C Dimensionless constant
- s Slop

q_e P

- i Intercept
- P/P₀ Relative pressure
- R Universal gas constant
- n Specific amount of adsorbed
- T Temperature, K/°C
- P Pressure, bar
- Q_{st} Isosteric heat of adsorption, kJ mol⁻¹
- ΔQ Normalize standard deviation

- N Number of adsorption isotherm data
- q Adsorption capacities obtained from experiment, wt%
- R² Coefficient of correlation
- V_{micro} Micropore volume, cm³ g⁻¹
- V_{meso} Mesopore volume, cm³ g⁻¹
- V_{total} Total pore volume, cm³ g⁻¹
- ΔH_{ads} Heat of adsorption, kJ mol⁻¹

SA_{BET} Surface area BET, m² g⁻¹

- V_p Pore volume, cm³ g⁻¹
- VH₂ Volume of H₂, $cm^3 g^{-1}$
- $DH_2 \qquad \text{Density of } H_2 \text{, } 0.0708 \text{ g cm}^{-3} \text{ of } H_2 \text{ at } 20 \text{ K}$

Greek letters

θ	Theta
ν	Wavenumber, cm ⁻¹
$ ho_v$	Volumetric density, kg m ⁻³
$ ho_g$	Gravimetric density, wt%
Subscript	
р	Porevolume
v	Volumetric

	~
g	Gravimetric

- BET Brunauer-Emmett-Teller
- ads Adsorption
- e Equilibrium
- t Toth Model
- s Sips Model
- m Monolayer for Langmuir constant and Volume
ACRONYMS

MOFs	Metal-organic frameworks
DOE	Department of Energy
PCPs	Porous coordination polymers
PCNs	Porous coordination networks
ZIFs	Zeolitic imidazolate frameworks
MIL	Materials of Institute Lavoisier
PXRD	Powder X-ray diffraction
TGA	Thermogravimetric analysis
FTIR	Fourier transforms infrared spectroscopy
EA	Elemental analysis
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
XPS	X-Ray photoelectron spectroscopy
SEM	Scanning electron microscopic
TEM	Transmission electron microscopic
NMR	Nuclear magnetic resonance
NLDFT	Non-linear density functional theory
BJH	Barrett-Joyner-Halenda
DA	Dubinin-Astakhov
DR	Dubinin-Radushkevic
НК	Horvath-Kawazoe
SF	Saito-Foley
ARE	Average relative error
RHA	Rice husk ash
HTC	Hydrothermal carbonizations
Li	Lithium
EDXS	Energy-dispersive X-ray spectrometry
BET	Brunauer-Emmett-Teller
CNT	Carbon nanotube
SWNT	Single walled carbon nanotube

AC	Activated carbon
Pt	Platinum
HRTEM	High resolution transmission electron microscopic
MWCNTs	Multi-walled carbon nanotubes
FCNF	Functionalized carbon nanofiber
HCl	Hydrochloric acid
HNO ₃	Nitric acid
H ₂ O	Distilled water
CMP	Conjugated microporous polymer
UV-vis	UV-visible Spectroscopy
Ar	Argon
Не	Helium
H_2	Dihydrogen
N_2	Nitrogen
CO ₂	Carbon dioxide
CH ₄	Methane
HMF	5-hydroxymethylfurfural
ppm	Parts per million
RT/r.t.	Room temperature
temp	Temperature
EtOH	Ethanol
DMF	Dimethylformamide
MeOH	Methanol
Atm	Atmospheres (pressure)
cm ³	Cubic centimeter
m^2	Square meter
g	Gram
mg	Milligram
h	Hour
rpm	Revolutions per minute
nm	Nanometer

eV	Electron volt
mmol	Millimole
Κ	Kelvin
D	Density
V	Volume
mM	Millimolar
μΜ	Micro Molar
cm	Centimeter
0	Degree
°C	Degree Celsius
μL	Microliter
a. u.	Arbitrary unit
min	Minute
mL	Milliliter
mm	Millimeter

Chapter 1 Introduction

1.1 An overview on hydrogen as an energy carrier

In the present scenario of escalating global energy demand and deteriorating environmental condition, there is a need for a sustainable and efficient source of energy [1]. In this regard, effective, efficient, and economical (3E's) energy technologies are the need of the hour and hence, such strategies have drawn great attention. To pursue the 3E's, utilizing hydrogen as the prime energy carrier sources may provide a sustainable solution [1-5]. Hydrogen has three times higher energy density than gasoline on a weight basis [3, 5]. To use hydrogen as an energy carrier, the three-step process - production, storage, and utilization is considered to be a better strategy (Fig. 1.1).



Fig. 1.1 Steps to use hydrogen as an energy carrier

Hydrogen can be produced by steam reforming, biomass gasification, electrolysis of water, coal gasification and thermochemical method, and feasibly used in various stationary and mobile applications, and producing water vapor as the only by-product when combined with oxygen in a fuel cell [5]. Providing a reasonably safe and affordable methodology to store and deliver hydrogen is still a challenge [2-5]. It is predicted that the total energy generated by economically developed countries, utilizes one-third of the energy in transportation sector. In the modern vehicle 400 km distance can be traveled with 24 kg of gasoline fuel, whereas to travel the same distance about 8 kg of hydrogen is required for the combustion engine driven vehicle and, 4 kg of hydrogen for a fuel cell-driven vehicle. It is estimated that to store 4 kg of hydrogen in gaseous phase at ambient temperature and atmospheric pressure, a container of 45 m³ volume will be required [2]. The key challenge in the exploitation of hydrogen as an energy carrier is adequate safety and effective storage. The U.S. Department of Energy (DOE) recently updated the requirements for onboard hydrogen storage systems (Table 1.1): 30 g L⁻¹ for volumetric capacity, and 4.5 wt% for gravimetric capacity by the year 2020, and 40 g L⁻¹, and 5.5 wt% by 2025, at an operating temperature of -40 to 60 °C and 12 bar of maximum delivery pressure [6].

Storage parameter	Units	2020	2025	Ultimate
System gravimetric capacity	kg H ₂ per	0.045	0.055	0.065
(net useful energy/max system mass)	kg system			
System volumetric capacity	kg H ₂ per L	0.030	0.040	0.050
(net useful energy/max system volume)	system			
Min/Max delivery temperature	°C	-40/85	-40/85	-40/85
Cycle life (1/4 tank to full)	Cycles	1500	1500	1500
Min/Max delivery pressure from storage	bar (abs)	5/12	5/12	5/12
system				
System fill time (for 5 kg H ₂)	min	3-5	3-5	3-5
Fuel purity (H ₂ from storage)	% H ₂	99.97 % (dry basis)		basis)
		SAE J2719 and		
		ISO/PDTS 14687-2		

 Table 1.1 DOE technical targets for onboard hydrogen storage for light-duty

 vehicles

1.2 Hydrogen storage technology

In the 21st century, hydrogen is globally accepted as one of the ideal green and clean energy fuel. It is well known that hydrogen has the highest energy per unit mass as compared to any other fuel. Hence, to employ the high energy density of hydrogen as a fuel, development of advanced, efficient and safe hydrogen storage methods, is still a critical challenge [3, 5]. Hydrogen can be stored by one of the following techniques: (i) as compressed hydrogen gas (high pressure around 700 bar), (ii) as liquid hydrogen (low temperature around 20 K), and (iii) in solid-state materials [2-5]. The compressed hydrogen and liquid hydrogen storage techniques are also known as conventional hydrogen storage method. Fig. 1.2 represents various hydrogen storage technologies [7]. A comparison of different hydrogen storage methods is given in Table 1.2 [8]. Hydrogen storage capacity is mainly quantified as volumetric and gravimetric method. In the volumetric method, the measurement of hydrogen capacity is quantified as volume by capacity with respect to change in hydrogen pressure. On the other hand, gravimetric method hydrogen capacity is directly measured by determining the change in the mass of adsorbent using a highly sensitive mass balance equipment [9].



Fig. 1.2 Hydrogen storage technologies [7]

	Operating cond	Volumetric	Gravimetric		
Storage method	Temperature (°C)	Pressure (bar)	density ρ _v (kg m ⁻³)	density ρ _g (wt%)	
High pressure compressed gas	Ambient	700	< 40	13	
Liquefaction	-252.87	1	70.8	Varies	
Physisorption	Variable (0 to -196)	0 to 100	20	~ 2	
Metal hydrides	Variable (0 to 400)	0 to 100	150	~ 2	
Complex metal hydrides	Variable	0 to 100	150	< 18	
Chemical storage	Variable	0 to 100	> 150	< 40	

Table 1.2 Comparison of different hydrogen storage methods [8]

1.2.1 Compressed hydrogen storage

To compress hydrogen gas to very high pressures (~ 350 and 700 bar) for mobile application, large amount of energy is required to achieve the sufficient amount of hydrogen fuel. Hence to store highly pressurized hydrogen gas, fabrication of large storage tanks is required, which can sustain high pressure of compressed hydrogen. The major obstacles in the implement compressed hydrogen technique for onboard mobile application are the safety issues and economic factors [3-5].

1.2.2 Liquid hydrogen storage

In the case of liquid hydrogen storage method, liquefaction of hydrogen is attained at low temperature of 20 K at 1 bar (boiling point of hydrogen). Further to minimize boil-off losses, large amount of energy is required to maintain the required lower temperature and cooling [3-5].

1.2.3 Solid-state hydrogen storage

Compressed gas and liquefied hydrogen storage technologies have serious challenges of safety, effectiveness, and economical operation for onboard storage systems. Therefore, to meet the prerequisite of potential applications, solid-state hydrogen storage is the most promising technology [2-5]. In solid materials, storage of hydrogen can be achieved by physisorption and chemisorption processes: i) physisorption involves adsorption of hydrogen through weak

dispersive attraction (van der Waals forces) with surface of the adsorbent, and ii) chemisorption involves binding of hydrogen molecules to the surface by strong chemical association or forming a new compound [2-5, 8, 9]. Conventional metal hydrides (e.g., LiNa₅, MmNi₅, and ZrMn₂), and complex metal hydrides or chemical hydrogen storage materials (e.g., LiBH₄, LiNH₂, Mg(BH₄)₂, Mg(NH₂)₂ and NaBH₄) are chemisorption based materials. These materials have shown high gravimetric storage uptakes. However, the strong chemical association in chemisorption process also lead to several challenges such as requirement of high temperature for hydrogen desorption, non-reversibility, and slow adsorption and desorption kinetics [2-5, 8-11]. Porous materials such as different types of carbon (activated carbon and nanotubes), zeolites, metal-organic frameworks (MOFs), covalent organic frameworks (COFs) are classified as physisorption based materials [2-5, 8-11]. Due to weak interaction between the adsorbent and hydrogen gas molecules, physisorption based materials require low activation energy as compared to chemisorption-based materials. Moreover, favorable thermodynamic and long-term cyclic stability is also an advantageous property of physisorption based materials. The above-mentioned important characteristics of physisorption based materials for hydrogen storage process are promising properties for onboard hydrogen storage applications [2-5, 8-11].

The traditional porous materials such as activated carbon, zeolite, silica, microporous polymer, and so on, have been extensivly explored for gas storage/separation application and mainly for hydrogen storage [8-11]. However, the criteria set for onboard hydrogen storage applications by DOE are not being completely satisfied by any of the available hydrogen storage methods and materials [6]. Among several materials (metal hydrides, carbon, zeolites, and complex metal hydrides) explored metal-organic frameworks (MOFs) have shown high potential for onboard hydrogen storage applications [8-11]. Hence, the present thesis mainly focuses on the physisorption based metal-organic framework materials for hydrogen storage application.

5

1.3 Metal-organic frameworks (MOFs) as physisorption

material

Developing new materials with versatile structures and relevent functionalities is a potential tool to achieve materials with tuned properties. In the past two decades, a new class of porous crystalline materials metal-organic frameworks (MOFs) has been extensively explored as a promising candidate for hydrogen storage materials. MOFs also known as porous coordination polymers (PCPs) or porous coordination networks (PCNs), are constructed by the linking of metal ions or clusters with the organic linkers to configure one, two, or three dimension framework structure [12-15]. The metal ions or metal clusters can be an element of transition metals, alkali metal, alkaline earth metals, lanthanides, or actinides. The organic linkers are typically multidentate molecules with N- or O donor atoms (pyridyl, polyamines, carboxylates, and so on). The constructed framework structure exhibits remarkable properties high surface area, large pore volume, extraordinary thermal and chemical stability, tunable pore structure and internal surface properties, and low density of framework [14-18]. These exceptional physical and chemical characteristics of MOFs making them suitable for a wide range of potential applications (Fig. 1.3), including gas storage, separation, catalysis, magnetism, optical, drug delivery, sensor, and luminescence [17, 18].

MOFs are typical hybrid organic-inorganic materials, generally synthesised by conventional (hydrothermal and solvothermal method) technique in a temperature range of ambient to ~ 250 °C [14, 16, 19]. Alternative synthesis approach such as microwave-assisted, electrochemical, mechanochemical, sonochemical and ultrasonic irradiation methods have also been explored to produce rapid, inexpensive, and uniform MOF structures in large scale [14, 16]. The structure, morphology and chemical state of the synthesised MOFs can be established by various characterisation techniques. The single crystal and powder X-ray diffraction method are used to the established crystal structure, crystallinity, and phase of the synthesised material. The pore textural characteristics (surface area pore volume and pore size) of the synthesised MOFs can be confirmed by

nitrogen sorption measurements. Morphology, thermal and chemical stability, function group, purity, and elemental composition can be investigated by the electron microscopy (SEM and TEM), thermal gravimetric technique and Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy (NMR) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) respectively [19, 20]. The details description of the characterisation technique is discussed in section 1.6.



Fig. 1.3 Potential application of MOFs

1.4 Development of MOFs for gas storage application

Since the invention of MOFs, considerable efforts have been devoted for the development of various MOF frameworks for gas storage applications. So far, huge number and variety of MOFs with high porosity, diverse structures, unique morphologies, versatile functionalities, and tailorable porosities have been developed. Fig. 1.4 demonstrates different phases for the development of MOFs for gas storage applications.

Despite the promising characteristic of MOFs, their application in the field of gas storage is disrupted by many challenging issues including stability, unutilized pore space, weak interaction of MOFs wall with gas molecules, and so on. In order to overcome these challenges, pre/*in situ* and post-synthesis strategies for the modification of pristine MOFs have been adopted to synthesise composites of MOFs having improved physical and chemical characteristics and hence enhanced gas storage performance. In an alternative approach a secondary metal element is introduced into framework structure to obtain bimetallic or mixed metal MOFs. The development of bi-metallic MOFs is a very promising approach to achieve enhanced gas storage, but there are several considerable challenges with bimetallic MOFs in terms of yield of a fragile framework, topology and functionality. On the other hand, core-shell MOFs have shown considerably high potential to overcome some of the challenges associated with mono or bimetallic MOFs.



Fig. 1.4 Developmental phases of MOFs for gas storage application

1.4.1 Zeolitic imidazolate frameworks (ZIFs)

In the last few years, MOFs with zeolitic topologies have become a hot topic in the field of material chemistry. Zeolitic imidazolate frameworks (ZIFs) are a new subclass of MOFs family, which normally acquire zeolitic topologies. In general, ZIF structures are mainly constructed by the coordination bonding of the transition metal ions/cluster (M = Zn(II), Co(II)) and imidazolate derivatives.

ZIFs are promising and widely used for hydrogen gas storage, due to their tailorable porosities, unique morphologies, and excellent thermal and chemical stability [20-25].

Among the wide varieties of available ZIFs (Fig. 1.5), ZIF-8 [Zn(Hmim)₂] (Hmim = 2-methylimidazole) and ZIF-67 [Co(Hmim)₂] having zeolite sod topology are the most explored ZIFs. The analogous isoreticular sodalite (SOD) topology and similar unit cell parameters for ZIF-8 (a = b = c = 16.9910 Å) and ZIF-67 (a = b = c = 16.9589 Å), and comparable ionic radii of Zn²⁺ (0.74 Å) and Co²⁺ (0.72 Å) facilitated the facile synthesis of bimetallic and core-shell ZIFs with tuned properties [20-25].



Fig. 1.5 Presents the ZIF-8 and ZIF-67 crystals, each row has the nets (blue line and black dot drawings) shown stacked on top of the tiles representing the subdivision of space (variously colored polyhedral shapes) in the net labeled with the three-letter net symbol, followed by the single crystal XRD structures of ZIFs corresponding to each of the nets. The largest cage in each ZIF is shown with ZnN₄ tetrahedra in blue and CoN₄ in pink. The yellow ball is placed in the structure for clarity and to indicate space in the cage. H atoms have been omitted [IM and IM-type links are shown in ball-and stick representation (C, black; N, green; O, red; Cl, pink)]. *Reproduced from ref. [25] with the permission of The American Association for the Advancement of Science*

1.4.2 Materials of Institute Lavoisier (MIL)

In 2004, Ferey and co-workers were the first to introduce the concept of MIL frameworks, where they developed a variety of MIL frameworks such as MIL-100, MIL-101(Cr) and MIL-101(Fe), MIL-53, and so on [26, 27]. Among a wide range of MOFs explored, MIL-101(Cr) has received the utmost attention. A chromium-based MIL-101 (in Fig. 1.6) has the molecular formula of $Cr_{3}F(H_{2}O)_{2}O[(O_{2}C)-C_{6}H_{4}-(CO_{2})]_{3}$.nH₂O (where n is ~25). MIL-101(Cr) is constructed from the linkage of 1,4-benzene dicarboxylate (1,4-BDC) and inorganic trimers consist of three chromium atoms arranged in an octahedral environment with four oxygen atoms of the bidentate dicarboxylate, one µ₃O atom, and one oxygen atom from the terminal water or fluorine group. Advantageously, MIL-101(Cr) displayed several promising features such as mesoporous zeotype structure with mobil thirty-nine (MTN) topology, giant cell volume (~702,000 Å^3), high BET and Langmuir surface area (~4100 \pm 200 m² g^-1 and 5900 \pm 300 m² g⁻¹), and excellent thermal and chemical stability over a wide range of temperature (350-400 °C) and moisture conditions, and availability of numerous unsaturated Cr metal sites. Moreover, MIL-101 also possesses two types of large mesoporous cages; where the smaller cage of diameter 29 Å is accessible through a pentagonal window of 12 Å aperture, while the larger cage of diameter 34 Å is accessible through both hexagonal and pentagonal windows of 14.5 x 16 Å² apertures [26-29].

Though the large pore volume and unsaturated open metal sites available in MOFs are the important factors to achieve high gas storage properties, the weak interaction of MOF walls and H_2 molecules adversely affect the H_2 adsorption properties of MOF, resulting in the underutilization of large pore volumes. To address this issue, several approaches, such as functionalization of the linker, loading of a metal nanoparticle, and other materials are being explored to improve the interaction between gas molecules and MOF walls [13, 29-32].



Fig. 1.6 (A and B) Ball-and-stick view and free dimensions (Å) of the pentagonal and hexagonal windows, (C and D) Ball-and-stick view of the two cages, chromium octahedra, oxygen, fluorine and carbon atoms are in green, red, red and blue, respectively. *Reproduced from ref.* [26] with the permission of The American Association for the Advancement of Science

1.5 Metal-organic frameworks for hydrogen storage

To meet DOE targets for the utilization of hydrogen gas for onboard mobile application, design and development of MOFs have attracted worldwide attention due to their inherent characteristics and diversity in structures. At the starting of the 21^{st} century, Yaghi and coworker were the first to explore MOF material for hydrogen storage. They developed a robust and highly porous cubic three-dimensional structure and extended the porous structure of MOF-5, having the composition of Zn₄O(BDC)₃ (BDC-1,4 benzene dicarboxylate). MOF-5 displayed higher thermal stability (300° to 400° C) and extraordinary high surface area of around 2500 to 3000 m² g⁻¹, and displayed a H₂ adsorption capacity of 4.5 wt% (at 78 K and near 1 atm), and 1.0 wt% (at room temperature and up to 20 bar pressure) [15]. This breakthrough report generated large interest between physicists and chemists to design and develop MOFs for hydrogen storage application. Hence, enormous efforts have been devoted for the investigation of hydrogen storage properties of MOFs at low temperatures (cryogenic) and ambient conditions at varying pressure range [9, 13, 15, 31-34]. The details of hydrogen storage at low temperature and ambient temperature are discussed in the following sections.

1.5.1 Low temperature (cryogenic) hydrogen storage in MOFs

At present, a large number of MOFs have been extensively explored for hydrogen gas storage. Literature revealed that most of the experimental data on hydrogen storage in MOFs are obtained at low pressure up to 1 bar and 77 K [31-34].

For high-pressure measurements, excess and absolute (or total) adsorption capacity is mainly used to describe hydrogen storage uptake in MOFs [31, 32]. For instance, recently Yaghi *et al.* demonstrated the highest H₂ uptake 86 mg g⁻¹ (excess) and 176 mg g⁻¹ (total) for newly developed MOF-210 at 77 K and 80 bar, which is higher than MOF-177 (7.5 wt%, 70 bar at 77 K) and IRMOF-20 (6.7 wt%, 80 bar at 77 K) [35, 36]. Hupp *et al.* also achieved 99.5 mg g⁻¹ (excess) at 77 K (56 bar), and 164 mg g⁻¹ (total) H₂ uptake for NU-100 at 77 K, 70 bar [37]. Ferey *et al.* reported a maximum hydrogen capacity of 3.3 wt% at 77 K (25 bar) for MIL-100, and 6.1 wt% at 77 K and 60 bar for MIL-101 [28]. Hydrogen uptake capacities evaluated for several other, pristine MOFs at low temperature 77 K are ZIF-8 (3.3 wt%, 30 bar), NOTT-103 (7.78 wt%, 60 bar), PCN-11 (5.23 wt%, 45 bar), and MIL-102 (1.0 wt%, 35 bar) [38-41]. The factors which mainly attributed to hydrogen uptake at low temperature (77 K) are surface area, pore size, porevolume, and open metal sites for pristine MOFs [31-37].

MOFs	Surface	Pore	Pressure	H_2	Ref.
	area	volume	(bar)	uptake	
	$(m^2 g^{-1})$	$(cm^{3} g^{-1})$		(wt%)	
MIL-100	2700	1.0	25	3.3	[28]
MIL-101	5500	1.9	60	6.1	
HKUST-1	1958		50	3.6	[46]
MOF-5	2296	1.19	50	4.7	
IRMOF-11	1984	0.68	35	3.5	[36]
IRMOF-6	2804	1.14	50	4.8	
IRMOF-20	4024	1.53	80	6.7	
MOF-177	4746	1.59	70	7.5	
ZIF-8			30	3.3	[38]
MIL-53(Al)	1100	0.59	16	3.8	[47]
MIL-53(Cr)	1100	0.56	16	3.1	
PCN-11	1931	0.91	45	5.23	[40]
PCN-10	1407	0.67	45	4.2	
MOF-5	3800		40	7.1	[48]
IRMOF-8	1818		15	3.6	[49]
PCN-68	5109	2.13	50	7.32	[50]
PCN-66	4000	1.63	45	6.65	
NOTT-101	2316	0.89	20	6.06	[39]
NOTT-102	2942	1.138	20	6.07	
NOTT-103	2929	1.142	60	7.78	
NOTT-105	2387	0.898	20	5.40	
MIL-102	42	0.12	35	1.0	[41]
MIL-101	2887	1.45	60	6.36	[51]
AC@MIL-101	3555	1.75	60	10.1	
MIL-101	3148	2.10	100	7.25	[45]
AC-MIL-101	3458	2.04	100	11.68	
Li@AC-MIL-101-727	2791	1.65	100	14.39	
MIL-101	2887	1.45	60	6.37	[44]
MIL-101@SWNT-8%	2998	1.36	60	9.18	

 Table 1.3 High-pressure hydrogen uptake performance at 77 K for selected porous MOFs

_

Several reports revealed that the porosity of MOFs is not fully utilized because of the weak interaction of MOF wall and gas molecules [13, 26, 29-32]. To further improve the hydrogen storage capacity of MOFs, different strategies such as impregnation, catenation, linker modification or functionalization, open metal site, and spillover effect have been explored to enhance the interaction of H₂ molecules to MOFs wall [39-35, 42, 43]. In this direction, several attempts

have been made to increase hydrogen uptake performance. For instance, singlewalled carbon nanotubes incorporated MIL-101 composite (SWNT@MIL-101) was synthesised by Jasra *et al.* to achieve an increase in H₂ storage capacity from 6.37 wt% for MIL-101 to 9.18% for SWNT@MIL-101 at 77 K and 60 bar, attributed to the generation of additional micropore volume and optimization into pore size [44]. Deschamps *et al.* developed a hybrid composite of MIL-101 by incorporating activated carbon (AC) and lithium doping at different concentrations and explored the hydrogen uptake performance. Results revealed that the optimum loading of lithium in the hybrid composite resulted in an improvement in hydrogen uptake as compared to the parent MIL-101 and hybrid composite AC-MIL-101. The observed enhancement in hydrogen uptake was attributed to the combined effect of activated carbon and doping of lithium-ion into the MOF framework [45].

Table 1.3 summarized the high-pressure hydrogen storage capacity of selected MOF at 77 K. These results inferred that despite high H_2 uptake was achived with many MOFs at 77 K, but acheving high H_2 uptake at ambient condition is still a challenge.

1.5.2 Ambient temperature hydrogen storage in MOFs

At ambient temperature, very poor hydrogen uptake performance (< 1 wt%) is observed in MOFs, because the binding energy between MOFs structure and hydrogen molecules are comparable to thermal vibration energies. Therefore, it is quite difficult to achieve high H_2 uptake performance with MOFs [31-34].

At ambient temperature, hydrogen uptake capacities for few of the pristine MOFs are MOF-5 (0.28 wt%, 65 bar), (HKUST-1 0.35 wt%, 65 bar), MIL-101 (0.43 wt%, 80 bar), MOF-5 (0.57 wt%, 100 bar) and PCN-68 (1.0 wt%, 90 bar), etc. [46, 28, 48, 50]. Several approaches are explored to improve hydrogen uptake performances of pristine MOFs at ambient condition. For instance, Yang *et al.* demonstrated improved hydrogen storage in IRMOF-1 and IRMOF-8 through bridged hydrogen spillover due to the doped metal catalysis Pt/AC at ambient conditions. Similarly, Anbia *et al.* and Park *et al.* developed Pt/CMK-3, MIL-101,

and Pt loaded CNT@MOF-5 hybrid composite and investigated hydrogen uptake performance at 298 K. Results revealed that due to the support of carbon materials and bridging, building or spillover effect plays an important role in achieving improved hydrogen uptake performance. Other strategies, such as the formation of MOFs composite with carbon-based materials and doping of metal particle and alkali metal also shown enhancement in hydrogen uptake as demonstrated by various studies. The high-pressure hydrogen storage capacity data at 298 K for selected MOFs structure are summarized in Table 1.4.

MOFs	Surface	Pore	Pressure	H_2	Ref.
	area	volume	(bar)	uptake	
	$(m^2 g^{-1})$	$(cm^{3} g^{-1})$		(wt%)	
MOF-5	2296	1.19	65	0.28	[46]
HKUST-1	1958		65	0.35	
ZIF-8			60	0.13	[38]
MIL-100	2700	1.0	73.3	0.15	[28]
MIL-101	5500	1.9	80	0.43	
MOF-5	3800		100	0.57	[48]
IRMOF-8	1818		30	0.4	[49]
PCN-68	5109	2.13	90	1.01	[50]
PCN-66	4000	1.63	90	0.785	
MIL-102	42	0.14	35	0.05	[41]
MOF-5	1810	0.271	95	0.30	[52]
MOF-MWCNT	2900	0.672	95	0.61	
MIL-101	3148	2.10	100	0.55	[45]
AC-MIL-101	3458	2.04	100	0.69	
Li@AC-MIL-101-727	2791	1.65	100	1.14	
MOF-5	757	0.45	100	0.30	[53]
Pt-MWCNT-MOF-5	1692	0.84	100	1.25	
MIL-101	2887	1.45	60	0.23	[44]
MIL-101@SWNT-8%	2998	1.36	60	0.64	
IRMOF-1	1021	0.68	100	0.4	[54]
IRMOF-1/Pt-AC	890	0.61	100	~3	
IRMOF-8	548	0.48	100	0.5	
IRMOF-8/Pt-AC	466	0.43	100	~4	
MIL-101TE	1270	1.56	20	0.55	[55]
MIL-101 TE:Pt-CMK-3	380	0.16	20	1.34	

 Table 1.4 High-pressure hydrogen uptake performance at 298 K for selected porous MOFs

1.6 Instruments for material characterisation

Instrumentation techniques are the key component to acquire qualitative and quantitative information of the structure, composition, morphology and chemical state of the materials [19, 20, 56]. This section presents a brief overview of important characterisation tool, which are used to characterise the developed MOFs in this thesis.

1.6.1 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) is a nondestructive technique, which plays a crucial role in the field of materials research. This technique is mostly used for the characterisation of crystalline materials, and it provides information related to a structural parameter such as phase, crystal structure, grain size, lattice parameter, crystallinity, crystal defects, and strain [20, 56]. In this thesis, the powder X-ray diffraction (PXRD) pattern was obtained using a Rigaku Smart Lab automated X-ray diffractometer system with monochromatic Cu K α 1 radiation (λ =1.5406 Å) at 40 kV and 30 mA, with a scan step size of 0.01° and a scan speed of 3° per minute at ambient temperature.

1.6.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique that is usually carried out to examine the thermal stability of a material. In this technique, the change in mass of a sample is monitored with the help of a thermobalance with respect to time or temperature, while the sample is heated at a constant rate [20]. In the present thesis, thermogravimetric analysis was carried out using a Mettler Toledo TGA/DSC1 instrument inflow of nitrogen gas at a heating rate of 5 °C/min from ambient temperature to 800 °C.

1.6.3 Fourier transforms infrared spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy (FTIR) is a nondestructive technique that mainly provides qualitative information of chemical bonding and molecular structure of organic compounds [20, 56]. Herein, the functional groups of adsorbents were identified by FTIR using PerkinElmer Spectrum Version 10.5.1 wavenumber (400-4000 cm⁻¹).

1.6.4 Raman spectroscopy

Raman spectroscopy quantify molecular vibrations are used to determine chemical structure, phase and polymorphism, crystallinity and molecular interaction, impurity and contamination of material [56]. Raman spectroscopic study of the developed MOFs was performed on STR 500 confocal micro Raman spectrometer (Make AIRIX Corp. Japan).

1.6.5 Elemental analysis (EA)

Elemental analysis is used to determine the elemental composition of the material. In the present study, elemental (C, H, N, and O) analyses of the samples were obtained using a Thermo Scientific analyzer.

1.6.6 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique widely used to estimate the metal ions at a low concentration level in a material [20, 56]. Herein, ICP-AES analysis was conducted using ARCONS instrument, which synchronizes with ICP spectrometer (SPECTRO, analytical instruments GmbH, Germany), with spectral wavelength range of 130 nm to 770 nm.

1.6.7 X-Ray photoelectron spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is a highly sophisticated tool used to quantify the elemental composition and chemical state of the material [20]. In the present thesis, the XPS analyses were conducted over Omicron ESCA (Electron Spectroscopy for Chemical Analysis), Oxford Instrument, Germany. Aluminum (Al) anode was used as Monochromatic X-ray energy source ~ 1486.7 eV for samples measurement, and resolution was confirmed by FWHM at about 0.60 eV. For XPS measurements, pellets of the materials were made with the help of a mechanical press.

1.6.8 Scanning electron microscope (SEM)

Scanning Electron Microscope (SEM) is an electron microscope, in which electron beam is focused across a surface of the sample, providing long depth high-resolution images of the sample surface [56]. In this thesis, the scanning electron microscopy (SEM) images were obtained using Carl Zesis Supra-55 equipment. Energy-dispersive X-ray spectroscopy (EDXS) was carried out using the EDXS Oxford instruments model X-Max attached with the Carl Zesis Supra-55 system.

1.6.9 Transmission electron microscope (TEM)

Transmission Electron Microscope (TEM) is an electron microscope, mostly used to characterise the sample morphology, crystalline structure, and elemental composition of the material. In this technique, an electron beam is transmitted through a specimen to form a high resolution of image [56]. For the present research work, the transmission electron microscopy (TEM) images and (EDXS) data was obtained using a JEOL (JEM-2100F) at operating voltage of 200 kV. Elemental mapping and line scan analysis was performed on FEI Tecnai G2, F30 TEM at an operating voltage of 200 kV. Sample preparation for TEM analysis was prepared by dispersing the material in methanol under ultrasound for 30 minutes, and a well-dispersed sample was spread over a carbon-coated Cu grid and dried at room temperature.

1.6.10 ¹³C Solid-state single pulse nuclear magnetic resonance (NMR) spectroscopy

¹³C Solid-State nuclear magnetic resonance (NMR) spectroscopy is a key tool to obtain the atomic-level structure of carbon-based materials. Based on the isotropic chemical shifts region, it provides information for aliphatic and aromatic carbons. ¹³C solid-state single pulse nuclear magnetic resonance spectra were acquired on a Jeol-ECX400, 400 MHz high resolution multinuclear FT-NMR spectrometer using 4 mm rotors spinning at a MAS frequency of vMAS=10kHz.

Relaxation delay was set for 5 s, and the number of scans were 8192 (for MIL-101) and 5120 (for C100-MIL-101 composite).

1.6.11 Nitrogen sorption isotherms

Nitrogen sorption isotherm analysis is used to evaluate pore textural properties, such as apparent surface area, pore-volume, and pore size distribution for porous materials. To obtain sorption isotherm curves non-reactive gases (N₂, Ar, and He) are used at cryogenic temperature. In general, N₂ gas sorption at cryogenic temperature (77 K) are employed to determine the pore textural characteristics of the studied material. The shapes of the isotherms curve provide valuable information about the nature of materials. The data obtained from the experimental investigation are used to the calculated apparent surface area, using different adsorption theories including Langmuir (monolayer) and BET (multilayer). To estimate pore volume (micro, meso and total) and pore size distribution, several methods such as, Non-Linear Density Functional Theory (NLDFT), Barrett-Joyner-Halenda (BJH), Dubinin-Astakhov (DA), Dubinin-Radushkevic (DR), Horvath-Kawazoe (HK), Saito-Foley (SF) and t-plot, etc. are generally applied [19, 20, 56].

Herein, the pore texture properties of the developed MOFs were measured on Quantachrome Autosorb-iQ automated gas sorption instrument using Nitrogen Sorption data obtained at 77 K. The measured isotherms were analyzed using Quantachrome® ASiQwinTM with inbuilt software for calculating the framework properties. Prior to characterisation, all the developed MOFs were activated under vacuum at the desired temperature for a specific time period.

1.6.12 Hydrogen sorption measurements

Low-pressure hydrogen sorption measurements were carried out on an Autosorb-iQ automated volumetric sorption instrument at 77 K and around 1 bar absolute pressure. High-pressure hydrogen adsorption measurements at near ambient conditions and up to 12 bar were carried out using volumetric sorption analyzer PCTPro (Setaram Instrumentation, France). Prior to adsorption isotherm measurements, samples were activated under vacuum at the desired temperature for a specific time period. After the activation process, samples were allowed to naturally be cool to room temperature. Further, the temperature of the measurement cell was maintained at the desired value using a Julabo FP 50 throughout during the hydrogen adsorption isotherm experiments.

1.7 Fundamentals of adsorption mechanism

Adsorption process refers to a surface phenomenon that causes accumulation of substance at the interface of two phases, such as solid/liquid and solid/gas. The substance accumulated on the surface of another substance is known as adsorbate, and solid surface on which adsorption takes place is called the adsorbent. Based on the interaction forces between the adsorbent and adsorbate, the adsorption process is classified as physical adsorption (or physisorption) and chemical adsorption (or chemisorption). Physisorption involves the weak van der Waals interactions of adsorbate with the adsorbent, while strong chemical interactions of adsorbate with the adsorbent play an important role in the chemisorption process [9, 33]. The following adsorption characteristics such as adsorption isotherm and equilibrium, adsorption kinetics, and adsorption thermodynamic properties are required to design and develop the adsorption based energy systems.



Fig. 1.7 Adsorption isotherms, q = f(P) at T

1.8 Adsorption equilibrium isotherm

An adsorption isotherm is a curve that expresses the variation in the amount of adsorbate adsorbed on the surface of adsorbent with the change in pressure at a constant temperature [57-59]. Adsorption equilibrium is established when an adsorbent, which is in contact with the surrounding adsorbate of a certain composition, is involved in adsorption process, the composition of adsorbent and adsorbate achieve an equilibrium state [57, 59]. In this regard, Fig. 1.7 represents, a typical adsorption isotherm, showing the relationship between the concentration of adsorbate in the adsorbent (q) with change in pressure (P), at a constant temperature (T) with the equation q = f(P) at T.

1.9 Adsorption equilibrium isotherm models

Adsorption isotherm models are described through different mathematical correlations, which provide fundamental information related to the selective adsorption process and the amount of adsorbate adsorbed under a given set of conditions [59]. The developed empirical and theoretical mathematical correlation plays an important role in the direction of modeling analysis of isotherms. These isotherm models correlated the experimental data in mathematical equations with two or three parameters. In general, three (or) multi models parameters provide a better fitting of experimental data and mathematical equation for isotherm model. In the past few years, a wide range of equilibrium isotherm models have been developed and studied to estimate adsorption kinetics, thermodynamic properties, and nature of the adsorption.

1.9.1 Two parameter isotherm models

The mathematical equation proposed by Langmuir, Freundlich, Temkin, Hill, and Dubinin-Radushkevich, are two-parameter isotherm models. A few of them used in the present thesis are discussed below [59].

1.9.1.1 *Langmuir isotherm model*

In 1916, Irving Langmuir proposed an adsorption isotherm model for gases adsorbed onto solid surface. Langmuir empirical model assumes monolayer adsorption at a finite number of localized sites and uniform distribution of adsorption over the homogenous surface [59, 60]. The non-linear Langmuir model adsorption isotherm is given as Eq. (1):

$$q_e = \frac{a_m b P_e}{1 + b P_e} \tag{1}$$

In Eq. (1), q_e is the amount of adsorbate adsorbed on adsorbent (wt%), P_e is the adsorbate pressure (bar), a_m (wt%), and b (bar⁻¹) is the Langmuir isotherm equation parameters.

1.9.1.2 Freundlich isotherm model

Freundlich empirical model describes multilayer adsorption with nonuniform distribution of adsorption over heterogeneous surface of adsorbent [59]. The adsorption isotherm of non-linear Freundlich model can be shown as Eq. (2):

$$q_e = k P_e^{\frac{1}{n}} \tag{2}$$

here, k and n are the Freundlich isotherm equation parameters that can be determined by the non-linear form of the Freundlich equation using the regression model.

1.9.2 Three parameter isotherm models

The adsorption isotherm equation established by Sips, Toth, Khan, Koble-Corrigan, and Radke-Prausnitz, are three-parameter isotherm models [59]. Few of these adsorption models used in the present thesis are elaborated below:

1.9.2.1 Toth isotherm model

Toth isotherm equation includes three parameters into an empirical model and is widely used as an improved Langmuir empirical model. Toth model is useful in predicting the heterogeneity adsorption system at low and high adsorbate concentrations [59, 61]. The non-linear Toth isotherm equation is commonly shown as (Eq. (3)):

$$q_e = \frac{k_t P_e}{\left(a_t + P_e\right)^{\frac{1}{t}}} \tag{3}$$

here, k_t , a_t , and t are the Toth isotherm equation parameters that can be determined by the Toth equation.

1.9.2.2 Sips isotherm model

Sips isotherm equation is a collective form of Langmuir and Freundlich's empirical model. At high concentration, the adsorbate equation predicts a Langmuir model, and at low concentration adsorbate, it describes the Freundlich model [59]. Sips empirical model is deduced to describe the heterogeneity of the adsorption system. The adsorption isotherm of the Sips model can be represented as Eq. (4):

$$q_e = \frac{k_s P_e^{t_s}}{1 + a_s P_e^{t_s}} \tag{4}$$

here, k_s, t_s, and a_s are the Sips isotherm equation parameters.

1.9.2.3 Multilayer physisorption isotherms

Brunauer–Emmett–Teller (BET) isotherm is a theoretical based mathematical equation, and is mostly applicable for gas/solid equilibrium state to estimate the surface area of the porous material. The specific surface area determined by the BET method, which was established by S. Brunauer, P. H. Emmett, and E. Teller (1938). In general, surface area for multilayer adsorption is determined in the relative pressure range of 0.05 to 0.30 [59, 62]. The BET equation for surface area calculation is given as Eq. (5):

$$\frac{1}{V[\left(\frac{P_0}{P}\right)-1]} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \left(\frac{P}{P_0}\right)$$
(5)

here, P is partial vapor pressure of adsorbate gas in equilibrium with surface at 77.4 K (liquid nitrogen), where at this temperature P_0 is the saturated vapor pressure of the adsorbed gas, V is volume of gas adsorbed per gram adsorbent at STP to make an apparent monolayer on the adsorbent, V_m is volume of the monolayer adsorbed gas per gram adsorbent, C is a dimensionless constant. The BET parameters obtained by the linear form of equation (5) using the plot of

$$\frac{1}{V[\left(\frac{P_0}{P}\right)-1]} \text{ against } \frac{P}{P_0}$$
Slope (s) = $\frac{C-1}{V_mC}$
Intercept (i) = $\frac{1}{V_mC}$
Solving for $V_m = \frac{1}{s+i}$

So, the total BET surface area is,

$$S_{BET} = \frac{V_m N A_m}{M_V}$$

where, N is Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), A_m is effective crosssectional area of the adsorbate molecules (0.162 nm^2 for N₂), M_v is volume occupied by 1 mole of the adsorbate gas at STP (22414 cm^3), and V_m is volume of monolayer adsorbed gas (cm³ g⁻¹).

1.10 Adsorption thermodynamics

To design and develop an adsorption-based energy system, various thermodynamic properties such as specific heat capacity, enthalpy, and entropy, isosteric heat of adsorption, Gibbs free energy, activation energy, and parameter, play a significant role. Thermodynamic properties are also helpful in predicting the mechanism of adsorption process and investigating the performance of adsorption-based systems. To investigate various adsorption thermodynamic properties, data obtained from the adsorption process, and isotherm model are helpful.

1.10.1 Isosteric heat of adsorption (Qst)

The isosteric heat of adsorption is the main indicator to evaluate the strength of the interaction force between adsorbate and adsorbent. Herein, isosteric heat of adsorption is calculated from the experimental data of adsorption isotherms at different temperature ranges. Isosteric heat of adsorption (Q_{st}) is calculated using the Clausius-Clapeyron equation from the available experimental data. The expression for the heat of adsorption is given by Eq. (6) as follows:

$$\Delta Q_{st} = -R \left[\frac{\partial \ln(P)}{\partial (\frac{1}{T})} \right]_{n}$$
(6)

here, P is pressure, T is temperature, n is the specific amount of gas adsorbed, and R is the universal gas constant. In the present study, the calculation performed with two adsorption isotherms measured at 77 K and 298 K with a suitable pressure range, and the amount of gas adsorbed (n) [38, 45].

1.11 Validation of adsorption isotherm equation

To determine the best fitting of the isotherm model into experimental adsorption data, validation of adsorption isotherm equation is necessary [59]. Various equations (expressed below) are used to validate the adsorption isotherm models equation.

1.11.1 Normalize standard deviation

The adsorption isotherm equation is used to validate based upon the values obtained for normalize standard deviation (ΔQ) and the coefficient of correlation (R^2) [59]. This can be represented as Eq. (7)

$$\Delta Q = 100 \sqrt{\frac{\sum [(q-q_e)/q]^2}{N-1}}$$
(7)

where, q and q_e are the adsorption capacities obtained from experiment and isotherm model, respectively, and N is the number of adsorption isotherm data points.

1.11.2 Average relative error

Average relative error (ARE) and the value of the coefficient of correlation (R^2) is used to validate the adsorption isotherm equation [59]. ARE can be represented as Eq. (8)

$$ARE = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q - q_e}{q} \right|$$
(8)

where, q and q_e are the adsorption capacities obtained from experiment and isotherm model, respectively, and N is the number of adsorption isotherm data points.

1.12 Motivation for the present research work

To accomplish high H₂ uptake over MOFs, various techniques are explored to fine-tune the morphology and topology of the MOFs. In this context, functionalization of organic linkers, incorporation of metal nanoparticles, suitable cations, or post-modification (composites) over single-metal MOFs has been widely investigated [31, 33, 42, 43]. Among several strategies, mixed metals or bimetallic MOFs designed by introducing new secondary metal ions/clusters into single-metal MOFs have been identified as one of the most facile routes to construct new materials with tuned properties [22, 63].

Among a wide range of MOFs explored, MIL-101 has received the utmost attention. Advantageously, MIL-101 displayed several promising features such as mesoporous zeotype structure with MTN topology, giant cell volume, high BET surface area, excellent thermal and chemical stability over a wide range of temperature and moisture conditions, and availability of unsaturated Cr metal sites. Though the large pore volume and unsaturated open metal sites available in MOFs are important factors to achieve high gas storage properties, the weak interaction of MOF walls and H₂ molecules adversely affect the H₂ adsorption properties of MOF, resulting in under-utilized of large pore volumes [26-29]. In the present thesis, different approaches have been employed achieve enhanced H₂ uptake: (i) Inducing *in situ* hydrothermal carbonization of glucose to synthesise carbon-MIL-101 hybrid composites, (ii) developed silica-rich MIL-101(Cr) hybrid composite and (iii) silica-rich MIL-101(Cr) hybrid composite doped with lithium metal ion for improving the interaction between gas molecules and MOF wall. Moreover, literature revealed that bimetallic ZIFs possess improved physical and chemical properties compared to the single-metal ZIFs, and therefore it is obvious to understand why these bimetallic ZIFs are being extensively explored for wide applications, including potential materials for enhanced gas storage [22, 63, 64]. Despite these encouraging findings, there are still several considerable challenges associated with the development and utilization of such bimetallic materials, such as fragile yields of the framework, segregation of metals, and unpredicted topologies and functionalities of bimetallic MOFs for advanced applications in gas storage and separation. In this thesis, we developed bimetallic core-shell ZIFs to overcome these short comings and to achieve enhanced H₂ uptake properties.

1.13 Objectives and scope of the present research work

The present thesis makes an attempt to address recent improvements in the development of metal-organic frameworks (MOFs) structure (mono-bi metallic, hybrid composite and core-shell structure) for solid-state hydrogen storage and its related applications. Therefore, considering the literature available for research reports in the area of development of MOFs for H_2 storage application, the following objectives are set for the present research work:

- To address the several challenges associated with bimetallic MOFs structure for gas storage application, synthesise core-shell MOFs, as an effective alternative way to tune and introduce new properties in MOFs and consequently to improve their performance for gas storage.
- To employ under-utilized large pore volume and unsaturated open metal sites available in MOFs for improved H₂ uptake, synthesise carbon-MIL-101 hybrid composites by inducing *in situ* hydrothermal carbonizations of glucose.
- To provide a better alternative for the established carbon-based MOFs composites for gas storage applications, utilize an inexpensive and waste by-product of the rice industry (silica-rich rice husk ash-RHA) to incorporate in MIL-101.

• To enhance the interaction of MOF wall and H₂ molecules by developing Li⁺ doped MOFs hybrid composite and investigate its H₂ uptake behavior.

1.14 Structure of the present thesis

The structure of the present thesis is as follows:

Chapter 1 discusses the introduction of hydrogen storage methods and materials, fundamentals of metal-organic frameworks, and their salient features, physical and chemical characteristics of MOFs, and the potential applications of MOFs. This chapter also summarizes the performance of different MOF structures for hydrogen storage and its related applications.

Chapter 2 presents the development of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks to achieve an unprecedented enhancement in H_2 storage, as compared to the monometallic ZIF-8 and ZIF-67 and the physical mixture of parent ZIFs, attributed to the core-shell morphology and the tuned porosity of the synthesised materials. These core-shell ZIFs also display improved CO₂ capture properties.

Chapter 3 describes the synthesis of carbon-MIL-101 hybrid composite by advantageously inducing *in situ* hydrothermal carbonizations (HTC) of glucose during the synthesis of MIL-101. Optimum incorporation of carbon content in MIL-101 induces significant tuning of porosity and textural properties of the carbon-MIL-101 hybrid composite to achieve enhanced hydrogen uptake.

Chapter 4 demonstrates the synthesis of hybrid composite of MIL-101(Cr) with silica-rich rice husk ash (RHA) by *in situ* incorporation of RHA and shows the improved low-pressure H_2 uptake capacities at 77 K and 1 bar, which is higher than the bare MIL-101 and comparable to most of the well-explored carbon-based MOF composites and other analogous systems.

Chapter 5 presents the enhanced hydrogen uptake achieved for RHA incorporated MIL-101 by controlled doping of Li^+ ion. Studies evidence that the content of Li^+ ion doping greatly influence the hydrogen uptake properties, attributed to the favorable Li^+ ion to H₂ interactions and the effect of silanol bonds of silica-rich rice-husk ash incorporated in MIL-101.

Chapter 6 summarizes the work presented in this thesis and the possible future work and scope.

1.15 References

- Turner J.A. (1999), A Realizable Renewable Energy Future, Science, 285, 687-689.
- [2] Schlapbach L., Zuttel A. (2001), Hydrogen-Storage Materials for Mobile Applications, Nature, 414, 353-358.
- [3] Van den Berg A.W.C., Arean C.O. (2008), Materials for Hydrogen Storage: Current Research Trends and Perspectives, Chem. Commun., 6, 668-681.
- [4] Durbin D.J., Malardier-Jugroot C. (2013), Review of Hydrogen Storage Techniques for on Board Vehicle Applications, Int. J. Hydrogen Energy, 38, 14595-14617.
- [5] Niaz S., Manzoor T., Pandith A.H. (2015), Hydrogen Storage: Materials, Methods and Perspectives, Renew. Sustain. Energy Rev, 50, 457-469.
- [6] www.energy.gov/sites/prod/files/2017/05/f34/fcto_targets_onboard_hydro
 storage explanation.pdf
- [7] Farrusseng D. (2011), Research Status of Metal-Organic Frameworks for On-Board Cryo-Adsorptive Hydrogen Storage Applications, Dailly A.
 Metal-Organic Frameworks: Applications from Cataysis to Gas storage, First Edition, Wiley-VCH Verlag GmbH & Co. KGaA, pp 151-169.
- [8] Zuttel A. (2003), Materials for Hydrogen Storage, Mater. Today, 6, 24-33.
- [9] Suh M.P., Park H.J., Prasad T.K., Lim D.W. (2012), Hydrogen Storage in Metal-Organic Frameworks, Chem. Rev., 112, 782-835.

- [10] Lim K.L., Kazemianl H., Yaakob Z., Daud W.R.W. (2010), Solid-state Materials and Methods for Hydrogen Storage: A Critical Review, Chem. Eng. Technol., 33, 213-226.
- [11] Felderhoff M., Weidenthaler C., Helmoltb R.V., Eberleb U. (2007), Hydrogen Storage: The Remaining Scientific and Technological Challenges, Phys. Chem. Chem. Phys., 9, 2643-2653.
- [12] Yaghi O.M., O'Keeffe M., Ockwig N.W., Chae H.K., Eddaoudi M., Kim J. (2003), Reticular Synthesis and the Design of New Materials, Nature, 423, 705-714.
- [13] Rowsell J.L.C., Yaghi O.M. (2005), Strategies for Hydrogen Storage in Metal-Organic Frameworks, Angew. Chem., Int. Ed., 44, 4670-4679.
- [14] Stock N., Biswas S. (2012), Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites, Chem. Rev., 112, 933-969.
- [15] Rosi N.L., Eckert J., Eddaoudi M., Vodak D.T., Kim J., O'Keeffe M., Yaghi O.M. (2003), Hydrogen Storage in Microporous Metal-Organic Frameworks, Science, 300, 1127-1129.
- [16] Lee Y.R., Kim J., Ahn W.S. (2013), Synthesis of Metal-Organic Frameworks: A Mini Review, Korean J. Chem. Eng., 30, 1667-1680.
- [17] Furukawa H., Cordova K.E., O'Keeffe M., Yaghi O.M. (2013), The Chemistry and Applications of Metal-Organic Frameworks, Science, 341, 1230444.
- [18] Kuppler R.J., Timmons D.J., Fang Q.R., Li J.R., Makal T.A., Young M.D., Yuan D., Zhao D., Zhuang W., Zhou H.C. (2009), Potential Applications of Metal-Organic Frameworks, Coord. Chem. Rev., 253, 3042-3066.
- [19] Butova V.V., Soldatov M.A., Guda A.A., Lomachenko K.A., Lamberti C. (2016), Metal-Organic Frameworks: Structure, Properties, Methods of Synthesis and Characterization, Russ. Chem. Rev., 85, 280-307.

- [20] Howarth A.J., Peters A.W., Vermeulen N.A., Wang T.C., Hupp J.T., Farha O.K. (2016), Best Practices for the Synthesis, Activation, and Characterization of Metal-Organic Frameworks, Chem. Mater., 29, 26-39.
- [21] Chen B., Yang Z., Zhu Y., Xia Y. (2014), Zeolitic Imidazolate Framework Materials: Recent Progress in Synthesis and Applications, J. Mater. Chem. A, 2, 16811-16831.
- [22] Eddaoudi M., Sava D.F., Eubank J.F., Adil K., Guillerm V. (2015), Zeolite-like Metal-Organic Frameworks (ZMOFs): Design, Synthesis, and Properties, Chem. Soc. Rev., 44, 228-249.
- [23] Park K.S., Ni Z., Cote A.P., Choi J.Y., Huang R., Uribe-Romo F.J., Chae H.K., O'Keeffe M., Yaghi O.M. (2006), Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks, Proc. Natl. Acad. Sci. USA., 103, 10186-10191.
- [24] Hayashi H., Cote A.P., Furukawa H., O'Keeffe M., Yaghi O.M. (2007),Zeolite a Imidazolate Frameworks, Nat. Mater., 6, 501-506.
- [25] Banerjee R., Phan A., Wang B., Knobler C., Furukawa H., O'Keeffe M., Yaghi O.M. (2008), High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO₂ Capture, Science, 319, 939-943.
- [26] Ferey G., Draznieks C.M., Serre C., Millange F., Dutour J., Surble S., Margiolaki I. (2005), A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area, Science, 309, 2040-2042.
- [27] Jhung S.H., Lee J.H., Yoon J.W., Serre C., Ferey G., Chang J.S. (2007), Microwave Synthesis of Chromium Terephthalate MIL-101 and Its Benzene Sorption Ability, Adv. Mater., 19, 121-124.
- [28] Latroche M., Surble S., Serre C., Mellot-Draznieks C., Llewellyn P.L., Lee J.H., Chang J.S., Jhung S.H., Ferey G. (2006), Hydrogen Storage in the Giant Pore Metal-Organic Frameworks MIL-100 and MIL-101, Angew. Chem., Int. Ed., 45, 8227-8231.
- [29] Hong D.Y., Hwang Y.K., Serre C., Ferey G., Chang J.S. (2009), Porous Chromium Terephthalate MIL-101 with Coordinatively Unsaturated Sites:

Surface Functionalization, Encapsulation, Sorption and Catalysis, Adv. Funct. Mater, 19, 1537-1552.

- [30] Hwang Y.K., Hong D.Y., Chang J.S., Jhung S.H., Seo Y.K., Kim J., Vimont A., Daturi M., Serre C., Ferey G. (2008), Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation, Angew. Chem., Int. Ed., 47, 4144-4148.
- [31] Sculley J., Yuan D., Zhou H.C. (2011), The Current Status of Hydrogen Storage in Metal-Organic Frameworks – Updated, Energy Environ. Sci., 4, 2721-2735.
- [32] Murray L.J., Dinca M., Long J.R. (2009), Hydrogen Storage in Metal-Organic Frameworks, Chem. Soc. Rev., 38, 1294-1314.
- [33] Langmi H.W., Ren J., North B., Mathe M., Bessarabov D. (2014), Hydrogen Storage in Metal-Organic Frameworks: A Review, Electrochim. Acta, 128, 368-392.
- [34] Hu Y.H., Zhang L. (2010), Hydrogen Storage in Metal-Organic Frameworks, Adv. Mater., 22, E117-E130.
- [35] Furukawa H., Ko N., Go Y.B., Aratani N., Choi S.B., Choi E., Yazaydin A.O., Snurr R.Q., O'Keeffe M., Kim J., Yaghi O.M. (2010), Ultrahigh Porosity in Metal-Organic Frameworks, Science, 329, 424-428.
- [36] Wong-Foy A.G., Matzger A.J., Yaghi O.M. (2006), Exceptional H₂ Saturation Uptake in Microporous Metal-Organic Frameworks, J. Am. Chem. Soc., 128, 3494-3495.
- [37] Farha O.K., Yazaydin A.O., Eryazici I., Malliakas C.D., Hauser B.G., Kanatzidis M.G., Nguyen S.T., Snurr R.Q., Hupp J.T. (2010), De Novo Synthesis of a Metal-Organic Framework Material Featuring Ultrahigh Surface Area and Gas Storage Capacities, Nat. Chem., 2, 944-948.
- [38] Zhou W., Wu H., Hartman M.R., Yildirim T. (2007), Hydrogen and Methane Adsorption in Metal-Organic Frameworks: A High-Pressure Volumetric Study, J. Phys. Chem. C, 111, 16131-16137.
- [39] Lin X., Telepeni I., Blake A.J., Dailly A., Brown C.M., Simmons J.M., Zoppi M., Walker G.S., Thomas K.M., Mays T.J., Hubberstey P., Champness N.R., Schrode M. (2009), High Capacity Hydrogen Adsorption in Cu(II) Tetracarboxylate Framework Materials: The Role of Pore Size, Ligand Functionalization, and Exposed Metal Sites, J. Am. Chem. Soc., 131, 2159-2171.
- [40] Wang X.S., Ma S., Rauch K., Simmons J.M., Yuan D., Wang X., Yildirim T., Cole W.C., López J.J., Meijere A.D., Zhou H.C. (2008), Metal-Organic Frameworks Based on Double-Bond-Coupled Di-Isophthalate Linkers with High Hydrogen and Methane Uptakes, Chem. Mater., 20, 3145-3152.
- [41] Surble S., Millange F., Serre C., Duren T., Latroche M., Bourrelly S., Llewellyn P.L., Ferey G. (2006), Synthesis of MIL-102, a Chromium Carboxylate Metal-Organic Framework, with Gas Sorption Analysis, J. Am. Chem. Soc., 128, 14889-14896.
- [42] Zhu Q.L., Xu Q. (2014), Metal-Organic Framework Composites, Chem. Soc. Rev., 43, 5468-5512.
- [43] Liu X.W., Sun T.J., Hu J.L., Wang S.D. (2016), Composites of Metal-Organic Frameworks and Carbon-Based Materials: Preparations, Functionalities and Applications, J. Mater. Chem. A, 4, 3584-3616.
- [44] Prasanth K.P., Rallapalli P., Raj M.C., Bajaj H.C., Jasra R.V. (2011), Enhanced Hydrogen Sorption in Single Walled Carbon Nanotube Incorporated MIL-101 Composite Metal-Organic Framework, Int. J. Hydrogen Energy, 36, 7594-7601.
- [45] Prabhakaran P.K., Deschamp J. (2015), Doping Activated Carbon Incorporated Composite MIL-101 using Lithium: Impact on Hydrogen Uptake, J. Mater. Chem. A, 3, 7014-7021.
- [46] Panella B., Hirscher M., Putter H., Müller U. (2006), Hydrogen Adsorption in Metal-Organic Frameworks: Cu-MOFs and Zn-MOFs Compared, Adv. Funct. Mater., 16, 520-524.
- [47] Ferey G., Latroche M., Serre C., Millange F., Loiseau T., Percheron-Guégan A. (2003), Hydrogen Adsorption in the Nanoporous Metal-

Benzenedicarboxylate $M(OH)(O_2C-C_6H_4-CO_2)$ (M = Al³⁺, Cr³⁺), MIL-53, Chem. Commun., 14, 2976-2977.

- [48] Kaye S.S., Dailly A., Yaghi O.M., Long J.R. (2007), Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn₄O (1,4-Benzenedicarboxylate)₃ (MOF-5), J. Am. Chem. Soc., 129, 14176-14177.
- [49] Dailly A., Vajo J.J., Ahn C.C. (2006), Saturation of Hydrogen Sorption in Zn Benzenedicarboxylate and Zn Naphthalenedicarboxylate, J. Phys. Chem. B, 110, 1099-1101.
- [50] Yuan D., Zhao D., Sun D., Zhou H.C. (2010), An Isoreticular Series of Metal-Organic Frameworks with Dendritic Hexacarboxylate Ligands and Exceptionally High Gas-Uptake Capacity, Angew. Chem., Int. Ed., 49, 5357-5361.
- [51] Rallapalli P.B.S., Raj M.C., Patil D.V., Prasanth K.P., Somani R.S., Bajaj H.C. (2013), Activated Carbon@MIL-101(Cr): A Potential Metal-Organic Framework Composite Material for Hydrogen Storage, Int. J. Energy Res., 37, 746-753.
- [52] Yang S.J., Choi J.Y., Chae H.K., Cho J.H., Nahm K.S., Park C.R. (2009), Preparation and Enhanced Hydrostability and Hydrogen Storage Capacity of CNT@MOF-5 Hybrid Composite, Chem. Mater., 9, 1893-1897.
- [53] Yang S.J., Cho J.H., Nahm K.S., Park C.R. (2010), Enhanced Hydrogen Storage Capacity of Pt-Loaded CNT@MOF-5 Hybrid Composites, Int. J. Hydrogen Energy, 35, 13062-13067.
- [54] Li Y., Yang R.T. (2006), Hydrogen Storage in Metal-Organic Frameworks by Bridged Hydrogen, J. Am. Chem. Soc., 128, 8136-8137.
- [55] Anbia M., Mandegarzad S. (2012), Enhanced Hydrogen Sorption on Modified MIL-101 with Pt/CMK-3 by Hydrogen Spillover Effect, J. Alloy Compd., 532, 61-67.
- [56] R. Kohli, K.L. Mittal, (2012) Developments in Surface Contamination and Cleaning, Detection, Characterization, and Analysis of Contaminants, Elsevier, Chapter 3, pp 107-178 (ISBN:978-1-4377-7883-0).

- [57] M. Suzuki, (1990) Adsorption Engineering, Elsevier Science Publishers, Tokyo.
- [58] D.D. Do, (1998) Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London.
- [59] Foo K.Y., Hameed B.H. (2010), Insights into the Modeling of Adsorption Isotherm Systems, Chem. Eng. J., 156, 2-10.
- [60] Langmuir I. (1916), The Constitution and Fundamental Properties of Solids and Liquids, J. Am. Chem. Soc., 38, 2221-2295.
- [61] Toth J. (1995), Uniform Interpretation of Gas/Solid Adsorption, Adv. Colloid Interface Sci, 55, 1-239.
- [62] Brunauer S., Emmett P.H., Teller E. (1938), Adsorption of Gases in Multimolecular Layers, J. Am. Chem. Soc., 60, 309-319.
- [63] Kaur G., Rai R.K., Tyagi D., Yao X., Li P.Z., Yang X.C., Zhao Y., Xu Q., Singh S.K. (2016), Room-Temperature Synthesis of Bimetallic Co-Zn Based Zeolitic Imidazolate Frameworks in Water for Enhanced CO₂ and H₂ Uptakes, J. Mater. Chem. A, 4, 14932-14938.
- [64] Yang X., Xu Q. (2017), Bimetallic Metal-Organic Frameworks for Gas Storage and Separation, Cryst. Growth Des., 17, 1450-1455.

Chapter 2

Core-Shell Zeolitic Imidazolate Frameworks: Synthesis, Characterisation and Hydrogen Storage

2.1 Introduction

For the hydrogen storage application, metal-organic frameworks (MOFs) generated great attention because of their exceptional physical and chemical characteristics such as high specific surface area, large porosity, and excellent thermal and chemical stability in various environments [1-5]. In this context, one of the widely explored MOFs is zeolite imidazolate frameworks (ZIFs), as they find various advanced properties for diverse applications in energy storage, gas adsorption and separation, catalysis, and so on [6-19]. In the recent past, a wide range of chemically distinct ZIFs were investigated, in which ZIF-8 [Zn(Hmim)₂] and ZIF-67 $[Co(Hmim)_2]$ frameworks have been extensively explored [6, 7, 12, 20, 21]. For gas storage applications over ZIF, various strategies are explored to effectively fine-tune the morphology and topology of ZIFs structure. In this context, functionalization of organic linker or post modification (composites) over single metal ZIFs has been widely investigated, albeit with limited results [6-9, 13-19, 22-25]. Among several strategies, mixed metal or bimetallic MOFs designed by introducing new secondary metal ions/cluster into single metal MOFs have been identified as one of the most facile routes to construct new materials with tuned properties. For instance, Botas et al. first time experimentally reported in situ substitution of Zn^{2+} ions in IRMOF-1 (MOF-5) by Co^{2+} (Co/Zn \leq 1:4), and achieved higher adsorption capacities of H₂, CO₂ and CH₄ at high pressure (up to 10 bar), where incorporation of Co^{2+} was expected to provide more assessable sites to gas molecules from unexposed metal sites [26]. Kaung et al. synthesised Co-doped ZnO ($Zn_{1-x}Co_xO$, x = 0.03, 0.05 and 0.10) for the development of diluted magnetic semiconductors [27]. Yamauchi et al. used a bimetallic ZIF $(Co_x, Zn_{1-x}(MeIm)_2)$ as template for the synthesis of highly porous carbon

materials [28]. Recently, we have also synthesised highly robust bimetallic $Co_x Zn_{100-x}$ -ZIF-8 (x = 25, 50, 75 and 90%), where $Co_{75} Zn_{25}$ -ZIF-8 displayed superior H₂ and CO₂ uptakes at 77 K and 298 K, respectively, at 1 bar. We demonstrated that by varying Co/Zn content in the bimetallic Co/Zn-ZIF, chemical heterogeneity and porosity can be fine-tuned and hence excellent gas uptake can be achieved [29]. Very recently, Verpoort et al. also reported similar bimetallic Zn/Co zeolitic imidazolate frameworks for gas (N₂, CO₂ and CH₄) sorption application and catalysis conversion of CO₂ to cyclic carbonates [30]. These recent findings displayed that bimetallic ZIF frameworks possesses improved physical and chemical properties compared to single metal ZIFs, and therefore it is obvious to understand why these bimetallic ZIF frameworks are being extensively explored for wide applications, including as potential materials for enhanced gas storage [26-30]. Despite these encouraging findings, there are several considerable challenges for the development and utilization of such bimetallic materials, as appropriately discussed by Xu et al., such as fragile yields of the framework, segregation of metals, unpredicted topologies and functionalities of bimetallic MOFs for advanced application in gas storage and separation [31].

In contrary to bimetallic MOFs, core-shell MOFs has shown considerably high potential to overcome some of the above highlighted challenges [31], for instance, intrinsic structural components of the participating MOFs remains intact and well understood for core-shell MOFs. Therefore, construction of such core-shell MOFs could be an effective alternative way to tune or introduce new fascinating properties in MOFs [32], and consequently to improve their performance for various advanced applications, in particular for gas storage and separation. Earlier reports in this direction demonstrated the potential of core-shell MOFs for wide application [32-39]. Rosi *et al.* reported a porous bio-MOF-11/14@bio-MOF-14 framework, which exhibited an enhanced CO₂ uptake (58.3 cm³ g⁻¹) compared to the parent bio-MOF-14 (44.8 cm³ g⁻¹) [33]. Facile construction of IRMOF-3@MOF-5, MOF-5@IRMOF-3@MOF-5 and their reversed structures with similar topology were also reported [34]. Szilagyi *et al.*

described the synthesis of IRMOF-2@MOF-5, Janus MOF-5@IRMOF-2 and vice *versa* and explored these MOFs for H_2 uptake (up to 25 bar) [35]. Yamauchi *et al.* also constructed ZIF-8@ZIF-67 frameworks and utilized these frameworks as a template to synthesise functionalized nanoporous hybrid carbon materials for electrochemical analysis [36]. A similar ZIF-67@ZIF-8 framework was reported by Li et al., which was transformed into Pd@H-Zn/Co-ZIF to achieve an enhanced catalytic activity for semi-hydrogenation of acetylene [37]. Feng et al. described a new approach, instead of seed-mediated growth, for the construction of multilayered core-shell ZIF-8@ZIF-67 and ZIF-8@ZIF-67@ZIF-8 structures. They demonstrated that under controlled slow nucleation process, double layered core-shell of ZIF-8@ZIF-67 and ZIF-67@ZIF-8 framework with the thick shell can be synthesised at room temperature [38]. Core-shell MIL-101@UiO-66 was also reported to show a significant enhancement in H_2 uptake (26% and 60%, as compared to the parent MIL-101 and UiO-66 respectively) [39]. Although coreshell MOFs displayed significantly improved properties than the parent MOFs, surprisingly, application of core-shell ZIF@ZIF was not explored extensively for gas storage application.

Herein, we synthesised core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks by a seed-mediated growth method, while keeping the Co-to-Zn molar ratio of ~0.50 for both the core-shell structures. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images, TEM-energy-dispersive X-ray spectrometry (EDXS) line scanning, and elemental mapping were probed to establish the core-shell structures, whereas X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses confirmed the electronic state and the molar composition of Zn and Co elements in the core-shell ZIFs. Core-shell ZIFs possesses unprecedented tuned framework properties (surface area, pore volume and pore size distribution). Remarkably, enhanced H₂ storage properties were achieved over the core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks, which is significantly higher than the parent ZIF-8. The obtained experimental data were fitted well with the Langmuir adsorption equilibrium isotherm model.

Moreover, core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks also displayed improved CO_2 capture properties compared to either of the parent ZIFs. To the best of our knowledge, the observed impressive H₂ storage and improved CO_2 capture are amongst the best reported till date, within the analogous class of core-shell ZIFs.

2.2 Experimental section

2.2.1 Chemicals and reagents

All these Chemical and reagents were analytical grade and used as delivered without further purification. These chemicals included Basolite[®] Z1200 (2-Methylimidazole zinc salt (ZIF-8), Sigma-Aldrich), cobalt (II) chloride hexahydrate (CoCl₂.6H₂O, 97-102% assay (by complexometry), Loba Chemie), zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O, \geq 96.0% assay, Merck), Polyvinylpyrrolidone ((C₆H₉NO)_n, Sigma-Aldrich) and 2-Methylimidazole (Hmim, 99% assay, Sigma-Aldrich). Acetone ((CH₃)₂CO, \geq 99%), methanol (CH₃OH, 99.7%) and distilled water obtained from Merck. Highly pure Certified He, N₂, CO₂ and H₂ gases used for the adsorption measurements are purchase from Inox air product Ltd, India.

2.2.2 Preparation of core-shell ZIF-8@ZIF-67 framework

The core-shell framework of ZIF-8@ZIF-67 was fabricated via adopting the seed-mediated growth method (Fig. 2.1a) as followed by Yamauchi *et al.* with minor modifications [36]. In this work, a commercially available Basolite[®] Z1200 seeds (known as ZIF-8 purchased from Sigma-Aldrich) were utilized as seed. Initially, 0.160 g of ZIF-8 seeds was dissolved in 20 mL methanol under ultrasound for 20 min at ambient temperature. 0.354 g CoCl₂·6H₂O and 1.790 g 2-Methylimidazole separately dissolved in 6 mL methanol solution. After forming a uniform solution of CoCl₂·6H₂O and 2-methylimidazole in methanol were stepwise injected into the core solution. Then the mixture was stirred for another 20 min and transferred to a 50 mL Teflon-lined autoclave. The mixture heated at 373 K for 12 h. The autoclave was allowed to cool to ambient temperature. The resultant ZIF-8@ZIF-67 solid was collected by centrifugation at 8000 rpm for 15 min. The obtained solid residue was washed with methanol for several times, collected by centrifugation at 8000 rpm for 8 min, and dried under vacuum at 373 K overnight. Typical elemental analysis showed the following composition: C: 47.88 wt%; H: 5.49 wt% and N: 22.64 wt%.

2.2.3 Preparation of core-shell ZIF-67@ZIF-8 framework

The ZIF-67@ZIF-8 core-shell framework prepared according to earlier reported seed-mediated growth method (Fig. 2.1a) by Li *et al.* with minor changes [37]. Initially, a homogenous methanolic solution of CoCl₂·6H₂O (1.092 g in 15 mL methanol) and 2-methylimidazole (1.232 g in 30 mL methanol) was prepared under ultra-sonication for 2 min at 313 K. In next step, a methanolic solution of Zn(NO₃)₂·6H₂O (1.116 g in 15 mL methanol) stepwise injected into above-prepared core solution. Then the mixture was ultra-sonicated for 20 minutes at ambient temperature. Finally, the resultant solid of ZIF-67@ZIF-8 was collected *via* centrifugation at 8000 rpm for 15 min. The solid residue was washed with methanol for several times and collected by centrifugation at 8000 rpm for 8 min and dried under vacuum at 373 K overnight. Typical elemental analysis showed the following composition: C: 47.86 wt%; H: 5.39 wt% and N: 22.73 wt%.

2.2.4 Preparation of ZIF-67 framework

ZIF-67 [Co(Hmim)₂] synthesised according to the previously reported procedure of Jing Yamauchi *et al* [36]. 519 mg CoCl₂.6H₂O, 2630 mg 2-Methylimidazole and 600 mg polyvinylpyrrolidone (PVP) first well dispersed in 80 mL methanol under stirring for 30 min at ambient temperature. Then the reaction mixture was kept at ambient temperature for overnight. The bright purple color mixture of ZIF-67 was collected by centrifugation at 8000 rpm for 15 min. The obtained solid residue was washed with methanol for several times, collected by centrifugation at 8000 rpm for 8 min, and dried under vacuum at 373 K overnight.

2.2.5 Preparation of physical mixture of ZIF-8+ZIF-67 frameworks

A physical mixture of ZIF-8 and ZIF-67 was prepared by mixing the commercial available ZIF-8 and synthesised ZIF-67 in Co:Zn molar ratio of 0.50, to meet with the ICP-AES analysis for ZIF-8@ZIF-67 (Co/Zn = 0.51) and ZIF-67@ZIF-8 (Co/Zn = 0.54). The physical mixture was further dried under vacuum at 373 K overnight.

2.2.6 Issues and challenges encountered while conducting experimental work

To ensure high purity and crystalline nature of material, removal of unreacted organic ligand/linker and metal salt impurity is necessary. In this regard, exploring an optimum condition of repeated and subsequent washing and solvent exchange process is required and is a challenging task. Moreover, applying this process also affect the yield and properties of syntthesised materials.

2.3 Material characterisation

The powder X-ray diffraction (PXRD) pattern for the samples was obtained using a Rigaku Smart Lab automated X-ray diffractometer system with monochromatic CuK α_1 radiation ($\lambda = 1.540593$ Å) at 40 kV and 30 mA. The diffraction angle in the range of 5-40° with a scan speed of 3° per minute and scan step size 0.01°. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC1 instrument; approximately 8 mg samples heated at a rate of 5 °C min⁻¹ from room temperature to 800 °C. The morphology of the sample was characterised using a Carl Zesis Supra-55 Scanning electron microscopic (FEG-TEM) image and energy dispersive X-ray spectrometer (EDXS) measurement was carried out with the help of a JEOL (JEM-2100F) at operating voltage of 200 kV. Elemental mapping and line scan analysis performed on FEI Tecnai G2, F30 TEM with operating voltage of 200 kV. The sample prepared for analysis was dispersed into methanol under ultrasound for 30 minutes. Then the well-dispersed sample was spread over carbon-coated Cu grid

and dried at room temperature. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique utilized for estimate metal ion at a low level. ICP-AES analysis conducted with the help of ARCONS instrument which synchronizes with ICP spectrometer (SPECTRO, analytical instruments GmbH, Germany) to the system. For estimation of Zn^{2+} and Co^{2+} metal ion sample was digested into 20 mL aqua regia solution. The UV-vis spectra studies have been performed on an Agilent Cary 60 spectrophotometer in the range 200-800 nm wavelength. The X-ray photoelectron spectroscopy (XPS) analysis technique measured the electronic state of the elements present into a core-shell framework structure. The XPS analysis conducted with the help of AXIS supra (Make: Kratos Analytical, UK) instrument. For measurement of XPS analysis small size of the pellet made with the help of the mechanical press. The framework structure dried at 393 K for 8 h under vacuum condition before performing XPS measurement. Initially, a wide scan of spectrum survey was carried out to pass energy at 160 eV, resolution 2 eV for core-shell structure. For knowing the electronic state of main elements (Zn^{2+} and Co^{2+}), the high-resolution scan was performed to pass energy at 20 eV and 0.5 eV resolutions. The functional groups of core-shell frameworks were identified by Fourier transform infrared spectroscopy (FTIR) using instruments of PerkinElmer Spectrum Version 10.5.1 in the 400-3000 cm⁻¹ range of wave number. The samples were dried under vacuum condition at 393 K for 12 h before the FTIR measurement. The elemental analysis of the core-shell framework was obtained using a Thermo Scientific analyzer. The N_2 adsorption-desorption isotherm of samples was performed using a Qunatachrom Autosorb-iQ automated volumetric sorption instrument at 77 K. The Brunauer-Emmett-Teller (BET) and Langmuir surface area calculated in the relative pressure range of 0.05 to 0.25. The total pore volume has measured at point $P/P_0 = 0.99$ using N₂ adsorption-desorption isotherm data. The pore size distribution was estimated based on the NLDFT theory. The sample was outgassed at 393 K for 12 h under ultra-high vacuum condition, before each measurement.

2.3.1 Evaluation of H₂ storage and CO₂ capture performance

The H₂ storage and CO₂ capture adsorption isotherms for core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 along with the parent ZIF-8, ZIF-67 and the physical mixture of ZIF-8+ZIF-67 were measured using the static volumetric technique by an apparatus from Qunatachrom Autosorb-iQ. The low pressure (~ 1 bar) H₂ gas adsorption isotherm was measured at 77 K, 298 K and CO₂ gas adsorption isotherm data was collected at 298 K. Before gas adsorption measurements the samples were dried at 393 K under vacuum for 12 h.

2.3.2 Adsorption equilibrium isotherm model

The experimental results and interaction over the surface (homogenous/heterogeneous) of gas molecules and behavior of interaction (monolayer/multilayer) were validated through the Langmuir and Freundlich isotherm equations at low pressure region (detailed in section 1.9.1.1 and 1.9.1.2). Langmuir equation assumes monolayer adsorption at finite number of localized sites and uniform distribution of adsorption over homogenous surface. The H₂ and CO₂ gas adsorption isotherm data of ZIF-8, ZIF-8@ZIF-67, ZIF-67@ZIF-8, and ZIF-67 at 77 K and 298 K respectively, used for the present model.

2.4 **Results and discussion**

2.4.1 Synthesis and morphology characteristics of core-shell ZIFs

Core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks were synthesised by a seed-mediated growth methodology under the solvothermal condition, as illustrated in Fig. 2.1a. Freshly prepared ZIF-67 seeds and commercially available ZIF-8 (Basolite[®] Z1200) were used as seed for the synthesis of core-shell ZIF-67@ZIF-8 and ZIF-8@ZIF-67 frameworks, respectively [36, 37]. A visible color change from pale white for ZIF-8 to offviolet and dark violet for core-shell ZIF-67@ZIF-8 and ZIF-8@ZIF-67 frameworks, respectively has also been observed during the synthesis of these core-shell ZIFs (Fig. 2.2). The UV-vis absorption spectra (Fig. 2.1b) well supported the formation of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks, where the presence of characteristic bands for the tetrahedral Co²⁺ at ~580 nm and ~540 nm with no significant shift, compared to that of the parent ZIF-67, suggests the presence of Co²⁺ in the ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks [29, 37, 40]. Notably, the analogous isoreticular sodalite (SOD) topology and similar unit cell parameters for ZIF-8 (a = b = c = 16.9910 Å) and ZIF-67 (a = b = c = 16.9589 Å), and comparable ionic radii of Zn²⁺ (0.74 Å) and Co²⁺ (0.72 Å) drive the facile synthesis of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks with a topology analogous to those of parent ZIF-8 and ZIF-67 [9, 12, 20, 27, 29].



Fig. 2.1 (a) Synthetic scheme of preparation of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8, (b) UV-visible spectra and (c) PXRD patterns of ZIF-8, ZIF-67, ZIF-8@ZIF-67, ZIF-8+ZIF-67 and ZIF-67@ZIF-8



Fig. 2.2 Photographs of the synthesised core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8, along with the parent ZIF-8 and ZIF-67 frameworks

Figure 2.1c illustrated the PXRD patterns of the synthesised core-shell ZIFs along with those of the parent ZIF-8 and ZIF-67. The presence of high intensity peaks in PXRD spectra is in good agreement with the highly crystalline nature of the synthesised core-shell ZIFs [36-38]. Diffraction peaks appeared at 20 value of 7.52, 10.53, 12.90, 14.86, 16.60, 18.21, 22.21, 24.66, 26.82 degrees were identified for (011), (002), (112), (002), (013), (222), (114), (233), (134) planes respectively [29]. The PXRD characteristics of the parent ZIF-8 (Basolite Z1200) resemble well with the earlier reported PXRD patterns of Basolite Z1200 [41]. Notably, no additional phase was found, and the close resemblance of PXRD diffraction peaks of core-shell ZIF frameworks with those of parent ZIF-8 and ZIF-67, suggesting that the intrinsic framework properties of the participating ZIF-8 and ZIF-67 remains intact during the formation of core-shell ZIFs [9, 12, 20, 21, 29]. Moreover, the PXRD pattern of the physical mixture of ZIF-8 and ZIF-67 also showed diffractions peaks analogous to the parent ZIFs (Fig. 2.1c). The TEM and SEM images established a well-defined rhombic dodecahedron topology with uniform size distribution independently for both the core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks (Fig. 2.3a, e). TEM-EDXS, line scan, and elemental mapping analyses further confirmed the composition and distribution of Zn and Co elements within the core-shell ZIFs (Fig. 2.3b-d, f-h and Fig. 2.4). Distribution of Zn in the core and Co at the shell in ZIF-8@ZIF-67 and analogously Co in the core and Zn at the shell in ZIF-67@ZIF-8 clearly evidenced the core-shell frameworks of the synthesised ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks [36-38]. Despite the fact that ZIF-67@ZIF-8 has larger particle size than the ZIF-8@ZIF-67, the core to shell thickness ratio was observed to be comparable for both the core-shell ZIFs (Table 2.1).



Fig. 2.3 (a,e) SEM images (*inset* TEM images) (b,f) line scanning, (c-d, g-h) elemental mapping of (a-d) ZIF-8@ZIF-67 and (e-h) ZIF-67@ZIF-8 frameworks

Table 2.1 Molar ratio of Co^{2+}/Zn^{2+} , Core Size (nm), Shell thickness (nm) of theZIF-8@ZIF-67 and ZIF-67@ZIF-8

ZIFs	Molar ratio of Co ²⁺ /Zn ²⁺	Core Size (nm)	Shell thickness (nm)	Ratio of Core Size/ Shell thickness
ZIF-8@ZIF-67	0.51	225	65	3.46
ZIF-67@ZIF-8	0.54	875	300	2.92



Fig. 2.4 EDXS plots of (a) ZIF-8@ZIF-67 and (b) ZIF-67@ZIF-8

Moreover, ICP-AES analysis also authenticated the comparable Co to Zn molar ratio for both the core-shell ZIF-8@ZIF-67 (Co/Zn = 0.51) and ZIF-67@ZIF-8 (Co/Zn = 0.54). XPS analysis was performed to establish the electronic states of Co and Zn elements present in the core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks (Fig. 2.5a,d). The high resolution spectra of Zn 2p (~1021 eV) and Co 2p (~781 eV) were in good agreement with those of the Zn^{2+} and Co^{2+} oxidation states (Fig. 2.5b,c,e,f). Moreover, the signals corresponding to Co^{2+} appeared to be of low intensity, suggesting the presence of Co (ZIF-67) in the core of ZIF-67@ZIF-8. Analogously, for ZIF-8@ZIF-67, the signals for Zn^{2+} was found to be of lower intensity due to the encapsulation of ZIF-8 in the ZIF-67 shell [27, 37]. The N 1s peak at ~399 eV was assigned to the N atom of the 2-methylimidazole linker. Moreover, an elemental analysis also confirms that almost similar wt % of C ~ 48, N ~ 23 and H ~ 5.5 are present in ZIF-8@ZIF-67 and ZIF-67@ZIF-8. Fourier transform infrared spectroscopy (FTIR) vibration bands for ZIF-8@ZIF-67 and ZIF-67@ZIF-8 showed characteristics bands at ~2929 and ~1581 cm⁻¹ assigned to C-H and C=N banding vibrations, respectively, suggesting that the 2-methylimidazole linker remains intact during the formation of core-shell ZIFs. Notably, the presence of vibration band at ~421 cm⁻¹, corresponding to Zn-N or Co-N bond stretching demonstrated the presence of Zn-imidazolate/Co-imidazolate linkage in the core-shell ZIFs (Fig. 2.6a) [37]. Thermogravimetric analysis (TGA) curves of ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks along with those of the parent ZIF-8 and ZIF-67 are shown in Fig. 2.6b. TGA curves of ZIF-8 and ZIF-67 matches well with the earlier reports [9, 12, 20, 21, 29, 36, 37]. Interestingly, core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 were thermally stable up to 370 °C and 340 °C, respectively, which is analogous to that of ZIF-67 (390 °C), but lower than ZIF-8 (410 °C). These results evidenced the presence of heterogeneity in the studied core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks [33, 36, 37].



Fig. 2.5 (a,d) Wide scan XPS and (b,c,e,f) respective high resolution XPS spectra showing Zn 2p and Co 2p core bands, of ZIF-8, ZIF-67, ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks



Fig. 2.6 (a) FTIR spectra, (b) TGA profiles, of the core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8, along with the parent ZIF-8 and ZIF-67

The surface area, total pore volume and pore size distribution of core-shell ZIF-8@ZIF-67, ZIF-67@ZIF-8 and the physical mixture of ZIF-8+ZIF-67 frameworks were analyzed by measuring N₂ adsorption-desorption isotherms at 77 K, where all the studied ZIF frameworks displayed type I isotherm (Fig. 2.7a, and Table 2.2). The pore size distributions were calculated by density functional theory (DFT), as shown in Fig. 2.7b [9, 10, 12, 20, 21, 29, 36, 37]. It is also observed that the estimated average pore size of ZIF-8@ZIF-67 (~ca. 1.20 nm), ZIF-67@ZIF-8 (~ca. 1.02 nm) and ZIF-8+ZIF-67 (~ca. 1.03 nm) frameworks are almost similar to those of the parent ZIF-8 (~ca. 1.11 nm) and ZIF-67 (~ca. 1.01 nm). Notably, BET surface area (1402.15 m² g⁻¹) and total pore volume of ZIF-8@ZIF-67 framework structure showed an increment by $ca. \sim 6\%$ (5.93%) and ca. ~15% (14.66%), respectively, as compared to the parent ZIF-8. Such enhancement may be due to the well grown ZIF-67 shell over the ZIF-8 core, without intercepting the pores of ZIF-8. In contrary, ZIF-67@ZIF-8 showed lower BET surface area (1271.82 m² g⁻¹) and total pore volume of ZIF-67@ZIF-8, ca. ~ 8.65% and $\sim ca$. 7% lower than the ZIF-67 core, presumably due to the blockage of the pore at the interface of the ZIF-8 shell and ZIF-67 core. BET surface area $(1295.64 \text{ m}^2 \text{g}^{-1})$ and total pore volume $(0.6871 \text{ cm}^3 \text{g}^{-1})$ of the physical mixture of ZIF-8 and ZIF-67 frameworks showed almost similar to the average value of parent ZIF-8 and ZIF-67. Hence, the above results clearly evidenced the distinct surface and porosity behavior of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8, brings in due to their core-shell topology, compared to the parent ZIF-8, ZIF-67 and the ZIF-8+ZIF-67 physical mixture. The close agreement in the observed trend in the pore volume and pore size of core-shell ZIFs with that of the respective core, inferred the predominant role of the core in controlling the growth of the shell in accordance with the core's crystal lattice of the core [32, 33].



Fig. 2.7 (a) N₂ sorption and (b) DFT pore size distribution of ZIF-8, ZIF-67, ZIF-8@ZIF-67, ZIF-67@ZIF-8 and ZIF-8+ZIF-67 physical mixture frameworks

Table 2.2 Surface area, pore volume, pore size and H₂ storage properties of coreshell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks along with ZIF-8, ZIF-67 and ZIF-8+ZIF-67 physical mixture

ZIFs	Surface Area ^[a]	Pore Volume ^[b]	Pore Size ^[c]	H ₂ uptake at 77 K, 1 bar		Reference	
	$(m^2 g^{-1})$	$(\mathbf{cm}^3 \mathbf{g}^{-1})$	(nm)	mmol g ⁻¹	wt %	-	
ZIF-8	1323.62	0.7633	1.11	7.08	1.43	This work	
ZIF-8@ZIF-67	1402.15	0.8752	1.20	10.07	2.03	This work	
ZIF-67@ZIF-8	1271.82	0.6797	1.02	8.37	1.69	This work	
ZIF-8+ZIF-67	1295.64	0.6871	1.03	7.69	1.55	This work	
ZIF-67	1392.30	0.7324	1.01	7.55	1.53	This work	
Co ₇₅ Zn ₂₅ -ZIF-8	1571.7	0.7750	1.97	7.69	1.55	[29]	

^[a] BET surface area,^[b]Total pore volume (estimated at P/P₀=0.99),^[c]Average pore radius

2.4.2 H₂ storage properties

Envisioned by the remarkably enhanced surface properties of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks, we explored the H_2 storage capacities of these frameworks. The H_2 adsorption isotherms were obtained at 77 K and 298 K, respectively in the pressure range of 0-1.0 bar (Fig. 2.8a-d, and Table 2.2). Interestingly, ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks

displayed enhanced H_2 storage capacities of 2.03 and 1.69 wt% respectively, compared to the parent ZIF-8 (1.43 wt%) and ZIF-67 (1.53 wt%) at 77K. Among both the studied core-shell ZIFs, ZIF-8@ZIF-67 framework outperformed over ZIF-67@ZIF-8 and showed remarkable enhancement in H₂ storage capacity by 41.95% than the core ZIF-8 and 32.68% more than the shell ZIF-67. Interestingly, the surface area of core-shell ZIF-8@ZIF-67 is almost analogous to the shell ZIF-67, while only 5.9% higher than the core ZIF-8. Notably, ZIF-67 having surface area analogous to ZIF-8@ZIF-67, exhibited much lower H₂ storage properties, suggesting that presumably the porous ZIF-67 shell complemented well with the core ZIF-8 to facilitate the observed enhancement in H₂ storage for core-shell ZIF-8@ZIF-67. In contrary, the other core-shell ZIF-67@ZIF-8 exhibited lower H₂ storage than the core-shell ZIF-8@ZIF-67 and only $10 \sim 18\%$ higher than the core ZIF-67 and shell ZIF-8, suggesting that the shell ZIF-8 significantly prevented the H_2 uptake by the core. Further, it was also noted that the H_2 adsorption isotherm was not saturated within the investigated pressure range up to 1 bar (Fig. 2.8b), suggesting that higher H_2 storage can be possible at high pressure. Notably, ZIF-8@ZIF-67 and ZIF-67@ZIF-8 exhibited very low H₂ uptake values of 0.084 wt% and 0.043 wt% at 298 K, nevertheless, the trend is consistent with that observed at 77 K (Fig 2.8d). It should be noted that in general, MOFs exhibited low H₂ uptake at 298 K even at high pressure, for instance, Yildirim *et.al* reported 0.13 wt% over ZIF-8 at 30 bar, and therefore, at low pressure there will be more uncertainty in the estimated H_2 uptake values [42a].

Further, to validate if the observed H₂ storage performance of core-shell ZIF frameworks is because of the structural modification due to their core-shell morphology, H₂ storage performance of the physical mixture of ZIF-8+ZIF-67 (Co:Zn = 0.50) was also evaluated. It should be noted that the physical properties of ZIF-8+ZIF-67 physical mixture was found to be the average of the parent ZIF-8 and ZIF-67, and hence a similar trend was also expected for the H₂ storage properties of the ZIF-8+ZIF-67 physical mixture. This was indeed the case, as H₂ storage of the physical mixture of ZIF-8+ZIF-67 (1.55 wt%) was found to be well

below the high performing core-shell frameworks (2.03 wt% for ZIF-8@ZIF-67) and is almost average of ZIF-8 and ZIF-67.



Fig. 2.8 (a) H_2 storage isotherm at 77 K with Langmuir model, (b) enlarged view of H_2 storage isotherm in the pressure range of 0.80-1.0 bar, (c) comparative H_2 storage, and (d) H_2 storage isotherm at 77 K and 298 K

Similar behavior has also been observed by Rosi *et al.*, where the coreshell II-bio-MOF-14 exhibited 4 fold lower N₂ gas adsorption compared to the grinded II-bio-MOF-14, which was attributed to the exposure of the core to the N₂ gas upon grinding [33]. This further elaborated the advantage with core-shell morphology, where the gas must have to pass through the shell before filling into the core [33]. Notably, the observed H₂ storage capacity of core-shell ZIFs was also found to be higher than the bimetallic Co₇₅Zn₂₅-ZIF-8 (1.55 wt%) and comparable to most of the similar class of MOFs (Table 2.3) [29, 31, 42]. The H₂ storage capacities were in the order of ZIF-8@ZIF-67 > ZIF-67@ZIF-8 > ZIF-67 > ZIF-8. Hence, the above observations clearly evidenced the special arrangement of ZIF-8 and ZIF-67 in core-shell topology is responsible for the observed

increment in H₂ adsorption properties of the studied core-shell ZIFs, and not just because of the mere presence of the individual components (ZIF-8 and ZIF-67). Notably, no visible changes in the diffraction patterns were observed in the PXRD patterns of the core-shell ZIFs before and after gas adsorption, suggesting that their core-shell structures remain intact (Fig. 2.9a). Moreover, to know the adsorption behavior of H₂ molecules, Langmuir and Freundlich equation (Fig. 2.8a, b, Fig. 2.9b and Table 2.4) were applied to fit the experimental H_2 adsorption isotherms of ZIF-8@ZIF-67, ZIF-67@ZIF-8, ZIF-8 and ZIF-67 frameworks. The fitting parameters and represented correlation coefficients (R^2) inferred a good agreement of experimental isotherm with Langmuir model ($R^2 \ge$ (0.9999) compared to Freundlich model, suggesting that the H₂ adsorption behavior of the studied core-shell frameworks adopts theoretically expects of the model [43, 44]. Moreover, the estimated heat of adsorption (ΔH_{ads}) ~3.45 and ~3.40 kJ mol⁻¹ for ZIF-8@ZIF-67 and ZIF-67@ZIF-8 respectively. Notably, the obtained ΔH_{ads} values were estimated over a large temperature difference (77-298 K) range and low pressure range (0-1 bar), which may lead to an uncertainty in ΔH_{ads} values. Nevertheless, the estimated ΔH_{ads} is in good agreement with other literature findings (~4.3 and ~3.8 kJ mol⁻¹ for MIL-101(Cr) and Li@AC-MIL-101-A, ~4.8 kJ mol⁻¹ for ZIF-8) [42].



Fig. 2.9 (a) PXRD patterns of ZIF-8@ZIF-67-B and ZIF-67@ZIF-8-B (before) and ZIF8@ZIF-67-A and ZIF-67@ZIF-8-A (after) gas adsorption (b) H₂ storage isotherm at 77 K with Freundlich model

	Surface Pore		H			
MOFs	area	volume	Р	<u> </u>		Ref.
	$(m^2 g^{-1})$	$(\mathbf{cm}^3 \mathbf{g}^{-1})$	(bar)	(K)		
ZIF-8@ZIF-67	1402.15	0.8752	1.0	77	2.03	This
ZIF-67@ZIF-8	1271.82	0.6797	1.0	77	1.69	work
ZIF-67	1392.30	0.7324	1.0	77	1.53	
Co ₇₅ Zn ₂₅ -ZIF-8	1571.7	0.7750	1.0	77	1.55	[29]
Ni-GO/MIL	2045	0.98	1.0	77	1.64	[45]
UMCM-1/C dots	3714	1.95	1.0	77	1.21	[46]
Li@AC-MIL-101	2791	1.65	1.0	77	1.60	[42b]
MIL-101	3148	2.10	1.0	77	1.20	
MOF-5/Pt-CNTs	1692	0.84	1.0	77	1.89	[47]
MOF-5	1758	0.82	1.0	77	1.20	
IRMOF-1+Pd	958	0.39	1.0	77	1.86	[48]
IRMOF-1	2885	1.18	1.0	77	1.15	
Pt/AC-MOF-5	740	0.80	1.0	77	1.395	[49]
MOF-5	670	0.79	1.0	77	1.399	
SodZMOF	361	0.13	10.0	77	1.6	[50]
4Li ⁺ Me-SodZMOF	334	0.12	10.0	77	1.18	
4Na ⁺ Me-SodZMOF	804	0.33	10.0	77	1.6	
4K ⁺ Me-SodZMOF	181	0.07	10.0	77	0.8	
MOF-5/MWCNT	2900	0.672	1.0	77	1.52	[51]
Li ⁺ Zn ₂ (NDC) ₂ (diPyNI)	802		1.0	77	1.63	[52]
Zn ₂ (NDC) ₂ (diPyNI)	756		1.0	77	0.93	
ZIF-67	1319.9		1.0	77	1.26	[53]
Cu/ZIF-67	1324.1		1.0	77	1.51	
MOF-2/FCNF	50		1.0	77	0.84	[54]
ZIF-8/GO	1161	0.718	1.06	298	0.068*	[55]
ZIF-8/Pt-GO	1101	0.684	1.06	298	0.312*	
HKUST-1	1131	0.601	1.06	298	0.014*	
HKUST-1/GO	955	0.509	1.06	298	0.0102*	
Pt@HKUST-1/GO	433	0.319	1.05	298	0.504*	

Table 2.3 Comparative surface area, pore volume and H_2 storage properties of several monometallic and bimetallic MOF materials

*Experimental data convert into mmol g^{-1} and wt%.

	Langmuir constants			Freundlich constants			
ZIFs	am	b	\mathbf{R}^2	K	n ⁻¹	\mathbf{R}^2	
ZIF-8	3.9752	0.5131	0.9999	1.4249	0.8634	0.9961	
ZIF-8@ZIF-67	7.7682	0.3370	0.9999	2.0237	0.8973	0.9972	
ZIF-67@ZIF-8	7.7184	0.2705	0.9999	1.6610	0.9038	0.9976	
ZIF-8+ZIF-67	3.7474	0.6036	0.9999	1.5348	0.8619	0.9971	
ZIF-67	4.8114	0.4365	0.9999	1.5302	0.8771	0.9965	

Table 2.4 Isotherm constants for the Langmuir and Freundlich model of ZIF-8, ZIF-8@ZIF-67, ZIF-67@ZIF-8, physical mixture ZIF-8+ZIF-67 and ZIF-67 H_2 storage at 77 K and 1 bar

2.4.3 CO₂ capture properties

Encouraged by the observed noteworthy enhancement in H₂ storage capacities of the studied core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks, performance of these core-shell ZIFs was also explored for CO₂ capture capacities at 298 K and 1 bar (Fig. 2.10, Tables 2.5 and 2.6). All ZIF frameworks displayed a linear increase in the CO₂ adsorption capacities with the increase in pressure (0-1.0 bar). Consistent with the advancement in surface and porosity properties of core-shell ZIF-8@ZIF-67 over ZIF-67@ZIF-8 frameworks and the parent ZIF-8 and ZIF-67, a two-fold increment in CO₂ capture capacities to 1.67 mmol g⁻¹ (7.35 wt%) was observed for core-shell ZIF-8@ZIF-67 as compared to the core ZIF-8 (0.83 mmol g⁻¹, 3.65 wt%) and shell ZIF-67 (1.11 mmol g⁻¹, 4.91 wt%). Analogously, the other core-shell ZIF-67@ZIF-8 also exhibited 18.54% more CO_2 capture than the core ZIF-67 and 59.45% than the shell ZIF-8. Nevertheless, the studied core-shell ZIFs exhibited comparable or even superior CO₂ capture capacities than most of the bimetallic ZIF or MOF frameworks at 1 bar and 298 K (Table 2.7). Hence, the easily tunable structure of core-shell frameworks by critically chosen core and the shell materials and exploiting the complementary inegration of core to shell, along with the other crucial factors such as surface functionalities, optimum porosity structure, the interaction between gas molecules and pore wall, and the chemical heterogeneity

of the core-shell frameworks has vital role in dfetermining the application of such materials in various fields including H_2 storage and CO_2 capture [29, 32-39, 67-69].



Fig. 2.10 (a) CO_2 capture isotherms at 298 K, 1 bar (b) enlarged view of CO_2 uptake in the pressure range of 0.02-0.15 bar

Table 2.5 Surface area, pore volume, pore size and CO2 capture properties ofcore-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks

ZIFs	Surface Area ^[a]	Pore Volume ^[b]	Pore Size ^[c]	CO ₂ Capture (mmol g ⁻¹), 298 K	
	$(m^2 g^{-1})$	$(cm^{3} g^{-1})$	(nm)	0.15 bar	1 bar
ZIF-8	1323.62	0.7633	1.11	0.096	0.83 (3.65 wt %)
ZIF-8@ZIF-67	1402.15	0.8752	1.20	0.168	1.67 (7.35 wt %)
ZIF-67@ZIF-8	1271.82	0.6797	1.02	0.145	1.32 (5.82 wt %)
ZIF-67	1392.30	0.7324	1.01	0.124	1.11 (4.91 wt %)

^[a] BET surface area,^[b]Total pore volume (estimated at P/P₀=0.99),^[c]Average pore radius



Fig. 2.11 Comparative CO₂ capture isotherms at 298 K, 1 bar

Entry	ZIFs	Freundlich constants					
		K	n ⁻¹	\mathbf{R}^2			
1	ZIF-8	3.4175	1.1277	0.9984			
2	ZIF-8@ZIF-67	6.7216	1.171	0.9999			
3	ZIF-67@ZIF-8	5.5154	1.1592	0.9987			
4	ZIF-67	4.3918	1.1031	1.000			

Table 2.6 Isotherm constants for the Freundlich model of ZIF-8, ZIF-8@ZIF-67, ZIF-67@ZIF-8 and ZIF-67 CO₂ capture at 298 K and 1 bar

 Table 2.7 Comparative surface area, pore volume, CO2 capture properties of

 several monometallic and bimetallic MOF materials

MOFs	Surface	Pore	CO ₂ capture		Ref.	
	area (m ² g ⁻¹)	volume (cm ³ g ⁻¹)	P (bar)	T (K)	mmol g ⁻¹	-
ZIF-8	1323.62	0.7633	1.0	298	0.83	
ZIF-8@ZIF-67	1402.15	0.8752	1.0	298	1.67	This
ZIF-67@ZIF-8	1271.82	0.6797	1.0	298	1.32	work
ZIF-67	1392.30	0.7324	1.0	298	1.11	
Co ₇₅ Zn ₂₅ -ZIF-8	1571.7	0.7750	1.0	298	0.90	[29]
MIL-101	3125.4	1.629	1.0	298	1.60	[56]
PEI-MIL-101-50	1802.7	0.901	1.0	298	4.00	
PEI-MIL-101-75	1112.6	0.526	1.0	298	4.64	
PEI-MIL-101-100	604.8	0.292	1.0	298	5.00	
PEI-MIL-101-125	182.9	0.095	1.0	298	4.35	
UiO-66/GO	1184	0.384	1.0	298	3.37	[57]
HKUST-1/HCM	516	0.26	1.0	298	2.75	[58]
MOF-2/FCNF	50		1.0	298	1.61	[54]
HKUST-1/AGO	1367	0.663	1.0	298	4.65	[59]
ZIF-L	161	0.066	1.0	298	0.94	[60]
ZIF-8			1.0		0.66	
ZIF-67	1319.9		1.0	298	0.94	[53]
Cu/ZIF-67	1324.1		1.0	298	1.18	
Zn/Ni-ZIF-8	1700		1.0	298	0.67	[61]
ED-ZIF-8	1428	0.75	25.0	298	10	[62]
Gro@MIL-101			25.0	298	22.4	[63]
HKUST-1/CNT/Li	857	0.69	18.0	298	15*	[64]
Zn/Co(0.5/0.5)-ZIF	1998	0.62	1.0	273	1.52*	[30]
ZIF-8/CNTs	1997	0.747	1.32	273	2.21	[65]
ZIF-8/GO	289	0.09	1.0	195	16.45	[66]
bio-MOF-II@bio-MOF-14			1.0	273	2.60*	[33]
bio-MOF-14			1.0	273	1.99*	

*Experimental data convert into mmol g-1 and wt%.

2.5 Conclusions

In conclusion, we demonstrated a facile synthesis of core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks through seed-mediated growth methodology. TEM, SEM, elemental mapping and line scan, PXRD and XPS authenticated the core-shell topology of the studied ZIFs. The ICP-AES analyses further evidenced an analogous Co to Zn composition for both the core-shell ZIFs. The observed remarkable enhancement in H₂ storage properties of the coreshell ZIFs compared to either of the parent ZIF-8 and ZIF-67, clearly evidenced the coherent synergy between the core and the shell, along with the tuned porosity (surface area and pore volume) behavior of the synthesised core-shell ZIFs. Further, the poor H₂ storage properties of the physical mixture of ZIF-8 and ZIF-67 authenticated the crucial role of core-shell morphology in achieving enhanced H_2 storage. Additionally, the synthesised core-shell ZIFs displayed improved CO_2 capture properties compared to the ZIF-8 and ZIF-67. The observed unprecedented advanced properties displayed by core-shell ZIFs for gas storage applications may present an opportunity to design new core-shell MOFs to achieve enhanced gas storage properties and several other advanced applications.

Note: The content of this chapter is published as Panchariya *et al.*, ACS Omega, 2018, 3, 1, 167-175, (DOI: 10.1021/acsomega.7b01693) and reproduced here with the permission of American Chemical Society.

2.6 References

- Turner J.A. (1999), A Realizable Renewable Energy Future, Science, 285, 687-689.
- [2] Morris R.E., Wheatley P.S. (2008), Gas Storage in Nanoporous Materials, Angew. Chem., Int. Ed., 47, 4966-4981.
- [3] Schlapbach L., Zuttel A. (2001), Hydrogen-Storage Materials for Mobile Applications, Nature, 414, 353-358.
- [4] (a) Zhou H.C., Long J.R., Yaghi O.M. (2012), Introduction to Metal-Organic Frameworks, Chem. Rev., 112, 673-674. (b) Blanco A.A.G.,

Vallone A.F., Gil A., Sapag K. (2012), A Comparative Study of Various Microporous Materials to Store Hydrogen by Physical Adsorption, Int. J. Hydrogen Energy, 37, 14870-14880. (c) Rallapalli P.B.S., Raj M.C., Patil D.V., Prasanth K.P., Somani R.S., Bajaj H.C. (2013), Activated Carbon@MIL-101(Cr): A Potential Metal-Organic Framework Composite Material for Hydrogen Storage, Int. J. Energy Res., 37, 746-753.

- [5] (a) Furukawa H., Cordova K.E., O'Keeffe M., Yaghi O.M. (2013), The Chemistry and Applications of Metal-Organic Frameworks, Science, 341, 1230444. (b) Nandi S., Luna P.D., Daff T.D., Rother J., Liu M., Buchanan W., Hawari A.I., Woo T.K., Vaidhyanathan R. (2015), A Single-ligand Ultra-microporous MOF for Precombustion CO₂ Capture and Hydrogen Purification, Sci. Adv., 1, No. e1500421.
- [6] Chen B., Yang Z., Zhu Y., Xia Y. (2014), Zeolitic Imidazolate Framework Materials: Recent Progress in Synthesis and Applications, J. Mater. Chem. A, 2, 16811-16831.
- [7] Eddaoudi M., Sava D.F., Eubank J.F., Adil K., Guillerm V. (2015),
 Zeolite-Like Metal-Organic Frameworks (ZMOFs): Design, Synthesis, and
 Properties, Chem. Soc. Rev., 44, 228-249.
- [8] Stock N., Biswas S. (2012), Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites, Chem. Rev., 112, 933-969.
- [9] Park K.S., Ni Z., Cote A.P., Choi J.Y., Huang R., Uribe-Romo F.J., Chae H.K., O'Keeffe M., Yaghi O.M. (2006), Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks, Proc. Natl. Acad. Sci. USA., 103, 10186-10191.
- [10] Hayashi H., Cote A.P., Furukawa H., O'Keeffe M., Yaghi O.M. (2007), Zeolite Imidazolate Frameworks, Nat. Mater., 6, 501-506.
- [11] Wu H., Zhou W., Yildirim T. (2007), Hydrogen Storage in a Prototypical Zeolitic Imidazolate Framework-8, J. Am. Chem. Soc., 129, 5314-5315.

- [12] Banerjee R., Phan A., Wang B., Knobler C., Furukawa H., O'Keeffe M., Yaghi O.M. (2008), High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO₂ Capture, Science, 319, 939-943.
- [13] Langmi H.W., Ren J., North B., Mathe M., Bessarabov D. (2014), Hydrogen Storage in Metal-Organic Frameworks: A Review, Electrochim. Acta, 128, 368-392.
- [14] Sumida K., Rogow D.L., Mason J.A., McDonald T.M., Bloch E.D., Herm Z.R., Bae T.H., Long J.R. (2012), Carbon Dioxide Capture in Metal-Organic Frameworks, Chem. Rev., 112, 724-781.
- [15] Bhattacharjee S., Jang M.S., Kwon H.J., Ahn W.S. (2014), Zeolitic Imidazolate Frameworks: Synthesis, Functionalization, and Catalytic/Adsorption Applications, Catal. Surv. Asia, 18, 101-127.
- [16] Lu G., Li S., Guo Z., Farha O.K., Hauser B.G., Qi X., Wang Y., Wang X., Han S., Liu X., DuChene J.S., Zhang H., Zhang Q., Chen X., Ma J., Loo S.C.J., Wei W.D., Yang Y., Hupp J.T., Huo F. (2012), Imparting Functionality to a Metal-Organic Framework Material by Controlled Nanoparticle Encapsulation, Nat. Chem., 4, 310-316.
- [17] Janiak C., Vieth J.K. (2010), MOFs, MILs and More: Concepts, Properties and Applications for Porous Coordination Networks (PCNs), New J. Chem., 34, 2366-2388.
- [18] Jiang H.L., Liu B., Akita T., Haruta M., Sakurai H., Xu Q. (2009), Au@ZIF-8: CO Oxidation over Gold Nanoparticles Deposited to Metal-Organic Framework, J. Am. Chem. Soc., 131, 11302-11303.
- [19] Lu G., Hupp J.T. (2010), Metal-Organic Frameworks as Sensors: A ZIF-8
 Based Fabry-Pérot Device as a Selective Sensor for Chemical Vapors and Gases, J. Am. Chem. Soc., 132, 7832-7833.
- [20] Shi Q., Chen Z., Song Z., Li J., Dong J. (2011), Synthesis of ZIF-8 and ZIF-67 by Steam-Assisted Conversion and an Investigation of Their Tribological Behaviors, Angew. Chem., Int. Ed., 50, 672-675.

- [21] Qian J., Sun F., Qin L. (2012), Hydrothermal Synthesis of Zeolitic Imidazolate Framework-67 (ZIF-67) Nanocrystals, Mater. Lett., 82, 220-223.
- [22] Tanabe K.K., Cohen S.M. (2011), Post Synthetic Modification of Metal-Organic Frameworks-A Progress Report, Chem. Soc. Rev., 40, 498-519.
- [23] Ahmed I., Jhung S.H. (2014), Composites of Metal-Organic Frameworks: Preparation and Application in Adsorption, Mater. Today, 17, 136-146.
- [24] Liu X.W., Sun T.J., Hu J.L., Wang S.D. (2016), Composites of Metal– Organic Frameworks and Carbon-Based Materials: Preparations, Functionalities and Applications, J. Mater. Chem. A, 4, 3584-3616.
- [25] Liu J., Thallapally P.K., McGrail B.P., Brown D.R., Liu J. (2012), Progress in Adsorption-Based CO₂ Capture by Metal-Organic Frameworks, Chem. Soc. Rev., 41, 2308-2322.
- [26] Botas J.A., Calleja G., Sanchez M.S., Orcajo M.G. (2010), Cobalt Doping of the MOF-5 Framework and Its Effect on Gas-Adsorption Properties, Langmuir, 26, 5300-5303.
- [27] Lu Y., Zhou Q., Chen L., Zhan W., Xie Z., Kuang Q., Zheng L. (2016), Templated Synthesis of Diluted Magnetic Semiconductors using Transition Metal Ion-Doped Metal-Organic Frameworks: The Case of Co-Doped ZnO, Cryst. Eng. Comm., 18, 4121-4126.
- [28] Tang J., Salunkhe R.R., Zhang H., Malgras V., Ahamad T., Alshehri S.M., Kobayashi N., Tominaka S., Ide Y., Kim J.H., Yamauchi Y. (2016), Bimetallic Metal-Organic Frameworks for Controlled Catalytic Graphitization of Nanoporous Carbons, Sci. Rep., 6, 30295.
- [29] Kaur G., Rai R.K., Tyagi D., Yao X., Li P.Z., Yang X.C., Zhao Y., Xu Q., Singh S.K. (2016), Room-Temperature Synthesis of Bimetallic Co-Zn Based Zeolitic Imidazolate Frameworks in Water for Enhanced CO₂ and H₂ Uptakes, J. Mater. Chem. A, 4, 14932-14938.
- [30] Zhou K., Mousavi B., Luo Z., Phatanasri S., Chaemchuen S., Verpoort F. (2017), Characterization and Properties of Zn/Co Zeolitic Imidazolate Frameworks vs. ZIF-8 and ZIF-67, J. Mater. Chem. A, 5, 952-957.

- [31] Yang X., Xu Q. (2017), Bimetallic Metal-Organic Frameworks for Gas Storage and Separation, Cryst. Growth Des., 17, 1450-1455.
- [32] Hirai K., Furukawa S., Kondo M., Uehara H., Sakata O., Kitagawa S. (2011), Sequential functionalization of porous coordination polymer crystals, Angew. Chem., Int. Ed., 50, 8057-8061.
- [33] Li T., Sullivan J.E., Rosi N.L. (2013), Design and Preparation of a Core-Shell Metal-Organic Framework for Selective CO₂ Capture, J. Am. Chem. Soc., 135, 9984-9987.
- [34] Koh K., Foy A.G.W., Matzger A. (2009), MOF@MOF: Microporous Core-Shell Architectures, J. Chem. Commun., 6162-6164.
- [35] Szilagyi P.A.G., Lutz M., Gascon J., Alcaniz J.J., Esch J.V., Kapteijn F., Geerlings H., Dam B., Krol R.V.D. (2013), MOF@MOF Core– Shell vs. Janus Particles and the Effect of Strain: Potential for Guest Sorption, Separation and Sequestration, Cryst. Eng. Comm., 15, 6003-6008.
- [36] Tang J., Salunkhe R.R., Liu J., Torad N.L., Imura M., Furukawa S., Yamauchi Y. (2015), Thermal Conversion of Core-Shell Metal-Organic Frameworks: A New Method for Selectively Functionalized Nanoporous Hybrid Carbon, J. Am. Chem. Soc., 137, 1572-1580.
- [37] Yang J., Zhang F., Lu H., Hong X., Jiang H., Wu Y., Li Y. (2015), Hollow Zn/Co ZIF Particles Derived from Core–Shell ZIF-67@ZIF-8 as Selective Catalyst for the Semi-Hydrogenation of Acetylene, Angew. Chem., Int. Ed., 54, 10889-10893.
- [38] Zhang J., Zhang T., Xiao K., Cheng S., Qian G., Wang Y., Feng Y. (2016), Novel and Facile Strategy for Controllable Synthesis of Multilayered Core–Shell Zeolitic Imidazolate Frameworks, Cryst. Growth Des., 16, 6494-6498.
- [39] Ren J., Musyoka N.M., Langmi H.W., North B.C., Mathe M., Kang X. (2014), Fabrication of Core-Shell MIL-101(Cr)@Uio-66(Zr) Nanocrystals for Hydrogen Storage, Int. J. Hydrogen Energy, 39, 14912-14917.

- [40] He M., Yao J., Liu Q., Wang K., Chen F., Wang H. (2014), Facile Synthesis of Zeolitic Imidazolate Framework-8 from a Concentrated Aqueous Solution, Micropor. Mesopor. Mat., 184, 55-60.
- (a) Butova V.V., Budnyk A.P., Bulanova E.A., Lamberti C., Soldatov A [41] V. (2017), Hydrothermal Synthesis of High Surface Area ZIF-8 with Minimal use of TEA, Solid State Sci., 69, 13-21. (b) Eiras D., Labreche Y., Pessan L.A. (2016), Ultem/ZIF-8 Mixed Matrix Membranes for Gas Separation: Transport and Physical Properties, Mater. Res., 19, 220-228. (c) Du M., Li L., Li M., Si R. (2016), Adsorption Mechanism on Metal-Organic Frameworks of Cu-BTC, Fe-BTC and ZIF-8 for CO₂ Capture Investigated by X-Ray Absorption Fine Structure, RSC Adv., 6, 62705-62716. (d) Peralta D., Chaplais G., Simon-Masseron A., Barthelet K., Pirngruber G.D. (2012), Separation of C6 Paraffins Using Zeolitic Imidazolate Frameworks: Comparison with Zeolite 5A, Ind. Eng. Chem. Res., 51, 4692-4702. (e) Chen H., Wang L., Yang J., Yang R.T. (2013), Investigation on Hydrogenation of Metal-Organic Frameworks HKUST-1, MIL-53, and ZIF-8 by Hydrogen Spillover, J. Phys. Chem. C, 117, 7565-7576.
- [42] (a) Zhou W., Wu H., Hartman M.R., Yildirim T. (2007), Hydrogen and Methane Adsorption in Metal-Organic Frameworks: A High-Pressure Volumetric Study, J. Phys. Chem. C, 111, 16131-16137. (b) Prabhakaran P.K., Deschamps J. (2015), Doping Activated Carbon Incorporated Composite MIL-101 using Lithium: Impact on Hydrogen Uptake, J. Mater. Chem. A, 3, 7014-7021.
- [43] Singh V.K., Kumar E.A. (2016), Measurement and Analysis of Adsorption Isotherms of CO₂ on Activated Carbon, Appl. Therm. Eng., 97, 77-86.
- [44] Foo K.Y., Hameed B.H. (2010), Insights into the Modeling of Adsorption Isotherm Systems, Chem. Eng. J., 156, 2-10.

- [45] Lee S.Y., Park S.J. (2013), Hydrogen Storage Behaviors of Ni-Doped Graphene Oxide/MIL-101 Hybrid Composites, J. Nanosci. Nanotech, 13, 443-447.
- [46] Li J.S., Tang Y.J., Li S.L., Zhang S.R., Dai Z.H., Si L., Lan Y.Q. (2015)
 Carbon Nano dots Functional MOFs Composites by a Stepwise Synthetic
 Approach: Enhanced H₂ Storage and Fluorescent Sensing, Cryst. Eng.
 Comm., 17, 1080-1085.
- [47] Yang S.J., Cho J.H., Nahm K.S., Park C.R. (2010), Enhanced Hydrogen Storage Capacity of Pt-loaded CNT@MOF-5 Hybrid Composites, Int. J. Hydrogen Energy, 35, 13062-13067.
- [48] Sabo M., Henschel A., Frode H., Klemm E., Kaskel S. (2007), Solution Infiltration of Palladium into MOF-5: Synthesis, Physisorption and Catalytic Properties, J. Mater. Chem., 17, 3827-3832.
- [49] Chien A.C., Chuang S.S.C. (2011), Static and Dynamic Hydrogen Adsorption on Pt/AC and MOF-5, Int. J. Hydrogen Energy, 36, 6022-6030.
- [50] Calleja G., Botas J.A., Sanchez M.S., Orcajo M.G. (2010), Hydrogen Adsorption Over Zeolite-Like MOF Materials Modified by Ion Exchange, Int. J. Hydrogen Energy, 35, 9916-9923.
- [51] Yang S.J., Choi J.Y., Chae H.K., Cho J.H., Nahm K.S., Park C.R. (2009), Preparation and Enhanced Hydrostability and Hydrogen Storage Capacity of CNT@MOF-5 Hybrid Composite, Chem. Mater., 21, 1893-1897.
- [52] Mulfort K.L., Hupp J.T. (2007), Chemical Reduction of Metal-Organic Framework Materials as a Method to Enhance Gas Uptake and Binding, J. Am Chem. Soc., 129, 9604-9605.
- [53] Yang H., He X.W., Wang F., Kang Y., Zhang J. (2012), Doping Copper into ZIF-67 for Enhancing Gas Uptake Capacity and Visible-Light-Driven Photocatalytic Degradation of Organic Dye, J. Mater. Chem., 22, 21849-21851.
- [54] Pachfule P., Balan B.K., Kurungot S., Banerjee R. (2012), One-Dimensional Confinement of a Nano sized Metal-Organic Framework in

Carbon Nanofibers for Improved Gas Adsorption, Chem. Commun., 48, 2009-2011.

- [55] Zhou H., Zhang J., Zhang J., Yan X.F., Shen X.P., Yuan A.H. (2015), Spillover Enhanced Hydrogen Storage in Pt-Doped MOF/Graphene Oxide Composite Produced via an Impregnation Method, Inorg. Chem. Commun., 54, 54-56.
- [56] Lin Y., Yan Q., Kong C., Chen L. (2013), Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO₂ Capture, Sci. Rep., 3, 1859.
- [57] Cao Y., Zhao Y., Lv Z., Song F., Zhong Q. (2015), Preparation and Enhanced CO₂ Adsorption Capacity of Uio-66/Graphene Oxide Composites, J. Ind. Eng. Chem., 27, 102-107.
- [58] Qian D., Lei C., Hao G.P., Li W.C., Lu A.H. (2012), Synthesis of Hierarchical Porous Carbon Monoliths with Incorporated Metal-Organic Frameworks for Enhancing Volumetric Based CO₂ Capture Capability, ACS Appl. Mater. Interfaces, 4, 6125-6132.
- [59] Policicchio A., Zhao Y., Zhong Q., Agostino R.G., Bandosz T.J. (2013), Superior Performance of Copper Based MOF and Aminated Graphite Oxide Composites as CO₂ Adsorbents at Room Temperature, ACS Appl. Mater. Interfaces, 6, 101-108.
- [60] Chen R., Yao J., Gu Q., Smeets S., Baerlocher C., Gu H., Zhu D., Morris W., Yaghi O.M., Wang H. (2013), A Two-Dimensional Zeolitic Imidazolate Framework with a Cushion-Shaped Cavity for CO₂ Adsorption, Chem. Commun., 49, 9500-9502.
- [61] Li R., Ren X., Feng X., Li X., Hu C., Wang B. (2014), A Highly Stable Metal- and Nitrogen-Doped Nanocomposite Derived from Zn/Ni-ZIF-8 Capable of CO₂ Capture and Separation, Chem. Commun., 50, 6894-6897.
- [62] Zhang Z., Xian S., Xia Q., Wang H., Li Z., Li J. (2013), Enhancement of CO₂ Adsorption and CO₂/N₂ Selectivity on ZIF-8 via Post synthetic Modification, AIche J., 59, 2195-2206.

- [63] Zhou X., Huang W., Miao J., Xia Q., Zhang Z., Wang H., Li Z. (2015), Enhanced Separation Performance of a Novel Composite Material GrO@MIL-101 for CO₂/CH₄ Binary Mixture, Chem. Eng. J., 266, 339-344.
- [64] Xiang Z., Hu Z., Cao D., Yang W., Lu J., Han B., Wang W. (2011), Metal-Organic Frameworks with Incorporated Carbon Nanotubes: Improving Carbon Dioxide and Methane Storage Capacities by Lithium Doping, Angew. Chem., Int. Ed., 50, 491-494.
- [65] Yang Y., Ge L., Rudolph V., Zhu Z. (2014), In-Situ Synthesis of Zeolitic Imidazolate Frameworks/Carbon Nanotube Composites with Enhanced CO₂ Adsorption, Dalton Trans., 43, 7028-7036.
- [66] Kumar R., Jayaramulu K., Maji T.K., Rao C.N.R. (2013), Hybrid Nanocomposites of ZIF-8 with Graphene Oxide Exhibiting Tunable Morphology, Significant CO₂ Uptake and other Novel Properties, Chem. Commun., 49, 4947-4949.
- [67] Song X., Oh M., Lah M.S. (2013), Hybrid Bimetallic Metal-Organic
 Frameworks: Modulation of the Framework Stability and Ultra large CO₂
 Uptake Capacity, Inorg. Chem., 52, 10869-10876.
- [68] Muhammad R., Rekha P., Mohanty P. (2016), Aminal Linked Inorganic-Organic Hybrid Nanoporous Materials (HNMs) for CO₂ Capture and H₂ Storage Applications, RSC Adv., 6, 17100-17105.
- [69] Rana M.K., Suffritti G.B., Demontis P., Masia M. (2013), Simulation Study of CO₂ Adsorption Properties in Small Zeolite Imidazolate Frameworks, Chem. Phys. Lett., 580, 99-102.
Chapter 3

Inducing *in situ* Hydrothermal Carbonization of Glucose to Synthesise carbon-MIL-101 Hybrid Composites: Synthesis, Characterisation and Hydrogen Storage

3.1 Introduction

In the past few decades, the family of porous materials, such as activated carbon, zeolites, covalent organic frameworks, and metal-organic frameworks (MOFs), has been the center of interest for hydrogen storage [1-10]. In particular, MOFs have attracted worldwide attention, due to their excellent physical and chemical characteristics [3, 6, 8-12]. Among a wide range of MOFs explored, MIL-101 has received utmost attention [13-16]. Advantageously, MIL-101 displayed several promising features such as mesoporous zeotype structure with MTN topology, giant cell volume, high BET surface area, excellent thermal and chemical stability over a wide range of temperature and moisture conditions, and availability of unsaturated Cr metal sites [13-16]. Moreover, MIL-101 also possesses two types of large mesoporous cages: the smaller cage of diameter 29 Å is accessible through a pentagonal window of 12 Å aperture, while the larger cage of diameter 34 Å is accessible through both hexagonal and pentagonal windows of 14.5 x 16 $Å^2$ apertures [13-16]. Though the large pore volume and unsaturated open metal site available in MOFs are important factors to achieve high gas storage properties, the weak interaction of MOF walls and H₂ molecules adversely affect the H₂ adsorption properties of MOF, resulting in the underutilization of large pore volumes [16-19]. To address this issue, researchers implied several approaches such as functionalization of linker, loading of metal nanoparticle and other materials for improving the interaction between gas molecules and MOF wall [17-20].

In the last few years, carbon-based MOF composite have been widely explored as one of the promising materials to achieve enhanced H₂ storage [1832]. Carbon materials, when incorporated in MOFs can tune the architectural structure due to their large surface site, strong dispersive force and optimized pore volume and size [21-32]. Park et al. explored CNT@MOF-5 and Pt-doped CNT@MOF-5 to achieve enhanced H₂ adsorption capacity as compared to the parent MOF-5 [23, 24]. Chuang et al. studied static and dynamic H₂ adsorption behavior of a physical mixture of 5 wt% Pt/AC (Pure graphite, Norit SX Ultra CAT) and MOF-5, wherein the observed high H_2 storage capacity was attributed to the dissociation of H_2 at high temperature and spillover at low temperature on Pt/AC [25]. AC@MIL-101 was also reported to show a significant enhancement (up to 10.1 wt% at 77.4 K and 60 bar) in H_2 uptake as compared to MIL-101 [26]. SWNT@MIL-101 MOF composite, synthesised by in situ incorporation of SWNT (6-10 wt%) during the synthesis of MIL-101, also resulted in an enhancement of hydrogen uptake capacities from 6.37 to 9.18 wt% at 77 K and 60 bar, and 0.23 to 0.64 wt% at 298 K and 60 bar [27]. The observed enhancement in H_2 uptake was attributed to the increase in the micropore volume and decrease in the pore size, due to the incorporation of SWNT in MIL-101 [27]. Deschamps et al. extensively explored carbon-MIL-101 hybrid material for achieving enhanced H₂ adsorption properties [28-30]. A combined effect of activated carbon (NORIT-RB3) and lithium doped MIL-101 was exploited for high-pressure (upto 100 bar) H₂ adsorption at 77 K and 298 K [28]. They also explored hybrid AC-MIL-101 for high pressure (50 bar) H₂ storage at 77 K and analyzed the hydrogen diffusion in hybrid AC-MIL-101 under the influence of temperature variation and different carbon loading [30]. Wei et al. utilized MIL-101/CMK-3 composite to achieve enhanced CO₂ uptake at 25 °C and 1 bar, which was attributed to the formation of additional micropores, increase in micropore-volume and the unsaturated metal site due to the presence of CMK-3 in MIL-101 [31].

Apart from the commercially available carbon-based materials, efforts have also been made towards exploring natural resources as carbon materials. For instance, hydrothermal carbonization (HTC) of biomass compounds (glucose, sucrose, xylose, fructose, starch, HMF, furfural, etc.) is considered as an important route to obtain micro-meso-macro structured carbon-based materials, under mild and environmentally benign conditions [33-38]. Despite that, very few reports are available on the utilization of biomass as a carbon source to synthesis carbon-MOF composite and its application for H₂ storage [33-39].

Here in, we synthesised carbon-MIL-101 hybrid composites by utilizing *in situ* hydrothermal carbonization (HTC) of glucose during the synthesis of MIL-101 under hydrothermalcondition and investigated their H₂ storage behavior. Carbon content in the synthesised carbon-MIL-101 composite was tuned by controlling the content of glucose and its effect on H₂ storage properties of MIL-101 was systematically investigated. Various spectro-analytical and microscopic techniques such as Raman, ¹³C solid-state NMR, FTIR, XPS, TEM, SEM images, and N₂ sorption measurements were employed to establish the evidence of *in situ* formation of carbon-MIL-101 hybrid composite. The synthesised carbon-MIL-101 composites displayed improved stability, porosity and textural properties, and hence enhanced H₂ storage behavior was achieved for these hybrid composites in comparison to the parent MIL-101, at 77 K and 1 bar.

3.2 Experimental section

3.2.1 Materials and reagents

High purity chemicals and solvents were used for the synthesis and purification of MIL-101 and carbon-MIL-101 composites. Chromium (III) nitrate nonahydrate (98%), terephthalic acid (H₂BDC) (98%), D-(+)-Glucose (anhydrous, 99%) were purchased from Thomas Baker, Sigma Aldrich and Alfa Aesar respectively. The certified highly pure (99.999%) grade H₂, He, and N₂ gases, purchased from Inox air product Ltd, India were used in this study.

3.2.2 Synthesis of MIL-101

Hydrothermal synthesis of MIL-101 was performed according to our previously reported procedure with minor modification in the purification process [32]. In a typical synthesis procedure, $Cr(NO_3)_3 \cdot 9H_2O$ (2.0 g, 5.0 mmol) and H₂BDC (0.833 g, 5.0 mmol) was dissolved in 12M HCl (0.416 mL, 5.0 mmol) in 30 mL of distilled water by sonication for 30 minutes at room temperature. The

mixture wastransferred to a 50 mL Teflon lined autoclave and heated at 493 K for 8 h. The autoclave was allowed to slowly be cooled down to room temperature to obtain a green crystalline material, which was separated by centrifugation (8000 rpm, 15 min). To remove the unreacted H₂BDC, the obtained solid was washed three times with 30 mL of hot distilled water followed by hot methanol, hot ethanol and acetone. To further assure the high purity of the final product, the green solid was sonicated for 30 mL in ethanol-H₂O mixture (v/v-95:5) and heated at 353 K for 12 h in an autoclave. The final product was separated by centrifugation (8000 rpm, 15 min), washed three times with 30 mL of hot ethanol, hot methanol and acetone, and dried under vacuum at 393 K for 12 h.

3.2.3 Hydrothermal carbonization (HTC) of glucose

In general, HTC of glucose can be achieved at the temperature range of 180-250 °C [33-41]. Moreover, HTC reaction condition may significantly influence the chemical nature and morphology of the obtained solid carbonaceous product, along with the liquid and gaseous products [37, 39-41]. Since, we attempted here to integrate HTC of glucose with the synthesis of MIL-101 to ensure the *in situ* generation and incorporation of carbonaceous product in MIL-101 framework; we performed HTC of glucose at 493 K for 8 h under hydrothermal condition. In a typical procedure, 0.1 g D-glucose was dissolved in 30 mL of distilled water and heated in an autoclave at 493 K for 8 h. Autoclave was allowed to slowly cooled down to room temperature and the obtained black solid was separated by centrifugation (8000 rpm, 30 min). The obtained black solid was washed three times with 30 mL of distilled water and thefinal product was dried under vacuum at 393 K for 12 h, Yield 11%.

3.2.4 Synthesis of carbon-MIL-101 hybrid composites

Carbon-MIL-101 hybrid composites with varying amount of carbon loading was synthesised by inducing *in situ* hydrothermal carbonization of glucose during the synthesis of MIL-101. In a typical procedure to synthesise C50-MIL-101 composite, 0.05 g D-glucose dissolved in 30 mL distilled water

was added to a mixture of $Cr(NO_3)_3$ ·9H₂O (2.0 g, 5.0 mmol), H₂BDC (0.833 g, 5.0 mmol) and 12M HCl (0.416 mL, 5.0 mmol) in 30 mL of distilled water, and was sonicated for 30 minutes at room temperature. The obtained mixture was heated in a 50 mL Teflon lined autoclave at 493 K for 8 h. After cooling the reaction mixture to room temperature, the obtained green crystallinesolid was separated by centrifugation (8000 rpm, 15 min). The solid green product was washed three times with 30 mL of hot distilled water followed by hot ethanol (30 mL), hot methanol (30 mL) and acetone (30 mL). Further, purification of the solid green product was performed using an analogous method used for the undoped MIL-101. The obtained solid was dried under vacuum at 393 K for 12 h. Carbon-MIL-101 hybrid composite with varying amount of carbon was obtained using 0.100 g, 0.150 g and 0.200 g of glucose respectively for C100-MIL-101, C150-MIL-101 and C200-MIL-101 under the reaction condition used to obtain C50-MIL-101 hybrid composite, Yield 50% - 60%. Physical mixture of carbon and MIL-101 was prepared by uniform mixing of carbon (obtained from HTC of glucose) and MIL-101.

3.3 Material characterisation and evaluation of H₂ uptake performance

Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku Smart Lab automated X-ray diffractometer system with Cu K α_1 radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA. The patterns were obtained in the range of 1.5-50° with a scan step size of 0.01° and scan speed of 3° per minute at ambient temperature. Raman Spectroscopic study of carbon-MIL-101 hybrid composites was performed on STR 500 confocal micro Raman spectrometer (Make AIRIX Corp. Japan). Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC1 instrument, in nitrogen at a heating rate of 5 °C/min from 25 °C to 800 °C. Fourier transform infrared (FTIR) spectra were obtained using PerkinElmer Spectrum Version 10.5.1 in the 400-3000 cm⁻¹ range of wave number. The elemental (C, H, N and O) analyses of the samples were obtained using a Thermo Scientific analyzer. Scanning electron microscopic images of the

samples were obtined using a Carl Zesis Supra-55 Scanning electron microscope at an accelerating voltage of 5 kV. The transmission electron microscopic (FEI-TEM) images, energy dispersive X-ray spectra (EDXS) and elemental mapping was obtined with the help of a Tecnai G^2 20 (FEI) S-Twin at operating voltage of 200 kV. Samples for TEM analysis was prespared by dispersing the sample in methanol under ultrasonication for 60 minutes, and then the well-dispersed sample was spread over carbon-coated Cu grid and dried at room temperature. ¹³C solid-state single pulse nuclear magnetic resonance (NMR) spectra were acquired on a Jeol-ECX400, 400 MHz high resolution multinuclear FT-NMR spectrometer using 4 mm rotors spinning at a MAS frequency of vMAS=10kHz. Chemical shifts were denoting by the δ in ppm. Relaxation delay was set for 5 s, and number of scans was 8192 (for MIL-101) and 5120 (for C-100-MIL-101 composite). The XPS analyses were conducted over Omicron ESCA (Electron Spectroscope for Chemical Analysis), Oxford Instrument, Germany. Aluminum (Al) anode was used as Monochromatic X-ray energy source ~ 1486.7 eV for samples measurement and resolution was confirmed by FWHM about 0.60 eV. Initially, a wide scan of spectrum survey was carried out for carbon-MIL-101 hybrid composite. To probe the electronic state of the elements (Cr, C and O), thehigh-resolution XPS scan was performed for respective elements. All the samples were dried at 393 K for 8 h under vacuum condition before performing XPS measurement. The textural properties of the carbon-MIL-101 hybrid composite were measured on Quantachrome Autosorb-iQ automated gas sorption instrument using N₂ adsorption-desorption at 77 K in the relative pressure range of 5.0 x $10^{-7} \le P/P_0 \le 1.00$. The measured isotherms were analyzed using Quantachrome® ASiQwinTM software for calculating the framework properties. The surface area was evaluated in the relative pressure range of $0.05 \le P/P_0 \le$ 0.20. Micropore volume was estimated using DA method. The total pore volume was determined using desorption isotherm data at $P/P_0 = 0.99$. The mesopore volume was calculated by difference of total pore volume and micropore volume. The NLDFT and DA (micropore) method was used to estimate the pore size distribution curve in using N₂ sorption data. The adsorbents were outgassed at 393

K for 8 h under ultrahigh vacuum before each measurement. Low-pressure hydrogen uptake measurements (up to 1 bar) were also performed on a Quantachrome Autosorb-iQ automated volumetric apparatus at 77 K.

3.3.1 Sips adsorption equilibrium isotherm models

The hydrogen adsorption isotherms of hybrid carbon-MIL-101 along with physical mixture and HTC of glucose at 77 K were modeled by fitting them to the non-linear form of three parameter Sips isotherm equation (detailed in section 1.9.2.2).

3.4 Results and discussion

Glucose, one of the important constituents of biomass, underwent carbonization under the hydrothermal conditions (453 ~ 523 K) [33-41]. Since HTC is a complex process, involving a sequence of reactions – dehydration, fragmentation, polymerization, aromatization and condensation, reaction product is greatly dependent on the reaction condition [37, 39-41]. Literatures also revealed that, in general, the reaction pathway of HTC of glucose consist of following steps: (i) dehydration to furans (5-HMF), and (ii) de-functionalization of furans into oxygen deficient aromatics and subsequently to carbonaceous solid product. Reaction parameters, such as temperature, time, precursor concentration, precursor carbohydrates, and pH value, involved in an HTC process, can greatly inflence the chemical nature and morphology (particle size and distribution) of the synthesised carbon materials [39-41]. Worthy to mention that the HTC condition for glucose coincide well with the synthetic reaction condition of MIL-101. We, therefore, exploited the advantage of hydrothermal carbonization (HTC) of glucose and incorporated this with the hydrothermal synthesis of MIL-101 to obtain carbon-MIL-101 hybrid composites. Initially, HTC of glucose was performed at 493 K for 8 h under hydrothermal condition (see experimental section) to obtain the solid carbonaceous material. Notably, the residual glucose could not be identified in the reaction mixture obtined after the reaction, suggesting the complete consumption of glucose. Since, our prime focus is the *in*

situ incorporation of carbonaceous solid products in MIL-101, hence we focused only on the solid carbonaceous product obtained from the HTC of glucose 493 K and 8 h, and extensively characterised it. Further, by inducing *in situ* HTC during the synthesis of MIL-101, we synthesised carbon-MIL-101 hybrid composites (C_x -MIL-101, where 'x' is the amount of glucose in mg) with varying carbon loading based on the amount of glucose used during the synthesis, under hydrothermal condition at 493 K for 8 h. Notably, pure MIL-101 was also synthesised under the hydrothermal condition at 493 K for 8 h, under analogous condition, carbon spheres (C100) were also obtained from glucose. Further, the physical mixture of MIL-101 and carbon was obtained by mixing the separately synthesised pure MIL-101 and carbon spheres.

The newly synthesised carbon-MIL-101 hybrid composites along with the carbon sphere, MIL-101 and the physical mixture of MIL-101 and carbon were extensively characterised by powder X-ray diffraction (PXRD), Raman and infrared (IR) spectroscopy, and thermogravimetric analysis (TGA) (Fig. 3.1). The elemental composition of the synthesised carbon-MIL-101 hybrid composite displayed an increment in the carbon content suggesting the loading of carbon in MIL-101. Moreover, the fall in O/C ratio with the increase in carbon content in carbon-MIL-101 hybrid composite as compared to the parent MIL-101, is also in line with the *in situ* HTC of glucose in MIL-101 (Table 3.1) [33, 36, 37, 39, 42]. FTIR spectra of all the synthesised carbon-MIL-101 hybrid composite showed (Fig. 3.1a) characteristics bands ($v_{O-C-O} \sim 1401 \text{ cm}^{-1}$, $v_{ph} \sim 585$ and 1629 cm⁻¹, $v_{c=c}$ ~ 1510 cm⁻¹) for dicarboxylate linker of MIL-101, suggesting that during the *in* situ HTC of glucose the framework of MIL-101 is well preserved. Further, the absence of any vibrations corresponding to glucose in the synthesised carbon MIL-101 hybrid composite, suggesting the successful HTC of glucose in MIL-101 [27, 28, 33]. The TGA curve of glucose-derived carbon spheres displayed two-stage weight loss (Fig. 3.1b). Unlike glucose, the first weight loss occurred at around 100 °C was due to the removal of residual moisture and the volatile matter, while the second major weight loss was observed between 200-550 °C. On the other hand, TGA curves of carbon-MIL-101 hybrid composite showed an

enhanced thermal stability and hydrophobicity upon carbon loading as compared to the parent MIL-101, which can be attributed to the tuning of pore of MIL-101 due to the *in situ* generated carbon materials in carbon-MIL-101 hybrid composites [26-29, 32, 33, 35, 43, 44].

Table 3.1 Elemental analysis (%), O/C, H/C ratio of carbon-MIL-101 hybridcomposite and HTC of glucose (C100)

MOFs	C (wt%)	H (wt%)	O (wt%)	(O/C) ^b	(H / C) ^b
MIL-101	35.35	2.26	29.01	0.61	0.76
C50-MIL-101	37.27	3.17	30.63	0.62	1.01
C100-MIL-101	39.19	3.33	29.23	0.56	1.02
C150-MIL-101	42.94	4.36	28.26	0.49	1.21
C200-MIL-101	44.31	4.82	27.08	0.46	1.29
C100	58.64	4.14	37.21 ^a	0.48	0.84

^aCalculated using a depletion method after C and H value.

^b O/C and H/C are given in atomic ratio.

PXRD patterns of carbon-MIL-101 hybrid composites displayed a notable loss in the intensity of the peaks present in the 2 θ range of 3° – 10°. This effect was more prominent with the increase in carbon loading in MIL-101. Nevertheless, carbon does not lead to any loss in the MIL-101 framework structure, as the characteristic 2 θ peaks for MIL-101 was retained in carbon-MIL-101 hybrid composites. As expected, the PXRD pattern of the physical mixture of MIL-101 and carbon follows the same pattern as of the parent MIL-101 and the carbon sphere (Fig. 3.1c) [26, 28, 32, 34, 37, 39, 43, 44]. Raman spectroscopy was probed to gain more insights on the HTC of glucose and its effect on the synthesised carbon-MIL-101 hybrid composites (Fig. 3.1d). Raman spectra of carbon obtained from HTC of glucose exhibited two distinct peaks at 1360 cm⁻¹ and 1580 cm⁻¹, assigned to D-band and G-band respectively. The presences of band in 1000 – 1900 cm⁻¹ range are of typical carbonized materials, supporting the carbonization of glucose [45, 46]. The carbon-MIL-101 hybrid composites exhibited prominent peaks at 1460 cm⁻¹ and 1580 cm⁻¹, where the peak at 1460 cm⁻¹ can be attributed to the stretching of carbon atoms infused aromatic rings [47].



Fig. 3.1 (a) FTIR spectra, (b) TGA curve, (c) PXRD pattern and (d) Raman spectra of carbon-MIL-101 hybrid composites, MIL-101, carbon (HTC of glucose), glucose and the physical mixture of MIL-101 and carbon (HTC of glucose)

The surface morphology of carbon-MIL-101 hybrid composites, along with the parent MIL-101 and glucose derived carbon spheres was investigated by field emission scanning electron microscopy (FE-SEM) (Fig. 3.2). The high-resolution FE-SEM images inferred the presence of a well-defined topology with uniform size distribution (*ca.* 100 nm) for all the hybrid composites. These results further suggesting that the typical octahedron topology of MIL-101 remained intact during the HTC of glucose, which is consistent with FTIR and PXRD results. Notably, FE-SEM images of carbon-MIL-101 hybrid composite displayed the uniform distribution of carbon particles in MIL-101, suggesting the close

interaction between MOF and carbon particles. In contrary to the carbon-MIL-101 hybrid composite, the physical mixture of MIL-101 and carbon displayed only randomly interacting MOF and carbon particles (Fig. 3.3).



Fig. 3.2 (a-f) SEM images of MIL-101, carbon-MIL-101 hybrid composites, and carbon sphere (HTC of glucose-C100)

The pore texture properties of carbon-MIL-101 hybrid composites along with the physical mixture and HTC of glucose were measured by nitrogen sorption isotherms at 77 K. Table 3.2 represents BET and Langmuir surface area and pore volume of the studied carbon-MIL-101 hybrid composites. The pure MIL-101 exhibited type I isotherm profile with BET surface area of 2441 m² g⁻¹, which is comparable to the literature reports (Table A1) [26-32, 43]. It is worth mentioning here that the different synthesis condition, additive, purification and activation method may influence the surface area value (Table A1). As inferred from Fig. 3.4a, the N₂ sorption isotherms of carbon-MIL-101 hybrid composites showed superior behavior compared to MIL-101, which can be attributed to the presence of high specific surface area and the formation of additional new pores (micro and mesopore) upon incorporation of carbon materials in MIL-101 (Fig. 3.4, 3.5). Moreover, the N₂ sorption behavior was also influenced by the amount of carbon loading in carbon-MIL-101 hybrid composites (Fig. 3.5). As compared to MIL-101, the BET surface area of carbon-MIL-101 hybrid composites showed an enhancement as higher as 27% and followed a trend of C100-MIL-101 > C150-MIL-101 > C50-MIL-101 > C200-MIL-101 > MIL-101. Therefore, amongst the synthesised carbon-MIL-101 hybrid composites, the C100-MIL-101 composite displayed the highest surface area (3102 m² g⁻¹ BET surface area and 4338 m² g⁻¹ Langmuir surface area), suggesting that C100-MIL-101 has the optimum loading of carbon to achieve superior surface properties and porosity. Notably, the physical mixture of MIL-101 and carbon sphere could not show any improvement in the surface area, suggesting the significance of *in situ* HTC of glucose for the synthesis of carbon-MIL-101 hybrid composites.



Fig. 3.3 (a-c) Schematic representation of the morphology evolution and (d–f) SEM images of the physical mixture of MIL-101 and carbon sphere (HTC of glucose-C100)

Table 3.2 Surface area, pore volume and H_2 storage properties of carbon-MIL-101 hybrid composites, MIL-101, HTC of glucose (C100) and the physical mixture of MIL-101 and carbon

	BET	Langmuir	Pore volume			H ₂ uptake		
Adsorbents	surface	surface	$(cm^{3} g^{-1})$			at 77 K and 1.0 bar		
	$(\mathbf{m}^2 \mathbf{g}^{\cdot 1})$	$(\mathbf{m}^2 \mathbf{g}^{-1})$	V _{micro}	V _{meso}	V _{total}	wt%	mmol g ⁻¹	mg g ⁻¹
MIL-101	2441	3430	1.08	0.16	1.24	1.46	7.28	14.69
C50-MIL-101	2590	3605	0.88	0.52	1.40	1.51	7.49	15.10
C100-MIL-101	3102	4338	1.03	0.63	1.66	1.62	8.03	16.21
C150-MIL-101	2619	3635	0.90	0.60	1.50	1.32	6.54	13.20
C200-MIL-101	2459	3434	0.85	0.83	1.68	1.29	6.41	12.93
C100+MIL-101	1758	2461	0.88	0.05	0.93	1.05	5.24	10.56
C100	133	974	0.07	0.09	0.16	0.63	3.13	6.32



Fig. 3.4 (a) N_2 sorption, (b) micropore size distribution by DA method, and (c,d) DFT pore size distribution of incremental and cumulative pore volume of carbon-MIL-101 hybrid composites, MIL-101 and the physical mixture of MIL-101 and HTC of glucose (C100)



Fig. 3.5 (a,b) Low-pressure ranges (up to 10^{-3} and 10^{-4}) profile for N₂ sorption isotherms of various adsorbents

Moreover, increasing the carbon loading beyond the optimized amount appeared to have detrimental effect on the surface area of carbon-MIL-101 composite, presumably due to the pore blockage [26-32]. The pore size distribution of carbon-MIL-101 hybrid composite, MIL-101 and HTC of glucose are estimated by Non-Local Density Function Theory (NLDFT) and Dubinin-Astakhov (DA) method using N₂ sorption data at 77 K [26-32]. The micropore analysis by DA method as shown in Fig. 3.4b, inferred that the pore radius shifted towards microporous region (0.81 nm) for carbon-MIL-101 hybrid composite as compared to MIL-101 (0.87 nm). Moreover, loading of carbon substantially influenced the microporous volume, where the C100-MIL-101 hybrid composite displayed the highest (1.03 cm³ g⁻¹) micropore volume (Table 3.2). However, further higher loading of carbon in MIL-101 led to a decrease in pore volume, inferred the pore tuning in the studied carbon-MIL-101 hybrid composites. The incremental NLDFT pore size distribution curves of carbon-MIL-101 hybrid composites displayed analogous pattern to that of MIL-101 (Fig. 3.4c). However, a visible shift in the pore diameter towards microporous region was observed for the carbon-MIL-101 hybrid composites as compared to MIL-101. A significant increment in micropore volume for carbon-MIL-101 hybrid composite evidenced the formation of additional micro pores due to the *in situ* HTC of glucose in MIL-101. The NLDFT pore size distributions for incremental and cumulative pore volume also correlated well with the above findings (Fig. 3.4c, d). Notably, with the large excess increase in carbon loading (beyond C100-MIL-101 composite), the mesoporous volume also increases, which can be attributed to the generation of additional pores due to the excess of carbon in and around MIL-101, at the same time micropores volume decreases significantly implies the filling of pores. Hence, C100-MIL-101 composite with optimum carbon loading displayed high surface area, high meso- and total pore volume, tuned micropore diameter and volume. Therefore, we further investigated the chemical structure of C100-MIL-101 hybrid composite by ¹³C NMR and X-ray photoelectron spectroscopy (XPS).



Fig. 3.6 (a) ¹³C solid-state NMR and (b-e) high-resolution XPS spectra of C 1s and Cr 2p for C100-MIL-101 composite and MIL-101

The ¹³C solid-state NMR spectra of MIL-101 after carbon incorporation shows the characteristics peaks of HTC carbon in hybrid C100-MIL-101 composite (Fig. 3.6a) [37, 39, 48-51]. The presence of prominent peak at 125-129 ppm, corresponding to C=C of aromatic rings further corroborated well with the aromatization of glucose (HTC of glucose) in MIL-101. Moreover, the presence

of low-intensity peaks at 20 ~ 40 ppm are the characteristics peaks for HTC of glucose (obtained at 200 ~ 240 °C) [37, 39]. Notably, such peaks are absent in the ¹³C NMR spectra of the parent MIL-101. Therefore, the solid-state ¹³C NMR characterisation of the carbon-MIL-101 hybrid composite underlined the evidence of *in situ* HTC of glucose in MIL-101. XPS results of MIL-101 and C100-MIL-101 hybrid composite indicating that the binding energy related to carbon in the MIL-101 framework changed upon carbon incorporation (Fig. 3.6b-e, Fig. 3.7). Narrowing down of carbon C1s peak in carbon-MIL-101 hybrid composite suggesting the incorporation of carbon in MIL-101 due to the *in situ* HTC of glucose (Fig. 3.6c, e). Notably, Cr 2p_{1/2} and Cr 2p_{3/2} peaks appeared at the same position in both MIL-101 and carbon-MIL-101 hybrid composite, evidenced that the MIL-101 framework was intact even after carbon incorporation (Fig. 3.6b, d) [44, 47].



Fig. 3.7 (a) Wide scan XPS spectra and (b-c) high-resolution XPS spectra showing O 1s for MIL-101 and C100-MIL-101 hybrid composite



Fig. 3.8 (a,c) SEM images and (b,d) TEM images (inset HR-TEM) of (a,b) MIL-101 and (c,d) C100-MIL-101 composite

The intrinsic surface morphology of pristine MIL-101 and C100-MIL-101 was also examined by transmission electron microscopy (TEM) (Fig. 3.8). TEM images of C100-MIL-101 composite inferred that the morphology of MIL-101 remains intact even upon incorporation of carbon in MIL-101. Notably, the presence of visible fringes in the HRTEM images of C100-MIL-101 further evidenced the presence of carbon in MIL-101.



Fig. 3.9 (a) Low-pressure hydrogen uptake (at 77 K), (b) Correlation of hydrogen uptake isotherm with Sips isotherm model, and (c) comparative hydrogen uptakes with BET surface area for carbon-MIL-101 hybrid composites, MIL-101, carbon (HTC of glucose) and the physical mixture of MIL-101 and carbon

Hydrogen adsorption studies were performed for MIL-101, carbon sphere and carbon-MIL-101 hybrid composite at 77 K and 1 bar pressure (Fig. 3.9 and Table 3.2). The hydrogen uptake capacity of MIL-101 was 1.46 wt% at 77 K and 1 bar, which is in line with the previous reports [28, 32]. As inferred from Fig. 3.9a, the hydrogen uptake capacity increased initially with the increase in the loading of carbon in MIL-101. Notably, C50-MIL-101 and C100-MIL-101 exhibited hydrogen uptake capacity of 1.51 wt% and 1.62 wt%, respectively, which is higher as compared to the parent MIL-101 (1.46 wt%) at 77 K and 1 bar. However, with the further increase in carbon loading hydrogen uptake capacity drastically deteriorated to 1.32 wt% and 1.29 wt% respectively for C150-MIL-101 and C200-MIL-101 composites. The above-enhanced hydrogen uptake properties of carbon-MIL-101 composites (C50-MIL-101 and C100-MIL-101) can be attributed to the formation of additional micropores and optimization of pore volume of MIL-101 upon carbon loading via in situ HTC of glucose in MIL-101. Pore textural properties validated that with the increase in carbon loading, surface area along with the meso- and total pore volume also increased significantly, while micro pore volume was optimized to the maximum value for C100-MIL-101 hybrid composite (Table 3.2). However, further increase in carbon loading in MIL-101 (C150-MIL-101 and C200-MIL-101) resulted in only a marginal increase in surface area, total pore volume as compared to MIL-101. Noticeably, the micropore volume for C150-MIL-101 and C200-MIL-101 composites decreased remarkably well below to that for MIL-101, presumably due to pore blockage of MIL-101 with the higher loading of carbon. Notably, the H₂ sorption isotherms for the studied carbon-MIL-101 hybrid composites are not yet fully saturated, and therefore higher H_2 adsorption capacity can be expected at higher pressures. Further, to evaluate the significance of *in situ* HTC of glucose for synthesising carbon-MIL-101 hybrid composites with tuned porosity and textural properties, N₂ sorption and H₂ storage capacity of the physical mixture of carbon and MIL-101 was also investigated. The N2 adsorption-desorption isotherms inferred no enhancement in the porosity and surface area for physical mixture. Furthermore, a hysteresis in N₂ and H₂ adsorption-desorption isotherm was observed for the physical mixture, which can be attributed to the different kinetics of the separately mixed carbon and MIL-101 composite (Fig. 3.9 and Fig. 3.10). Notably, the hydrogen uptake capacity of the physical mixture was also found to be well below to that for C100-MIL-101 hybrid composite. The hydrogen uptake capacities were in the order of C100-MIL-101 > C50-MIL-101 > MIL-101 > C150-MIL-101 > C200-MIL-101 > C100+MIL-101 hybrid composite. Hence, above findings clearly demonstrated the significance of in situ HTC of glucose during the synthesis of MIL-101, obtain carbon-MIL-101 hybrid composite with tuned porosity, textural properties and superior hydrogen capacities.

Notably, the observed H₂ uptake capacities of the studied carbon-MIL-101 hybrid composite are comparable or even higher than several other important

MOFs and their carbon composites extensively explored for H_2 uptake (Table 3.3). For instance, recently we incorporated activated carbon during the synthesis of MIL-101 and observed hydrogen uptake of 1.48 wt% for AC-MIL-101 at 77 K and 1 bar [32]. Analogously, for carbon nanodots (C-dots) functionalized UMCM-1 composite (Cdots@UMCM-1) a hydrogen uptake of 1.2 wt% was observed, which was attributed to the interaction between the polar functional groups at surface of C dots and H_2 molecules [53]. The hybrid composite of acid treated multi-walled carbon nanotubes (MWCNTs) and MOF-5 exhibited an enhancement in the hydrogen capacity from 1.2 wt% to 1.52 wt% at 77 K and 1 bar as compared to the parent MOF-5 [23]. A very low hydrogen uptake (0.84 wt%) was observed for a functionalized carbon nanotube (FCNF) hybrid MOF composite (MOF@FCNF) [24]. Further, inducing interpenetrated structure with high mesoporosity in MOF-5 by incorporation of MWCNT also resulted in an enhancement of H₂ uptake (2.02 wt%) at 77 K and 1 bar [54]. Doping Li in AC@MIL-101 and Zn-based MOF also resulted in an enhancement in H₂ uptake to 1.60 wt% and 1.63 wt%, respectively [28, 55].



Fig. 3.10 N₂ sorption analysis of physical mixture C100+MIL-101

MOFs	Surface Pore		H_2	Ref.
	area volume		uptake	
	$(m^2 g^{-1})$	$(cm^{3} g^{-1})$	(wt%)	
MIL-101	2441	1.24	1.46	
C50-MIL-101	2590	1.40	1.51	Present
C100-MIL-101	3102	1.66	1.62	study
C150-MIL-101	2619	1.50	1.32	
C200-MIL-101	2459	1.68	1.29	
C100+MIL-101	1758	0.93	1.05	
Li@AC-MIL-101	2791	1.65	1.60	[28]
MIL-101	3148	2.10	1.20	
MIL-101	2323		1.40	[32]
AC-MIL-101	2619	2.79	1.48	
RHA-MIL-101	2524	1.95	1.54	
UMCM-1	4150	2.14	1.11	[52]
Cdots@UMCM-1a	3714	1.95	1.21	
MOF-177	3275	2.65	1.32	[56]
MOF-177	3100	1.58	1.50	[57]
MOF-5/MWCNT	2900	0.765	1.52	[23]
MOF-5	1810	0.552	1.20	
FCNF	23		0.27	[53]
MOF-2	39		0.63	
MOF@FCNF	50		0.84	
MOF-5/Pt-MWCNT	1692	0.84	1.89	[24]
MOF-5	1758	0.82	1.20	
MOF-5/MWCNT	805		2.02	[54]
C075Zn25-ZIF-8	1571.7	0.7750	1.55	[11]
Pt/AC-MOF-5	740	0.30	1.395	[25]
MOF-5	670	0.31	1.399	
SodZMOF	361	0.13*	1.6	[58]
4Li ⁺ Me-SodZMOF	334	0.12*	1.18	
4Na ⁺ Me-odZMOF	804	0.33*	1.6	
4K ⁺ Me-SodZMOF	181	0.07*	0.8	
Li ⁺ Zn ₂ (NDC) ₂ (diPyNI)	802	0.30	1.63	[55]
Zn ₂ (NDC) ₂ (diPyNI)	756	0.34	0.93	
ZIF-67	1319.9		1.26	[59]
Cu/ZIF-67	1324.1		1.51	
Ni-GO/MIL	2045	0.98	1.64	[60]
ZIF-8	1810	0.66	1.29	[61]
ZIF-11	1947	0.58	1.37	

Table 3.3 Comparative charts for the surface area, pore volume, and H_2 uptake data for selected MOFs at 77 K and 1 bar

* H₂ adsorption at 10 bar

Sips isotherm	ks	ts	as	\mathbf{R}^2	ARE (%)
models parameters					
MIL-101	1.93677	0.62386	0.30988	0.9998	1.54
C50-MIL-101	2.41191	0.70758	0.60332	0.9997	1.11
C100-MIL-101	2.69470	0.73114	0.67213	0.9998	1.45
C150-MIL-101	2.01852	0.73295	0.53611	0.9999	1.23
C200-MIL-101	1.79208	0.69984	0.38844	0.9998	0.59

 Table 3.4 Isotherm constants for the three-parameter Sips isotherm models of

 carbon-MIL-101 hybrid composites and MIL-101

Further, three parameter non-linear sips isotherm model was employed to describe the H₂ adsorption behavior for carbon-MIL-101 hybrid composites (Fig. 3.9b and Table 3.4) [62]. The fitting parameters and correlation coefficient ($R^2 \ge 0.999$) inferred a good agreement with the experimental H₂ isotherms. The above observation inferred that the enhanced hydrogen uptake was presumably adopted a non-linear multilayer adsorption behavior due to the heterogeneity in the surface of the carbon-MIL-101 hybrid composites induced by *in situ* HTC of glucose in MIL-101.

3.5 Conclusion

In summary, we explored a simple approach to synthesis carbon-MIL-101 hybrid composite by inducing *in situ* HTC of glucose in MIL-101 under hydrothermal condition to achieve enhanced H₂ uptake. The presence of carbon in MIL-101 was established by Raman, SEM, TEM, TGA, ¹³C solid-state NMR, and XPS investigations. Incorporation of an optimum amount of carbon in MIL-101 remarkably influenced the porosity and textural properties of the carbon-MIL-101 hybrid composite. Results inferred that among the synthesised carbon-MIL-101 hybrid composites, the C100-MIL-101 hybrid composite displayed higher surface area and pore volume than the parent MIL-101. Hence, an increment of 11% in hydrogen uptake (1.62 wt%) was observed for C100-MIL-101 composite as

compared to the MIL-101 at 77 K and 1 bar. However, higher carbon loading in MIL-101 resulted in pore filling and reduction in surface area and micropore volume, and hence exhibited significant loss in H₂ uptake. Notably, the physical mixture of MIL-101 and carbon also displayed poor H₂ uptake under analogous conditions, significantly endorsed the importance of *in situ* incorporation of carbon in MIL-101. Therefore, our results substantiate the importance of *in situ* HTC of glucose during the synthesis of MOF to develop carbon-MOF hybrid composites with superior porosity and surface area, and hence enhanced H₂ uptake properties.

Note: The content of this chapter is published as Panchariya *et al.*, Energy & Fuels, 2019, 33, 10123-10132, (DOI:10.1021/acs.energyfuels.9b01809) and reproduced with the permission of American Chemical Society.

3.6 References

- [1] Turner J.A. (1999), A Realizable Renewable Energy Future, Science, 285, 687-689.
- [2] Graetz J. (2009), New Approaches to Hydrogen Storage, Chem. Soc. Rev., 38,73-82.
- [3] Morris R.E., Wheatley P.S. (2008), Gas Storage in Nanoporous Materials, Angew. Chem., Int. Ed., 47, 4966-4981.
- [4] Durbin D.J., Malardier-Jugroot C. (2013), Review of Hydrogen Storage Techniques for on Board Vehicle Applications, Int. J. Hydrogen Energy, 38, 14595-14617.
- [5] Schlapbach L., Zuttel A. (2001), Hydrogen-Storage Materials for Mobile Applications, Nature, 414, 353-358.
- [6] Zuttel A. (2003), Materials for Hydrogen Storage, Mater. Today, 6, 24-33.
- [7] Murthy S.S., Kumar E.A. (2014), Advanced Materials for Solid State Hydrogen Storage: Thermal Engineering Issues, Appl. Therm. Eng., 72, 176-189.

- [8] Langmi H.W., Ren J., North B., Mathe M., Bessarabov D. (2014), Hydrogen Storage in Metal-Organic Frameworks: A Review, Electrochim. Acta, 128, 368-392.
- [9] Suh M.P., Park H.J., Prasad T.K., Lim D.W. (2012), Hydrogen Storage in Metal-Organic Frameworks, Chem. Rev., 112, 782-835.
- [10] Furukawa H., Cordova K.E., O'Keeffe M., Yaghi O.M. (2013), The Chemistry and Applications of Metal-Organic Frameworks, Science, 341, 1230444.
- [11] Kaur G., Rai R.K., Tyagi D., Yao X., Li P.Z., Yang X.C., Zhao Y., Xu Q., Singh S.K. (2016), Room-Temperature Synthesis of Bimetallic Co-Zn Based Zeolitic Imidazolate Frameworks in Water for Enhanced CO₂ and H₂ Uptakes, J. Mater. Chem. A, 4, 14932-14938.
- [12] Panchariya D.K., Rai R.K., Kumar E.A., Singh S.K. (2018), Core-shell Zeolitic Imidazolate Frameworks for Enhanced Hydrogen Storage, ACS Omega, 3, 167-175.
- [13] Ferey G., Draznieks C.M., Serre C., Millange F., Dutour J., Surble S., Margiolaki I. (2005), A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area, Science, 309, 2040-2042.
- [14] Jhung S.H., Lee J.H., Yoon J.W., Serre C., Ferey G., Chang J.S. (2007), Microwave Synthesis of Chromium Terephthalate MIL-101 and Its Benzene Sorption Ability, Adv. Mater., 19, 121-124.
- [15] Latroche M., Surble S., Serre C., Mellot-Draznieks C., Llewellyn P.L., Lee J.H., Chang J.S., Jhung S.H., Ferey G. (2006), Hydrogen Storage in the Giant Pore Metal-Organic Frameworks MIL-100 and MIL-101, Angew. Chem., Int. Ed., 45, 8227-8231.
- [16] Hong D.Y., Hwang Y.K., Serre C., Ferey G., Chang J.S. (2009), Porous Chromium Terephthalate MIL-101 with Coordinatively Unsaturated Sites: Surface Functionalization, Encapsulation, Sorption and Catalysis, Adv. Funct. Mater, 19, 1537-1552.

- [17] Hwang Y.K., Hong D.Y., Chang J.S., Jhung S.H., Seo Y.K., Kim J., Vimont A., Daturi M., Serre C., Ferey G. (2008), Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation, Angew. Chem., Int. Ed., 47, 4144-4148.
- [18] Sculley J., Yuan D., Zhou H.C. (2011), The Current Status of Hydrogen Storage in Metal-Organic Frameworks – Updated, Energy Environ. Sci., 4, 2721-2735.
- [19] Murray L.J., Dinca M., Long J.R. (2009), Hydrogen Storage in Metal-Organic Frameworks, Chem. Soc. Rev., 38, 1294-1314.
- [20] Rowsell J.L.C., Yaghi O.M. (2005), Strategies for Hydrogen Storage in Metal-Organic Frameworks, Angew. Chem., Int. Ed., 44, 4670-4679.
- [21] Zhu Q.L., Xu Q. (2014), Metal-Organic Framework Composites, Chem. Soc. Rev., 43, 5468-5512.
- [22] Liu X.W., Sun T.J., Hu J.L., Wang S.D. (2016), Composites of Metal-Organic Frameworks and Carbon-Based Materials: Preparations, Functionalities and Applications, J. Mater. Chem. A, 4, 3584-3616.
- [23] Yang S.J., Choi J.Y., Chae H.K., Cho J.H., Nahm K.S., Park C.R. (2009), Preparation and Enhanced Hydrostability and Hydrogen Storage Capacity of CNT@MOF-5 Hybrid Composite, Chem. Mater., 9, 1893-1897.
- [24] Yang S.J., Cho J.H., Nahm K.S., Park C.R. (2010), Enhanced Hydrogen Storage Capacity of Pt-Loaded CNT@MOF-5 Hybrid Composites, Int. J. Hydrogen Energy, 35, 13062-13067.
- [25] Chien A.C., Chuang S.S.C. (2011), Static and Dynamic Hydrogen Adsorption on Pt/AC and MOF-5, Int. J. Hydrogen Energy, 36, 6022-6030.
- [26] Rallapall P.B.S., Raj M.C., Patil D.V., Prasanth K.P., Somani R.S., Bajaj H.C. (2013), Activated Carbon@MIL-101(Cr): A Potential Metal-Organic Framework Composite Material for Hydrogen Storage, Int. J. Energy Res., 37, 746-753.

- [27] Prasanth K.P., Rallapalli P., Raj M.C., Bajaj H.C., Jasra R.V. (2011), Enhanced Hydrogen Sorption in Single Walled Carbon Nanotube Incorporated MIL-101 Composite Metal-Organic Framework, Int. J. Hydrogen Energy, 36, 7594-7601.
- [28] Prabhakaran P.K., Deschamp J. (2015), Doping Activated Carbon Incorporated Composite MIL-101 using Lithium: Impact on Hydrogen Uptake, J. Mater. Chem. A, 3, 7014-7021.
- [29] Yu Z., Deschamps J., Hamon L., Prabhakaran P.K., Pre P. (2017), Hydrogen Adsorption and Kinetics in MIL-101(Cr) and Hybrid Activated Carbon-MIL-101(Cr) Materials, Int. J. Hydrogen Energy, 42, 8021-8031.
- [30] Yu Z., Deschamps J., Hamon L., Prabhakaran P.K., Pre P. (2017), Modeling Hydrogen Diffusion in Hybrid Activated Carbon-MIL-101(Cr) Considering Temperature Variations and Surface Loading Changes, Microporous Mesoporous Mater, 248, 72-83.
- [31] Zhang Z., Wang H., Chen X., Zhu C., Wei W., Sun Y. (2015), Chromium-Based Metal-Organic Framework/Mesoporous Carbon Composite: Synthesis, Characterization and CO₂ Adsorption, Adsorption, 21, 77-86.
- [32] Panchariya D.K., Rai R.K., Kumar E.A., Singh S. K. (2019), Silica-Rich MIL-101(Cr) for Enhanced Hydrogen Uptake, J. Porous Mater., 26, 1137-1147.
- [33] Titirici M.M., Antonietti M. (2010), Chemistry and Materials Options of Sustainable Carbon Materials Made by Hydrothermal Carbonization, Chem. Soc. Rev., 39, 103-116.
- [34] Titirici M.M., White R.J., Falco C., Sevilla M. (2012), Black Perspectives for a Green Future: Hydrothermal Carbons for Environment Protection and Energy Storage, Energy Environ. Sci., 5, 6796-6822.
- [35] Krishnan D., Raidongia K., Shao J., Huang J. (2014), Graphene Oxide Assisted Hydrothermal Carbonization of Carbon Hydrates, ACS Nano, 8, 449-457.

- [36] Sevilla M., Fuertes A.B., Mokaya R. (2011), High Density Hydrogen Storage in Superactivated Carbons from Hydrothermally Carbonized Renewable Organic Materials, Energy Environ. Sci., 4, 1400-1410.
- [37] Titirici M.M., White R.J., Brun N., Budarin V.L., Su D.S., Monte F.D., Clark J.H., MacLachlan M.J. (2015), Sustainable Carbon Materials, Chem. Soc. Rev., 44, 250-290.
- [38] Zhang P., Qiao Z., Dai S. (2015), Recent Advances in Carbon Nanospheres: Synthetic Routes and Applications, Chem. Commun., 51, 9246-9256.
- [39] Falco C., Baccile N., Titirici M.M. (2011), Morphological and Structural Differences between Glucose, Cellulose and Lignocellulosic Biomass Derived Hydrothermal Carbons, Green Chem., 13, 3273-3281.
- [40] Hu B.B., Wang K., Wu L., Yu S.H., Antonietti M., Titirici M.M. (2010), Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass, Adv. Mater., 22, 813-828.
- [41] Funke A., Ziegler F. (2010), Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering, Biofuels Bioprod. Biorefin., 4, 160-177.
- [42] Falco C., Caballero F.P., Babonneau F., Gervais C., Laurent G., Titirici M.M., Baccile N. (2011), Hydrothermal Carbon from Biomass: Structural Differences between Hydrothermal and Pyrolyzed Carbons via ¹³C Solid State NMR, Langmuir, 27, 14460-14471.
- [43] Lin Y., Yan Q., Kong C., Chen L. (2013), Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO₂ Capture, Sci. Rep., 3, 1859.
- [44] Gong J., Michalkiewicz B., Chen X., Mijowska E., Liu J., Jiang Z., Wen X., Tang T. (2014), Sustainable Conversion of Mixed Plastics into Porous Carbon Nanosheets with High Performances in Uptake of Carbon Dioxide and Storage of Hydrogen, ACS Sustainable Chem. Eng., 2, 2837-2844.
- [45] Sheng C. (2007), Char Structure Characterised by Raman Spectroscopy and its Correlations with Combustion Reactivity, Fuel, 86, 2316-2324.

- [46] Cuesta A., Dhamelincourt P., Laureyns J., Martinez-Alonso A., Tascon J.M.D. (1994), Raman Microprobe Studies on Carbon Materials, Carbon, 32, 1523-1532.
- [47] Sevilla M., Fuertes A.B. (2009), Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides, Chem. Eur. J., 16, 4195-4203.
- [48] Cendak T., Zunkovic E., Godec T.U., Mazaj M., Logar N.Z., Mali G. (2014), Indomethacin Embedded into MIL-101 Frameworks: A Solid-State NMR Study, J. Phys. Chem. C, 118, 6140-6150.
- [49] Horcajada P., Serre C., Vallet-Regi M., Sebban M., Taulelle F., Ferey G.
 (2006), Metal-Organic Frameworks as Efficient Materials for Drug Delivery, Angew. Chem., Int. Ed., 45, 5974-5978.
- [50] Goesten M.G., Juan-Alcaniz J., Ramos-Fernandez E.V., Gupta K.B.S.S., Stavitski E., Bekkum H.V., Gascon J., Kapteijn F. (2011), Sulfation of Metal-Organic Frameworks: Opportunities for Acid Catalysis and Proton Conductivity, J. Catal., 281, 177-187.
- [51] Luo X., Shena T., Ding L., Zhong W., Luo J., Luo S. (2016), Novel Thymine-Functionalized MIL-101 Prepared by Post-Synthesis and Enhanced Removal of Hg²⁺ from Water, J. Hazard. Mater., 306, 313-322.
- [52] Li J.S., Tang Y.J., Li S.L., Zhang S.R., Dai Z.H., Si L., Lan Y.Q. (2015), Carbon Nanodots Functional MOFs Composites by A Stepwise Synthetic Approach: Enhanced H₂ Storage and Fluorescent Sensing, Cryst. Eng. Comm., 17, 1080-1085.
- [53] Pachfule P., Balan B.K., Kurungot S., Banerjee R. (2012), One-Dimensional Confinement of A Nano sized Metal-Organic Framework in Carbon Nanofibers for Improved Gas Adsorption, Chem. Commun., 48, 2009-2011.
- [54] Jiang H., Feng Y., Chen M., Wang Y. (2013), Synthesis and Hydrogen-Storage Performance of Interpenetrated MOF-5/MWCNTs Hybrid Composite with High Mesoporosity, Int. J. Hydrogen Energy, 38, 10950-10955.

- [55] Mulfort K.L., Hupp J.T. (2007), Chemical Reduction of Metal-Organic Framework Materials as a Method to Enhance Gas Uptake and Binding, J. Am. Chem. Soc., 129, 9604-9605.
- [56] Saha D., Wei Z., Deng S. (2008), Equilibrium, Kinetics and Enthalpy of Hydrogen Adsorption in MOF-177, Int. J. Hydrogen Energy, 33, 7479-7488.
- [57] Li Y., Yang R.T. (2007), Gas Adsorption and Storage in Metal-Organic Framework MOF-177, Langmuir, 23, 12937-12944.
- [58] Calleja G., Botas J.A., Sanchez M.S., Orcajo M.G. (2010), Hydrogen Adsorption Over Zeolite-Like MOF Materials Modified by Ion Exchange, Int. J. Hydrogen Energy, 35, 9916-9923.
- [59] Yang H., He X.W., Wang F., Kang Y., Zhang J. (2012), Doping Copper into ZIF-67 for Enhancing Gas Uptake Capacity and Visible-Light-Driven Photocatalytic Degradation of Organic Dye, J. Mater. Chem. A, 22, 21849-21851.
- [60] Lee S.Y., Park S.J. (2013), Hydrogen Storage Behaviors of Ni-Doped Graphene Oxide/MIL-101 Hybrid Composites, J. Nano sci. Nanotech, 13, 443-447.
- [61] Park K.S., Ni Z., Cote A.P., Choi J.Y., Huang R., Uribe-Romo F.J., Chae H.K., O'Keeffe M., Yaghi O.M. (2006), Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks, Proc. Natl. Acad. Sci. U. S. A., 103, 10186-10191.
- [62] Foo K.Y., Hameed B.H. (2010), Insights into the Modeling of Adsorption Isotherm Systems, Chem. Eng. J., 156, 2-10.

Chapter 4

Silica-rich MIL-101(Cr): Synthesis, Characterisation and Hydrogen Storage

4.1 Introduction

MOFs display tunable physical (porosity and framework) and chemical properties, such as high surface area, high pore volume, low density framework and tunable pore size and ultra-high porosity, due to the available flexibility in judicial choice of organic linkers and inorganic nodes [1-13]. Hence, MOFs, have received extensive attention for various applications like gas storage, separation, catalysis, magnetism, drug delivery, and luminescence [4, 8, 13-15]. Among several MOFs explored for H₂ storage applications, MIL-101 has received more attention due to its large surface area (BET > 4100 m² g⁻¹, Langmuir > 5400 m² g⁻¹ ¹), large mesoporous cage (29 Å ~ 34 Å). Strategies to accomplish high H₂ uptakes over MOFs, depend on several parameters and efficient surface to H_2 interactions is essentially one of the important parameters [16-18]. This can be achieved by incorporation of metal nanoparticles, suitable cations and modification or functionalization of organic linkers [9, 10]. Moreover, hybrid structures, such as composites of porous MOF materials, possess high surface area and functionalized/activated porous framework [4, 19-21]. Extensive research in this direction has resulted in the development of several materials with high hydrogen uptake capacities, for instance AC@MIL-101 (50.5 mmol g⁻¹ at 60 bar and 77 K), SWCNT@MIL-101 (3.2 mmol g⁻¹ at 60 bar and 298 K), Pt/AC-MIL-101 (7.2 mmol g⁻¹ at 100 bar and 298 K), Pd@MIL-101 (1.2 mmol g⁻¹ at 45 bar and 298 K) and so on [22-27]. Literature has revealed that composites of MOFs with carbon-based materials have been extensively explored for gas storage application, even at low pressure (77 K and 1 bar) [20-24, 26, 28-33]. For low pressure (77 K and 1 bar) hydrogen storage, Deschamps et al. reported recently that doping Li in AC@MIL-101 sample resulted in an enhancement in H₂ uptake to 1.60 wt% compared to bare MIL-101, when high affinity of Li toward hydrogen molecules is attributed to the observed enhancement in H₂ uptake for Li@AC-MIL-101 [31]. Mulfort *et al.* reported 1.63 wt% H₂ uptake over Li doped MOF at 77 K and 1 bar [32]. A H₂ uptake of 1.52 wt% was also reported by Wang *et al.* over CNT@MOF-5, under analogous conditions [33].

On the other hand, Zeolitic materials exhibit appreciable affinity towards the adsorption and activation of small molecule, such as H_2 , N_2 or O_2 [34]. In particular, the –OH groups of Zeolite are expected to undergo weak interaction with H_2 molecule, as also probed by extensive infrared studies [34]. Analogous to Zeolitic materials, surface of silica materials is also enriched by silanols (Si–OH), and these silanol bonds also show similar behavior as observed for Zeolitic –OH bonds [35-37]. Hence, silica materials were also explored for the hydrogenation reactions, where the controlled experiments using D_2 or HD, probed by infrared spectroscopic studies, inferred that the silanol bonds exhibit high affinity towards H_2 molecules [28, 34, 36, 37]. Therefore, it is obvious to explore, *why silica* (*silica-rich*) materials, which is available in abundance, can't be used as a hydrogen storage material.

Despite the high potential of silica materials, surprisingly, application of composites of MOF with silica-rich materials for gas sorption, in particular, H₂ storage remains elusive, compared to carbon incorporated MOF composites. In order to explore silica (or silica-rich materials as an alternative to carbon based materials for H₂ storage application, a new hybrid composite of MIL-101 was developed by incorporating silica-rich Rice husk ash (RHA) to achieve improved H₂ storage properties (1.54 wt% at 77 K and 1 bar). In this study, RHA, an inexpensive and waste by-product of the rice industry, was incorporated into MIL-101 *in situ* during the synthesis *via* hydrothermal technique. Activated carbon incorporated composite of MIL-101 (AC-MIL-101) was also synthesised analogously using crystalline Darco-100. Incorporation of RHA or AC into MIL-101 and the structural, morphological and chemical properties of the newly synthesised composites of MIL-101 were probed by PXRD, FTIR, SEM and EDXS/elemental mapping studies. Porous properties (surface area, pore size

distribution, total pore volume) and thermal stabilities of the newly synthesised MIL-101 composites were determined by N_2 adsorption desorption isotherm and TGA studies. Furthermore, H_2 uptake properties of as-synthesised RHA-MIL-101 composite were evaluated at 77 K and 1 bar and thoroughly compared with those of established carbon-based MIL-101 composites and bare MIL-101. Moreover, the obtained experiment data were fitted using non-linear two parameters and three parameters adsorption equilibrium isotherm models.

4.2 Experimental details

4.2.1 Reagents and materials

Chromium (III) nitrate nonahydrate (98%) was supplied by Thomas Baker. Benzene-1-4-dicarboxylic acid (H₂BDC, 98%) was purchased from Sigma Aldrich. Acetone (\geq 99%), nitric acid (68-70%), hydrochloric acid (36.5-38%) and distilled water were obtained from Merck. Ethanol (99.9%) was bought from S D Fine Chemical. All these reagents and materials were used as supplied by supplier without further purification. Helium, nitrogen and hydrogen gases were used for obtaining the framework properties and low-pressure adsorption measurements were certified ultra-high purity (99.999%) grade was purchased from Inox air product ltd, India. The Rice husk ash (RHA, Nishant Enterprises India) and activated charcoal-DARCO-100 mesh particle size (AC, Sigma Aldrich) were obtained and used for *in situ* during the synthesis of MIL-101.

4.2.2 Preparation of MIL-101 adsorbent

MIL-101 adsorbent was synthesised according to the procedure reported by Lin *et al.* with minor modifications of the purification process [38, 39]. The MIL-101 adsorbent was synthesised by hydrothermal reaction. 2.0 g of $Cr(NO_3)_3 \cdot 9H_2O$ was mixed with 0.833 g of C_6H_4 -1,4-(COOH)₂ 0.416 mL of 12M HCl and 30 mL of distilled water in a 50 mL Teflon lined autoclave. The mixture was sonicated for 30 minutes for obtaining uniform solution. The mixture was then heated at 493 K for 8 hours. After the reaction, Teflon lined autoclave was cooled down to ambient temperature. The generated green color crystals were separated from the solution by centrifugation at around 6000 rpm for 15 minutes. To remove unreacted regents, the generated green crystals were washed twice with hot distilled water, acetone and hot ethanol respectively. After that, precipitated green crystals were transferred in to a 50 mL Teflon lined autoclave and mixed with 30 mL mixture of hot ethanol (95%) and distilled water (5%). The mixture was sonicated for 30 minutes and heated at 353 K for 8 hours. Then, the autoclave was cooled to ambient temperature and the mixture was decanted from the mixture, the green crystal adsorbent was dehydrated at 353 K under low vacuum condition for 12 hours [39]. The final adsorbent was obtained with a yield of ~ 60% based on chromium.

4.2.3 Pre-treatment of rice husk ash (RHA) and activated charcoal (AC)

Pre-treatment process was performed to obtain uniform particle size, purity and functionalized form of supplied rice husk ash (RHA) and activated charcoal (AC). The supplied product contained impurities (moisture, oxide layer, etc.) and non-uniform particle size. Uniform particle size was obtained by solid grinding of material for 60 minutes and sieving by 200-micron mesh size sieves. Impurities in the materials were removed by heating them at 393 K under 10^{-3} mbar vacuum conditions for 12 hours. Uniform particle size and purified RHA and AC were functionalized by the treatment of (1:1, v/v) HNO₃/Distilled water.

4.2.4 Preparation of RHA-MIL-101 and AC-MIL-101 hybrid composites

Figure 4.1 represents the synthetic scheme of hybrid composite. In a typical procedure to synthesise RHA-MIL-101 hybrid composite, 0.0125 g of functionalized and purified RHA was mixed with $Cr(NO_3)_3 \cdot 9H_2O$ (2.0 g), C_6H_4 -1,4-(COOH)₂ (0.833 g), 12 M HCl (0.416 mL) and 30 mL distilled water in a 50 mL Teflon lined autoclave. The reaction mixture was sonicated for 30 minutes and then heated at 493 K for 8 hours in a programable oven. After cooling to ambient temperature, the obtained green crystalline solid was washed twice with hot distilled water, acetone and hot ethanol respectively to remove any unreacted

organic linker or metal salt. Further purification was conducted by sonicating the green solid in 30 mL mixture of hot ethanol (95%) and distilled water (5%) in a 50 mL Teflon lined autoclave for 30 minutes, followed by heating at 353 K for 8 hours in a programable oven. The final product was activated in vacuum at 353 K for 12 hours.

AC-MIL-101 hybrid composite was also obtained under analogous reaction condition by using 0.0125 g of functionalized and purified AC.

4.2.5 Preparation of physical mixture of AC and RHA with MIL-101 adsorbent

A physical mixture of AC and RHA with MIL-101 was prepared by mixing the AC and RHA with pre-synthesised MIL-101 (as per section 4.2.2), in same weight ratio used for the synthesis of RHA-MIL-101 and AC-MIL-101 hybrid composites. The physical mixture was further dried under vacuum at 393 K for 12 hours. Here, physical mixtures are denoted as AC+MIL-101 and RHA+MIL-101.



Fig. 4.1 Synthetic scheme of the hybrid composites of MIL-101

4.3 Instruments for physical characterisation

Powder X-ray diffraction (PXRD) data was obtained using a Rigaku Smart Lab automated X-ray diffractometer system with Cu K α radiation ($\lambda = 1.5406$ Å). The data was obtained in the range of $2-30^{\circ}$ with a scan step of 0.01° and scan speed of 3° per minute at ambient temperature. The functional groups of adsorbents were identified by Fourier transform infrared spectroscopy (FTIR) using instruments of PerkinElmer Spectrum Version 10.5.1 in the 500-4000 cm⁻¹ range of wave number. The adsorbents were dried under vacuum condition at 393 K for 6 hours before the FTIR analysis. The scanning electron microscopy (SEM) images were captured using Carl Zesis Supra-55 equipment. Energy dispersive Xray spectroscopy (EDXS) was carried out using EDXS Oxford instruments model X-Max attached with Carl Zesis Supra-55 system. The elemental analysis of the adsorbents was obtained using a Thermo Scientific analyzer. Thermo gravimetric analysis (TGA) was conducted using Mettler Toledo TGA/DSC1 instrument at a heating rate of 5 °C/min room temperature to 800 °C. The framework properties of the adsorbents were measured on Quantachrome Autosorb-iQ automated gas sorption instrument using Nitrogen adsorption-desorption at 77 K in the relative pressure range of $0.025 \le P/P_0 \le 1.00$. The measured isotherms were analyzed using Quantachrome® ASiQwinTM software for calculating the framework properties. The framework properties include BET and Langmuir surface areas, total pore volume and pore size distribution. The isotherms data in the P/P_0 range of 0.05-0.20 was used to calculate surface area. The total pore volume was determined using desorption isotherm data at $P/P_0 = 0.99$. The NLDFT method was used to estimate the pore size distribution curve in MIL-101 and composite of RHA-MIL-101 and AC-MIL-101. Before measurement of the N₂ adsorptiondesorption isotherm, the adsorbents were outgassed at 393 K for 8 hours to remove the impurities.
4.3.1 Hydrogen adsorption measurement

4.3.1.1 Low pressure hydrogen adsorption measurements

Low pressure hydrogen adsorption measurements (up to 1 bar) were performed on a Quantachrome Autosorb-iQ automated volumetric apparatus at liquid nitrogen temperature. For this purpose, approximate 50~100 mg of adsorbents was filled into sample a cell (glass filler rod~6mm) and degassed under ultra-high vacuum at 393 K for 8 hours, before measuring hydrogen adsorption isotherms. The hydrogen sorption measurement of synthesised materials was carried out twice.

4.3.2 Adsorption equilibrium isotherm models

The hydrogen adsorption isotherms of MIL-101, RHA-MIL-101 and AC-MIL-101 at 77 K were modelled by fitting them to the non-linear form of two parameter isotherms; Langmuir and Freundlich isotherm equations, and three parameter isotherms; Toth and Sips isotherm equations (detailed in section 1.9.1/1.9.2) [40, 41].

4.4 **Results and discussion**

Hybrid composite RHA-MIL-101 was prepared by in situ incorporation of pre-treated RHA during the synthesis of MIL-101 following the process reported by Lin *et al.*, with minor modifications on purification procedure [38, 39]. Analogously, AC-MIL-101 was also prepared by incorporation of Darco-100 in MIL-101. To have the best evaluation of the hydrogen uptake properties of RHA-MIL-101 and AC-MIL-101, the reported optimum amount of 12.5 wt% was considered as the standard for AC and RHA both [23, 31]. It was expected that more amount of AC and RHA incorporation would result in decrease of crystalline nature, change in the surface morphology, and complete filling and blockage of the pores [23, 38]. The as-synthesised MIL-101, RHA-MIL-101 and characterised AC-MIL-101 samples were by PXRD. FTIR, SEM. EDXS/elemental mapping, TGA and N₂ adsorption-desorption studies.

The PXRD patterns of MIL-101, RHA-MIL-101, and AC-MIL-101, samples, as shown in Fig. 4.2(a), indicates that the framework of MIL-101 remains intact even after incorporation of RHA and AC in MIL-101. Moreover, compared to MIL-101 and AC-MIL-101, the observed decrease in the relative intensity of the diffraction peaks, in the range of $2\theta = 3^{\circ}$ to 16° for RHA-MIL-101, can be attributed to the presence of amorphous RHA within the pores of MIL-101. FTIR spectrum of MIL-101, RHA-MIL-101 and AC-MIL-101 also confirm the incorporation of RHA and AC in MIL-101 (Fig. 4.2b) [16, 23, 24]. Characteristics bands of MIL-101 framework, at 1635 cm⁻¹ are assigned to O-H banding vibrations and a strong band at 1400 cm⁻¹ attributed to the symmetric O-C-O vibration of terephthalate in MIL-101 framework, are present in all these samples, suggesting the existence of MIL-101 framework. Moreover, for RHA-MIL-101 samples, band observed at 1637 cm⁻¹ corresponds to the Si-OH band stretching and the signature band at 1111 cm⁻¹ due to the Si-O-Si vibration band, along with bands at 802 cm⁻¹ and 972 cm⁻¹ for symmetric Si-O-Si stretching and Si-O vibrations, support the incorporation of RHA in MIL-101. Moreover, presence of bands between 2800~3000 cm⁻¹, corresponding to C-H bond stretching, along with bands at 1168, 1021, 885, 748 cm⁻¹ for C-H deformation vibrations, are consistent with analogues MIL-101 and AC-MIL-101 systems [22, 31, 36, 42, 43].



Fig. 4.2 (a) PXRD patterns and (b) FTIR vibration bands of MIL-101, RHA-MIL-101, AC-MIL-101, RHA and AC (*inset* shows the enlarged view of FTIR vibration bands of RHA-MIL-101 in the range of $800-1200 \text{ cm}^{-1}$)



Fig. 4.3 (a-d) SEM images and (*inset*) particle size distribution of (a-b) RHA-MIL-101, (c) MIL-101, (d) AC-MIL-101, (e) physical mixture of RHA+MIL-101, (f) physical mixture of AC+MIL-101, (g) pure AC and (h) pure RHA

The SEM images (Fig. 4.3) of MIL-101, RHA-MIL-101 and AC-MIL-101 samples display their octahedron morphologies with particle size in the range of

100~400 nm. These observations suggest that the architecture of MIL-101 remains intact even upon incorporation of RHA and AC in MIL-101, which is consistent with PXRD data [16, 23, 24]. Notably, SEM images of RHA-MIL-101 and AC-MIL-101, shows only the octahedron morphologies of MIL-101, while RHA and AC, used during the synthesis of these hybrid composites, was not observed, suggesting the successful *in situ* incorporation of RHA and AC in MIL-101 for RHA-MIL-101 and AC-MIL-101, respectively. To further ensure this, morphological behavior of the physical mixture of RHA+MIL-101 and AC+MIL-101 was also studied by SEM, where RHA and AC was clearly observed separated from MIL-101 octahedron (Fig. 4.3).

EDXS spectra and elemental mapping (Fig. 4.4 and Table 4.1) of these samples reveal the presence of Cr and Si for RHA-MIL-101 in the ratio of 13.7 (Cr:Si), suggesting the incorporation of RHA in MIL-101. AC-MIL-101 shows an enhanced C:Cr ratio of 22.04, compared to C:Cr ratio of 8.71 in bare MIL-101, supporting the incorporation of AC in MIL-101. Moreover, elemental analysis of pure AC (C = 82.15%, H = 1.27% and N = 0.17%) is also in agreement with the incorporation of AC in MIL-101 [24].

Fig. 4.4 (a-c) Elemental mapping, showing carbon (C), chromium (Cr) and silica (Si), and (d-f) EDXS analysis of (a,d) MIL-101, (b,e) AC-MIL-101 and (c,f) RHA-MIL-101

$MOFs \rightarrow$	MIL-101	RHA-MIL-101	AC-MIL-101
Element 🗸			
Cr (Atomic %)	10.30	7.42	4.34
C (Atomic %)	89.70	92.04	95.66
Si (Atomic %)		0.54	
Ratio (Cr:Si)		13.7	
Ratio (C:Cr)	8.71	12.4	22.04

Table 4.1 Quantitative analysis of EDXS data for MIL-101, RHA-MIL-101 andAC-MIL-101

To understand further the framework properties of RHA-MIL-101 and AC-MIL-101, their porosity characteristics are assured by measuring N_2 adsorption and desorption isotherms at 77 K. As shown in (Fig. 4.5 and Table 4.2), the observed type II isotherms and quantitative data (Langmuir and BET surface area, total pore volume, NLDFT pore size distribution) clearly suggest that the framework structure of MIL-101 is intact even after incorporation of RHA and AC, which is in good agreement with the FTIR, PXRD and SEM results. The BET surface area measured for synthesised MIL-101 in this present work by using hydrochloric acid as additive and minor modification on purification are comparable to earlier reported data (Table A1). However, we observed that the obtained BET surface area of synthesised MIL-101 lower than the earlier reported and this difference may be due to the different synthesis condition, additive, purification and activation method utilized (Table A1). It is interesting to note, that RHA shows type III isotherm (Fig. 4.5a, b) for a mesoporous/amorphous structure, when incorporated in MIL-101 exhibit type II isotherm. Compared to bare MIL-101, an enhancement by 8.64% (2524.71 m² g⁻¹) in the BET surface area and 8.17% (3485.49 m² g⁻¹) in Langmuir surface area of RHA-MIL-101 is observed, whereas, for AC-MIL-101 an enhancement of 12.74% and 12.73% respectively for BET (2619.99 m² g⁻¹) and Langmuir $(3632.48 \text{ m}^2 \text{ g}^{-1})$ surface is observed.

Table 4.2 N_2 adsorption and desorption properties, and low-pressure hydrogen uptake isotherms of MIL-101, RHA-MIL-101, AC-MIL-101 and pure AC, RHA at 77 K

MOFs	BET surface	Langmuir surface	Total pore volume	H ₂ uptal and up	ke at 77 K to 1 bar
	area (m ² g ⁻¹)	area (m ² g ⁻¹)	$(P/P_0=0.99)$ $(cm^3 g^{-1})$	(wt%)	(mg g ⁻¹)
MIL-101	2323.89	3222.24	2.07	1.40	14.06
RHA-MIL-101	2524.71	3485.49	1.95	1.54	15.40
AC-MIL-101	2619.99	3632.48	2.79	1.48	14.87
AC	940.48	1246.93	0.86	1.09	10.91
RHA	14.04	19.51	0.04	0.03	0.30

Fig. 4.5 (a) N_2 isotherms, (b) Enlarge view of N_2 isotherms (P/P₀=0.1 to 0.9) (c) Pore size distribution and (d) TGA curve of prepared MIL-101, RHA-MIL-101, AC-MIL-101 and pure AC, RHA

Moreover, pore volume and pore size are decreased by ca. 6% and ca. 13% respectively, for RHA-MIL-101, compared to MIL-101, suggesting the incorporation of mesoporous/amorphous silica in the larger pores of MIL-101. The incorporation of silica-rich RHA in MIL-101 resulted in the interaction of silanols groups of RHA with the cage of MIL-101 which may induce the slight change in the pore parameters [37]. In contrary to RHA-MIL-101, incorporation of AC in MIL-101 result in the increase in pore size and consequently the pore volume by *ca.* 19% and *ca.* 34%, respectively, presumably due to the formation of additional pore upon incorporation of AC in MIL-101. The NLDFT pore size distribution curves (Fig. 4.5c) also assist this outcome [16, 23, 28, 42, 43]. The enhancement in the surface area of AC-MIL-101, in comparison of MIL-101, can also be attributed to the formation of additional micropores and defective crystalline structures upon incorporation of AC in MIL-101 [23]. Further, to investigate the role of *in situ* incorporated RHA and AC in fine tuning of the porosity and surface behavior of RHA-MIL-101 and AC-MIL-101, synthesised physical mixture of AC+MIL-101 and RHA+MIL-101 were also explored for N2 sorption isotherms studies (Fig 4.6). The measured BET surface area and pore volume of AC+MIL-101 (449 m² g⁻¹, 0.33 cm³ g⁻¹) and RHA+MIL-101 (522 m² g⁻¹) ¹, 0.41 cm³ g⁻¹). Notably, the physical mixture does not show any enhancement in the porosity or surface area. Moreover, it also shows a hysteresis during N₂ sorption measurements, which can be attributed to the different kinetics of the separately mixed materials (RHA, AC and MIL-101). This study confirms that the in situ incorporation of RHA and AC in MIL-101 resulted in the fine-tuning of the porosity and enhancement in surface area of MIL-101. Earlier reports on AC@MIL-101 also showed an enhancement in the surface area due to the generation of additional pores upon incorporation of AC [23]. Morsali et al. have also observed that the interaction of silanol bonds of mesoporous silica (SBA-15) with the metal centers of MOF-5 induced the fine tuning of pores [37].

Further, TGA studies of RHA-MIL-101 and AC-MIL-101 samples (Fig. 4.5d) reveal that the thermal stabilities of these composites are analogous to that of bare MIL-101 [24]. TGA profiles of these composites showing two distinct

weight loss steps; first, being in the range of up to 300 °C corresponding to the loss of guest water molecules from the large (d = 3.4 nm) and small cage (d = 2.9 nm) of MIL-101 frameworks. The second step weight loss in the range of 300-400 °C is due to the decomposition of framework by the elimination of organic groups [22, 23, 26, 31].

Fig. 4.6 (a) N_2 adsorption desorption isotherms and (b) NLDFT pore size distribution of AC+MIL-101 and RHA+MIL-101

H₂ sorption isotherm of RHA-MIL-101 at 77 K and 1 atm are measured to evaluate the effect of silica-rich materials on the H₂ sorption properties of MIL-101, and its H_2 uptake properties are compared with bare MIL-101 and AC-MIL-101. As shown in (Fig. 4.7, and Table 4.2), the H₂ uptake of RHA-MIL-101 at 77 K and 1 atm is 15.40 mg g^{-1} (1.54 wt%) compared to 14.06 mg g^{-1} (1.40 wt%) of MIL-101. It is worth noting that RHA-MIL-101 exhibits higher H₂ uptake as compared to the AC-MIL-101 (14.8 mg g⁻¹, 1.48 wt%). The observed enhanced H₂ uptake capacity shown by RHA-MIL-101 is comparable and even higher than several important MOFs and their composites with carbon-based materials, which are extensively explored as important hydrogen storage materials (Table 4.3). For instance, 1.60 wt% of H₂ uptake is reported for Li doped AC@MIL-101 and 1.63 wt% for a Li doped Zn based MOF [31, 32]. Analogously, for CNT@MOF-5, 1.52 wt% H₂ uptake is reported [33]. Roswell et al. achieved H₂ uptakes in the range of 0.89 wt% to 1.62 wt% (IRMOF-11) [44]. Lan et al. reported the carbon nanodots functional UMCM-1 composite materials for enhanced H_2 uptake (1.21) wt%) at 77 K and 1 bar, where the enhanced H_2 uptakes of UMCM-1/C dots was

due to the interactions between polar functional groups (like –OH) at the surface of the Carbon dots and H₂ molecules [45]. Yang *et al.* examined hydrogen adsorption capacities (at 1.01 bar and 77 K) of low silica type X zeolite (Si/Al~1.0) fully exchange by alkali or alkali earth metal cation Li⁺-LSX(1.50 wt%), Na⁺-LSX (1.46 wt%), K⁺-LSX (1.33 wt%), Ca⁺-LSX (1.27 wt%) and Mg⁺-LSX (0.83 wt%), our results reveal that the RHA-MIL-101 (1.54 wt%) display better adsorption capacities than alkali doped metal LSX [46, 47]. Therefore, the notable increment in H₂ uptake by ~ 9% over RHA-MIL-101, clearly demonstrate the significance of silica-rich materials, where interactions between silanol bonds and H₂ molecules presumably plays a determining role (Fig. 4.8) [7]. Further, the H₂ sorption isotherms of RHA-MIL-101 (along with others) are not fully saturated, higher adsorption capacities may be expected under higher pressure.

Fig. 4.7 (a) Low pressure hydrogen uptake isotherms and (b) comparative hydrogen uptakes for MIL-101, RHA-MIL-101 and AC-MIL-101 at 77 K, (c) Correlation of hydrogen uptake isotherm for RHA-MIL-101 with two parameter (Langmuir and Freundlich) and three parameter (Toth and Sips) non-linear isotherm model

Table 4.3 Comparative	charts for	the:	surface	area,	pore	volume	and	H_2	uptake
data for selected MOFs a	t 77 K and	d 1 b	ar						

Materials	SA _{BET}	Vp	H ₂ uptake	Reference
	$(m^2 g^{-1})$	(cm ³ g ⁻¹)	(wt%)	
RHA-MIL-101	2524	1.95	1.54	This work
AC-MIL-101	2619	2.79	1.48	This work
Li@AC-MIL-101	2791	1.65	1.60	[31]
MIL-101	3148	2.10	1.20	[31]
Li ⁺ Zn ₂ (NDC) ₂ (diPyNI)	802		1.63	[32]
Zn ₂ (NDC) ₂ (diPyNI)	756		0.93	[32]
CNT@MOF-5	2900	1.43	1.52	[33]
MOF-177	4526*	1.61	1.25	[44]
IRMOF-18	1501*	0.53	0.89	[44]
IRMOF-11	1911*	0.68	1.62	[44]
IRMOF-1	3362*	1.19	1.32	[44]
IRMOF-8	1466*	0.52	1.50	[44]
UMCM-1/C dots	3714	1.95	1.21	[45]
Li-LSX (low Silica Zeolite)	717	0.56	1.50	[46]
Na-LSX (low Silica Zeolite)	642	0.34	1.46	[46]
K-LSX (low Silica Zeolite)	570	0.33	1.33	[46]
Ca-LSX (low Silica Zeolite)	669	0.36	1.27	[47]
Mg-LSX (low Silica Zeolite)	442	0.34	0.83	[47]
Ni-GO/MIL	2045	0.98	1.64	[48]
IRMOF-20	3409	1.53	1.32	[49]
MOF-5/Pt-CNTs	1692	0.84	1.89	[50]
MOF-5	1758	0.82	1.20	[50]
IRMOF-1+Pd	958	0.39	1.86	[51]
IRMOF-1	2885	1.18	1.15	[51]
Pt/AC-MOF-5	740	0.80	1.395	[52]
MOF-5	670	0.79	1.399	[52]
ZIF-8	1810	0.66	1.29	[53]
ZIF-11	1947	0.58	1.37	[53]
MOF-177	3275	2.65	1.32	[54]
MOF-177	3100	1.58	1.50	[55]
SodZMOF	361	0.13	1.6	[56]
4Li ⁺ Me-SodZMOF	334	0.12	1.18	[56]
4K ⁺ Me-SodZMOF	181	0.07	0.8	[56]

*Langmuir surface area

Fig. 4.8 Plausible weak interactions of silanol bonds with hydrogen molecules contributing in the observed improved H₂ uptake properties of RHA-MIL-101

Further, to describe the adsorption behavior of H₂, two parameters (Langmuir and Freundlich equations) and three parameters (Toth and Sips equations), non-linear isotherm models (Fig. 4.7c, Fig. 4.9 and Table 4.4) are applied to fit the experimental H₂ adsorption isotherms of RHA-MIL-101, AC-MIL-101 and MIL-101 materials. The fitting parameters and represented correlation coefficients (R²) and normalized standard deviation inferred a good agreement of experimental isotherm. The three parameter equations provide better fitting than the two parameter equations. The adsorption capacities as estimated by the three parameters are strongly influenced by the incorporated RHA and AC materials. The results prove that the best fits for two and three parameter equation sequence of RHA-MIL-101is Toth > Sips > Freundlich > Langmuir, due to excess heterogeneity, provided on adsorbent surface, and also the combined effects of low and high concentration of adsorbate [40, 41]. The degree of the best fitting for all models for the explanation of adsorption isotherms H₂ on MIL-101 and AC-MIL-101, are Sips > Toth > Freundlich > Langmuir. The above observations suggest that the H₂ adsorption behavior of the studied RHA-MIL-101 composites, presumably, adopts non-uniform multi-layer adsorption behavior, due to its heterogeneous surface [40, 41].

Fig. 4.9 Correlation of hydrogen uptake for MIL-101 and AC-MIL-101 with two (Langmuir and Freundlich) and three parameter (Toth and Sips) non-linear isotherm model

Table	4.4	Isother	n const	tants fo	r the	two	(Langn	nuir a	nd Fr	eundli	ch) a	and t	three
(Toth	and S	Sips) pa	rameter	risothe	rm mo	odels	of MII	101,	RHA	-MIL	-101	and	AC-

Isotherm	MIL-101	RHA-MIL-101	AC-MIL-101
models			
	Three Paran	neter Isotherm mod	lels
Toth			
\mathbf{k}_{t}	1.4437	1.5677	1.5821
$a_t (10^{-2})$	2.1270	3.6428	9.2396
1/t	0.4927	0.5151	0.6044
\mathbb{R}^2	0.9997	0.9999	0.9997
$\Delta Q(\%)$	0.2071	0.0117	0.1099
Sips			
$\mathbf{k}_{\mathbf{s}}$	1.7976	2.0867	2.7377
as	0.6212	0.6470	0.7463
ts	0.2632	0.3608	0.8356
\mathbb{R}^2	0.9999	0.9998	0.9999
$\Delta Q(\%)$	0.1405	0.0509	0.0172
	Two Param	eter Isotherm mod	els
Langmuir			
a_{m}	2.0784	2.2428	2.1304
b	1.9556	1.9720	2.1782
\mathbf{R}^2	0.9896	0.9912	0.9955
$\Delta Q(\%)$	0.4154	0.5476	0.3307
Freundlich			
k	1.4370	1.5524	1.5286
\mathbf{n}^{-1}	0.5376	0.5352	0.5196
\mathbf{R}^2	0.9921	0.9987	0.9957
$\Delta Q(\%)$	0.3042	0.1581	0.4307

MIL-101

4.5 Conclusions

To conclude, the experiment has demonstrated a simple approach to incorporate RHA, an inexpensive and waste by-product of the rice industry, into MIL-101 under hydrothermal conditions, and its structural, morphological and properties are established by SEM, PXRD, TGA, FTIR, chemical EDXS/elemental mapping studies, which confirms the incorporation of RHA into MIL-101 without any significant distortion in the framework of MIL-101. Moreover, N₂ adsorption desorption isotherm and TGA studies revealed that RHA-MIL-101 composite also possess high surface area, optimized pore size and high thermal stability. Furthermore, RHA-MIL-101 composite displayed enhanced H₂ uptake properties at 77 K and 1 bar, which is ca 9.1 % higher than the bare MIL-101 and comparable to most of the well explored MOFs and their composites with carbon-based materials. The work affirms that interaction between the polar silanol groups (present at the surface of RHA) and H_2 molecules are responsible for the observed improved H_2 uptake properties, and therefore silica-rich materials have high potential to be a better alternative to carbon materials as composites fillers. Further investigations are underway in the laboratory, to evaluate the high-pressure hydrogen uptake properties of RHA-MIL-101 and other analogous silica-rich composites.

Note: The content of this chapter is published as Panchariya *et al.*, Journal of Porous Materials, 2019, 26, 4, 1137-1147, (DOI: 10.1007/s10934-018-0710-4) and reproduced with the permission of Springer Nature.

4.6 References

- Schlapbach L., Zuttel A. (2001), Hydrogen-Storage Materials for Mobile Applications, Nature, 414, 353-358.
- [2] Zuttel A. (2003), Materials for Hydrogen Storage, Mater. Today, 6, 24-33.
- [3] Graetz J. (2009), New Approaches to Hydrogen Storage, Chem. Soc. Rev., 38, 73-82.

- [4] Rowsell J.L.C., Yaghi O.M. (2005), Strategies for Hydrogen Storage in Metal-Organic Frameworks, Angew. Chem., Int. Ed., 44, 4670-4679.
- [5] Murthy S.S., Kumar E.A. (2014), Advanced Materials for Solid State Hydrogen Storage: Thermal Engineering Issues, Appl. Therm. Eng., 72, 176-189.
- [6] Langmi H.W., Ren J., North B., Mathe M., Bessarabov D. (2014), Hydrogen Storage in Metal-Organic Frameworks: A Review, Electrochim. Acta, 128, 368-392.
- [7] Suh M.P., Park H.J., Prasad T.K., Lim D.W. (2012), Hydrogen Storage in Metal-Organic Frameworks, Chem. Rev., 112, 782-835.
- [8] Rosi N.L., Eckert J., Eddaoudi M., Vodak D.T., Kim J., O'Keeffe M., Yaghi O.M. (2003), Hydrogen Storage in Microporous Metal-Organic Frameworks, Science, 300, 1127-1129.
- [9] Sculley J., Yuan D., Zhou H.C. (2011), The Current Status of Hydrogen Storage in Metal-Organic Frameworks – Updated, Energy Environ. Sci., 4, 2721-2735.
- [10] Murray L.J., Dinca M., Long J.R. (2009), Hydrogen Storage in Metal-Organic Frameworks, Chem. Soc. Rev., 38, 1294-1314.
- [11] Yaghi O.M., O'Keeffe M., Ockwig N.W., Chae H.K., Eddaoudi M., Kim J. (2003), Reticular Synthesis and the Design of New Materials, Nature, 423, 705-714.
- [12] Long J.R., Yaghi O.M. (2009), The Pervasive Chemistry of Metal-Organic Frameworks, Chem. Soc. Rev., 38, 1213-1214.
- [13] Kaur G., Rai R.K., Tyagi D., Yao X., Li P.Z., Yang X.C., Zhao Y., Xu Q., Singh S.K. (2016), Room-Temperature Synthesis of Bimetallic Co-Zn Based Zeolitic Imidazolate Frameworks in Water for Enhanced CO₂ and H₂ Uptakes, J. Mater. Chem. A, 4, 14932-14938.
- [14] Kuppler R.J., Timmons D.J., Fang Q.R., Li J.R., Makal T.A., Young M.D., Yuan D., Zhao D., Zhuang W., Zhou H.C. (2009), Potential Applications of Metal-Organic Frameworks, Coord. Chem. Rev., 253, 3042-3066.

- [15] Meek S.T., Greathouse J.A., Allendorf M.D. (2011), Metal-Organic Frameworks: A Rapidly Growing Class of Versatile Nanoporous Materials, Adv. Mater. 23, 249-267.
- [16] Ferey G., Draznieks C.M., Serre C., Millange F., Dutour J., Surble S., Margiolaki I. (2005), A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area, Science, 309, 2040-2042.
- [17] Horcajada P., Serre C., Vallet-Regi M., Sebban M., Taulelle F., Ferey G.
 (2006), Metal-Organic Frameworks as Efficient Materials for Drug Delivery, Angew. Chem., Int. Ed., 45, 5974-5978.
- [18] Hwang Y.K., Hong D.Y., Chang J.S., Jhung S.H., Seo Y.K., Kim J., Vimont A., Daturi M., Serre C., Ferey G. (2008), Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation, Angew. Chem., Int. Ed., 47, 4144-4148.
- [19] Bhattacharjee S., Chen C., Ahn W.S. (2014), Chromium Terephthalate Metal-Organic Framework MIL-101: Synthesis, Functionalization, and Applications for Adsorption and Catalysis, RSC Adv., 4, 52500-52525.
- [20] Liu X.W., Sun T.J., Hu J.L., Wang S.D. (2016), Composites of Metal-Organic Frameworks and Carbon-Based Materials: Preparations, Functionalities and Applications, J. Mater. Chem. A, 4, 3584-3616.
- [21] Janiak C., Vieth J.K. (2010), MOFs, MILs and More: Concepts, Properties and Applications for Porous Coordination Networks (PCNs), New J. Chem., 34, 2366-2388.
- [22] Prasanth K.P., Rallapalli P., Raj M.C., Bajaj H.C., Jasra R.V. (2011), Enhanced Hydrogen Sorption in Single Walled Carbon Nanotube Incorporated MIL-101 Composite Metal-Organic Framework, Int. J. Hydrogen Energy, 36, 7594-7601.

- [23] Rallapall P.B.S., Raj M.C., Patil D.V., Prasanth K.P., Somani R.S., Bajaj H.C. (2013), Activated Carbon@MIL-101(Cr): A Potential Metal-Organic Framework Composite Material for Hydrogen Storage, Int. J. Energy Res., 37, 746-753.
- [24] Panchariya D.K., Rai R.K., Singh S.K., Kumar E.A., (2017), Synthesis and Characterization of MIL-101 Incorporated with Darco type Activated Charcoal, Mater. Today Proc., 4, 388-394.
- [25] Szilagyi P.A., Callini E., Anastasopol A., Kwakernaak C., Sachdeva S., Krol R.V.D., Geerlings H., Borgschulte A., Zuttel A., Dam B. (2014), Probing Hydrogen Spillover in Pd@MIL-101(Cr) with a Focus on Hydrogen Chemisorption, Phys. Chem. Chem. Phys., 16, 5803-5809.
- [26] Anbia M., Mandegarzad S. (2012), Enhanced Hydrogen Sorption on Modified MIL-101 with Pt/CMK-3 by Hydrogen Spillover Effect, J. Alloys Compd., 532, 61-67.
- [27] Lin K.S., Adhikari A.K., Su Y.H., Shu C.W., Chan H.Y. (2012), Synthesis, Characterization, and Hydrogen Storage Study by Hydrogen Spillover of MIL-101 Metal-Organic Frameworks, Adsorption, 18, 483-491.
- [28] Zhu Q.L., Xu Q. (2014), Metal-Organic Framework Composites, Chem. Soc. Rev., 43, 5468-5512.
- [29] Stock N., Biswas S. (2012), Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites, Chem. Rev., 112, 933-969.
- [30] Jiang H., Feng Y., Chen M., Wang Y. (2013), Synthesis and Hydrogen-Storage Performance of Interpenetrated MOF-5/MWCNTs Hybrid Composite with High Mesoporosity, Int. J. Hydrogen Energy, 38, 10950-10955.
- [31] Prabhakaran P.K., Deschamp J. (2015), Doping Activated Carbon Incorporated Composite MIL-101 using Lithium: Impact on Hydrogen Uptake, J. Mater. Chem. A, 3, 7014-7021.

- [32] Mulfort K.L., Hupp J.T. (2007), Chemical Reduction of Metal-Organic Framework Materials as a Method to Enhance Gas Uptake and Binding, J. Am. Chem. Soc., 129, 9604-9605.
- [33] Yang S.J., Choi J.Y., Chae H.K., Cho J.H., Nahm K.S., Park C.R. (2009), Preparation and Enhanced Hydrostability and Hydrogen Storage Capacity of CNT@MOF-5 Hybrid Composite, Chem. Mater., 9, 1893-1897.
- [34] Sigl M., Ernst S., Weitkamp J., Knozinger H. (1997), Characterization of the Acid Properties of [Al]-, [Ga]- and [Fe]-HZSM-5 by Low-Temperature FTIR Spectroscopy of Adsorbed Dihydrogen and Ethylbenzene Disproportionation, Catal. Lett., 45, 27-33.
- [35] Hohmeyer J., Kondratenko E.V., Bron M., Krohnert J., Jentoft F.C., Schlogl F., Claus P. (2010), Activation of Dihydrogen on Supported and Unsupported Silver Catalysts, J. Catal., 269, 5-14.
- [36] Rajagopal V.K., Guthrie R.D., Fields T., Davis B.H. (1996), Hydrogenation Catalysis by Thermally Activated Silica, Catal. Today, 31, 57-63.
- [37] Karimi Z., Morsali A., (2013), Modulated Formation of Metal-Organic Frameworks by Oriented Growth over Mesoporous Silica, J. Mater. Chem. A, 1, 3047-3045.
- [38] Lin Y., Yan Q., Kong C., Chen L. (2013), Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO₂ Capture, Sci. Rep., 3, 1859.
- [39] Bromberg L., Diao Y., Wu H., Speakman S.A., Hatton T.A. (2012), Chromium(III) Terephthalate Metal-Organic Framework (MIL-101): HF-Free Synthesis, Structure, Polyoxometalate Composites, and Catalytic Properties, Chem. Mater., 24, 1664-1675.
- [40] Foo K.Y., Hameed B.H. (2010), Insights into the Modeling of Adsorption Isotherm Systems, Chem. Eng. J., 156, 2-10.
- [41] Singh V.K., Kumar E.A. (2016), Measurement and Analysis of Adsorption Isotherms of CO₂ on Activated Carbon, Appl. Therm. Eng., 97, 77-86.

- [42] Du X., He J. (2012), Amino-Functionalized Silica Nanoparticles with Center-Radially Hierarchical Mesopores as Ideal Catalyst Carriers. Nanoscale, 4, 852-859.
- [43] Balas F., Manzano M., Horcajada P., Vallet-Regi M. (2006), Confinement and Controlled Release of Bisphosphonates on Ordered Mesoporous Silica-Based Materials, J. Am. Chem. Soc., 128, 8116-8117.
- [44] Rowsell J.L.C., Millward A.R., Park K.S., Yaghi O.M. (2004), Hydrogen Sorption in Functionalized Metal-Organic Frameworks, J. Am. Chem. Soc., 126, 5666-5667.
- [45] Li J.S., Tang Y.J., Li S.L., Zhang S.R., Dai Z.H., Si L., Lan Y.Q. (2015), Carbon Nanodots Functional MOFs Composites by A Stepwise Synthetic Approach: Enhanced H₂ Storage and Fluorescent Sensing, Cryst. Eng. Comm., 17, 1080-1085.
- [46] Li Y., Yang R.T. (2006), Hydrogen Storage in Low Silica Type X Zeolites, J. Phys. Chem. B, 110, 17175-17181.
- [47] Wang L., Yang R.T. (2010), Hydrogen Storage Properties of Low Silica Type X Zeolites, Ind. Eng. Chem. Res., 49, 3634-3641.
- [48] Lee S.Y., Park S.J. (2013), Hydrogen Storage Behaviors of Ni-Doped Graphene Oxide/MIL-101 Hybrid Composites, J. Nano sci. Nanotech, 13, 443-447.
- [49] Rowsell J.L.C., Yaghi O.M. (2006), Effects of Functionalization, Catenation, and Variation of the Metal Oxide and Organic Linking Units on the Low-Pressure Hydrogen Adsorption Properties of Metal-Organic Frameworks, J. Am. Chem. Soc., 128, 1304-1315.
- [50] Yang S.J., Cho J.H., Nahm K.S., Park C.R. (2010), Enhanced Hydrogen Storage Capacity of Pt-Loaded CNT@MOF-5 Hybrid Composites, Int. J. Hydrogen Energy, 35, 13062-13067.
- [51] Sabo M., Henschel A., Frode H., Klemm E., Kaskel S. (2007), Solution Infiltration of Palladium into MOF-5: Synthesis, Physisorption and Catalytic Properties, J. Mater. Chem., 17, 3827-3832.

- [52] Chien A.C., Chuang S.S.C. (2011), Static and Dynamic Hydrogen Adsorption on Pt/AC and MOF-5, Int. J. Hydrogen Energy, 36, 6022-6030.
- [53] Park K.S., Ni Z., Cote A.P., Choi J.Y., Huang R., Uribe-Romo F.J., Chae H.K., O'Keeffe M., Yaghi O.M. (2006), Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks, Proc. Natl. Acad. Sci. U. S. A., 103, 10186-10191.
- [54] Saha D., Wei Z., Deng S. (2008), Equilibrium, Kinetics and Enthalpy of Hydrogen Adsorption in MOF-177, Int. J. Hydrogen Energy, 33, 7479-7488.
- [55] Li Y., Yang R.T. (2007), Gas Adsorption and Storage in Metal-Organic Framework MOF-177, Langmuir, 23, 12937-12944.
- [56] Calleja G., Botas J.A., Sanchez M.S., Orcajo M.G. (2010), Hydrogen Adsorption over Zeolite-Like MOF Materials Modified by Ion Exchange, Int. J. Hydrogen Energy, 35, 9916-9923.

Chapter 5

Lithium-doped Silica-rich MIL-101(Cr): Synthesis, Characterisation and Hydrogen Storage

5.1 Introduction

Globally, efforts are being made to achieve U. S. Department of Energy (DOE) targets for volumetric (30 g L^{-1}) and gravimetric (4.5 wt%) hydrogen storage [1, 2]. Among several strategies such as metal hydrides, porous materials and complex metal hydrides explored to establish an efficient hydrogen economy, utilization of metal-organic frameworks (MOFs) has shown high potential for onboard hydrogen storage applications [3-5]. The extraordinary features such as high crystallinity and ultra-micro porosity of MOFs projected these materials as promising candidates for gas storage application [4, 6-10]. In this direction several MOFs have been extensively explored to achieve enhanced H_2 uptake capacity at 77 K under varying pressure of H_2 gas. For instance, MOF-210 (8.6 wt%, 80 bar), MOF-177 (7.5 wt%, 70 bar), IRMOF-20 (6.7 wt%, 80 bar), NU-100 (9.95 wt%, 56 bar), MOF-5 (4.5 wt%, 1 bar), MIL-101 (6.1 wt%, 60 bar) ZIF-8 (3.3 wt%, 30 bar) are few of the promising results for H_2 storage in MOFs [11-16]. In particular reference to MOF-5, inelastic neutron scattering spectroscopic studies indicated that H_2 molecules preferentially interact with two well-defined binding sites (Zn and BDC linker) of the MOF-5 framework [14].

However, the large volume of MOFs usually remains under-utilized due to the weak interaction of H₂ molecules with MOF wall [17-20]. In this direction, strategies of impregnating or doping of low weight alkali metal ions (e.g. Li⁺, Na⁺) in MOFs are turned out as a better way to utilize high porosity of MOFs for enhanced hydrogen uptake performance [21, 22]. In general, alkali metal ions show high affinity towards H₂ molecules *via* electrostatic charge-quadrupole and charge induced dipole interactions [21, 22]. For instance, Mulfort and Hupp reported Li-doped MOF, synthesised by chemical reduction with Li⁰, for

enhanced hydrogen uptake and attributed the observed enhancement in hydrogen adsorption to Li-H₂ charge interactions [23-25]. Doping Li⁺ ions in non-catenated hydroxyl-functionalized MOF also enhanced hydrogen uptake (1.32 wt% for Li_{0.20}-MOF), but hydrogen uptake decreased significantly upon increasing the Lidoping content (0.77 wt% for Li_{2.62}-MOF) [26]. Analogously, higher hydrogen uptake is also achieved by doping Li⁺ ions in a Mn based MOF Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀]₂, where BTT is 1,3,5-benzenetristetrazolate [27]. Eddaoudi *et al.* however, could not achieve enhanced H₂ uptake upon Li⁺ ion doping, but noticed remarkable enhancement (up to 50%) in the isosteric heat of adsorption for H₂ storage in Li⁺ ions doped MOF, attributed to the favorable interaction of Li^+ ions and H_2 molecules [28]. Li^+ ion doped MIL-53(Al) and hydroxyl-modified MIL-53(Al) exhibited significantly improved H₂ uptakes as 1.84 wt% and 1.7 wt%, respectively [29, 30]. ¹³C solid state NMR accounted the interaction of Li⁺ ion with the carboxylate of terephthalic linker in MIL-53(Al) [30]. Trapping Li⁺ ions in crown-ether functional of Zn-MOF-crown significantly enhanced H₂ uptake capacity to 104.8 mL g⁻¹ compared to the undoped Zn-MOFcrown (72.5 mL g⁻¹), attributed to the efficient Li⁺ ion to H₂ interactions [31]. Lidoped MOF-5 also exhibited an enhancement of 24% in H₂ uptake compared to the parent MOF-5 [32]. Exchanging piperazine (ppz) in NOTT-200 with Li^+ ion also showed an enhancement in H₂ uptake from 0.96 wt% (ppz-NOTT-200) to 1.02 wt% (Li⁺-NOTT-201), albeit the enhancement was attributed to the increase in porosity by replacing the bulky ppz with Li⁺ ion [33, 34]. On the other hand, hybrid composites of MOFs synthesised by incorporation of activated carbon (AC-MIL-101), carbon nanotubes (SWCNT-MIL-101) or silica-rich rich husk ash (RHA-MIL-101) have shown improved hydrogen uptake properties, owing to the enhancement in interactions with H₂ molecules [35-37]. Further, doping Li⁺ ions in the hybrid composite AC-MIL-101, Deschamps et al. reported enhancement in H₂ uptake (1.60 wt%) for Li-doped AC-MIL-101 (Li-AC-MIL-101) compared to MIL-101 (1.20 wt%) at 1 bar and 77 K [35]. At 100 bar, Li-AC-MIL-101 and Li-MIL-101 exhibited 14.4 wt% and 7.9 wt% H₂ uptake respectively, which is appreciably higher than the respective undoped AC-MIL-101 (11.7 wt%) and MIL-101 (7.2 wt%) at 77 K [35]. Analogously, Li@SWNT-MIL-101 also exhibited enhanced H₂ uptake (1.04 wt%) compared to 0.49 wt% for undoped SWNT-MIL-101 at 90 bar and 298 K [36]. The observed enhancement in H₂ uptake for Li-doped MOF composites is attributed to the Li⁺ ion to H₂ interactions and pore tuning due to the incorporation of AC/SWNT in MIL-101 [35, 36].

Evidences for the crucial role of Li⁺ ions in enhancing the H₂ uptake properties of porous frameworks have also been strongly supported by various simulation-assisted studies [21, 22, 38-46]. Most of these studies revealed that Li⁺ ions mainly located either near the planer core of organic linker or the carboxylate oxygen atoms [21, 22, 38, 39]. Literature revealed that due to the better charge to size ratio, Li⁺ ions exerts stronger interactions with H₂ molecules. However, increase in the clustering of H₂ molecules over Li⁺ disturb the charge transfer ability of Li^+ and hence weakens the binding interactions of the subsequent H_2 molecules to Li^+ ions [42]. Using density functional calculations, Ahuja *et al.* proposed that Li⁺ ions interact with the carboxylate oxygen of the BDC linkers in MOF-5, where three H₂ molecules can bind with each Li⁺ ions compared to one H₂ molecules per BDC unit [22]. The first principal simulation studies evidenced that Li atoms may interact with the sp^2 aromatic rings of the BDC linkers, which causes the charge separation. Consequently, more positive Li atom strongly stabilize molecular H₂, and hence facilitate higher H₂ adsorption (5.2 wt% for Li-MOF-C30 as compared to undoped MOF-C30 (< 1 wt%, at 300K and 100 bar) [38]. Studies also revealed that in Li-doped MOFs, the interaction of Li-H₂ molecules superseded the interactions of H_2 molecules to the MOF framework [39]. Froudakis et al. employed Grand Canonical Monte Carlo (GCMC) simulations to investigate the interaction behavior of H₂ molecules with the Lidoped IRMOF-14. Studies revealed that the strong charge distribution from H_2 molecules to the Li atom induced very strong dipoles for enhanced Li-to- H_2 binding [21]. Charge distribution from Li atom to COF framework was also studied using first principles calculations on Li doped covalent organic frameworks (COFs), where Li atoms doped in COFs are more positively charged by 0.3 e per Li atom [43]. Such positively charged Li atoms interact more strongly

with H₂ molecules via a dative bond between H₂ σ bond electrons and the empty 2s orbitals of Li atom [21, 44]. Notably, clustering of Li atoms in COFs may inhibit the charge transfer from Li to COFs and thus adversely affect H₂ uptake properties of COFs with higher Li doping [43]. Analogous computational studies over Li doped conjugated microporous polymer (CMP) revealed the preferential clustering of H₂ molecules around Li atom compared to that with the C=C and aromatic rings of the CMP framework. Such enhancement in H₂ uptake of Li-CMP compared to CMP was due to Li doping rather than the CMP porous network. However, higher loading of Li in CMP also resulted in the loss in H₂ uptake due to the clustering of Li⁺ ions in CMP [45].

Theoretical predictions on H₂ uptake properties of Li-coated fullerenes (C₆₀) impregnated in MOF-5 and IRMOF-10, also inferred that H₂ molecules favorably interacts with Li atoms [46]. Charge transfer from Li atoms to the framework linker and C₆₀ resulted in a highly positively charged Li atom, which induced strong electrostatic-charge induced dipole interactions of Li to H₂ molecules. Theoretical GCMC simulations over MIL-101(Cr) and Li⁺-MIL-101(Cr) revealed that indeed the Li⁺ ion sites are the most favorable sites for the clustering of H₂ molecules in Li⁺-MIL-101(Cr). Results inferred that doping Li⁺ ions in MIL-101(Cr) also resulted in the increase in heat of adsorption (12.0 kJ mol⁻¹) as compared to 6.6 kJ mol⁻¹ for undoped MIL-101(Cr). However, doping of Li⁺ ions in MIL-101(Cr) resulted in a significant loss in total pore volume of the framework and hindrance to the free interaction of H₂ molecules with Cr metal unsaturated sites [41].

Previously, we investigated the hydrogen uptake properties of RHA-MIL-101 (RHA is rice husk ash), where the observed enhancement in hydrogen uptake properties is attributed to the plausible involvement of silanol bonds to H₂ molecules interactions and pore-tuning due to the incorporation of silica-rich RHA in MIL-101 [37]. Here in, we are interested to further enhance the H₂ uptake capacity of RHA-MIL-101 by Li⁺ ion doping. We investigated the effect of Li⁺ ion doping (in varying concentration) and pore tuning on hydrogen uptake properties of Li-doped RHA-MIL-101. Several spectro-analytical techniques are probed to investigate and establish the morphological and chemical properties of the synthesised Li-doped RHA-MIL-101. Hydrogen uptake capacity for the high performing Li-doped RHA-MIL-101 is also estimated at 1 bar (77 K) and 12 bar (298 K).

5.2 Experimental section

5.2.1 Materials

High purity chemical reagents and metal salts are procured from Sigma-Aldrich, Thomas Baker, Merck and S.D. Fine Chemical, and are used without further purification, unless and otherwise specified. The gases used for measurements of framework properties and hydrogen adsorption analysis are of ultra-high purity (Inox air product Ltd, India). The Rice husk ash (RHA) is provided by the Nishant Enterprises, India, and is used for the synthesis of RHA-MIL-101 composite.

5.2.2 Synthesis of Li-doped RHA-MIL-101

At an outset, hybrid composite RHA-MIL-101 is synthesised following our previously reported method with some modification [37]. Typically, purified RHA (12.5 mg) is added in a mixture of $Cr(NO_3)_3.9H_2O$ (2.0 g) and terephthalic acid (0.833 g) in 30 mL distilled water containing 0.416 mL of HCl. Mixture is sonicated for 30 min and heated at 493 K for 8 h in a 50 mL Teflon lined reactor. The obtained solid is separated by centrifugation at 6000 rpm for 15 min, and is repeatedly washed with hot distilled water, acetone and hot ethanol. Further, the solid residue is dispersed in 30 mL ethanol-water (95:1 v/v) and heated at 353 K for 8 h in a Teflon reactor. The obtained solid is pre-activated under ultra-high vacuum at 393 K for 12 h. Further the pre-activated RHA-MIL-101 (100 mg) is added to 1 mM LiCl in DMF-H₂O (100 mL, 50:1 v/v), and the mixture is stirred at room temperature for 8 h. Solid residue is collected by centrifugation (8000 rpm, 15 min) and washed with DMF (10 mL x 10). Further, the solid residue is activated at 433 K for 8 h to obtain 0.06Li-RHA-MIL-101. Concentration of leftover Li⁺ ions in the combined solution of mother liquor and DMF washing is analyzed by ICP to quantify the loading content of Li⁺ ions in *x*Li-RHA-MIL-101. The estimated value displays the amount of Li⁺ ion loaded into the formed product. Li-doped RHA-MIL-101 composites with varying doping amount are analogously synthesised using 5 mM, 10 mM and 100 mM solution of LiCl in DMF-H₂O (50:1 v/v).

5.3 General methods and instruments

Powder X-ray diffraction (PXRD) measurements are performed using a Rigaku Smart Lab 15 automated X-ray diffractometer system with Cu Ka radiation ($\lambda = 1.540593$ Å) over a wide range of $3^{\circ} < 2\theta < 24^{\circ}$, 40 K eV and 30 mA with 3° min⁻¹ scan speed in 0.02° s⁻¹ scan step at room temperature. Fourier transform infrared (FTIR) spectra are recorded on a PerkinElmer Spectrum Two FTIR spectrometer at the range of 500-4000 cm⁻¹. The scanning electron microscopic (SEM) images are collected using Carl Zesis Supra-55 equipment at an operating voltage of 5 kV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis is conducted on ARCOS, simultaneous ICP spectrometer (make: SPECTRO, analytical instruments GmbH, Germany) (spectral wavelength range: 130 nm to 770 nm). Low-pressure hydrogen and nitrogen sorption measurements are carried out on an AutosorbiQ automated volumetric sorption instrument at 77 K and relative pressure ($P/P_0 \sim 1.0$). The data points obtained from nitrogen sorption analysis are used to calculate framework properties such as Brunauer-Emmett-Teller (BET) and Langmuir surface area, total pore volume and pore size distribution. The inbuilt software (Quantachrome® ASiQwinTM) is used to determine the value of both surface area in the relative pressure range of $0.05 \le P/P_0 \le 0.20$, and pore volume. Micropore volume is measured using DA method (up to $P/P_0 \sim 0.1$) and total pore volume is calculated at $P/P_0 = 0.99$. The pore size distribution curve is drawn by adopting a nonlocal density functional theory (NLDFT) method for incremental and cumulative pore volume with respect to half pore width. We also measured N_2 adsorption isotherms in the low-pressure range ($P/P_0 < 0.01$) at 77 K. The BET surface area for both RHA-MIL-101 and 0.06Li-RHA-MIL-101 are calculated by

fitting to the BET equation ($0.007 < P/P_0 < 0.04$). Moreover, micropore volume is estimated by Horváth-Kawazoe (HK) and Dubinin-Astakhov (DA) methods in the respective pressure range of $10^{-6} < P/P_0 < 0.15$ and $0.0001 < P/P_0 < 0.10$. Prior to characterisation, all the synthesised materials (RHA-MIL-101 and *x*Li-RHA-MIL-101) are activated under vacuum at 433 K for overnight.

5.3.1 Hydrogen adsorption measurements

Low-pressure hydrogen sorption measurements are carried out on an AutosorbiQ automated volumetric sorption instrument at 77 K and relative pressure (P/P₀ ~1.0). High-pressure hydrogen adsorption measurements at 298 K and up to 12 bar are carried out using volumetric sorption analyzer PCTPro (Setaram Instrumentation, France). Prior to adsorption isotherm measurements, samples are activated under vacuum at 433 K for 12 h. After activation process samples are allowed to cool down naturally to room temperature. Further, the temperature of the measurement cell is maintained at 298 K using a Julabo FP 50 throughout during the hydrogen adsorption isotherm experiment.

5.3.2 Adsorption equilibrium isotherm model

The hydrogen adsorption isotherms of RHA-MIL-101 and *x*Li-RHA-MIL-101 at 77 K were modelled by fitting them to the non-linear equation of three parameter Sips isotherm model (detailed in section 1.9.2.2).

5.3.3 Isosteric heat of adsorption (Q_{st})

In the present study, the calculation is performed with two adsorption isotherms at measured temperature 77 K pressure range (0–1 bar) and 298 K pressure range (0–12 bar), and a different amount of adsorbed gas (n) in the range of 0.3 to 0.4 wt%.

5.4 **Results and discussion**

At an outset, we synthesised RHA-MIL-101 by incorporating rice husk ash (RHA) in situ during the synthesis of MIL-101, following our previously reported procedure [37]. We demonstrated that RHA-MIL-101 exhibited high thermal and chemical stability, tuned porous structure and enhanced hydrogen uptake properties and herein, was further modified RHA-MIL-101 by Li⁺ ion doping and systematically investigated the effect of Li⁺ ion doping on the hydrogen storage properties of Li-doped RHA-MIL-101. In recent past several methodologies for Li^+ ion loading in MOFs have been explored [27-36], we choose to use a simple immersion technique to efficiently synthesise Li-doped RHA-MIL-101. Typically, pre-treated RHA-MIL-101 is dispersed in a DMF- H_2O solution containing Li^+ ions (as LiCl) in a specific concentration (1 mM-100 mM). In order to investigate the effect of Li⁺ ion loading, we also synthesised Lidoped RHA-MIL-101 with varying concentration of Li⁺ ions (see experimental section). ICP analysis inferred the presence of Cr, Si and Li in xLi-RHA-MIL-101, and evidence the loading of a significant amount of Li^+ ions in xLi-RHA-MIL-101. Consequently, Li-doped RHA-MIL-101 with varying Li^+ ion loading (0.06, 0.32, 0.63 and 6.09 wt%) are designated as xLi-RHA-MIL-101, where x is Li⁺ ion loading in wt%. An apparent color change from light green (for undoped RHA-MIL-101) to olive green (for xLi-RHA-MIL-101) can also be seen during the synthesis of Li-doped RHA-MIL-101 (Fig. 5.1) [24, 25]. PXRD patterns (Fig. 5.2a) of the synthesised xLi-RHA-MIL-101 with varying Li^+ ion doping is consistent with the undoped RHA-MIL-101 [37], suggesting the framework structure and the crystallinity of RHA-MIL-101 are intact upon Li⁺ ion doping. FTIR of the xLi-RHA-MIL-101 corroborated well with that of undoped RHA-MIL-101 (Fig. 5.2b). The presence of characteristics bands for Si-OH (1637 cm⁻ ¹), Si-O-Si (585 cm⁻¹) and Si-O (801 cm⁻¹) evidenced the presence of silica-rich rice husk ash (RHA) in xLi-RHA-MIL-101. Moreover, the appearance of bands at 1400 cm⁻¹ and 1511 cm⁻¹ corresponding to O-C-O symmetric vibration (dicarboxylate) and C=C stretching vibration (benzene ring) inferred the presence of MIL-101 framework [35-37, 47-49].

Fig. 5.1 Photographs of undoped RHA-MIL-101 and Li-doped RHA-MIL-101

Fig. 5.2 (a) PXRD and (b) FTIR of RHA-MIL-101 and xLi-RHA-MIL-101

Fig. 5.3 FESEM images of (a-b) RHA-MIL-101, (c) 0.06Li-RHA-MIL-101, (d) 0.3Li-RHA-MIL-101, (e) 0.6Li-RHA-MIL-101 and (f) 6.0Li-RHA-MIL-101

FESEM images of *x*Li-RHA-MIL-101 inferred the presence of a welldefined octahedron topology with uniform size (*ca.* 200 nm) distribution, evidenced the intactness of the framework morphology of RHA-MIL-101 upon Li⁺ ion doping (Fig. 5.3). TGA plots of the *x*Li-RHA-MIL-101 exhibited that all the Li-doped RHA-MIL-101 are stable up to 300 °C (Fig. 5.4). Among the observed two distinct weight loss steps, the first step (up to 300 °C) corresponds to the loss of guest water molecules from the large (d = 3.4 nm) and small (d = 2.9 nm) cages, while the second step (300-400 °C) is due to the loss of organic linker leading to the framework decomposition of *x*Li-RHA-MIL-101 [35-37].

Fig. 5.4 TGA of RHA-MIL-101 and xLi-RHA-MIL-101

Further, framework properties of *x*Li-RHA-MIL-101 are investigated by performing N₂ sorption studies at 77 K (Fig. 5.5a, b). All the quantitative data, surface area (Langmuir and BET), pore volume and pore size distribution are displayed in Table 5.1. The estimated BET surface area and total pore volume of the undoped RHA-MIL-101 are 2525 m² g⁻¹ and 1.95 cm³ g⁻¹, respectively [37]. On the other hand, *x*Li-RHA-MIL-101 displayed distinct behavior, where surface area and pore volume are significantly dependent on the content of Li⁺ ion doping in RHA-MIL-101. It is evident that silanol bonds may show enhanced interactions with Li⁺ ions, which may further facilitate efficient loading of Li⁺ ion in RHA-MIL-101 [50]. Moreover, the Li⁺ ion may also occupy the available pores in the framework structure [35]. Consequently upon Li⁺ ion loading with varying concentration in RHA-MIL-101, a gradual decrease in pore volume from 1.53 cm³ g⁻¹ (for 0.06Li-RHA-MIL-101) to 0.55 cm³ g⁻¹ (for 6.0LI-RHA-MIL-101) is observed, evidenced the pore filling due to Li⁺ ion doping in RHA-MIL-101. Though for lowest Li⁺ ion doping (0.06Li-RHA-MIL-101), an enhanced surface area of 2942 m² g⁻¹ is observed, with subsequent increase in Li⁺ ion doping content BET surface area significantly decreased to 1073 m² g⁻¹ (for 6.0Li-RHA-MIL-101), which is *ca*. 58% drop compared to the undoped RHA-MIL-101. The higher surface area of 0.06Li-RHA-MIL-101 can be attributed to the formation of additional adsorptive sites with lower Li⁺ ion doping, whereas filling of pore resulted in the observed decrease in surface area for 6.0Li-RHA-MIL-101 [35].

Fig. 5.5 (a) N_2 sorption isotherms, (b) NLDFT incremental pore size distribution for RHA-MIL-101 and *x*Li-RHA-MIL-101

To further investigate the effect of Li⁺ ions doping in the porous properties of RHA-MIL-101, N₂ adsorption isotherms (Fig. 5.6) for RHA-MIL-101 and 0.06Li-RHA-MIL-101 are conducted in the low-pressure range (P/P₀ < 0.01) at 77 K. The BET surface area for both RHA-MIL-101 and 0.06Li-RHA-MIL-101 are calculated by fitting to the BET equation (0.007 < P/P₀ < 0.04), where the BET surface area of 0.06Li-RHA-MIL-101 (2716 m² g⁻¹) is found to be higher than that of undoped RHA-MIL-101 (2314 m² g⁻¹) [23]. Moreover, micropore volume is estimated by Horváth-Kawazoe (HK) and Dubinin-Astakhov (DA) methods in the respective pressure range of $10^{-6} < P/P_0 < 0.15$ and $0.0001 < P/P_0 < 0.10$. Notably, the estimated micropore volume by DA and HK methods evidenced the increase in micropore volume upon Li⁺ ion doping 0.06Li-RHA-MIL-101 ($V_{DA} \sim$ 1.48 cm³ g⁻¹ and $V_{HK} \sim 1.25$ cm³ g⁻¹) as compared to the undoped RHA-MIL-101 (V_{DA} ~ 1.29 cm^3 g^{\text{-1}} and V_{HK} ~ 1.08 cm^3 g^{\text{-1}}), evidenced the superior porous properties for 0.06Li-RHA-MIL-101 compared to the undoped RHA-MIL-101. Nevertheless, the observed trend is consistent with the loading of Li^+ ions in xLi-RHA-MIL-101. In accordance with the observed trend in surface area and pore volume for xLi-RHA-MIL-101, the NLDFT pore size distribution also demonstrated that upon Li⁺ ion loading, pores in the mesoporous region are filled and new smallest pores are generated (Fig. 5.5b). It is evident that after Li⁺ ion doping the micropore volume fraction (V_{micro}/V_{total}) increased from 0.64 (in undoped RHA-MIL-101) to above 0.90 (in xLi-RHA-MIL-101) (Table 5.1 and Table 5.2).

Table 5.1 N_2 and H_2 low-pressure adsorption measurements of undoped RHA-MIL-101 and xLi-RHA-MIL-101

Adsorbents	SA _{BET} (m ² g ⁻¹)	Pore v (cm	volume ³ g ⁻¹)	H ₂ uptake at 77 K and 1.0 bar	
		Vmicro	V _{total}	mmol g ⁻¹	wt%
RHA-MIL-101	2525	1.25	1.95	7.64	1.54
0.06Li-RHA-MIL-101	2942	1.42	1.53	13.13	2.65
0.3Li-RHA-MIL-101	2141	1.03	1.11	12.00	2.42
0.6Li-RHA-MIL-101	1825	0.87	0.95	8.39	1.69
6.0Li-RHA-MIL-101	1073	0.52	0.55	7.82	1.58

In this connection, simulation assisted studies revealed that Li^+ ions interact favorably with the carboxylate oxygen atoms or the planer core of organic linker [21, 22, 38, 39]. Studies also indicated a charge transfer from Li to the framework, which resulted in a more positively charged Li^+ ion for enhanced Li-to-H₂ molecules interactions [38, 43, 46]. For instance, dispersion of Li^+ ions in

C₆₀-IRMOF-10 composite facilitated enhanced Li⁺ to C₆₀ interactions and hence the highly positively charged Li⁺ ion exhibited enhanced binding with H₂ molecules [46]. It is evident that Li⁺ ions are the most favorable sites for the interactions of H₂ molecules, and these interactions superseded the interaction of H₂ molecules with the framework [21, 22, 38-46]. However, clustering of Li⁺ ions in the pores of MOFs/COFs may have several adverse effects: it hinders the interaction of H₂ molecules with framework, less positively charged Li atoms due to the poor Li-to-framework interactions, and significant loss in the pore volume [41, 43, 45].

Fig. 5.6 (a) N₂ sorption isotherms and b) low pressure range (P/P₀ \leq 0.01) profile for N₂ adsorption isotherms of RHA-MIL-101 and 0.06Li-RHA-MIL-101

	Pore volume (cm ³ g ⁻¹)			H_2 u	ptake	Pore filling (%)	
Adsorbents	Vmicro	V _{total}	V _{micro} /V _{total}	NH2 (wt%)	V _{H2} (cm ³ g ⁻¹)	V _{micro}	\mathbf{V}_{total}
RHA-MIL-101	1.25	1.95	0.64	1.54	0.218	17%	11%
0.06Li-RHA-MIL-101	1.42	1.53	0.93	2.65	0.374	26%	24%
0.3Li-RHA-MIL-101	1.03	1.11	0.93	2.42	0.341	33%	31%
0.6Li-RHA-MIL-101	0.87	0.95	0.92	1.69	0.239	27%	25%
6.0Li-RHA-MIL-101	0.52	0.55	0.95	1.58	0.223	43%	43%
$V_{H_2} = (N_{H_2}/100) / D_{H_2}$ (1)	$DH_2 = 0.0$	0708 g ci	m^{-3} of H_2 at 2	20 K) ^[52]			

Table 5.2 Correlation of H_2 adsorption and pore volume in undoped RHA-MIL-101 and *x*Li-RHA-MIL-101

Fig. 5.7 (a) low-pressure hydrogen sorption isotherms at 77 K, and (b) correlation between surface area, total pore volume and hydrogen capacities for RHA-MIL-101 and *x*Li-RHA-MIL-101

Hydrogen sorption isotherms of the synthesised Li-doped RHA-MIL-101 (xLi-RHA-MIL-101) are measured at 77 K, 1 bar (Fig. 5.7a). Interesting to note that, Li⁺ ion doping content significantly influenced the hydrogen uptake properties of xLi-RHA-MIL-101. Results inferred that with the lowest content of Li^+ ion, 0.06Li-RHA-MIL-101 displayed significant enhancement of 72% in H₂ uptake (2.65 wt%) compared to the undoped RHA-MIL-101 (1.54 wt%) [37]. Moreover, 0.06Li-RHA-MIL-101 showed a hydrogen uptake of 0.49 wt% (4.9 mg g⁻¹) at 12 bar and 298 K, which is still 20% higher than the undoped RHA-MIL-101 (0.39 wt%) (Fig. 5.8a, b). Notably, the obtained hydrogen uptake (at 298 K and 12 bar) of undoped RHA-MIL-101 and 0.06Li-RHA-MIL-101 is in good agreement with those reported for pristine MIL-101 (0.55 wt% at 298 K and 20 bar) [51]. Further, increasing the Li⁺ ion content in *x*Li-RHA-MIL-101 resulted in a gradual loss in H_2 uptake. Nevertheless, the hydrogen uptake value of 2.42 wt% for 0.3Li-RHA-MIL-101 is still 57% higher than the parent RHA-MIL-101. Further, higher Li⁺ ion doping content in xLi-RHA-MIL-101 only marginally increased the H₂ uptake of 0.6Li-RHA-MIL-101 (1.69 wt%) and 6.0Li-RHA-MIL-101 (1.58 wt%). Analogous loss in H₂ uptake is also observed by Hupp *et* *al.*, where in Li_{2.62}-MOF having higher Li-content displayed lower H₂ uptake (0.77 wt%) compared to Li_{0.20}-MOF (1.32 wt%) with lower Li-content [26].

Further, the experimental H₂ adsorption isotherms of xLi-RHA-MIL-101 fitted well with the three parameters Sips non-linear isotherm model (Fig. 5.8c and Table 5.3). The observed trend is consistent with a non-uniform multilayer adsorption behavior for Li-doped RHA-MIL-101 [37]. Considering the density of 0.0708 g cm⁻³ of H₂ at 20 K [52], the volume of H₂ adsorbed in 0.06Li-RHA-MIL-101 is 0.374 cm³ g⁻¹, which is *ca*. 26% of the micropore volume of 1.53 cm³ g^{-1} . Similarly, 26 – 43% pore filling is also observed for all other Li⁺ ion doped RHA-MIL-101 (Table 5.2). These values are reasonable considering that the undoped RHA-MIL-101 displayed only 11% pore filling, evidenced the pore filling by Li⁺ ions in xLi-RHA-MIL-101. Figure 5.7b also inferred a fair correlation of H_2 uptake with BET surface area and pore volume [24, 53]. Though the observed trend in H_2 uptake is well in accordance with the trend observed for surface area of xLi-RHA-MIL-101, 0.06Li-RHA-MIL-101 having lowest Li⁺ ion doping exhibited high surface area (2942 m² g⁻¹), optimum pore volume (1.53 cm³ g^{-1}), and presumably well exposed available Li^+ ions, which resulted in the observed significantly enhanced H_2 uptake (2.65 wt%). It is evident from N_2 sorption studies that higher loading of Li⁺ ion resulted in pore filing of RHA-MIL-101. Consequently, the limited availability of Li⁺ ion resulted in the observed lower H₂ uptake for 0.6Li-RHA-MIL-101 and 6.0Li-RHA-MIL-101. It is worth noting here, that 0.3Li-RHA-MIL-101 displayed 57% higher H₂ uptake (2.42 wt%) compared to the undoped RHA-MIL-101, despite that the surface area of 0.3Li-RHA-MIL-101 is 15% lesser than the undoped RHA-MIL-101. These findings indeed evidenced the role of Li⁺ ions in achieving enhanced H₂ uptake properties for xLi-RHA-MIL-101. Notably, xLi-RHA-MIL-101 also exhibited hysteresis loop, which decreases with the increase in Li⁺ ion content. Notably, hysteresis loop may appear due to the pseudo-entrapment of H_2 molecules in the pores or a favorable interaction of H₂ molecule with adsorbent wall [54-56]. This behavior is also observed in metal hydrides, where a large difference in the adsorption and desorption is observed. Therefore, the enhanced Li^+ ion to H_2

interactions in Li-doped RHA-MIL-101 are presumably the origin of such behavior, where H₂ desorption process occurred at slower rate. However, such hysteresis can also be due to the different kinetics of materials and capillary condensation phenomena [35, 56-58]. Moreover, the isosteric heat of adsorption (Q_{st}) values (Fig. 5.8d) estimated for 0.06 Li-RHA-MIL-101 is in the range of 4.9 – 4.6 kJ mol⁻¹ and is higher than those of undoped RHA-MIL-101 (4.5 – 4.3 kJ mol⁻¹). Though the Q_{st} values are estimated over a large temperature and pressure difference range (at 77 K, 1 bar, and 298 K, 12 bar), and therefore may led to an uncertainty in the estimated Q_{st} values, the Q_{st} values are reasonably consistent with the Q_{st} values reported for analogous MOFs (Table 5.2) [23, 24, 26, 30, 35].

Fig. 5.8 (a-b) High-pressure hydrogen adsorption profiles at 298 K for undoped RHA-MIL-101 and 0.06Li-RHA-MIL-101 (c) Sips non-linear isotherm model of hydrogen uptake for undoped RHA-MIL-101 and *x*Li-RHA-MIL-101 (d) Isosteric heat of adsorption (at 77 K and 298 K) (Q_{st}) for undoped RHA-MIL-101 and 0.06Li-RHA-MIL-101
RHA-MIL-101 and xLi-RHA-MIL-101 Sips Isotherm models parameters **Adsorbents** \mathbf{R}^2 ks ts $\Delta Q(\%)$ \mathbf{a}_{s} 0.1082 RHA-MIL-101 2.0867 0.3608 0.6470 0.9998 0.06Li-RHA-MIL-101 1.3939 -0.4607 0.4273 0.9993 0.3625 0.3Li-RHA-MIL-101 2.5014 0.0020 0.5412 0.9993 0.4631

-0.2630

0.2070

0.5110

0.5995

0.9989

0.9996

0.0947

0.1013

1.2542

1.9199

0.6Li-RHA-MIL-101

6.0Li-RHA-MIL-101

Table 5.3 Isotherm constants for the three-parameter Sips isotherm models of



Fig. 5.9 Comparative hydrogen adsorption profile for RHA-MIL-101 and *x*Li-RHA-MIL-101

Hence, these finding are consistent with the observed trend in H₂ uptake of *x*Li-RHA-MIL-101, where Li⁺ ion to hydrogen molecules interaction presumably plays crucial role, which is also well complemented by the silanol bonds of RHA and tuned porosity [35-37]. It is worth noting that the observed 72% enhancement in hydrogen uptake upon Li⁺ ion doping in RHA-MIL-101 (2.65 wt% H₂ uptake for 0.06Li-RHA-MIL-101) is significant and superior than most of the previously reported analogous MIL-101 composites with Li⁺ ions doping (Fig. 5.9) [35, 36].

Deschamps *et al.* observed enhancement in H_2 adsorption from 1.20 wt% for MIL-101 upon Li loading (727 ppm) in AC (activated carbon) incorporated MIL-101 (1.60 wt%) at 77 K and 1 bar. Inducing enhanced Li⁺ ion to H₂ interactions, increment in hydrogen uptake from 0.49 wt% (for MIL-101) to 1.043 wt% (for Li@SWNT-MIL-101), at 298 K and 90 bar, was also reported [35, 36]. Hupp et al. also observed similar enhancement in H₂ uptake in Zn-MOF upon Li⁺ ion doping (1.63 wt%) compared to 0.93 wt% (for undoped Zn-MOF) [23]. Therefore, our experimental findings evidenced that Li⁺ ion doping significantly tuned the hydrogen adsorption properties of RHA-MIL-101 and are much superior than most of the previously reported Li-doped MOFs (Table 5.4). It is also evident from previous theoretical investigations over Li-MIL-101(Cr), that doping of Li⁺ ions in MIL-101(Cr) framework induced the clustering of H₂ molecules around Li⁺ ions, as evident by the increase in heat of adsorption for H₂ uptake from 6.6 kJ mol⁻¹ (for undoped MIL-101) to 12.0 kJ mol⁻¹ (for Li-doped MIL-101) [41]. Density functional calculations also suggested that each Li⁺ ions can interact with three H₂ molecules, where the crucial charge transfer from Li⁺ ions to the framework generated more positively charged Li atoms for strong binding with H₂ molecules [21, 22, 38-46]. Since, the interaction of Li⁺ ions with H_2 molecules is a dominating factor during low pressure H_2 uptake, it has been proposed that Li⁺ ions doping in MIL-101(Cr) changes the adsorption sites rather than creating additional anchoring sites in Li⁺-MIL-101(Cr) for interaction with H₂ molecules [41]. Therefore, the observed superior H₂ uptake properties of 0.06Li-RHA-MIL-101 over the undoped RHA-MIL-101 can be attributed to the favorable interactions of Li⁺ ions to H₂ molecules along with the improved porous properties of Li doped RHA-MIL-101 (0.06Li-RHA-MIL-101). Hence, our findings are promising and showing the usefulness of Li⁺ ion doping to achieve enhanced hydrogen uptake properties.

Pore Surface H_2 Qst area volume uptake (kJ **MOFs** Ref. $(m^2 g^{-1})$ $(cm^{3}g^{-1})$ mol^{-1}) (wt%) RHA-MIL-101 2525 4.5-4.3 **This** 1.95 1.54 2942 4.9-4.6 work 0.06Li-RHA-MIL-101 1.53 2.65 0.3Li-RHA-MIL-101 2141 1.11 2.42 --0.6Li-RHA-MIL-101 1825 0.95 1.69 --6.0Li-RHA-MIL-101 1073 0.55 1.58 -- $Zn_2(NDC)_2(diPyNI)$ 802 0.30 0.93 5.6-3.4 [23] Li⁺.Zn₂(NDC)₂(diPyNI) 6.1-5.0 756 0.34 1.63 Li⁺.Zn₂(NDC)₂(diPyNI) 676 0.34 1.23 6.3-5.6 [24] $Zn_2(NDC)_2(diPyTz)$ 400 0.16 1.12 8.5-6.5 [25] Li.Zn₂(NDC)₂(diPyTz) 526 0.19 1.46 8.3-6.1 1 (DO-MOF) 810 0.35 1.23 6.3-4.7 [26] $1 - Li_{0.20}$ 840 0.46 1.32 6.3-6.6 270 $1-Li_{2.62}$ 0.20 0.77 5.6-0.5 DMA-rho-ZMOF 0.95 8.0 ----[28] 0.91 9.1 Li-rho-ZMOF ----MIL-53(Al) 976 1.53 1.66 6.4-5.1 [30] Li-MIL-53(Al) 958 1.84 6.3-4.9 1.34 $0.65^{[a]}$ Zn-MOF-Crown(ether) ___ 1101.4 0.56 [31] Li⁺@Zn-MOF-Crown(ether) $0.94^{[a]}$ 893.6 0.49 --(1-ppz-solv) (NOTT-200) 180 0.136 0.96 9.03 [33] (1-Li-solv) (NOTT-201) 580 0.239 1.02 10.10 $0.74^{[b]}$ (NOTT-206) ~0 7.81 ~3 [34] $0.90^{[b]}$ 9.13 Li in (NOTT-207) 474 0.206 1.02^[b] 0.287 8.73 (NOTT-208) 687 1.32^[b] 12.04 Li in (NOTT-209) 729 0.303 3148 4.3 MIL-101 2.10 1.20 [35] Li@AC-MIL-101 2791 1.65 1.60 3.3 MIL-101(Cr) 2537 1.75 2.37 [59] -- $Li \cdot MIL - 101(Cr)$ 3.39 1840 1.38 __ $Cu_3(BTC)_2$ 1587 0.73 2.41 ---Li•Cu₃(BTC)₂ 795 0.51 3.50 -- $Me_2NH_2[In(L)].(DMF).(CH_3CN).(H_2O)_4$ 820 0.326 1.39 7.57 [60] $Li_{0.5}(H_3O)_{0.5}[In(L)].(H_2O)_5.(C_3H_6O)_{0.5}$ 1024 0.419 1.66 6.13 SodZMOF 361 0.13 $1.6^{[c]}$ --[61] $1.18^{[c]}$ 4Li⁺Me-SodZMOF 334 0.12 --Converted ^[a]cm³g⁻¹ to wt%; ^[b]mmol g⁻¹ to wt%; ^[c]uptake at 10 bar

Table 5.4 Comparison of surface area, pore volume and H_2 uptake data for selected Li⁺-doped MOFs at 77 K and 1 bar

5.5 Conclusions

In summary, we demonstrated a simple strategy to significantly enhance hydrogen uptake capacity of RHA incorporated MIL-101 by Li⁺ ion doping. Modulating the Li⁺ ion doping content, we achieved up to 72% enhancement in H₂ uptake as compared to the undoped RHA-MIL-101, where 0.06Li-RHA-MIL-101 with the lowest Li⁺ ion doping content (0.06 wt%) exhibited H₂ uptake as high as 2.65 wt% (1 bar at 77K). However, increasing the Li⁺ ion content resulted in lower H₂ uptake, attributed to the pore filling (lower pore volume and surface area). Nevertheless, all Li-doped RHA-MIL-101 exhibited higher hydrogen uptakes compared to the undoped RHA-MIL-101. We anticipated that the enhanced Li⁺ ion to hydrogen molecules interaction along with the cooperative effect of silanol bonds and tuned porosity provided a favorable environment for the observed enhanced hydrogen uptake for the Li-doped RHA-MIL-101 (*x*Li-RHA-MIL-101). The present study provided a facile route to synthesise new hybrid MOFs by incorporating rice husk ash (a waste material) and Li⁺ ion doping for hydrogen gas storage applications.

Note: The content of this chapter is published as Panchariya *et al.*, Chemistry-An Asian Journal, 2019, 14, 3728-3735, (DOI:10.1002/asia.201900833) and reproduced here with the permission of Wiley VCH.

5.6 References

- [1] Schlapbach L., Zuttel A. (2001), Hydrogen-Storage Materials for Mobile Applications, Nature, 414, 353-358.
- [2] www.energy.gov/sites/prod/files/2017/05/f34/fcto_targets_onboard_hydro
 _storage_explanation.pdf
- [3] Graetz J. (2009), New Approaches to Hydrogen Storage, Chem. Soc. Rev., 38, 73-82.
- [4] Morris R.E., Wheatley P.S. (2008), Gas Storage in Nanoporous Materials, Angew. Chem., Int. Ed., 47, 4966-4981.

- [5] Langmi H.W., Ren J., North B., Mathe M., Bessarabov D. (2014), Hydrogen Storage in Metal-Organic Frameworks: A Review, Electrochim. Acta, 128, 368-392.
- [6] Suh M.P., Park H.J., Prasad T.K., Lim D.W. (2012), Hydrogen Storage in Metal-Organic Frameworks, Chem. Rev., 112, 782-835.
- [7] Furukawa H., Cordova K.E., O'Keeffe M., Yaghi O.M. (2013), The Chemistry and Applications of Metal-Organic Frameworks, Science, 341, 1230444.
- [8] Yaghi O.M., O'Keeffe M., Ockwig N.W., Chae H.K., Eddaoudi M., Kim J. (2003), Reticular Synthesis and the Design of New Materials, Nature, 423, 705-714.
- [9] Kaur G., Rai R.K., Tyagi D., Yao X., Li P.Z., Yang X.C., Zhao Y., Xu Q., Singh S.K. (2016), Room-Temperature Synthesis of Bimetallic Co-Zn Based Zeolitic Imidazolate Frameworks in Water for Enhanced CO₂ and H₂ Uptakes, J. Mater. Chem. A, 4, 14932-14938.
- [10] Panchariya D.K., Rai R.K., Kumar E.A., Singh S.K. (2018), Core-shell Zeolitic Imidazolate Frameworks for Enhanced Hydrogen Storage, ACS Omega, 3, 167-175.
- [11] Furukawa H., Ko N., Go Y.B., Aratani N., Choi S.B., Choi E., Yazaydin A.O., Snurr R.Q., O'Keeffe M., Kim J., Yaghi O.M. (2010), Ultrahigh Porosity in Metal-Organic Frameworks, Science, 329, 424-428.
- [12] Wong-Foy A.G., Matzger A.J., Yaghi O.M. (2006), Exceptional H₂
 Saturation Uptake in Microporous Metal-Organic Frameworks, J. Am.
 Chem. Soc., 128, 3494-3495.
- [13] Farha O.K., Yazaydin A.O., Eryazici I., Malliakas C.D., Hauser B.G., Kanatzidis M.G., Nguyen S.T., Snurr R.Q., Hupp J.T. (2010), De Novo Synthesis of a Metal-Organic Framework Material Featuring Ultrahigh Surface Area and Gas Storage Capacities, Nat. Chem., 2, 944-948.
- [14] Rosi N.L., Eckert J., Eddaoudi M., Vodak D.T., Kim J., O'Keeffe M., Yaghi O.M. (2003), Hydrogen Storage in Microporous Metal-Organic Frameworks, Science, 300, 1127-1129.

- [15] Zhou W., Wu H., Hartman M.R., Yildirim T. (2007), Hydrogen and Methane Adsorption in Metal-Organic Frameworks: A High-Pressure Volumetric Study, J. Phys. Chem. C, 111, 16131-16137.
- [16] Latroche M., Surble S., Serre C., Mellot-Draznieks C., Llewellyn P.L., Lee J.H., Chang J.S., Jhung S.H., Ferey G. (2006), Hydrogen Storage in the Giant Pore Metal-Organic Frameworks MIL-100 and MIL-101, Angew. Chem., Int. Ed., 45, 8227-8231.
- [17] Hong D.Y., Hwang Y.K., Serre C., Ferey G., Chang J.S. (2009), Porous Chromium Terephthalate MIL-101 with Coordinatively Unsaturated Sites: Surface Functionalization, Encapsulation, Sorption and Catalysis, Adv. Funct. Mater, 19, 1537-1552.
- [18] Hwang Y.K., Hong D.Y., Chang J.S., Jhung S.H., Seo Y.K., Kim J., Vimont A., Daturi M., Serre C., Ferey G. (2008), Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation, Angew. Chem., Int. Ed., 47, 4144-4148.
- [19] Sculley J., Yuan D., Zhou H.C. (2011), The Current Status of Hydrogen Storage in Metal-Organic Frameworks - Updated, Energy Environ. Sci., 4, 2721-2735.
- [20] Murray L.J., Dinca M., Long J.R. (2009), Hydrogen Storage in Metal-Organic Frameworks, Chem. Soc. Rev., 38, 1294-1314.
- [21] Mavrandonakis A., Tylianakis E., Stubos A.K., Froudakis G.E. (2008), Why Li Doping in MOFs Enhances H₂ Storage Capacity? A Multi-scale Theoretical Study, J. Phys. Chem. C, 112, 7290-7294.
- [22] Blomqvist A., Araujo C.M., Srepusharawoot P., Ahuja R. (2007), Li-Decorated Metal-Organic Framework 5: A Route to Achieving a Suitable Hydrogen Storage Medium, Proc. Natl. Acad. Sci. USA, 104, 20173-20176.
- [23] Mulfort K.L., Hupp J.T. (2007), Chemical Reduction of Metal-Organic Framework Materials as a Method to Enhance Gas Uptake and Binding, J. Am. Chem. Soc., 129, 9604-9605.

- [24] Mulfort K.L., Hupp J.T. (2008), Alkali Metal Cation Effects on Hydrogen Uptake and Binding in Metal-Organic Frameworks, Inorg. Chem., 47, 7936-7938.
- [25] Mulfort K.L., Wilson T.M., Wasielewski M.R., Hupp J.T. (2009), Framework Reduction and Alkali-Metal Doping of A Triply Catenating Metal-Organic Framework Enhances and then Diminishes H₂ Uptake, Langmuir, 25, 503-508.
- [26] Mulfort K.L., Farha O.K., Stern C.L., Sarjeant A.A., Hupp J.T. (2009), Post-Synthesis Alkoxide Formation within Metal-Organic Framework Materials: A Strategy for Incorporating Highly Coordinatively Unsaturated Metal Ions, J. Am. Chem. Soc., 131, 3866-3868.
- [27] Dinca M., Long J.R. (2007), High-Enthalpy Hydrogen Adsorption in Cation-Exchanged Variants of the Microporous Metal-Organic Framework Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀]₂, J. Am. Chem. Soc., 129, 11172-11176.
- [28] Nouar F., Eckert J., Eubank J.F., Forster P., Eddaoudi M. (2009), Zeolite-Like Metal-Organic Frameworks (ZMOFs) as Hydrogen Storage Platform: Lithium and Magnesium Ion-Exchange and H(2)-(Rho-ZMOF) Interaction Studies, J. Am. Chem. Soc., 131, 2864-2870.
- [29] Himsl D., Wallacher D., Hartmann M. (2009), Improving the Hydrogenadsorption Properties of a Hydroxy-modified MIL-53(Al) Structural Analogue by Lithium Doping, Angew. Chem., Int. Ed., 48, 4639-4642.
- [30] Kubo M., Shimojima A., Okubo T. (2012), Effect of Lithium Doping into MIL-53(Al) through Thermal Decomposition of Anion Species on Hydrogen Adsorption, J. Phys. Chem. C, 116, 10260-10265.
- [31] Bai L., Tu B., Qi Y., Gao Q., Liu D., Liu Z., Zhao L., Li Q., Zhao Y. (2016), Enhanced Performance in Gas Adsorption and Li Ion Batteries by Docking Li⁺ in A Crown Ether-Based Metal-Organic Framework, Chem. Commun., 52, 3003-3006.

- [32] Chu C.L., Chen J.R., Lee T.Y. (2012), Enhancement of Hydrogen Adsorption by Alkali-Metal Cation Doping of Metal-Organic Framework-5, Int. J. Hydrogen Energy, 37, 6721-6726.
- [33] Yang S.H., Lin X., Blake A.J., Walker G.S., Hubberstey P., Champness N.R., Schroder M. (2009), Cation-Induced Kinetic Trapping and Enhanced Hydrogen Adsorption in a Modulated Anionic Metal-Organic Framework, Nat. Chem., 1, 487-493.
- [34] Yang S., Martin G.S.B., Titman J.J., Blake A.J., Allan D.R., Champness N.R., Schroder M. (2011), Pore with Gate: Enhancement of the Isosteric Heat of Adsorption of Dihydrogen via Postsynthetic Cation Exchange in Metal-Organic Frameworks, Inorg. Chem., 50, 9374-9384.
- [35] Prabhakaran P.K., Deschamp J. (2015), Doping Activated Carbon Incorporated Composite MIL-101 using Lithium: Impact on Hydrogen Uptake, J. Mater. Chem. A, 3, 7014-7021.
- [36] Prabhakaran P.K., Deschamp J. (2015), Room Temperature Hydrogen Uptake in Single Walled Carbon Nanotubes Incorporated MIL-101 Doped with Lithium: Effect of Lithium Doping, J. Porous Mater., 22, 1635-1642.
- [37] Panchariya D.K., Rai R.K., Kumar E.A., Singh S. K. (2019), Silica-Rich MIL-101(Cr) for Enhanced Hydrogen Uptake, J. Porous Mater., 26, 1137-1147.
- [38] Han S.S., Goddard III W.A. (2007), Lithium-Doped Metal-Organic Frameworks for Reversible H₂ Storage at Ambient Temperature, J. Am. Chem. Soc., 129, 8422-8423.
- [39] Dalach P., Frost H., Snurr R.Q., Ellis D.E. (2008), Enhanced Hydrogen Uptake and the Electronic Structure of Lithium-Doped Metal-Organic Frameworks, J. Phys. Chem. C, 112, 9278-9284.
- [40] Klontzas E., Mavrandonakis A., Tylianakis E., Froudakis G.E. (2008), Improving Hydrogen Storage Capacity of MOF by Functionalization of the Organic Linker with Lithium Atoms, Nano Lett., 8, 1572-1576.

- [41] Ghoufi A., Deschamps J., Maurin G. (2012), Theoretical Hydrogen Cryostorage in Doped MIL-101(Cr) Metal-Organic Frameworks, J. Phys. Chem. C, 116, 10504-10509.
- [42] Lochan R.C., Head-Gordon M. (2006), Computational Studies of Molecular Hydrogen Binding Affinities: The Role of Dispersion Forces, Electrostatics, and Orbital Interactions, Phys. Chem. Chem. Phys., 8, 1357-1370.
- [43] Cao D., Lan J., Wang W., Smit B. (2009), Lithium-Doped 3D Covalent Organic Frameworks: High-Capacity Hydrogen Storage Materials, Angew. Chem., Int. Ed., 48, 4730-4733.
- [44] Vitillo J.G., Damin A., Zecchina A., Ricchiardi G., (2005), Theoretical Characterization of Dihydrogen Adducts with Alkaline Cations, J. Chem. Phys., 122, 114311.
- [45] Li A., Lu R.-F., Wang Y., Wang X., Han K.-L., Deng W.-Q., (2010), Lithium-Doped Conjugated Microporous Polymers for Reversible Hydrogen Storage, Angew. Chem., Int. Ed., 49, 3330-3333.
- [46] Rao D., Lu R., Xiao C., Kan E., Deng K. (2011), Lithium-Doped MOF Impregnated with Lithium-Coated Fullerenes: A Hydrogen Storage Route for High Gravimetric and Volumetric Uptakes at Ambient Temperatures, Chem. Commun., 47, 7698-7700.
- [47] Rajagopal V.K., Guthrie R.D., Fields T., Davis B.H. (1996), Hydrogenation Catalysis by Thermally Activated Silica, Catal. Today, 31, 57-63.
- [48] Du X., He J. (2012), Amino-Functionalized Silica Nanoparticles with Center-Radially Hierarchical Mesopores as Ideal Catalyst Carriers. Nanoscale, 4, 852-859.
- [49] Balas F., Manzano M., Horcajada P., Vallet-Regi M. (2006), Confinement and Controlled Release of Bisphosphonates on Ordered Mesoporous Silica-Based Materials, J. Am. Chem. Soc., 128, 8116-8117.
- [50] Macon A.L.B., Jacquemin M., Page S.J., Li S., Bertazzo S., Stevens M.M., Hanna J.V., Jones J.R. (2017), Lithium-Silicate Sol-Gel Bioactive

Glass and the Effect of Lithium Precursor on Structure-Property Relationships, J. Sol-Gel Sci. Technol., 81, 84-94.

- [51] Anbia M., Mandegarzad S. (2012), Enhanced Hydrogen Sorption on Modified MIL-101 with Pt/CMK-3 by Hydrogen Spillover Effect, J. Alloy Compd., 532, 61-67.
- [52] Lin X., Jia J., Zhao X., Thomas K.M., Blake A.J., Walker G.S., Champness N.R., Hubberstey P., Schroder M. (2006), High H₂ Adsorption by Coordination-Framework Materials, Angew. Chem., Int. Ed., 45, 7358-7364.
- [53] Frost H., Snurr R.Q. (2007), Design Requirements for Metal-Organic Frameworks as Hydrogen Storage Materials, J. Phys. Chem. C, 111, 18794-18803.
- [54] Kang J., Wei S.H., Kim Y.H. (2010), Microscopic Theory of Hysteretic Hydrogen Adsorption in Nanoporous Materials, J. Am. Chem. Soc., 132, 1510-1511.
- [55] Wu H., Thibault C.G., Wang H., Cychosz K.A., Thommes M., Li J. (2016), Effect of Temperature on Hydrogen and Carbon Dioxide Adsorption Hysteresis in an ultra-microporous MOF, Micropor. Mesopor. Mater., 219, 186-189.
- [56] Zhao X.B., Xiao B., Fletcher A.J., Thomas K.M., Bradshaw D., Rosseinsky M.J. (2004), Hysteretic Adsorption and Desorption of Hydrogen by Nanoporous Metal-Organic Frameworks, Science, 306, 1012-1015.
- [57] Seki K. (2002), Dynamic Channels of a Porous Coordination Polymer Responding to External Stimuli, Phys. Chem. Chem. Phys., 4, 1968-1971.
- [58] Tabares L.C., Navarro J.A.R., Salas M. (2001), Cooperative Guest Inclusion by a Zeolite Analogue Coordination Polymer. Sorption Behavior with Gases and Amine and Group 1 Metal Salts, J. Am. Chem. Soc., 123, 383-387.
- [59] Xiang Z., Hu Z., Yang W., Cao D. (2012), Lithium Doping on Metal-Organic Frameworks for Enhancing H₂ Storage, Int. J. Hydrogen Energy, 37, 946-950.

- [60] Yang S., Lin X., Blake A.J., Thomas K.M., Hubberstey P., Champness N.R., Schroder M. (2008), Enhancement of H₂ Adsorption in Li⁺-Exchanged Co-Ordination Framework Materials, Chem. Commun., 6108-6110.
- [61] Calleja G., Botas J.A., Sanchez M.S., Orcajo M.G. (2010), Hydrogen Adsorption over Zeolite-Like MOF Materials Modified by Ion Exchange, Int. J. Hydrogen Energy, 35, 9916-9923.

Chapter 6

Conclusions and Future Scope

6.1 Conclusion drawn from the present studies

The present thesis mainly deals with the development of MOFs (MIL or ZIF frameworks) for hydrogen storage application. In these studies, core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks, carbon-MIL-101, RHA-MIL-101, and AC-MIL-101 hybrid composite, and Li-doped RHA-MIL-101 were synthesised. The structural, morphological, physical and chemical properties of the newly synthesised MOFs were investigated by the several spectro-analytical and microscopic techniques such as PXRD, Raman, FTIR, TGA, elemental analysis, TEM and SEM images, TEM-EDXS line scanning and elemental mapping, XPS, ICP-AES, and ¹³C solid-state NMR. Porous properties including surface area, pore-volume, pore size distribution of the newly synthesised coreshell ZIFs frameworks, hybrid composites, and Li doped MOFs were evaluated by N₂ sorption isotherm. Hydrogen storage performance of the developed MOFs was evaluated at low pressure and temperature (77 K and 298 K). Experimental results of H_2 storage uptakes correlated well with the Langmuir, Freundlich, Toth, and Sips adsorption isotherms model. The heat of adsorption (Q_{st}) was also estimated using Clausius-Clapeyron equation from the available experimental data for the newly developed MOFs. The obtained results reveal that the above established MOFs displayed improved stability, porosity, and textural properties, and hence, enhanced H_2 storage behavior was observed for these developed MOFs in comparison to the parent MOFs.

Chapter 2 deals with the several major challenges, such as, fragile yields of the framework, segregation of metals, and unpredicted topologies and functionalities, associated with bimetallic MOFs and its consequences on gas storage properties. To provide a better solution, construction of the core-shell ZIFs (ZIF-8@ZIF-67 and ZIF-67@ZIF-8) was carried out by seed mediated growth method, by controlled elemental composition of Co:Zn ~0.50 for both the core-shell ZIF frameworks. The above attempt could be an effective alternative way to tune or introduce improved properties in ZIFs. The synthesised core-shell ZIFs were characterised by several physical and chemical characterisation techniques including TEM and SEM images, TEM-EDXS line scanning, and elemental mapping. Core-shell ZIFs also possessed unprecedented tuned framework properties. Core-shell ZIF-8@ZIF-67 and ZIF-67@ZIF-8 frameworks conferred enhanced H_2 (2.03 wt% and 1.69 wt%) storage properties at 77 K and 1 bar, which is *ca*. 41% and 18%, respectively higher than the parent ZIF-8. Notably, the distinctly remarkable H_2 storage properties shown by both the coreshell ZIFs over the bimetallic Co/Zn-ZIF and the physical mixture of ZIF-8 and ZIF-67, clearly evidenced the unique structural properties (confinement of porosity) and elemental heterogeneity due to the core-shell morphology of the outperforming core-shell ZIFs.

In chapter 3, attempt has been made to utilize the under-utilized large pore volumes and unsaturated open metal sites available in MIL-101 to enhance the interaction of H_2 molecules with the MIL-101 framework. So, in this direction, a sustainable methodology was explored to synthesise carbon-MIL-101 hybrid composites by inducing *in situ* hydrothermal carbonizations of glucose during the synthesis of MIL-101. Various spectro-analytical and microscopic techniques such as Raman, ¹³C solid-state NMR, FTIR, XPS, TEM, SEM images, and N₂ sorption measurements were employed to establish an evidence the *in situ* formation of carbon-MIL-101 hybrid composite. The synthesised carbon-MIL-101 composites displayed improved stability, porosity, and textural properties due to the formation of the hybrid composites, in comparison to the parent MIL-101. Optimum incorporation of carbon content in MIL-101 induced significant tuning of porosity and textural properties of the carbon-MIL-101 hybrid composite, and hence an enhanced hydrogen uptake was achieved. An increment of 11% in hydrogen uptake (1.62 wt%) was observed for C100-MIL-101 composite as compared to the MIL-101 at 77 K and 1 bar. However, higher carbon loading in MIL-101 resulted in pore filling and reduction in surface area and micropore volume, and hence exhibited significant loss in H₂ uptake.

In chapter 4, effort has been made to provide a better alternative for the established carbon-based MOFs composites for hydrogen gas storage. In this direction, an inexpensive and waste by-product of the rice industry (rice husk ash-RHA) was incorporated in MOF framework to synthesise silica-rich MIL-101 composite. The structural, morphological and chemical properties of the synthesised silica-rich MIL-101 composite was established by SEM, PXRD, TGA, FTIR, and EDXS/elemental mapping studies, which confirm the incorporation of RHA in MIL-101 without any significant distortion in the framework of MIL-101. The as-synthesised RHA-MIL-101 composite displayed enhanced BET surface area (8.6%) compared to the bare MIL-101. Moreover, pore volume and pore size were decreased by ca. 6% and ca. 13%, respectively, for RHA-MIL-101, compared to MIL-101, suggesting the incorporation of silica in the larger pores of MIL-101. H₂ sorption isotherm of RHA-MIL-101 at 77 K and 1 atm was measured to evaluate the effect of silica-rich materials on the H_2 sorption properties of MIL-101, and its H₂ uptake properties was compared with the bare MIL-101 and AC-MIL-101. Results inferred that RHA-MIL-101 exhibited improved hydrogen uptake properties, attributed to the bifunctional properties of the synthesised RHA-MIL-101, abundance of silanol bonds of RHA (which shows high affinity towards H₂ molecules), and tuned porous properties of RHA-MIL-101. Therefore silica-rich materials have high potential to be a better alternative to carbon materials as composites fillers.

Chapter 5 further extended the scope and application of silica-rich MOF composite in hydrogen gas storage. Herein, effort has been made to increase the interaction of H₂ molecules with MOFs wall or structure via alkali metal (lithium ion) doping in systematical order (1 mM to 100 mM). Several spectro-analytical techniques such as PXRD, FTIR, ICP-AES, TGA, and SEM images were probed to investigate and establish the morphological and chemical properties of the synthesised Li-doped RHA-MIL-101. The enhanced hydrogen uptake was achieved for RHA incorporated MIL-101 by controlled doping of Li⁺ ion. Studies evidenced that the content of Li⁺ ion doping greatly influenced the hydrogen



uptake properties, attributed to the favorable Li^+ ion to H_2 interactions and the effect of silanol bonds of silica-rich rice-husk ash incorporated in MIL-101.

Fig. 6.1 Comparative chart of hydrogen uptake from the present research work

6.2 Contributions from the present work

Figure 6.1 demonstrates a comparative chart of hydrogen uptake performance of all the MOFs explained in the present research work. Among the synthesised various MOFs, core-shell ZIF-8@ZIF-67 and Li-doped RHA-MIL-101 exhibited significantly enhanced hydrogen uptake by 42% and 72%, respectively as compared to the respective parent MOFs ZIF-8 and RHA-MIL-101. Moreover, RHA-MIL-101 composite appeared as a promising alternative to carbon-MOF composites. *In situ* carbonization of glucose during the syntheses of MIL-101 demonstrated an energy efficient process to synthesise carbon-MOF composites. Despite that, the developed MOFs exhibited promising results for hydrogen storage; further efforts need to be focused to meet the DOE criteria of hydrogen storage materials. Here, an attempt has been made to provide a new direction in the field of materials research to achieve the established goal for hydrogen storage.

6.3 Limitations of the present work

- In the present thesis, hydrogen storage capacity was evaluated at 77 K (cryogenic temperature) and 1 bar. However, most of applications require the operating conditions near around the ambient conditions; hence the storage capacity need to measure near ambient condition.
- The MOFs developed for the current studies is laboratory level/scale in mg or gram quantity. To synthesis MOFs in industrial scale efficient methodologies need to be developed.

6.4 Scope for future work

- Further study is needed to examine the hydrogen uptake performance of developed MOFs at different temperature (from cryogenic to ambient) and varying pressure range.
- To understand inter-particular diffusion phenomena and hydrogen sorption rates of the developed MOFs, kinetic measurements are required to be performed.
- The adsorption thermodynamic properties such as enthalpy, entropy, Gibbs free energy, specific heat capacity, isosteric heat of adsorption, and activation energy are required to be studied for the developed MOFs.
- The present study can also be extended for the developed MOFs for storage and separation application of various other gases (CO₂, CH₄, CO₂/N₂, CO₂/SO₂) also.
- The developed simple, cost-effective, and efficient methodologies for the production of MOF composites can also be extended for mass scale synthesis of other MOFs.
- The developed MOFs can also be utilized for other potential application such as catalysis, drug delivery, magnetism, luminescence and sensors.

APPENDIX-A

Table .	A1	Comparison	of	surface	areas	of repor	ted	MIL-101(Cr)	according t	0
additive	e, tir	ne, temperati	ıre	(synthes	is and	activatio	on) a	and purification	n steps	

Additive	Time	Tempera	ature (°C)	SBET	Pu	rification ste	eps	Ref.
	(h)	Synthesis	Activation	$(\mathbf{m}^2 \mathbf{g}^{-1})$	Filtration	Solvent	Fluoride	
						treatments	-anion exchange	
HCl	8	220	120	2441		hot H ₂ O/	exenange	Present
-	-	-	-			acetone/		study
						hot EtOH/		
						hot MeOH		
						and hot		
						EtOH		
						(93%) + H ₂ O (5%)		
HC1	8	220	120	2324		hot $H_2O/$		[1]
ner	U	220	120	2021		acetone/		[-]
						hot EtOH		
						and hot		
						EtOH		
						(95%) +		
	0	200	140	2014		$H_2O(5\%)$		[2]
пг	0	200	140	2014				[2]
HF	8	200	80	1765		DMF/EtOH		
HF	8	220	150	2390	OF	DMF/H ₂ O/		[3]
	0	220	00	2240	OF	EtOH	MILE/hot	F 4 1
пг	0	220	80	2540	OF	H ₂ O	H ₂ O	[4]
NaAc	12	220	150	2341		DMF/EtOH		[5]
HF/	10	210	150	2083		DMF/EtOH		[6]
$C_2H_4O_2$	0		• • • •	1105				
	8	210	200	1137		DMF		[7]
HF	8	220	150	2345	OF	EtOH		[8]
HF	8	220	90	2220	DF	hot DMF/		[9]
HF	10	220	100	2213	OF	EtOH DMF/H ₂ O	NH₄F	[10]
	- •							[-•]
HF	8	220	130	2052		H ₂ O/EtOH/		[11]
HF	8	220	150	2100	DF	DMF/H ₂ O		[12]
HF	8	220	150	1815	DF	H ₂ O		
	0	0		1010				

HF	8	220	160	2191	DF	(95%EtOH + 5%H ₂ O)	NH ₄ F	[13]
HF	8	220	150	2231	DF	(95%EtOH		[14]
HF	8	220	150	2663.7	DF	+ 5%H ₂ O) (95%EtOH		[15]
HF	8	220	150	1638		+ 5% H ₂ O) DMF/EtOH		[16]
HF	8	220	150	2563		MeOH	95% ethanol⊥	[17]
HF	8	220	150	2549		EtOH/H ₂ O	NH ₄ F	[18]
HF	8	220	210	2578	OF	H ₂ O/DMF/ EtOH		[19]
HF	8	220	200	2552		DMF		[20]
HF	8	210	70	2661		DMF/EtOH		[21]
HF	8	220		1452	OF	H_2O		[22]
HF	8	220	100	2454	OF	$H_2O/(95\%)$ EtOH + 5% H_2O		
HF	8	220	100	2868	OF	$H_2O/(95\%)$ EtOH + 5%	NH ₄ F	
HF	8	220	200	2452	DF	H ₂ O/EtOH	$\rm NH_4F$	[23]
HF	8	220	150	2674		DMF/EtOH		[24]
HF	8	220	80	2693	OF	H_2O		[25]
NaOH	6	210	150	2735		H ₂ O/DMF		[26]
HF	8	220	150	2800	DF			[27]
HF	8	220	100	2800	DF	EtOH	$\rm NH_4F$	[28]
HF	8	220	150	2962	OF	H ₂ O/EtOH		[29]

*DF: Double filtration

#OF: One-time filtration

EtOH- Ethanol, MeOH-Methanol, NH₄F- Ammonium fluoride, DMF- N,N-Dimethylformamide

A.1 References

- Panchariya D.K., Rai R.K., Kumar E.A., Singh S.K. (2019), Silica-Rich MIL-101(Cr) for Enhanced Hydrogen Uptake, J. Porous Mater., 26, 1137-1147.
- [2] Santiago-Portillo A., Navalon S., Cirujano F.G., Xamena F.X.L.I., Alvaro M., Garcia H. (2015), MIL-101 as Reusable Solid Catalyst for Autoxidation of Benzylic Hydrocarbons in the Absence of Additional Oxidizing Reagents, ACS Catal., 5, 3216-3224.
- [3] Behvandi A., Safekordi A.A., Khorasheh F. (2017), Removal of Benzoic Acid from Industrial Wastewater using Metal-Organic Frameworks: Equilibrium, Kinetic and Thermodynamic Study, J. Porous Mater., 24, 165-178.
- [4] Hassan H.M.A., Betiha M.A., Mohamed S.K., El-Sharkawy E.A., Ahmed E.A. (2017), Stable and Recyclable MIL-101(Cr)-Ionic Liquid Based Hybrid Nanomaterials as Heterogeneous Catalyst, J. Mol. Liq., 236, 385-394.
- [5] Shen T., Luo J., Zhang S., Luo X. (2015), Hierarchically Mesostructured MIL-101 Metal-Organic Frameworks with Different Mineralizing Agents for Adsorptive Removal of Methyl Orange and Methylene Blue from Aqueous Solution, J. Environ. Chem. Eng., 3, 1372-1383.
- [6] Zhu M., Hu P., Tong Z., Zhao Z., Zhao Z. (2017), Enhanced Hydrophobic MIL(Cr) Metal-Organic Framework with High Capacity and Selectivity for Benzene VOCs Capture from High Humid Air, Chem. Eng. J., 313, 1122-1131.
- [7] Ren J., Musyoka N.M., Langmi H.W., Segakweng T., North B.C., Mathe M., Kang X. (2014), Modulated Synthesis of Chromium-Based Metal-Organic Framework (MIL-101) with Enhanced Hydrogen Uptake, Int. J. Hydrogen Energy, 39, 12018-12023.
- [8] El-Shall M.S., Abdelsayed V., Khder A.E.R.S., Hassan H.M.A., El-KaderiH.M., Reich T.E. (2009), Metallic and Bimetallic Nanocatalysts

Incorporated into Highly Porous Coordination Polymer MIL-101, J. Mater. Chem., 19, 7625-7631.

- [9] Maksimchuk N.V., Timofeeva M.N., Melgunov M.S., Shmakov A.N., Chesalov Y.A., Dybtsev D.N., Fedin V.P., Kholdeeva O.A. (2008), Heterogeneous Selective Oxidation Catalysts Based on Coordination Polymer MIL-101 and Transition Metal-Substituted Polyoxometalates, J. Catal., 257, 315-323.
- [10] Gordon J., Kazemian H., Rohani S. (2015), MIL-53(Fe), MIL-101, and SBA-15 Porous Materials: Potential Platforms for Drug Delivery, Mater. Sci. Eng. C, 47, 172-179.
- [11] Jangodaz E., Alaie E., Safekordi A.A., Tasharrofi S. (2018), Adsorption of Ethylbenzene from Air on Metal-Organic Frameworks MIL-101(Cr) and MIL-53(Fe) at Room Temperature, J. Inorg. Organomet. Polym. Mater., 28, 2090-2099.
- [12] Gobara H.M., Mohamed R.S., Hassan S.A., Khalil F.H., El-Sall M.S. (2016), Pt and Ni Nanoparticles Anchored into Metal-Organic Frameworks MIL-101 (Cr) as Swift Catalysts for Ethanol Dehydration, Catal. Lett., 146, 1875-1885.
- [13] Fazaeli R., Aliyan H., Banavandi R.S. (2015), Sunlight Assisted Photodecolorization of Malachite Green Catalyzed By MIL-101/Graphene Oxide Composites, Russ. J. Appl. Chem., 88, 169-177.
- [14] Szilagyi P.A., Callini E., Anastasopol A., Kwakernaak C., Sachdeva S., Van de Krol R., Geerlings H., Borgschulte A., Zuttel A., Dam B. (2014), Probing Hydrogen Spillover in Pd@MIL-101(Cr) with a Focus on Hydrogen Chemisorption, Phys. Chem. Chem. Phys., 16, 5803-5809.
- [15] Chen C., Zhang M., Guan Q., Li W. (2012), Kinetic and Thermodynamic Studies on the Adsorption of Xylenol Orange onto MIL-101(Cr), Chem. Eng. J., 183, 60-67.
- [16] Mohammadkhani Z., Abedi S., Morsali A., Abbasi A.R., Ebrahimzadeh M.E., Babaei F., Matikolaei M.K. (2018), Effects of Pore Size and Surface

Area on CH_4 And CO_2 Capture in Mesostructured MIL-101, J. Iran. Chem. Soc., 1, 137-142.

- [17] Suresh M., Raju B.D., Rao K.S.R., Reddy K.R., Srinivasu M.L.K.P. (2014), Metal-Organic Framework MIL-101(Cr) for Dehydration Reactions, J. Chem. Sci., 126, 527-532.
- [18] Ye S., Jiang X., Ruan L.W., Liu B., Wang Y.M., Zhu J.F., Qiu L.G. (2013), Post-Combustion CO₂ Capture with the HKUST-1 and MIL-101(Cr) Metal-Organic Frameworks: Adsorption, Separation and Regeneration Investigations, Microporous Mesoporous Mater., 179, 191-197.
- [19] Liu Y.Y., Zeng J.L., Zhang J., Xu F., Sun L.X. (2007), Improved Hydrogen Storage in the Modified Metal-Organic Frameworks by Hydrogen Spillover Effect, Int. J. Hydrogen Energy, 32, 4005-4010.
- [20] Musyoka N.M., Ren J., Annamalai P., Langmi H.W., North B.C., Mathe M., Bessarabov D. (2016), Synthesis of a Hybrid MIL-101(Cr)/ZTC Composite for Hydrogen Storage Applications, Res. Chem. Intermed., 42, 5299-5307.
- [21] Mu M., Yan X., Li Y., Chen L. (2017), Post-Modified Acid-Base Bifunctional MIL-101(Cr) for One-Pot Deacetalization-Knoevenagel Reaction, J. Nanopart. Res., 19, 148.
- [22] Lin K.S., Adhikari A.K., Su Y.H., Shu C.W., Chan H.Y. (2012), Synthesis, Characterization, and Hydrogen Storage Study by Hydrogen Spillover of MIL-101 Metal-Organic Frameworks, Adsorption, 18, 483-491.
- [23] Bullot L., Vieira-Sellaï L., Chaplais G., Simon-Masseron A., Daou T.J., Patarin J., Fiani E. (2017), Adsorption of 1,2-Dichlorobenzene and 1,2,4-Trichlorobenzene in Nano- and Microsized Crystals of MIL-101(Cr): Static and Dynamic Gravimetric Studies, Environ. Sci. Pollut. Res., 24, 26562-26573.

- [24] Chowdhury P., Bikkina C., Gumma S. (2009), Gas Adsorption Properties of the Chromium-Based Metal-Organic Framework MIL-101, J. Phys. Chem. C, 113, 6616-6621.
- [25] Senkovska I., Kaskel S. (2008), High Pressure Methane Adsorption in the Metal-Organic Frameworks Cu₃(btc)₂, Zn₂(bdc)₂dabco, and Cr₃F(H₂O)₂O(bdc)₃, Microporous Mesoporous Mater., 112, 108-115.
- [26] Khan N.A., Kang I.J., Seok H.Y., Jhung S.H. (2011), Facile Synthesis of nano-sized Metal-Organic Frameworks, Chromium-benzenedicarboxylate, MIL-101, Chem. Eng. J., 166, 1152-1157.
- [27] Llewellyn P.L., Bourrelly S., Serre C., Vimont A., Daturi M., Hamon L., Weireld G.D., Chang J.S., Hong D.Y., Hwang Y.K., Jhung S.H., Ferey G. (2008), High Uptakes of CO₂ And CH₄ in Mesoporous Metals-Organic Frameworks MIL-100 and MIL-101, Langmuir, 24, 7245-7250.
- [28] Kim H.Y., Kim S.N., Kim J., Ahn W.S. (2013), Liquid Phase Adsorption of Selected Chloroaromatic Compounds over Metal-Organic Frameworks, Mater. Res. Bull., 48, 4499-4505.
- [29] Huang X.X., Qiu L.G., Zhang W., Yuan Y.P., Jiang X., Xie A.J., Shen Y.H., Zhu J.F. (2012), Hierarchically Mesostructured MIL-101 Metal-Organic Frameworks: Supramolecular Template-Directed Synthesis and Accelerated Adsorption Kinetics for Dye Removal, Cryst. Eng. Comm., 14, 1613-1617.

APPENDIX-B

Uncertainty and Error of Experiment

The specifications of various instruments used in the present work are given below:

B.1 Weighing Balance

Limit values Make: Mettler Toledo Model: ME204 Maximum Capacity: 220 g Readability: 0.1 mg Repeatability (at nominal load): 0.1 mg Linear deviation: 0.2 mg Sensitivity temperature drift: 2 ppm/°C

B.2 Thermostatic Bath

Make: Julabo Model: FP 50 Temperature range: -50 to 200°C Stability: ±0.01°C Flow range: 11 to 16 l/min Heating Capacity: 2000 W

B.3 Sorption Experimental Setup (Low Pressure measurement and BET measurement)

Make: Quantachrome Instruments Model: autosorb iQ₂ TPX Analysis stations: Two Pressure transducers: 1 torr, 10 torr, 1000 torr, 0.1 torr (optional) Pressure accuracy*: 1000 torr (<±0.11 % of full scale) : 10 torr (<±0.12 % of reading) : 0.1 torr, 1 torr (<±0.15 % of reading) Ultimate vacuum, analysis[#]: 5x10⁻¹⁰ mbar Ultimate vacuum, degas[#]: 5x10⁻¹⁰ mbar Degassing temperature: 350°C (450°C with quartz glassware) *transducer manufacture specification [#] vacuum pump, manufacturer specification

B.4 High Pressure Sorption Experimental Setup

Make: SETARAM Instrumentation

Model: PCTPro

Temperature range: - 260°C to 500°C with different sample holders options

Calibrated reservoirs: 2 High pressure calibrated volumes (Evo version)

5 High pressure calibrated volumes (E&E version)

Operating pressure range: From vacuum to 200 bar

Pressure regulation: Automated PID software controlled

Aliquot sizing - Fixed P, ΔP or $f(\Delta P)$

Pressure measurements: 4 pressure transducers

Pressure regulation: 2 transducers for vacuum to 200 bar Experiment pressure: 1 transducer for vacuum to 200 bar 1 transducer for vacuum to 5 bar

Accuracy: 1% of the reading

High accuracy option: Accuracy < 0.12% of the reading (vacuum to 5 bar) Accuracy < 0.025% full scale (vacuum to 200 bar)

Maximum sensitivity: 3 µmole of gas (with the MicroDoser attachment)

B.5 Experimental Uncertainty and Error Analysis

The objective of uncertainty analysis is to quantify the variations of output due to the variation of input. The main role of uncertainty analysis is to evaluate error in the calculations. For the gas sorption measurements, the possible error might be due to error in measurement of multiple parameters. The parameters such as void volume calculation, weight of material, temperature deviations and variations in pressure measurement affect the final estimation of adsorbed quantity. In order to minimize the error during the experimental work, the experimental workstation is calibrated with the known sample using the standard procedure. In the present study, low pressure sorption instrument was calibrated as per autosorb iQ and ASiQwin gas sorption system operating manual with standard material. High-pressure sorption workstation was calibrated with standard material (Palladium) supplied from the manufacturer [1, 2]. The explanation of measurement parameter is discussed in the 1.6.11 and 1.6.12 section.

B.6 References

- [1] QuantaChrome Inc., "Autosorb iQ and ASiQwin Gas Sorption System Operating Manual," *Characterizing Porous Materials and Powders*. QuantaChrome Inc., Boynton Beach, FL.
- [2] AN695- Hydrogen sorption studied by manometric (Sievert's) techniques alone and coupled to calorimetry.

APPENDIX-C

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Dec 27, 2019

This Agreement between Mr. DHARMENDRA KUMAR PANCHARIYA ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	4734731079816
License date	Dec 23, 2019
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Chemistry - An Asian Journal
Licensed Content Title	Lithium-Doped Silica-Rich MIL-101(Cr) for Enhanced Hydrogen Uptake
Licensed Content Author	Dharmendra K. Panchariya, E. Anil Kumar, Sanjay K. Singh
Licensed Content Date	Sep 11, 2019
Licensed Content Volume	14
Licensed Content Issue	20
Licensed Content Pages	8
Type of Use	Dissertation/Thesis
Requestor type	Author of this Wiley article
Format	Print and electronic
Portion	Full article
Will you be translating?	No
Title of your thesis / dissertation	Synthesis and Characterisation of Metal Organic Frameworks based Hydrogen Storage Materials
Expected completion date	Mar 2020
Expected size (number of pages)	200
Requestor Location	Mr. DHARMENDRA KUMAR PANCHARIYA SB-224 B
	Indian Institute of Technology Indore
	Simrol Campus, Khandwa Road
	Indore, 403002
	Attn: Mr. DHARMENDRA KUMAR PANCHARIYA
Publisher Tax ID	EU826007151
Total	0.00 USD
Terms and Conditions	
	TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a'Wiley Company') or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively 'WILEY'). By clicking 'accept' in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ('CCC's Billing and Payment terms and conditions'), at the time that you opened your RightsLink account (these are available at any time at <u>http://mvaccount.copyright.com</u>).

Terms and Conditions

The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

SPRINGER NATURE LICENSE TERMS AND CONDITIONS

Dec 27, 2019

This Agreement between Mr. DHARMENDRA KUMAR PANCHARIYA ("You") and Springer Nature ("Springer Nature") consists of your license details and the terms and conditions provided by Springer Nature and Copyright Clearance Center.

License Number	4734740097235
License date	Dec 23, 2019
Licensed Content Publisher	Springer Nature
Licensed Content Publication	Journal of Porous Materials
Licensed Content Title	Silica rich MIL-101(Cr) for enhanced hydrogen uptake
Licensed Content Author	Dharmendra K. Panchariya, Rohit K. Rai, E. Anil Kumar et al
Licensed Content Date	Jan 1, 2019
Licensed Content Volume	26
Licensed Content Issue	4
Type of Use	Thesis/Dissertation
Requestor type	academic/university or research institute
Format	print and electronic
Portion	full article/chapter
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	yes
Title	Synthesis and Characterisation of Metal Organic Frameworks based Hydrogen Storage Materials
Institution name	n/a
Expected presentation date	Mar 2020
Requestor Location	Mr. DHARMENDRA KUMAR PANCHARIYA SB-224 B
	Simrol Campus. Khandwa Road
	Indore, 453552
	India
	Attn: Mr. DHARMENDRA KUMAR PANCHARIYA
Iotal	0.00 USD
Terms and Conditions	

Springer Nature Customer Service Centre GmbH Terms and Conditions

This agreement sets out the terms and conditions of the licence (the Licence) between you and Springer Nature Customer Service Centre GmbH (the Licensor). By clicking 'accept' and completing the transaction for the material (Licensed Material), you also confirm your acceptance of these terms and conditions.

1. Grant of License

 The Licensor grants you a personal, non-exclusive, non-transferable, world-wide licence to reproduce the Licensed Material for the purpose specified in your order only. Licences are granted for the specific use requested in the order and for no other use, subject to the conditions below.

 2. The Licensor warrants that it has, to the best of its knowledge, the rights to license reuse of the Licensed Material. However, you should ensure that the material you are requesting is original to the Licensor and does not carry the copyright

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE LICENSE TERMS AND CONDITIONS

Dec 27, 2019

This Agreement between Mr. DHARMENDRA KUMAR PANCHARIYA ("You") and The American Association for the Advancement of Science ("The American Association for the Advancement of Science") consists of your license details and the terms and conditions provided by The American Association for the Advancement of Science and Copyright Clearance Center.

License Number	4736970197649
License date	Dec 27, 2019
Licensed Content Publisher	The American Association for the Advancement of Science
Licensed Content Publication	Science
Licensed Content Title	A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area
Licensed Content Author	G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki
Licensed Content Date	Sep 23, 2005
Licensed Content Volume	309
Licensed Content Issue	5743
Volume number	309
Issue number	5743
Type of Use	Thesis / Dissertation
Requestor type	Scientist/individual at a research institution
Format	Print and electronic
Portion	Figure
Number of figures/tables	1
Order reference number	
Title of your thesis / dissertation	Synthesis and Characterisation of Metal Organic Frameworks based Hydrogen Storage Materials
Expected completion date	Mar 2020
Estimated size(pages)	200
Requestor Location	Mr. DHARMENDRA KUMAR PANCHARIYA SB-224 B Indian Institute of Technology Indore
	Simrol Campus, Khandwa Road
	India
	Attn: Mr. DHARMENDRA KUMAR PANCHARIYA
Total	0.00 USD
Terms and Conditions	

American Association for the Advancement of Science TERMS AND CONDITIONS

Regarding your request, we are pleased to grant you non-exclusive, non-transferable permission, to republish the AAAS material identified above in your work identified above, subject to the terms and conditions herein. We must be contacted for permission for any uses other than those specifically identified in your request above. The following credit line must be printed along with the AAAS material: "From [Full Reference Citation]. Reprinted with permission

The following credit line must be printed along with the AAAS material: "From [Full Reference Citation]. Reprinted with permission from AAAS."

All required credit lines and notices must be visible any time a user accesses any part of the AAAS material and must appear on any printed copies and authorized user might make. This permission does not apply to figures / photos / artwork or any other content or materials included in your work that are credited

This permission does not apply to figures / photos / artwork or any other content or materials included in your work that are credited to non-AAAS sources. If the requested material is sourced to or references non-AAAS sources, you must obtain authorization from

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE LICENSE TERMS AND CONDITIONS

Dec 27, 2019

This Agreement between Mr. DHARMENDRA KUMAR PANCHARIYA ("You") and The American Association for the Advancement of Science ("The American Association for the Advancement of Science") consists of your license details and the terms and conditions provided by The American Association for the Advancement of Science and Copyright Clearance Center.

License Number	4736961483397
License date	Dec 27, 2019
Licensed Content Publisher	The American Association for the Advancement of Science
Licensed Content Publication	Science
Licensed Content Title	High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO2 Capture
Licensed Content Author	Rahul Banerjee, Anh Phan, Bo Wang, Carolyn Knobler, Hiroyasu Furukawa, Michael O'Keeffe, Omar M. Yaghi
Licensed Content Date	Feb 15, 2008
Licensed Content Volume	319
Licensed Content Issue	5865
Volume number	319
Issue number	5865
Type of Use	Thesis / Dissertation
Requestor type	Scientist/individual at a research institution
Format	Print and electronic
Portion	Figure
Number of figures/tables	1
Order reference number	
Title of your thesis / dissertation	Synthesis and Characterisation of Metal Organic Frameworks based Hydrogen Storage Materials
Expected completion date	Mar 2020
Estimated size(pages)	200
Requestor Location	Mr. DHARMENDRA KUMAR PANCHARIYA SB-224 B Indian Institute of Technology Indore Simrol Campus, Khandwa Road Indore, 453552 India Attr. Mr. DHARMENDRA KUMAR PANCHARIYA
Total	0.00 USD

Terms and Conditions

American Association for the Advancement of Science TERMS AND CONDITIONS

Regarding your request, we are pleased to grant you non-exclusive, non-transferable permission, to republish the AAAS material identified above in your work identified above, subject to the terms and conditions herein. We must be contacted for permission for any uses other than those specifically identified in your request above.

The following credit line must be printed along with the AAAS material: "From [Full Reference Citation]. Reprinted with permission from AAAS."

All required credit lines and notices must be visible any time a user accesses any part of the AAAS material and must appear on any printed copies and authorized user might make.





Dharmendra Kumar Panchariya

Ph.D. Scholar, Heat Transfer Lab, Discipline of Mechanical Engineering and Member of Organometallics and Nanotech Catalysis Group, Discipline of Chemistry Indian Institute of Technology Indore, Simrol Indore 453552 India **E-Mail:** phd1401203004@iiti.ac.in, dharm03021989@gmail.com

Education Qualifications

2014-Present	<i>Ph.D.</i> (<i>Mechanical Engineering</i>) Indian Institute of Technology Indore, Indore, India	9.63 (CPI)
2010-2012	<i>M. Tech</i> (<i>Thermal System Design</i>) Sardar Vallabhbhai National Institute of Technology, Surat, India	87.77% (Honours)
2006-2010	B.E (Mechanical Engineering) Chhattisgarh Swami Vivekanand Technical University, Bhilai, India	79.81% (Honours)
2005-2006	Intermediate- Physics, Chemistry, Mathematics Chhattisgarh Board of Secondary Education, Raipur, India	82.40%
2003-2004	Senior Secondary - Science, Mathematics, English, Social Science Chhattisgarh Board of Secondary Education, Raipur, India	81.50%
	Work experiences	
2014 to 2019	Teaching Assistant Indian Institute of Technology Indore, India	
2013 to 2014	Temporary Faculty National Institute of Technology Raipur, India	
2010 to 2012	Teaching Assistant Sardar Vallabhbhai National Institute of Technology, Surat, In	dia

Awards and Responsibilities

- GATE (Graduate Aptitude Test Exam)- National Level Qualifying Exam for Scholarship Award for Postgraduate and Ph.D. Programs - qualified in 2010, 2012, 2013.
- > Alumni Joint Secretaries, IIT Indore (2015-16)

Workshops and Certified Courses Attended

- I have attained a day workshop on "Hydrogen Storage Materials" conducted at Indian Oil R&D Centre, Faridabad, 7th December 2018.
- Certified course on Advance Diploma in C, C++ Programme.
- GIAN Course on "Introduction to Heat Pipe Science and Technology" By Prof. Manfred Groll. University of Stuttgart, Germany.
- GIAN Course on "Second Law Analysis of Thermal Energy Storage Systems" By Prof. Bale V. Reddy. Faculty of Engineering and Applied Science, University of Ontario Institute of Technology.
- GIAN Course on "Introduction to Thermal System Design" By Prof. Srinivas Garimella. Director of the Sustainable Thermal Systems Laboratory at Georgia Institute of Technology.
- GIAN Course on "Adsorption Science & Technology for Cooling & Desalination Applications" By Prof. Bidyut Baran Saha. Professor and Principal Investigator Thermal Science and Engineering Division, International Institute for Carbon-Neutral Energy Research (WPI-I²CNER)/Department of Mechanical Engineering, Kyushu University/ Japan

Technical Training & Industry Visits

Summer training at Bhilai Steel Plant, Bhilai, India	Duration 6 weeks (2007-08)
Summer training at Electric Loco Shed, Bhilai, India	Duration 6 weeks (2008-09)
Visited on Sardar Sarovar Dam and Power station, Gujarat, India	One Day Visit (2010-11)
Visited on Jalaram Cottex Pvt. Ltd., Jasdan, Gujarat, India	One Day Visit (2011-12)
Visited on Agrawal Oil Mills, Udaipur, Rajasthan, India	One Day Visit (2011-12)

Participated in the Training Program on "Uses of E-Resources" Organized by Central Library, NIT, Raipur (Sept. 2014)

Personal Details

Date of Birth: 03/02/1989 Marital Status: Married Gender: Male Nationality: Indian Languages: Hindi, English, Rajasthani, Gujarati, Chhattisgarhi Residency Address: Qtr No. III/27, BSNL Type III Qtr, Scheme-44, Khatiwala Tank, Indore-452014, India