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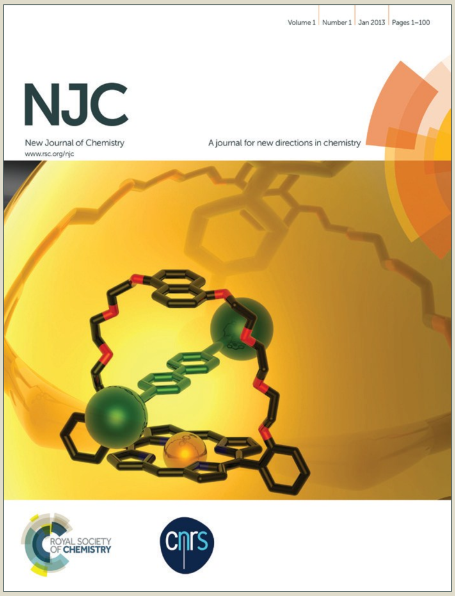

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# Facile one-pot tandem reductive amination of aldehydes from nitroarenes over a hierarchical ZSM-5 zeolite containing palladium nanoparticles

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In the present work, palladium nanoparticles supported on hierarchical ZSM-5 zeolite (Pd/H-hierarchical ZSM-5) was evaluated as a novel acid-metal bi-functional heterogeneous catalyst for direct one-pot reductive amination of nitroarenes using aldehyde in the presence of $NaBH_4$ and water as a mild reducing agent and green solvent, respectively. The structural and morphological properties of the prepared catalyst were investigated by XRD, BET, FT-IR, $NH_3$-TPD, SEM, TEM, XPS, DRS-UV and ICP-AES techniques. The reaction was carried out at room temperature, in short reaction time without producing any by-products. The stability of the catalyst was good and it could be reused six times without much loss of activity in reductive amination reaction.

**KEYWORDS:** Tandem reductive amination; Hierarchical ZSM-5 zeolite; Palladium nanoparticles; Heterogeneous catalyst; Acid-metal bifunctional catalyst.

## 1. Introduction

Amines are basically valuable compounds, which have been widely used in dyes, rubber materials, agricultural chemicals, herbicides, chelating agents, pharmaceuticals, surfactant textile auxiliaries, polymers.[1] There are several methods for the preparation of substituted amines: (a) using alkyl halides or sulfonates as alkylating agents, alkylation of ammonia, primary or secondary amines; (b) reduction of nitrogen-containing functional groups such as nitro, carboxamide derivatives, cyano, and azide and (c) reaction of aldehydes or ketones with ammonia, primary or secondary amines in presence of different reducing agents which for this transformation, the two synthetic methods were commonly used: direct and indirect methods.[2-4]

Direct Reductive amination represents one of the most convenient and versatile methods of amine synthesis that offers significant advantages over other amine syntheses, like facilitating the separation steps, the mild reaction conditions, wide commercial availability of substrates and increasing yields.[5] Also, the operational simplicity and reducing the use of reagents adds to the values of this method as a practical alternative to the reductive amination of carbonyl compounds.[6] In this regards, one of the economical and clean pathways is direct reductive amination of aldehydes and ketones using nitroarenes instead of amines. In recent years, few studies have been reported on these types of three-step reactions ,which start by using nitroarenes and usually need several hours to perform reaction.[7-13] In this method, after reduction of nitroarenes to amines, the carbonyl compounds react with amines to produce imines. Finally, the C=N bond of the imine is hydrogenated with hydride compounds or molecular hydrogen ($H_2$) to yield the secondary and tertiary amines. (Scheme 1).[10, 12,13]

Bi-functional catalysts can be used to perform one-pot cascade reductive amination reaction with nitroarenes in three steps, which have to have metallic and acidic character. In this respect, recently a variety of catalytic systems have been developed[7,11] which in the midst of them, heterogeneous catalysts have many benefits like recovery capabilities and easy separation in comparison to homogeneous ones.[7,8,11,14,15]

Recently, various metal nanoparticles have been used as hydride transfer catalysts in the reduction systems, for instance: Pt, Ni, Cu, and Pd.[16-19] However, an effective control of particle size and a uniform dispersion of nanoparticles in catalytic applications are typically anticipated. Nonetheless, nanoparticles usually aggregate to yield bulk-like materials that extremely reduce the activity of catalysts and selectivity. Accordingly, they must be immobilized in the pores of heterogeneous supports such as ordered mesoporous silica[20] or embedded in matrices such as macromolecular organic ligands or polymers.[21-23]

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† Electronic supplementary information (ESI) available: XRD pattern, FT-IR spectrum, $N_2$ adsorption/desorption isotherm, physicochemical properties and pore size distribution of H-hierarchical ZSM-5. See DOI: 10.1039/x0xx00000x

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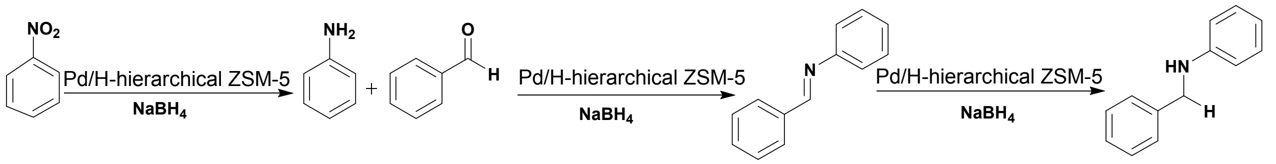

**Scheme 1**. Reaction steps and intermediates proposed in the direct one-pot reductive amination of aldehydes from nitroarenes.

It has been proven that in the direct reductive amination of carbonyl compounds with nitrobenzene, the acidic properties of supports can be effective to boost the reaction.[24,25] Since zeolites are good candidates among the variety of the supports to be used in this reaction. Despite that, because of diffusion restriction in its microporous framework, the results indicated a clogging and poisoning.[26] During the past decade, significant efforts have been devoted to developing methods that introduce mesoporosity in zeolite materials with shape selective properties by different methods that decreasing accessibility limitations and the diffusion of larger molecules in biomass promotion.[27] The conflation of mesopores in the zeolite materials can decrease pore blockage due large molecules adsorbing to the surface and thus enhance activation of the support.[28,29]

To address this issue, we will introduce synthesis and application of dispersed palladium nanoparticles incorporated in ZSM-5 zeolite with hierarchy structure as a novel acid-metal bi-functional heterogeneous catalyst. Furthermore, the catalyst was used effectively for the direct one-pot reductive amination of nitroarenes compounds using aldehyde in the presence of a small amount of $NaBH_4$ as a reducing agent and water as a green solvent at room temperature without any by-products.

## 2. EXPERIMENTAL

### 2.1. Catalyst Characterization

The samples were analyzed using the X-ray powder diffraction (XRD) of the catalyst was performed on a Bruker D8Advance X-ray diffractometer using nickel-filtered Cu Kα radiation at 40 kV and 20 mA. FT-IR spectroscopy (using a Perkin-Elmer 65 in KBr matrix in the range of 4000-400 $cm^{-1}$). The BJH pore size distribution, BET specific surface areas and MP-plot of the samples were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature using a Series BEL SORP 18. Temperature-programmed desorption of $NH_3$ ($NH_3$-TPD) was recorded on FINESORB-3010 equipped with a thermal conductivity detector. The DRS UV-vis Spectrophotometer was recorded with JASCO spectrometer, V-670 from 190 to 2700 nm. Moreover, X-ray photoelectron spectrum (XPS) was carried out recorded on ESCA SSX-100 (Shimadzu) using a non-monochromatized Mg Kα X-ray as the excitation source. In order to get detailed information on the size of Pd nanoparticles Transmission Electron Microscope (TEM) observations were performed with on a Philips CM30 electron microscope at an accelerating voltage of 300.00 kV. Scanning Electron Microscope (SEM) studies were performed on Hitachi S4160 FESEM. The Pd amount content of the catalyst was appraised estimated by inductively coupled plasma atomic emission spectrometry (ICP-AES) using perkin-Elmer optima 4300.

The products were characterized by $^{13}C$ NMR and $^{1}H$ NMR spectra (Bruker DRX-500 Avance spectrometer at 125.47 MHz and 500.13, respectively). Melting points were measured with an electro thermal 9100 apparatus. All the products were known compounds and they were characterized by $^{1}H$ NMR, $^{13}C$ NMR and FT-IR.

### 2.2. Catalyst Preparation

**2.2.1. Preparation of KIT-6**. Firstly, pursuant to the reported procedure, high quality ordered mesoporous KIT-6 was prepared to generate the hierarchical zeolite.[30] The large pore 3D (*Ia3d*) cubic mesostructure, designated as KIT-6, was prepared using tetraethylorthosilicate (TEOS) and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) template as the silica precursor and a structure directing agent, respectively. The detailed synthesis procedures are explained as follows: 6 g of n-butanol (0.161 mol) and 6 g (1.03 mmol) of P123 were dissolved in 270 g (15 mol) of distilled water and 11.4 g (0.115 mol) of concentrated hydrochloric acid (37 wt. % HCl). Then after, 12.9 g (0.061 mol) of TEOS was added to this mixture. The mixture was stirred for 24 h at 318 K in order to form the mesostructure product. Finally, the reaction mixture was heated for 24 h at 370 K for hydrothermal treatment under static conditions. The solid product filtered, washed with deionized water and dried at 373 K. Subsequently, the samples were calcined for 6 h at 823 K to remove the organic template.

**2.2.2. Preparation of hierarchical ZSM-5 zeolite.** Hierarchical zeolite prepared by KIT-6 as an indirect template (silica source) via the method described in recent literature.[31] In brief, solution of sodium aluminate and tetrapropylammonium hydroxide (TPAOH, 40 wt.%) were impregnated into 1 g of KIT-6 powder. The synthesis gel ($Al_2O_3$:$60SiO_2$:$4Na_2O$:$4800H_2O$:18TPAOH) was obtained as the final molar ratio. The mixture was stirred for 12 h at 293 K. Then, the aged synthesis mixture was transferred into a Teflon-lined stainless steel autoclave followed by reaction for 48 h at 448 K. Then, the solid product was filtered, washed with deionized water and dried at room temperature at 393 K overnight. In the end, the sample was calcined for 6 h at 823 K

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to remove the TPAOH template, and the hierarchical ZSM-5 zeolite was obtained.

**2.2.3. Preparation of acidic hierarchical zeolite (H-hierarchical ZSM-5).** The acid form of hierarchical zeolite was prepared by ion-exchange method. In short, 1 g of hierarchical zeolite was mixed up with 100 mL aqueous solutions of NH4Cl (1 M) in the reflux condition for 48 h, then the mixture was washed with deionized water, dried for 12 h at 383 K and finally was calcined for 6 h at 823 K to prepare H-hierarchical ZSM-5.

**2.2.4. Preparation of palladium nanoparticles supported on hierarchical zeolites (Pd/H-hierarchical ZSM-5).** Pd/H-hierarchical ZSM-5 was prepared through in situ reduction of Pd ions inside the channels of H-mZSM-5, according to our previous report.[32] The preparation of Pd/H-hierarchical ZSM-5 was carried out as follows:

H-hierarchical ZSM-5 (0.1 g) and 10 mL of an aqueous acidic solution ($C_{HCl}$ = 0.09 M) of $Pd(OAc)_2$ (0.0088 g, 0.0392 mmol) were placed in a round bottom flask. The mixture was heated to for 5 h at 353 K while being stirred. Next, 0.6 mL (2.47 mmol) aqueous solution of $N_2H_4{\bullet}H_2O$ (80 vol.%) was added to the mixture drop by drop in 20–25 min. Afterward, the solution was stirred for 1 h at 333 K. After that, it was filtered and washed sequentially with methanol and chloroform to remove excess $N_2H_4{\bullet}H_2O$ and was dried at room temperature to yield Pd/H-hierarchical ZSM-5 zeolite. The Pd content of the catalyst was estimated by decomposing the accurate amount of the catalyst by hydrochloric acid, nitric acid, fluoric acid and perchloric acid. ICP-AES estimated 0.332 mmolg$^{-1}$ Pd content of Pd/H-hierarchical ZSM-5.

**2.3. General procedure for direct reductive amination of aldehydes from nitroarenes.** A mixture of nitrobenzene (2 mmol) and benzaldehyde (2 mmol) in water (3 mL) was placed in a round bottom flask and stirred for 1 min at room temperature. Afterward, to the resulting mixture, Pd/H-hierarchical ZSM-5 (0.04 g) and $NaBH_4$ (6 mmol) were added and the mixture was stirred at room temperature until TLC showed the complete disappearance of the benzaldehyde. Then, the reaction mixture was quenched with water (10 mL) and the product was extracted with diethylether (2 × 10 mL). After they finished, the organic phase was dried over anhydrous $Na_2SO_4$, filtered and concentrated. In the end, the products were obtained very pure just by extract with diethylether in the majority of the reactions. In a few cases, column chromatography was used to obtain the pure product. The product was identified with a melting point, FT-IR spectroscopy techniques, $^1$HNMR and $^{13}$CNMR.

## 3. RESULTS AND DISCUSSION

As a first step towards the accomplishment of the synthesis of the hierarchical zeolite, high quality ordered mesoporous KIT-6 silica was prepared by sol-gel technique. After that, KIT-6 was used as an indirect template for the synthesis of zeolite. Moreover, the acid form of hierarchical zeolite was prepared by ion-exchange method. Furthermore, palladium nanoparticles have been reduced by hydrazine hydrate and immobilized on hierarchical zeolite. Subsequently, the Pd/H-hierarchical ZSM-5 zeolite with excellent properties was fabricated by this simple method for the reductive amination of nitro aromatic compounds in water medium and in the presence of low amount of $NaBH_4$ as a reducing agent.

### 3.1. Catalyst characterization

The expected crystalline structure of H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5 were confirmed by powder XRD measurements in Fig. 1S (ESI†) and Fig. 1, respectively. The major phases of H-hierarchical ZSM-5 show reflections at 2θ values of 7-9° and 23-25°, which completely agree with the characteristic peaks of MFI structure.[33] In addition, the wide-angle XRD pattern of the Pd/H-hierarchical ZSM-5 (2θ = 5-90◦) (Fig. 1) show peaks of 2θ values 39.92°, 46.54°, 67.90° and 82.0°, which are assigned to the corresponding (111), (200) and (220) and (311) indices of the face-centered cubic (*fcc*) lattice of metallic Pd.[34,35] The XRD results imply that after the immobilized of palladium nanoparticles on hierarchical zeolites, zeolite structure has not changed, indicating a successful synthesis of the Pd/H-hierarchical ZSM-5 (Fig. 1).

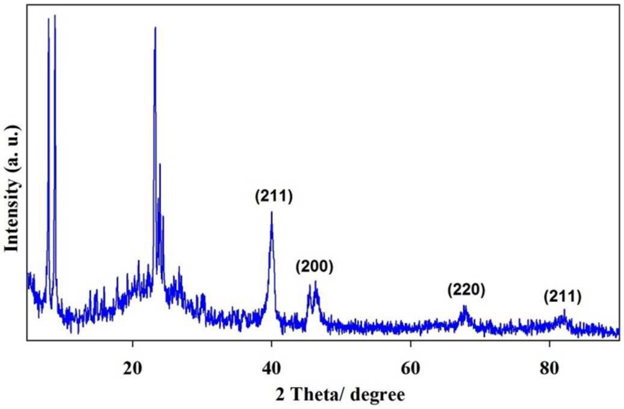

**Figure 1.** XRD pattern of Pd/H-hierarchical ZSM-5 (2θ = 5-90).

The FT-IR spectra were carried out to identify of pure H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5, which are shown in Fig. 2S (ESI†) and Fig. 2. A broad band at around 3440 cm$^{-1}$ is observed in both samples which represent the O-H stretching vibration of the adsorbed water molecules and hydroxyl groups of zeolite surface. Additionally, the band around ~3650 cm$^{-1}$ is generally attributed to the bending vibration of Si-OH-Al groups that shown to be acidic (more specifically Bronsted acid sites) and in agreement with prior reports.[36,37] The band at about 1630 cm$^{-1}$ can be attributed to adsorbed water, which is principally close to related reports.[38,39] The peaks around 1220 cm$^{-1}$ (external asymmetric stretch), 1150-1050 cm$^{-1}$ (internal asymmetric stretch), ~800 cm-1 (symmetric stretch) and 450 cm$^{-1}$ (T–O bend) are characteristic of highly siliceous materials. In the FT-IR spectra of H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5, the new band at around 550 cm$^{-1}$ corresponds to the double five rings

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(Si–O–Si or Al–O–Si groups) of the typical structure of MFI-type zeolites.[31] Both the FT-IR spectra and the XRD can represent that MFI-type zeolite (H-hierarchical ZSM-5) has been successfully synthesized.

Furthermore, the ratio of the intensities of 550 and 450 $cm^{-1}$ bands was used to figure out the (IR) crystallinity of the prepared samples. The results roll up in Table 1.

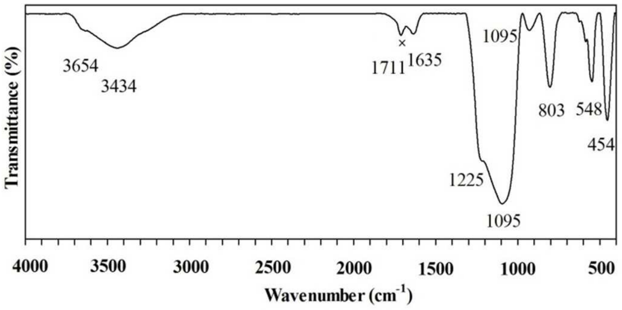

**Figure 2.** FT-IR spectrum of Pd/H-hierarchical ZSM-5. (× Impurity: carbonyl bond of acetone, which was used for rinse off the silicon wafer while preparation of KBr pellet).

High IR crystallinity matters to a high degree of ordering of the aluminosilicate (Al–O–Si) phase in a manner similar to that in ZSM-5 zeolite.[40]

The BET specific surface areas, the pore sizes and the pore volumes of both samples were computed by BET, BJH, MP-Plot and *t*-Plot methods (Table 1). The $N_2$ adsorption–desorption isotherms for these samples are shown in Fig. 3S (ESI†) and Fig. 3. Moreover, the corresponding pore size distribution curves (micro and meso pores) are drawn in Fig. 4-5S (ESI†) and Figs. 4-5 for H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5, respectively. As shown, according to the IUPAC nomenclature, two samples demonstrate isotherms of type IV, which are the typical characteristics of mesostructure materials (Fig. 3 and 3S (ESI†)).[41]

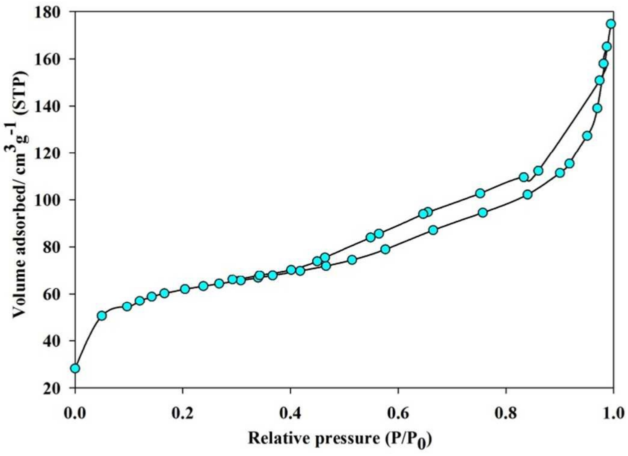

**Figure 3.** $N_2$ adsorption/desorption isotherm of Pd/H-hierarchical ZSM-5.

As shown, the H-hierarchical ZSM-5 can be applicable as a suitable supply for the deposition of palladium nanoparticles with a high BET surface area (223 $m^2$ $g^{-1}$), pore size (4.6 nm) and pore volume (0.26 $cm^3$ $g^{-1}$) (Table 1). In addition, the co-presence of micropores is suggested by *t*-Plot and MP-Plot methods (Table 1). Apparently these results demonstrate the formation of a new hierarchical zeolitic structure with an acceptable porosity and surface area. Based on the results, H-hierarchical ZSM-5 illustrates both mesoporous and microporous structures.

All three cases of the specific surface area, pore diameter (calculated by BJH) and pore volume of Pd/H-hierarchical ZSM-5 are lower than those of H-hierarchical ZSM-5 (Table 1), according to this results, palladium nanoparticles distributed on the outer surface and their incorporation inside the (micro and meso) pores of the hierarchical zeolites. Nonetheless, this isotherm is still similar to type IV that is the characteristic of a mesoporous material.

Fig 4S (ESI†) and Fig. 4 shows the pore size distribution curves (using BJH method) of the synthesized zeolite. As can be seen, the samples of H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5 have a narrow range pore size distribution with a pore diameter of about ~4 nm displaying the existence of a mesoporous structure in these zeolites. After the incorporation of palladium nanoparticles, the pore size distribution has slightly changed that indicates the distribution of palladium nanoparticles on the surface of zeolites.

MP-Plot methods and *t*-Plot corroborate the presence of microporosity of H-hierarchical ZSM-5 zeolite structures as well (Table 1, Fig. 5S(ESI†)). These microporous structures are still visible after the incorporation of palladium nanoparticles (Fig. 5).[42-44]

The aforementioned results indicate that H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5 still show a hierarchical structure with a suitable surface area, pore diameter and pore volume, which make it reasonable to act as a catalyst.

According to the TPD results, the numbers of acid sites were 0.96 mmol $g^{-1}$ and 0.90 mmol $g^{-1}$ for H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5, respectively (Table 1), which indicates that despite of distribution palladium nanoparticles on H-hierarchical ZSM-5, the acidic properties of Pd/H-hierarchical ZSM-5 are still maintained.

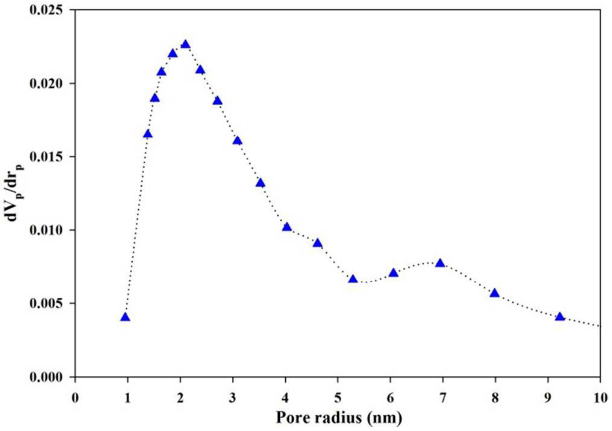

**Figure 4.** Pore size distribution of Pd/H-hierarchical ZSM-5 obtained by BJH method.

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**Table 1.** Physicochemical properties of H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5 samples obtained from $N_2$ adsorption.

| Sample | $S_{BET}$ ($m^2g^{-1}$)[a] | $V_{mesopore}$ ($cm^3g^{-1}$)[a] | $D_{mesopore}$ (nm)[a] | $D_{mesopore}$ (nm)[b] | $S_{micropore}$ ($m^2g^{-1}$)[c] | $S_{micropore}$ ($m^2g^{-1}$)[d] | $V_{micropore}$ ($cm^3g^{-1}$)[c] | $D_{micropore}$ (nm)[c] | IR crystallinity (%)[e] | $NH_3$ chemisorbed (mmol/g)[f] |
|---|---|---|---|---|---|---|---|---|---|---|
| H-hierarchical ZSM-5 | 223 | 0.26 | 4.60 | 4.80 | 269 | 293 | 0.10 | 0.7 | 99 | 0.96 |
| Pd/H-hierarchical ZSM-5 | 154 | 0.23 | 4.1 | 4.20 | 236 | 234 | 0.07 | 0.7 | 94 | 0.90 |

[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] The micropore surface area was estimated by the *t*-plot analysis using the adsorption branch of the isotherm curves. [e] IR crystallinity defined as $(I_{550}/I_{450})/0.72\times100\%$ [40] with $I_{550}$ and $I_{450}$ the intensities of the bands at 550 and 450 $cm^{-1}$, respectively. [f] $NH_3$ TPD.

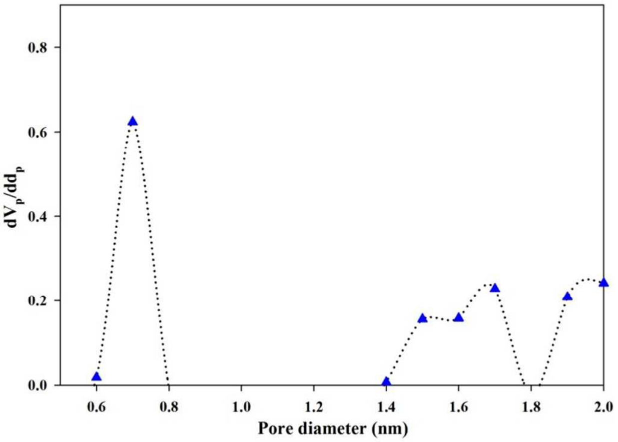

**Figure 5.** Pore size distribution of Pd/H-hierarchical ZSM-5 obtained by MP-Plot method.

Fig. 6 presents the result of the UV-vis spectrum of Pd/H-hierarchical ZSM-5. After reduction of $Pd^{2+}$/H-hierarchical ZSM-5 by hydrazine hydrate the UV-vis spectrum of $Pd^0$/H-hierarchical ZSM-5 was studied.

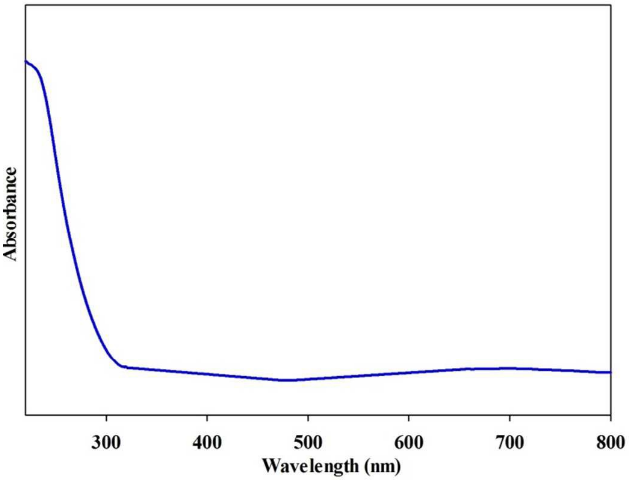

**Figure 6.** UV-vis spectrum of Pd/H-hierarchical ZSM-5.

According to the literature results, the UV-vis spectrum of $Pd(OAc)_2$ revealing a peak at 400 nm refer to the existence of $Pd^{2+}$.[45] As mentioned in Section 2, we used hydrazine hydrate as a reduction agent to prepare Pd nanoparticle supported on hierarchical zeolite from $Pd^{2+}$/H-hierarchical ZSM-5. In spite of a fact that we just mentioned, there were not any peaks at 400 nm in the UV-vis spectrum of Pd/H-hierarchical ZSM-5, which illustrated a complete reduction of $Pd^{2+}$ to Pd nanoparticles.

The chemical composition of Pd/H-hierarchical ZSM-5 was also analysed by XPS (Fig. 7). The XPS results of Pd nanoparticles dispersed in H-hierarchical ZSM-5 zeolite for Pd 3d spectrum with the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ lying at about 335.3 and 340.7 eV, respectively (Fig. 7). Which indicate Pd nanoparticles are stable as a metallic state in H-hierarchical ZSM-5 zeolite (the XPS spectrum of $Pd^{2+}$ ions appears two peaks at about 337 and 342 eV refer to Pd $3d_{5/2}$ and $3d_{3/2}$[46]) in comparison to the standard binding energy ($Pd^0$ with Pd $3d_{5/2}$ of about 335 eV and $Pd_{3/2}$ of about 340 eV[47]). In this context, it could be concluded that the Pd peaks in H-hierarchical ZSM-5 shifted to higher binding energy toward $Pd^0$ standard binding energy. As we know, the situation of Pd 3d peak is generally influenced by the local chemical/physical environment around Pd species besides the formal oxidation state, and shifts to higher binding energy when the charge density around it decreases.[21,47]

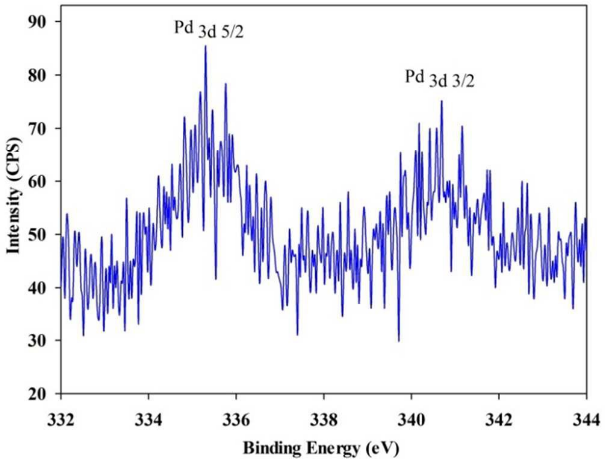

**Figure 7.** XPS spectrum of $Pd_{3d}$ of Pd/H-hierarchical ZSM-5.

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In other words, the existence of the acidic sites of the zeolite (with the electron withdrawing nature) around the $Pd^0$ species conduct toward a decrease in the charge density around $Pd^0$ and the slight increase in binding energy.[37]

The full XPS spectrum of Pd/H-hierarchical ZSM-5 showed peaks of silicon, aluminum, carbon, oxygen and palladium. The presence of Al, Si and O confirm that ZSM-5 was obtained. Carbon has also been detected after the template removal corresponds to remaining organic template of TPAOH inside the zeolite pores (Fig. 8). Recent studies have surely shown that even after template removal, a small amount of template stays inside the small cages in the MFI type zeolite.[48-50] Moreover, calibration of XPS instrument is done by using the binding energy of the reference substance which always causes present carbon pollution with a C1s binding energy of 284 eV.[51,52]

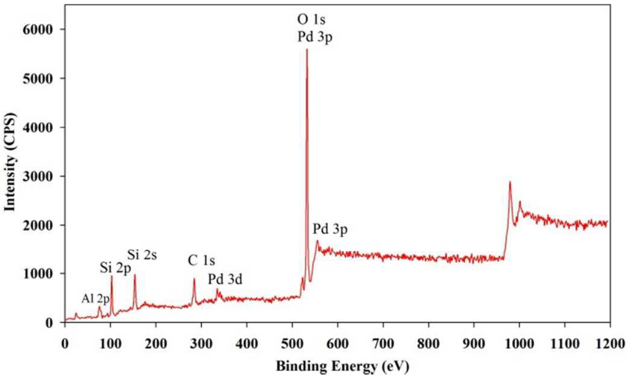

**Figure 8.** Full XPS spectrum of Pd/H-hierarchical ZSM-5.

In order to gain insights into the morphology of the catalyst, TEM analyses were carried out on H-hierarchical ZSM-5 (a) and Pd/H-hierarchical ZSM-5 (b-d), which depicted in Fig. 9. This images are demonstrated the formation of the ordered mesostructure in H-hierarchical ZSM-5 with pore diameter about 6-7 nm and the distribution of the palladium nanoparticles in the H-hierarchical ZSM-5 (Fig. 9 (a-c)).

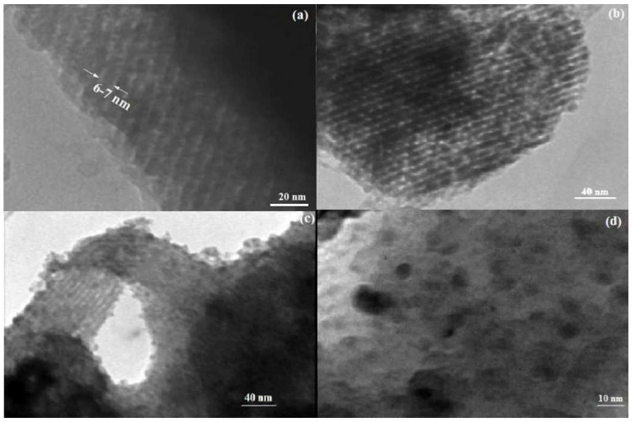

**Figure 9.** Transmission electron microscopy (TEM) of (a) H-hierarchical ZSM-5 and (b-d) Pd/H-hierarchical ZSM-5.

Also, the TEM images of Pd/H-hierarchical ZSM-5 (Fig. 9b-c) indicative of the places with darker contrast. Apparently, it could be related to the presence of palladium nanoparticles. Also, the small dark dots in the images with an average diameter of ~3-6 nm can be related to palladium nanoparticles and are located into the mesopores (Fig. 9d). As shown, the mesopore structure still remains after the incorporation of Pd nanoparticles in H-hierarchical ZSM-5 (Fig. 9b-c).

The SEM was conducted to identify the morphologies of H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5 that are shown in Fig. 10. In this regard, H-hierarchical ZSM-5 has a crystalline structure with small cubic regular particles and a size about 3 μm (Fig. 10a). As shown, it can be concluded that there is no difference in particle surface morphology between the H-hierarchical ZSM-5 and Pd/H-hierarchical ZSM-5 (Fig. 10b), indicating that the supporting of Pd nanoparticles takes place inside the channels of H-hierarchical ZSM-5 which is not detectable in the SEM images (these particles shown in the TEM section). This observation is also supported by the decrease in pore volume and in surface area as shown in Table 1. It’s also noteworthy to mention that, the crystalline structure of the zeolite is not destroyed during the loading of Pd nanoparticles on the H-hierarchical ZSM-5.

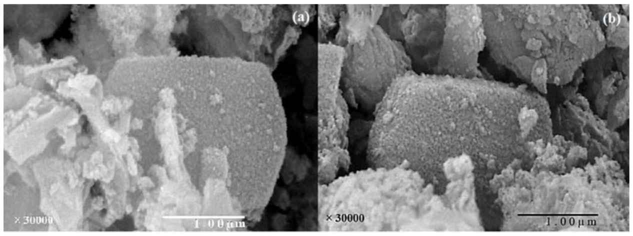

**Figure 10.** Scanning electron microscopy (SEM) photographs of (a) H-hierarchical ZSM-5 and (b) Pd/H-hierarchical ZSM-5.

### 3.2. Catalytic activity

Synthesized Hierarchical zeolite was characterized by several methods in the previous section. Here we introduce the application of this catalyst to the reductive amination reaction because it has many specific characteristics contrast to traditional zeolite. Over the past two decades, many studies devoted to industrial and academic research groups to the development of environmentally friendly synthesis. Accordingly, using water as a reaction medium in transition metal-catalyzed processes has merited increasing attention and nowadays it is one of the most essential targets of sustainable chemistry.[53,54] Water is an inexpensive, nontoxic solvent, readily available, non-inflammable that provides significant advantages over common organic solvents both from an environmental and an economic standpoint.[11,55] Thus, the effect of different parameters on the one-pot tandem reductive amination of aldehydes with nitroarenes over Pd/H-hierarchical ZSM-5 as acid-metal bifunctional catalyst was surveyed at room temperature in water and the results are as follows:

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**Table 2.** Effect of $Pd(OAc)_2$ molar ratio on the catalytic activity.[a]

| Entry | $Pd(OAc)_2$ (wt%) | Pd content of catalyst (mmol/g catalyst)[b] | Reaction time (min) | Conversion of benzaldehyde (%)[c] | Yield (%)[c] amine | Yield (%)[c] imine |
|---|---|---|---|---|---|---|
| 1 | 4.2 | 0.167 | 20 | 65 | 55 | 45 |
| | | | 45 | 100 | 98d | 2 |
| 2 | 8.1 | 0.332 | 20 | 100 | 98d | 2 |
| 3 | 11.6 | 0.464 | 18 | 100 | 98d | 2 |
| 4 | 15 | 0.598 | 15 | 100 | 98d | 2 |

[a] Reaction conditions: benzaldehyde (2 mmol), nitrobenzene (2 mmol), Pd/H-hierarchical ZSM-5 (0.10 g), $H_2O$ (3 mL) and $NaBH_4$ (6 mmol) at room temperature. [b] Estimated by ICP-AES. [c] Conversion of benzaldehyde and yield were analyzed by GC, and n-dodecane was used as the internal standard. [d] Isolated yield after work-up.

At the first screening of experiments, different amounts of $Pd(OAc)_2$ were examined to recognize the effect of palladium nanoparticles concentration on the reaction. So, while the other parameters were constant, the amount of $Pd(OAc)_2$ to prepare Pd/H-hierarchical ZSM-5 was changed from 4.2 wt% to 15 wt% and then measured by the ICP-AES technique which showed in Table 2. As can be seen in Table 2, the activity of catalytic increased steadily between 4.2 and 8.1 wt%. By increasing the amount of $Pd(OAc)_2$. As the catalytic reaction mechanism involves Pd 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 palladium nanoparticles, and a larger amount of hydrides can be transferred to the nitro compounds and then imine groups through the catalyst.[56] The excess amount of $Pd(OAc)_2$ cause the reaction time decrease with mild slope and because of the expensive price of palladium acetate, we chose 8.1wt% of $Pd(OAc)_2$ as an optimum amount.

The effect of $NaBH_4$ amount (as a hydride donor) on the reductive amination was investigated in the presence of Pd/H-hierarchical ZSM-5. The results revealed that there is a direct relationship between yield and the amount of $NaBH_4$ up to 6 mmol (Table 3). With further increase in the $NaBH_4$ amount, the yield of the reaction leveled off at 98% between 6 and 8 mmol $NaBH_4$. Fewer values were not enough for the reduction of the amount of nitro and imine compounds and the excess amount didn't have any effect on the reaction as well. Therefore, the best value of $NaBH_4$ was 6 mmol.

The effect of amount of Pd/H-hierarchical ZSM-5 was determined for the reductive amination reaction. It can be seen that with an increase in the amount of the catalyst from 0.03 g to 0.04 g, a considerable decrease in the reaction time was observed from 38 to 20 minutes (Table 4) which are due to the availability of more acidic and metallic sites.

**Table 3.** Effect of $NaBH_4$ on the direct one-pot reductive amination.[a]

| Entry | Amount of $NaBH_4$ (mmol) | Reaction time (min) | Conversion of benzaldehyde (%)[b] | Yield (%)[b] amine | Yield (%)[b] imine |
|---|---|---|---|---|---|
| 1 | 2 | 20 | 36 | 21 | 15 |
| | | 60 | 77 | 66 | 11 |
| 2 | 4 | 20 | 62 | 53 | 9 |
| | | 35 | 95 | 90 | 5 |
| 3 | 6 | 20 | 100 | 98[c] | 2 |
| 4 | 8 | 20 | 100 | 98[c] | 2 |

[a] Reaction conditions: benzaldehyde (2 mmol), nitrobenzene (2 mmol), Pd/H-hierarchical ZSM-5 (0.10 g) and $H_2O$ (3 mL) at 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 4.** Effect of catalyst amount on the direct one-pot reductive amination reaction.[a]

| Entry | Amount of catalyst (g) | Reaction time (min) | Yield of amine (%)[b] |
|---|---|---|---|
| 1 | 0.03 | 20 | 74[c] |
| | | 38 | 98 |
| 2 | 0.04 | 20 | 98 |
| 3 | 0.05 | 20 | 98 |
| 5 | 0.10 | 20 | 98 |

[a] Reaction conditions: benzaldehyde (2 mmol), nitrobenzene (2 mmol), $H_2O$ (3 mL) and $NaBH_4$ (6 mmol) at room temperature. [b] Isolated yield after work-up. [c] Yield was analyzed by GC, and n-dodecane was used as the internal standard.

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As shown from this table, a higher amount of catalyst (0.05 g) had no any appreciable effect on the yield. It might be mentioned that using low amounts of $NaBH_4$ and catalysts in this reaction shows the extraordinary catalytic activity of this catalyst.

The reusability of the catalyst was tested by using Pd/H-hierarchical ZSM-5 in recycling experiments (Chart 1). After each cycle, the catalyst was filtered off, washed with water (10 mL) and ethanol (3 mL × 5 mL). Thereafter, it was dried in an oven at 60 ˚C and reused in the reaction with a fresh reaction mixture. It should be noted that after each run, some of the catalysts were lost in the filtration process.

Herein, to solve this problem, after each run the amount of remaining catalyst was determined and the molar ratio of the reactants was changed according to the remaining amount of the catalyst. Nonetheless, it's noteworthy that there was a very low amount of lost catalyst after each cycle.

The catalyst was reused up to 6 times without any modification and 17% loss of activity was observed. It's noticeable that there was very low Pd leaching (2.7 % measured by ICP-AES) during the reaction and the catalyst exhibited high stability even after six runs (Chart 1).

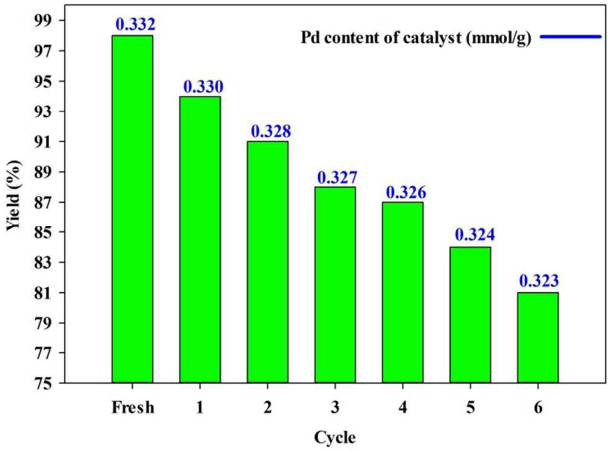

**Chart 1.** The catalysts reusability and leaching of palladium for direct one-pot reductive amination reaction.

Moreover, the XRD pattern of the used catalyst after five cycles showed that the structure of the catalyst is well retained (Fig. 11). Also, the XRD pattern in $2\theta = 45\text{-}75^{\circ}$ shows the reflections at $45^{\circ}$ and $53^{\circ}$ suggesting that during the reaction, the palladium nanoparticles remain in the form of a crystal. On the other hand, XRD analysis of reused Pd/H-hierarchical ZSM-5 indicates the presence of palladium crystals to form both, metallic and hydride. At room temperature, palladium hydrides may contain two crystalline α and β, phases. The existence of Palladium metal hydrides is the result of the very high tendency of palladium nanoparticles to accept the hydride ions and then conversion to palladium hydride. This process is faster in the presence of $NaBH_4$.[57]

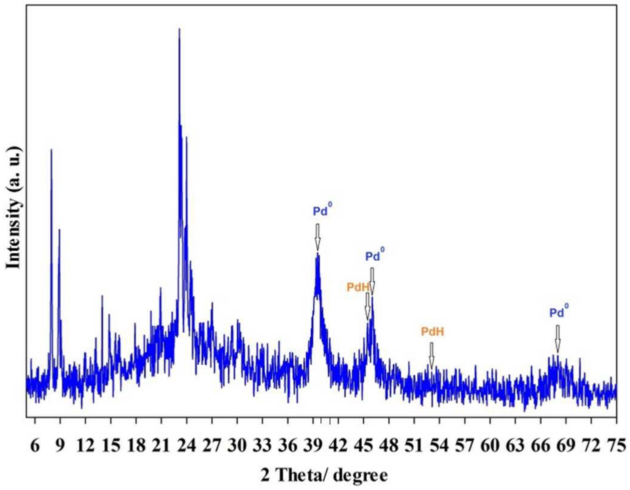

**Figure 11.** XRD patterns of the used Pd/H-hierarchical ZSM-5 after the fifth run of the recycle reaction.

It should be mentioned that in the presence of palladium hydride, the efficiency of the catalyst doesn't detract since palladium hydride is reversible in metallic form by slightly heating. In addition, the existence of palladium hydride crystal in reused catalyst indicates that this catalyst is very suitable for hydride transfer.

SEM images of the catalyst recovered from the fifth run of the recycle reaction are presented in Fig. 12, too. In contrast, between these images and SEM images of the fresh catalysts (Fig. 10), it's indicated that the structure of the ZSM-5 zeolite is well retained even after the fifth runs of the recycle reaction. Since, the catalysts exhibit high stability over 6 runs which is essential for the applications of catalyst.

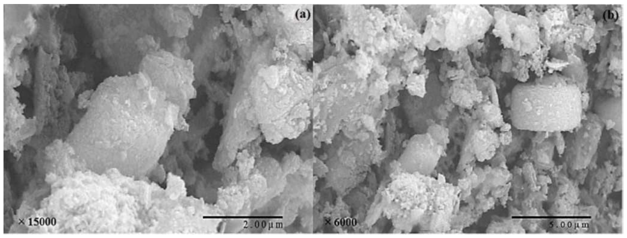

**Figure 12.** Scanning electron microscopy (SEM) photographs of the used Pd//H-hierarchical ZSM-5 catalyst after the fifth run of the recycle reaction.

The catalytic activity of the Pd/H-hierarchical ZSM-5 in the reductive amination was compared with H-hierarchical ZSM-5, $Pd^{2+}$/H-hierarchical ZSM-5, Pd/H-ZSM-5 (prepared based on traditional ZSM-5) and without a catalyst. The results are presented in Table 5. The result emphasizes the important role of the acid-metal catalyst in this reaction. As shown, the reaction efficiency without catalyst will be only 5% as long as 100 minutes (entry 1).

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**Table 5.** Effect of catalyst for the direct one-pot reductive amination.[a]

| Entry | catalyst | Reaction time (min) | Yield of amine (%)[b] |
|---|---|---|---|
| 1 | Without catalyst | 100 | 5 |
| | | 20 | 5 |
| 2 | H-hierarchical ZSM-5 | 55 | 20 |
| | | 20 | 15 |
| 3 | $Pd^{2+}$/H-hierarchical ZSM-5 | 55 | 45 |
| | | 20 | 25 |
| 4 | Pd/H-ZSM-5 | 55 | 75 |
| | | 20 | 55 |
| 5 | Pd/H-hierarchical ZSM-5 | 20 | 98[c] |

[a] Reaction conditions: benzaldehyde (2 mmol), nitrobenzene (2 mmol), catalyst (0.04 g), $NaBH_4$ (6 mmol) and $H_2O$ (3 mL) at room temperature. [b] Yield was analyzed by GC, and n-dodecane was used as the internal standard. [c] Isolated yield after work-up.

There is the important point that $NaBH_4$ act as a mild hydride donor agent, which is poor reagent for reducing nitro groups. By using the H-hierarchical ZSM-5 catalyst (entry 2), with increase acid sites of the zeolite the nitro group activated and so the yield slightly increased. (20% yield in 55 minutes). Using $Pd^{2+}$/H-hierarchical ZSM-5 (entry 3), the yield of nitro benzene reduction was increased to 45% due to the role of Pd ions as species to transfer hydride ions from $NaBH_4$ to nitro groups. Also, using Pd/H-ZSM-5 (traditional ZSM-5) (entry 4), the reaction performance was increased to 75% because of the role of palladium nanoparticles as species to transfer hydride ions from $NaBH_4$ to nitro groups. In order to prove the efficiency of the hierarchical structure of Pd/H-hierarchical ZSM-5 than traditional Pd/H-ZSM-5 zeolite, they compare with each other that Pd/H-hierarchical ZSM-5 showed the higher performance (entries 3 and 4). In fact the hierarchical structure containing micro/mesoporous buildings cause easier access of reactants to the active sites of the catalyst.

In catalyst study, one interesting point is heterogeneous nature. In this context, heterogeneity test was performed. In this regard, the catalyst was separated from the reaction mixture at approximately 50% conversion of the starting material through centrifugation.

The reaction progress in the filtrate was monitored (Fig.13). No further reductive amination reaction occurred even at addition times, representing that the nature of reaction process is heterogeneous and there is not any progress for the reaction in homogeneous phase.

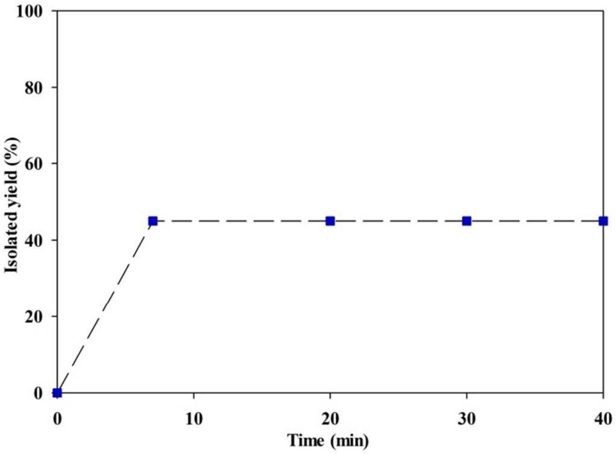
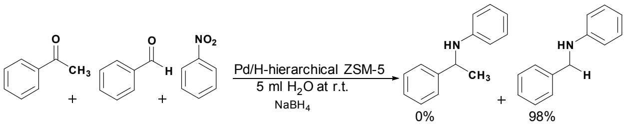


**Figure 13.** Heterogeneity test for direct one-pot reductive amination.

Under the optimized reaction conditions, the scope of the reaction was explored with structurally and electronically diverse aldehydes with a wide range of nitroarenes. Reactions were investigated at room temperature in water at different times, which mentioned in Table 6. The results show that all reactions are almost completed within 17 to 45 min at room temperature (Table 6). The reaction rate goes up by the decrease electron density at the nitro group with locating electron-withdrawing group on the nitro aromatic ring (entry 2). On the other hand, electron-donating groups show the reverse effect and cause the reaction rate decreased (entries 3 and 4). Actually, by decreasing the electron density of the nitro groups, the tendency of nitro groups to accept the hydride ions is increased. In contrast, the existence of electron-donating groups on the benzaldehyde ring cause increases in the reaction rate (entries 5 and 8). Actually, the electron-donating groups stabilize the protonated carbonyl bond intermediate and cause an increase in the reaction rate.

Additionally, the direct reductive amination from nitroarene was performed on a 20-time scale-up (Table 6, entry 9), which the results represent the high activity of the catalyst.

As shown in Scheme 2, this process is highly selective for the preparation of amines from aldehydes in the presence of ketones and only secondary amines of the aldehydes is produced.



**Scheme 2.** Selective reductive amination of aldehyde from nitroarenes.

According to the results, it can be found that the catalyst afforded an average to excellent yields of the amine products. Compared with the other studies on the tandem reductive amination of aldehydes the significant advantages of our method are:[7-9,11-15,58-60]

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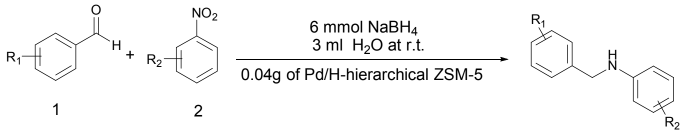
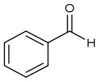
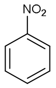
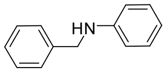
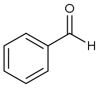
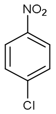
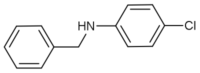
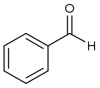
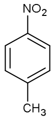
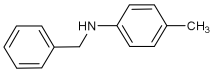
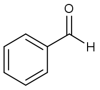
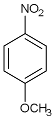
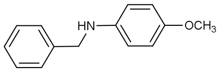
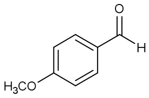
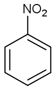
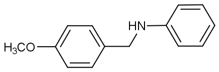
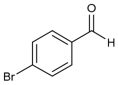
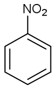
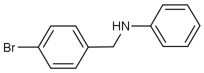
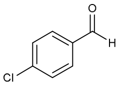
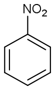
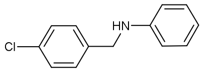
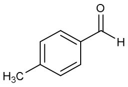
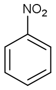
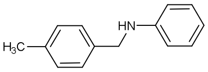
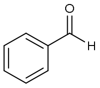
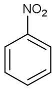
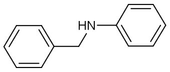
**Table 6.** Direct one-pot reductive amination of aldehydes with nitroarenes over Pd/H-hierarchical ZSM-5.[a]



| Entry | 1 | 2 | Product | Yield (%)[b] | Time (min) | TON/TOF ($h^{-1}$)[c] |
|---|---|---|---|---|---|---|
| 1 |  |  |  | 98 | 20 | 148/443 |
| 2 |  |  |  | 98 | 17 | 148/521 |
| 3 |  |  |  | 92 | 30 | 138/277 |
| 4 |  |  |  | 96 | 35 | 144/248 |
| 5 |  |  |  | 96 | 10 | 144/867 |
| 6 |  |  |  | 97 | 27 | 146/325 |
| 7 |  |  |  | 96 | 35 | 144/248 |
| 8 |  |  |  | 95 | 15 | 143/572 |
| 9 |  |  |  | 90[d] | 45 | 135/181 |

[a] Reaction conditions: aldehyde (2 mmol), nitro aromatic compound (2 mmol), $NaBH_4$ (6 mmol), Pd/H-hierarchical ZSM-5 (0.04 g) and $H_2O$ (3 mL) at room temperature. [b] Isolated yield after work-up. [c] Turn-over number (mol product/mol Pd) and turn-over frequency (mol product/(mol Pd.h)). [d] Scale-up condition: benzaldehyde (40 mmol) , nitrobenzene (40 mmol) , catalyst (0.80 g), $NaBH_4$ (120 mmol) and $H_2O$ (150 mL) at room temperature.

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- The use of water as a green solvent;
- Green and simple reaction system;
- The fast reaction rate with high TOF and TON;
- The use of very low amount of catalyst and $Pd(OAc)_2$;
- The reaction was performed under mild conditions at room temperature;
- The use of heterogeneous catalyst and elimination of toxic reagents;
- Wide substrate scope and generality;
- The catalyst is highly selective and versatile;
- Expensive and toxic ligands are not needed;
- The high yields of the products;
- According to the XPS and UV-vis results, the synthesized palladium nanoparticles by this method are quite stable and can be kept under an inert atmosphere for several months.
- The reactions are relatively more environmentally friendly with easy and efficient recyclability of the catalyst.

These advantages make the present method to be considered as a convenient alternative method for the reductive amination of aldehydes. Also, these advantages make this methodology attractive for the development of large-scale industrial synthesis.

## 4. CONCLUSIONS

In one word, we have developed a simple and highly efficient and eco-friendly method for one-pot reductive amination using a stable and recoverable catalyst that immobilized Pd on hierarchical zeolite under mild conditions. The existence of both acid and metal in the structure of Pd/H-hierarchical ZSM-5 as a bi-functional heterogeneous catalyst plays an important role to conduct this tandem reaction in one-pot. Moreover, this method can be used to produce a variety range of amines in good to excellent yields. This catalyst exhibits high activity/stability even after six cycles. It offers an economical and clean method for the one-pot synthesis of amines from nitrobenzenes and attractive for the development of large-scale industrial synthesis.

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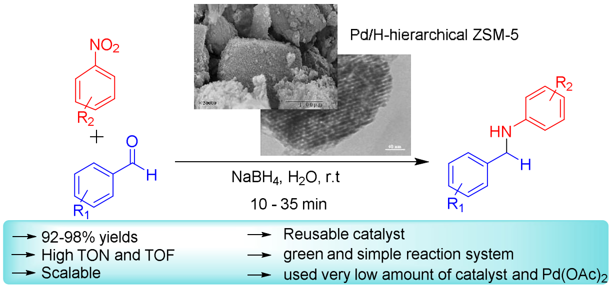
# Table of Contents

Palladium nanoparticles embedded hierarchical zeolite acts as acid-metal bi-functional catalyst for efficient reductive amination of aldehyde from nitroarenes.

# graphical abstract



→ 92-98% yields
→ High TON and TOF
→ Scalable
→ Reusable catalyst
→ green and simple reaction system
→ used very low amount of catalyst and $Pd(OAc)_2$