MIL-101 Supported Nanoparticle Catalysts: Synthesis, Characterization and Catalytic Properties

M.Sc. Thesis

By AJAY



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MIL-101 Supported Nanoparticle Catalysts: Synthesis, Characterization and Catalytic Properties

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Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science





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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "MIL-101 Supported Nanoparticle Catalysts: Synthesis, Characterization and Catalytic Properties" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2015 to June 2016 under the supervision of Dr Sanjay K. Singh, Assistant Professor, Indian Institute of Technology, Indore.

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.

AJAY

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

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AJAY has successfully given his M.Sc.	. Oral Examination held on
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Date:	Date:

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Ajay, IIT Indore

Dedication I would like to dedicate this thesis to my Parents

Abstract

Highly active, robust and stable bimetallic NiPd, CuPd and CoPd alloy nanoparticle catalysts stabilized by MIL-101 framework, (M/Pd atomic ratio = 95:5, M = Ni, Cu and Co) were synthesized and their catalytic activity for Suzuki reaction at moderate reaction conditions was explored. In contrary to monometallic counterparts, a significant enhancement in catalytic activity was observed with these bimetallic NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 alloy nanoparticle catalysts. Among the synthesized catalysts, NiPd/MIL-101 and CuPd/MIL-101 displayed higher catalytic activity for the synthesis of biaryls for a wide range of substituted aryl halides and arylboronic acids having electron donating and electron withdrawing substituents, whereas CoPd/MIL-101 was found to be poorly active. Catalytic efficiency of the synthesized CuPd/MIL-101 was found to be highest followed by NiPd/MIL-101, whereas CoPd/MIL-101 was found to be poorly active for Suzuki reaction. The observed high catalytic activity displayed by NiPd/MIL-101 and CuPd/MIL-101 was attributed to the synergistic effect brings in by electronic charge transfer from Ni or Cu to Pd, and high dispersity of NiPd and CuPd nanoparticles on MIL-101.

LIST OF PUBLICATIONS

Synergistic Catalysis with MIL-101 Stabilized Highly Active Bimetallic NiPd and CuPd Alloy Nanoparticle Catalysts for C–C Coupling Reactions

Ajay Dhankhar, Rohit K. Rai, Deepika Tyagi, Yao Xin, and Sanjay K. Singh*

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MOF supported nanoparticle catalytic system for Suzuki Miyaura reaction

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TABLE OF CONTENTS

LIST OF FIGURES	vii-viii
LIST OF TABLES	ix
NOMENCLATURE	x
ACRONYMS	xi

Chapter 1 Introduction and Reaction Scheme

2 1	Conoral	11
Chapter 2	Experimental Section	
1.2	Reaction Scheme	10
1.1g	Theme of our work	9
1.1f	Overview of previous work	7-9
1.1e	MIL-101 (MIL: Materials from the Institute Lavoisier)	6-7
1.1d	MOFs as a support	5-6
1.1c	Problems associated with nanoparticle synthesis	4-5
1.1b	Overview of Suzuki Reaction	2-4
1.1a	Bimetallic Nanoparticles	1-2
1.1	Introduction	1-9

2.1	General	11
2.2	Synthesis of MIL-101	11-12

2.3	Synthesis of NiPd/MIL-101, 12	
	CuPd/MIL-101 and CoPd/MIL-101	
	nanoparticle catalysts	
2.4	Procedure for catalytic Suzuki reaction	13
Chapter 3	Results and Discussion	14-26
Chapter 4	Conclusion and scope of future w	vork
4.1	Conclusion	27
4.2	Scope of future work	27
APPENDIX-A	NMR data of coupled products	28-36
	Poster Abstract	37
REFERENC	ES	38-47

LIST OF FIGURES

Figure Description		
No.		No.
Figure 1.	Figure illustrating using MOF as a support to NPs and some examples of their diverse catalytic applications.	6
Figure 2.	Structure of MIL-101 having pentagonal and hexagonal windows	7
Figure 3.	Powder XRD pattern of synthesized MIL-101.	14
Figure 4.	SEM image of synthesized MIL-101.	14
Figure 5.	TEM and SEM images of synthesized NiPd/MIL- 101.	15
Figure 6.	TEM and SEM images of synthesized CuPd/MIL- 101.	16
Figure 7.	TEM and SEM images of synthesized CoPd/MIL- 101.	16
Figure 8.	EDS analyses of synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101.	17
Figure 9.	Elemental mapping of synthesized NiPd/MIL-101 and corresponding SEM image.	17
Figure 10.	Elemental mapping of synthesized CuPd/MIL-101 and corresponding SEM image.	17

Figure 11.	Elemental mapping of synthesized CoPd/MIL-101 18 and corresponding SEM image.				
Figure 12.	PXRD pattern of synthesized MIL-101 and NiPd/MIL-101.	19			
Figure 13.	PXRD pattern of synthesized MIL-101 and CuPd/MIL-101.	20			
Figure 14.	PXRD pattern of synthesized MIL-101 and CoPd/MIL-101.	20			
Figure 15.	TGA curve of synthesized MIL-101.				
Figure 16.	TGA curve of synthesized NiPd/MIL-101.	22			
Figure 17.	TGA curve of synthesized CuPd/MIL-101. 22				
Figure 18.	TGA curve of synthesized CoPd/MIL-101. 23				
Figure 19.	Comparison of catalytic conversion for cross 24 coupled product in Suzuki reaction of 4- iodoanisole and phenylboronic acid at room				

іх

temperature in water-ethanol solution.

LIST OF TABLES

Table No.	Description	Page No.
Table 1.	ICP and EDS data of the synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 nanoparticle catalysts.	18
Table 2.	Catalytic activity of NiPd/MIL-101 and CuPd/MIL-101 catalysts for Suzuki reaction	25-26

NOMENCLATURE

Å	Angstrom
⁰ / ₀	Percent
μm	Micrometer
nm	Nanometer
kV	Kilovolt
mA	Milliampere
mg	Milligram
G	Gram
mmol	Millimole
mL	Milliliter
λ	Wavelength

ACRONYMS

NPs	Nanoparticles
MOFs	Molecular Organic Frameworks
MIL	Materials from the Institite Lavoisier
TMS	Tetramethylsilane
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
EDS	Energy dispersive spectrometry
XRD	X-ray diffraction
TGA	Thermo gravimetric analysis
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
OWR	Overwhelming reduction
NMR	Nuclear Magnetic Resonance
TOF	Turnover Frequency
MOCVD	Metal-organic chemical vapour deposition

Chapter 1:

Introduction and Reaction Scheme:

1.1 Introduction:

1.1a Bimetallic Nanoparticles:

In the last few decades, scientific and industrial attention has been focused on bimetallic nanoparticles (NPs) in the field of catalysis. Heterometallic NPs composed of two or more different metals with various nanostructures such as alloys, core-shell etc have been synthesized using various synthetic approaches [1-13]. The scientific and industrial attention is due to high synergic and cooperative interactions between the individual metal components which lead to the superior catalytic performance [1-33]. Synergistic itself is defined as various parts working together to produce effective results. Synergistic interactions between metals involve a) structural tuning, b) electronic tuning as transfer or exchange of electrons between the metals and c) adsorption and stabilization of reactants and intermediates. This accounts for the enhancement in the catalytic activity of the bimetallic NP catalysts [1-25]. As the catalytic activity of any catalyst is closely related to the catalyst surface, so the appropriate modification of the surface by introducing another component or by changing the composition or morphology of different elements present in the catalyst, can lead to increased catalytic activity. First principle studies have shown that the bimetallic catalysts performance is subjected to surface electronic states, which are greatly diversified by changing geometrical parameters of the catalyst [34-36]. The addition of second metal can lead to tailor the electronic and geometrical changes and thereby increasing the catalytic performance of the catalyst. Bimetallic NPs displays unique properties that are not plausible with monometallic counterparts [1-13]. Use of bimetallic or multi metallic systems is important in the regard that it can slice down the high cost associated with many expensive metals. Moreover, the composition of different metals present in the catalyst can be optimized according to the reaction conditions.

1.1b Overview of Suzuki Reaction:

Suzuki reaction is one of the favourite reactions in organic chemistry for the synthesis of biaryls. It is classified as coupling reaction where the coupling partners are arylboronic acids and aryl halides. For this reaction, Pd based catalysts are of primary choice and they had been used in the past as active catalysts for several other coupling reactions [37-44]. The detailed mechanism for Suzuki reaction involves multi steps (Scheme 1) [81]. The first step is oxidative addition of Pd(0) to the halides to form organopalladium(II) species. In most of the cases it is the rate determining step. This species on reaction with base gives an intermediate which undergoes transmetalation to form another organopalladium species. In the final step reductive elimination occurs which leads to formation of coupled product and restores the original Pd(0) and completes the catalytic cycle. As the first step is oxidative addition, this sometimes leads to leaching and the outcome of this is that Pd remains in +2 oxidation state and not available for the catalytic cycle. This reaction can proceed through three possible mechanisms wiz homogeneous, heterogeneous and semi-heterogeneous. In homogeneous mechanism the Pd gets dispersed in the solution whereas in heterogeneous mechanism, Pd remains in Pd(0) form during the catalytic cycle. Considerable progress has been achieved by carrying out the reaction in a heterogeneous system by means of fastening the catalysts onto solid supports with nano size clusters. In case of semiheterogeneous mechanism, Pd gets leached out from the surface after first oxidative addition and follows the homogeneous mechanism thereafter. The active species Pd(0) again deposited on the nanoclusters after reductive elimination to generate coupled products. The advantage of heterogeneous catalyst is that it offers simple separation and recovery and thus there is an ease of recyclability. Pd NPs are considered heterogeneous in nature. Although Pd is considered as the

most active metal for various coupling reactions, being a noble metal, the high cost associated with Pd catalyst and its relative abundance, possess a problem. This all has ignited researcher's mind for developing a low-cost high-performing heterogeneous catalyst, free from Pd or with a low content of Pd. Alloying Pd with other metals can overcome this situation, by using the synergistic interactions between Pd and the other metal. In this regard, several reports come into sight on bimetallic catalysts, such as PdAu, PdAg, PdRu, PdCo, PdNi or PdCu as active catalysts for Suzuki reaction [41-69]. Among the number of catalysts available for Suzuki reaction, PdNi and PdCu catalysts are of particular interest. The reason for this lies behind the abundant availability and low cost associated with these metals (Ni or Cu) [47-69]. In this context, Rai et al. recently reported a class of highly active bimetallic NiPd alloy NPs as an efficient catalyst with high Ni to Pd atomic ratios for Suzuki reaction, where significant Ni to Pd interactions contribute in the observed high catalytic activity. Various NiPd bimetallic alloy NP catalysts were synthesized with different molar ratios having low Pd content. Ni to Pd interactions was found to be highest when NiPd were used in the ratio of 99:1. NiPd bimetallic NPs were also found to be active for other coupling reactions wiz Heck and Sonogashira reactions [52, 53].



Scheme 1. Schematic representation of different mechanisms exhibited for Suzuki reaction (Reproduced with permission).

1.1c Problems associated with nanoparticles synthesis:

NPs aggregation is one of the common problems encountered during NPs synthesis. Due to high surface energy and large surface area, their thermodynamic stability is decreased [70-72]. To produce stable NPs, it is necessary to terminate the growth of NPs during their synthesis and for this; various methodologies have been devised [73-75]. One of the popularly used methods used is by immobilizing active catalyst on a support, because aggregation of NPs has been retarded by immobilizing them on a support during their synthesis [14-25, 37-40, 54-69]. The properties of supported NPs is dependent on its morphological environment (size and shape), metal dispersion and electronic properties of the metals. In this context, a huge number of porous materials such as metals organic frameworks (MOFs) [14-25, 37-40], metal oxides [54-59], graphene [60-63], polymers [64-66] and carbon [67-69], have been designed and used as a supports for metal NPs immobilization. The fusion of porous materials and NPs opens up

a new era of research in the direction of efficient green catalysis having high conversions, selectivity and yields. Using of supports not only prevents aggregation, but it also suppresses the catalyst poisoning and leaching problem associated with NPs.

1.1d MOFs as a support:

Because of the excellent physical and chemical properties exhibited by MOFs, MOFs are of particular interest among the various supports used for immobilizing the metal NPs. MOFs are the crystalline nanoporous coordination polymers; build from multidendate organic ligands, using metal ions as templates. Due to diverse number of organic ligands available including several metal ions and guest molecules, MOFs are user and reaction friendly. They exhibit exceptional physical properties such as high surface area, well-defined pore structures and low density. Moreover, the chemical properties of MOFs are flexible and can be tuned as per requirement [14-25, 76]. Due to chemical tailoring of inner surface of channels and cavities present in them, MOFs are very promising for various applications including size selective catalysis (Figure 1) [14-25]. Various metal NPs can be immobilized on the MOFs or can be encapsulated within the pores of the MOF. Two approaches have been used in the past decades for the immobilization of NPs in MOFs. In "ship-in-a bottle" approach, the introduction of metal precursors into the pre-synthesized MOF matrix is carried out and subsequent reduction or decomposition of the precursors was done to yield metal NPs. The second approach is the "bottle-around-ship" or "template synthesis" which involves the assembly of MOF precursors around pre-synthesized metal NPs.



Figure 1. Figure illustrating using MOF as a support to NPs and some examples of their diverse catalytic applications.

<u>1.1e MIL-101 (MIL: Materials from the Institute</u> Lavoisier):

MIL-101 is an example of MOF that is known for its high pore volume and a large surface area. It has large pore diameter having hexagonal and pentagonal windows of large aperture. Both hydrophilic and hydrophobic moieties and networks are present for the selective adsorption of substrates and intermediates (Figure 2) [78, 80]. Moreover, it shows high stability such as high thermal stability and it is chemically resistive to most of the solvents and reaction conditions. Due to its exceptional physical and chemical properties, it is one of the primary choices to be used as support for immobilizing metal NPs.



Figure 2. Structure of MIL-101 having pentagonal and hexagonal windows (Reprinted with permission from open access of journal *Membranes* **2013**, *3*, 331-353).

1.1f Overview of previous work:

In recent years, the main focus was on the development of catalytic systems based on monometallic NPs immobilized on various MOFs for Suzuki reaction [37-40]. In this context, Yuan *et al.* reported the Pd NPs supported on MIL-101 framework as highly active catalyst for Suzuki and Ulmann coupling reactions in aqueous media [37]. This work represented the first MOF supported NP catalytic system for coupling reactions. Water mediated coupling reaction of aryl chlorides over a heterogeneous Pd catalyst was demonstrated using MIL-101 as a support. Similarly, Puthiaraj *et al.* developed Pd NPs immobilized on MIL-125 framework for coupling of aryl chlorides and arylboronic acids for Suzuki reaction [38]. Good yields were obtained in case of *para-* and *meta-* substituted substrates whereas, slightly lower yields in case of *ortho-* substituted substrates. The catalyst was found to be free from the necessity of external additives, inert atmosphere or highly toxic organic solvents. Shang *et al.* reported Pd NPs encapsulated

inside the pores of MIL-101 for Suzuki and Heck cross coupling reactions [40]. Duly dispersed Pd NPs were encapsulated inside the cages of MIL-101 through a double solvent method followed with subsequent reduction by NaBH₄. The as prepared catalyst was recyclable for at least five consecutive cycles. Despite of these reports on monometallic NPs immobilized on MOFs, there are very few reports available for MOF immobilized bimetallic NPs [14, 19-21]. Chen et al. reported a number of bimetallic NPs encapsulated in MIL-101 framework as efficient catalysts for hydrolytic dehydrogenation of ammonia borane [14]. A seed-mediated synthetic approach was used to reduce the non-noble metal precursors (Ni²⁺, Co²⁺, Fe²⁺, etc.) using the trace amount of noble metal precursors (Ag²⁺, Pd²⁺, Pt²⁺, Au³⁺, etc.) at room temperature. The catalytic activity displayed by these bimetallic systems is higher than monometallic counterparts whereas, the catalytic activity of AgNi/MIL-101 was found to be highest for dehydrogenation of ammonia borane. Hermannsdorfer et al. reported PdNi NPs encapsulated within the pores of MIL-101 framework for cyclohexanone oxidation [19]. MOCVD (metal-organic chemical vapour deposition) method was used to load the metal organic precursors into the porous structure of MIL-101. The reduction of loaded precursors was carried out by using hydrogen as reducing agent. The as synthesized catalyst displayed superior catalytic activity for oxidation of cyclohexanone. Jiang et al. studied PdAg NPs stabilized by MIL-101 for one-pot cascade catalytic reaction, utilizing the host-guest cooperation and bimetallic synergy of Pd and Ag [20]. Lewis acidity offered by MIL-101 and bimetallic synergy between Pd and Ag attributed to the observed high catalytic activity. Pd offered high hydrogenation activity and Ag improves the selectivity. One pot multistep conversion of nitroarene to secondary arylamine had been explored. Recently, Trivedi et al. reported MIL-101 supported bimetallic PdCu NPs as an efficient catalyst for chromium reduction and conversion of carbon dioxide at room temperature [21]. The catalytic activity of these PdCu/MIL-101 was found to be 3 to 5 times superior than PdCu NPs. Being heterogeneous in nature, PdCu/MIL-

101 catalyst was found to be recyclable and easy to handle. However in spite of these reports, till present, there are no reports for MIL-101 stabilized bimetallic NPs for Suzuki reaction.

1.1g Theme of our work:

Keeping in view the superior catalytic performance of bimetallic NPs stabilized on MOFs, we figured to synthesize bimetallic NPs (NiPd, CuPd and CoPd) immobilized on MIL-101 framework and to explore their catalytic performance for Suzuki reaction. Synergistic interactions between Pd and the other metal along with MIL-101 support can lead to higher catalytic activity for Suzuki reaction. Therefore, herein we synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 catalysts, and investigated their catalytic activity for Suzuki reaction with a wide range of aryl halides substrates having electron donating and electron withdrawing substituents under moderate reaction conditions in water-ethanol solution. With the CuPd/MIL-101 and NiPd/MIL-101 catalyst, a significant enhancement in the catalytic activity was observed whereas CoPd/MIL-101 catalyst was very poorly active. Catalytic efficiency of the synthesized CuPd/MIL-101 was found to be highest followed by NiPd/MIL-101, whereas CoPd/MIL-101 was found to be poorly active for Suzuki reaction.

1.2 Reaction Scheme:



Scheme 2. Schematic representation of bimetallic NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 catalysts for Suzuki reaction.

Chapter 2:

Experimental Section:

2.1 General:

High-purity chemicals were used for the experiments. NMR spectra were recorded on a BrukerAvance 400 spectrometer. Chemical shifts are referenced to internal solvent resonances and reported relative to tetramethylsilane (TMS). Transmission electron microscopic (TEM) images were obtained with a JEM-1400 microscope (JEOL) operated at 100-120 kV. Scanning electron microscopy (SEM) images and Energy dispersive spectrometry (EDS) analysis were performed on Carl Zeiss supra 55 and field-emission JSM-7001F (JEOL) operated at 15 kV. Powder X-ray diffraction (XRD) measurements were performed for the dried samples of catalyst on a Shimadzu XRD-6000 Labx diffractometer at 40 kV and 30 mA using Cu K α radiation (λ = 1.5418 Å). Thermo gravimetric analysis (TGA) was performed on Mettler Toledo TGA/DSC analyzer. The apparatus was loaded with *ca*. 4 mg of sample under the flow of N₂ gas at a heating rate of 5 °C/min from room temperature to 800 °C. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis was performed using ARCOS, simultaneous ICP spectrometer.

2.2 Synthesis of MIL-101:

Synthesis of MIL-101 was carried out according to reported procedure with some modifications [76]. In an autoclave, chromium nitrate nonahydrate (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol), and deionized water (20 mL) were mixed and extensively sonicated to obtain a dark blue colored suspension. The resulting suspension was placed in a Teflon-lined autoclave and heated in an oven at 218 °C for 18 h. After cooling the suspension to room temperature, the MIL-101 solids were separated from water by centrifugation (5,000 rpm \times 2, for 10 min) and washed twice with suitable amount of water, methanol and acetone respectively. The green colored suspension of MIL-101 in acetone was further centrifuged and redispersed in N,N-dimethylformamide (20 mL). Suspension was sonicated for 10 min and then kept at 70 °C in an oven for 12 h. The resulting solids were separated by centrifugation, washed twice with methanol and acetone respectively, dried at 75 °C overnight and then under vacuum at 100 °C for 2 days.

2.3 Synthesis of NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 catalysts:

For the synthesis of MPd/MIL-101 (M = Ni, Cu and Co) catalysts, typically 200 mg of dehydrated MIL-101 was suspended in 40 mL of dry *n*-hexane and the mixture was sonicated for about 20 min until it became homogeneous. After stirring for a while, 0.36 mL of aqueous solution containing potassium tetrachloropalladate(II) and respective metal salt solution (NiCl₂·6H₂O, CuCl₂·3H₂O and CoCl₂·6H₂O) in 5:95 molar ratio, was added dropwise over a period of 20 min with constant vigorous stirring. The resulting solution was continuously stirred for 3.5 h. Solid $M^{2+}Pd^{2+}/MIL-101$ obtained was isolated from the supernatant by decanting the solution. The solids were dried at room temperature and then at 30 °C under vacuum for 1 h. The molar contents of M²⁺Pd²⁺ added to 200 mg MIL-101 powder were kept constant to 0.068 mmol. The reduction of the $M^{2+}Pd^{2+}/MIL-101$ was carried out using an overwhelming reduction (OWR) approach where a freshly prepared 0.6 M aqueous NaBH₄ solution (5 mL) was added to the suspension of the $M^{2+}Pd^{2+}/MIL-101$ in hexane with vigorous stirring. The synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 was collected by centrifugation and dried at 100 °C under vacuum prior to use for catalytic reaction. All monometallic analogues of the previously synthesized catalysts (Ni/MIL-101, Co/MIL-101, Cu/MIL-101 and Pd/MIL-101) were also prepared following the above procedure.

2.4 Procedure for catalytic Suzuki reaction:

To the reaction vessel, 10 mg of catalyst was suspended in a waterethanol solution (1:1 v/v, 20 mL). To it, arylboronic acid (1.2 mmol), aryl halide (1.0 mmol) and base (2.0 mmol) were added. The resulting suspension was stirred at room temperature (for aryl iodides) and at 50 °C (for aryl bromides) for the desired reaction time. Progress of the reaction was monitored by TLC. Upon completion, the mixture was centrifuged at 6000 rpm to separate the catalyst. The reaction mixture was extracted with dichloromethane (3 × 10 mL), and the organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The obtained cross coupled product was identified based on earlier reports. Isolated yields were reported based on the purified products obtained from the catalytic reaction. All the products were characterized by ¹H and ¹³C NMR spectroscopy.

Chapter 3:

Results and Discussion:

MIL-101 powder synthesized using hydrothermal method, was characterized using powder XRD and SEM analysis. The diffraction peak positions and relative intensities of the peaks of synthesized MIL-101, matches to those of reported patterns (Figure 3) [76]. The SEM micrograph of synthesized MIL-101 powder reveals octahedral shape of the particles (Figure 4).



Figure 3. Powder XRD pattern of synthesized MIL-101.



Figure 4. SEM image of synthesized MIL-101.

Double solvent method was used for immobilizing of NPs on MIL-101 framework. The synthesis of NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 catalysts was done by impregnation of Pd²⁺ and

Ni²⁺/Cu²⁺/Co²⁺ precursors on activated MIL-101 [77]. Typically, to a suspension of MIL-101 in *n*-hexane, an aqueous solution of the desired metal precursors was added dropwise over a period of 20 min with constant vigorous stirring. The solids obtained after impregnation of metal salts on MIL-101 were dried under vacuum, and the precursors were reduced by OWR approach using NaBH₄ as a reducing agent. In the similar fashion, monometallic Pd/MIL-101, Ni/MIL-101, Cu/MIL-101 and Co/MIL-101 were also synthesized. The synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 were characterized using various spectroscopic techniques. Powder XRD, ICP-AES, TEM, SEM, EDX and elemental mapping of the synthesized NPs supported on MIL-101 were taken to obtain their electronic and compositional information. From the SEM and TEM micrographs of the synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101, a uniform particle size (120~150 nm) of MIL-101 supports (Figures 5–7) was estimated. Due to the very high distribution of bimetallic alloy NPs throughout MIL-101 framework, their particle size cannot be estimated with complete accuracy.



Figure 5. a) TEM and b) SEM images of synthesized NiPd/MIL-101.



Figure 6. a) TEM and b) SEM images of synthesized CuPd/MIL-101.



Figure 7. a) TEM and b) SEM images of synthesized CoPd/MIL-101.

Moreover, the main problem associated with NPs, aggregation, was also not observed on the surface of MIL-101. This is further supported by the EDS (Figure 8) and elemental mapping (Figure 9-11) of synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101. EDS and elemental mapping of the synthesized catalysts, taken by dispersing the solid catalysts in methanol, showed the presence of both the metals Pd and M (M = Ni, Cu and Co) in the catalyst. The various peaks obtained in the EDS spectra corresponding to Pd and M (M = Ni, Cu and Co) have been shown in their spectrum.



Figure 8. EDS analyses of synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101.



Figure 9. Elemental mapping of synthesized NiPd/MIL-101 and corresponding SEM image.



Figure 10. Elemental mapping of synthesized CuPd/MIL-101 and corresponding SEM image.



Figure 11. Elemental mapping of synthesized CoPd/MIL-101 and corresponding SEM image.

EDS analysis showed that the theoretical relative ratios of Pd and M (M = Ni, Cu and Co) used in the synthesis of NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 (95:5) was in good agreement with the molar ratios of the respective precursors used. This is further supported by the ICP-AES analysis of the synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101. The Pd to M (M = Ni, Cu and Co) atomic ratio in the synthesized catalysts corresponds well with the proposed compositions (Table 1).

Table 1. ICP and EDS data of the synthesized NiPd/MIL-101,CuPd/MIL-101 and CoPd/MIL-101 catalysts.

Entry	Catalysts	Theoretical Pd Molar ratio	EDS Data	ICP-AES Data
1	NiPd/MIL-101	5	4.5	5.8
2	CuPd/MIL-101	5	4.7	5.4
3	CoPd/MIL-101	5	4.9	5.2

To further characterize the catalyst powder XRD was taken for the synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 catalysts. In the powder XRD pattern of the synthesized NiPd/MIL- 101, no peaks were detected for metal NPs (Figure 12). Moreover, reduction in the intensity of diffraction peaks below 10°, was observed in the PXRD pattern. The MIL-101 diffractions get broadened after NPs immobilization. The reduction in intensities of diffraction peaks and the broadening of MIL-101 diffractions after NPs incorporation was described by partial damage of MIL-101 structure and due to metal infiltration into the pores of MIL-101 [19, 78]. PXRD pattern of CuPd/MIL-101 (Figure 13) and CoPd/MIL-101 (Figure 14) were analogues to PXRD pattern of NiPd/MIL-101. Analogously, reduction in diffraction intensities and broadening of MIL-101 diffractions was observed. Moreover, PXRD pattern of synthesized catalysts indicates alloy formation with no segregation of either atom as no individual peaks for Pd, Ni, Cu or Co was detected.



Figure 12. PXRD pattern of synthesized MIL-101 and NiPd/MIL-101.



Figure 13. PXRD pattern of synthesized MIL-101 and CuPd/MIL-101.



Figure 14. PXRD pattern of synthesized MIL-101 and CoPd/MIL-101.

Thermo gravimetric analysis (TGA) curves of synthesized MIL-101, NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 were obtained by heating the samples in N₂ atmosphere at a rate of 5 °C/min. TGA curve of MIL-101 (Figure 15) exhibited four step weight loss in the 25-200 °C (~ 10 wt%), 210-350 °C (~ 60 wt%), 360-600 °C (~ 5 wt%) and 610-800 °C(~ 6 wt%). These four steps of weight loss corresponds to a) the loss of water molecules, b) the loss of hydroxylic groups, c) the degradation of the dicarboxylate linkers, and d) the fusion and decomposition of chromium(III) oxide cluster respectively [76].



Figure 15. TGA curve of synthesized MIL-101.

TGA patterns for NiPd/MIL-101 (Figure 16), CuPd/MIL-101 (Figure 17) and CoPd/MIL-101 (Figure 18) showed analogues pattern to that of MIL-101 framework, suggesting the integrity of framework remains intact. Moreover, the stability of the MIL-101 was also enhanced after immobilization of NPs as the second step of weight loss increases from ~350 °C to 400 °C and the weight loss is also ~40% during this step. Thus, immobilizing NPs on MIL-101 framework leads to increase in its thermal stability.



Figure 16. TGA curve of synthesized NiPd/MIL-101.



Figure 17. TGA curve of synthesized CuPd/MIL-101.



Figure 18. TGA curve of synthesized CoPd/MIL-101.

Catalytic activity of synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 catalysts was investigated for the Suzuki reaction. Phenylboronic acid and 4-iodoanisole were taken as a model substrate and the reaction was performed in water-ethanol solution at room temperature. A significant enhancement in the catalytic activity of the NiPd/MIL-101 and CuPd/MIL-101 catalyst was observed in comparison of CoPd/MIL-101 catalyst (Figure 19). Due to the synergic interactions between Pd and other metal (Ni or Cu), which facilitated the highly active catalyst system, a great enhancement in the catalytic activity of NiPd/MIL-101 and CuPd/MIL-101 catalysts was observed. The alloy components of these bimetallic NPs facilitate the formation of Pd-M (M = Ni, Cu) bonds which tuned the electronic charge transfer, resulted in a highly negatively charged Pd centre, a favorable site for facile oxidative addition of aryl halides [52, 53, 55]. The higher catalytic activity observed in case of CuPd/MIL-101 catalyst was presumably due to electronic charge transfer in the valance shell of Pd,

which makes Pd more electron rich centre and enhanced the catalytic activity of the catalyst [52, 53, 79].



Figure 19. Comparison of catalytic conversion for cross coupled product in Suzuki reaction of 4-iodoanisole and phenylboronic acid at room temperature in water-ethanol solution.

With the CuPd/MIL-101 and NiPd/MIL-101 catalyst, a significant enhancement in the catalytic activity was observed whereas CoPd/MIL-101 catalyst was very poorly active. Catalytic efficiency of the synthesized CuPd/MIL-101 was found to be highest followed by NiPd/MIL-101, whereas CoPd/MIL-101 was found to be poorly active for Suzuki reaction. Notably, with monometallic Pd/MIL-101, 94% conversion to the cross coupled was obtained (Figure 19) whereas, Ni/MIL-101, Cu/MIL-101 and Co/MIL-101 were inactive for the Suzuki reaction. Moreover, a remarkable impact on the enhancement of the catalytic reaction was shown by MIL-101. An enhancement of *ca.* 20% in TOF (h^{-1}) values with the supported NiPd/MIL-101 bimetallic alloy NPs in comparison to the earlier reported NiPd NPs under analogous reaction conditions [52, 53]. This can be described as due to high dispersity of NPs on MIL-101 framework and thus preventing agglomeration of NPs. Catalytic activity of synthesized NiPd/MIL-101, CuPd/MIL-101 and CoPd/MIL-101 towards Suzuki reaction was explored under the optimized reaction conditions in water-ethanol (1:1, v/v) at room temperature or ~50 °C (Table 2) with a wide range of substituted aryl halides (iodo and bromo) substituents and arylboronic acids [52,53]. From the results obtained with catalytic Suzuki reaction, we can conclude that CuPd/MIL-101 catalyst performed significantly well for a wide range of substituted aryl bromides/iodides having electron donating (Table 2, entries 1-2, 5, 11) and electron withdrawing (Table 2, entries 6-7 and 9-10) substituents to obtain corresponding biaryl products in good to excellent yields (65~97%). In comparison to CuPd/MIL-101, NiPd/MIL-101 catalyst also showed excellent yields with aryl halides having electron donating substituents (Table 2, entries 1-2, 5, 11), whereas poor yields were obtained with electron withdrawing substituents (Table 2, entries 6-7 and 9). In contrary to the high yields obtained with aryl iodides and aryl bromides, reaction with aryl chlorides under analogous modified reaction conditions showed poor conversion. A maximum of only 15% conversion to the cross coupled products with CuPd/MIL-101 was obtained (Table 2, entry 12) whereas, Pd-Ni/MIL-101 was found to be inactive for aryl chlorides.

R	B(OH) ₂ + X = I, E	X R'	M _{0.05} Pd _{0.95} /MIL M = Ni, Cu base, H ₂ O-C ₂ H ₅ OI rt or 50 °C	101	R'
Entry	Aryl- boronic acid	Aryl halide	Biaryl product	Con./Sel Pd-Ni/MIL-10	.(Yield) 1 Pd-Cu/MIL-101
1	B(OH) ₂	CH ₃	CH3	94/99(91)	92/99(87)
2	B(OH));	OCH3		93/99(90)	96/99(92)

Table 2. Catalytic activity of NiPd/MIL-101 and CuPd/MIL-101catalysts for Suzuki reaction.



Reaction conditions: arylboronic acid (1.2 mmol), aryl halide (1.0 mmol), NaOH (2.0 mmol), catalyst (10 mg), $H_2O-C_2H_5OH$ (1:1 v/v, 20 mL), room temperature; for aryl bromides: K_2CO_3 (2.0 mmol), 50 °C; for aryl chlorides, 80 °C. Conversion and selectivity were determined by ¹H NMR. Isolated yields of the purified products are given in the parentheses.

Chapter 4:

Conclusion and scope of future work:

4.1 Conclusion:

In summary, we synthesized highly active bimetallic NiPd/MIL-101 and CuPd/MIL-101 catalysts and investigated their catalytic activity for Suzuki reaction in water-ethanol solution for a wide range of substituted aryl halides and arylboronic acids. The catalytic activity displayed by these bimetallic MIL-101 stabilized shows high reactivity and tolerance towards various electron-donating and electronwithdrawing substituents of aryl halides and arylboronic acids. In comparison to bimetallic counterparts, monometallic Ni/MIL-101, Cu/MIL-101 and Co/MIL-101 catalysts were found to be inactive for the Suzuki reaction. Catalytic efficiency of the synthesized CuPd/MIL-101 was found to be highest followed by NiPd/MIL-101, whereas CoPd/MIL-101 was found to be poorly active for Suzuki reaction. The high catalytic activity displayed by the catalysts was attributed to the activation of the Pd center by electron charge transfer from Ni or Cu to the Pd, along with high dispersity, facilitating of the alloy NPs on MIL-101 framework and thus prevented the agglomeration of NPs.

4.2 Scope of future work:

The catalytic activity of MIL-101 stabilized bimetallic alloy NPs can be studied for various other organic reactions such as oxidation and coupling reactions. Various other multimetallic or bimetallic combinations of metals can be prepared, immobilized on different types of MOFs and their catalytic activity can be tested for various other reactions accordingly under optimized reaction conditions. Characterization data of coupling products



Biphenyl: ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 7.61$ (d, 4H, J = 8Hz), 7.45 (t, 4H, J = 8Hz), 7.36 (t, 2H, J = 8Hz), ¹³C NMR (100 MHz, CDCl₃, ppm): 141.2, 128.7, 127.2, 127.1.



4-Methoxybiphenyl: ¹**H NMR (400 MHz, CDCl₃, ppm):** δ = 7.56-7.52 (m, 4H), 7.42 (t, 2H, *J* = 8Hz), 7.30 (t, 1H, *J* = 8Hz), 6.98 (d, 2H, *J* = 8Hz), 3.86 (s, 3H), ¹³**C NMR (100 MHz, CDCl₃, ppm):** 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.



4-Methylbiphenyl: ¹**H NMR** (**400 MHz**, **CDCl**₃, **ppm**): δ = 7.71 (d, 2H, *J* = 4Hz), 7.63 (d, 2H, *J* = 8Hz), 7.55 (t, 2H, *J* = 8Hz), 7.45 (t, 1H, *J* = 4Hz), 7.37 (d, 2H, *J* = 8Hz), 2.52 (s, 3H). ¹³**C NMR** (**100 MHz**, **CDCl**₃, **ppm**): 141.1, 138.4, 137.1, 129.5, 128.7, 127.1, 127.0, 21.1.



4-Cyanobiphenyl: ¹**H NMR (400 MHz, CDCl₃, ppm):** δ = 7.74- 7.68 (m, 4H), 7.59 (d, 2H, *J* = 8Hz), 7.49 (t, 2H, *J* = 8Hz), 7.43 (t, 1H, *J* = 8Hz). ¹³**C NMR (100 MHz, CDCl₃, ppm):** 145.6, 139.1, 132.5, 129.1, 128.5, 127.6, 127.1, 118.9, 110.8.



4-Bromobiphenyl: ¹H NMR (**400** MHz, CDCl3, ppm): δ = 7.68-7.64 (m, 5H), 7.46 (t, 3H, *J* = 8Hz), 7.36 (t, 1H, *J* = 8Hz). ¹³C NMR (**100** MHz, CDCl₃, ppm): 140.7, 140.1, 129.1, 128.8, 128.5, 127.5, 127.3, 127.



3-Nitrobiphenyl: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.42 (s, 1H), 8.16, (d, 1H, *J* = 8Hz), 7.88 (d, 1H, *J* = 8Hz), 7.60-7.55 (m, 3H), 7.46 (t, 2H, *J* = 8 Hz), 7.39 (t, 1H, *J* = 8Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 148.7, 142.7, 138.6, 132.9, 129.6, 129.1, 128.5, 127.1, 121.9, 121.8.



2-Hydroxybiphenyl: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.46-7.43 (m, 4H), 7.36 (t, 1 H, *J* = 8Hz) 7.23-7.20 (m, 2H), 6.95 (t, 2H, *J* = 8Hz), 5.26 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.3, 137.1, 130.2, 129, 128.1, 127.6, 122.3, 120.8, 115.9.

Spectra of cross coupled products



Figure A1. ¹H and ¹³C NMR spectra of biphenyl.



Figure A2. ¹H and ¹³C NMR spectra of 4-methoxybiphenyl.



Figure A3. ¹H and ¹³C NMR spectra of 4-methylbiphenyl.



Figure A4. ¹H and ¹³C NMR spectra of 4-cyanobiphenyl.



Figure A5. ¹H and ¹³C NMR spectra of 4-bromobiphenyl.



Figure A6. ¹H and ¹³C NMR spectra of 3-nitrobiphenyl.



Figure A7. ¹H and ¹³C NMR spectra of 2-hydroxybiphenyl.

MOF supported nanoparticle catalytic system for Suzuki Miyaura reaction

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Abstract

A highly active, robust and stable bimetallic Pd-M (M = Cu, Ni, Co) alloy nanocatalysts, supported on MIL-101 framework, having low Pd content (M/Pd atomic ratio = 95:5) was synthesized by using double solvents method combined with a liquid-phase concentration-controlled reduction strategy¹. A comparative study of the catalytic activity of these MOF supported nanoparticles was done for Suzuki Miyaura coupling reaction at moderate reaction conditions in presence of 0.34 mol% catalyst. In contrary to monometallic counterparts, great enhancement in catalytic activity was observed with these bimetallic nanocatalysts. Among the studied bimetallic Pd-M/MIL-101 anaocatalysts, Pd-Cu/MIL-101 and Pd-Ni/MIL-101 displayed high catalytic activity for the synthesis of biaryls with a wide range of substituted aryl halides and aryl boronic acids having electron donating and electron withdrawing substituents, whereas Pd-Co/MIL-101 was found to be poorly active. In contrary to Pd-Ni alloy nanocatalysts with same Ni to Pd atomic ratio³, Pd-Ni supported on MIL-101 displayed 20% higher TOF values at same reaction conditions, due to more dispersity of nanoparticles on MIL-101 framework and thus preventing agglomeration.



Fig. a) Schematic representation and b) TOF comparison for Suzuki Miyaura reaction

References: (1) Zhu, Q. L.; Li, J.; Xu, Q. J. Am. Chem. Soc. 2013, 135, 10210-10213

(2) Rai, R. K.; Gupta, K.; Behrens, S.; Li, J.; Xu, Q.; Singh, S. K. *ChemCatChem* **2015**, 7, 1806 - 1812

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75

Figure A8. Poster Abstract.

- Jiang H. L., Xu Q. (2011), Recent progress in synergistic catalysis over heterometallic nanoparticles, J. Mater. Chem., 21, 13705-13725.
- [2] Singh A. K., Xu Q. (2013), Synergistic catalysis over bimetallic alloy nanoparticles, ChemCatChem, 5, 652-676.
- [3] Balanta A., Godard C., Claver C. (2011), Pd nanoparticles for C–C coupling reactions, Chem. Soc. Rev., 40, 4973-4985.
- [4] Aijaz A., Xu Q. (2014), Catalysis with metal nanoparticles immobilized within the pores of Metal-Organic Frameworks, J. Phys. Chem. Lett., 5, 1400-1411.
- [5] Kim C. R., Uemura T., Kitaqawa S. (2016), Inorganic nanoparticles in porous coordination polymers, Chem. Rev., DOI: 10.1039/c5cs00940e.
- [6] Wang D., Peng Q., Li Y. (2010), Nanocrystalline intermetallics and alloys, Nano Res., 3, 574-580.
- [7] Su R., Tiruvalam R., Logsdail A. J., He Q., Downing C. A., Jensen M. T., Dimitratos N., Kesavan L., Wells P. P., Bechstein R., Jensen H. H., Wendt S., Catlow C. R. A., Kiely C. J., Hutchings G. J., Besenbacher F. (2014), Designer Titaniasupported Au-Pd nanoparticles for efficient photocatalytic hydrogen production, ACS Nano, 8, 3490-3497.
- [8] Jiang H. L., Akita T., Ishida T., Haruta M., Xu Q. (2011), Synergistic catalysis of Au@Ag core-shell nanoparticles stabilized on Metal-Organic Framework, J. Am. Chem. Soc., 133, 1304-1306.
- [9] Singh S. K., Xu Q. (2009), Complete conversion of hydrous hydrazine to hydrogen at room temperature for chemical hydrogen storage, J. Am. Chem. Soc., 131, 18032-18033.
- [10] Singh S. K., Xu Q. (2010), Bimetallic Ni-Pt nanocatalysts for selective decomposition of hydrazine in aqueous solution to hydrogen at room temperature for chemical hydrogen storage, Inorg. Chem., 49, 6148-6152.

- [11] Li J., Zhu Q. L., Xu Q. (2015), Non-noble bimetallic CuCo nanoparticles encapsulated in the pores of metal-organic frameworks: synergetic catalysis in the hydrolysis of ammonia borane for hydrogen generation, Catal. Sci. Technol., 5, 525-530.
- [12] Goksu H., Ho S. F., Metin O., Korkmaz K., Garcia A. M., Gultekin M. S., Sun S. H. (2014), Tandem dehydrogenation of ammonia borane and hydrogenation of nitro/nitrile compounds catalyzed by graphene-supported NiPd alloy nanoparticles, ACS Catal., 4, 1777-1782.
- [13] Ahmed M. S., Jeon S. (2014), Highly active graphenesupported Ni_xPd_{100-x} binary alloyed catalysts for electrooxidation of ethanol in an alkaline media, ACS Catal., 4, 1830-1837.
- [14] Chen Y. Z., Liang L., Yang Q., Hong M., Xu Q., Yu S. H., Jiang H. L. (2015), A seed-mediated approach to general and mild synthesis of nonnoble metal nanoparticles stabilized by a Metal-Organic Framework for highly efficient catalysis, Mater. Horiz., 2, 606-612.
- [15] Chen Y. Z., Xu Q., Yu S. H., Jiang H. L. (2015), Tiny Pd@Co core-shell nanoparticles confined inside a Metal-Organic Framework for highly efficient catalysis, Small, 11, 71-76.
- [16] Shen K., Chen L., Long J., Zhong W., Li Y. (2015), MOFs-Templated Co@Pd core-shell NPs embedded in N2doped carbon matrix with superior hydrogenation activities, ACS Catal., 5, 5264-5271.
- [17] Çetinkaya Y., Metin O., Balci M. (2016), Reduced graphene oxide supported nickel-palladium alloy nanoparticles as a superior catalyst for the hydrogenation of alkenes and alkynes under ambient conditions, RSC Adv., 6, 28538-28542.
- [18] Dai H., Cao N., Yang L., Su J., Luo W., Cheng G. (2014), AgPd nanoparticles supported on MIL-101 as high performance

catalysts for catalytic dehydrogenation of formic acid, J. Mater. Chem. A, 2, 11060-11064.

- [19] Hermannsdçrfer J., Friedrich M., Miyajima N., Albuquerque R.
 Q., Mmel S. K., Kempe R. (2012), Ni/Pd@MIL-101: Synergistic catalysis with cavity-conform Ni/Pd nanoparticles, Angew. Chem. Int. Ed., 51, 11473-11477.
- [20] Chen Y. Z., Zhou Y. X., Wang H., Lu J., Uchida T., Xu Q., Yu S. H., Jiang H. L. (2015), Multifunctional PdAg@MIL-101 for one-pot cascade reactions: Combination of host-guest cooperation and bimetallic synergy in catalysis, ACS Catal., 5, 2062-2069.
- [21] Trivedi M., Bhaskaran, Kumar A., Singh G., Kumar A., Rath N. P. (2016), Metal-organic framework MIL-101 supported bimetallic Pd-Cu nanocrystals as efficient catalysts for chromium reduction and conversion of carbon dioxide at room temperature, New J. Chem., 40, 3109-3118.
- [22] Long J., Liu H., Wu S., Liao S., Li Y. (2013), Selective oxidation of saturated hydrocarbons using Au-Pd Alloy nanoparticles supported on Metal-Organic Frameworks, ACS Catal., 3, 647-654.
- [23] Huang Y., Zhang Y., Chen X., Wu D., Yi Z., Cao R. (2014), Bimetallic alloy nanocrystals encapsulated in ZIF-8 for synergistic catalysis of ethylene oxidation degradation, Chem. Commun., 50, 10115-10117.
- [24] Tang M., Mao S., Li M., Wei Z., Xu F., Li H., Wang Y. (2015), RuPd alloy nanoparticles supported on N^Ddoped carbon as an efficient and stable catalyst for benzoic acid hydrogenation, ACS Catal., 5, 3100-3107.
- [25] Yang Q., Xu Q., Yu S. H., Jiang H. L. (2016), Pd Nanocubes@ZIF-8: Integration of plasmon-driven photothermal conversion with a Metal-Organic Framework for efficient and selective catalysis, Angew Chem. Int. Ed., 55, 3685-3689.

- [26] Yin L. X., Liebscher J. (2007), Carbon-Carbon coupling reactions catalyzed by heterogeneous palladium catalysts, Chem. Rev., 107, 133-173.
- [27] Durand J., Teuma E., Gómez M. (2008), An overview of palladium nanocatalysts: Surface and molecular reactivity, Eur. J. Inorg. Chem., 23, 3577-3586.
- [28] Fihri A., Bouhrara M., Nekoueishahraki B., Basseta J. M., Polshettiwar V. (2011), Nanocatalysts for Suzuki crosscoupling reactions, Chem. Soc. Rev., 40, 5181-5203.
- [29] Molnar A. (2011), Efficient, selective, and recyclable palladium catalysts in carbon-carbon coupling reactions, Chem. Rev., 111, 2251-2320.
- [30] Deraedt C., Astruc D. (2014), "Homeopathic" palladium nanoparticle catalysis of cross carbon-carbon coupling reactions, Acc. Chem. Res., 47, 494-503.
- [31] Narayanan R. (2010), Recent advances in noble metal nanocatalysts for Suzuki and Heck cross-coupling reactions, Molecules, 15, 2124-2138.
- [32] Cai S., Wang D., Niu Z., Li Y. (2013), Progress in organic reactions catalyzed by bimetallic nanomaterials, Chin. J. Catal., 34, 1964-1974.
- [33] Rai R. K., Tyagi D., Gupta K., Singh S. K. (2016), Activated nanostructured bimetallic catalysts for C–C coupling reactions: recent progress, Catal. Sci. Technol., 6, 3341-3361.
- [34] Grob A. (2006), Reactivity of bimetallic systems studied from first principles, Top. Catal., 37, 29–39.
- [35] Ham H. C., Hwang G. S., Han J., Nam S. W., Lim T. H. (2010), Geometric parameter effects on ensemble contributions to catalysis: H₂O₂ formation from H₂ and O₂ on AuPd alloys. A first principles study, J. Phys. Chem. C, 114, 14922–14928.
- [36] Hansgen D. A., Vlachos D. G., Chen J. G. (2010), Using first principles to predict bimetallic catalysts for the ammonia decomposition reaction, Nat. Chem., 2, 484–489.

- [37] Yuan B., Pan Y., Li Y., Yin B., Jiang H. (2010), A highly active heterogeneous palladium catalyst for the Suzuki-Miyaura and Ullmann coupling reactions of aryl chlorides in aqueous media, Angew. Chem. Int. Ed., 49, 4054-4058.
- [38] Puthiaraj P., Ahn W. S. (2015), Highly active palladium nanoparticles immobilized on NH₂-MIL-125 as efficient and recyclable catalysts for Suzuki-Miyaura cross coupling reaction, Catal. Commun., 65, 91-95.
- [39] Pourkhosravani M., Dehghanpour S., Farzaneh F. (2016), Palladium nanoparticles supported on zirconium Metal Organic Framework as an efficient heterogeneous catalyst for the Suzuki-Miyaura coupling reaction, Catal. Lett., 146, 499-508.
- [40] Shang N., Gao S., Zhou X., Feng C., Wang Z., Wang C. (2014), Palladium nanoparticles encapsulated inside the pores of a metal-organic framework as a highly active catalyst for carbon-carbon cross-coupling, RSC Adv., 4, 54487-54493.
- [41] Song H. M., Moosa B. A., Khashab N. M. (2012), Waterdispersable hybrid Au-Pd nanoparticles as catalysts in ethanol oxidation, aqueous phase Suzuki-Miyaura and Heck reactions, J. Mater. Chem., 22, 15953-15959.
- [42] Fang P. P., Jutand A., Tian Z. Q., Amatore C. (2011), Au-Pd core-shell nanoparticles catalyze Suzuki-Miyaura reactions in water through Pd leaching, Angew. Chem. Int. Ed., 50, 12184-12188.
- [43] Wang F., Li C., Chen H., Jiang R., Sun L. D., Li Q., Wang J., Yu J. C., Yan C. H. (2013), Plasmonic harvesting of light energy for Suzuki coupling reactions, J. Am. Chem. Soc., 135, 5588-5601.
- [44] Chen M., Zhang Z., Li L., Liu Y., Wang W., Gao J. (2014), Fast synthesis of Ag-Pd@reduced graphene oxide bimetallic nanoparticles and their applications as carbon-carbon coupling catalysts, RSC Adv., 4, 30914-30922.
- [45] Nasrollahzadeh M., Azarian A., Mahame M., Ehsani A. (2015), Synthesis of Au/Pd bimetallic nanoparticles and their

application in the Suzuki coupling reaction, J. Ind. Eng. Chem., 21, 746-748.

- [46] Nasrollahzadeh M., Sajadi S. M., Vartoonia A. R., Khalaj M. (2014), Journey on greener pathways: use of Euphorbia condylocarpa M. bieb as reductant and stabilizer for green synthesis of Au/Pd bimetallic nanoparticles as reusable catalysts in the Suzuki and Heck coupling reactions in water, RSC Adv., 4, 43477-43484.
- [47] Thathagar M. B., Beckers J., Rothenberg G. (2002), Coppercatalyzed Suzuki cross-coupling using mixed nanocluster catalysts, J. Am. Chem. Soc., 124, 11858-11859.
- [48] Coggan J. A., Hu N. X., Goodbrand H. B., Bender T. P., Crosscoupling reactions, US Patent, 2006/0025303A1.
- [49] Wu Y., Wang D., Zhao P., Niu Z., Peng Q., Li Y. (2011), Monodispersed Pd-Ni nanoparticles: Composition control synthesis and catalytic properties in the Miyaura-Suzuki Reaction, Inorg. Chem., 50, 2046-2048.
- [50] Xiang J., Li P., Chong H., Feng L., Fu F., Wang Z., Zhang S., Zhu M. (2014), Bimetallic Pd-Ni core-shell nanoparticles as effective catalysts for the Suzuki reaction, Nano Res., 7, 1337-1343.
- [51] Seth K., Purohit P., Chakraborti A. K. (2014), Cooperative catalysis by palladium-nickel binary nanocluster for Suzuki-Miyaura Reaction of ortho-heterocycle-tethered sterically hindered aryl bromides, Org. Lett., 16, 2334-2337.
- [52] Rai R. K., Gupta K., Behrens S., Li J., Xu Q., Singh S. K. (2015), Highly active bimetallic nickel-palladium alloy nanoparticle catalyzed Suzuki-Miyaura reactions, ChemCatChem, 7, 1806-1812.
- [53] Rai R. K., Gupta K., Tyagi D., Mahata A., Behrens S., Yang X., Xu Q., Pathak B., Singh S. K. (2016), Access to highly active Ni-Pd bimetallic nanoparticle catalysts for C-C coupling reactions, Catal. Sci. Technol., DOI: 10.1039/C6CY00037A.

- [54] Tan L., Wu X., Chen D., Liu H., Meng X., Tang F. (2013), Confining alloy or core-shell Au-Pd bimetallic nanocrystals in silica nanorattles for enhanced catalytic performance, J. Mater. Chem. A, 1, 10382-10388.
- [55] Saha J., Bhowmik K., Das I., De G. (2014), Pd-Ni alloy nanoparticle doped mesoporous SiO₂ film: the sacrificial role of Ni to resist Pd-oxidation in the C-C coupling reaction, Dalton Trans., 43, 13325-13332.
- [56] Xiao Q., Sarina S., Jaatinen E., Jia J. F., Arnold D. P., Liu H. W., Zhu H. Y. (2014), Efficient photocatalytic Suzuki crosscoupling reactions on Au-Pd alloy nanoparticles under visible light irradiation, Green Chem., 16, 4272-4285.
- [57] Zhang S., Chang C., Huang Z., Ma Y., Gao W., Li J., Qu Y. (2015), Visible-light-activated Suzuki-Miyaura coupling reactions of aryl chlorides over the multifunctional Pd/Au/porous nanorods of CeO₂ catalysts, ACS Catal., 5, 6481-6488.
- [58] Zheng Z., Li H., Liu T., Cao R. (2010), Monodisperse noble metal nanoparticles stabilized in SBA-15: Synthesis, characterization and application in Microwave assisted Suzuki-Miyaura coupling reaction, J. Catal., 270, 268-274.
- [59] Kim M. R., Choi S. H. (2009), One-step synthesis of Pd-M/ZnO (M=Ag, Cu, and Ni) catalysts by γ-irradiation and their use in hydrogenation and Suzuki reaction, J. Nanomater., DOI: 10.1155/2009/302919.
- [60] Feng Y. S., Lin X. Y., Hao J., Xu H. J. (2014), Pd-Co bimetallic nanoparticles supported on graphene as a highly active catalyst for Suzuki-Miyaura and Sonogashira crosscoupling reactions, Tetrahedron, 70, 5249-5253.
- [61] Metin O., Ho S. F., Alp C., Can H., Mankin M. N., Gultekin M. S., Chi M., Sun S. (2013), Ni/Pd core/shell nanoparticles supported on graphene as a highly active and reusable catalyst for Suzuki-Miyaura cross-coupling reaction, Nano Res., 6, 10-18.

- [62] Hu J., Wang Y., Han M., Zhou Y., Jiang X., Sun P. (2012), A facile preparation of palladium nanoparticles supported on magnetite/s-graphene and their catalytic application in Suzuki-Miyaura reaction, Catal. Sci. Technol., 2, 2332-2340.
- [63] Chen M., Zhang Z., Li L., Liu Y., Wang W., Gao J. (2014), Fast synthesis of Ag-Pd@reduced graphene oxide bimetallic nanoparticles and their applications as carbon-carbon coupling catalysts, RSC Adv., 4, 30914-30922.
- [64] Kutubi Md. S., Sato K., Wada K., Yamamoto T., Matsumura S., Kusada K., Kobayashi H., Kitagawa H., Nagaoka K. (2015), Dual lewis acidic/basic Pd_{0.5}Ru_{0.5}-Poly(N-vinyl-2-pyrrolidone) alloyed nanoparticle: outstanding catalytic activity and selectivity in Suzuki-Miyaura cross-coupling reaction, ChemCatChem, 7, 3887-3894.
- [65] Wang S. B., Zhu W., Ke J., Lin M., Zhang Y. W. (2014), Pd-Rh nanocrystals with tunable morphologies and compositions as efficient catalysts toward Suzuki cross-coupling reactions, ACS Catal., 4, 2298-2306.
- [66] Miyamura H., Choo G. C. Y., Yasukawa T., Yoo W. J., Kobayashi S. (2013), A heterogeneous layered bifunctional catalyst for the integration of aerobic oxidation and asymmetric C-C bond formation, Chem. Commun., 49, 9917-9919.
- [67] Nasrollahzadeh M., Jalehb B., Ehsani A. (2015), Preparation of carbon supported CuPd nanoparticles as novel heterogeneous catalysts for the reduction of nitroarenes and the phosphine-free Suzuki-Miyaura coupling reaction, New J. Chem., 39, 1148-1153.
- [68] Tang W., Li J., Jin X., Sun J., Huang J., Li R. (2014), Magnetically recyclable Fe@Pd/C as a highly active catalyst for Suzuki coupling reaction in aqueous solution, Catal. Commun., 43, 75-78.
- [69] Lipshutz B. H., Nihan D. M., Vinogradova E., Taft B. R., Boskovic Z. V. (2008), Copper + Nickel-in-Charcoal (Cu-

Ni/C): A Bimetallic, heterogeneous catalyst for crosscouplings, Org. Lett., 10, 4279-4282.

- [70] Mirkin C. A. (2005), The beginning of a small revolution, Small, 1, 14–16.
- [71] Schmid G., Maihack V., Lantermann F., Peschel S. (1996), Ligand-stabilized metal clusters and colloids: properties and applications, *J. Chem. Soc. Dalton Trans.*, 589-595.
- [72] Doyle A., Shaikhutdinov S. K., Jackson S. D., Freund H. J.
 (2003), Hydrogenation on metal surfaces: why are nanoparticles more active than single crystals?, Angew. Chem., 115, 5398–5401.
- [73] Dahl J. A., Maddux B. L. S., Hutchinson J. E. (2007), Toward greener nanosynthesis, Chem. Rev., 107, 2228–2269.
- [74] Toshima N. (2003), Special Issue on the IUPAC 10th International Symposium on Macromolecule-Metal Complexes: Macromol. Symposia, 204, 219–226.
- [75] Astruc D., Lu F., Aranzaes J. R. (2005), Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis, Angew. Chem. Int. Ed., 44, 7852– 7872.
- [76] 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.
- [77] Zhu Q. L., Li J., Xu Q. (2013), Immobilizing metal nanoparticles to Metal-Organic Frameworks with size and location control for optimizing catalytic performance, J. Am. Chem. Soc., 135, 10210-10213.
- [78] Ferey G., Draznieks C. M., Serre C., Millange F., Dutour J., Surble S., Margiolaki I. (2005), A chromium terephthalatebased solid with unusually large pore volumes and surface area, Science, 309, 2040-2042.

- [79] Korzec M., Bartczak P., Niemczyk A., Szade J., Kapkowski M., Zenderowska P., Balin K., Lelatko J., Polanski J. (2014), Bimetallic nano-Pd/PdO/Cu system as a highly effective catalyst for the Sonogashira reaction, J. Catal., 313, 1-8.
- [80] Jeazet H. B. T., Koschine T., Staudt C., Raetzke K., Janiak C. (2013), Correlation of gas permeability in a Metal-Organic Framework MIL-101(Cr)-polysulfone mixed-matrix membrane with free volume measurements by Positron Annihilation Lifetime Spectroscopy (PALS), Membranes, 3, 331-353.
- [81] Lorenzo M. P. (2012), Palladium nanoparticles as efficient catalysts for Suzuki cross-coupling reactions, J. Phys. Chem. Lett., 3, 167–174.