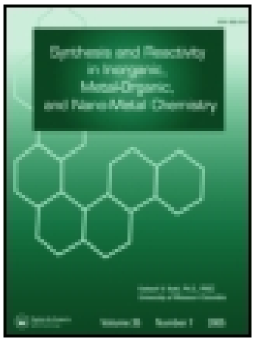

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Effective hydrogenation of haloaromatic nitro compounds catalysed by iridium nanoparticles deposited on Multi-Wall Carbon Nanotubes

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Abstract

Iridium nanoparticles immobilized on Multi-Wall Carbon Nanotubes composites (Ir/MWCNTs) were synthesized using anhydrous iridium trichloride as a precursor. The as-prepared composites were applied as catalysts for the hydrogenation of haloaromatic nitro compounds at room temperature and balloon hydrogen pressure in a methanol/water mixture, showing a selectivity of 99.9% to p-chloroaniline at complete conversion of p-chloronitrobenzene. Moreover, the catalysts also exhibited excellent catalytic properties for the reactants with electron-accepting, electron-donating and heterocycle groups. The high activity and selectivity of the catalyst was probably attributed to the interaction such as competitive adsorption and hydrogen bonding between solvent water and reactants.

Keywords

Selective hydrogenation, iridium, haloaromatic nitro compounds, Multi-Wall Carbon Nanotubes

1. Introduction

Synthesis of haloaromatic amines from hydrogenation of haloaromatic nitro-compounds is of great concern due to their useful applications in manufacture of dyes, drugs, herbicides, pesticides, and fine chemicals[1]. Catalytic hydrogenation is an energy-saving and high efficiency technology that has been widely applied for liquid phase hydrogenation of haloaromatic nitro-compounds using supported metals such as Ru[2-6], Pt[5, 7-11], Ir[12, 13] and Pd[14-17] as catalysts and molecular hydrogen as a reducing agent. Among these catalysts, Ru is proved to be highly selective to haloaromatic amines with relatively low activity, whereas Pd possesses the highest catalytic activity with the lowest selectivity due to the severely side reaction of hydrogenolysis via the scissoring the carbon-halogen bonds. However, the catalysts based in iridium are rarely investigated even though they exhibit relatively high activities in the hydrogenation of haloaromatic nitro-compounds because of the severely hydrogenolysis of carbon-halogen bonds during the hydrogenation process resulting in a low selectivity to the corresponding amines. In order to suppress the side reaction of hydrogenolysis, large amount of modifiers and promoters should be introduced into the reaction systems to modify the catalytic properties of iridium catalysts. For example, Xu et al. reported the synthesis of bimetallic Ru-Ir/Al_2O_3 catalyst for the selective hydrogenation of p-chloronitrobenzene (p-CNB) to p-chloroaniline (p-CAN)[18]. Promoters such as ethylenediamine are required to improve the catalytic property of the catalyst, therefore extra work should be done to isolate and purify the resulting amines. Campos and co-workers prepared commercial ZrO_2 supported iridium catalyst for the hydrogenation of substituted aromatic nitrobenzenes without any additives, in which the catalytic performance of iridium catalyst was attributed to the good stability of the support to active phase even the catalyst was prepared by impregnation[12]. Fan et al. synthesized Ir/$ZrO_2 \cdot xH_2O$ catalyst by co-precipitation method, showing an excellent activity and selectivity for the hydrogenation of haloaromatic nitro compounds[13].

In recent years, great attention has been focused on the applications of carbon nanotubes as catalyst supports owing to their special properties such as high tensile strength, large surface area, high electric and thermal conductivity[11, 19]. In the area of nitro group hydrogenation, the multi-wall carbon nanotubes supported (MWCNTs) Pt catalyst exhibited 100% conversion of nitrobenzene and 100% selectivity towards aniline under a solvent-free condition; however they require a high reaction temperature of 60 °C and hydrogen pressure of 4.0 MPa. Therefore, how to alleviate the reaction conditions while maintain catalytic activity and selectivity of the heterogeneous catalysts is a tremendous challenge. Nevertheless, there is a lack of information available on the application of MWCNTs as a carrier for depositing iridium catalysts for the hydrogenation of haloaromatic nitro-compounds to the corresponding amines. To this end, the aim of this work is to explore the MWCNTs as a support to immobilize the iridium nanoparticles for the selective hydrogenation of haloaromatic nitro-compounds to the corresponding amines under mild conditions. The Ir/MWCNTs catalyst was easily prepared with the use of $IrCl_3$ as a precursor and $NaBH_4$ as a reducing agent. The catalytic property of the pre-synthesized Ir/MWCNTs catalyst was tested in an alcohol/water medium with the use of p-CNB as a model reactant.

2. Experiment

2.1 Chemicals

Anhydrous iridium trichloride($IrCl_3$) was purchased from the Kunming Institute of Precious Metals, China. MWCNTs (500 m^2/g) were purchased from the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. Other chemicals and solvents (analytical grade reagents) were supplied from the Aladdin Industrial Corporation, China, and used as received without further purification.

2.2 Catalyst preparation

Ir/MWCNTs was prepared as follows: 30.0 mg of $IrCl_3$ was dissolved in 15 mL water and transferred into a 50 mL round-bottom-flask containing MWCNTs (1.5 g). Then the mixture was stirring overnight and reduced by an aqueous of $NaBH_4$ (1.5mol/L, 2 mL). The resulting black solid was washed with water and ethanol several times, dried at 60 °C under vacuum for 12 h. The content of Ir was 1.1 wt.% estimated by the ICP.

2.3 Catalyst characterization

Transmission electron microscopy (TEM) measurements were carried out on a FEI Tecnai G20 instrument operated at an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were performed on a Rigaku X-ray diffractometerD/max-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) over the range of 10-90°. XPS was performed on a Thermo ESCALAB 250 Axis Ultra spectrometer using a monochromatic Al Kα (hv = 1486.6 eV). All binding energy (BE) values were referenced to C1s peak of contaminant carbon at 284.6 eV. 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 um film) and nitrogen was used as a carrier gas.

2.4 Activity test

Typically, hydrogenation of halo-aromatic nitro-compounds was conducted as following：A desired amount of catalyst (10.0mg), solvent(total volume:7 mL), substrate(1.0 mmol) was introduced into a 25 mL round-bottom-flask equipped with a balloon and treated under vacuum to remove the air in the reactor. Then high purity hydrogen was charged into the reactor. The reaction was conducted under balloon hydrogen pressure with a stirring rate of 1200 rpm when the reaction temperature reached 25 °C. The recyclability of the catalyst was performed as the following procedures. After the catalytic run was finished, the catalyst was collected by centrifugation and washed with water and ethanol three times and kept into the reactor for the next run.

3. Results and discussion

3.1 Characterization of Ir/MWCNTs

The morphology of Ir nanoparticles (NPs) was characterized by TEM. As shown in Fig.1, Ir NPs was demonstrated to be well-distributed on the surface of MWCNTs with an average size of 2.5 nm. EDX characterization exhibited that Ir NPs were successfully immobilized on the surface of the MWCNTs via reaction of Ir^{4+} ion using $NaBH_4$ as a reducing agent. The crystal structure of Ir/MWCNTs was characterized by XRD and the result was shown in Fig.2a. The characteristic peak situated at $2\theta = 25.8^{\circ}$ was estimated to be the (002) plane of graphite. No peaks toward metallic Ir NPs were detected because of the small particle sizes of Ir, indicating that the Ir NPs were well-dispersed on the surface of MWCNTs which is in agreement with the TEM results. The electronic state of Ir species on MWCNTs was measured by XPS. As shown in Fig.3, Ir^{4+} ion was partly reduced to metallic Ir, which was confirmed by the binding energy values measured at 61.7 and 64.9 eV. However, the binding energy was 0.6 eV higher than that of the standard state of Ir(0), indicating that metallic Ir was at an electron deficient state in Ir/MWCNTs. In addition, two peaks at 63.5 and 66.8 eV belonged to the iridium oxide were distinctively observed, which was probably assigned to the oxidation of air and/or incomplete reduction of iridium oxide. However, the high activity of the catalyst Ir/MWCNTs indicates that the iridium oxide could be reduced during the hydrogenation process due to the fact that the iridium oxide was inactive to catalyze the nitro group prior to reduction.

Catalytic property of Ir/MWCNTs was investigated using p-CNB as a model substrate at 25 °C and balloon hydrogen pressure. The products for the hydrogenation of p-CNB were p-CAN and p-CNSB detected by the GC-MS. Blank test or using MWCNTs as the catalyst showed no conversion of p-CNB, indicating Ir NPs were the indispensible active sites for obtaining a high yield of p-CAN. Regarding the reaction medium, previous reports have indicated that adding adequate amount of water to replace organic solvent can significant increase catalytic property of supported catalysts for the hydrogenation of nitro-groups[6, 20]. To this end, we investigated the effect of water on the catalytic property of the Ir/MWCNTs and the results are illustrated in Fig.4a. It can be seen that the catalyst Ir /MWCNTs showed a low activity for the hydrogenation of p-CNB in methanol without the introduction of water. The conversion of p-CNB achieved 86.9% with a selectivity of 77.8% toward p-CAN due to the formation of large amount of intermediates p-CNSB (20.1%) in a long reaction time of 120 min (Fig.4a). When 28% methanol was replaced by water, the conversion of p-CNB increased to 100% with a selectivity of 87.5% to p-CAN and 11.8% to p-CNSB in a short reaction time of 60 min (Fig.4b). The selectivity of p-CAN could reach 99.5% with the elevation of reaction time to 120 min as a result of the further hydrogenation of the intermediate p-CNSB to the desired product p-CAN. The promotional effect of water on the selective hydrogenation of nitro groups was attributed to the competitive adsorption between water and methanol on the surface of the support and the formation of hydrogen bonds between the product and water in the solvent. It was reported that a water film would be formed on the surface of the hydrophilic support, which reduced the adsorption of methanol on the surface of catalyst due to the competitive adsorption of water [6, 13]. When the products were generated, they were easily escaped from the active site of the catalyst and resulted in a high yield due to the formation of hydrogen bonds between the products and water. The detection of high selectivity of the intermediate p-CNSB confirmed our suggestion. On the other hand, water can also inhibit the re-adsorption of p-CAN and avoid further hydrolysis of the carbon-halorine bonds. As a consequence, much higher catalytic activity in the hydrogenation of p-CNB was observed in such a methanol/water mixture. Up to now, the most successful example of Ir catalysts were reported by Campos et al. [12] and Fan et al. [13], in which a complete conversion of haloaromatic nitro compounds was achieved with a high selectivity to the corresponding amines(>99%) in the presence of commercial ZrO_2

supported iridium and Ir/ZrO_2•$x$$H_2O$. The Ir/MWCNTs catalyst also showed comparable catalytic activity and selectivity with the reported results.

We also investigated the catalytic property of Ir/MWCNTs in other alcohol/water mixture and the results listed in Table 1. As expected, the catalyst showed low activity toward p-CNB hydrogenation using alcohols such as methanol, ethanol and i-propanol as sole solvents. The addition of water significantly increased not only the catalytic activity but also the selectivity to p-CAN. Therefore, it can be concluded that the protic solvents such as methanol, ethanol, and i-propanol exhibit higher catalytic activity than that of non-protic solvents like 1,4-dioxide and THF, which was in agreement with the reported literature[6, 13]. Interestingly, the addition of water not only can enhance the catalytic activity and selectivity of Ir/MWCNTs toward p-CNB hydrogenation in protic solvents but also in non-protic solvent. Our results made further support to the previous reports [4, 6, 7, 10, 13].

Following the catalytic hydrogenation of p-CNB catalyzed by catalyst Ir/MWCNTs presented above, we have investigated hydrogenations of other haloaromatic nitro compounds. The results are presented in Table 2. The catalyst Ir/MWCNTs remained high efficiency in the investigated substrates containing electron-donating groups or electron-withdrawing groups. For example, chloronitrobenzenes can be quickly hydrogenated to the desired product in 2 h. In addition, other reactants with electron-donating groups, such as --OH, --CH_3, and --OCH_3 also can be hydrogenated to the corresponding amines with extremely high yield (>99%). The reactants with electron-accepting and heterocycle groups also can be hydrogenated to the corresponding amines.

Reusability of catalyst is of great importance in view of industrial applications. Therefore, we investigated the reusability of Ir/MWCNTs by performing five consecutive runs under the same reaction conditions. The catalyst Ir/MWCNTs showed good recyclability as shown in Fig.5. From the XRD (Fig.2b) and TEM (Fig.6) characterizations of the catalyst recycled five times, the structure and morphology of the catalyst did not changed obviously, which was attributed to the good recyclability, exhibiting some promise in use of practical applications.

4. Conclusion

In summary, the Ir NPs immobilized on MWCNTs was synthesized by impregnation and applied as catalysts for the hydrogenation of a variety of aromatic nitro compounds at 25 °C under balloon hydrogen pressure in methanol/water mixture. The catalyst Ir/MWCNTs exhibited high efficiency for the clean synthesis of amines due to the completely suppress the hydrolysis side reaction of hydrodechlorination of carbon-chroline bond in the substrate and the products. Moreover, the catalyst Ir/MWCNTs was quite stable and can be recycled at least five times without significant deactivation. Therefore, the present work provides a kind of more robust and eco-friendly catalytic system in view of the development of a sustainable catalytic route for the production of aromatic amines.

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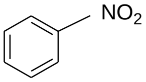
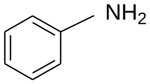
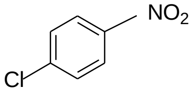
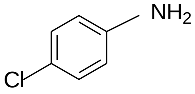
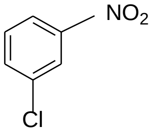
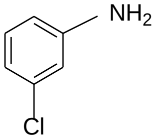
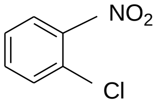
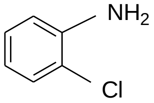
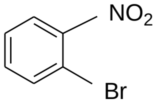
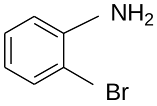
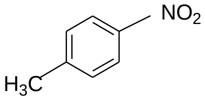
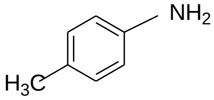
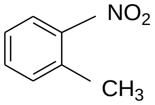
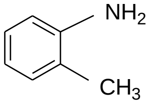
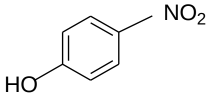
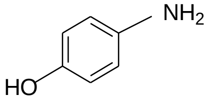
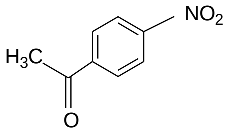
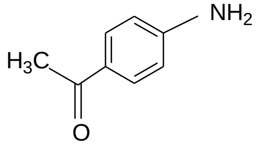
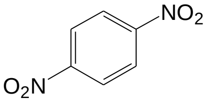
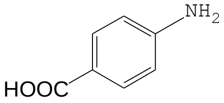
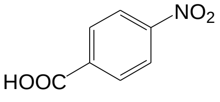
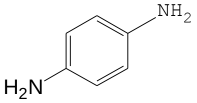
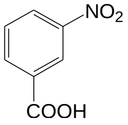
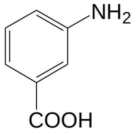
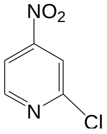
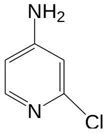
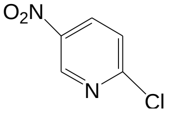
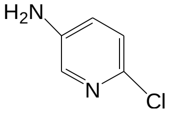
Table 1 Effect of solvent on hydrogenation of *p*-CNB[a]

Solvents	water	Conversion (%)	Selectivity (%)	
			p-CAN	*p*-CNSB
Methanol	No	86.9	77.8	20.1
	Yes	100(60)	99.5	0.5
Ethanol	No	98.7	88.8	10.8
	Yes	100(80)	97.3	2.3
i-propanol	No	23.1	60.7	37.9
	Yes	100(80)	98.9	0.4
1,4-dioxide	No	10.5	54.9	44.7
	Yes	16.8	82.4	17.3
THF	No	12.7	34.1	64.7
	Yes	40.3	79.5	19.7

[a]Reaction conditions: catalyst,10 mg; p-CNB,1 mmol; temperature, 25 °C; pressure, 1atm; reaction time, 120 min. [b] reaction time was 80 min.

Table 2 Hydrogenation of Catalyst for the hydrogenation of different substrates

Entry	Nitro-aromatics	Product	Time (h)	Conversion (%)	Selectivity (%)
1			2.5	100	99.9
2			2	100	99.5
3			2	100	95.4
4			2	99.7	99.4
5			3	88.7	99.0
6			2.5	100	99.0
7			2.5	100	95.9
8			3	91.2	86.8

9			3	95.3	95.8
10			6	95	97
11			4	96	98
12			5	94	96
13			2	100	99.0
14			2	100	99.2

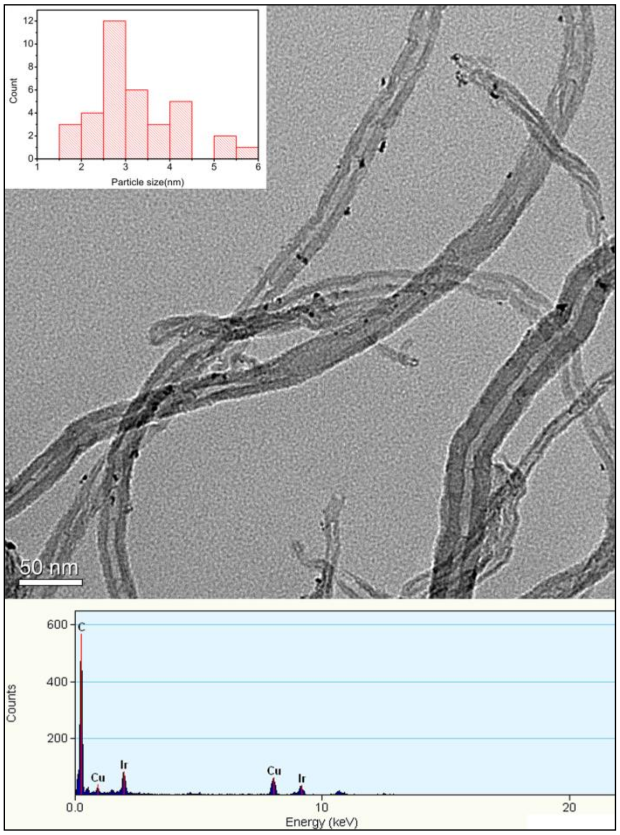


Fig.1 TEM image of catalyst Ir/MWCNTs

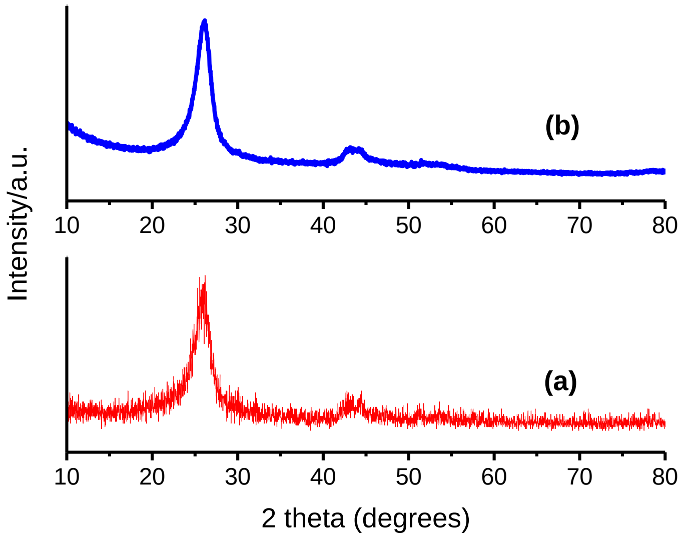


Fig.2 XRD patterns of fresh Ir/MWCNTs (a) and the catalyst recycled five times (b).

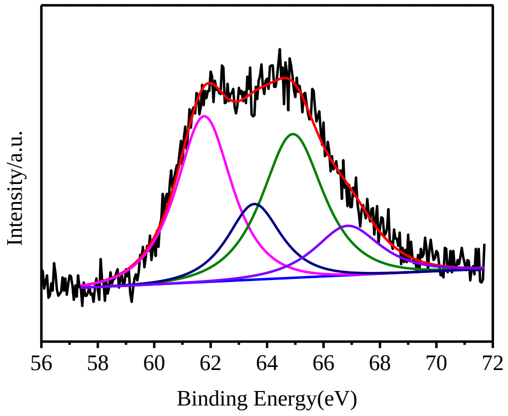


Fig.3 XPS spectrum of Ir/MWCNTs

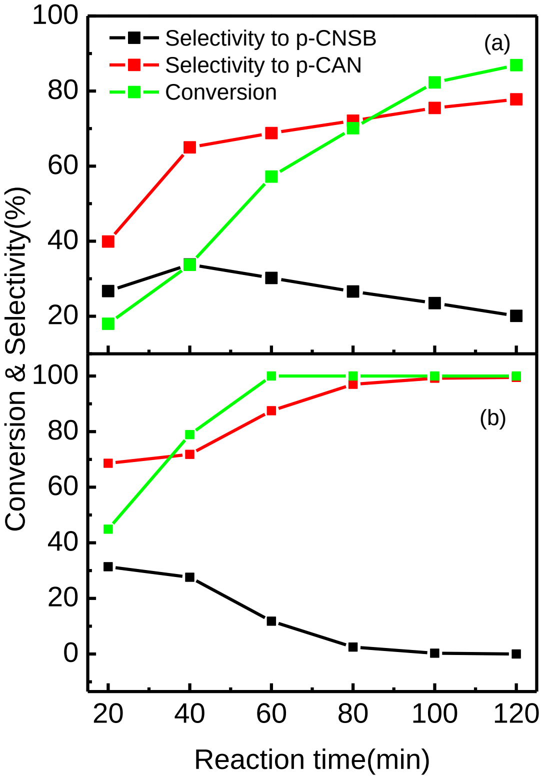


Fig.4 Catalytic properties of Ir/MWCNTs in methanol (a) and methanol/water mixture (volume ratio: 5:2) (b)

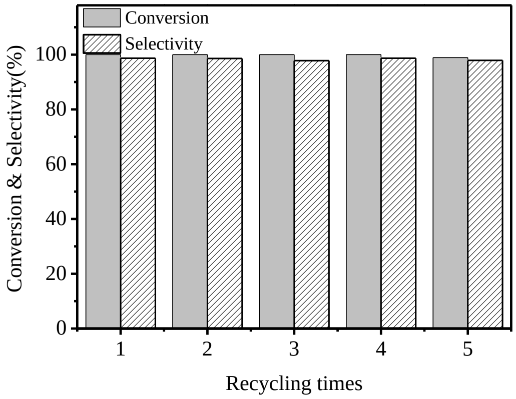


Fig.5 Recyclability of catalyst Ir/MWCNTs

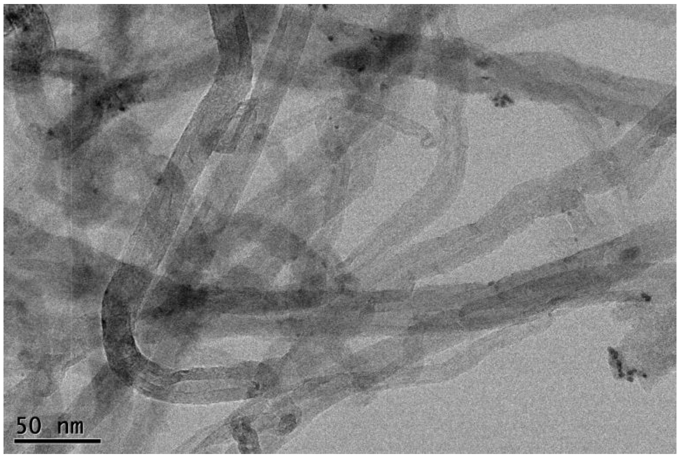


Fig.6 TEM image of Ir/MWCNTs recycled five times.