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One-pot synthesis of aluminum oxyhydroxide matrix-entrapped Pt nanoparticles as an excellent catalyst for the hydrogenation of nitrobenzene

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Aluminum oxyhydroxide matrix-entrapped Pt nanoparticles (Pt/AlO(OH)) were synthesized *via* a one-pot procedure, by the reduction of Pt^{4+} followed by the hydrolysis of $Al(O\text{-}sec\text{-}Bu)_3$. Small and well-dispersed Pt nanoparticles were entrapped into an aluminum oxyhydroxide matrix and confirmed by TEM characterization. FTIR analysis indicated that the Pt/AlO(OH) catalyst had a large amount of surface hydroxyl groups, which potentially improves its dispersibilty in aqueous solution. The as-prepared catalyst was used for the hydrogenation of nitrobenzene to aniline at 30 °C and atmospheric hydrogen pressure. Compared with other alcohol–water media, the hydrogenation reaction in a methanol–water medium exhibited a maximum turnover frequency (TOF) of 3620 h^{-1}. A complete conversion of nitrobenzene with a selectivity of 99.0% was obtained with an increase of time to 150 min.

Introduction

Aniline has been recognized as an attractive intermediate for the production of polyurethanes, dyes, pharmaceuticals, explosives and other fine chemicals.[1] In comparison with the other techniques that have been employed for the production of aniline, the catalytic method is gaining increasing attention since it is considered to be the "green" pathway, with the combined advantages of environmental friendliness and atom economy. Especially, the catalytic hydrogenation of nitrobenzene (NB) to aniline in an aqueous solution using transition or noble metals as catalysts, is the subject of the most extensive studies. Water, the most benign, abundant and inexpensive media, can be used as a solvent or additive for a wide range of chemical transformations, particularly hydrogenation. A number of groups have demonstrated that the addition of water into the reaction system can significantly improve the catalytic performance of heterogeneous catalysts. For example, Pietrowski *et al.*[2] found that the addition of water in methanol can significantly increase the activity of a Ru/MgF_2 catalyst. Very recently, Zhao and co-workers[3] studied the effect of water on the hydrogenation of *o*-chloronitrobenzene over Pt/C and Pd/C catalysts in ethanol, *n*-heptane and compressed carbon dioxide at 35 °C and 4.0 MPa H_2. In a previous study,[4] we also found that hydrous zirconia-supported Ir NPs exhibited an excellent catalytic activity and selectivity for the hydrogenation of haloaromatic nitro-compounds. This was attributed to the formation of hydrogen bonds between the substrate and the hydroxyl groups, to activate the N=O bond in the nitro group.[4] It was proposed that the carriers of catalysts with abundant hydroxyl groups would exhibit a higher activity and selectivity in the presence of water.

Among the catalysts that have been employed, a number of supported noble and non-noble transition metal NPs (*e.g.* Ru,[2,5–7] Pt,[1,8–13] Pd[14–17] and Ni[18–22]) have been synthesized for the production of aniline from the hydrogenation of nitrobenzene, among which Pt-based catalysts are highly valued. Apart from the commonly used supports, a variety of carriers such as gum acacia,[23] reduced graphene oxide (RGO),[12] and carbon nanotubes[1] have been explored in recent years, to deposit Pt as an effective catalyst in the hydrogenation of NB. Despite the advantage of convenience, most of the Pt-supported catalysts prepared by the impregnation method lack adhesion between the Pt particles and the support, which severely affects their interaction and inhibits further enhancement of their catalytic properties. Thus, improving the adhesion between the Pt particles and the support is strongly related to the further exploration of the catalytic potentials of Pt catalysts for the hydrogenation of nitrobenzene. Up to now, this has still remained a big challenge.

Bearing this in mind, we propose our work, which involves the preparation and characterization of AlO(OH)-supported Pt NPs with a smaller particle size, as well as the study of their catalytic properties. The Pt/AlO(OH) catalyst can be easily obtained through the entrapped Pt nanoparticles in the supporting AlO(OH) matrix, which was generated from the hydrolysis of $Al(O\text{-}sec\text{-}Bu)_3$. The catalytic performance of the

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Pt/AlO(OH) was investigated for the hydrogenation of NB, and was found to be excellent at 30 °C with atmospheric hydrogen pressure in a methanol–water medium.

The morphology of the as-prepared Pt/AlO(OH) was characterized by TEM and the results are illustrated in Fig. 1. The TEM image of the Pt/AlO(OH) exhibits a nanofiber profile which is characteristic for the aluminum oxyhydroxide matrix. High resolution transmission electron microscopy (HRTEM) was applied to detect the details of the Pt NPs. It can be seen that the Pt NPs are well dispersed on the aluminum oxyhydroxide matrix with a mean particle size of 2.0 nm. In the EDX analysis, the signals of Pt and Al were distinctly detected, and the loading of Pt was estimated to be 2.6 wt%, in agreement with the ICP results.

The XRD pattern of the Pt/AlO(OH) was also investigated. As can be seen from Fig. 2, the diffraction peaks appear at 28.2, 38.4, 40.5, 45.8, 49.3, and 65.2° which correspond to (021), (130), (111), (131), (002), and (200) Bragg diffractions of AlO(OH) (JCPDS no. 74-1895), respectively. Interestingly, no obvious diffraction signals have been detected for the Pt phase, possibly due to the small size and well-dispersing condition of the Pt particles.

The XPS elemental survey scans of the surface of the Pt/AlO(OH) show that the peaks corresponding to oxygen, carbon, platinum and aluminum are distinctly detected. High resolution XPS was carried out to determine the electronic state of the Pt in AlO(OH). As shown in Fig. 3, in spite of the partial overlap between the Al_{2p} and Pt_{4f} peaks, the resolution of the XPS measurement is high enough to distinguish the electronic state of Pt. The binding energies of the $Pt4f_{5/2}$ and $Pt4f_{3/2}$ levels in the catalyst are 74.0 and 77.7 eV respectively, which was attributed to the lower charge density of the Pt NPs. As it is well-known that $NaBH_4$ can reduce Pt^{4+} ions readily, the presence of a lower charge density of Pt NPs can be ascribed to the heating treatment of the as-prepared catalyst in the air, which is in agreement with the literature.[23] Moreover, the high yield of the desired product confirmed that most of the Pt NPs could be reduced during the hydrogenation process.

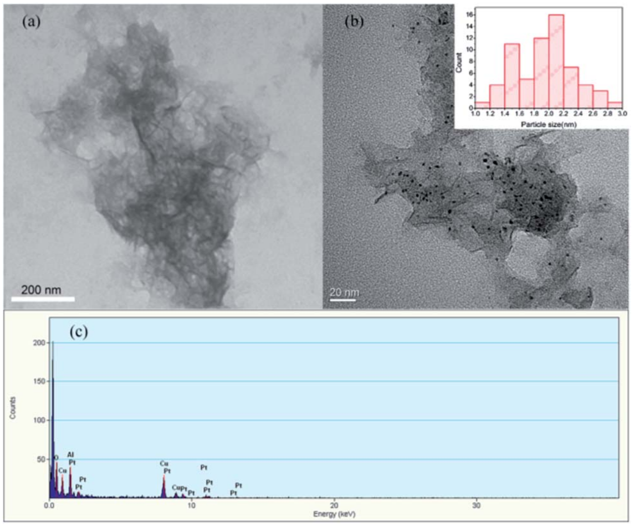


Fig. 1 (a) TEM image of Pt/AlO(OH), (b) HRTEM image of Pt/AlO(OH) (inset is the size distribution of the Pt nanoparticles) and (c) EDX of Pt/AlO(OH).

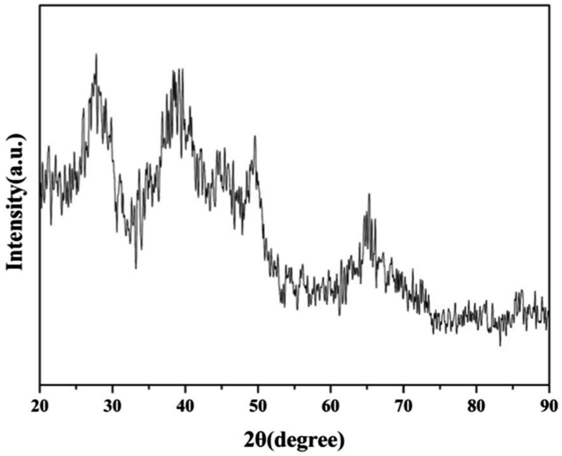


Fig. 2 XRD pattern of the Pt/AlO(OH) catalyst.

The surface functional groups of the Pt/AlO(OH) were detected and characterized by infrared spectroscopy. The results shown in Fig. 4 exhibit two strong peaks at 3439 and 1648 cm^{-1} which can be attributed to the stretching and bending modes of the adsorbed water,[24] indicating that the catalyst prepared by the hydrolysis of Al(O-*sec*-Bu)$_3$ contained a large amount of hydroxyl groups. The peak at 1067 cm^{-1} was attributed to the asymmetric stretching vibration of (OH)–Al═O,[24,25] and the peaks at 762 and 632 cm^{-1} were assigned to the bending of (AlO)–O–H and (OH)–Al═O,[25] respectively, indicating that the formation of the Pt/AlO(OH) was concomitant with the XRD results.

The catalytic properties of Pt/AlO(OH) were investigated by the hydrogenation of NB in a methanol–water mixture, at 30 °C and balloon hydrogen pressure. A blank test, or just an AlO(OH) catalyst, showed no activity toward NB hydrogenation, indicating that the Pt species provide the active sites for the reduction of NB. Fig. 5 shows the continuous conversion of NB with increasing reaction time. The conversion of NB reached

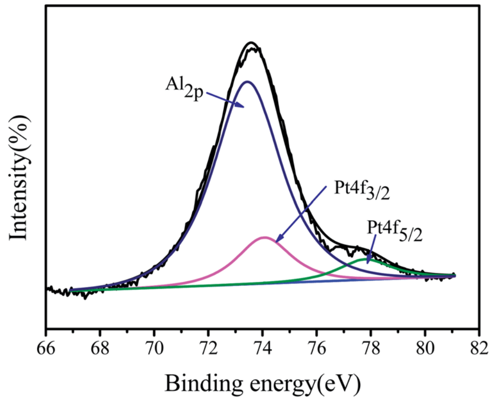


Fig. 3 XPS pattern of the Pt/AlO(OH) catalyst.

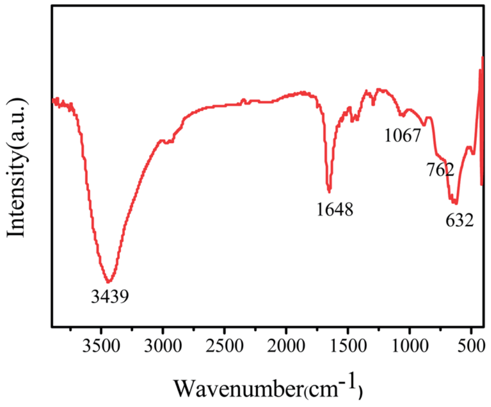


Fig. 4 FTIR pattern of the Pt/AlO(OH) catalyst.

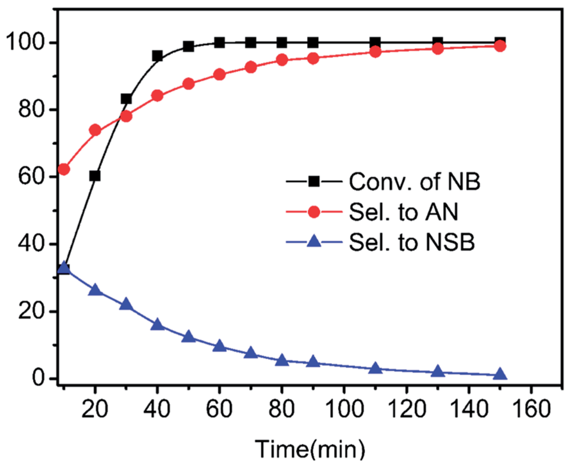


Fig. 5 Effect of reaction time on the hydrogenation of NB over Pt/AlO(OH).

99.0% with a 90.6% selectivity for AN within 60 min. The selectivity of AN increased to 99.0% as a result of the further hydrogenation of the intermediate NSB to AN, in a reaction time of 150 min. Apart from NSB no other by-products were detected, which contributed to a high yield of AN. Compared with the reported Pt-based catalytic systems, which are highly selective to the hydrogenation of nitrobenzene, the catalytic performance of the Pt/AlO(OH) in methanol–water medium is the best one. Sreedhar *et al.*[23] reported the synthesis of a Pt/GA catalyst for the hydrogenation of NB to AN in water; they could obtain a 88% yield of AN with a TOF of 52 h^{-1}, at room temperature under atmospheric pressure. Liu *et al.*[1] reported the solvent-free hydrogenation of NB to AN using Pt/MWCNTs as a catalyst. They could achieve a 100% conversion of NB and 100% selectivity to AN with the highest TOF of 66 900 h^{-1}. However, this reaction should be performed at 4.0 MPa H_2 and 60 °C. Later they reported the catalytic hydrogenation of NB over CeO_2 nanowire-supported Pt nanoparticles, which yielded a 92.0% conversion of NB and a 99.7% selectivity to aniline at 60 °C and 2 MPa H_2. However, the expensive equipment for the synthesis of the CeO_2 nanowires in supercritical CO_2-expanded ethanol hinders its application.[10] By using Pt/AlO(OH) as a catalyst, we can obtain a 99% yield of AN with a TOF of 724 h^{-1} at 30 °C under balloon hydrogen pressure.

Solvents strongly affect the catalytic properties of heterogeneous catalysts, and low boiling point alcohols such as methanol, ethanol and i-propanol *etc.* were commonly employed in the hydrogenation of nitro-compounds. Thereby, we investigated the catalytic performances of Pt/AlO(OH) in different media, including nonprotonic and protonic solvents. The results are illustrated in Table 1. Generally, when protonic alcohols were used as solvents, the Pt/AlO(OH) catalyst showed a higher activity and selectivity, whereas the activity and selectivity obtained in the nonprotonic solvents were not satisfactory. Particularly, the turnover frequency (TOF) achieved in the methanol solution was up to 3260 h^{-1}, which was much higher than that of other solvents. Thus, further investigations were focused on catalytic reactions carried out in the methanol medium.

Recently, several groups have reported that the addition of water into the lower boiling point alcohols can significantly enhance the catalytic performance of the catalysts. To this end,

Table 1 Hydrogenation of NB to AN over a Pt/AlO(OH) catalyst with different solvents[a]

Solvents	Conversion (%)	Selectivity (%) AN	NSB	Others	TOF[b] (h^{-1})
Methanol	72.6	78.0	18.9	3.1	3620
Ethanol	48.3	71.0	29.0	0	2412
n-Propanol	11.2	62.5	37.5	0	396
i-Propanol	21.8	56.9	41.2	1.9	1512
Ethyleneglycol	6.3	100	0	0	324
THF	7.7	62.0	38.0	0	360
1,4-Dioxane	6.0	9.0	91.0	0	324
Cyclohexane	49.6	98.8	1.2	0	2448
Hexane	28.3	95.9	4.1	0	1404

[a] *Reaction conditions*: 0.07 mol% of platinum; methanol–water solvent, 5 mL (volume ratio = 3 : 2); temperature, 30 °C; hydrogen pressure, 1 atm; time, 30 min. [b] Turnover frequency was calculated by the overall rate of nitrobenzene conversion normalized by the number of active sites over the specified time. The total active site number originated from the metal dispersion and all of the supported metal atoms. The Pt dispersion (D) was estimated by the equation: $D = 6(a_m/v_m)/d$, where the value of a_m/v_m was equal to 1.87 Angstrom,[3] and d was the average diameter of Pt estimated from TEM.

Table 2 Hydrogenation of NB to AN over a Pt/AlO(OH) catalyst in a mixed solvent of H_2O and methanol[a]

Water content (volume %)	Conversion (%)	Selectivity (%) AN	NSB	Others
0	72.6	78.0	18.9	3.1
20	76.5	76.3	20.3	3.2
40	83.3	78.1	21.9	0
60	78.9	76.4	14.8	8.8
80	66.3	90.0	10.0	0
100	37.7	92.5	7.5	0

[a] *Reaction conditions*: 0.07 mol% of platinum; methanol–water solvent, 5 mL (volume ratio = 3 : 2); temperature, 30 °C; hydrogen pressure, 1 atm; time, 30 min.

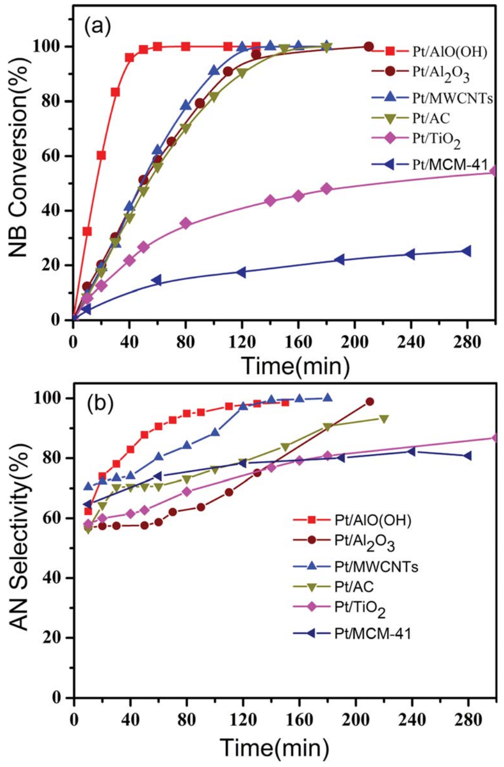


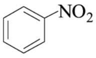
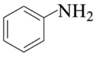
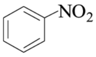
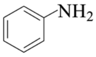
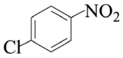
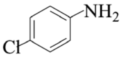
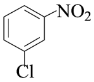
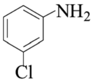
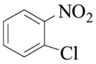
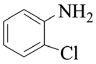
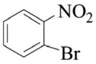
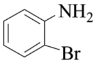
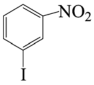
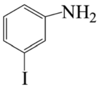
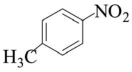
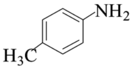
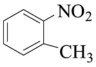
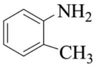
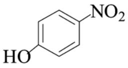
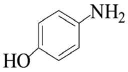
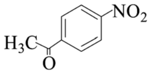
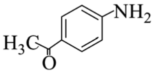
Fig. 6 Effect of different supports on the hydrogenation of NB.

the effect of water content on the hydrogenation of NB was also studied, with the results shown in Table 2. As can be observed, the hydrogenation of NB in pure methanol exhibited a conversion of 72.6% and a selectivity of 78.0%, with a large amount of intermediate nitroso-benzene (NSB) and other by-products. The conversion and selectivity for NB hydrogenation both increased when 20% of the methanol was replaced by H_2O. An even higher conversion of NB and selectivity to AN (83.3% and 78.1%) can be achieved in the 40% water and 60% methanol mixture. However, a negative effect on the catalytic activity of the Pt/AlO(OH) was detected when the water content was elevated to 60%. The conversion of NB was reduced to 37.7% when pure water was used as a solvent, with the highest selectivity to AN, at 92.5%. Similar phenomena have been witnessed and reported by other groups when studying the catalytic behavior of SiO_2 and active carbon (AC)-supported heterogeneous catalysts in alcohol–water mixtures.[3] Our results further confirmed that the addition of adequate water can improve the catalytic properties of the catalysts. The promotional effect of the water may be considered to arise from the interaction of the reactants through the hydrogen bonds and an enhanced solubility of hydrogen in the reaction medium. It was proposed that the formation of hydrogen bonds, such as OH⋯O and OH⋯N bonding between water and nitrobenzene, would weaken the N–O bond on nitrobenzene, hence facilitating the hydrogenation of the NO_2 group. Meanwhile, it is worth pointing out that the competition between water and methanol for surface adsorption may also contribute to the resulting high activity. Such competition may reduce the adsorption of methanol on the surface of the catalyst as the formation of a water film occurs on the surface of the hydrophilic catalyst. Further increasing the content of water in the reaction media, however, leads to a decrease of catalytic activity. This can probably be attributed to the reduced solubility of the hydrogen. With the decreasing solubility of the hydrogen, the rate determining step was constrained by the mass transfer of hydrogen, which resulted in a lower reaction rate.

It is well-known that the catalytic performance of the active species can be significantly influenced by the support in catalytic hydrogenation reactions. As a comparison, the catalytic properties of TiO_2, Al_2O_3, MWCNTs, MCM-41 and AC-supported platinum catalysts (these catalysts were prepared by an impregnation method with the same loading of Pt) were also investigated for the hydrogenation of NB, and the results are shown in Fig. 6. It can be seen that different carriers show varied catalytic behaviour for the hydrogenation of NB. In comparison with other supported catalysts, our synthesized Pt/AlO(OH) nanocomposites still hold first position in terms of both activity and selectivity. The hydrogenation rates increase in the order: Pt/AlO(OH) > Pt/MWCNTs > Pt/Al_2O_3 > Pt/AC > Pt/TiO_2 > Pt/MCM-41. Concerning the selectivity, Pt/AlO(OH) and Pt/MWCNTs exhibited a high selectivity for producing aniline in a short reaction time relative to the other counterparts. Typically, the selectivity in a reaction time of 90 min increases in the order: Pt/AlO(OH) > MWCNTs > Pt/MCM-41 > Pt/AC > Pt/TiO_2 > Pt/Al_2O_3.

We also surveyed the catalytic performance of Pt/AlO(OH) for hydrogenating other nitroarenes with electron-donating groups or electron-withdrawing groups. The results are shown in

Table 3 Hydrogenation of different nitroarenes over Pt/AlO(OH)[a]

Entry	Substrates	Product	Time[b] (min)	Selectivity (%)
1			150	99
2			150	98[c]
3			150	98
4			150	99
5			160	99
6			180	98
7			400	90
8			150	97
9			220	98
10			240	99
11			240	99

[a] *Reaction conditions*: 0.07 mol% of platinum; methanol–water solvent, 5 mL (volume ratio = 3 : 2); temperature, 30 °C; hydrogen pressure, 1 atm.
[b] Time needed for obtaining the maximum selectivity of the corresponding amines (all of the investigated substrates achieved 100% conversion).
[c] The Pt/AlO(OH) catalyst was reused five times.

Table 3. The catalyst shows excellent catalytic properties for the complete hydrogenation of the chloronitrobenzenes and *o*-bromonitrobenzene with a high yield of the corresponding amines of 98%. However, it should be noted that the hydrogenation of *m*-iodonitrobenzene requires a longer reaction time (400 min) for a 90% yield of *m*-iodoanline, which is probably attributed to the deactivation of the Pt nanocatalyst caused by the formation of I^- anions from the dehalogenation side reaction. Apart from that, the other substituted nitroarenes can be hydrogenated to the corresponding amines with a high yield and efficiency. The excellent catalytic activity of the Pt/AlO(OH) catalyst can probably be attributed to the following aspects: (1) the small Pt particle size with a higher dispersion enables more active sites to be available for the hydrogenation reaction; (2) the Pt/AlO(OH) catalyst with a large amount of hydroxyl groups, together with water as a solvent, facilitates the hydrogenation of NB through the activation of the N=O bonds in the NB.[2,4] In terms of the selectivity, owing to the large amount of hydroxyl groups on the surface of the support, a water film is formed. This makes desorption of the hydrogenated product AN from the active sites easy, prohibiting the side reaction between the methanol solvent and the AN. Therefore, a higher selectivity was observed in the present work.[4,26] The cycling catalytic test of the as-prepared Pt/AlO(OH) (Table 3) indicated its fine stability, with no loss of activity in the hydrogenation of the NB for five runs and with negligible leaching of Pt (0.11%, assessed by ICP).

Conclusions

In summary, Pt/AlO(OH) was synthesized by a facile one-pot process employing H_2PtCl_6 and Al(O-*sec*-Bu)$_3$ as precursors. It was applied for the catalytic hydrogenation of nitroarenes in a methanol–water medium under mild conditions. It can be seen that Pt nanoparticles are small and well dispersed on the AlO(OH) matrix. The Pt/AlO(OH) catalyst exhibited a much better catalytic performance than other Pt based catalysts prepared by impregnation method using common supports, such as MWCNTs, MCM-41, AC, TiO_2 and Al_2O_3. In addition, this material is quite stable and can be reused five times without loss of any activity and selectivity. This advanced composite material provides a kind of novel and effective catalyst with great promise for the hydrogenation of nitroarenes in practical applications.

Experimental

Catalyst preparation

All aromatic compounds (A.R.), solvents (A.R.), and reagents (A.R.) were used as received. Pt/AlO(OH) was prepared by a one-pot procedure from $H_2PtCl_6 \cdot 6H_2O$ and Al(O-*sec*-Bu)$_3$. Typically, $H_2PtCl_6 \cdot 6H_2O$ (250 mg), PVP (640 mg), ethanol (8.0 mL) and Al(O-*sec*-Bu)$_3$ (9.0 g) were added into a 100 mL round-bottom-flask equipped with a condenser. Then the mixture was heated to 50 °C and an ethanol solution of $NaBH_4$ (54 mg in 4.0 mL ethanol) was added drop by drop. Then 2.0 mL of water was quickly injected into the flask under vigorous stirring. The black suspension was further stirred for 30 min before cooling down to room temperature. The black solid was filtered, washed with acetone and dried in an oven at 120 °C for 1 h. The Pt content estimated by ICP was 2.6 wt%.

Characterization

Transmission electron microscopy (TEM) measurements were carried out on a JEOL model 2010 instrument operated at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/max-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) over the range of 10–90°. X-ray photoelectron spectroscopy (XPS, Kratos XSAM800) spectra were obtained using Al Ka radiation (12 kV and 15 mA) as an excitation source ($h\nu = 1486.6$ eV) and Au (BE Au4f = 84.0 eV) and Ag (BE Ag3d = 386.3 eV) as references. All binding energy (BE) values were referenced to the C1s peak of contaminant carbon at 284.6 eV. A Fourier transform infrared spectrum was recorded with a Nicolet 6700 (resolution 0.4 cm^{-1}) infrared spectrometer. All hydrogenation samples were analyzed by gas chromatography (Agilent 7890 A) with a FID detector and PEG-20M supelco column (30 m × 0.25 mm, 0.25 um film) and nitrogen was used as a carrier gas.

Activity test

The catalytic hydrogenation of nitrobenzene and other nitro-compounds was carried out in a 25 mL round-bottom flask equipped with a balloon. Typically, the procedure for the hydrogenation of nitrobenzene was as follows: the desired amounts of catalyst, nitroarenes (0.07 mol% of platinum), and solvent (5.0 mL) were charged to the flask. The reactor was vacuumed and flushed with pure hydrogen. Then the flask was put into a water bath. When the designated reaction temperature was reached, the stirring rate was adjusted to 1200 rpm in order to eliminate the mass transformation limitation and then the reaction time was counted. Aquilots of 0.1 mL were withdrawn at various time intervals and analyzed by gas chromatography.

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