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Efficient Transfer Hydrogenation of 4-Nitrophenol using Ammonia Borane over Metal-Organic Framework Derived Bimetallic Nanoparticles

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Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal ions and organic linkers connected through covalent bonds. To synthesize bimetallic nanoparticles ammonia borane was used as a reducing agent was used on metal ions contained in MOF-74(Cu, Ni). Monometallic Cu and Ni nanoparticles were also synthesized from their corresponding MOF-74 materials. The nanoparticles generated through this methodology were effectively stabilized by the linker of MOF. These nanoparticles were then employed for the transfer hydrogenation of 4-nitrophenol to 4-aminophenol. Among the 5 different catalysts tested, Cu_xNi_{1-x} exhibited exceptional catalytic activity towards 4-nitrophenol reduction within 2 min, indicating a synergistic effect between copper and nickel in the bimetallic catalyst. Additionally, these catalysts demonstrated good stability and recyclability up to 5 cycles.

Keywords: 4-Nitrophenol, Metal nanoparticles, Metal-organic frameworks, Ammonia borane, Transfer hydrogenation.

INTRODUCTION

Nitrophenols are widely employed in various industrial sectors like the pharmaceutical industry, dye manufacturing, agricultural chemicals and laboratory reagents and they have a negative impact on environment of a biological system [1-4]. 4-Nitrophenol (4-NP) derivatives are widely used for the synthesis of fungicides, herbicides, pesticides, *etc*. [2,5]. Because of this, it is one of the most common pollutants in agricultural and industrial wastewater. Significantly, human nerve and blood systems can be harmed by 4-NP [6,7]. In order to avoid their adverse impact, it is necessary to transform nitrophenols into less hazardous and more practical compounds. There have been numerous techniques discovered to remove 4-NP. They are chemical and photodegradation [8], biodegradation [9], adsorption [10], microwave-assisted catalytic oxidation [11], electrocoagulation [12], electro-fenton method [13], electrochemical treatment [14], reductive methods, *etc*. [15]. Among these methods, reductive methods of 4-NP are notable and beneficial since reduction treatments would convert the nitro group of 4-NP to an amine group, resulting in 4-aminophenol (4-AP). The conversion of 4-NP to 4-AP is a significant transformation, it is a less toxic product and is employed as an intermediate in the manufacture of many medications like paracetamol and in fine chemicals and dyes [16,17].

4-Nitrophenol (4-NP) was reduced using two different methods: (i) direct hydrogenation and (ii) transfer hydrogenation. Direct hydrogenation is the process of converting various functional groups into appropriate hydrogenated products by using molecular hydrogen (H_2) as a reducing agent in the presence of suitable catalysts [18-24]. Yin *et al.* [21] developed few Ni catalysts supported on Kieselguhr, TiO_2 and Al_2O_3 for the hydrogenation of 4-NP, utilizing molecular H_2 gas as the source of hydrogen. The reaction is carried out at a controlled temperature of 110 ºC for a duration of 8 h to ensure complete conversion. Subsequently, the resulting reaction products are subjected to analyze *via* HPLC to identify the products and assess their purity. Among the catalysts tested, the Ni@Kieselguhr catalyst exhibits higher activity, due to its lower acidity compared to the others. However, this approach required a high reaction temperature and a lengthy reaction time. Similarly, Liu *et al.* [22] developed a nickel nanoparticle supported on boehmite for the reduction of nitrophenol and *p*-chloro nitrophenol using 1.5 MPa of hydrogen pressure at 100 ºC. However, but this

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reaction took 3 h for the completion of the reaction [22]. As an evident from these two examples, usually, direct hydrogenation requires high pressure and temperature and requires specialized equipment [23,24]. Inspite of that, longer reaction times (a few hours) are reported to attain full conversions. In order to overcome the limitations associated with direct hydrogenation, transfer hydrogenation has been developed to carry out the reactions at milder conditions.

Transfer hydrogenation involves the transfer of hydrogen atoms from a hydrogen source to a reducible substrate in the presence of a catalyst, resulting in the reduction of corresponding substrates [25,26]. In organic synthesis, transfer hydrogenation is commonly used for the reduction of alkynes, alkenes, nitro groups and carbonyl compounds [27]. In transfer hydrogenation reactions, different hydrogen sources have been employed, including formic acid, isopropanol, hydrazine, sodium borohydride and ammonia borane. These hydrogen sources most commonly employed for the reduction of nitro compounds. A study conducted by Ahn *et al.* [28] focused on the utilization of Pd/NH_2-UiO-66 metal-organic framework (MOF) catalyst for the conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using formic acid as hydrogen source. The reaction was carried out at 60 ºC and took 7 h to reach completion. While formic acid offers the advantages of easy handling and the avoidance of high temperature and pressure conditions, its use in transfer hydrogenation reactions is limited due to its the longer reaction times required for complete conversion. Yu *et al.* [29] also developed a catalyst Pd/CS (carbon nanospheres) for the reduction of different nitro compounds. In their study, hydrazine hydrate was utilized as a source of hydrogen. The reduction reaction was conducted at 80 ºC and required 24 h to complete the reaction. Even though it is a safer reducing agent but requires longer reaction times. In comparison to formic acid and hydrazine hydrate, $NaBH_4$ offers several advantages as a hydrogen source in transfer hydrogenation reactions. Gu & Liu [30] developed a Pd@Co-MOF catalyst for the transformation utilizing $NaBH_4$ as hydrogen source. The reaction was completed in a short time of 1.33 min at room temperature. Similarly, Ishida *et al.* [31] reported the use of an Au/PMMA catalyst for the same transformation, employing $NaBH_4$ as hydrogen source. In this case, the reaction reached completion within 10 min at room temperature.

Recently, ammonia borane (AB) has gained significant attention among researchers due to its favourable characteristics. Ammonia borane is known for its high hydrogen content, with a composition of 19.6% hydrogen by weight and is stable and can be easily handled during the reaction. Another advantageous property of AB is the presence of polarized hydrogen atoms, which can enhance reaction rates by facilitating the transfer of hydrogen during transfer hydrogenation reactions [32]. These advantageous characteristics make AB as a promising option for various applications, particularly in the field of hydrogen storage and hydrogen as source in transfer hydrogenation reactions [33,34]. Metin *et al*. [35] successfully developed a catalyst system of Ag@Pd core/shell nanoparticles assembled on reduced graphene oxide for the reduction of nitro compounds. The reaction was carried out using AB as the hydrogen source at room temperature. Remarkably, they achieved the corresponding amine products within 5 min. This study demonstrates the effectiveness of the Ag@Pd core/shell nanoparticles supported on reduced graphene oxide as a highly efficient catalyst system for the reduction of nitro compounds using AB as hydrogen source. Lang *et al*. [36] also conducted a study on CoNi alloy nanoparticles embedded on Al_2O_3 nanosheets for the hydrogenation of nitro compounds and the hydrolysis of AB. Their research yielded the desired products in a short time of 5 min. These findings suggest that AB serves as an effective transfer hydrogenating agent. The reduction of 4-NP has traditionally been investigated using a variety of metal catalysts, *e.g*. palladium [37], platinum [38], gold [39], copper and nickel. However, Cu and Ni catalysts have been of great interest because of their low-cost availability and high catalytic efficiency in more hydrogenation reactions. However, in recent years, there has been growing interest in the application of metal-organic frameworks (MOFs) [40] and their derived metal nanoparticles for catalysing the transfer hydrogenation reaction of 4-NP.

MOFs are a class of porous crystalline materials formed by the combination of metal ions or clusters, coordinated with organic ligands. A well-designed structure and high surface area with active functionalities in their pores can be advantageous for catalytic applications [41]. When these MOFs are undergoing thermal or chemical treatment, they can yield metal nanoparticles with exceptional catalytic properties [42]. In this work, selected M-MOF-74 (M = Cu, Ni) as a precursor was used for the synthesis of effective catalysts for the transformation of 4-NP. These MOFs undergo chemical reaction with ammonia borane reducing agent to afford Cu and Ni nanoparticles stabilized with linker (Cu, Ni, $Cu_{0.9}Ni_{0.1}$, $Cu_{0.5}Ni_{0.5}$ and $Cu_{0.1}Ni_{0.9}$).

EXPERIMENTAL

Nitrophenol (≥99%) was purchased from Spectro Chem, 2,5-dihydroxy terephthalic acid, >98%) purchased from Tokyo Chemical Industry. Nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$, ≥ 95%) from Merck Life Science Pvt. Ltd. Copper nitrate trihydrate ($Cu(NO_3)_2\cdot 3H_2O$, 98%) was procured from Avra Synthesis Pvt. Ltd. Ammonia borane (H_3NBH_3) was synthesized according to the previously reported method [43].

General procedure

Synthesis of Cu/Ni nanoparticles: To synthesize Cu NPs, 10 mg of Cu-MOF-74 was added to a vial containing 10 mL of water-methanol (1:1) followed by the addition of 10 mmol of ammonia borane (AB) while continuing to stir for 10 min at room temperature. After the completion of reaction, black particles were separated by centrifugation and subsequently washed with water, methanol and then dried in vacuum. A similar procedure was followed for the synthesis of Ni NPs using MOF-74 (Ni).

Synthesis of bimetallic Cu_xNi_x (x = 0.1 to 0.9) nanoparticles: The same method used to synthesize Cu NPs was applied to the synthesis of bimetallic Cu-Ni NPs, with the exception that bimetallic MOF samples were employed in place of monometallic MOF ones. In order to achieve different compositions of Ni and Cu nanoparticles, specific bimetallic MOFs corresponding to the desired compositions were employed in the synthesis process.

Transfer hydrogenation of 4-nitrophenol (4-NP) with bimetallic Cu/Ni NPs: In a 15 mL glass vial, 0.646 mmol of 4-nitrophenol (4-NP) (3.75 mL, 0.1725 mM) solution was added, followed by 3.23 mmol of ammonia borane (AB) (4NP: AB mole ratio 1:5) followed by the addition of 1.5 mg of catalysts. The reaction vial was then sealed with a cap and stirred for 2 min. Following the completion of the reaction, 10 µL of reaction mixture was taken in a cuvette and diluted with 3.5 mL of distilled water. The UV-vis spectra were recorded using the UV-2600-SHIMADZU instrument and the percentage of conversation was calculated using the formula below:

$$\text{Conversion (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i is the absorbance of 4-NP at the initial time and C_f is the absorbance of 4-NP after completion of the reaction.

RESULTS AND DISCUSSION

In this study, Cu and Ni metal ions were specifically selected for the synthesis of bimetallic MOF-74 materials, due to its flexibility in synthesizing these MOFs using various metal ions. The as-synthesized MOF-74 materials were subjected to reduction using ammonia borane, which is known to reduce both Cu^{2+} and Ni^{2+} effectively to their respective zero oxidation state in aqueous solutions. Ammonia borane can disrupt the bond between metal and linker, leading to the formation of metal nanoparticles stabilized by the linker.

Morphology studies: TEM bright field images (Fig. 1) revealed the presence of agglomerated nanoparticles with an average particle size of 27.6, 12.4 and 8.2 nm for Cu, $Cu_{0.9}Ni_{0.1}$, $Cu_{0.5}Ni_{0.5}$, respectively. The $Cu_{0.1}Ni_{0.9}$ and NiNPs were found to be amorphous in nature using powder X-ray diffraction technique [44]. The inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis revealed a Cu content of 98.8 wt.% in Cu NPs and Ni content in Ni NPs was found to be 32.8 wt.%. The bimetallic $Cu_{0.9}Ni_{0.1}$ material has a Cu content of 72.2 wt.% and Ni content of 6.3 wt.%. The ICP-OES analysis of $Cu_{0.5}Ni_{0.5}$ material revealed a Cu content of 20.2 wt.% and Ni content of 18.7 wt.% and finally, the $Cu_{0.1}Ni_{0.9}$ material was found to contain 2.8 wt.% of Cu and 32.9 wt.% of Ni. The energy dispersive X-ray analysis (EDAX) spectrum further confirmed the presence of both Cu and Ni elements in the bimetallic nanoparticles (Fig. 2).

Transfer hydrogenation of 4-NP with M-MOF-74 (M = Cu, Ni) derived nanocatalysts: The as-synthesized bimetallic metal nanoparticles were successfully employed for the transformation of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using AB hydrogen source (**Scheme-I**). In this study, the catalytic performance of M-MOF-74 (M = Cu,Ni) derived bimetallic

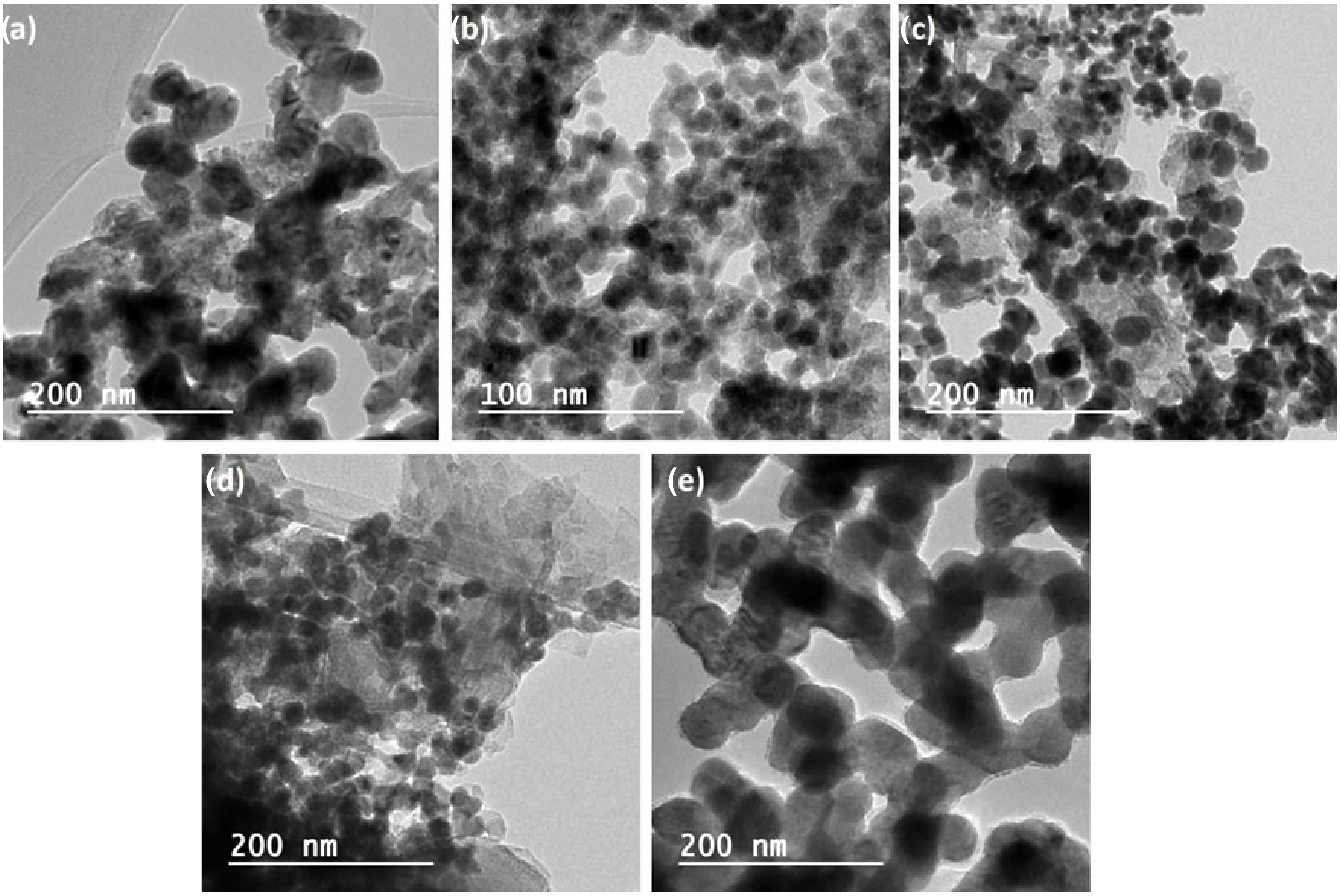


Fig 1. Transmission electron microscopy bright field image (TEM-BF) of M-MOF-74 derived metal NPs; (a) Cu NPs, (b) $Cu_{0.9}Ni_{0.1}$, (c) $Cu_{0.5}Ni_{0.5}$, (d) $Cu_{0.1}Ni_{0.9}$, (e) Ni NPs

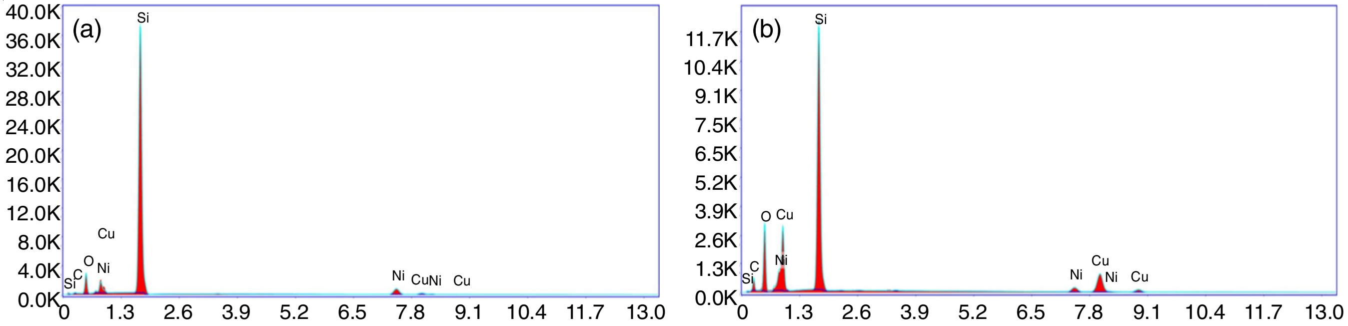
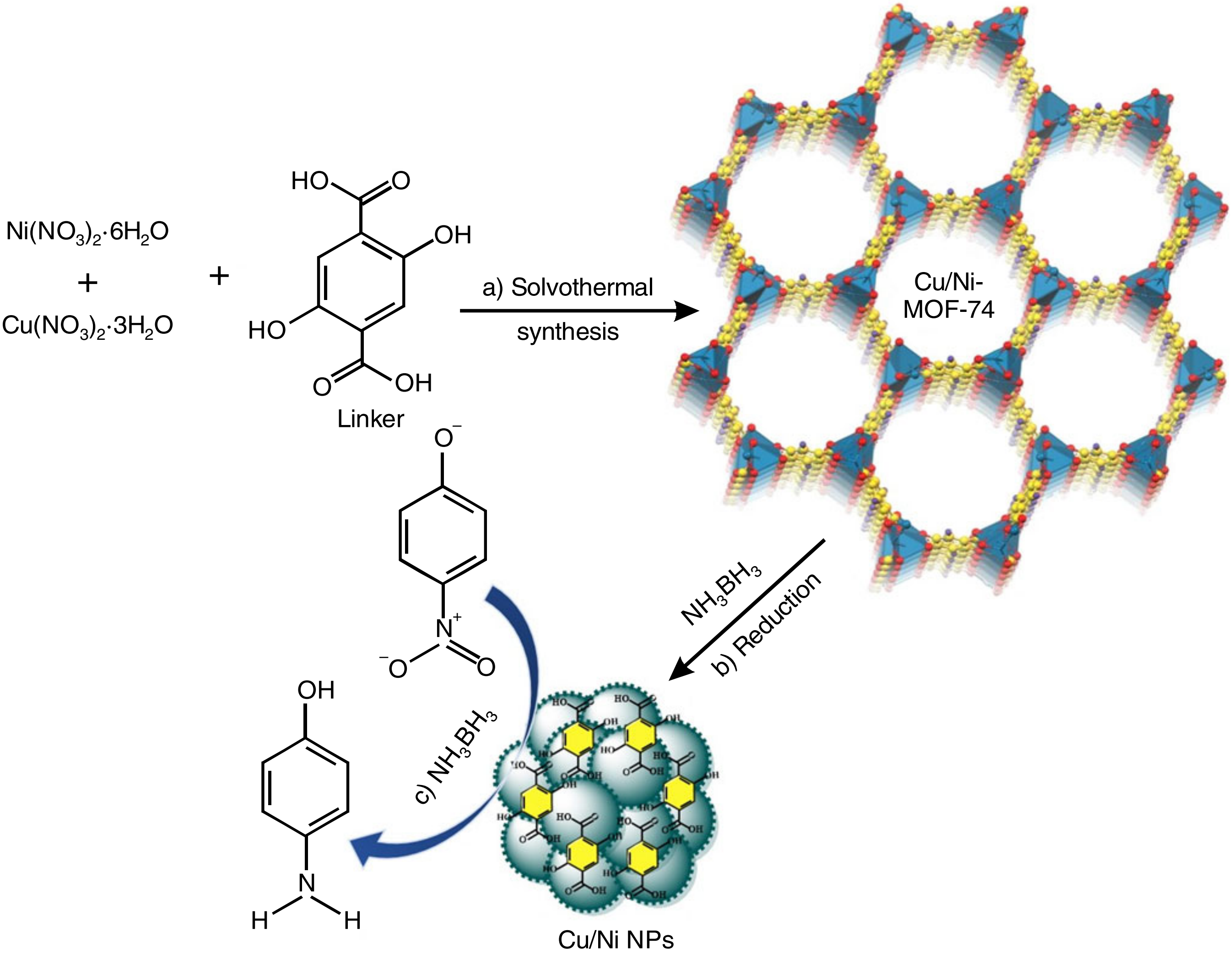
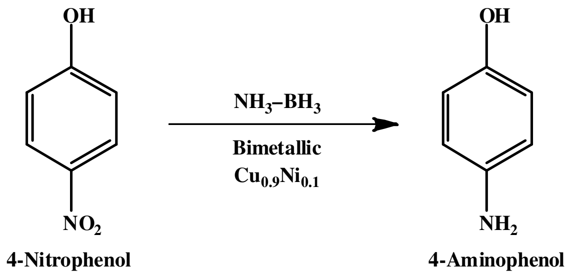


Fig. 2. Energy dispersive X-ray analysis (EDAX) spectrum of M-MOF-74 derived metal NPs; (a) $Cu_{0.5}Ni_{0.5}$ and (b) $Cu_{0.9}Ni_{0.9}$



Scheme-I: (a) Schematic representation of M-MOF-74 (Cu, Ni) solvothermal synthesis using Cu, Ni metal salts and 2,5-dihydroxy terephthalic acid organic linker, (b) MOF-74 (Cu, Ni) reduction with AB, (c) Reduction of 4-NP with Cu-Ni NPs using AB as H_2 source

nanoparticles were explored for the transformation of 4-NP to 4-AP. The reduction reaction of 4-NP usually takes place in aqueous medium, in aqueous medium 4-NP exhibit an intensive absorption peak at λ_{max} = 317 nm, which has been shifted to λ_{max} = 400 nm after the addition of AB due to the formation of phenoxide compound (Fig. 3a). This can be identified by colour change from light yellow to bright yellow. A 4-NP transfer hydrogenation reaction is performed at room temperature with a mole ratio of 1:5, AB to 4-NP, and a metal content of 1.28 wt.% relative to 4-NP. When added AB to 4-NP solution, the formation of 4-nitrophenolate anion is observed. After the addition of catalyst, the intensity of 4-nitrophenolate anion peak decreased and a new peak appeared at 296 nm corresponds to 4-AP. Also, we also conducted 4-NP transfer hydrogenation over the rest of catalysts derived from M-MOF-74 (Cu, $Cu_{0.9}Ni_{0.1}$, $Cu_{0.5}Ni_{0.5}$, $Cu_{0.1}Ni_{0.9}$ and Ni). Among five different M-MOF-74 derived bimetallic catalysts $Cu_{0.9}Ni_{0.1}$ showed best catalytic performance as shown in Fig. 3b,c and Table-1.



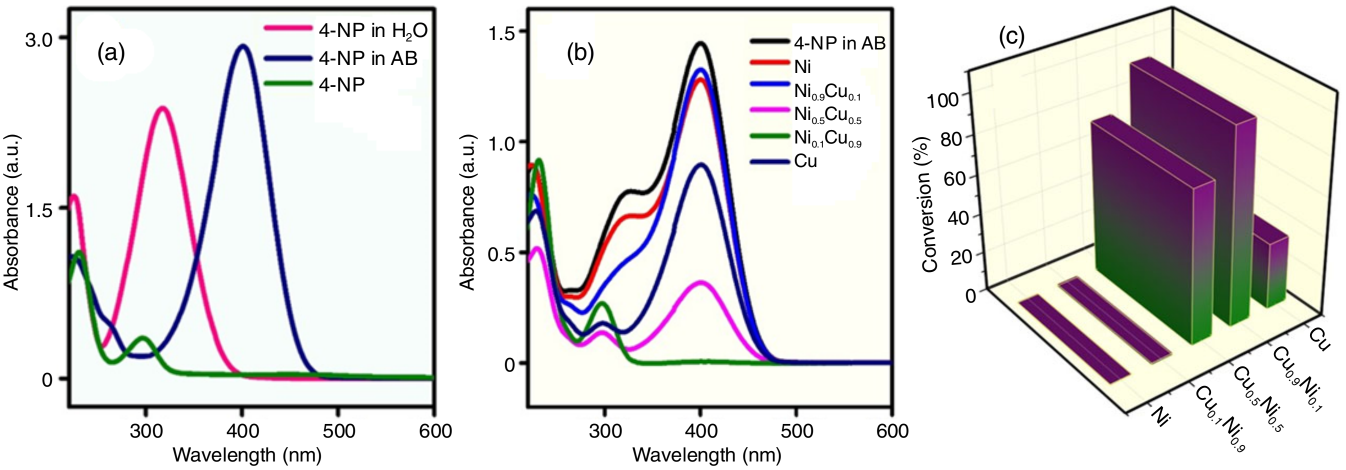


Fig. 3. (a) Reduction of 4-NP to 4-AP with $Cu_{0.9}Ni_{0.1}$ catalyst, (b) UV-vis spectra of 4-NP, 4-nitrophenolate anion and 4-AP, (c) M-MOF-74 (Cu, Ni) derived catalysts 4-NP reduction spectrum, (d) Comparison of conversation percent of 4-NP with M-MOF-74 (Cu, Ni) derived catalysts; AB = ammonia borane

TABLE-1
COMPARISON OF M-MOF-74 (Cu, Ni) DERIVED BIMETAL CATALYSTS ACTIVITY TOWARDS 4-NP REDUCTION

Catalyst	Wt.% of metal w.r.t. 4-NP	Conversion time (min)	Conversion (%)
Cu	1.28	2	34.2
$Cu_{0.9}Ni_{0.1}$	1.28	2	> 99
$Cu_{0.5}Ni_{0.5}$	1.28	2	78.2
$Cu_{0.1}Ni_{0.9}$	1.28	2	< 1
Ni	1.28	2	< 1

We further investigated the reaction kinetics over $Cu_{0.9}Ni_{0.1}$ catalyst. Since excess AB was used during the 4-NP transfer hydrogenation, the process followed a pseudo-first order kinetics. Following equation was used to calculate the rate constant [45]:

$$\ln\left(\frac{C_t}{C_o}\right) = -k_{app} \times t$$

where C_t and C_o are the concentration of 4-NP at time t and the initial concentration obtained from high absorbance peak at 400 nm, respectively and k_{app} is the apparent rate constant. The effect of different parameters like, effect of AB mole ratio, 4-NP concentration and concentration of AB was also examined. It is expected that rate of the reaction increases with increase in 4-NP to AB mole ratio from 1:1 to 1:3 (Fig. 4a). 4-NP moles maintained as 0.8266 mmol and AB amount increased from 0.8266, 1.6532 and 2.4798 mmol. The catalyst amount was maintained at 1.5 mg catalyst (1 wt.% metal content with respect to 4-NP) in all these studies. The obtained rates (k) were 3.46×10^{-1}, 9.57×10^{-2} and 4.07×10^{-2} min^{-1} corresponding to 1:3, 1:2 and 1:1 of 4-NP and AB mole ratios, respectively (Fig. 4b). This is because the availability of high hydrogen source enables faster transfer hydrogenation. Coming to 4-NP concentration effect as the concentration of 4-NP decreased from 1.725×10^{-1} to 4.312×10^{-2} mM, the 4-NP conversion also decreased (Fig. 4c). This could be ascribed to decrease in the availability of 4-NP near the active sites of $Cu_{0.9}Ni_{0.1}$catalyst with a decrease in 4-NP concentration. The observed rate constants were 3.46×10^{-1}, 2.26×10^{-1} and 6.36×10^{-2} min^{-1} for 1.725×10^{-1} mM, 8.625×10^{-2} mM and 4.312×10^{-2} mM, respectively (Fig. 4d). The catalytic performance of $Cu_{0.9}Ni_{0.1}$catalyst was also studied with different AB concentrations. As the concentration of AB increased rate of the reactionalso increased (Fig. 4e) and the rate constants are 3.46×10^{-1}, 1.42×10^{-1} and 9.87×10^{-2} min^{-1} for 3.26 mM, 1.63 mM and 8.1×10^{-1} mM, respectively (Fig. 4f). All the observed kinetic data is consistent with pseudo-first order kinetics, where the rate of 4-NP reduction is only affected by the concentration of a single substrate with remaining conditions intact.

Comparative studies: Furthermore, Table-2 provides the comparison studies of the catalytic activities between various reported catalysts and the catalysts used in present study for the transfer hydrogenation of 4-NP with AB and $NaBH_4$, which show better performance for the transfer hydrogenation of 4-NP. The remarkable aspect is that the reaction was completed with low metal content and within a short time of 2 min.

The activity of catalyst was compared by TOF calculation, where the activity of $Cu_{0.9}Ni_{0.1}$ catalyst was found to be 918.6 h^{-1}. In comparison to the Cu and Ni-based catalysts that have

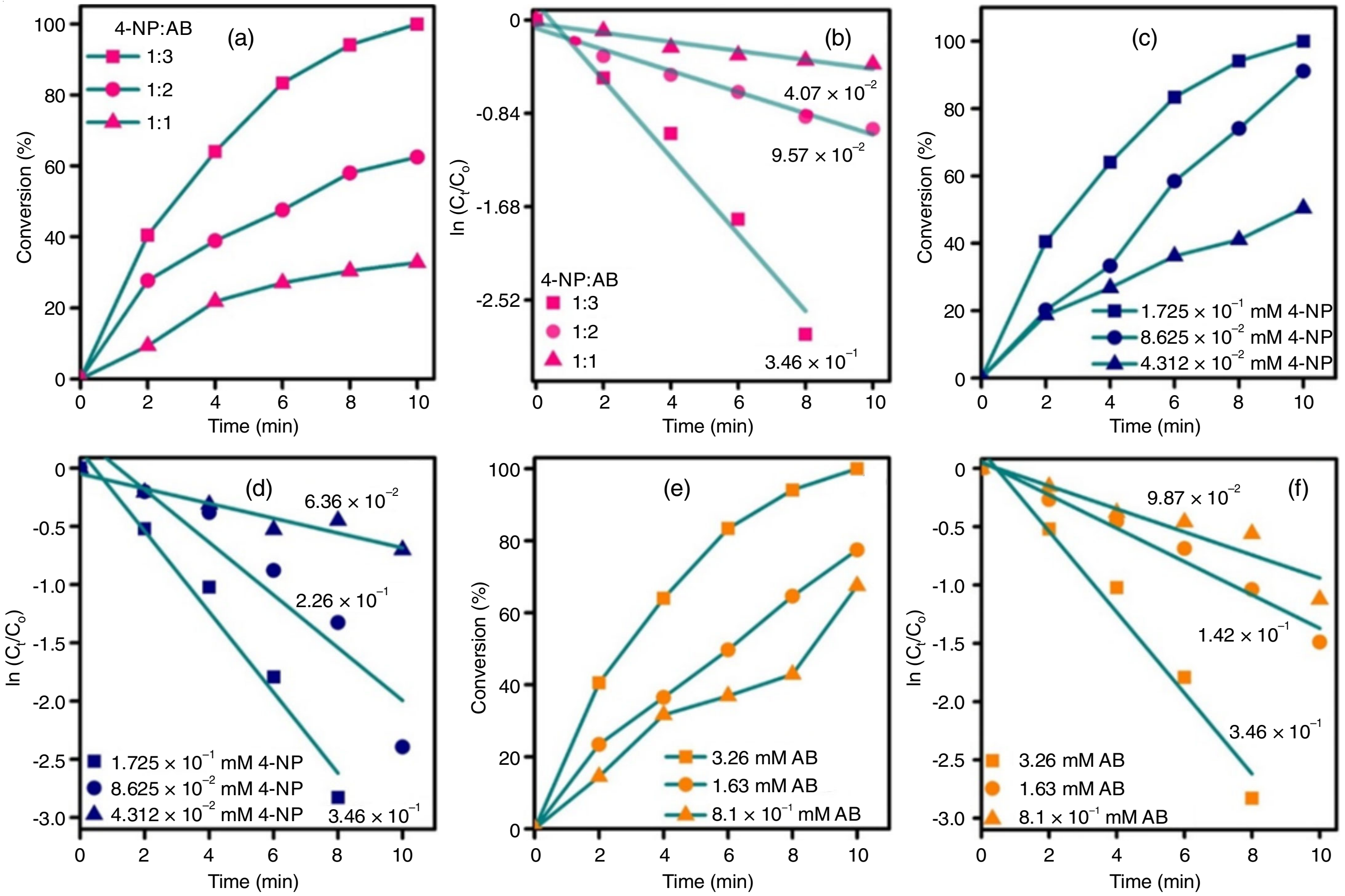


Fig. 4. (a and b) Mole ratio effect of 4-NP with AB, under reaction conditions of 0.8266 mmol of 4-NP, 0.8266, 1.6532 and 2.4798 mmol of AB, and 1.5 mg catalyst (1 wt% metal content with respect to 4-NP), (c and d) Concentration effect of 4-NP under reaction conditions of AB concentration: 3.26 mM, 4-NP concentration: 1.725×10^{-1}, 8.625×10^{-2}, and 4.312×10^{-2} mM and 1 wt% metal content with respect to 4-NP, (e and f) Concentration effect of AB with reaction conditions of 4-NP concentration 1.725×10^{-1} mM, AB concentrations- 3.26 mM, 1.63 mM, 8.1×10^{-1} and 1 wt% metal content with respect to 4-NP. All these experiments were carried out under room temperature

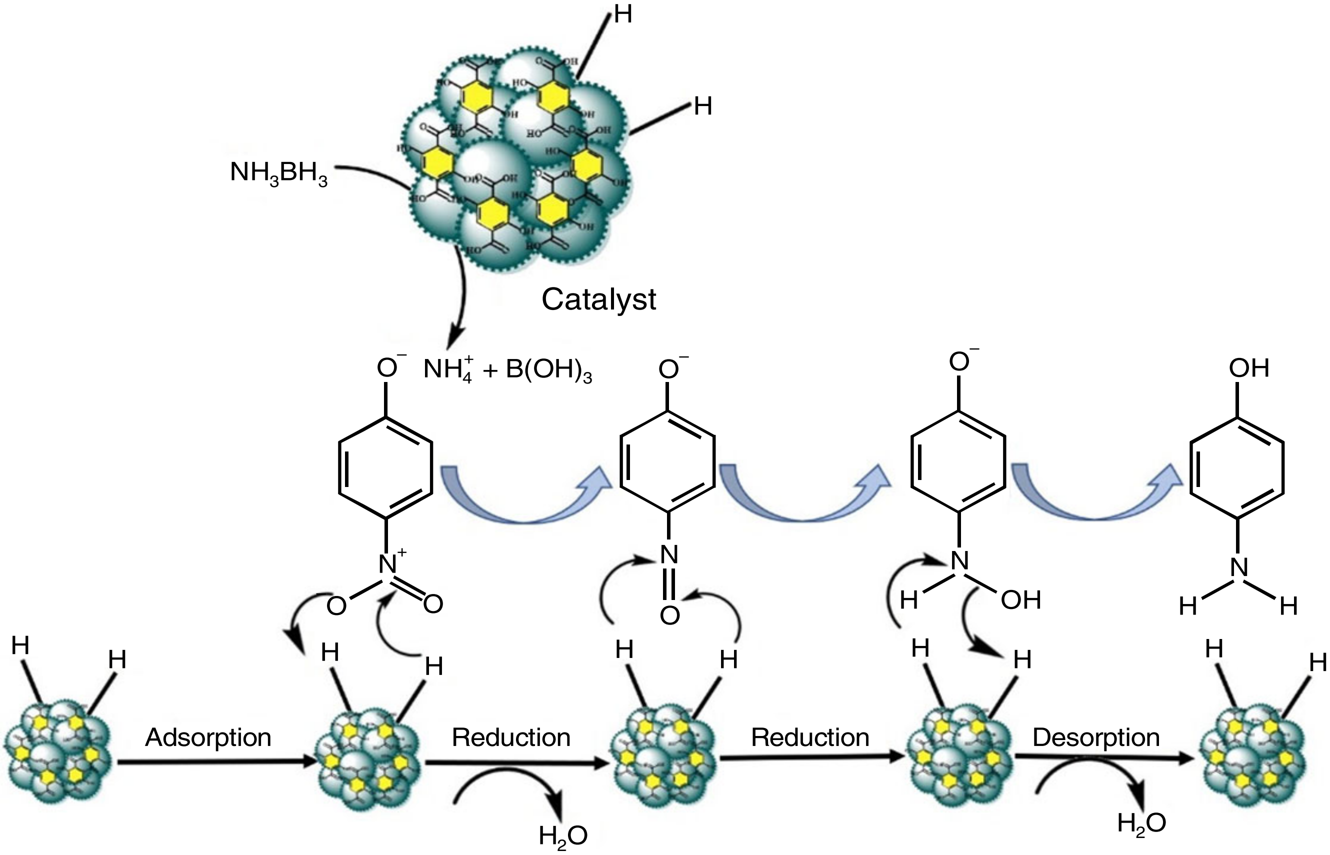
TABLE-2
COMPARISON OF 4-NP REDUCTION OVER VARIOUS Cu AND Ni CATALYST WITH NH_3BH_3 AND $NaBH_4$ HYDROGEN SOURCES

Catalyst	Reducing agent	Catalyst amount	Temp. (°C)	Solvent	Conversion (%)	Time (min)	Ref.
CuO	NH_3BH_3	5 mol%	50	MeOH	91.0	90	[50]
G-$Cu_{36}Ni_{64}$	NH_3BH_3	9.8 mM	RT	MeOH	97.0	30	[51]
CuNi@MIL-101	NH_3BH_3	3.75%	RT	MeOH/H_2O	> 99.0	4	[52]
Cu@Cu_2O	NH_3BH_3	20.0 mg	30	MeOH	97.0	5	[53]
NiO/CuOHNSs@C	$NaBH_4$	50 µL, 1 mg/mL	RT	H_2O	> 99.0	3	[54]
Cu/C-PC	$NaBH_4$	1.5 mg	RT	H_2O	> 99.0	3	[55]
CuO-RGO composite	$NaBH_4$	0.50 mg	RT	H_2O	> 99.0	–	[56]
Cu/Ag bimetallic NPs	$NaBH_4$	18 mg	RT	H_2O	> 99.0	4	[57]
Co_3O_4-CuO	$NaBH_4$	0.1 g/L (200 µL)	RT	H_2O	> 99.0	4	[58]
Ni/SG-SWCNTs	$NaBH_4$	15 mg	RT	H_2O	> 99.0	28	[59]
Cu cages	$NaBH_4$	(0.1 mL, 0.2 mg/mL)	RT	H_2O	> 99.0	6	[60]
Cu-Ni/GP	$NaBH_4$	10 mg	RT	H_2O	> 99.0	7	[46]
Cu/CS-CMM	$NaBH_4$	Cu/CS-CMM strip	RT	H_2O	75	12	[47]
$Cu_{0.9}Ni_{0.1}$	NH_3BH_3	1.5 mg	RT	H_2O	> 99.0	2	This work

been reported in the past, which of synthesized MOF-74(Cu, Ni) in the present work has one of the finest performances. Khan *et al*. [46] synthesized a Cu-Ag and Cu-Ni bimetallic nanoparticles for the reduction reaction 4-NP. This catalyst showed TOF value of 85.83 h^{-1} while, Cu/CS-CMM catalyst for 4-NP reduction have 103.3 h^{-1} TOF [47]. And, also different metal catalysts Au and Ag showed less TOF compared to the present results. These findings suggest that the synthesized catalyst [MOF-74(Cu, Ni)] is the potential candidate for the transformation of 4-NP to 4-AP.

Scheme-II illustrates the most likely mechanism for the transfer hydrogenation of 4-NP over $Cu_{0.9}Ni_{0.1}$. Over metal NPs surface, AB hydrolyses to produce MH_x [48]. As a result, 4-NP absorbs hydrogens, which reduces the nitro group to a nitroso group by releasing a water molecule. This will form hydroxylamine after being further reduced with two more hydrogens and thereafter reduced to 4-AP [49].

Furthermore, the catalyst ability was examined by separation of catalyst after each cycle by centrifugation. Only a slight decrease in activity was observed during the five cycles (Fig. 5a). In order to confirm the heterogeneous nature of the synthesized catalysis, a hot filtration test was performed by isolating $Cu_{0.9}Ni_{0.1}$ catalyst from the reaction mixture after 5 min of reaction time. The presence of catalyst resulted in 64% conversion (Fig. 5b)



Scheme-II: Proposed mechanism of 4-NP reduction over M-MOF-74 derived $Cu_{0.9}Ni_{0.1}$ catalyst with AB hydrogen source

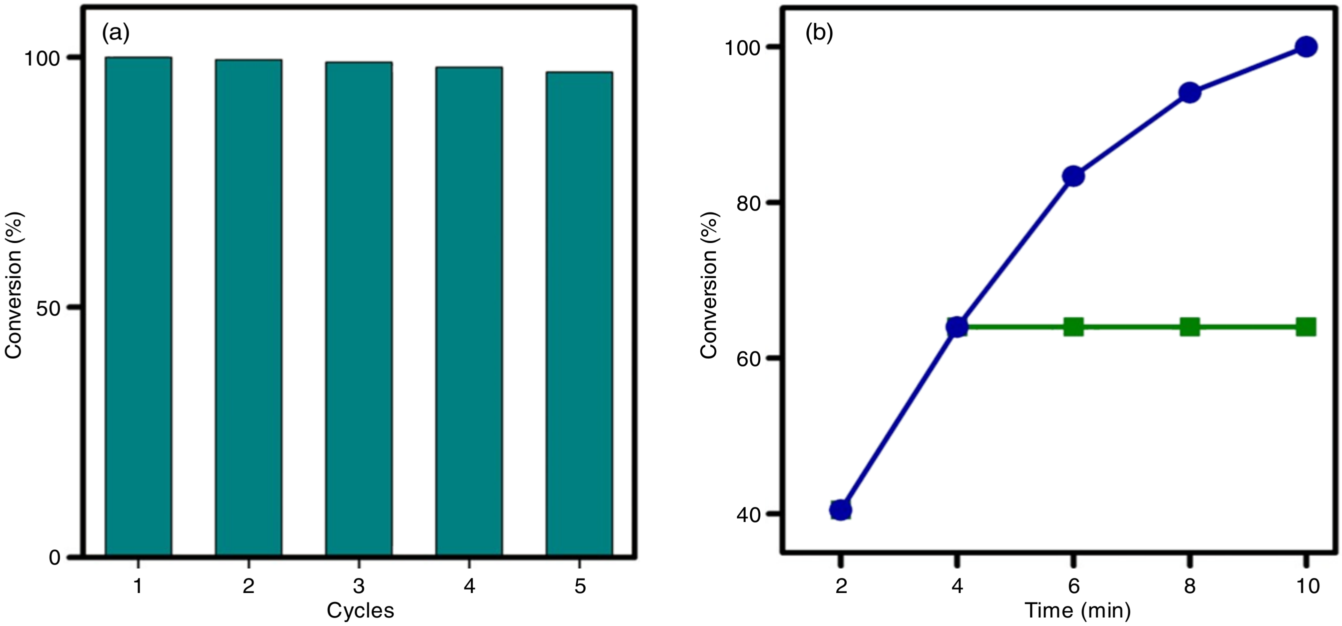


Fig. 5. (a) Recyclability of $Cu_{0.9}Ni_{0.1}$ catalyst for the reduction of 4-NP to 4-AP, (b) Hot filtration test

of 4-NP but after the removal of catalyst, the reaction does not carried indicating that the catalyst was crucial in facilitating the reaction. This result is consistent with a heterogeneous catalytic mechanism where the catalyst surface provided a site for reactant adsorption and activation.

Conclusion

In this work Cu, Ni, and their bimetallic nanoparticles were derived from MOF-74 in water-methanol (1:1). The as-synthesized nanocatalysts were tested for the transfer hydrogenation of 4-nitrophenol (4-NP). Among the 5 catalysts studied, $Cu_{0.9}Ni_{0.1}$ catalyst demonstrated the superior catalytic activity in the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using ammonia borane (AB). An attractive TOF of 918.6 h^{-1} was displayed by the catalyst. The reaction proceeded rapidly, with a reaction time of only 2 min. Kinetic analysis revealed that the reaction followed pseudo-first-order kinetics. Additionally, the $Cu_{0.9}Ni_{0.1}$ catalysts exhibited excellent recyclability up to five cycles and showed stability throughout the reaction.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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