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ARTICLE TYPE

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/AIO(OH)) was synthesized via a one-pot procedure from the reduction of Pt⁴⁺ and followed by the hydrolysis of Al(O-sec-Bu)₃. Small and well-dispersed Pt nanoparticles were entrapped into aluminum oxyhydroxide matrix confirmed by the characterization of TEM. FTIR analysis indicated that Pt/AIO(OH) catalyst had a large amount of surface hydroxyl groups, which potentially improve their dispersibility in the 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 methanol/water media exhibited the maximum turnover frequency (TOF) of 3620 h⁻¹. A complete conversion of nitrobenzene with a selectivity of 99.0 % was obtained with the elevation of the 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, catalytic method is gaining an increasing attention since it is considered to be the “green” pathway with combined advantages of environmental friendliness and atomic economy. Especially, catalytic hydrogenation of nitrobenzene (NB) to aniline in an aqueous solution using transition or noble metals as catalysts receives 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 catalyst Ru/MgF₂. Very recently, Zhao and co-workers³ 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 H₂. In a previous study⁴, we also found that the hydrous zirconia supported Ir NPs exhibited excellent catalytic activity and selectivity for the selective hydrogenation of haloaromatic nitro-compounds, which was attributed to the formation of hydrogen bond between substrate and the hydroxyl groups to activate the N=O bond in nitro group⁴. It was proposed that the carriers of catalysts with abundant hydroxyl groups would exhibit 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}, Pd¹⁴⁻¹⁷ and Ni¹⁸⁻²²) have been synthesized for the production of aniline from the hydrogenation of nitrobenzene, among which Pt-based catalysts are highly appreciated. Apart from the commonly used supports, a variety of carriers such as gum acacia²³, reduced graphene oxide (RGO)¹², carbon nanotubes¹, have been explored to deposit Pt as effective catalysts in the hydrogenation of NB in recent years. Despite of the advantage of convenience, most of the Pt supported catalysts prepared by impregnation method lack adhesion between the Pt particles and the support, which severely affect their interaction and further enhancement of the catalytic property. Thus to improve 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, still remains as a big challenge.

Bearing this in mind, we proposed our work involved the preparation and characterization of AIO(OH) supported Pt NPs with a smaller particle size as well as the study of their catalytic properties. The catalyst Pt/AIO(OH) can be easily obtained through the entrapped Pt nanoparticles into the support AIO(OH) matrix, which was generated from the hydrolysis of Al(O-sec-Bu)₃. The catalytic performance of Pt/AIO(OH) was investigated for the hydrogenation of NB. The catalyst exhibited excellent catalytic property for the hydrogenation of NB at 30 °C and atmospheric hydrogen pressure in a methanol/water media.

The morphology of the as-prepared Pt/AIO(OH) was characterized by TEM and the results are illustrated in Fig. 1. The TEM image of Pt/AIO(OH) exhibits a nanofiber profile which is characteristic for the aluminum oxyhydroxide matrix. A 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 signal 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.

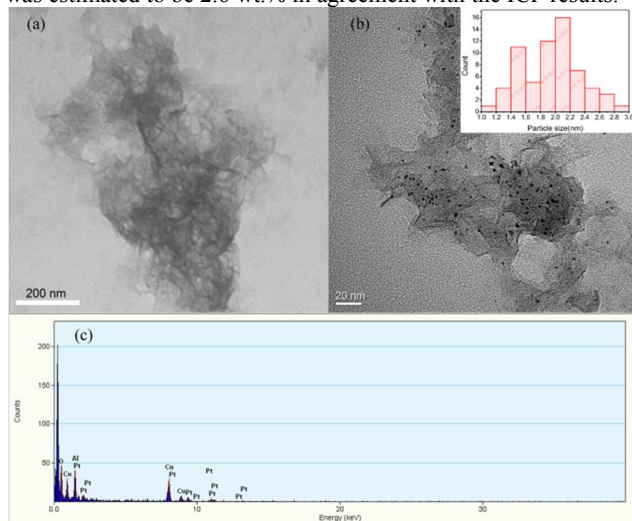


Figure 1 TEM image of (a) Pt/AIO(OH), (b) HRTEM image of Pt/AIO(OH) (inset is the size distribution of Pt nanoparticles) and (c) EDX of Pt/AIO(OH).

The XRD pattern of Pt/AIO(OH) also was 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 are corresponding 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 arising from the small size and well-dispersing condition of Pt particles.

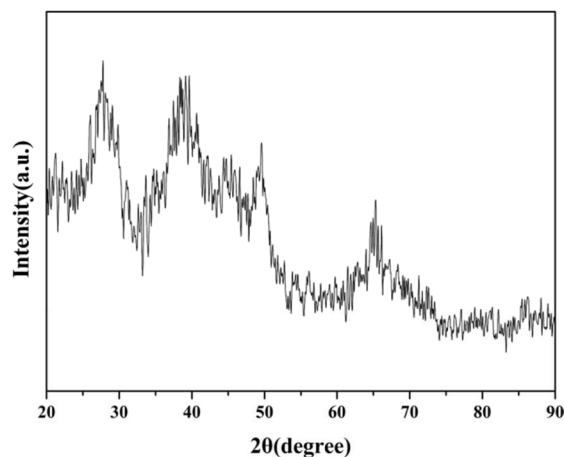


Fig.2 XRD pattern of catalyst Pt/AIO(OH)

The XPS elemental survey scans of the surface of the Pt/AIO(OH) shows 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 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 XPS measurement is high enough to distinguish the electronic state of Pt. The binding energy of $Pt_{4f_{5/2}}$ and $Pt_{4f_{3/2}}$ level in the catalyst is

74.0 and 77.7 eV respectively, which was attributed to the lower charge density of Pt NPs. As it is well-known that $NaBH_4$ can

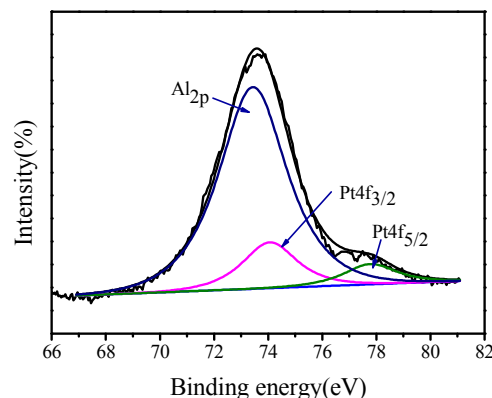


Fig.3 XPS pattern of catalyst Pt/AIO(OH)

reduce Pt^{4+} ion readily, the presence of 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 literature²³. Moreover, the high yield of the desired product confirmed that most of the Pt NPs could be reduced during the hydrogenation process.

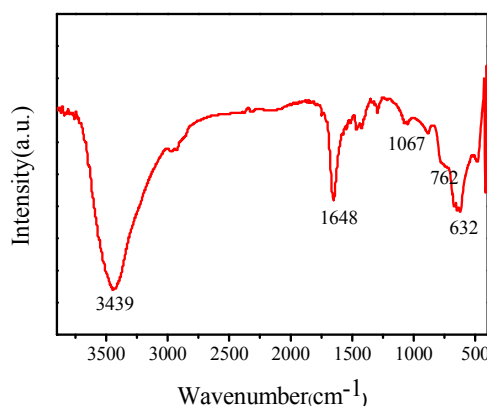


Fig.4 FTIR pattern of catalyst Pt/AIO(OH)

The surface functional groups of Pt/AIO(OH) was detected and analyzed by the characterization of infrared spectra. The characterized results showed in Fig.4 exhibited two strong peaks at 3439 and 1648 cm^{-1} which can be attributed to the stretching and bending modes of the adsorbed water²⁴, indicating that the catalyst prepared by the hydrolysis of $Al(O\text{-}sec\text{-}Bu)_3$ containing a large amount of hydroxyl groups. The peak at 1067 cm^{-1} was attributed to the asymmetric stretching vibration of $(OH)\text{-}Al=O$ ^{24, 25}, and the peaks at 762 and 632 cm^{-1} were assigned to the bending of $(AlO)\text{-}O\text{-}H$ and $(OH)\text{-}Al=O$ ²⁵, respectively, indicating that the formation of Pt/AIO(OH) concomitant with the XRD results.

Catalytic property of Pt/AIO(OH) was investigated by the hydrogenation of NB in methanol/water mixture at 30 °C and balloon hydrogen pressure. Blank test or only AlO(OH) as a catalyst showed no activity toward NB hydrogenation, indicating

that Pt species provide the active sites for the reduction of NB. Fig. 5 shows the continuous conversion of NB with the increase

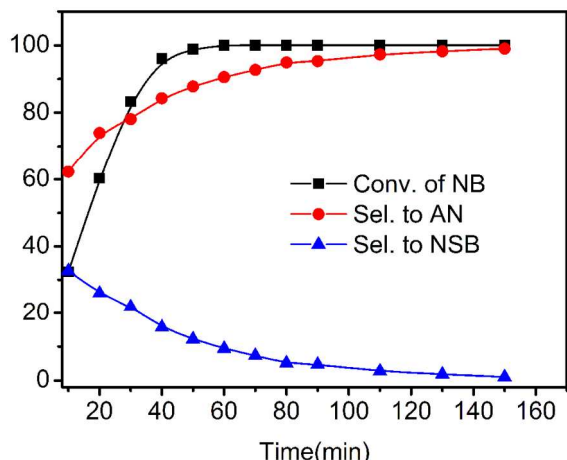


Fig. 5 Effect of reaction time on the hydrogenation of NB over Pt/AIO(OH)

of reaction time. The conversion of NB reached 99.0% with 90.6 % selectivity of AN was achieved within 60 min. The selectivity of AN increased to 99.0 % as a result of the further hydrogenation of the intermediate NSB to AN with 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 hydrogenation of nitrobenzene, the catalytic performance of Pt/AIO(OH) in methanol/water media is the best one. Sreedhar et al. [45] reported the synthesis of catalyst Pt/GA for the hydrogenation of NB to AN in water, they can 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 can achieve a 100 % conversion of NB and 100% selectivity to AN with the highest TOF of 66900 h⁻¹. However, this reaction should be performed at 4.0 MPa H₂ and 333 K. Later they reported the catalytic hydrogenation of NB over CeO₂ nanowires supported Pt nanoparticles, which yielded a 92.0 % conversion of NB and 99.7 % selectivity to aniline at 333 K and 2 MPa H₂, but the expensive equipments for the synthesis of CeO₂ nanowires in supercritical CO₂ expanded ethanol hinders its application¹⁰. By using Pt/AIO(OH) as a catalyst, we can obtained a 99% yield of AN and 724 h⁻¹ at room temperature under balloon hydrogen pressure.

Solvents strongly affect the catalytic property of heterogeneous catalysts, and low boiling point alcohols such as methanol, ethanol and *i*-propanol etc. were commonly employed in the nitro-compounds hydrogenation. Thereby, we investigated the catalytic performances of Pt/AIO(OH) in different media including the nonprotonic and protonic solvents and the results are illustrated in Table 1. Generally, when the protonic alcohols were used as solvent, the catalyst Pt/AIO(OH) showed relatively 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 can be 3260 h⁻¹, which was much higher than that of other solvents. Thus, further investigations were focused

on the catalytic reactions carried out in the methanol media.

Table 1 Hydrogenation of NB to AN over Pt/AIO(OH) catalyst with different solvents^a

| solvents | Conversion(%) | Selectivity (%) | | | TOF(h ⁻¹) ^b |
|----------------|---------------|-----------------|------|--------|------------------------------------|
| | | AN | NSB | Others | |
| 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; solvent methanol/water, 5 mL(volume ratio=3:2); temperature, 303 K; 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 sites number was 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 equal to 1.87 Angstrom [3], d was the average diameter of Pt estimated from TEM.

Table 2 Hydrogenation of NB to AN over Pt/AIO(OH) catalyst in mixed solvent of H₂O and methanol

| 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 |

Reaction conditions: Reaction conditions: 0.07 mol% of platinum; solvent methanol/water, 5 mL(volume ratio=3:2); temperature, 303 K; hydrogen pressure, 1 atm; time, 30 min.

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, the effect of water content on the hydrogenation of NB was also studied with results shown in Table 2. As can be observed, the hydrogenation of NB in pure methanol exhibited a conversion of 72.6 % and 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 % methanol was replaced by H₂O. Even higher conversion of NB and selectivity to AN (83.3% and 78.1%) can be achieved in the 40 % water and methanol mixture. However, a negative effect on catalytic activity of Pt/AIO(OH) was detected

when the content of water 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 of 92.5 % to AN. Similar phenomena have been witnessed and reported by other groups when studying the catalytic behavior of SiO₂ and active carbon supported heterogeneous catalysts in the alcohol/water mixtures. Our results further confirmed that the addition of adequate water can improve the catalytic property of the catalysts. The promoting effect of water may be considered from the interaction of reactants through the hydrogen bond and enhanced solubility of hydrogen in the reaction media. It was proposed that the formation of hydrogen bond 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 NO₂ group. Meanwhile, it is worth pointing out that the competition between water and methanol on surface adsorption may also contribute to the resulting high activity. Such competition may reduce the adsorption of methanol on the surface of catalyst as the formation of a water film on the surface of the hydrophilic catalyst. Further increasing the content of water in the reaction media, however, lead to a decrease of catalytic activity probably attributed to the reduced solubility of hydrogen. With the decreasing of solubility of hydrogen, the rate determining step was constrained by the mass transfer of hydrogen, which resulted in a lower reaction rate.

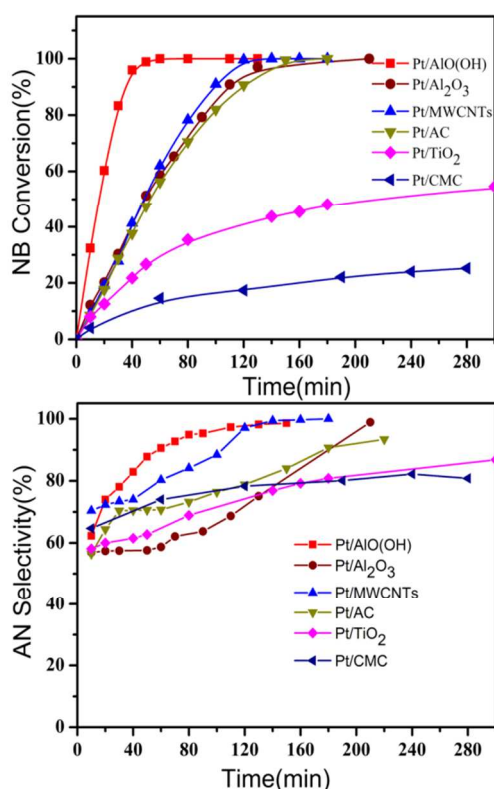


Fig. 6 Effect of supports on the hydrogenation of NB over Pt/AlO(OH)

It is well-known that the catalytic performance of the active species can be significantly influenced by the supports in the catalytic hydrogenation reactions. As comparison, catalytic properties of TiO₂, Al₂O₃, MWCNTs, CMC and AC supported

platinum catalysts (these catalysts were prepared by 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 manners for the hydrogenation of NB. In comparison with other supported catalysts, our synthesized Pt/AlO(OH) nanocomposites still holds the first position in terms of both activity and selectivity. The hydrogenation rates increase in the order: Pt/AlO(OH) > Pt/MWCNTs > Pt/Al₂O₃ > Pt/AC > Pt/TiO₂ > Pt/CMC. Concerning the selectivity, Pt/AlO(OH) and Pt/MWCNTs exhibited a high selectivity for producing aniline in a short reaction time relative of other counterparts. Typically, the selectivity in a reaction time of 90 min increase in the order: Pt/AlO(OH) > MWCNTs > Pt/CMC > Pt/AC > Pt/TiO₂ > Pt/Al₂O₃.

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

| Entry | Substrates | Product | Time (min) ^b | Sele. (%) |
|-------|------------|---------|-------------------------|-----------------|
| 1 | | | 150 | 99 |
| 2 | | | 150 | 98 ^c |
| 3 | | | 150 | 91 |
| 4 | | | 150 | 98 |
| 5 | | | 150 | 99 |
| 6 | | | 160 | 99 |
| 7 | | | 180 | 98 |
| 8 | | | 400 | 90 |
| 9 | | | 150 | 97 |
| 10 | | | 220 | 98 |
| 11 | | | 240 | 99 |
| 12 | | | 240 | 99 |

^a Reaction conditions: Reaction conditions: 0.07 mol% of platinum; solvent methanol/water, 5 mL (volume ratio=3:2); temperature, 303 K; hydrogen pressure, 1 atm; ^b Time for the obtaining the maximum selectivity of the corresponding amines (All of the investigated substrates achieved 100 % conversion); ^c The catalyst Pt/AlO(OH) was reused five times.

We also surveyed the catalytic performance of Pt/AlO(OH) for hydrogenating other nitroarenes with electron-donating groups or electron-withdrawing groups and the results are shown in Table 3. The catalyst shows excellent catalytic property for the complete hydrogenation of the chloronitrobenzenes and o-bromonitrobenzene with a high yield of the corresponding amines to 98 %. However, it should be noted that the hydrogenation of m-iodonitrobenzene require a longer reaction time (400 min) for

90 % yield of m-iodoaniline, which is probably attributed to the deactivation of the Pt nanocatalyst caused by the formation of I anions from dehalogenation side reaction. Except that, the other substituted nitroarenes can be hydrogenated to the corresponding amines with a high yield (97 %) and efficiency. The excellent catalytic activity of the catalyst Pt/AlO(OH) probably attributed to the following aspects: (1) the small Pt particle size with a higher dispersion enable the more active sites available for the hydrogenation reaction; (2) the catalyst Pt/AlO(OH) with large amount of hydroxyl groups and together with solvent water facilitate the hydrogenation of NB through the activation of the N=O bond in the NB^{2,4}. In term of the selectivity, owing to the large amount of hydroxyl groups on the surface of the support, a water film will be formed which makes the desorption of the hydrogenated product AN from the active sites easily, prohibiting the side reaction between the solvent methanol and AN. Therefore, a higher selectivity was observed in the present work^{4, 26}. The cycling catalytic test of as-prepared Pt/AlO(OH) (Table 3) indicated its fine stability with no loss of activity in the hydrogenation of NB for five runs and negligible leaching of Pt (0.11 %, assessed by ICP).

Conclusions

In summary, Pt/AlO(OH) was synthesized by a facile one-pot process employing H₂PtCl₆ and Al(O-sec-Bu)₃ as precursors and applied for the catalytic hydrogenation of nitroarenes in methanol/water media under mild conditions. It can be seen that Pt nanoparticles are small sized and well dispersed on the AlO(OH) matrix. The catalyst Pt/AlO(OH) exhibited excellent catalytic performance than other Pt based catalysts prepared by impregnation method using common supports such as MWCNTs, CMC, AC, TiO₂ and Al₂O₃. 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 hydrogenation of nitroarenes in practical application.

Experimental

Catalyst preparation

All aromatic compound (A.R.), solvents (A.R.), and reagents (A.R.) were used as received. Pt/AlO(OH) was prepared by a one-pot procedure from H₂PtCl₆·6H₂O and Al(O-sec-Bu)₃. Typically, H₂PtCl₆·6H₂O (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 NaBH₄ (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 vigorously 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 K α radiation (40 kV, 20 mA) over the range of 10-90°. X-ray photoelectron spectroscopy (XPS, Kratos XSAM800) spectra was obtained by using Al K α radiation (12 kV and 15 mA) as an excitation source (h ν = 1486.6 eV) and Au (BE Au4f = 84.0 eV) and Ag (BE Ag3d = 386.3 eV) as reference. All binding energy (BE) values were referenced to C1s peak of contaminant carbon at 284.6 eV. A Fourier transform infrared spectrum was recorded with a Nicolet 6700 (resolution 0.4cm⁻¹) infrared spectrometer. All hydrogenation samples were analyzed by gas chromatography (Agilent 7890A) with a FID detector and PEG-20M supelco column (30 m×0.25 mm, 0.25 μ m film) and nitrogen was used as a carrier gas.

Activity test

The catalytic hydrogenation of nitrobenzene and other nitro-compounds were carried out in a 25 mL round-bottom flask equipped with a balloon. Typically, the procedures for the hydrogenation of nitrobenzene were as following: 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 counted. Aliquots of 0.1 ml were withdrawn at various time intervals and analyzed by the gas chromatography.

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