Synthesis and characterization of magnetically recoverable, reusable and hybrid core-shell supported nickel nanocatalyst for TH of carbonyl compounds into alcohols at room temperature

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Abstract. Nickel nanoparticles stabilised by Fe_3O_4-Lignin a core-shell (Fe_3O_4-Lignin@Ni-NPs) were synthesised in water. Different methods have been used to characterise the Fe_3O_4-Lignin@Ni-NPs, including UV-Visble and fourier transform infrared (FT-IR)spectroscopy, energy dispersive X-ray (EDX) spectra, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM)and tunnelling electron microscopy. (TEM). Ni-NPs as prepared to have an average size of about 15 nm, which was consistent with the size predicted by PXRD. As the corresponding alcohol products were obtained in good to outstanding yields of up to 99% in quick reaction times of 1.25 to 3.0 h, this heterogeneous and magnetically recoverable catalyst has shown promising activity in the transfer hydrogenation of carbonyl compounds. Additionally, the catalyst could be readily recovered using an external magnet by filtration and repurposed up to six times with continued catalytic activity.

Keywords: Nickelnanoparticles, Lignin,Fe_3O_4, Nanocatalyst, Transfer hydrogenation

1 Introduction

The design and development of an efficient, stable, recoverable and reusable catalyst are the main difficulties facing the chemist. Heterogeneous catalysis has been used to address the majority of these issues. Catalysts supported by magnetic metal oxides are typically heterogeneous. It has been established that using magnetic metal oxides to support catalysts is an environmentally friendly method because these supports are non-toxic and these catalysts are magnetically recoverable and recyclable [1]. However, problems with end product contamination, leaching, aggregation, stabilization, and deactivation have been reported for catalysts with M-NPs backed by bare-metal oxides. Metal oxide nanoparticles may catalyse the oxidation and/or other reactions of organic substrates and/or products into undesirable compounds. These undesirable processes render such catalysts inert, non-recoverable, and

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eventually wasteful. Furthermore, because these supports are non-toxic and these catalysts are magnetically recoverable and recyclable, it has been determined that this technique is a sustainable one. Additionally, in large-scale manufacturing, particularly for pharmaceuticals where the impurity profile would be strictly regulated, the purification of metal-contaminated organic products would become a significant issue [1-6].

Natural biopolymers have recently come to light as excellent supports for metal nanoparticles (M-NPs) due to their abundance, safety, non-toxicity, biodegradability, biocompatibility, and environmental friendliness. The natural biopolymers agarose, alginate, arabinogalactan, cellulose, chitosan, lignin, pectin, and starch have been used as stabilisers or capping agents for M-NPs (Biopolymer@M-NPs, M = Ni, Pd, Pt, Ag, and Au) and have demonstrated exciting applications in chemistry as catalysts [7] biology [10,11], medicine [12-13], and material science [14,15]. Additionally, nickel nanoparticles (Ni-NPs) stabilised by a variety of supports [16-17] even biopolymers like agarose [18], cellulose [19], and lignin [20]. Very scant supported by have been used to stabilize but convert carbonyl molecules into alcohols [21-23].

At this moment, core-shell supported M-NPs (Core-Shell@M-NPs) catalysts have received a lot of interest. These hybrid supports or core shells made specifically from sources of inorganic and organic origin were found to be much more desirable and promising supports for M-NPs [24-26]. The organic shell serves as an auxiliary linker for the core and M-NPs in inorganic-organic@M-NPs catalysts, stabilizing metal nanoparticles and avoiding direct contact between the core and organic substrates and products, thereby preventing unfavorable oxidation and other reactions by metal oxide core. Additionally, for the reaction to occur, the organic solvent, substrates, and reagents can spread through the organic shell [27,28]. Synthesized metal nanoparticles with 'hybrid' core-shell supports [29-32], where the core is a magnetic metal oxide and the shell is a biopolymer, have found uses in biology, medicine, and catalysis [33-37]. Fe_3O_4 and biopolymer (chitosan, alginate, and cellulose) nanocomposites have been synthesised and used as supports for M-NPs [38-40]. Fe_3O_4 and lignin nanocomposite has been synthesised [41,42] and has been used as a support for Pd-NPs [42,43]. As nickel nanoparticles supported by hybrid core-shell nanocomposites have never been reported, it would be beneficial to synthesise magnetic, non-toxic, and inexpensive Fe_3O_4-lignin core-shell-supported nickel nanoparticles (Ni-NPs) [24-26]. And lignin, the only aromatic polysaccharide, is the second most abundant biopolymer, the safest, cheapest, sustainable, renewable, and biocompatible material [44,45]. In addition to stabilising M-NPs by ligating functional groups like arene, alkene, alcohol, phenol, carboxyl, carbonyl, and ether, lignin also serves as a reducing agent. Here, a simple synthesis of a nickel nanocatalyst supported by Fe_3O_4-lignin and its catalytic activity in the conversion of carbonyl compounds into alcohols are described.

2 Experimental

2.1 Materials and methods

All of AR Grade the chemicals, reagents and substrates brought from Spectrochem Ind. Pvt. Ltd., and used straight away without further purification. From Sigma-Aldrich India, obtained ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), anhydrous ferric chloride ($FeCl_3$), nickel chloride hexahydrate ($NiCl_2.6H_2O$), and high molecular weight alkaline lignin from St. Louis, MO, USA. The solvents were purified using widely accepted techniques. Silicagel 250-400 mesh for thin layer chromatography (TLC)was purchased from Merck Ind. Ltd. sold.

2.2 Synthesis of Fe_3O_4-Lignin@Ni-NPs

Under magnetic stirring, a standard aqueous solution of $NiCl_2.6H_2O$ (100 mL,0.237 g, 1 mmol) was combined with Fe_3O_4-Lignin (0.5 g). After stirring the resulting heterogeneous mixture for 30 min; this reaction mixture was added dropwise hydrazine hydrate (2 mL). The entire reaction mixture was then refluxed for 6 h while being constantly stirred. An external magnet was used to separate the solid from the reaction mixture after cooling it. This solid was washed with DI water (20 mL) followed by dry ethanol (20 mL). The resulting black solid was dried for two hours at 100° C in a vacuum oven. After that, Fe_3O_4-Lignin@Ni-NPs was collected as a fluffy black powder.

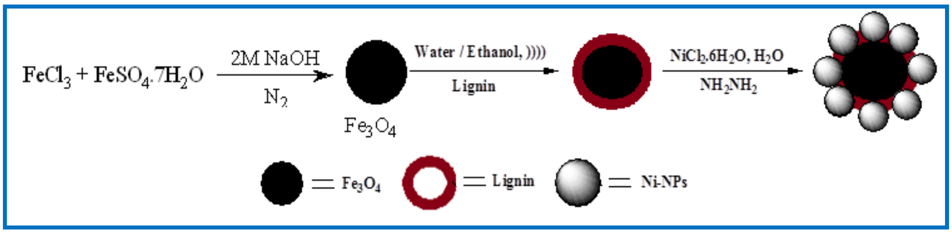
2.3 General procedure for transfer hydrogenation reaction

A carbonyl compound (1.0 mmol), Fe_3O_4-Lignin@Ni-NPs (0.05 g), solvent (10 mL), and hydrogen donor (1.0 mmol) were added to a two-neck round-bottom flask. At room temperature, this reaction mixture was magnetically stirred in a dry nitrogen environment. TLC was used in conjunction with an appropriate solvent system to check the progress of the reaction. After the reaction was finished, the catalyst was separated by magnetic filtration and the solvent was removed on a rotary evaporator. The organic product was extracted twice into dichloromethane (2×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed on a rotary evaporator. By using an appropriate solvent system and column chromatography, the crude products of each reaction were purified. Using ^1H NMR spectroscopy, the structures of each alcohol product were verified.

3 Results and discussion

3.1 Synthesis of Fe_3O_4, Fe_3O_4-Ligninand Fe_3O_4-Lignin@Ni-NPs

With a slight modification to the method described in the published literature [46,47], magnetic iron (II/III) oxide nanoparticles (Fe_3O_4-NPs) were made by chemically precipitating Fe^{3+} and Fe^{2+} ions from solutions of ferrous sulphate heptahydrate ($FeSO_4$ $7H_2O$) and anhydrous ferric chloride ($FeCl_3$) in a 2:1 molar ratio. Sonicating a mixture of lignin and Fe_3O_4-NPs in ethanol: water (1:1) system at ambient temperature to 40 °C results in the formation of a heterogeneous Fe_3O_4-Lignin nanocomposite solid. This solid was extracted using magnetic decantation, and it was then vacuum-dried at room temperature. Ni-NPs were synthesized by reducing a standard solution of nickel (II) sulphate hexahydrate in DD (doubly distilled) water with hydrazine hydrate while having Fe_3O_4-Lignin as a Core-Shell form of support. A black solid that had developed after the reaction mass had been cooled was separated by an external magnet. The wet-solid had been cleaned with DI water to get rid of any inorganic contaminants and then washed with dry ethanol. This Fe_3O_4-Lignin@Ni-NPs solid was dried for a couple of hours at 100 °C in a vacuum oven before being collected finally as a fluffy black powder. The different functional groups of lignin are anticipated to coordinate to the Ni-NPs that prevented their agglomeration and stabilizing them that have thus been formed.



Scheme 1 Synthesis of **Fe_3O_4-Lignin@Ni-NPs**.

Since Fe_3O_4 is the catalyst's primary core component, the catalyst (Fe_3O_4-Lignin@Ni-NPs) develops magnetic attraction and can subsequently be retrieved using magnetic separation. The only aromatic biopolymer with several ligating functionalities hydroxyl, carbonyl, and carboxyl groups are present in lignin that can bind both metal ions and metal nanoparticles, lignin acts as a shell around the Fe_3O_4 core, protecting it from agglomeration and leaching. Lignin is a natural, abundant, non-toxic, environmentally benign, biodegradable carbohydrate-based polymer. This heterogeneous nickel nanocatalyst is sustained by an inorganic-organic core-shell (Fe_3O_4-Lignin) but is insoluble in highly polar solvents like DMSO, DMF, and water. It was also found to be highly stable because no significant changes were noticed after being kept for a long time. This support has the advantages of being biodegradable, cheap, easily accessible, reusable, sustainable, eco-friendly, and non-toxic.

3.2 Characterization of Fe_3O_4-Lignin@Ni-NPs

3.2.1 UV-Visible Spectroscopy

The UV-visible spectra of an aqueous solution of Ni(II) and **Fe_3O_4-Lignin@Ni-NPs'**are depicted in **Fig. 1**. Ni(II) has been reduced to Ni(0) because the bands around λ_{max}, 300 nm, and 430 nm have been found to be absent.

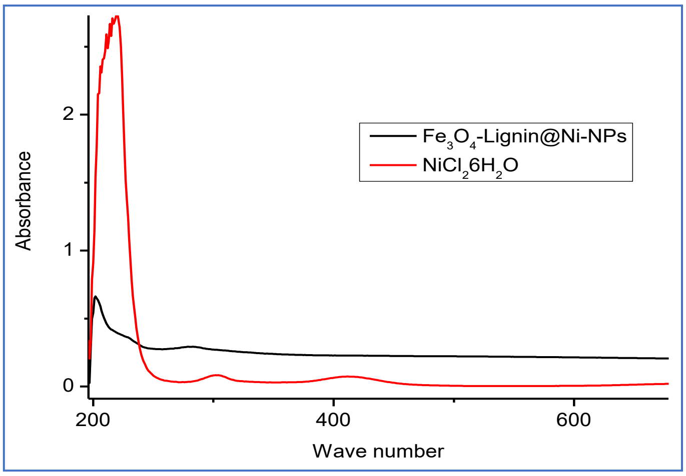


Fig.1 UV-Visible spectra of $NiCl_2.6H_2O$ (Red) and **Fe_3O_4-Lignin@Ni-NPs**(Black).

3.2.2 FT-IR spectroscopy

Fig. 2 displays the FT-IR spectrum of **Fe_3O_4-Lignin@Ni-NPs**. The various bands found in the IR spectrum of **Fe_3O_4-lignin@Ni-NPs** were appeared at υ,3417, 2935, 2112, 1603, 1509, 1463, 1420, 1267, 1214, 1127, 1080, 1032, 982, 675, 634, and 577 cm^{-1}. These bands have been evaluated in comparison to the IR spectra of lignin and lignin modified with Fe_3O_4 [41,42]. The presence of hydroxyl (O-H) groups was responsible for the wide band seen at υ,3417 cm^{-1}. At υ,2935 and 1462 cm^{-1}, respectively, observed the aliphatic C-H (methyl and methylene both merged) vibrational and deformation bands. Typical aromatic ring bands were observed at υ,1595 and 1512 cm^{-1}. The O-H group bending vibrations were detected at a wavenumber of υ,1373 cm^{-1}, while C-O stretching and aromatic vibrations were appeared at υ,1269 and 1221 cm^{-1}, respectively. Dialkyl ether linkages were seen at υ,1127 cm^{-1} and C-O deformation of bands of methoxy group was observed at υ,1030 cm^{-1}. The vibrations of Fe-O bonds of iron oxide appear in **Fe_3O_4-Lignin@Ni-NPs** betweenυ,675 to 577 cm^{-1}.

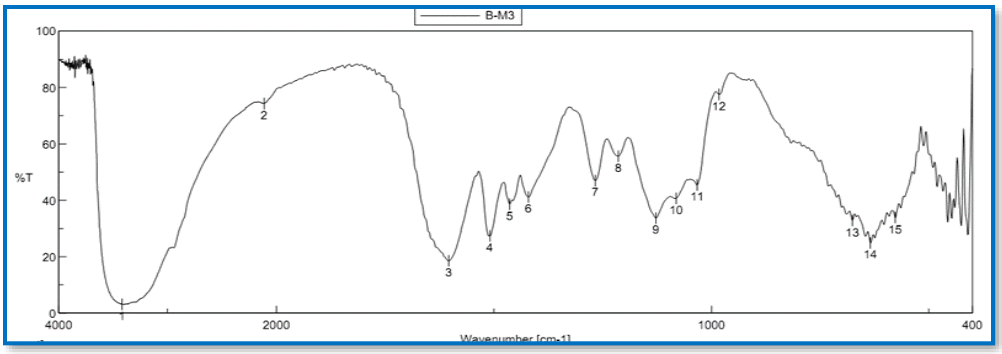


Fig.2 FT-IR spectrum of **Fe_3O_4-Lignin@Ni-NPs**.

3.2.3 Powder X-Ray Diffraction (PXRD)

The powder X-ray diffraction pattern of Fe3O4-Lignin@Ni-NPs is displayed in **Fig. 3**. The distinct characteristic peaks at 2θ values of 35.3, 43.0, 53.3, 57.09, and 62.5° correlate to the diffraction of the Fe_3O_4 lattice planes (220), (311), (400), (422), (511) and (440) [48]. The distinctive signals of the *fcc* and *hcp* crystalline phases of Ni are visible as peaks at 2θ values 37.10°, 43.30°, 62.87°, and 76.50°. According to the PXRD pattern the Ni-NPs had been effectively grafted onto the Fe_3O_4-Lignin, an inorganic-organic hybrid core-shell support.

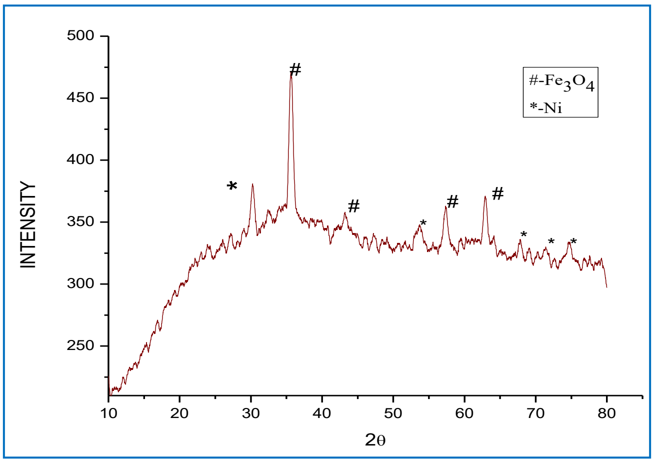
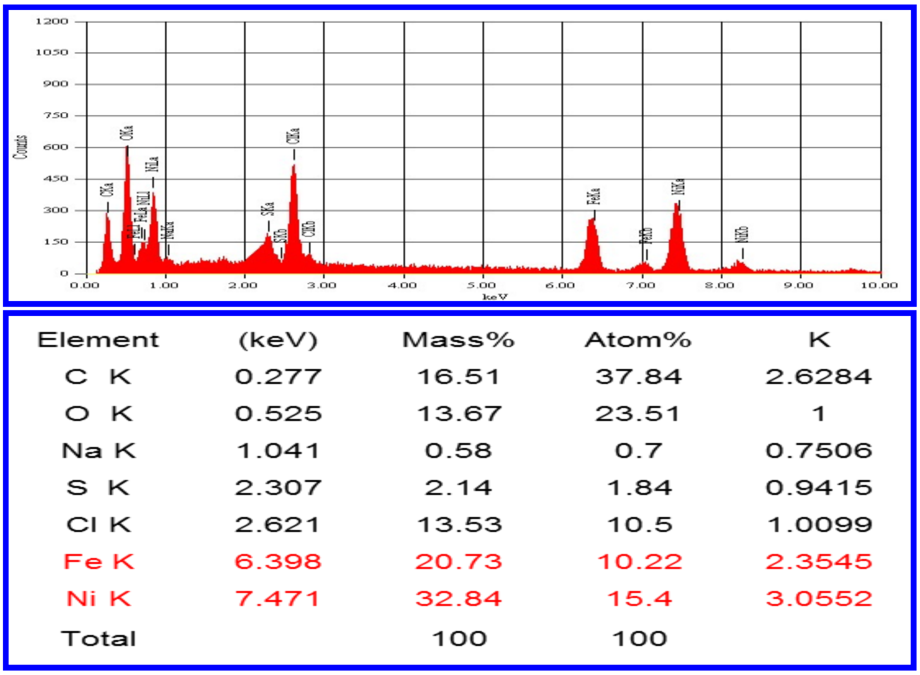


Fig.3 Powder X-Ray diffraction pattern of **Fe_3O_4-Lignin@Ni-NPs**.

3.2.4 Energy Dispersive X-ray analysis (EDX)

According to energy dispersive (EDX) X-ray spectrum (**Fig. 4**) the iron and nickel were found in the **Fe_3O_4-lignin@Ni-NPs** catalyst. It was observed that lignin was loaded with 20.73% iron and 32.84% nickel. Additionally, the EDX spectrum displayed the typical carbon and oxygen signals of the lignin.



Element	(keV)	Mass%	Atom%	K
C K	0.277	16.51	37.84	2.6284
O K	0.525	13.67	23.51	1
Na K	1.041	0.58	0.7	0.7506
S K	2.307	2.14	1.84	0.9415
Cl K	2.621	13.53	10.5	1.0099
Fe K	6.398	20.73	10.22	2.3545
Ni K	7.471	32.84	15.4	3.0552
Total		100	100	

Fig. 4 EDX spectrum of **Lignin-Fe_3O_4@Ni-NPs**.

3.2.5 Scanning Electron Microscopy (SEM)

The SEM pictures of **Fe_3O_4-Lignin@Ni-NPs** from various angles are presented in **Fig. 5**. These pictures demonstrated how evenly distributed the Ni-NPs are on the Fe_3O_4-Lignin.

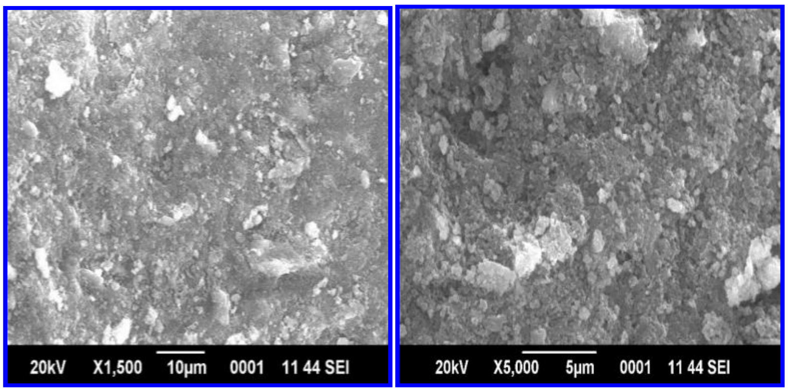


Fig.5SEM images of **Fe_3O_4-Lignin@Ni-NPs**.

3.2.6 Transmission Electron Microscopy (TEM)

TEM images of nickel nanoparticles stabilized by Fe_3O_4@ligninare shown in **Fig. 6**. These TEM images demonstrated that Ni-NPs were monodispersed and had both spherical and hexagonal morphology. The TEM pictures also demonstrated that the Ni-NPs had an almost uniform particle size distribution, with an average particle size of 15-20 nm.

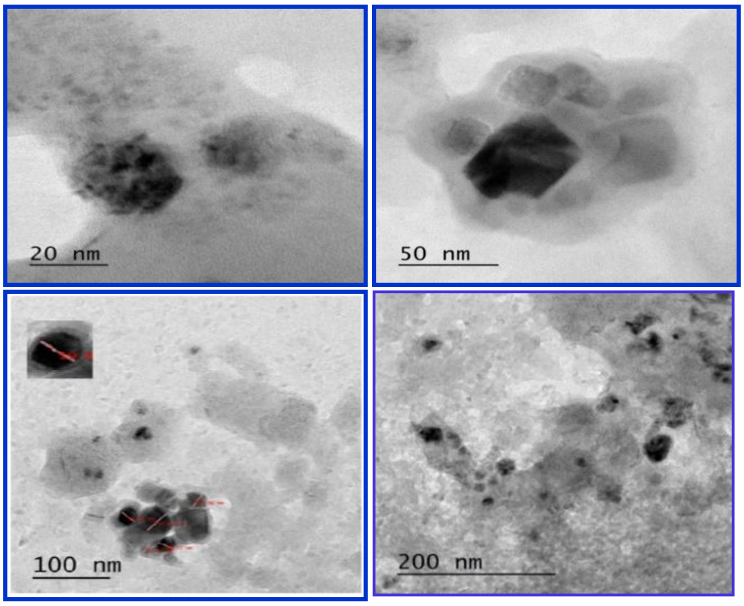


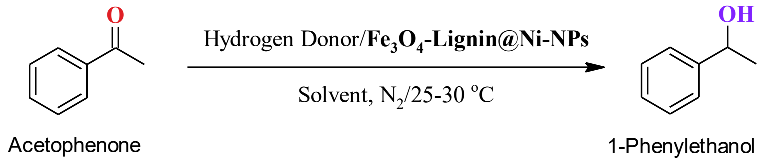
Fig. 6TEM images of **Fe_3O_4-Lignin@Ni-NPs**.

3.3 Applications of Fe_3O_4-Lignin@Ni-NPs in the TH of carbonyl compounds

3.3.1Optimizationstudies of hydrogen donor, solvent and reactions conditions

The effectiveness of the magnetic core-shell supported nickel nanoparticles (Fe_3O_4-Lignin@Ni-NPs) catalyst in the transfer hydrogenation (TH) of carbonyl compounds, including aldehydes and ketones, into primary and secondary alcohols was evaluated. The substrate for the optimisation experiments used was acetophenone. Selectively employing hydrogen sources, ammonium formate ($HCOONH_4$) and isopropanol (IPA). TH studies were conducted in a few examples of popular industrially useful organic solvents such as tetrahydrofuran (THF), acetonitrile, methanol, and *n*-hexane. The amount of the catalyst used was 0.05 g for all the optimization reactions. (What about the catalyst's dosage impact.) All of the reactions were carried out in an inert N2 environment with magnetic stirring at room temperature (25–30 °C). **Table 1** lists the experimental findings and conclusions of these optimization investigations. Short reaction periods of 1.5 h were used for the reactions. These experimental findings demonstrated that the ammonium formate was found to be a compatible and efficient hydrogen source, and that THF, used as the solvent, produced the highest yield (85%) of the reduction product 1-phenyl ethanol. (**Table 1**, **Entry 1**).

Table 1 Optimization of **Fe_3O_4-Lignin@ Ni-NPs**catalyzedTH of acetophenone[a].



Entry	Solvent	Hydrogen donor	Time (h)	Yield (%)[b]	TON	TOF
1	Tetrahydrofuran (THF)	Ammonium formate	1.5	85	3046.59	2031.06
2	Methanol	Ammonium formate	1.5	80	2867.38	1911.58
3	*n*-Hexane	Ammonium formate	1.5	59	2114.69	1409.79
4	Acetonitrile	Ammonium formate	1.5	62	2222.22	1481.48
5	Tetrahydrofuran	IPA	1.5	60	2150.53	1433.68
6	Methanol	IPA	1.5	55	1971.32	1314.21
7	*n*-Hexane	IPA	1.5	50	1792.11	1194.74
8	Acetonitrile	IPA	1.5	45	1612.90	1075.26

[a]Reactions conditions: Acetophenone (1.0 eq.), hydrogen donor (1.0 eq.), **Fe_3O_4-Lignin@Ni-NPs** (50mg) and solvent (10 times of acetophenone),T = 25-30 °C, N_2 atmosphere. [b]The isolated yields are given for the products.

3.3.2 Scope of the catalyst **Fe_3O_4-Lignin@ Ni-NPs** in the TH of aldehydes and ketones

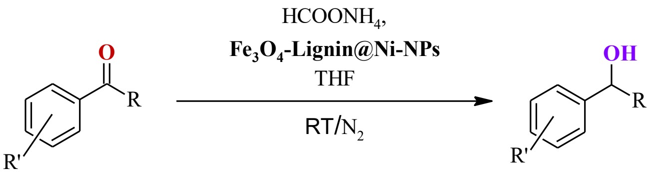
The efficiency of the **Fe_3O_4-Lignin@Ni-NPs** catalyst has been evaluated for the transfer hydrogenation of different substituted carbonyl compounds, aromatic aldehydes and ketones including heterocyclic ones, into the corresponding alcohols. As long as the carbonyl compounds were fully reduced, the TH reactions were carried out using the previously optimized reaction conditions, such as ammonium formate as a hydrogen source in THF at RT under nitrogen atmosphere. The product yields, TON, and TOFare provided in **Table 2**. On TLC, the reactions were routinely observed. Within 1.0 to 3.0 h, TH of any of the carbonyl compounds used in this study was transformed into the respective alcohols. The catalyst was found to be effective in the conversion of carbonyl compounds into corresponding alcohols in high yields and with shorter reaction periods when done at room temperature. This nickel nanocatalyst was also found to be highly active in the TH of aldehydes than ketones, which is the fact that aldehydes can attack the catalytically active site more readily than ketones because there is less steric resistance. Hence, carbonyl group of aldehydes can be reduced more readily than ketones.

In 1.25 and 1.5 h at room temperature, this catalyst could convert benzaldehyde and acetophenone into benzyl alcohol and 1-phenyl ethanol, producing 87 and 85% yields, respectively (**Table 2, Entry 1 and Entry 2**). The Ni nanocatalysts supported by ceria [49] and biopolymer [50] were used for the TH of carbonyl compounds in to alcohols and reported that these catalysts required in large amount though they resulted in a 98% yield of 1-phenylethanol. Further, in the latter caseH_2 gas under pressure was used as hydrogen donor. TH reaction of acetophenone (95%, 2 h) and benzaldehyde (99%, 3 h) by supported mesoporous carbon material supported nickel nanoparticles produces higher yields of respective alcohols but at 80 °C in slightly large reaction times and still larger reaction times (48 h) were reported in case if ionic liquids are used [51]. Higher yields of alcohols were produced by a mesoporous silica supported Ni-NPs catalyst in shorter reaction periods (45–60 min), but at temperatures of 100–110 °C in the presence of a base. Ni NPs were prepared by using lithium and DTBB for the TH of acetophenone at 76 °C with IPA as the hydrogen donor, and the result was 94% 1-phenylethanol. TH of acetophenone produces 86% 1-Phenylethanol catalyzed by Ni-NPs supported on polyionic in 48 h and under refluxing conditions.

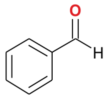
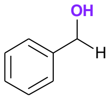
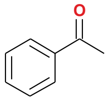
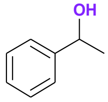
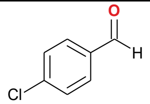
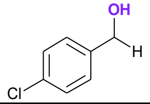
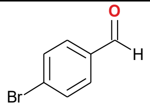
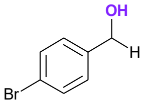
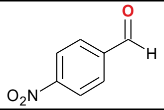
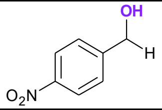
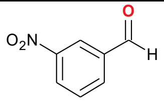
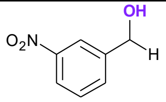
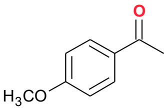
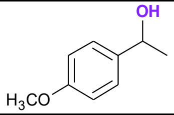
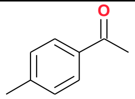
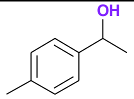
By selectively reducing the carbonyl group in the presence of other substituted functional groups like cyano, halo, methoxy, and nitro, the freshly synthesized nickel nanocatalyst's chemoselectivity was further evaluated. TH reaction of 4-chloro or 4-bromo benzaldehydes produced 90% and 96% yields of the respective alcohols without affecting C–X (X = Br, Cl) bond in 1.5 h(**Table 2**, **Entries 3** and **4**).This catalyst produced 91 and 95% isolated yields of the corresponding alcohols from 3-nitro and 4-nitrobenzaldehydes on TH in 2.5 and 1.5 h respectively (**Table 2**, **Entries 5** and **6**). This is linked to the substituent's increasing ability to withdraw electrons and the position of the substituent on the aromatic ring. The rate of heterogeneous catalytic reactions solely relies on the polarizability of the carbonyl group on the co-ordinatively unsaturated site of the catalyst because the reactions move through a six-membered cyclic transition state. Due to the reduced polarizability of the carbonyl group, it was found that when electron-donating OCH_3 and CH_3 groups were substituted at the *para* position of the acetophenone, the yields of the corresponding alcohols have been decreased by 82 and 70%, respectively (**Table 2**, **Entries 7** and **8**). This catalyst found to required very short reaction periods when compared to the reported similar type of Ni-NPs catalysts supported by polyionic liquid, CMK-3, and ceria though produce the alcohol product 4-methyl acetophenone in a high yield of 94% but requires longer reaction times and under refluxion conditions. In presence of the electron-withdrawing cyano group,*para*-

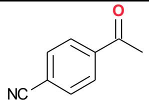
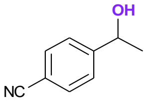
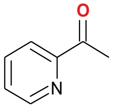
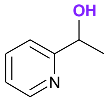
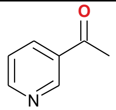
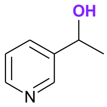
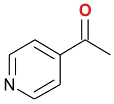
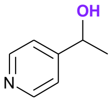
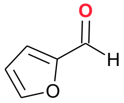
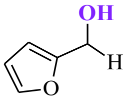
cyanoacetophenone generated 85% of the corresponding alcohol. (**Table 2**, **Entry 9**). When compared to the reported catalysts, the heteroaromatic carbonyl compounds also demonstrated to show good conversion in to respective alcohols (**Table 2**, **Entries 10, 11** and **12**). In conclusion, the catalyst **Fe_3O_4-Lignin@Ni-NPs** has been found to be very promising in terms yield of alcohol, reaction conditions like reaction duration and temperature, and cost of reagents and other materials.

Table 2 The catalytic transfer hydrogenation of carbonyl compounds in to alcohols using**Fe_3O_4-Lignin@ Ni-NPs**^{b} as catalyst.



R = H, CH_3; R^1 = H, CH_3, NO_2, Cl, Br, OCH_3, CN

Entry	Substrate	Product	Time (h)	Yield(%)^b	TON^c	TOF^d
1			1.25	87	3118.27	2494.61
2			1.50	85	3036.59	2024.39
3			1.50	90	3225.80	2150.53
4			1.50	96	3440.86	2293.90
5			1.00	95	3405.01	3405.01
6			2.50	91	3261.64	1304.65
7			1.50	82	2939.06	1959.37
8			1.00	70	2508.96	2508.96

9			2.50	85	3046.59	13218.
10			2.00	38	1362	681
11			2.00	90	3225.80	1612.9
12			2.00	98	3512.54	1756.27
13			3.00	40	1433.69	477.89

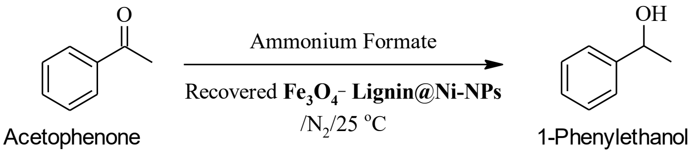
[a] Reactions were carried out with carbonyl compound (1.0 eq.), ammonium formate (1.0 eq.), **Fe_3O_4-Lignin@ Ni-NPs** (0.050 g) and THF (10 times with respect to carbonyl compound) at room temperature in an inert N_2atmosphere.

[b] The isolated yields are given for the products.

3.4 Recovery and reuse of the catalyst

An external magnet was used to retrieve the catalyst form the reaction system after each recycle. The same carbonyl compound underwent hydrogenation in five additional reactions using the recovered catalyst (**Table 3, Entry 2**) from the previous reaction under the same reaction circumstances. The reactions were found to be finished in the typical time range of 1.3 to 2 h, yielding products between 84% and 70% (**Table 3**).

Table 3 The catalytic reduction of acetophenone in to 1-phenyl ethanol using recovered using **Fe_3O_4-Lignin@Ni-NPs**.



Entry	**Catalyst**	**Reuse Stage**	**Time (h)**	**Yield[b] (%)**	**TON**	**TOF**
1	Fresh	1	1.30	84	3010.75	2315.96
2	Recovered from **Entry 1**	2	1.30	74	2652.32	2040.24
3	Recovered from **Entry 2**	3	1.40	73	2616.48	1868.91
4	Recovered from **Entry 3**	4	1.50	72	2580.64	1720.42
5	Recovered from **Entry 4**	5	2.00	72	2580.64	1290.32

6	Recovered from **Entry 5**	6	2.00	70	2508.96	1254.48

[a]Reactions were carried out with acetophenone (1.0 eq.), ammonium format (1.0 eq.), **Fe_3O_4-Lignin@ Ni-NPs** (0.050 g) and THF (10 times) at room temperature under stirring in an inert atmosphere of N_2.[b]The isolated yields are given for the products.

After the THreaction of each substrate the catalyst was separated by centrifugation, the residue washed with absolute ethanol (2-3 times) and then dried overnight in hot air oven. The recovered catalyst was reused for 6 runs and found that the catalyst does not to lose its efficiency. These observations revealed that the new **Fe_3O_4-Lignin@Ni-NPs** catalyst is advantageous as it avoids tedious purification process organic product. The recovered catalyst after 6 repeated usage has been characterized by TEM analysis. The TEM images of reused **Fe_3O_4-Lignin@Ni-NPs**are shown in **Fig. 7**.

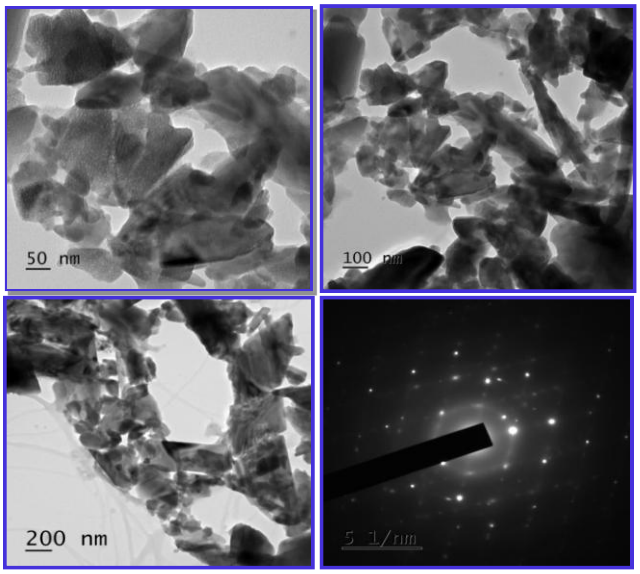


Fig. 7 TEM images of reused **Fe_3O_4-Lignin@Ni-NPs**.

3.5 Fe_3O_4-Lignin@Ni-NPscalcined at different temperatures

Fe_3O_4-Lignin@Ni-NPshas been calcined at different temperatures. The calcined material has been characterized by PXRD and TEM analysis.

3.5.1 PXRD spectra of **Fe_3O_4-Lignin@Ni-NPs**

PXRD patterns of calcined **Fe_3O_4-Lignin@Ni-NPs** are shown in **Fig.8**. It is obvious that the well-defined peaks. It is observed that peaks are sharp with high intensity for higher calcinations time which means that bigger particle size may be generated by increasing the calcination time. It is observed that increasing the calcination temperatures from 300 to 600 °C leads to increase in the crystallite size since crystallite growth is thermally accelerated.

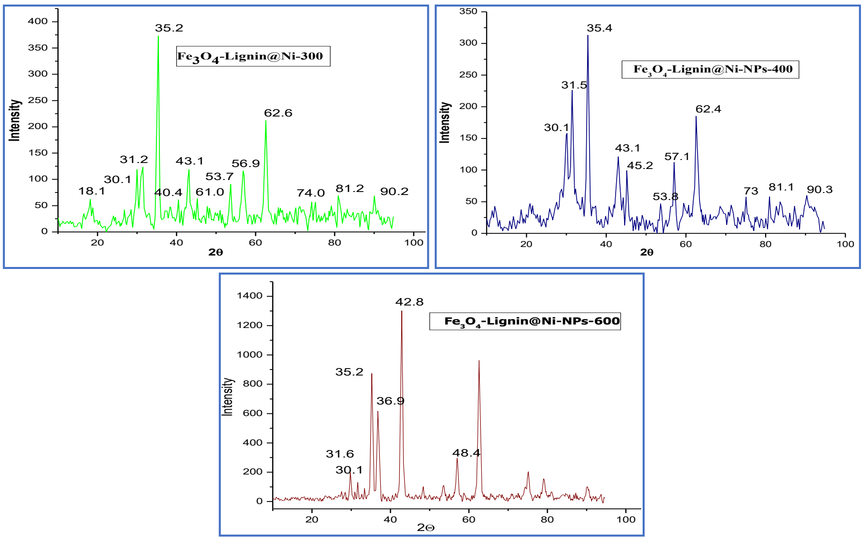


Fig. 8 PXRD spectra of **Fe_3O_4-Lignin@Ni-NPs** calcined at 300 °C, 400 °C and 600 °C

3.5.2 Transmission Electron Microscopy

After its sixth cycle of reuse, **Fe_3O_4-Lignin@Ni-NPs**was calcined at 600 °C whose TEM pictures at various magnifications are shown in **Fig. 9**. The pictures showed that the Ni-NPs aggregate slightly and were almost spherical in form. These TEM images of **Fe_3O_4-Lignin@Ni-NPs**revealed that the typical particle size was in the range of 25 to 30 nm.

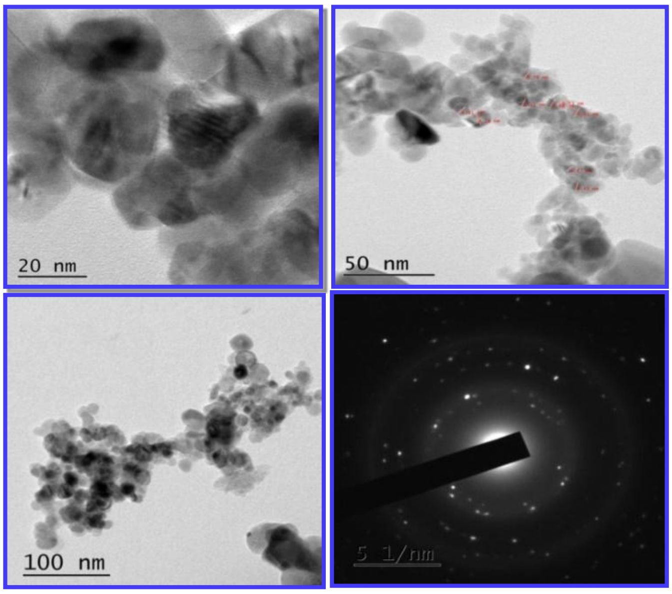


Fig.9 TEM images of **Fe_3O_4-Lignin@Ni-NPs** calcined at 600 °C and SAED image.

4 Conclusions

Fe_3O_4-Lignin was successfully synthesized using a green method, and it was used as a strong support for Ni(0) nanoparticles (Ni-NPs). Lignin is a non-toxic, eco-friendly biopolymer that has been effectively used to transform Ni(II) ions into Ni-NPs, stabilize/support Ni-NPs, and form a protective shell for Fe_3O_4-NPs. The **Fe_3O_4-Lignin@Ni-NPs** nanocatalyst is heterogeneous, magnetic, stable, and its size, shape, and have been characterized by methods such as UV-Visible, FT-IR, PXRD, SEM, TEM, EDX, and PXRD. TEM images showed that the particles' size and form change and their intensity rises after calcinations at 300, 400, and 600 °C. The catalytic effectiveness of the nickel nano catalyst **Fe_3O_4-Lignin@Ni-NPs** in the transfer hydrogenation of various substituted aromatic, hetroaromatic aldehydes, and ketones in to the corresponding alcohols has been effectively investigated. Under agreeable reaction conditions, the catalyst was found to be effective and highly selective for reduction carbonyl groups, yielding products up to 95% yield. Additionally, the catalyst avoids the need for costly chemicals and high temperatures and improves product yields in a shorter amount of time. The catalyst was retrieved using an external magnet and reused for up to six cycles before needing any additional modifications.

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