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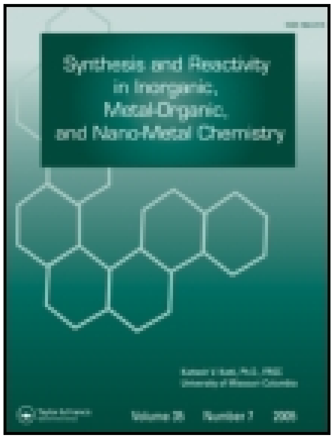

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Effective Hydrodechlorination of 4-Chlorophenol Over Pd Deposited on Multiwall Carbon Nanotubes

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Multiwall carbon nanotubes (MWCNTs) supported Pd nanoparticles were prepared by impregnation method and characterized by TEM, XRD, XPS, and FT-IR. The as-prepared catalyst Pd/MWCNTs exhibited excellent catalytic property for the hydrodechlorination (HDC) of 4-chlorophenol (4-CP) in aqueous medium without any additives under mild conditions. The results indicated that the choice of support and the introduction of metal ions played a significant role in the catalytic property for HDC of 4-CP. The high catalytic performance of Pd/MWCNTs was attributed to the highly dispersed Pd nanoparticles on the support MWCNTs and the interaction between support and metal actives.

Keywords 4-chlorophenol, hydrochlorination, multiwall carbon nanotubes, palladium nanoparticles

INTRODUCTION

Chlorophenols are known as commercially important chemicals and are widely applied as intermediates or end products in the production of pesticides, herbicide and disinfector.[1] The residue of these compounds is harmful to the environment and human beings since these chlorinated phenols are persistent toxic pollutants and recalcitrant to chemical and biological degradations. Therefore, removal of these compounds is an emerging process. Great efforts have been put into detoxifying the aqueous wastes containing chlorophenols through methodologies based on photochemical oxidation, thermal combustion, biodegradation, and incineration, which generate various by-products and pose many problems for the environment. The treatment of these toxic pollutants facilitated by liquid phase dechlorination has attracted investigative attention since this process is judged as simple, safe, and effective. Especially, the HDC of chlorophenols using noble metal as catalysts involving molecular hydrogen as a hydrogen source, currently receive a constant growth of interest. The catalytic HDC is an environmentally friendly and highly efficient route for decomposing these compounds under relatively mild conditions without the formation of the toxic by-products. Various heterogeneous metal catalysts (Pd,[2–5] Pt,[6,7] Rh,[8–11] Ni[12–15]) have been applied either in bulk or supported forms for the treatment of wastewaters containing chlorophenols. Pd nanoparticles are reported to be among the most promising ones because the HDC reaction can be performed at ordinary temperature and atmospheric pressure.[16]

Recent researches focused on the development of Pd catalysts have demonstrated that the choice of support has significant influence on the dispersion and electronic properties of the Pd species,[3] which affects the reaction rates of the catalytic HDC of chlorophenols. Among the commonly used supports, it has been reported that the use of Al_2O_3 can improve the stability of active species of the catalyst. However, this metal oxide support is more sensitive to HCl produced during the HDC process. Furthermore, the support activated carbon (AC) also has been extensively investigated for the HDC of chlorophenols because of its high surface area and particularly physical and chemical properties, but their applications should be carefully considered due to its strong adsorption properties based on surface area, pore size distribution, and surface composition. Very recently, the synthesis of new carbon materials or their composites has been exploited for the removal of wastewaters containing chlorophenols. For example, Jin et al.[2] reported the catalytic HDC of 4-CP over mesoporous silica–carbon nano-composite (MSCN) supported palladium catalyst, which attained 100% removal efficiency at 258–313 K under ordinary hydrogen pressure by using triethylamine (Et_3N) as a base additive. The catalytic activity of the Pd/MSCN catalyst was much higher than that of the commercial active carbon supported Pd. The catalytic HDC over Pd catalysts often requires the presence of base to neutralize hydrochloric acid formed in the reaction in order to prevent the deactivation of the catalyst. However, the addition of additives needs extra work to segregate the additives from the reaction mixture with the purpose of avoiding the secondary pollution to the environment.

Carbon nanotubes, with high tensile strength, large surface area, and high electric and thermal conductivity,[17] is considered to be an attractive material for a wide range of

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application especially as a catalyst support. Thus, the carbon nanotubes supported metals have been widely investigated as catalysts and have shown promising applications in catalysis.[17–19] Compared to carbon black and porous carbons, carbon nanotubes supported catalyst has the advantages of excellent resistance against corrosion and better contact between the reactant and the catalytic component.[17] But there are few researches concerning the employment of the carbon nanotubes supported catalysts for the treatment of chlorinated organic compounds. Recently, Song et al.[18] prepared NH_3 modified carbon nanofibers (CNFs) supported Pd catalyst for the catalytic HDC of chlorobenzene. Although the Pd/CNFs catalyst showed high activity and stability, one limitation of the reaction system is that the treatment procedure must be conducted in NH_3 atmospheric at 1123 K.

To date, it is still a big challenge over most of the previous heterogeneous catalysts in view of developing a highly active and recyclable system for the HDC of chlorophenols under mild conditions without any additives. Herein we prepared Pd/MWCNTs catalyst by an impregnation method using $PdCl_2$ as precursor and MWCNTs as support. The as -prepared catalyst Pd/MWCNTs was applied for the HDC of 4-CP under mild conditions without any promoters. Effects of supports, organic solvents and metal ions were also investigated. The catalyst Pd/MWCNTs showed much higher removal efficiency than the Pd/C catalyst and can be recycled six times without loss of any activity.

EXPERIMENTAL

Materials

Palladium chloride ($\geq$59.5%) was purchased from the Kunming Institute of Precious Metals, China. MWCNTs (500 m^2/g) were purchased from the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. Ethylene glycol (EG, 99%) and sodium borohydride ($NaBH_4$) were purchased from Alfa Aesar and used as received. Other solvents were analytical grade and used as received.

Instruments

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 diffractometerD/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 was obtained by using Al Ka radiation (12 kV and 15 mA) as an excitation source (hv = 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 0.4 cm^{-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 um film) and nitrogen was used as a carrier gas.

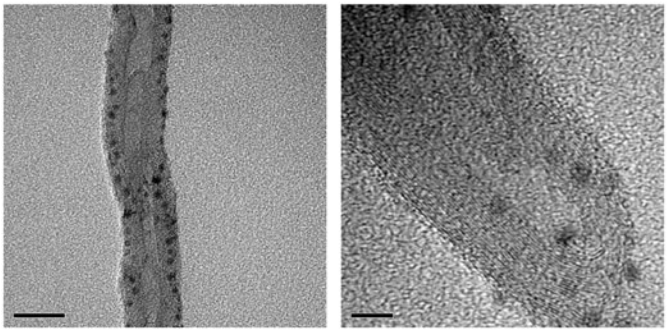

FIG. 1. TEM morphology of the Pd/MWCNTs catalyst and the mapping pattern of the Pd/MWCNTs.

Preparation of Pd/MWCNTs

Typically, 3.5 mg/mL $PdCl_2$ (10 mL) aqueous solution was placed into a 50 mL round-bottom flask and 500 mg MWCNTs was also added into the flask. The aqueous solution of $NaBH_4$ (75 mg, 5 mL) was slowly dropped into the solution under vigorous stirring. After stirring for 3 h, the product was washed with distilled water several times and dried under vacuum at 323 K for 12 h. The Pd loading was 1.0 wt% measured by ICP.

Activity Test

The HDC reaction was carried out in a 25 mL round-bottom flask. A typical procedure for the HDC of 4-CP is as following: The desired amounts of catalyst (5 mg), 4-CP (2.5 g/L), and solvent (5.0 mL) were charged to the flask equipped with a balloon. The reactor was vacuumed and flushed with pure hydrogen. When the designated reaction temperature was reached, the stirring rate was adjusted to 1200 rpm, and reaction time was accounted. Many experimental data were obtained by repeating the reaction two or three times and they had the good repeatability.

RESULTS AND DISCUSSION

Characterization of Pd/MWCNTs

Transmission electron microscopy (TEM) experiments have been carried out to detect a possible structure of the Pd particles (Figure 1). These images show that the Pd nanoparticles dispersed well on the support MWCNTs with a mean particle size of 2.1 nm. The compositional analysis carried out by energy-dispersive X-ray spectroscopy (EDS) measurements demonstrates that the presence of Pd element and the Pd loading is about 1.1 wt%, which agrees well with the ICP result.

The crystal structure of the purified MWCNTs and Pd/MWCNTs were characterized by powder X-ray diffraction (XRD) and the results were shown in Figure 2. It can be seen that the diffraction peak at $2\theta = 25.8°$ is estimated to be the

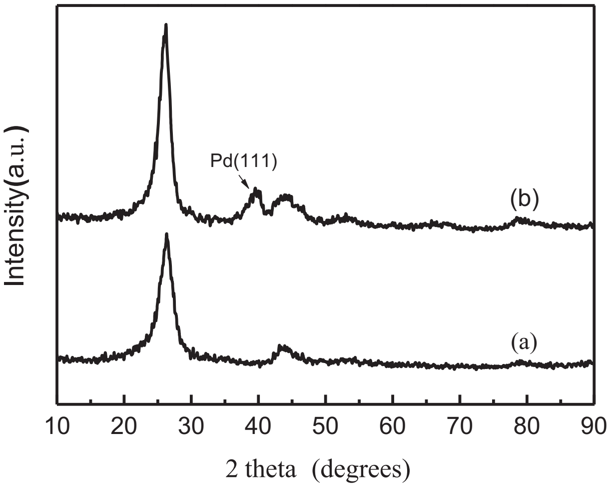

FIG. 2. XRD patterns of the MWCNT (a) and Pd/MWCNT (b) catalysts.

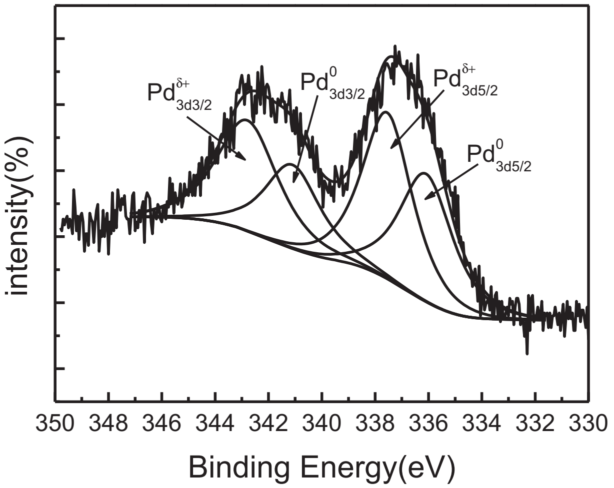

FIG. 3. XPS pattern of the Pd/MWCNT catalysts.

(002) plane of graphite (Figure 2). The characteristic peaks of concentrated nitric acid treated MWCNTs show no difference compared with the pristine MWCNTs. The diffraction peak at $2\theta = 40.1^\circ$ is attributed to the (111) plane of the Pd (Figure 2).

The electronic state of the Pd species on the MWCNTs was measured with the XPS. The pattern of Pd/MWCNTs catalyst is illustrated in Figure 3. The Pd_{3d} peaks in XPS spectra show that besides the binding energy values at 336.0 eV and 341.1 eV, which are attributed to the $3d_{5/2}$ and $3d_{3/2}$ peaks of metallic palladium, the binding energy values at 337.5 eV and 342.7 eV are assigned to the $3d_{5/2}$ and $3d_{3/2}$ peaks of palladium oxide, respectively. The presence of palladium oxide should be owing to the oxidation of air to nano-palladium particles and the incomplete reduction of palladium oxide. Pd(0) was the active species for the reaction because the catalyst was not active to catalyze the HDC prior to reduction and the palladium oxide also can be reduced during the HDC process.

Fourier transforms infrared (FTIR) spectra of MWCNTs and Pd/MWCNTs were also measured. Figure 4 shows the IR spectrum of MWCNTs, the characteristic absorption peaks at 3425 cm^{-1} and 1383 cm^{-1} are assigned to the O-H stretching mode; the peaks at 1584 cm^{-1} and 1046 cm^{-1} are ascribed to the C-O stretching modes, respectively, indicating that the surface of MWCNTs was decorated with carboxyl groups, thus providing some reactive and anchoring sites for nucleation and growth of Pd particles. An almost identical IR spectrum of Pd/MWCNTs was observed after immobilization of palladium on the surface of MWCNTs (Figure 4), but the characteristic peaks of MWCNTs in Pd/MWCNTs are shifted to higher wavenumbers (1584–1630 cm^{-1} and 3425–3438 cm^{-1}), which are attributed to the interaction between Pd and MWCNTs.[20]

Optimization of Reaction Conditions

The catalytic properties of the Pd/MWCNTs catalysts were investigated using the HDC of 4-CP as a model reaction, which has been proved to be an effective way to evaluate the removal efficiency of noble metal nanocatalysts. The HDC of 4-CP was negligible without catalyst or in the presence of pure MWCNTs at the same conditions, which shows that the presence of palladium is indispensable for high catalytic activity. Generally, the HDC of 4-CP results in the production of three products, that are phenol, cyclohexanol, and cyclohexanone.[2] Compared with the reactant 4-CP, the three products detected are lowly toxic and useful as intermediates in production of high value-added chemicals. However, only phenol was detected as product in the present system.

The progression of the reductive HDC process at various temperatures is shown in Figure 5. As expected, the HDC rates of the reactions were clearly increased with the elevation of the reaction temperature. The reaction time for complete conversion of 4-CP was 30 min and 40 min at the temperature of 293 K and 298 K in water under atmospheric pressure, respectively;

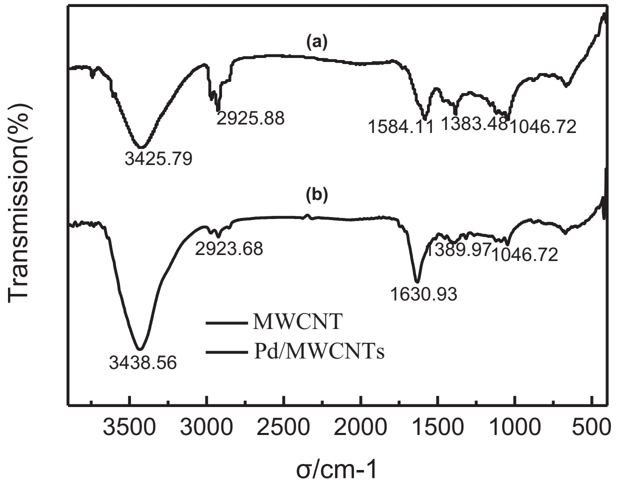

FIG. 4. FTIR morphology of (a) MWCNT and (b) Pd/MWCNT catalysts.

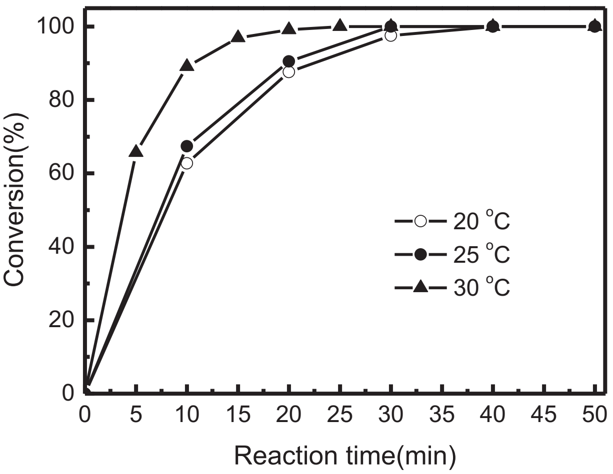

FIG. 5. Effect of reaction time on 4-CP hydrodechlorination.

when the reaction temperature was increased to 303 K, the 4-CP was completely transformed to phenol and cyclohexanone within 25 min. The results indicate that higher temperature facilitated the breaking down of the Cl–C bond to accelerate the reaction.

The effect of initial concentration of 4-CP removal efficiency was investigated in the range from 2.0 g/L to 3.5 g/L over the Pd/MWCNTs catalyst. The results presented in Figure 6 show that the removal percentages of 4-CP reached 94.3%, 89.1%, 74.6%, and 67.4% each after 10 min, and then reached 100%, 100%, 96.6%, and 90.5%, respectively, after 20 min of the reaction within the investigated range. Moreover, the reaction time for achieving the complete removal efficiency increased with the increase of the initial concentration. For 2.0 g/L 4-CP, it was completely hydrodechlorinated within 15 min, while it needed 40 min when the concentration of 4-CP increased to 3.5 g/L. The time for complete hydrodechloriation of 4-CP were 15, 20, 30, and 40 min, respectively. Though the time for complete removal of 4-CP increased with increasing initial 4-CP concentrations, the absolute removal amount increased.

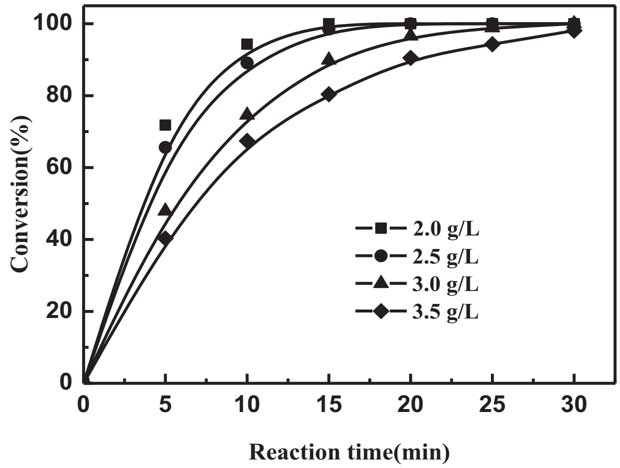

FIG. 6. Effect of initial concentration on 4-CP hydrodechlorination.

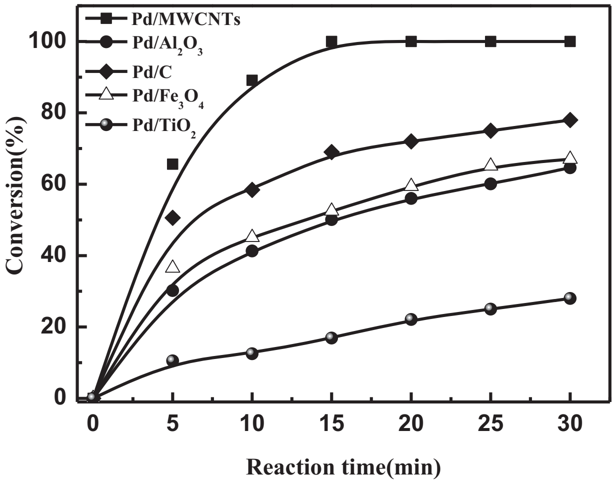

FIG. 7. Effect of supports on 4-CP hydrodechlorination.

Effect of Supports

It is reported that the choice of the solid support has a significant influence on the catalytic activity and selectivity. We also compared the activity of Pd/MWCNTs with those of Pd deposited on Al_2O_3, C, TiO_2 and Fe_3O_4 prepared by a similar method and the results were illustrated in Figure 7. The results reveal that the Pd/MWCNTs catalyst possess very high activity in aqueous medium, approaching almost 100% conversion of 4-CP over a period of 20 min, whereas the Pd/TiO_2 catalyst exhibits lower activity in terms of about 28% conversion within a period of 30 min. The Al_2O_3, TiO_2, and Fe_3O_4 supported Pd catalysts show a moderate activity. In this region of study, the activity of the catalysts varied in the order: Pd/MWCNTs > Pd/C > Pd/Fe_3O_4 > Pd/Al_2O_3 > Pd/TiO_2.

Effect of Different Solvents

The effects of different solvents on 4-CP removal efficiency are presented in Figure 8. As shown in Figure 8, the removal percentages of 4-CP was 100% within 15 min when using water as the reaction medium. In contrast, the addition of organic solvents both protic solvent such as methanol, ethanol, and n-propanol, and aprotic solvent such as cyclohexane and 1,4-dioxane resulted in decrease of removal efficiency under identical reaction conditions. As can be seen in Figure 8, when using the polar solvents methanol, ethanol, and n-propanol as the solvents, the removal percentages decreased to 49.6%, 37.5%, 27.8%, and 27.2% within 60 min, respectively. In contrast, when using nonpolar cyclohexane and 1,4-dioxane as solvents, the conversion of 4-CP was 24.3% in cyclohexane, and the lowest removal efficiency of 3.6% was obtained in 1,4-dioxane with the same reaction time. Compared to the HDC process in aqueous solution, the Pd/MWCNTs catalyst exhibited relatively low activities in the investigated organic solvents which was ascribed to the

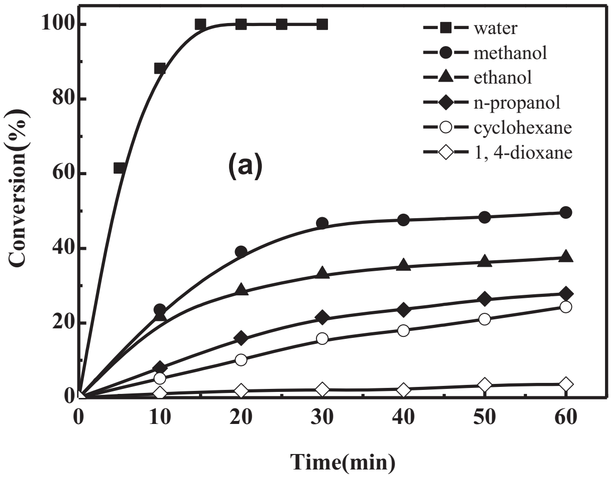

FIG. 8. Effect of solvent on 4-CP hydrodechlorination.

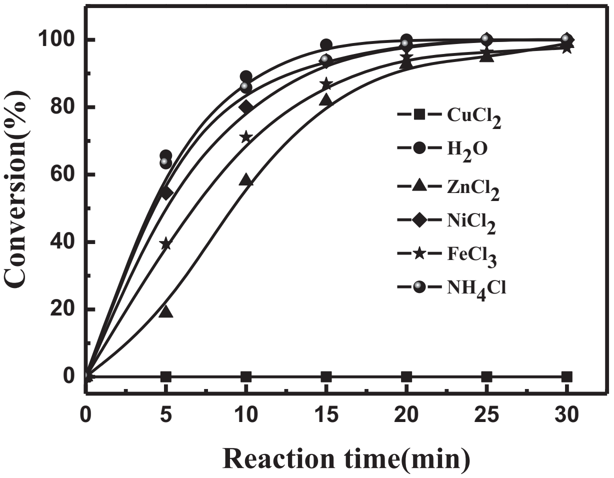

FIG. 9. Effect of metal ions on 4-CP hydrodechlorination.

probably adsorption of organic solvents on the surface of the catalysts and blocking some of active sites.

Effects of Metal Ion in Aqueous Solutions

The influence of metal ions on the catalytic HDC of 4-CP in aqueous media also was investigated by introducing a series of metal ions into the reaction mixture. Figure 9 shows the effects of some metal ions on the HDC of 4-CP in water. It was clearly indicated that the presences of metal ions such as Cu^{2+}, Ni^{2+}, Fe^{3+}, and Zn^{2+} were disadvantageous to the HDC of 4-CP. Only about 39.5% and 18.9% 4-CP were hydrogenated after 5 min when $FeCl_3$ or $ZnCl_2$ (0.6 mmol) was added into the reaction mixture; however 65.6% 4-CP was converted with the same reaction time in the absence of metal ions. Compared with $FeCl_3$ and $ZnCl_2$, the effects of $NiCl_2$ or NH_4Cl were weak, but the complete reactions still needed about 25 min, 25 min, and 30 min, respectively, while the complete conversion in water only needed 20 min. However, we found that with the addition of the same amount of $CuCl_2$ into water, the considerably remarkable deactivation of the catalyst was observed within 30 min. Our results showed that the addition of metal ions into the reaction system suppressed the activity of the catalyst and led to the decrease of the HDC rate. This phenomenon was possibly attributed to the adsorption of metal ions on the active sites of Pd/MWCNTs to lead to the deactivation of the catalyst as reported by Xia et al.[21] The inhabitation action of heavy metal ions, such as Fe^{3+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, was assigned to a metallic ions connecting with their orbitals and d-electrons, their d-electrons take part in the intermetallic bonds between the toxic metal and the catalyst and resulted in highly toxicity to the Pd catalyst. However, the Pd catalyst is not poisoned if the metal ions, such as Na^+, have no d-electron to form the bond between the metal and the catalyst.[21]

Stability of the Catalyst

The reusability of the Pd/MWCNTs catalyst was tested using 4-CP as a substrate at the same reaction conditions. After completion of the reaction, the catalyst was separated from the reaction system by centrifugation, and the supernatant liquid was removed. The recovered catalyst was thoroughly washed for three times with ethanol and dried in vacuum at room temperature for next use. Reusing the Pd/MWCNTs catalyst in six consecutive cycles showed that the catalytic activity remained without a significant loss of removal efficiency (Figure 10). Moreover, Metal leaching measurement investigated by ICP analysis of the catalyst indicates that the Pd leaching was negligible. The composition of the Pd/MWCNTs catalyst remained virtually unchanged as the fresh catalyst, which are attributed to the high recyclability of the catalyst.

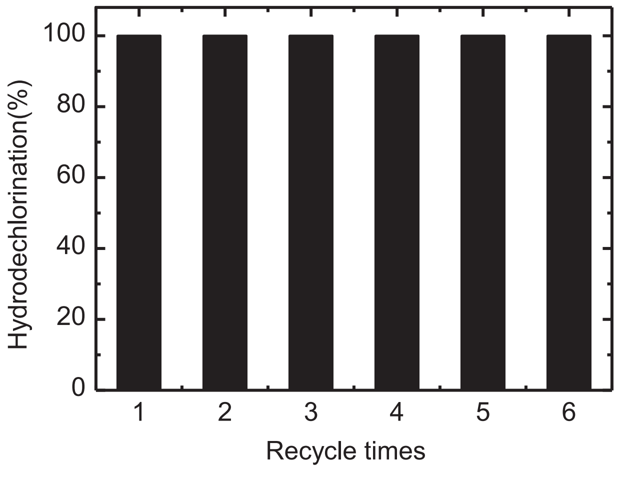

FIG. 10. Stability of the Pd/MWCNTs.

CONCLUSION

In conclusion, Pd/MWCNTs catalyst was prepared using the impregnation method and the catalytic property of HDC of 4-CP over the catalyst was investigated. Pd/MWCNTs exhibited higher stability compared to the commonly used support such as C, Al_2O_3, TiO_2, and Fe_3O_4. Moreover, the introduction of metal ions into the mixture led to the deactivation of the catalyst to some extent because of the interaction between the toxic metal and the catalyst. In addition, the Pd/MWCNTs catalyst was quite stable and could be reused six times without significant deactivation.

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