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Catalytic hydrodechlorination reaction of chlorophenols by Pd nanoparticles supported on graphene

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Abstract Chlorophenols are widely used as industrial chemicals such as herbicides, insecticides, wood preservatives, and disinfectants. However, chlorophenols are very toxic materials and they have become the cause of current environmental issues. Hydrodechlorination (HDC) reaction is a more environmentally friendly removal method of chlorophenols than other methods. In this paper, Pd–modified graphene was prepared and applied to HDC reaction. Pd supported on graphene (refer to Pd/G) was prepared using the recently reported microwave irradiation method. The Pd(II)/GO was made by impregnation methods of palladium precursors in solution phase and was subsequently reduced to Pd/G by microwave irradiation. The morphological and chemical structure of the Pd/G was characterized by XRD, SEM, ICP-MS, EDS, and TEM. It was found that the graphene-based Pd catalyst showed the highest catalytic performance among Pd/Y, Pd/MCM-41, and Pd/G catalysts. This is attributed to the smaller particle size and higher dispersions of Pd nanoparticles on the graphene surface. The catalytic HDC of chlorophenols was investigated. For HDC reaction, 100 ppm solution of chlorophenols such as 4-chlorophenol, six isomers of dichlorophenol, and 2,3,5-trichlorophenol in isopropanol was treated with catalyst and base, such as Na_2CO_3 and K_2CO_3, under a hydrogen gas at ambient pressure. The progress of the chlorophenol decomposition was analyzed with GC. All chlorophenols were completely decomposed within 2 h in the 3 % Pd/G catalyst. The reaction pathway of chlorophenols was elucidated

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from the conversion of chlorophenols and selectivities of products. The reuse of the catalyst was also studied. The performance of the recycled catalyst in HDC reaction up to six successive runs was observed.

Keywords Hydrodechlorination · Chlorophenol · Dichlorophenols · Trichlorophenol · Pd–graphene

Introduction

Chlorophenols are usually used as the intermediates for organic synthesis, and are extensively employed as pesticides, herbicides, disinfectants, and wood preservatives. Chlorophenols and their derivatives are carcinogenic, persistent, and bioaccumulative [1]. Chlorinated phenols have been detected in groundwater, surface water, air, and soils as a result of their improper disposal, leaching from landfills, and the incineration of chlorinated wastes. Contamination of water and soil by chlorine–substituted phenolic compounds now represents a significant environmental burden due to their widespread industrial use, inherent toxicity, and persistence in the environment [2, 3]. The toxic chlorophenols have become current environmental concerns. The toxicity of these compounds is connected with the chlorine content, and their biodegradability is strongly affected by chlorine substitution in the molecules. The group of chlorophenols comprises of 19 different chlorinated-phenol isomers, including pentachlorophenol, three tetrachlorophenols, six trichlorophenols, six dichlorophenols, and three monochlorophenols. Most chlorophenols are listed as priority pollutants by the U.S. EPA [4, 5]. Under certain conditions, chlorophenols occurred in the aqueous environment can be transformed to more toxic polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. Highly chlorinated aromatic compounds are recalcitrant towards disposal. Biological treatment of low concentration of such materials in aqueous waste streams often leaves the chlorinated compounds untreated or required several days. Therefore chlorophenols, even at a trace level, need to be removed from water [6]. Several methods have been developed for treating chlorophenol-contaminated media, including thermal treatment, sonification, ozonation, electrochemical treatment, Fenton-type oxidative degradation, advanced oxidation, bioremediation, phytodegradation, reductive dechlorination by zero valence metals and bimetallics known as dissolving metal reductions, adsorption on diversified materials, and catalytic hydrodechlorination (HDC) [7].

Hydrodechlorination (HDC) reaction by novel metals such as palladium and rhodium is more environmentally friendly than other methods [1, 8–10]. Supports used for palladium catalysts are carbon, silica, alumina, zeolite, and *meso* porous materials. Although these supports allow efficient recycling, a decrease in the activity of catalysts is frequently observed. Therefore, the development of heterogeneous palladium nanoparticles that combine high activity, stability, and recyclability is an important goal of nanomaterials research that is likely to have a considerable impact on chemical and pharmaceutical industries in the future. Recently, graphene has been considered as a potential support system for palladium-catalyzed reactions [11]. Graphene has a one-atom-thick planar sheet of sp^2-hybridized carbon atoms and because of the excellent mechanical flexibility, graphene is a very appealing matrix to encapsulate nanoparticles against their physical and chemical instability during use. Since graphene has excellent electron capture and transport properties, large specific surface area, good affinity toward organic molecules, and high thermal, chemical, and mechanical stability, it represents desirable characteristics as supports for metallic nanoparticles in efficient and recyclable catalysts that allow for industrial applications within environmentally benign processes [12].

In this study, palladium nanoparticles supported on graphene (refer to Pd/G) were prepared by microflow H_2 reduction [13], sodium borohydride ($NaBH_4$) reduction, or microwave irradiation method [14]. Microwave irradiation has been demonstrated for the synthesis of a variety of nanoparticles including metals, metal oxides, bimetallic alloys, and semiconductors with controlled size and shape without the need for high temperature or high pressure. Unlike conventional thermal heating, microwave irradiation allows better control of the extent of graphene oxide (GO) reduction by $NaBH_4$ or hydrazine hydrates as both the microwave irradiation power and time can be adjusted to yield a nearly complete concurrent reduction of GO and the palladium salt. These Pd/G catalysts were utilized in adsorption and HDC of chlorophenols. The catalytic HDC of chlorophenols, such as 4-chlorophenol, six isomers of dichlorophenol, and 2,3,5-trichlorophenol, by Pd/G were investigated. The recyclability of the catalysts was also studied using 4-chlorophenol as a model compound.

Experimental

Materials and methods

High-purity graphite powder (99.99 %) and palladium acetate [$Pd(OAc)_2$, 99.99 %] were purchased from Sigma-Aldrich and used as received. 4-Chlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol, 3,4-dichlorophenol, 3,5-dichlorophenol, and 2,3,5-trichlorophenol were purchased from Sigma-Aldrich and used as received. Powder XRD analyses were performed on a multi-purpose high-performance X-ray diffractometer D/max-2500 (Rigaku). The diffraction data were recorded for 2θ angles between 6.0° and 80°. SEM measurements were performed using a S-4700 FE-SEM (Hitachi). TEM measurements were performed using a JEM-200FS (HT) FE-TEM (JEOL). ICP-MS data were obtained from Agilent 7500A and EDS data were measured using EDS 1600 (Shimadzu).

Preparation of Pd/G nanoparticles and other catalysts

Graphene oxide (GO) was prepared by the oxidation of high-purity graphite powder with $H_2SO_4/KMnO_4$ according to the method of Hummers and Offeman [15]. Briefly, graphite (2.0 g) was added to concentrated H_2SO_4 (50 ml) in an ice bath, and $NaNO_3$ (1.0 g) and $KMnO_4$ (7.0 g) were slowly added under continuous stirring. After 2 h, the suspension was removed from the ice bath and warmed to 35 °C. The whole batch was carefully poured into a 1-l flask in an ice bath, and H_2O_2 (30 %) was added until gas was no longer detected. Then, the suspension was filtered and washed with 0.1 M HCl solution and water. After repeated washing of the resulting yellowish-brown cake with hot water, the powder was dried at room temperature under vacuum overnight. For the preparation of palladium nanoparticles supported on graphene (3 % Pd/G), 500 mg of the dried GO in 250 ml of deionized water and then an added 32 mg of palladium acetate were sonicated until a homogeneous yellowish brown dispersion was obtained. The solution was placed inside a conventional microwave after adding 100 μl of the reducing agent hydrazine hydrate. The microwave oven (Daewoo MW8119SB) was then operated at full power (1000 W), 2.45 GHz, in 30-s cycles (on for 10 s, off and stirring for 20 s) for a total reaction time of 60 s. The yellowish brown solution of $Pd(OAc)_2$–GO changed to a black color, indicating the completion of the chemical reduction to reduced-graphene. The Pd/G sheets were separated by using an Eppendorf 5804 centrifuge operated at 5000 rpm for 15 min and dried overnight under vacuum.

For comparison of the catalytic activity of Pd/G with other Pd-based catalysts, Pd–MCM-41 and Pd–Y were prepared. The preparation and characterization of these catalysts were described elsewhere [16]. Pd–MCM-41 was synthesized by hydrogen-flow reduction of $[Pd(NH_3)_4]^{2+}$-modified MCM-41, which was prepared by impregnation method using an aqueous solution of $[Pd(NH_3)_4]Cl_2$ in water. Pd–Y was prepared by ion-exchange method of zeolite Y followed by hydrogen-flow reduction. Palladium contents of these catalysts were determined by EPMA as ~3 wt%.

Reaction procedure for hydrodechlorination of chlorophenols

For HDC reaction, 10 ml of 100 ppm solution of 4-chlorophenol in isopropanol was treated with catalyst (50 mg of 3 % Pd/G), base (K_2CO_3, 100 mg) under a hydrogen gas at ambient pressure. The progress of the chlorophenol-decomposition was checked with GC. In order to find the effect of base in the reaction, various solid bases, such as Na_2CO_3, NaOAc, or KF/Al_2O_3, were added for HDC reaction instead of K_2CO_3 [17].

Results and discussion

Recently, the synthesis of metal nanoparticles by the chemical reduction of metal salts has been widely studied because of their applicability to catalysis. Among them, palladium-catalyzed hydrogenation reactions and cross-coupling reactions have drawn much attention in organic synthesis due to its industrial potential for the synthesis of chemicals and their intermediates. Although homogeneous palladium catalysts exhibit higher activity and selectivity for cross-coupling reactions, the uses of homogeneous Pd catalysts are restricted in large-scale reactions due to the contamination of products [18]. Tedious separation and recycling of the palladium catalyst are other major drawbacks of the homogeneous catalysts. In order to address these problems, heterogeneous Pd catalysts have been employed in recent years. Palladium has been supported on materials such as activated carbon, polymers, zeolites, silica, molecular sieves, clays, carbon nanotubes, and graphene. Among them, graphene has been considered as a potential support system for palladium-catalyzed reactions [12]. Although graphene allows efficient recycling, a decrease in the activity of catalysts is frequently observed. Therefore, the development of heterogeneous palladium nanoparticles supported on graphene that combine high activity, stability, and recyclability is an important goal of nanomaterials research that is likely to have a considerable impact on the chemical and pharmaceutical industries in the future. In this study, Pd nanoparticles supported on graphene (Pd/G) were prepared using the recently reported microwave irradiation method. The Pd(II)/GO was made by impregnation methods of palladium precursors in solution phase and were subsequently reduced to Pd/G.

The morphological and chemical structure of the Pd/G was characterized by XRD, SEM, ICP-MS, EDS, and TEM. The morphologies of the Pd/G were found by SEM and TEM. The structure of the catalyst was determined by XRD. The broad peak of 24.8° shows most of the GO was reduced into graphene. The 39.1° peak is characteristic for Pd(111) and other peaks represent Pd(200) and Pd(220) plane. Palladium content in the catalyst was measured by EDS and ICP. As depicted in Fig. 1, a lot of palladium nanoparticles responded as black dots in the image of the Pd/G catalyst. The average particle diameter of Pd NPs by hydrogen reduction was

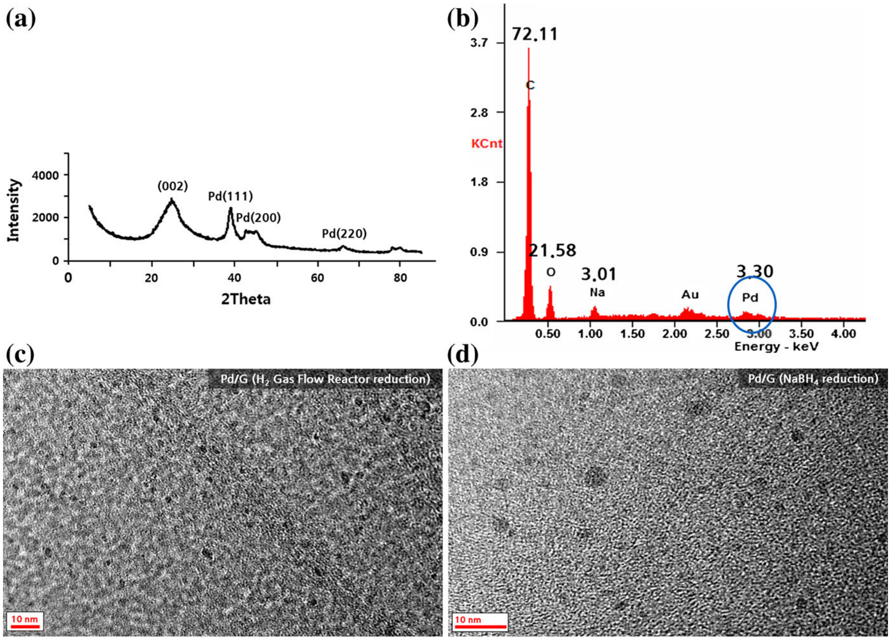


Fig. 1 **a** XRD patterns of Pd/G, **b** EDS analysis of Pd content in Pd/G, **c** TEM image of Pd/G (H_2 gas flow reactor reduction), and **d** TEM image of Pd/G ($NaBH_4$ reduction)

determined to be 2.0 ± 0.5 nm where more than 50 nanoparticles were randomly chosen and measured in an effort to achieve the desired statistical significance. The diameter of Pd NPs by sodium borohydride reduction was determined to 3.0 ± 0.5 nm, and the sizes of the catalysts were 5–8 μm indicated by SEM images. Palladium content of 3 % Pd/G was measured by EDS (3.3 %) and ICP-MS (3.2 %).

In order to test the degradation efficiency of the Pd/G catalyst in HDC reaction, variable amounts of the catalyst were added in the HDC reaction. Thus, 10 ml of 100 ppm solution of 4-chlorophenol in isopropanol was treated with catalyst (50, 100, or 150 mg of 3 % Pd/G), base (K_2CO_3, 100 mg) under a hydrogen gas at ambient pressure. The progress of the chlorophenol-decomposition was checked with GC/FID. As shown in Table 1, with 50 mg of 3 % Pd/G, 41.4 % of 4-chlorophenol was decomposed within 1 h and 4-chlorophenol had completely disappeared in 2 h. With 100 mg of 3 % Pd/G, 85.4 % of 4-chlorophenol was decomposed within 1 h and 4-chlorophenol had completely disappeared in 2 h. With 150 mg of 3 % Pd/G, 4-chlorophenol had completely disappeared within 1 h. From these results, we decided that 50 mg of catalyst was sufficient for degradation of 100 ppm chlorophenol solution. Next, in order to find the effect of base in the HDC reaction, various solid bases, such as Na_2CO_3, NaOAc, or KF/Al_2O_3, were tested for HDC reaction instead of K_2CO_3. As shown in Table 2, other bases Na_2CO_3, NaOAc, and KF/Al_2O_3, were also effective in HDC reaction. It is found that the degradation rate is faster with Na_2CO_3 than with K_2CO_3. Interestingly, when NaOAc was employed as a base, no cyclohexanone conversion was detected. It seems that chlorophenol substrate structures and base may change the mechanism of HDC reaction. The catalytic performance of Pd/G for the HDC of 6 dichlorophenol isomers was also investigated and the results are shown in Table 3. These Pd/G catalysts were also showed excellent catalytic activities for the HDC of dichlorophenols with reaction time of 2 h in the same condition. It seems that dechlorination rate was increasing with the increasing number of chlorine substituents. The dechlorination reaction rate appeared to be increased in the order of para- or ortho- > meta-position to hydroxyl group because of the electronic and steric hindrance of the substrate. The authors also prepared the palladium catalysts

Table 1 Hydrodechlorination of 4-chlorophenol (100 ppm) in 10 ml of isopropanol with various amounts of 3 % Pd/G and 100 mg of K_2CO_3

Time (h)	50 mg			100 mg			150 mg		
	Conv. (%)	X^{a}_{PhOH}	X^{b}_{Cone}	Conv. (%)	X_{PhOH}	X_{Cone}	Conv. (%)	X_{PhOH}	X_{Cone}
1	41.4	100.0	0.0	85.4	100.0	0.0	100.0	81.6	18.4
2	93.1	85.2	14.8	100.0	65.1	34.9	100.0	49.2	50.8
3	100	78.2	21.8	100.0	54.8	45.2	100.0	37.6	62.4
6	100	57.1	42.9	100.0	41.4	58.6	100.0	26.5	73.5

[a] X_{PhOH}: % selectivity of phenol

[b] X_{Cone}: % selectivity of cyclohexanone

Table 2 Hydrodechlorination of 4-chlorophenols (100 ppm) in 10 ml of isopropanol with 50 mg of 3 % Pd/G and 100 mg of base

Entry	Base	1 h			2 h		
		Conv. (%)	X^{a}_{PhOH}	X^{b}_{Cone}	Conv. (%)	X_{PhOH}	X_{Cone}
1	K_2CO_3	41.4	100.0	0.0	93.1	85.2	14.8
2	KF/Al_2O_3	91.7	85.1	14.9	100.0	79.2	20.8
3	Na_2CO_3	100.0	81.5	18.5	100.0	70.4	29.6
4	NaOAc	87.4	100.0	0.0	100.0	100.0	0.0

[a] X_{PhOH}: % selectivity of phenol

[b] X_{Cone}: % selectivity of cyclohexanone

Table 3 Hydrodechlorination of dichlorophenols (100 ppm) in 10 ml of isopropanol with 50 mg of 3 % Pd/G and 100 mg of K_2CO_3

Entry	Compound	1 h			2 h		
		Conv. (%)	X^{a}_{PhOH}	X^{b}_{Cone}	Conv. (%)	X_{PhOH}	X_{Cone}
1	4-Chlorophenol	41.4	100.0	0.0	93.1	85.2	14.8
2	2,3-Dichlorophenol	100.0	82.4	17.6	100.0	59.1	40.9
3	2,4-Dichlorophenol	100.0	100.0	0.0	100.0	24.4	75.6
4	2,5-Dichlorophenol	59.2	100.0	0.0	100.0	72.0	28.0
5	2,6-Dichlorophenol	100.0	100.0	0.0	100.0	61.5	38.5
6	3,4-Dichlorophenol	82.0	100.0	0.0	100.0	56.3	43.7
7	3,5-Dichlorophenol	49.8	100.0	0.0	90.9	67.7	32.3

[a] X_{PhOH}: % selectivity of phenol

[b] X_{Cone}: % selectivity of cyclohexanone

Table 4 Comparison of degradation efficiency of the catalysts (Pd/G, Pd–Y, and Pd–MCM-41)

Entry	Compound	1 h			2 h		
		Pd/G	Pd–Y	Pd–MCM-41	Pd/G	Pd–Y	Pd–MCM-41
1	4-Chlorophenol	41.4	35.1	19.4	100	65.5	55.7
2	2,4-Dichlorophenol	100	2.6	0	100	15.7	9.8
3	2,6-Dichlorophenol	100	42.1	15.3	100	100	28.7
4	3,4-Dichlorophenol	82.0	56.6	4.0	100	100	8.9

HDC reaction condition: Chlorophenols (100 ppm) in 10 ml of isopropanol were treated with 50 mg of catalysts using K_2CO_3 as base, and the degradation efficiency was checked after 1 and 2 h of reaction time, respectively

supported on zeolite (Pd–Y) and mesoporous material (Pd–MCM-41) for comparison of degradation efficiency of Pd/G catalyst with other Pd based catalysts. The results of HDC reaction efficiency of the catalysts was listed in Table 4 [17]. For comparison same palladium content (3 %) of Pd–Y and Pd–MCM-41 catalysts were prepared, and chlorophenols (100 ppm) in 10 ml of isopropanol were treated with

50 mg of catalysts using K_2CO_3 as base, and the degradation efficiency was checked after 1 and 2 h of reaction time, respectively. In the case of 4-chlorophenol, 41.4 % of 4-chlorophenol was decomposed within 1 h and 4-chlorophenol was completely disappeared in 2 h with Pd/G catalyst. However, 65.5 % of 4-chlorophenol was decomposed with Pd–Y and 55.7 % of 4-chlorophenol was decomposed with Pd–MCM-41 in 2 h, respectively. Activity of Pd/G catalyst in decomposition of dichlorophenols, such as 2,4-dichlorophenol, 2,6-dichlorophenol, and 3,4-dichlorophenol, was also better than decomposition of dichlorophenols with Pd/Y or Pd/MCM-41 under the same reaction conditions. The graphene-based Pd catalyst showed the highest catalytic performance among Pd/Y, Pd/MCM-41, and Pd/G catalysts. It seems that these results were due to high dispersity of palladium nanoparticles on the graphene surface, the higher specific surface area, and good affinity toward organic molecules especially aromatic compounds [17].

In order to find out the application of Pd/G catalyst to the environmentally polluted chlorophenol samples, mixture of dichlorophenol isomers (100 ppm, 10 ml in isopropanol) was decomposed under the same reaction conditions. As shown in Fig. 2, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, and 2,6-dichlorophenol disappeared within 2 h but 3,4-dichlorophenol and 3,5-dichlorophenol decomposed in 3 h because chlorine atoms in the *meta* position of phenol may be reduced very slowly in an HDC reaction, and monochlorophenols were not detected because produced monochlorophenols were simultaneously dechlorinated to phenol, and finally phenol was converted to cyclohexanone. In order to compare the Pd content of the catalyst in trichlorophenol HDC reaction, 1, 2, 3, 4, and 5 % Pd/G were prepared. When trichlorophenol were tried to decompose with these catalyst, 2,3,5-trichlorophenol was also degraded in 2 h with 2, 3, 4, or 5 % Pd/G. However, when 1 % Pd/G was used as a catalyst, dechlorination reaction took much

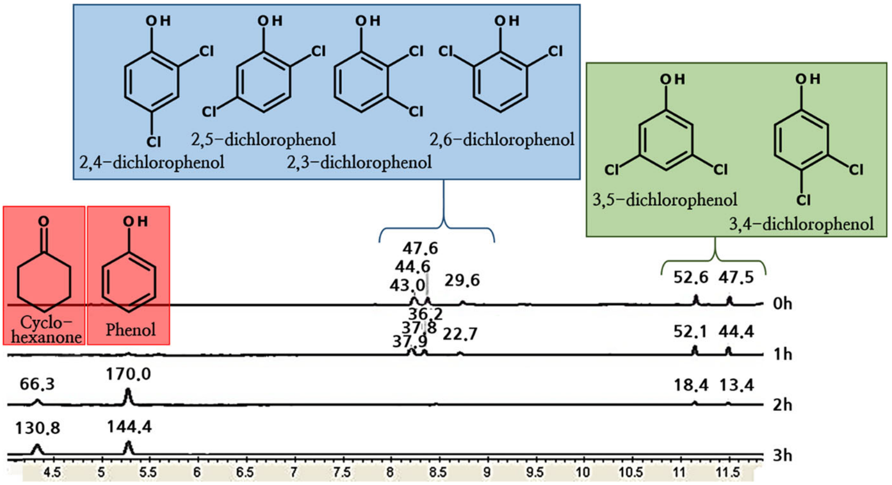


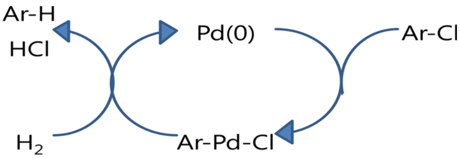
Fig. 2 Hydrodechlorination reaction of six isomers of dichlorophenol (100 ppm) in 10 ml of isopropanol with 50 mg of 3 % Pd/G. Dichlorophenols were completely decomposed within 3 h and phenol and cyclohexanone were produced

Table 5 Hydrodechlorination of 2,3,5-trichlorophenols (100 ppm) in 10 ml of isopropanol with 50 mg of Pd/G catalyst and 100 mg of K_2CO_3

Catalyst	Time (h)	Conv. (%)	X^{a}_{PhOH}	X^{b}_{Cone}
1 % Pd/G	1	45.3	0.0	0.0
	2	49.9	0.0	100.0
	3	53.7	0.0	100.0
	5	66.1	0.0	100.0
2 % Pd/G	1	54.8	29.0	71.0
	2	94.1	21.0	79.0
	3	100.0	0.0	100.0
	5	100.0	0.0	100.0
3 % Pd/G	1	70.0	48.0	52.0
	2	100.0	3.5	96.5
	3	100.0	0.0	100.0
	5	100.0	0.0	100.0
4 % Pd/G	1	79.6	39.5	60.5
	2	98.4	2.2	97.8
	3	100.0	0.0	100.0
	5	100.0	0.0	100.0
5 % Pd/G	1	92.9	42.7	57.3
	2	100.0	0.0	100.0
	3	100.0	0.0	100.0
	5	100.0	0.0	100.0

[a] X_{PhOH}: % selectivity of phenol

[b] X_{Cone}: % selectivity of cyclohexanone



Scheme 1 Feasible mechanism of HDC reaction of chlorophenols

time (Table 5). It is found that HDC reaction is finished through hydrogenolysis of C–Cl bond and hydrogen-substitution resulting phenol, and further hydrogenation of phenol yielding cyclohexanone [18]. This result was similar to reports of Dong group [19]. The feasible mechanism of HDC reaction with Pd/G is shown in Scheme 1.

Recovery and reuse of the catalyst and leaching of palladium nanoparticles in reaction medium are important issues when HDC reactions are carried out under heterogeneous conditions for industrial applications. Since it has been reported that the catalytic activity of the Pd NPs can be gradually poisoned by HCl formed during HDC reaction in spite of the addition of base, after the first cycle of the reaction the recovered catalyst was washed with alcohol and dried thoroughly for recycling study. It has been reported that the remaining oxygen functional groups of reduced graphene oxide can avoid the agglomeration and leaching of the Pd nanoparticles through interaction between the nanoparticles and the functional groups of graphene sheets, guaranteeing the high activity of the Pd/G. The performance of the recycled

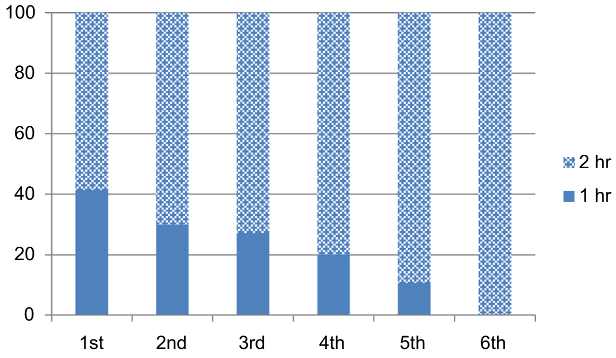


Fig. 3 Degradation yield of the recycled catalyst Pd/G

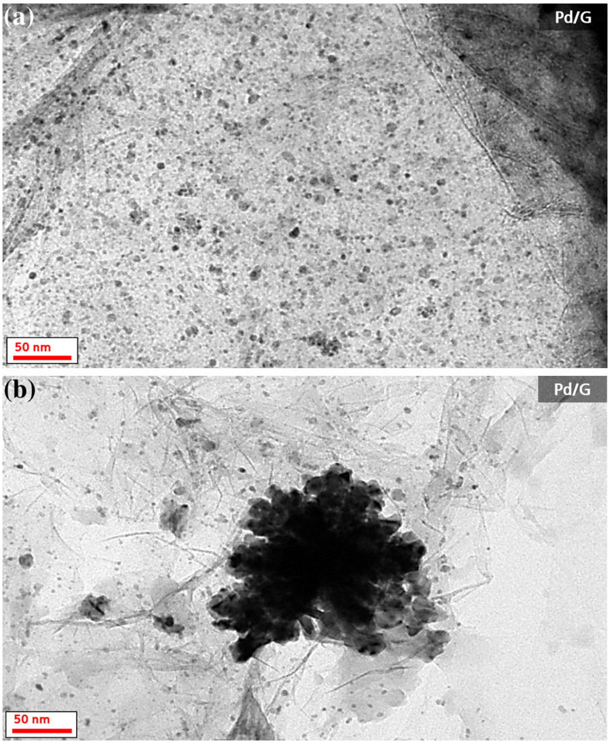


Fig. 4 **a** TEM image of Pd/G catalyst after first run and **b** TEM image of Pd/G catalyst after sixth run

catalyst in HDC reaction up to six successive runs is shown in Fig. 3. The reusability of the Pd/G nanocatalyst indicates that no obvious loss of activity with decreased reaction rate was detected for 4-CP HDC after the catalyst was reused six times without leaching of Pd but aggregation of Pd NPs was observed after six-recycle of the catalyst (Fig. 4).

Conclusions

For HDC reaction of 4-chlorophenol, 10 ml of 100 ppm solution of 4-chlorophenol in isopropanol was treated with catalyst (50 mg of 3 % Pd/G) and base (K_2CO_3, 100 mg) under hydrogen gas at ambient pressure. After 1 h, 41.4 % of 4-chlorophenol was decomposed and 4-chlorophenol completely disappeared in 2 h. It was found that all bases including K_2CO_3, KF/Al_2O_3, Na_2CO_3, and NaOAc are applicable for this reaction. These Pd/G catalysts also showed excellent catalytic activities for the HDC of dichlorophenols with the reaction time of 2 h in the same conditions. It seems that the reaction rate for dechlorination increased in the order of *para*- or *ortho*- > *meta*-position to hydroxyl group because of the electronic and steric hindrance of the substrate. Trichlorophenols were tried to decompose with these catalysts, 2,3,5-trichlorophenol were also degraded in 2 h with 2, 3, 4, or 5 % Pd/G. However, when 1 % Pd/G was used as a catalyst, dechlorination reaction took a lot of time. Final product was detected to be cyclohexanone in all Pd/G catalysts. The reusability of the Pd/G nanocatalyst indicates that no obvious loss of activity with decreased reaction rate was detected for 4-chlorophenol HDC after the catalyst was reused six times without leaching of Pd but aggregation of Pd nanoparticles was observed after six-recycle of the catalyst.

Pd nanoparticles of 1, 2, 3, 4, and 5 % supported on graphene (Pd/G) were easily prepared by H_2 reduction or $NaBH_4$ reduction. The HDC reaction of chlorophenols was catalyzed by Pd/G with base additives such as K_2CO_3 or Na_2CO_3 at room temperature. 4-Chlorophenol (100 ppm) was completely decomposed with Pd/G in 2 h. 2,3,5-TCP was also decomposed within 2 h. The reaction process of HDC was monitored by GC/FID and can be explained feasible degradation process with GC detection of degradation intermediates. It is found that Pd/graphene was an efficient catalyst for remediation of chlorophenols and can be recycled several times without decreasing activity.

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