Catal Lett (2008) 124:268–276
DOI 10.1007/s10562-008-9452-2

A Green Reduction of Aromatic Nitro Compounds to Aromatic Amines Over a Novel Ni/SiO_2 Catalyst Passivated with a Gas Mixture

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Received: 14 January 2008 / Accepted: 20 February 2008 / Published online: 14 March 2008

Abstract An efficient, mild and practical method for the reduction of aromatic nitro compounds using Ni/SiO_2 as catalyst is reported. The catalyst has been prepared and characterized by XRD, FT-IR, TEM, SEM successfully. The Ni loading is about 55 wt.%. The prominent merit of the Ni/SiO_2 catalyst passivated with a gas mixture is that it can be stored safely in air below 423 K and needs no activation before use. In the catalytic test, Ni/SiO_2 is found to be a highly efficient and reusable catalyst for the reduction of various aromatic nitro compounds. This catalyst is applicable for the preparation of various aromatic amines with different groups, the conversion and selectivity are almost up to 100%. Moreover, it is inexpensive, can be prepared and scaled up easily.

Keywords Ni/SiO_2 · Passivated · Aromatic nitro compounds · Aromatic amines · Catalytic hydrogenation

1 Introduction

Aromatic nitro compounds are important intermediates for agrochemicals, pharmaceuticals, dyestuffs, urethanes and other industrially important products [1–3]. The oldest and industrially practiced method is the Bechamp reduction [4], which has a history of 150 years up to now.

Nowadays, numerous methods for the reduction of aromatic nitro have been reported in the literatures, such as catalytic hydrogenation [5–20], catalytic transfer hydrogenation [21–29], CO/H_2O conditions [30–32] and other reduction systems [33–48]. The important developed catalytic systems are listed as follows, MCM-41-silylamine palladium(II)/THF[5],poly(4-vinylpyridine-co-N-vinylpyrrolidone)-Pd (0)/EtOH [6], Au/SiO_2/EtOH [7], nanosized nickel/EtOH [8], Au-Pt-NH_2-Si-MCM-41/CH_3OH [9], Au/Al_2O_3 [10], silica sol–gel encaged Pd-[Rh(cod) Cl]$_2$/n-heptane [11], nanosized NiCoB amorphous alloy/CH_3OH [12], PSF-Pd/DMF [13], Ni/SiO_2 [14], PVPA-Pd/EtOH/KOH [15], zero-valent iron powder/CH_3CN/phosphate buffer [16], Au/TiO_2 or Au/Fe_2O_3 [17, 18], Co-colliod or NiPd-colliod/THF [19], Au/ZrO_2/EtOH [20], $LaMO_3$/KOH/propan-2-ol [21], $La_{1-x}Sr_xFeO_3$/KOH/propan-2-ol [22], Co(II)/mesoporous aluminophosphate/KOH/iPrOH [23], Ni-MCM-41/iPrOH/KOH [24], hydrazine hydrate/ferrihydrite/EtOH [25], Polymer-Supported Formate and Magnesium/MeOH [26], Polymer-Supported Formate/Pd-C/ MeOH [27], CeO_2–SnO_2/hydraine/MeOH [28], Heteropolyacid/MeOH/N_2H_4 [29], $RhCl_3$/CO/H_2O [30], $Ru_3(CO)_{12}$/CO/H_2O [31], Se/NaOAc/DMF/CO/H_2O [32], Sm/NH_4Cl,MeOH/ultrasound [33], $N_2H_4{\cdot}H_2O$/Fe_xO_y/EtOH [34], $NaBH_4$/Raney nickel/CH_3OH [35], Raney Ni/$N_2H_4{\cdot}HCOOH$/CH_3OH [36], Zn/ammonium salts/ionic liquids/H_2O [37], P-[(phpy)(CO)$_2$ RuCl]$_2$/DMF [38], HI [39], S8/$NaHCO_3$/DMF [40], $N_2H_4{\cdot}H_2O$/EtOH [41], Microwave/Alumina-Supported Hydrazine/$Fe(NO_3)_3{\cdot}9H_2O$ [42], KF/PMHS/Pd(OAc)$_2$/THF/H_2O [43], Mn/$CuCl_2$/THF/H_2O [44], Sm/I_2/CH_3OH [45], In/NH_4Cl/H_2O/EtOH [46], $FeCl_3$/Zn/DMF/H_2O [47], FeS/NH_4Cl/H_2O/MeOH [48], Mg–Fe Hydrotalcite/$N_2H_4{\cdot}H_2O$/MeOH [49]. However, some difficulties is still existed, such as (1) seriously environmental pollution from residue, (2) expensive or

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sensitive to air, (3) significant limitations based on safety and handling considerations, (4) strong acidic or alkaline media, (5) the reaction conditions of most of these methods can destroy many sensitive functional groups.

With the increasing interest in human health and environmental protection, more attention is being paid to "green chemistry". Therefore, it is necessary to develop an efficient, mild and practical method for the reduction of aromatic nitro compounds.

To our knowledge, the catalytic reduction of nitro groups using passivated Ni/SiO_2 catalyst has not been reported before. In this paper, we report a high efficient and environmentally friendly method for preparing aromatic amines by the reduction of aromatic nitro compounds, using a novel Ni/SiO_2 catalyst passivated with a gas mixture. The major advantage of this catalyst is that it can be stored safely in air below 423 K and needs no activation before use. Additionally, other merits of our catalytic systems are as follows, (1) this catalyst can be easily prepared and is low-cost; (2) the mild reaction conditions (about 383 K, 2.5 MPa); (3) the catalytic system is environmentally friendly, using ethanol as sole solvent, without remnants of chemical; (4) in most cases, the product can be conveniently separated using filtration or magnetic separation; (5) high conversion and selectivity can be obtained, almost without by-products; (6) it can be reused five times without loss of catalytic activity; (7) sensitive functional groups, such as –OH, –Cl, –CH_3, –CHO, –CH_2OH, –$COCH_3$, –OCH_3 and –$NHCOCH_3$, remain unaffected in the reaction condition.

2 Experimental

2.1 The Preparation of Ni/SiO_2 Catalyst

Some commercial diatomite is added to an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1.0 mol/L nickel nitrate solution) and stirred for 1 h at 323 K. 10 mL monodisperse silica sol is added into the above mixture and stirred for 1 h. Then, an aqueous solution of $(NH_4)_2CO_3$ is dropped. After stirring for 20 h, the resulting solid is filtered, washed, extruded forming, dried at 333 K for 24 h and crushed to powder. Finally, the sample is reduced in H_2 for 4 h at 773 K, and passivated with a gas mixture (3% N_2 in air) until it is cooled to room temperature. The Ni loading is about 55 wt.% and the BET is 180 m^2/g.

2.2 Characterization of the Catalyst

The content of nickel in Ni/SiO_2 was determined by atomic absorption spectroscopic analysis on a varian-AA240 spectrometer. Total surface area determination was performed in a Micromeritics ASAP 2010. Powder X-ray diffraction (XRD) for samples was measured with XRD-6000 diffractometer made in Japan, using Cu Kα radiation ($\lambda = 0.15418$ nm). TEM measurements were taken on a Hitachi-600 electron microscope, and samples were suspended in ethanol and ultrasonically dispersed. SEM-EDAX measurements were taken on a Hitachi S-4800 electron microscope. Fourier transform infrared (FT-IR) spectra was recorded with a Nicolet NEXUS 670 FT-IR instrument with a DTGS detector.

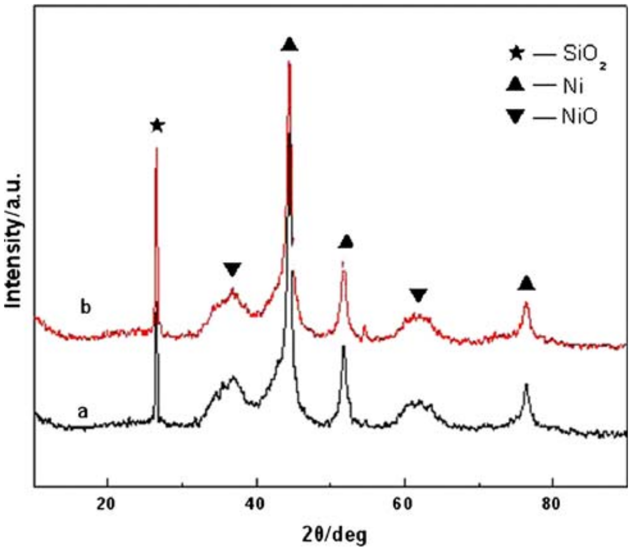

Fig. 1 The XRD patterns of Ni/SiO_2 catalysts. (**a**) Fresh catalyst; (**b**) reused catalyst (after five times use)

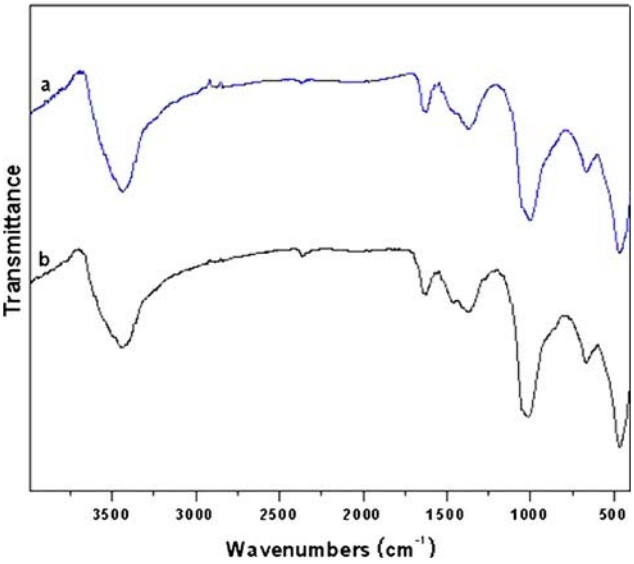

Fig. 2 FT-IR spectra of Ni/SiO_2 catalysts. (**a**) Fresh catalyst; (**b**) reused catalyst (after five times use)

2.3 General Procedure for the Catalytic Test

The catalytic hydrogenations were carried out in a 100 mL stainless steel reactor equipped with a magnetic stirrer. In a typical reaction procedure, substrates (1.0 g) and 20 mL ethanol (solvent) were mixed with passivated Ni/SiO_2 catalyst (0.1 g). The reactor was flushed three times with 0.5 MPa H_2 and pressurized to the desired pressure. Then, it was heated to the desired temperature in an oil bath with stirring. After reaction, the reactor was cooled in an ice-water bath and then slowly depressurized. Finally, the catalyst was separated, and the reactants and products were

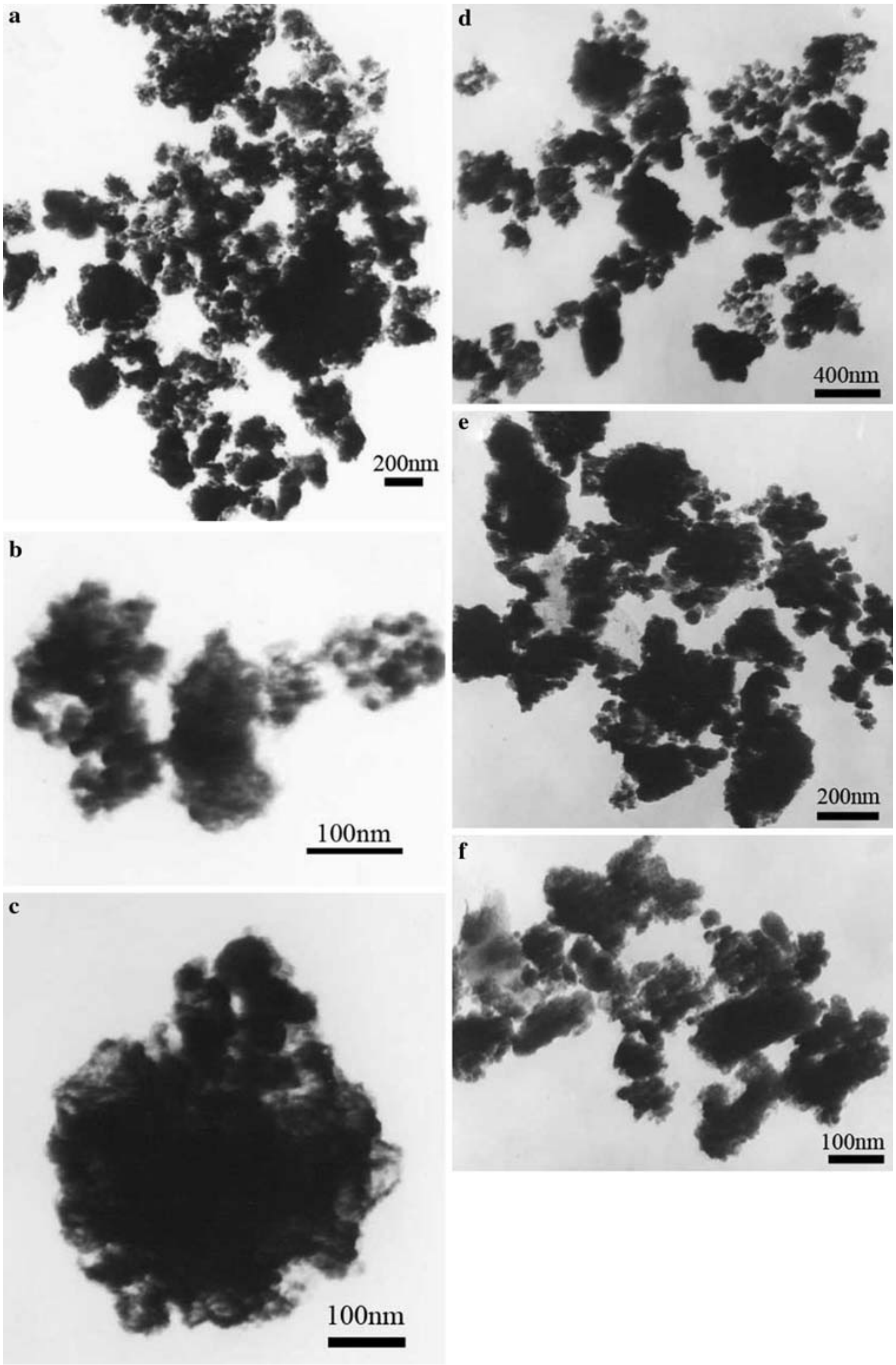

Fig. 3 TEM images of Ni/SiO_2 catalysts a, b, c: fresh catalyst; d, e, f: reused catalyst (after five times use)

analyzed by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6890N/5973N).

3 Results and Discussion

3.1 Catalyst Characterization

Figure 1 illustrates the wide-angle powder XRD patterns (in the 2θ range of 10–90°) of the fresh Ni/SiO_2 (Fig. 1a) and the reused one (Fig. 1b). The fresh Ni/SiO_2 shows three diffraction peaks in the 2θ of 44.3, 51.7, and 76.3, which correspond to metallic nickel. The peaks attributed to nickel oxide are observed at 36.7 and 61.2 in 2θ, and the peak attributed to SiO_2 is observed at 26.7 in 2θ. The result is basically consistent with the related reports in characterization [50]. In addition, there exist no other peaks, indicating the interaction of the Ni and carrier SiO_2 is weak. By comparing the XRD pattern of the reused Ni/SiO_2 with that of the fresh one, we find that the structure of the catalyst does not change significantly after multiple repeated uses, indicating the catalyst is stable and can be reused.

Figure 2 shows the IR spectra of the fresh and reused Ni/SiO_2 catalysts in the wave range from 4000 to 400 cm^{-1}. In the spectrum of the fresh Ni/SiO_2, the maximal absorptions at 1002, 663 and 468 cm^{-1} are attributed to an anti-symmetric stretch, symmetric stretch and bending mode of Si–O–Si, respectively. The strong and wide absorption band at 3429 cm^{-1} of the catalyst samples indicates that there are plenty of –OH groups on the surface of the Ni/SiO_2 catalyst. The presence of Si–OH shows that the sample does not have a completely condensed network. The band at 1625 cm^{-1} is attributed to adsorbed water, which is basically similar to the related reports [51]. By comparing the spectrum of the reused Ni/SiO_2 with that of the fresh one, we find there is not noticeable changes in Fig. 2a and b, which agrees with the above XRD analysis.

The representative electron micrographs (TEM) of the Ni/SiO_2 catalysts samples are presented in Fig. 3. We can find that the catalyst is mainly in amorphous phase, agglomerates partially, and there exists large amount of interspersed particles, including the interspersed Ni and NiO particles. The diameter of the Ni/SiO_2 powder is about 30 nm. Moreover, compared the TEM of the reused Ni/SiO_2 with that of the fresh one, we find that no remarkable change occurs in the bulk structure of the catalyst due to the repeated uses. This result suggests that the catalyst is stable during reaction.

Usually, SEM is used to determine the particle size and particle morphology of the synthesized sample. The representative scanning electron microscopy (SEM) of the Ni/SiO_2 catalyst samples were presented in Fig. 4. It is clear that most of the catalyst particles are in good dispersibility, although some agglomerates are detected. From SEM, we can see that the diameter of the main spherical particles are about 10 um.

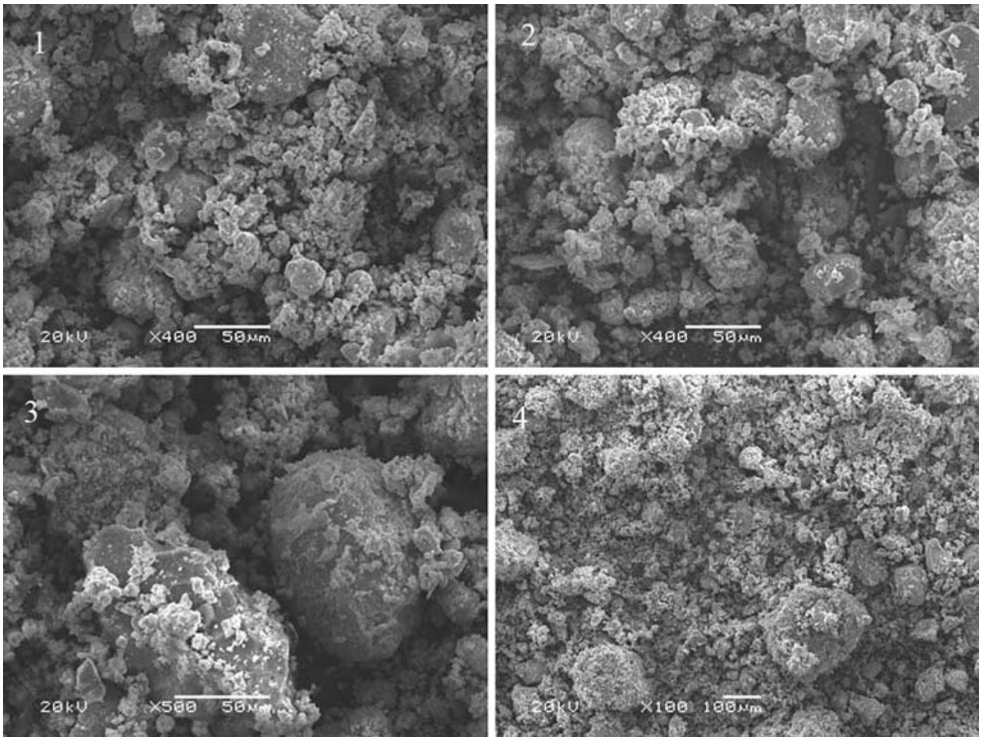

Fig. 4 SEM images of Ni/SiO_2 catalyst (fresh catalyst)

Table 1 Catalytic hydrogenation of various aromatic nitro compounds over Ni/SiO$_2$[a]

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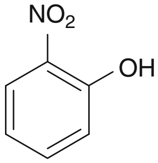
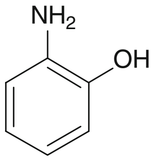
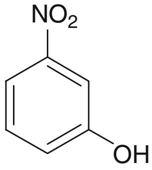
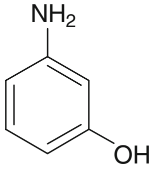
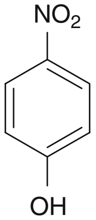
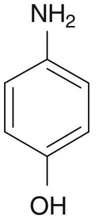
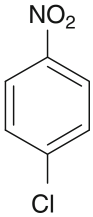
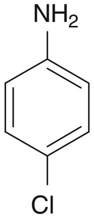
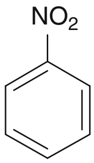
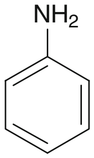
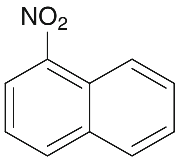
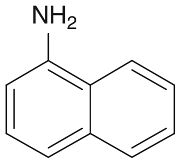
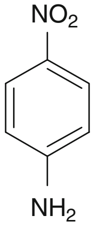
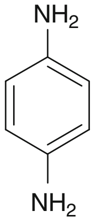
1			7	2.5	100	100
2			7	2.5	100	100
3			7	2.5	100	100
4			7	2.5	100	93.5
5			7 10	2.5 2.5	100 100[b]	100 100[b]
6			7	2.5	100	100
7			8	2.5	100	100

Table 1 continued

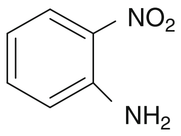
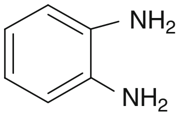
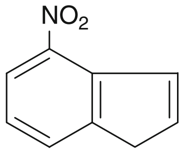
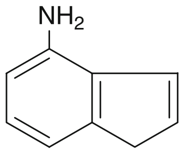
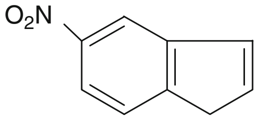
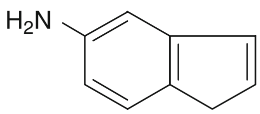
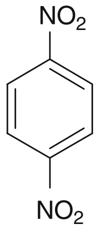
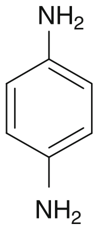
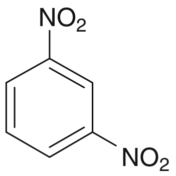
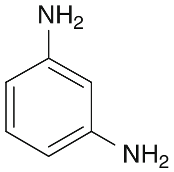
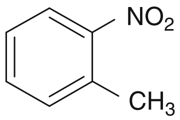
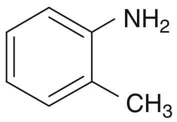
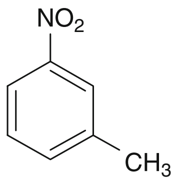
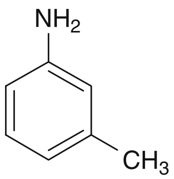
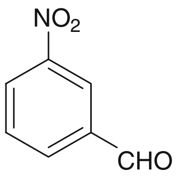
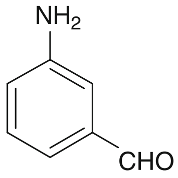
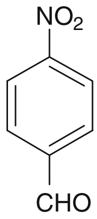
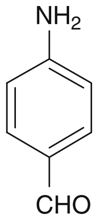
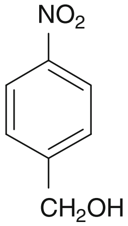
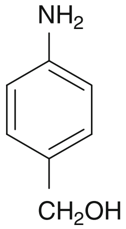
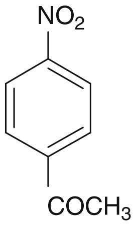
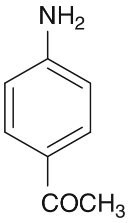
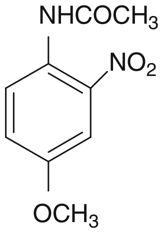
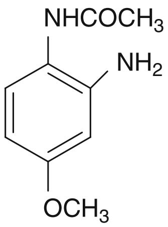
Entry	Substrate	Product	Time (h)	Pres. (MP)	Conv. (%)	Sel (%)
8			8	2.5	100	100
9			8	2.8	100	100
10			8	2.5	100	100
11			9	3	100	100
12			9	3	100	100
13			7	2.5	100	99.3
14			7	2.5	100	99.5

Table 1 continued

Entry	Substrate	Product	Time (h)	Pres. (MP)	Conv. (%)	Sel (%)
15			6	2	100	100
16			6	2	100	90.1
17			6	2	100	99.1
18			7	2.5	100	82.1
19			7	2.5	100	100

[a] Reaction conditions: 0.1 g catalyst, 1.0 g substrate, 20 mL ethanol, 383 K

[b] Reused catalyst (after five times uses)

3.2 Catalytic Hydrogenation of Aromatic Nitro Compounds to Aromatic Amines Over the Novel Ni/SiO_2 Catalyst

Table 1 shows the catalytic hydrogenation results of various aromatic nitro compounds over Ni/SiO_2 catalyst.

In most cases, the reaction condition (383 K, 2.5 Mpa, 6–7 h) was sufficient to give satisfactory conversion and selectivity. In our study, the passivated Ni/SiO_2 catalyst can reduce various kinds of aromatic nitro compounds easily and achieve excellent conversion and selectivity, though the substrates have some sensitive functional groups, such as –OH, –Cl, $–CH_3$, –CHO, $–CH_2OH$, $–COCH_3$, $–OCH_3$ and $–NHCOCH_3$.

High selectivity of aromatic amines is achieved while using the passivated Ni/SiO_2 as catalyst, and the probable reason is that the passivated Ni/SiO_2 catalyst has lower activity and doesn't destroy sensitive groups in comparison with other reported catalysts, such as Raney Ni, Pd(0) and Pd/C [5, 6, 8, 11, 13, 27, 35, 36]. Different from that reported in some previous work [35], higher selectivity for aromatic aldehydes is obtained (entry 15,16) using the passivated Ni/SiO_2 catalyst. Meanwhile, dinitro compounds (entry 11, 12) are also reduced with high conversion and selectivity, and this result is better than previous work [7]. There is only slight dechlorination (entry 4) in our case. However, we can also find that the selectivity for some aromatic amine (entry 4, 16, 18) is not very high while using the passivated Ni/SiO_2 as catalyst. Moreover, the selectivity of 82.1% is obtained in the case of entry 18, which is lower than that reported in Ref. [7]. Maybe our experiment condition is slightly high for entry 18, some ketone reduced to alcohol.

It should be pointed out that the novel Ni/SiO_2 catalyst passivated with a gas mixture need no activation before use and is reported to do this job for the first time. The reaction conditions employed in our study is relatively mild for the reduction of the aromatic nitro compounds compared with other reported systems, which need high pressure or the medium of acid and alkali [4, 15, 21–24]. This catalyst shows higher chemoselectivity for aromatic amine than other reported catalysts, is easily scaled up and applicable for preparing different substituted aromatic amines on a large scale.

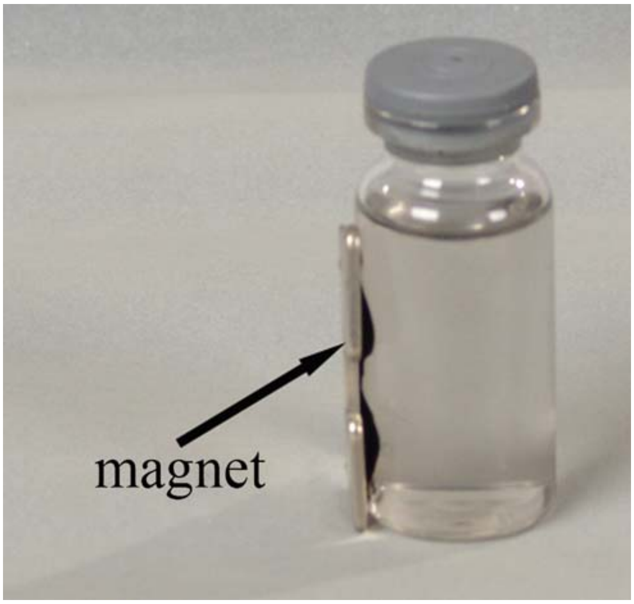


Fig. 5 Magnetic recovery of the Ni/SiO_2 catalysts

3.3 Catalyst Recycling Tests

From Fig. 5, we can see that the Ni/SiO_2 catalyst shows obvious magnetism. It can be separated from a reaction mixture easily in a relatively low magnetic field by using a small laboratory magnet and recovered quantitatively by simply filter. Moreover, after magnetic recovery, the catalyst can be dispersed readily for further use. The catalyst recycling experiment demonstrates that the conversion and selectivity are almost unchanged after using five times (Table 1, entry 5^b).

4 Conclusion

In summary, an efficient, mild and practical method for the reduction of aromatic nitro compounds employing Ni/SiO_2 catalyst is reported. The novel passivated Ni/SiO_2 catalyst has an excellent conversion and selectivity for the hydrogenation of aromatic nitro compounds. This catalytic system is simple, inexpensive, easily scaled up and applicable for preparing different substituted aromatic amines on a large scale.

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