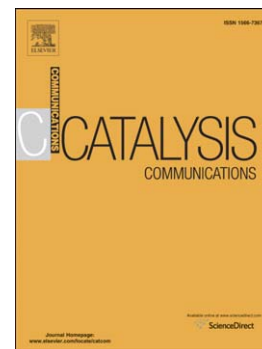# Accepted Manuscript

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Synthesis and characterization of hierarchical ZSM-5 zeolite containing Ni nanoparticles for one-pot reductive amination of aldehydes with nitroarenes

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Abstract

In this paper, we wish to report the synthesis and characterization of Nickel nanoparticles supported on acidic form of ZSM-5 zeolite (Ni/H-mZSM-5) with microporous/mesoporous hierarchical structure. This catalyst was effectively employed as novel acid-metal bi-functional heterogeneous catalyst for direct one-pot reductive amination of aldehydes with nitroarenes in the presence of $NaBH_4$ as a mild reducing agent. Excellent yields at room temperature and short reaction time in aqueous media conditions were obtained.

Keywords: Hierarchical zeolite, reductive amination, Nickel nanoparticles, Acid-metal bi-functional catalyst, One-pot reaction.

1. Introduction

Amines and their derivates are very important industrial organic compounds that have found widespread applications such as pharmaceuticals, agrochemicals, dyes, and fine chemicals [1]. Reductive amination of carbonyl compounds with amines is useful synthetic route for the preparation of amines and their derivatives. To achieve this, several methods have been developed [2]. However, one of the major pathways is direct reduction of nitroarenes to amine and then further transformation is carried out by amination to obtain their amine derivatives in one-pot which is an important issue in chemistry owing to several inherent advantages such as simplifying separation steps, reducing the use of reagents, and increasing yields [3]. Recently, few studies have been reported on these types of three-step reactions which start by using nitroarenes. In this approach, the nitroarenes are reduced to amines and then the carbonyl compounds are reacted with amines to form imines, which are then reduced to new amines by the pre-generated hydrides [3].

To carry out one-pot tandem reductive amination reaction from nitroarenes in three steps, bi-functional catalysts can be used which must have acidic and metallic character. In this regard, several catalytic systems have been recently developed [3-5] which among them, heterogeneous catalysts in comparison to homogeneous ones have many advantages such as separation and recovery capabilities [6].

It has been proved that in the direct reductive amination of carbonyl compounds using nitrobenzene, acidic properties of supports can be helpful to promote the reaction [4,5]. Hence, among the various types of the supports, zeolites are good candidates to be used in this reaction. Nevertheless, the results indicated a poisoning and clogging because of diffusion limitation in its microporous network [7]. In recent years, hierarchical zeolites have been synthesized to exploit

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the shape selective properties of microporous zeolites while decreasing the diffusion and accessibility limitations of larger molecules in biomass upgrading [8]. The incorporation of mesopores in the zeolite material can reduce pore blockage caused by large molecules adsorbing to the surface and thus increase activation of the support [9]. In addition, according to the recent reports, hierarchical zeolites showed better catalytic activity in organic reactions than the mesoporous aluminosilicate catalysts such as Al-MCM-41, Al-MCM-48, … [10-12]. Unfortunately, despite the large pores of ordered mesoporous aluminosilicate materials, the amorphous walls of these materials were not able to match the stability, acid strength and catalytic activity typically associated with crystalline zeolites.

Herein, Hierarchical H-mZSM-5 zeolite containing Ni nanoparticles was synthesized as a novel acid-metal bi-functional heterogeneous catalyst. Then, it was used effectively for the direct one-pot reductive amination of aldehydes with nitroarenes compounds at room temperature and in aqueous media conditions.

2. Experimental

2.1. Catalyst preparation

Firstly, high quality ordered mesoporous silica KIT-6 was prepared according to the reported procedure [13]. Then, Ni/H-mZSM-5 was synthesized as the following:

At first, KIT-6 was used as an indirect template (silica source) for the synthesis of hierarchical mZSM-5 zeolite. A solution of sodium aluminate and tetrapropylammonium hydroxide (TPAOH, 40 wt.%) was impregnated into 1 g of KIT-6 powder. The final molar ratio of the resulting synthesis gel was Al_2O_3:60SiO_2:4Na_2O:4800H_2O:18TPAOH. The mixture was stirred for 12 h at room temperature. Then, the aged synthesis mixture was transferred into a

Teflon-lined stainless steel autoclave followed by reaction at 448 K for 48 h. The solid product was then filtered, washed with deionized water and dried in air at 393 K overnight. Finally, the sample was calcined at 823 K for 6 h to remove the TPAOH template and the hierarchical mZSM-5 product was obtained.

In the second step, the obtained mZSM-5 was ion-exchanged with 100 mL aqueous solution of NH_4Cl (1 M) in the reflux condition for 48 h, washed with deionized water, dried at 383 K for 12 h and calcined at 823 K for 6 h to prepare hierarchical H-mZSM-5.

In the third step, Ni/H-mZSM-5 was prepared through *in situ* reduction of Ni ions inside the channels of H-mZSM-5, according to our previous report [14].

2.2. General procedure for one-pot reductive amination of aldehydes with nitroarenes

A mixture of benzaldehyde (2 mmol), nitrobenzene (2 mmol) in water (5 mL) was placed in a round bottom flask and stirred for 1 min at room temperature. Then, to the resulting mixture, $NaBH_4$ (6 mmol) and Ni/H-mZSM-5 (0.05 g) were added and the mixture was stirred under room temperature until TLC showed complete disappearance of the benzaldehyde. After that, the reaction mixture was quenched with water (10 mL) and the product was extracted with diethylether (2×10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The products were obtained very pure just by extraction with diethylether in majority of the reactions. In a few cases column chromatography was used to obtain the pure product. The product was identified with melting point, ^{1}HNMR, ^{13}CNMR and FT-IR spectroscopy techniques.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of H-mZSM-5 and Ni/H-mZSM-5 are depicted in Fig. 1. H-mZSM-5 shows reflections at 2θ values of 7-9˚ and 23-25˚, which agree well with the characteristic peaks of MFI structure [15]. In the Ni/H-mZSM-5, nickel peak cannot be seen in XRD due to the homogeneity of the Ni nanoparticles in the Ni/H-mZSM-5 and it just shows an amorphous pattern at 2θ values of about 44˚ (it should be mentioned that the nanoparticles which are located inside the pores are not observed in the XRD pattern [16]). In order to prove the existence of the Ni species in the hierarchical zeolite, Ni/H-mZSM-5 catalyst was exposed to temperature (400˚C). On heating, amorphous Ni changed to crystalline, thus appeared as a peak [17]. The XRD pattern of Ni/H-mZSM-5 sample heated at 400˚C can be seen in Fig. 1 (inside). After calcination at 400 ˚C, XRD pattern of residue shows a broad peak with low intensity (about 44˚) which can be attributed to the small size of nickel nanoparticles [18] (the size of nickel nanoparticles was determined using TEM images and will be described in the next section). However, the peak at 2θ = 44.29˚, corresponds to the plane (111) of fcc nickel [17]. Nevertheless, as can be seen, after deposition of nickel nanoparticles on hierarchical zeolites, zeolite structure has not changed, representing a successful synthesis of the catalyst (Fig. 1).

<Fig. 1>

The BET specific surface areas, the pore volumes and the pore sizes of H-mZSM-5 and Ni/H-mZSM-5 samples were calculated using BET, BJH and MP-Plot methods (Table 1). The N_2 sorption isotherms for these samples are shown in Fig. 2. [19], which are the typical characteristics of mesoporous materials (Figs. 2). It is seen that H-mZSM-5 has a high BET surface area (223 m^2 g^{-1}) and pore size (4.6 nm) which indicates its applicability as a suitable

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supply for the deposition of Ni nanoparticles (Table 1). Furthermore, MP-Plot method confirm the existence of microporosity within the H-mZSM-5 and Ni/HmZSM-5 structures (Table 1), which after incorporation of nickel nanoparticles, these microporous structures are still visible [20-22]. Also, the specific surface area, pore volume and pore diameter (calculated by BJH) of Ni/H-mZSM-5 is lower than that of H-mZSM-5 (Table 1); Which is due to the distribution of nickel nanoparticles on the surface of the hierarchical zeolites.

Also, according to the TPD results, the numbers of acid sites were 0.96 mmol/g for H-mZSM-5 and 0.92 mmol/g for Ni/H-mZSM-5 (Table 1), respectively; which indicates that despite the deposit of nickel nanoparticles on H-mZSM-5, acidic properties of Ni/H-mZSM-5 are still maintained.

<Table 1>, <Fig. 2>

SEM images of H-mZSM-5 and Ni/H-mZSM-5 are given in Fig. 3. The synthesized H-mZSM-5 is small cubic regular particles with a crystalline form structure and a size about 5 μm (Fig. 3a). It is necessary to mention that most of the Ni nanoparticles are incorporated inside the zeolite mesoporous structure which is not detectable in the SEM images (these particles can be seen in the TEM images). It should be mentioned that after loading of Ni nanoparticles on the surface of H-mZSM-5, the crystalline structure of the zeolite is not destroyed.

<Fig. 3>

The morphology of hierarchical H-mZSM-5 and the distribution of the Ni nanoparticles in the Ni/H-mZSM-5 were studied by TEM observations. The typical TEM micrographs (Fig. 4a and b) clearly show that the H-mZSM-5 and Ni/H-mZSM-5 have an ordered mesostructure with a pore diameter of about 5 nm. In the TEM image of Ni/H-mZSM-5 (Fig. 4c), the places with darker contrast can be related to the presence of nickel nanoparticles (Fig. 4c). The small dark

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spots in the images can be related to Ni nanoparticles with average diameter of ~3-5 nm, which are located into the support channels.

<Fig. 4>

In order to investigate the state of the Ni in the hierarchical zeolite, an XPS study was carried out on the Ni/H-mZSM-5 catalyst (Fig. 5). The XPS result of Ni nanoparticles dispersed in H-mZSM-5 media for Ni2p spectrum with the binding energies of $Ni2p_{3/2}$ and $Ni2p_{1/2}$ lying at about 852.7 and 870.4 eV, respectively (see Fig. 5a), meaning that Ni nanoparticles are stable in metallic state in H-mZSM-5 [17]. Also, the XPS spectrum shows two additional, slightly higher energy bands at 857.5 and 872.9 eV, though in relatively weak intensities, attributable to Ni(II) $2p_{3/2}$ and Ni(II) $2p_{1/2}$, respectively. By comparing to the spectral data for NiO, these bands indicate the presence of a small amount of NiO, presumably in the form of a thin oxide film on the surface of Ni nanoparticles. Upon argon ion bombardment, the former two bands of Ni^0 gain intensity while the latter two bands of Ni(II) loose intensity relatively. This observation supports the assumption that NiO is formed on the surface of nanoparticles. Therefore, the oxidized Ni may come from partial oxidation during XPS sampling, whereby the Ni nanoparticles are exposed to air for a few seconds [17,23].

The full XPS spectrum of Ni/H-mZSM-5 showed peaks of silicon, aluminum, carbon, oxygen and nickel. Carbon peaks correspond to remaining organic template of TPAOH inside the zeolite channels (Fig. 5b). Recent studies have undoubtedly shown that even after template removal, small amount of template stays inside the small cages in the MFI structure [24-26]. In addition, calibration of XPS instrument is done by using the binding energy of a known compound which always cause present carbon contamination with a C_{ls} binding energy of 284.4 eV [18,27].

<Fig. 5>

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3.2. Catalytic activity

Ni/H-mZSM-5 hierarchical zeolite was used as an acid-metal bifunctional catalyst for the one-pot reductive amination of aldehydes with nitroarenes. This reaction was carried out in water as a green solvent and in room temperature.

To identify the effect of nickel nanoparticles concentration on the reduction amination reaction, different amounts of $NiCl_2.6H_2O$ were examined. The amount of $NiCl_2.6H_2O$ to prepare Ni/H-mZSM-5 was changed from 2 mmol/g to 10 mmol/g while the other values were constant. Ni contents of the catalysts were determined by Atomic Absorption method and are presented in Table 2. As shown in Table 2, the catalytic activity was improved by increasing the amount of $NiCl_2.6H_2O$ from 2 to 5 mmol/g. As the catalytic reaction mechanism involves Ni nanoparticle mediated electron transfer from BH_4^- ion to the nitro compounds (in the first step) and to the imine intermediates (in the third step), the amount of H^- sites on the catalyst surface are increased by increasing nickel nanoparticles, and a larger amount of hydrides can be transferred to the nitro compounds and then imine groups through the catalyst [28]. According to the results, the catalyst prepared by 5 mmol/g $NiCl_2.6H_2O$ showed the best catalytic activity.

However, by further increasing the amount of $NiCl_2.6H_2O$ (more than 5 mmol/g), the catalytic activity was reduced, which can be attributed to after a certain amount of nickel chloride increases, a larger amount of nanoparticles is loaded on the surface of the zeolite that may have caused the hierarchical zeolite pores to narrow. Actually, by increasing the amount of $NiCl_2$, the nanoparticle size will increase [29,30], the pore size will narrow in some places and it can reduce the rate of reactants diffusion through the pores. Therefore, lower activity of the catalyst prepared with higher $NiCl_2$ concentration will be expected. However, it doesn't mean that the pores are entirely clogged.

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<Table 2>

The reusability of the catalyst was studied by using Ni/H-mZSM-5 in recycling experiments. After each cycle, the catalyst was filtered off, washed with water (10 mL) and ethanol (3 mL $\times$ 5 mL). Then, it was dried in an oven at 60 °C and reused in the reductive amination reaction. The results showed that the recycled catalyst could be reused six times (Table 3). It should be mentioned that there was very low Ni leaching (about 3%) during the reaction and the catalyst exhibited high stability even after six recycles. In addition, the XRD pattern of the used catalyst after five runs showed that the structure of the catalyst is well retained (Fig. 6).

<Table 3>, <Fig. 6>

The catalytic activity of the Ni/H-mZSM-5 in the reductive amination was compared with H-mZSM-5, Ni/H-ZSM-5 (prepared based on traditional ZSM-5) and without catalyst. The results are given in Table 4. The result highlights the important role of the catalyst in this reaction. As can be seen, the reaction performance without catalyst will be only 5% (entry 1). It is noteworthy to mention that $NaBH_4$ is considered a mild hydride donor agent, which is not a good reagent for reducing nitro groups. By using H-mZSM-5 catalyst (entry 2), the yield was increased slightly because the acid sites of the zeolites cause nitro groups to activate. Using Ni/H-ZSM-5 (traditional ZSM-5) (entry 3), the yield of product was increased to 81% due to the role of Ni nanoparticles as important species to transfer hydride ions from $NaBH_4$ to nitro groups. Comparing the activity of Ni/H-ZSM-5 and Ni/H-mZSM-5, the latter showed the best performance (entries 3 and 4), which corresponds to the hierarchical structure of Ni/H-mZSM-5. The hierarchical structure containing microporous and mesoporous buildings cause easier access of reactants to the active sites of the catalyst.

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<Table 4>

In further studies, the one-pot reductive amination of a wide range of other benzaldehydes and nitroarenes consist of electron-donating and electron-withdrawing groups over Ni/H-mZSM-5 as catalyst were conducted. The results show that all reactions are almost completed within 40 min at room temperature (Table 5). Existence of electron-withdrawing group on the nitro aromatic ring, which decrease electron density at the nitro group, cause increase in the reaction rate (entry 6) whereas electron-donating groups, shows reverse effect and cause decrease the reaction rate (entries 7 and 8). Actually, by decreasing the electron density over the nitro groups, the tendency of nitro groups to accept the hydride ions is increased. On the other hand, the existence of electron-donating groups on the benzaldehyde ring, cause increases in the reaction rate (entries 2-5). Actually, the electron-donating groups stabilize the protonated carbonyl bond intermediate and cause increase in the reaction rate.

Moreover, the one-pot reductive amination was performed on a 15-time scale-up (Table 5, entry 9), which the results represents the high activity of the catalyst.

In a further study, to clarify the role of solvent, the reaction was carried out in the presence of DMF (dimethylformamide) as an aprotic solvent (Table 5, entry 1). The results showed that the reaction time was increased, drastically. However, the reaction was completed after 80 min. Actually, in this type of reaction, in the steps of reduction of nitroarenes or imine intermediate, there is requirement of a hydride and a proton. Hydride is given by $NaBH_4$ and proton can be provided either by water or acid catalyst. According to the results, in the absence of water, the proton is given by acid catalyst and this process takes a longer time because this proton should be given back from the reactants. In addition, water as a polar protic solvent stabilizes the polar

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reaction intermediates and cause increase the reaction rate. Therefore, the role of water as polar protic solvent is important.

<Table 5>

Actually, there are a few reports on the one-pot reductive amination of benzaldehydes and nitroarenes which in compare with them; Ni/H-mZSM-5 catalyst shows reasonable yield at room temperature in short reaction time [4-6, 31]. Most importantly, water was used as a green solvent in this procedure.

4. Conclusion

In summary, Ni/H-mZSM-5 as a hierarchical zeolite with mesoporous-microporous structure was successfully synthesized and exhibited good catalytic performance in one-pot reductive amination of benzaldehydes and nitroarenes at room temperature in water. The existence of both acid and metal in the structure of Ni/H-mZSM-5 as a bi-functional heterogeneous catalyst plays an important role to carry out this three-step reaction in one-pot. Additionally, the catalyst could be removed from the reaction medium easily and can be reused for several cycles without any significant decrease in the catalytic activity/stability.

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Figure Captions:

Fig. 1. XRD patterns of H-mZSM-5 and Ni/H-mZSM-5 (2θ = 5–30) and inside: Ni/H-mZSM-5 burned in 400 °C for 4 h (2θ = 30-66).

Fig. 2. N_2 adsorption/desorption isotherms of H-mZSM-5 and Ni/H-mZSM-5.

Fig. 3. Scanning electron microscopy (SEM) photographs of (a) H-mZSM-5 and (b) Ni/H-mZSM-5.

Fig. 4. Transmission electron microscopy (TEM) of (a) H-mZSM-5 and (b) Ni/H-mZSM-5.

Fig. 5. a) XPS spectrum of Ni2p of Ni/H-mZSM-5, b) Full XPS spectrum of Ni/H-mZSM-5.

Fig. 6. XRD patterns of the used Ni/H-mZSM-5 catalyst after the fifth run of the recycle reaction and inside: used Ni/H-mZSM-5 after the fifth run of the recycle reaction burned in 400 °C for 4 h (2θ = 30-66).

Scheme 1.

Fig. 1

Fig. 1

Fig. 2

Fig. 2

Fig. 3

Fig. 3

Fig. 4

Fig. 4

Fig. 5

Fig. 5

Fig. 6

Fig. 6

Scheme 1

Table 1. Physicochemical properties of H-mZSM-5 and Ni/H-mZSM-5 samples obtained from N_2 adsorption.

Sample	S_{BET} $(m^2g^{-1})^a$	$V_{mesopore}$ $(cm^3g^{-1})^a$	$D_{mesopore}$ $(nm)^b$	$S_{micropore}$ $(m^2g^{-1})^c$	$V_{micropore}$ $(cm^3g^{-1})^c$	$D_{micropore}$ $(nm)^c$	NH_3 chemisorbed $(mmol/g)^d$
H-mZSM-5	223	0.26	4.60	269	0.10	0.7	0.96
Ni/H-mZSM-5	60	0.23	2.4	85	0.08	0.8	0.92

[a] Calculated by BET method.

[b] Mean pore diameter determined by using BJH method from the adsorption branch of the isotherm curves.

[c] Calculated by MP-Plot method.

[d] NH_3 TPD.

Table 2. Effect of $NiCl_2.6H_2O$ molar ratio on the catalytic activity.[a]

Entry	$NiCl_2 \cdot 6H_2O$ (mmol/g)	Ni content of catalyst (mmol/g Ni/H-mZSM-5)	Reaction time (min)	Conversion of benzaldehyde (%)[b]	Yield (%)[b]	
					amine	imine
1	2	0.9	35	60	60	40
			60	100	98[c]	2
2	5	2.32	35	100	98[c]	2
			60	100	98[c]	2
3	7	2.8	35	81	70	30
			60	100	98[c]	2
4	10	3.24	35	76	55	45
			60	100	98[c]	2

[a] Reaction conditions: benzaldehyde (2 mmol), nitrobenzene (2 mmol), Ni/H-mZSM-5 (0.05 g), H_2O (5 mL), $NaBH_4$ (6 mmol), room temperature.
[b] Conversion of benzaldehyde and yield were analyzed by GC, and n-dodecane was used as the internal standard.
[c] Isolated yield after work-up

Table 3 The catalysts reusability and leaching of Ni for the direct one-pot reductive amination.[a]

Cycle	Ni content of catalyst (mmol/g Ni/H-mZSM-5)	Yield (%)[b]
Fresh	2.32	98
1	2.29	92
2	2.28	88
3	2.26	84
4	2.25	79
5	2.24	74

[a] Reaction conditions: benzaldehyde (2 mmol), nitrobenzene (2 mmol), Ni/H-mZSM-5 (0.05 g), H_2O (5 mL), $NaBH_4$ (6 mmol), room temperature.
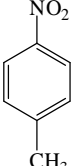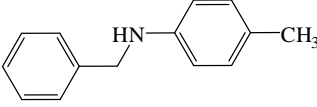[b] Isolated yield after work-up.

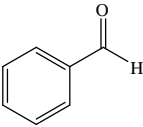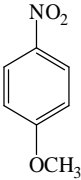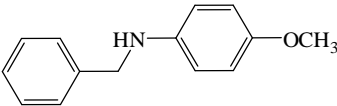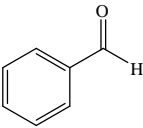**Table 4.** Effect of catalyst for the direct one-pot reductive amination.[a]

Entry	catalyst	Reaction time (min)	Yield (%)[b]
1	Without catalyst	100	5
2	H-mZSM-5	55	20
3	Ni/H-ZSM-5	105	81
4	Ni/H-mZSM-5	35	98

[a] Reaction conditions: aldehyde compound (2 mmol), nitro aromatic compound (2 mmol), catalyst (0.05 g), $NaBH_4$ (6 mmol), H_2O (5 mL), room temperature.
[b] Isolated yield after work-up.

Table 5. Direct one-pot reductive amination of aldehydes with nitroarenes over Ni/H-mZSM-5.[a]

Entry	1	2	Product	Yield (%)[b]	Time (min)	TON/TOF (h^{-1})[c]
1				98	35	16.9/29.0
				95[d]	80	16.4/12.3
2				96	30	16.5/33.1
3				95	40	16.4/24.6
4				96	45	16.5/22.1
5				97	35	16.7/28.7
6				97	30	16.7/33.4
7				93	40	16.0/24.1

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| 8 | (benzaldehyde) | (4-nitroanisole, NO$_2$/OCH$_3$) | (N-benzyl-4-methoxyaniline, HN—OCH$_3$) | 95 | 40 | 16.4/24.6 |
| 9 | (benzaldehyde) | (nitrobenzene, NO$_2$) | (N-benzylaniline, HN) | 84[e] | 65 | 14.5/13.4 |

[a] Reaction conditions: aldehyde compound (2 mmol), nitro aromatic compound (2 mmol), Ni/H-mZSM-5 (0.05 g), NaBH$_4$ (6 mmol), H$_2$O (5 mL), room temperature.

[b] Isolated yield after work-up.

[c] Turn-over number (mol product/mol Ni) and turn-over frequency (mol product/(mol Ni.h)).

[d] Reaction conditions: aldehyde compound (2 mmol), nitro aromatic compound (2 mmol), Ni/H-mZSM-5 (0.05 g), NaBH$_4$ (6 mmol), DMF (5 mL), room temperature.

[e] Scale-up condition: benzaldehyde (30 mmol) , nitrobenzene (30 mmol) , catalyst (0.75 g), NaBH$_4$ (90 mmol), H$_2$O (150 mL), room temperature.

Highlights

► Hierarchical H-mZSM-5 zeolite containing Ni nanoparticles was synthesized.

► Ni/H-mZSM-5 was prepared as novel acid-metal bi-functional heterogeneous catalyst.

► Ni/H-mZSM-5 was used for one-pot reductive amination of aldehydes with nitroarenes.

► Excellent yields at room temperature in water were obtained.

► The stability of the catalyst was excellent and could be reused 6 times.