Development of Catalysts for Hydrogen Production Reactions

M.Sc. THESIS

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of

Master of Science

By

Pranjal Gupta



Department of Chemistry

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DECLARATION

I hereby certify that the work which is being presented in the report entitled "**Development** of Catalysts for Hydrogen Production" is an authentic record of my own work carried out during the period from July 20, 2022 to May 15, 2023 under the supervision of **Prof. Sanjay** Kumar Singh.

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.

Gupta

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

Signature of the supervisor

Prof. Sanjay Kumar Singh

Pranjal Gupta has successfully given his M.Sc. oral examination held on May 17, 2023.

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Signature of the supervisor

Prof. Sanjay Kumar Singh

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Dedicated to my parents and all well-wishers.....

Abstract

Due to the increase in the standard of living and the growing population, the energy consumption of the world is extensively increasing. To fulfill the energy demands, the consumption of fossil fuels is increasing, leading to CO₂ emission that has negative environmental outcomes. Hydrogen is identified as an alternate source of energy as it is efficient, clean, and renewable. But the production of hydrogen selectively at low cost, with high efficiency, and at ambient conditions are the primary challenges. This thesis is based on the development of heterogeneous catalysts for hydrogen production. Our main aim is to synthesize a catalyst that can effectively produce hydrogen from various hydrogen carriers using less base or base free under mild reaction conditions. This thesis comprises of 4 chapters. The 1st chapter describes the advantages of hydrogen as an alternate energy source and its challenges in storage and transportation. In the 2nd chapter, the literature reports on hydrogen production using various homogenous and heterogeneous catalysts are explained. In the 3rd chapter, I have discussed the experiments performed and obtained results. In the 4th and last chapter, I have concluded my work with my major findings in the form of a short summary.

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ACRONYMS

СТАВ	Cetyltrimethyl Ammonium Bromide
EDS	Energy Dispersive X-Ray Spectroscopy
GC-TCD	Gas Chromatography-Thermal Conductivity Detector
LOHCs	Liquid Organic Hydrogen Carriers
MOFs	Metal Organic Frameworks
NP's	Nanoparticles
PVP	Polyvinylpyrrolidone
PEMFCs	Proton Exchange Membrane Fuel Cells
PXRD	Powder X-Ray Diffraction
RPM	Rotation Per Minute
SEM	Scanning Electron Microscope

NOMENCLATURE

°C	Degree Celsius
g	Gram
h	Hour
mL	Millilitre
min	Minutes
mmol	Millimole
RB	Round Bottom
Ref.	Reference
Sel.	Selectivity
Т	Temperature
t	Time

Chapter 1: Introduction

1.1 General introduction

The world's energy consumption is experiencing a significant upward trend due to the escalation of living standards and population growth. The consequent increase in energy demand necessitates substantial growth in energy production capacity and a diversified and secure range of energy sources.^[1] Hydrogen, recognized as a globally accepted as a clean fuel and a primary energy source,^[2] stands out among various existing energy strategies for its capacity to generate only water as a byproduct when utilized in fuel cells. However, hydrogen poses a challenge in terms of storage and transportation due to its high energy density.



Fig 1: Pictorial representation of hydrogen generation and utilization

The scientific community has taken a keen interest in developing materials for hydrogen storage that can safely and efficiently store and release hydrogen (see Figure 1). Over the past few decades, a plethora of hydrogen storage materials, including metal hydrides, MOFs, and on-board reforming of hydrocarbons into hydrogen and other organic materials, have been developed. However, none of these have demonstrated the capability to fulfill all the necessary requirements for transport, such as gravimetric and volumetric H_2 capacities, temperature and pressure handling, by-

product recycling, cost-effectiveness, and other considerations. Hydrogen storage is widely regarded as a bottleneck problem for the progression of the hydrogen economy.^[3] In this context, liquidorganic hydrogen carriers (LOHCs) are attracting attention as organic substances in a liquid or semi-solid state that can store hydrogen and release it with the assistance of suitable catalysts.^[4]

The storage of H₂ in liquid-organic hydrogen carrier (LOHC) systems has received significant attention as compared to conventional storage systems. A suitable LOHC medium must facilitate fully reversible hydrogen storage via catalytic processes and possess desirable attributes such as thermal stability, low melting points, favourable hydrogenation thermodynamics and kinetics, large-scale availability, and compatibility with the existing fuel energy infrastructure to ensure practical applications. Several LOHCs have been reported, including methanol, formaldehyde, formic acid, ethanol, perhydro dibenzyl toluene and dibenzyl toluene, diphenyl ether and furfuryl alcohol, methylcyclohexane, toluene, naphthalene, and decalin, among others.^[5]



Fig 2: Representation of the LOHC system

Hydrazine

•

Hydrazine (N_2H_4) is a colorless, highly reactive, and toxic compound that has found numerous applications across various industries. In recent years, hydrazine has gained attention as a potential source of hydrogen gas, a clean and efficient fuel. Through controlled decomposition or reaction with catalysts, hydrazine can release hydrogen gas, which can be utilized in fuel cells or other hydrogenbased energy systems.

The decomposition of hydrazine can occur through various pathways, including thermal decomposition, catalytic decomposition, and reaction with other compounds. The decomposition reactions typically involve the breaking of N-N bonds within the hydrazine molecule, resulting in the formation of different reaction products.

N ₂ H ₄ →	$N_2 + 2H_2$	ΔG (273 K) = -1.46 eV	Path 1
3N ₂ H ₄ ►	$4\mathrm{NH}_3$ + N_2		Path 2
N ₂ H ₄ →	$4/3NH_3 + 1/3N_2$	∆G (273 K) = -1.72 eV	

Hydrazine decomposition has attracted significant research interest due to its potential applications in hydrogen production, as one of the primary decomposition products is hydrogen gas (H₂). Hydrogen is considered a clean and efficient fuel, and hydrazine offers a high hydrogen content, making it a promising candidate for hydrogen generation.

However, hydrazine decomposition is a complex process influenced by various factors, such as temperature, pressure, catalysts, reaction medium, and additives. The control of reaction conditions and catalyst selection is crucial for optimizing the decomposition efficiency, selectivity, and stability of the process.

 $NH_2NH_2 + H_2O \longrightarrow H_2NNH_3^+ + OH^-$

In the presence of the reaction medium, the concentration of $N_2H_5^+$ increases, leading to competition with the deprotonation of hydrazine and the formation of NH₃. To enhance the selectivity of hydrogen generation, a base is typically added to the reaction medium, which can increase the basicity of the catalyst's surface and inhibit the formation of basic ammonia.

Researchers have focused on developing catalysts that can enhance the decomposition rate and selectivity towards desired products, such as hydrogen.^[15-18] Different catalysts, including metals and metal nanoparticles supported on various materials, have been investigated for their catalytic activity in hydrazine decomposition.

Overall, hydrazine decomposition is a subject of significant scientific and technological interest due to its potential for hydrogen generation and its broader implications in energy, materials, and chemical industries.

However, it is important to note that hydrazine is highly toxic and poses significant health and safety risks. It is a potent irritant to the skin, eyes, and respiratory system. Proper handling, storage, and disposal procedures are essential to minimize exposure and prevent accidents.

1.2 Literature review

Dehydrogenation is a catalytic process that involves the removal of hydrogen from an organic compound. For instance, alcohols can be dehydrogenated to produce aldehydes and ketones, accompanied by the release of hydrogen.^[6] During dehydrogenation, the carbon atom undergoes a reduction in electron density, and the loss of electrons is associated with oxidation. When any alkane is subjected to heat in the presence of a suitable catalyst, it can undergo a dehydrogenation reaction, resulting in the corresponding alkene with a loss of two hydrogen atoms. Additionally, hydrogen gas is a highly valued clean fuel with considerable energy potential, particularly when produced from renewable resources. Nonetheless, hydrogen gas challenging.

In recent years, considerable research efforts have been directed towards the development of hydrogen storage materials, as handling and storing gaseous H₂ is challenging. Among the various materials explored, methanol (MeOH) has been identified as one of the most promising hydrogen carriers due to its high H₂ content (12.6 wt% H₂) and its usage in fuel cells. The dehydrogenation of MeOH is an endothermic reaction, which necessitates both dehydrogenation catalysts and large temperatures.^[7] In this regard, several heterogeneous and homogeneous catalytic systems have been explored. Methanol is inexpensive and can be produced from biomass,^[8] and as an industrial by-product, and this makes it a promising source of hydrogen. The traditional methanol-water reforming procedure creates large concentrations of CO along with hydrogen and typically needs higher temperatures (>200 °C) for hydrogen generation. The Pt catalyst in can be harmed by trace levels of CO (up to 100 ppm) (PEMFCs). This makes the use of the traditional reforming process unsuitable in portable applications like hydrogen vehicles.^[9]

$$CH_3OH + H_2O \longrightarrow 3H_2 + CO_2 \qquad \Delta G = 9.0 \text{ kJ mol}^{-1} \qquad (1)$$

The entire reforming reaction can be classified into three primary phases of straightforward reactions, denoted as reactions (2) – (4). The first stage in the dehydrogenation of methanol, is the most challenging of the three since it is an uphill reaction ($\Delta G > 0$). Reaction no. (3) and (4) are down-hill reactions ($\Delta G < 0$) making the subsequent dehydrogenation of formaldehyde and formic acid significantly smoother. Even if the subsequent stages can be catalysed with a large reaction rate at low temperatures, the uphill reaction (2) makes it difficult for the entire methanol-water reforming reaction to proceed.^[10]

$$CH_3OH \longrightarrow HCHO + H_2 \qquad \Delta G = 63.7 \text{ kJ mol}^{-1}$$
 (2)

$$HCHO + H_2O \longrightarrow HCOOH + H_2 \quad \Delta G = -21.7 \text{ kJ mol}^{-1}$$
(3)

HCOOH
$$\longrightarrow$$
 CO₂ + H₂ $\Delta G = -33.0 \text{ kJ mol}^{-1}$ (4)

Researchers recently developed some highly active as well as selective molecular catalysts to catalyse methanol-water reforming at a lower temperature (100 °C) and produce pure H_2 with only a trace of, or even completely without CO. In order to attain high activity, alkaline reagents were typically introduced to the reaction system as consumptive additives. However, the alkaline solution can be neutralized by the acidic CO₂ gas produced during the reforming of methanol. Homogeneous catalysis for acceptorless alcohol dehydrogenation into carbonyl compounds relies on active catalysts such as Ru, Ir, and Os complexes.^[11] While comprehensive reviews exist regarding the of alcohol progress homogenously-driven acceptorless dehydrogenation, they are subject to the common drawbacks associated with homogeneous catalysis, such as complex recycling and the use of additives, which limit their potential for large-scale applications.^[12]

In order to overcome the drawbacks associated with homogenous catalysis, heterogeneous catalysts of transition metals such as Pd, Pt, and Ru have been explored as efficient and active options for

dehydrogenation. Another approach involves removing the H₂ acceptor to produce both an important carbonyl compound and H₂ gas. Although acceptorless dehydrogenation reactions are less favoured thermodynamically than oxidation reactions,^[13] they offer benefits such as reducing the threat of over-oxidation to carboxylic acids. Furthermore, such reactions are significant for H₂ production from

Table	Table 1: Comparison table for the different wt % of liquid hydrogen storage system						
Sr.	Liquid	Reaction equation	wt %				
No	hydrogen						
	carriers						
1.	CH ₃ CH ₂ OH	a) $CH_3CH_2OH \longrightarrow CH_3CHO + H_2$	4.34				
		b) $CH_3CH_2OH + H_2O \longrightarrow CH_3COOH + 2H_2$	6.25				
2.	CH ₃ OH	a) $CH_3OH \longrightarrow HCHO + H_2$	6.25				
		b) $CH_3OH + H_2O \longrightarrow HCOOH + 2H_2$	8				
		c) $CH_3OH + H_2O \longrightarrow CO_2 + 3H_2$	12.5				
3.	НСНО	$HCHO + H_2O \longrightarrow CO_2 + 2H_2$	8.4				
4.	НСООН	HCOOH \rightarrow CO ₂ + H ₂	4.3				
5.	NH ₂ NH ₂	$NH_2NH_2 \rightarrow 2H_2 + N_2$	12.5				

alcohols and for H-transfer reactions.

In order to overcome the challenges associated with homogeneous catalysis, researchers have focused on the development of heterogeneous catalysts of transition metals such as Pd, Pt, and Ru, which have demonstrated high activity and efficiency for dehydrogenation.^[14] Additionally, an alternative approach involves the elimination of the hydrogen acceptor and production of both an important carbonyl compound and H₂ gas. Among the transition metals tested for dehydrogenation, Ru, Pt, Pd, Re, Ag, Au, Fe, Mn, Cu, Co, Ni, and some alloys have been identified as active catalysts, with Ru and Cu catalysts being of particular interest. While noble metals like Ru, Pd, and Pt have excellent catalytic activity, they are also expensive, and

alternative non-noble metals such as Ni, Co, Mn, Cu, and Fe have been explored due to their lower cost and demonstrated activity towards the dehydrogenation process.

Anhydrous hydrazine is explosive if we use metal catalyst so another its liquid form known as hydrazine monohydrate (H₂NNH₂.H₂O) is a safe it wt%.^[17] option and contains hydrogen 7.9 The activity of monometallic NPs (Rh, Ru, Co, Ir, Cu, Ni, Fe, Fe, and Pd) as catalysts for hydrazine decomposition has been investigated. Ni, Cu, Fe, and Pt were found to be inactive for the decomposition. However, Ir, Co, and Ru showed low selectivity toward hydrogen, whereas Rh nanoparticles exhibited a selectivity of 43.8% at 25 °C.^[18] The selectivity of the hydrazine decomposition reaction can be influenced by factors such as the presence of N₂H₅⁺, the use of a base, and the choice of catalyst. Jang et al. have demonstrated that a 2% Ir honeycomb catalyst can rapidly decompose hydrazine hydrate near ambient temperature. They have also designed a catalytic system for catalyst recovery and confirmed the material's stability. The findings suggest that Ir NPs supported on γ -Al₂O₃ could be an effective catalyst for this decomposition, and that the catalyst could be recovered and used multiple times without significant degradation.

1.3 Research gaps

The dehydrogenation has been investigated utilizing diverse catalytic system, including both homogeneous and heterogeneous types, yet there is a need for enhanced activity. The objective is to achieve more efficient hydrogen production at low temperatures using environmentally friendly solvents. However, numerous studies have identified the requirement for organic solvents or additives that are not conducive to the sustainability of the process. Therefore, there is a demand for a cost-effective catalytic system for dehydrogenation that addresses these challenges.

1.4 Objectives for the development of catalyst for the hydrogen production

High Activity: The catalyst should exhibit a high level of activity for the specific hydrogen production reaction, enabling efficient and rapid conversion of the reactants into hydrogen. This involves designing catalysts with optimized surface properties, active sites, and composition to enhance their catalytic activity.

Selectivity: The catalyst should demonstrate high selectivity towards hydrogen production, minimizing unwanted side reactions or by-products. Selectivity is crucial for achieving high purity and quality of the produced hydrogen.

Stability and Durability: The catalyst should possess excellent stability and durability under the reaction conditions, maintaining its activity over prolonged operation. This involves developing catalyst materials that are resistant to deactivation, poisoning, or structural changes caused by the reaction environment.

Low Energy Requirements: The catalyst should enable hydrogen production with low energy requirements, promoting energy efficiency in the process. Catalyst design should aim to reduce activation barriers and optimize reaction kinetics, allowing for hydrogen production at lower temperatures and pressures.

Cost-effectiveness: The catalyst synthesis should strive for costeffectiveness, utilizing readily available and affordable materials. This includes exploring alternative catalyst compositions and structures that minimize the use of expensive or rare elements, while still maintaining high activity and selectivity. **Scalability:** The catalyst synthesis should be scalable, allowing for the production of catalysts in larger quantities for industrial-scale hydrogen production. This involves considering the feasibility of the catalyst synthesis process in terms of scalability, reproducibility, and ease of manufacturing.

Compatibility: The catalyst should be compatible with the specific hydrogen production method or reactor design. This involves considering factors such as catalyst particle size, morphology, and support materials to ensure optimal interaction with reactants and efficient utilization of the catalyst.

Environmental Sustainability: The catalyst synthesis process should aim for environmental sustainability by minimizing the use of hazardous or environmentally harmful substances. This includes exploring green and sustainable synthesis methods, utilizing renewable resources, and minimizing waste generation during catalyst production.

Chapter 2:

Experimental section:

2.1 Material and instrumentation:

All reagents and solvents for the synthesis and analysis were purchased from Merck Sigma Aldrich, TCI, and used as received without further purifications. Powder X-ray diffraction (P-XRD) measurements were performed using Rigaku Smart Lab, Automated Multipurpose X-ray diffractometer at 40 KV and 30 mA (Cu α λ = 1.5418 A).

2.2 Synthesis of NiFe catalyst

In the synthesis of NiFe nanocatalyst at first 0.012 g of NiCl₂.6H₂O and 0.014 g of FeSO₄.7H₂O were dissolved in 1 mL of water to which 50 mg of cetyltrimethylammonium bromide is added with constant stirring. After 15 min aqueous solution of sodium borohydride (1 mL, 0.025 g) was added under inert conditions with continuous stirring. The content in RB is stirred to obtain a black suspension of Ni₁Fe₁ which is our desired catalyst. Similarly, Ni₃Fe₁ and Ni₁Fe₃ was prepared with same approach by taking NiCl₂.6H₂O and FeSO₄.7H₂O in the molar ratio of 3:1 and 1:3 respectively. The synthesized Ni₁Fe₁ nanocatalyst was washed with distilled water and dried in complete vacuum for characterization.^[3]

2.3 Decomposition of hydrazine monohydrate using NiFe at different reaction conditions

For decomposition of hydrazine the substrate taken is hydrazine monohydrate (2 mmol) in 50 mL two-neck RB which contains NiFe nanocatalyst in 2 mL of water. The reaction RB is then connected to dehydrogenation setup with fixed temperature and the nanocatalyst solution is stirred at 970 RPM for 10 minutes then addition of NaOH (0.5 M) took place. After confirming that the whole setup is leak-proof, 2 mmol of hydrazine monohydrate injected with the help of 500 μ L glass syringe followed by continuous monitoring of the reaction with respect to the volume of gas released over the course of time.

Chapter 3:

Results and discussion:

3.1 Characterization of Catalyst

As synthesized Ni₁Fe₁ nanocatalyst was characterized by P-XRD and FE-SEM.

Powder X-ray diffractogram of Ni_1Fe_1 peak in the 2 θ range of 42°- 45° shifts towards higher 2 θ value with the increase of Ni content in Ni-Fe nanoparticles, suggesting the presence of metallic nickel and iron in alloy form.^[17]



Fig. 3 P-XRD pattern of synthesized Ni₁Fe₁ nanocatalyst

FE-SEM was carried out to know the morphology of synthesized NiFe nanocatalyst.



Fig 4: SEM image of synthesized Ni₁Fe₁

3.2 Optimization of catalytic decomposition reaction

H ₂ NNH ₂ .H ₂ O	NiFe (5 mol%)	>
2 mmol	70°C, H ₂ O (3 mL)	-

Table 2: Effect of different NiFe molar ratios on catalytic hydrogen production from hydrazine monohydrate.

Entry	NiFe ratio	Volume of gas released (mL)	Volume of gas released (mmol)	Time (min)	n(N ₂ +H ₂)/n(N ₂ H ₄)	n(N ₂ +H ₂)/n(Catalyst)	
1	1:0	46	1.9	220	0.94	19	
2	3:1	54	2.2	190	1.10	22	
3	1:1	58	2.4	103	1.18	24	
4	1:3	44	1.8	138	0.90	18	
5	0:1	0	0	180	0	0	
Reaction conditions: Hydrous hydrazine (2 mmol), catalyst (5 mol %), water (3 mL), 70°C, air atmosphere, t (min).							



Fig 5: Effect of different NiFe molar ratios on catalytic hydrogen production from hydrazine monohydrate.

At an outset, we have screened the NiFe catalyst with varying its molar concentration as discussed in the table 2 below. Firstly, we have used only Ni nanoparticles as a catalyst and observed that only 46 mL of gas was released in 220 min (Table 2, entry 1). Moreover, varying the NiFe ratios by 3:1, 1:1, and 1:3 the evolution of gas was observed 54 mL, 58 mL and 44 mL in the 190, 103 and 138 min respectively (Table 2, entry 2-4). To check whether Fe has any significant effect in the production of gas we checked only Fe NPs as catalyst and found that Fe alone has not very prominent effect in the generation of gas (Table 2, entry 5). But when Ni and Fe molar ratio is 1:1 it shows very good results for gas production, it because Ni and Fe show synergistic effect in the catalytic reaction.

H₂NNH₂.H₂O 2 mmol

Ni₁Fe₁ (5 mol%) 70°C, Base (0.5 M), H₂O (3 mL)

Table	Table 3: Effect of different bases on the catalytic hydrogen production from hydrazine									
monoh	monohydrate.									
Entry	Base	Volume of gas released (mL)	Volume of gas released (mmol)	Time (min)	$n(N_2+H_2)/n(N_2H_4)$	$n(N_2+H_2)/n(Catalyst)$				
1	NaOH	86	3.5	335	1.75	35				
2	КОН	90	3.7	369	1.84	37				
3	3 K ^t _{OBu} 92 3.8 432 1.88 38									
Reaction air atmos	Reaction conditions: Hydrous hydrazine (2 mmol), Ni ₁ Fe ₁ (5 mol%), water (3 mL), 70°C, air atmosphere, t (min), base (0.5 M).									



Fig 6: Effect of different bases on the catalytic hydrogen production from hydrazine monohydrate.

Notably, we discovered that, the base plays an important role in the production of hydrogen and nitrogen. In the presence of a base, reaction goes via pathway 1 (as discussed above) and shows greater selectivity towards H_2 and N_2 . Without the base, there is a production of ammonia was observed. Based on the results, the reaction with bases apart from NaOH, such as KOH, and K^tOBu showed a comparable activity (Table 3, entry 1-3). $H_2NNH_2.H_2O$ $Ni_1Fe_1 (5 \text{ mol}\%)$ 1-3).

Table 4: Effect of surfactant on the catalytic hydrogen production from hydrazine monohydrate.									
Entry	Surfactant	Volume of gas released (mL)	Volume of gas released (mmol)	Time (min)	$n (N_2 + H_2) / n(N_2 H_4)$	n (N ₂ + H ₂) /n(Catalyst)			
1	Without	82	3.3	335	1.67	33			
2	PVP	100	4.1	186	2.04	41			
3	CTAB	98	4	174	2.00	40			
Reaction	on conditions	Reaction conditions: Hydrous hydrazine (2 mmol), Ni ₁ Fe ₁ (5 mol%), water (3 mL), 70°C, air							

atmosphere, NaOH (0.5 M), t min



Fig 7: Effect of surfactant on the catalytic hydrogen production from hydrazine monohydrate.

Further, we screenned different sufactants with NiFe catalyst. Surfactant plays very important role in stabilizing the nanoparticles. We used PVP and CTAB as a surfactant, the production of gas increases, as well as the reaction time decreases to half as compared to without any surfactant. Based on the results (Table 4, entries 1-3) it is concluded that the use of surfactant enhances the reaction rate also enhances the gas production.

H₂NNH₂.H₂O Ni₁Fe₁ 2 mmol 70°C, NaOH (0.5 M), H₂O (3 mL)

Table 5: Effect of catalytic loading on the catalytic hydrogen production from hydrazine monohydrate. Volume $n (N_{1} + H_{2})/n(N_{1} + H_{4})$ $n(N_{2} + H_{2})$ Ni₁Fe₁ Volume Time Entry of gas of gas (min) /n(Catalyst) released released (mL)(mmol) 1 5 335 1.67 33 82 3.3 mol% 2 7.5 92 3.8 240 38 1.88 mol% 3 10 100 4.1 178 2.04 41 mol% Reaction conditions: Hydrous hydrazine (2 mmol), Ni₁Fe₁ (5 mol%), water (2 mL), 70°C, air atmosphere, NaOH (0.5 M), t min.

Fig 8: Effect of catalytic loading on the catalytic hydrogen production from hydrazine monohydrate.

To optimize the catalyst loading we tried various mol percentages of the catalyst with respect to hydrazine monohydrate. we varied the mol percentage from 5-10 mol percentage and observed that, with an increase in the catalyst loading the gas production also increased within less time (Table 5, Fig. 8).



Fig 8: Effect of catalytic loading on the catalytic hydrogen production from hydrazine monohydrate.

 $\begin{array}{c} H_2NNH_2.H_2O \\ 2 \text{ mmol} \end{array} \qquad \begin{array}{c} Ni_1Fe_1 \ (5 \text{ mol}\%) \\ \hline 70^\circ C, \text{ NaOH} \ (0.5 \text{ M}), H_2O \ (3 \text{ mL}) \end{array}$

 Table 6: Effect of reaction atmosphere on the catalytic hydrogen production from hydrazine

 monohydrate.

Entry	Atmosphere	Volume of gas released (mL)	Volume of gas released (mmol)	Time (min)	n(N ₂ +H ₂)/n(N ₂ H ₄)	n(N ₂ +H ₂)/n(Catalyst)	
1	Air	82	3.3	335	1.67	33	
2	Argon	92	3.8	335	1.88	38	
Reaction conditions: Hydrous hydrazine (2 mmol), Ni ₁ Fe ₁ (5 mol%), water (3 mL), 70°C, NaOH							

(0.5 M), t min



Fig 9: Effect of reaction atmosphere on the catalytic hydrogen production from hydrazine monohydrate.

Notably when reaction is performed in inert atmosphere it shows slightly better results than in air it could be due to the oxidation of Ni and Fe NPs. From here (Table 6, entry 1-2) we have concluded that the decomposition of hydrazine monohydrate in inert produces more gas than in air (Table 6, Fig. 9).

H₂NNH₂.H₂O 2 mmol

 $\frac{\text{Ni}_{1}\text{Fe}_{1} \text{ (5 mol\%) (with CTAB)}}{70^{\circ}\text{C}, \text{NaOH}, \text{H}_{2}\text{O} \text{ (3 mL)}}$

Table 7: Effect of base concentration on the catalytic hydrogen production from hydrazine monohydrate.							
Entry	NaOH concentration (M)	Volume of gas released (mL)	Volume of gas released (mmol)	Time (min)	$n(N_2+H_2)/n(N_2H_4)$	n(N ₂ +H ₂)/n(Catalyst)	
1	0	72	2.9	192	1.47	29	
2	0.25	86	3.5	154	1.75	35	
3	0.50	98	4	174	2.00	40	
4	0.75	106	4.3	185	2.16	43	
5	1	124	5.1	184	2.53	51	
Reaction conditions: Hydrous hydrazine (2 mmol), Ni ₁ Fe ₁ (5 mol%), with CTAB, water (3 mL), 70°C. NaOH, air atmosphere, t min.							



Fig 10: Effect of base concentration on the catalytic hydrogen production from hydrazine monohydrate.

After getting the best base for the catalytic reaction. Further, we checked the best base concentration for this reaction. Here we observed that with the increase in base concentration, the amount of gas is also increased within less time (Table 7, Fig. 9).

H ₂ NNH ₂ .H ₂ O	Ni ₁ Fe ₁ (5 mol%)	_
2 mmol	NaOH (0.5 M), H ₂ O (3 mL)	

Table 8: Effect of temperature on the catalytic hydrogen production from hydrazine monohydrate.						
Entry	Т (°С)	Volume of gas (mL)	Volume of gas (mmol)	Time (min)	$n(N_2+H_2)/n(N_2H_4)$	$n(N_2+H_2)/n(Catalyst)$
1	30	0	0	180	0	0
2	50	50	2.1	720	1.02	20
3	70	82	3.3	335	1.67	33
4	90	108	4.4	277	2.20	44
Reaction conditions: Hydrous hydrazine (2 mmol), Ni ₁ Fe ₁ (5 mol%), water (3 mL), air atmosphere, NaOH (0.5 M), t min.						



Fig 11: Effect of temperature on the catalytic hydrogen production from hydrazine monohydrate.

Following an assessment of the aforementioned parameters in the catalytic reaction, we proceeded to conduct a temperature-dependent analysis. Our findings indicated that higher temperatures, ranging from 30-90 °C, resulted in a notable increase in reaction rate. Specifically, we observed a positive correlation between temperature and reaction speed.





Fig 12: Time course plot for production of gas under optimized reaction conditions.

3.3 Recyclability of Ni₁Fe₁ nanocatalyst



Fig 13: Long-term stability and recyclability experiment for the Ni₁Fe₁ catalyzed decomposition of hydrazine monohydrate.

Chapter 4:

Conclusion and Future plan:

Different molar ratios (1:1, 1:3 and 3:1) of NiFe catalysts have been synthesized and characterized by PXRD and FESEM analysis. Complete decomposition of hydrazine monohydrate was observed over Ni₁Fe₁ catalyst at 70°C. Also, we have checked the recyclability of Ni₁Fe₁ nanocatalyst, we found it is active to next three cycles. The evolved gas was measured by water displacement method and characterised by GC-TCD analysis. Different parameters (effect of temperature, base concentration, catalyst loading, atmosphere and surfactant) were examined.

In future, I will proceed with other bi-metallic catalyst which can effectively work in decomposition of hydrous hydrazine at lower temperature and lower base concentration or at base free conditions. Also, will examine the role of various supports for the decomposition of hydrous hydrazine with NiFe nanoparticles.

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