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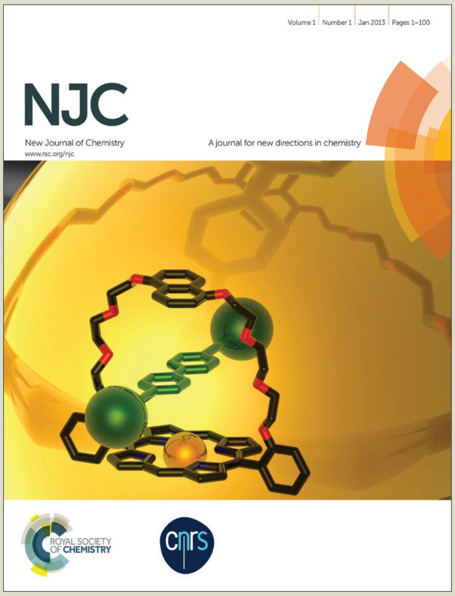

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ARTICLE

Convenient Preparation of Pd/RGO Catalyst for the Efficient Hydrodechlorination of Various Chlorophenols

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Uniformly dispersed Pd nanoparticles supported on reduced graphene oxide (RGO) has been conveniently synthesized by a facile one-pot approach through the co-reduction of sodium tetrachloropalladate(II) and graphene oxide (GO) using $NaBH_4$ as reducing agent. The catalytic activity of Pd/RGO was investigated for aqueous hydrodechlorination (HDC) of chlorophenols at room temperature and hydrogen balloon pressure without any additives. Results indicated that Pd/RGO exhibited excellent activity with a reaction rate of 280.0 $min^{-1}\cdot g_{pd}^{-1}$ for the hydrodechlorination (HDC) of 4-CP. Furthermore, the Pd nanoparticles supported on RGO is easily recoverable and can be reused four times without obvious leaching and loss of activity.

1. Introduction

Chlorophenols (CPs) have been widely used as pesticides, fungicides, herbicides, dyes, solvents, disinfectants and wood preservatives in industry and agriculture.[1, 2] However, the CPs residues would have adverse effect on the environment since CPs can hardly be biodegraded or self-cleaned in the environment. Nowadays, varied techniques have been adopted to dispose the residual CPs, among which catalytic hydrodechlorination (HDC) has been demonstrated as a cost-effective and environment-friendly technology.[3] The HDC of CPs by various heterogeneous catalysts containing noble metals (e.g., Pd,[1,3-6] Rh,[2,7-11] Pt [2,7]) has attracted tremendous interest due to their high reactivity.

Catalyst support plays a critical role in enhancing the activity of noble metals due to the improved dispersion of metal nanoparticles (NPs). Pd NPs deposited on conventional carriers, i.e., active carbon,[12] Al_2O_3 [2,8] and pillared clays,[7,9] have been tested as catalysts for CPs degradation. Recently, graphene has been identified as an excellent stabilizer [11] due to its excellent tolerance to HCl and high ability to improve the metal NPs dispersion. Although the Pd/RGO had good reactivity towards the 4-CP HDC, the Pd/RGO preparation was tedious and the reduction conditions of GO was rigorous to some extent. In the current work, a facile one-pot synthetic method was developed to prepare Pd/RGO NPs via a co-reduction of sodium tetrachloropalladate(II) and GO by sodium borohydride. The as-prepared Pd/RGO catalyst was found to exhibit high activity and stability in the HDC of 4-CP under moderate conditions.

2. Experimental Section

2.1 Reagents and materials

$Na_2PdCl_4\cdot 6H_2O$ were purchased from Kunming Institute of Precious Metals, China. Graphite powder and sodium borohydride ($NaBH_4$) were obtained from Aladdin Industrial Inc., China. Other solvents were analytical grade and used as received.

Graphene oxide (GO) was prepared according to the improved Hummer's method. [13] Typically, graphite powder (3.0 g) and $KMnO_4$ (18.0 g) were transferred into a 500 mL round-bottom-flask. And then the mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was slowly dropped into the flask under vigorous stirring. The mixture was heated to 50 °C and stirred for another 24 h and then 400 mL of ice containing 3 ml of 30% H_2O_2 were poured into the flask. The resulting suspension was centrifuged and washed with deionized water, HCl (36% wt.%), and absolute ethanol several times. The obtained solid as the aim product was dried under vacuum at room temperature for 12h.

Pd/RGO catalyst was synthesized using a one-pot co-reduction described as follows. GO (150 mg) was dispersed in 50 mL of deionized water under ultrasonication, giving a uniform suspension in which a 2.88 mL of Na_2PdCl_4 with a Pd concentration of 1.61mg/mL was slowly added with continuously stirring. Afterwards, a 10mL aqueous solution of $NaBH_4$ (150mg) was added dropwise into the mixture at 0 °C. The resulting black solid was obtained by centrifugation and washed with water and absolute ethanol several times. Finally, the black solid was dried under vacuum at 60 °C for 12 h, yielding the aim Pd/ RGO catalyst.

2.2 Activity tests

The catalytic activity of Pd/RGO towards the degradation of CPs was evaluated at 25 °C and hydrogen balloon pressure. Typically, 5.0 mg of Pd/RGO was added into a 25 mL two-necked round-bottom flask equiped with a hydrogen balloon. Then 5.0 mL of 4-CP aqueous solution with a 4-CP concentration of 2.5 g/L was transferred into the flask under continuous stirring. The catalyst concentration was kept at 1.0 g/L. The reaction temperature was controlled by a water bath. The flask was purged with pure hydorgen several times to remove the air. The reaction time was set at zero, when the temperature of reactant solution was stable. During the course of the reaction, samples were withdrawn from the flask periodically by a syringe and analyzed by GC (Agilent 7890A) with a FID detector

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and PEG-20M capillary column (30 m×0.25 mm, 0.25 μm film). Nitrogen acted as carrier gas.

3. Results and Discussion

3.1 Characterizations of the Pd/ RGO catalyst

TEM image (Fig.1a) of Pd/RGO with a Pd loading of 3.0 wt.% demonstrates that Pd NPs are uniformly dispersed on the surface of RGO sheets, which is probably assigned to the interaction between the Pd ions and oxygen-containing groups of GO, inhibiting the aggregation of Pd NPs during the reduction process. As shown in Fig. 1b, however, Pd/RGO NPs begun to aggregate after the fifth run. Strong diffraction peak at 2θ=26.4° of graphite shown in the insert of Fig. 1c was found to disappear, and a new peak at 2θ=10.0° corresponding to the plane of GO appears. It was clearly vestified that the successful oxidation of graphite to GO. In addition, the disappearance of the characteristic peaks of GO suggests the efficient reduction of GO. The two new peaks at the position of 25.4° and 43.1° are attributed to the (002) and (100) reflections of RGO, respectively. Those new peaks of Pd/RGO at 2θ=39.1°, 45.4°, 66.1°, which correspond to the (111), (200), and (220) planes of Pd (JCPDS card No. 87-0637), demonstrate that Pd NPs are indeed loaded on RGO surface through the one-pot co-reduction procedure.

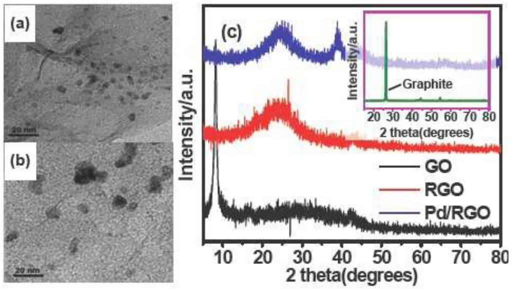

Fig. 1 TEM images of Pd/RGO (a) and Pd/RGO after five runs (b) as well as XRD patterns of GO, RGO and Pd/RGO (c). The insert of Fig. 1c displays the XRD pattern of graphite.

To determine the surface compositions and the electronic states of each element on the surface of Pd/RGO, the XPS elemental survey scans of Pd/RGO was firstly conducted (Fig. 2). The results obtained show the existence of Pd, oxygen, and carbon on the RGO surface. The C1s spectrum could be deconvoluted into four peaks which attribute the C–C, C–OH, C–O–C and HO–C=O, respectively. The declined peak intensities of oxygen-containing groups on RGO surface suggest the successful reduction of GO (Fig.2b and 2c). The binding energy of $Pd3d_{5/2}$ level in Pd/RGO is 335.8 eV, which is higher than that (= 335.0 eV) of the standard zero-valent state of Pd. The increase in binding energy of Pd(0) results from the electron transformation from palladium to RGO due to the strong interaction between Pd and RGO.[14] The peak at 337.9 eV is assigned to the oxidation state of Pd species, [15] and to some extent the presence of oxidation state of Pd facilitates the HDC of 4-CP as reported in Dr. Seoane' work. [16]

In fact, those facts mentioned above were also verified by the changed FT-IR adsorptions of the surface oxygen-containing functional groups on GO and RGO-supported Pd NPs (Fig. 3). Namely, for GO the broad characteristic band at 3420 cm^{-1} is attributed to the O-H stretching vibration arising from hydroxyl groups. The absorption bands associated with the C=O stretching are at 1730 cm^{-1}, and the C–O stretching at 1040 cm^{-1} and the C=C peak at 1610 cm^{-1} from unoxidized sp^2 C–C bonds are detected. The adsorption at 1230 cm^{-1} and 1040 cm^{-1} are attributed to the C=O vibrations and C–O groups situated at the edges of GO. This testifies the oxygen–containing groups on the GO surface, providing reactive anchoring sites for Pd ions and inhibiting the aggregation of Pd NPs during the reduction process. GO is successfully reduced in aqueous phase using $NaBH_4$, which is provided an evidence from the decreased intensity of the peaks corresponding to the oxygen-containing groups. Accordinally, based on the above-mentioned characterizations we believe that the the desired Pd/RGO catalyst was obtained with the convenient co-reduction process.

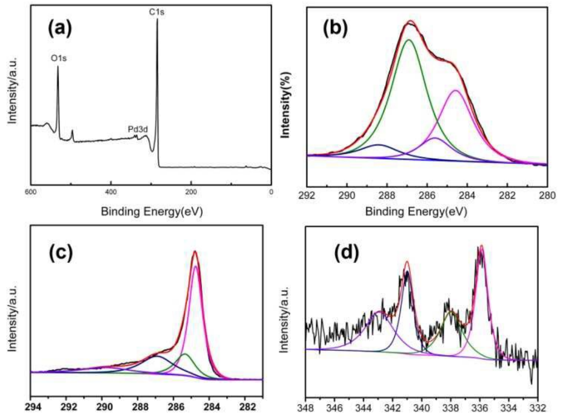

Fig. 2 XPS scans of Pd/RGO (a); XPS spectra of C_{1s} peaks of GO (b), RGO(c) and Pd 3d peaks of Pd/RGO (d).

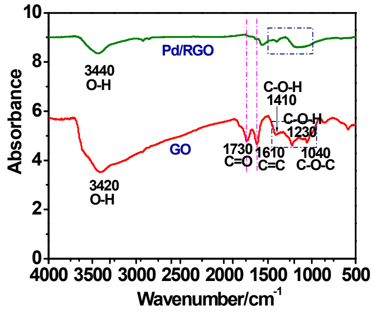

Fig. 3 Distinguishabe FT-IR adsorptions of GO and RGO-supported Pd NPs.

3.2 Effect of varied solvents on the HDC of 4-chlorophenol

In this case, effects of varied solvents, including water, methanol, ethanol, cyclohexane and 1,4-dioxane, on the catalytic preformance of Pd/RGO were firstly evaluated for the HDC of 4-CP (Fig.4). It can be seen that Pd/RGO displayed distinguishable reactivity in various solvents. Specifically, 4-CP could be completely converted to phenol in 90 min when water acted as green solvent. Meanwhile, the reactivity of Pd/RGO in protic solvents and aprotic solvents were obviously decreased. The initial HDC rates of 4-CP over Pd/RGO in different solvents exhibited a marked dependence on the reaction media and decreased in the order: water > methanol > ethanol > cyclohexane>1,4-dioxane.

With respect to product distributions, the main product was phenol and only trace amount of cyclohexanone (<0.1%) was detected. This fact was probably attributed to the low concentration of catalyst (1.0 g/L) and high initial concentration of 4-CP (2.5 g/L) as well as low reaction temperature (25 ^{o}C).[17] Additionally, the low reaction temperature also contributed to the low selectivity to cyclohexanone, [17] which was confirmed by observing the increase of cyclohexanone selectivity to 0.9 % when the reaction was conducted at elevating temperature of 40 ^{o}C (Fig.S1). Furthermore, the product distributions did not vary obviously regardless of the solvents. The solvent with high dielectric constant and low molar volume is beneficial to the HDC reaction. On the one hand, the solvent with higher dielectric constant provides stronger ionic forces to stabilize the electropositive arenium intermediate. On the other hand, the solvent with low molar volume means that more solvent molecular available to interact with the charged reaction intermediate, which obviously accelerates the HDC reaction of 4-CP. Thereupon, the highest catalytic activity of Pd/RGO for the HDC of 4-CP in water was ascribed to the properties of water. In comparison with the other four organic media, the highest activity of Pd/RGO for the HDC of 4-CP in water was due to the well-organized structure of water originated from the formation of an H-bonding between the dissolving ions and water with the highest/lowest values of dielectric constant and molar volume. [18]

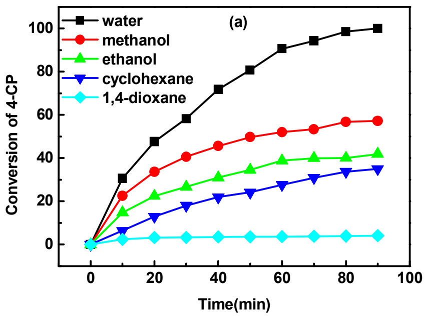

Fig. 4 Effect of different solvents on the conversion of 4-CP.

3.3 Kinetics and recycling test of catalyst

As illustrated in Fig.5, the kinetic study showed that the conversion of 4-CP increased with the elevation of reaction temperature in the range from 298 to 313 K. Meantime, there is no noticeable change towards the product distributions regardless of the temperature variation. Rate constants (k_{obs}) are determined from the slope of the linear part of each plot in Fig.5(a). The activation energy (E_a) is calculated using the Arrhenius equation (Eq. 1). Consequently, the activation energy is estimated to be 61.5 kJ/mol based on the slope of the lnk-(1/T) plot shown in Fig.5(b). The kinetic reaction rate of 4-CP HDC catalyzed by Pd/RGO was compared with the reported results. The catalyst Pd/Al_2O_3 reported by Diaz et al.[2] showed a kinetic reaction rate of 3.33 min^{-1}•g^{-1} and Pd/pillared clays reported by Molina et al.[19] exhibited a reaction rate of 7.6 min^{-1}•g^{-1}, respectively. Increasing reaction rate to 13.2 min^{-1}•g^{-1} was detected by Liu et al.[17] with a Pd/dendritic mesoporous silica nanospheres. Noteworthyly, in our case the highest reaction rate of 280.0 min^{-1}•g^{-1} was observed at the same reaction temperature when the HDC of 4-CP was catalyzed by Pd/RGO, which was probably ascribed to the strong interaction between Pd and RGO as well as the presence of electron-deficient Pd on RGO surface.

$$k_{obs} = Ae^{-E_a/RT} \quad \text{………………} \ (1)$$

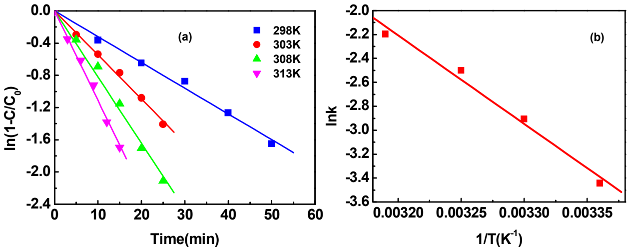

Fig. 5 Effect of temperature on the reactivity of Pd/RGO for the HDC of 4-CP. Dependant of ln*k* upon 1/T based on the rearranged Arrhenius equation is shown in Fig. 5(b).

The stability and recyclability of Pd/RGO for the HDC of 4-CP was investigated with successive runs under the operated conditions. After each run, the solid catalyst was separated from the reactor by centrifugation and the supernatant liquid was removed. The black solid was thoroughly washed three times with ethanol, dried in vacuum, and reused for next run. As shown in Fig.6, the catalyst is quite stable and no loss of activity for the HDC of 4-CP was detected after the catalyst was reused four times. Howbeit, the activity of Pd/RGO begun to decrease after the fifth run. Pd leching test was firstly conducted by ICP and the results indicate that the Pd leaching is negligible (0.4 ppm). In addition, XRD investigation shows that the crystalline structure of the recovered catalyst is mostly retained after five catalytic cycles (Fig.S2). The suface property of the recycled catalyst analyzed by XPS (Fig.S3) shows that the binding energy of Pd(0) in the recovered catalyst was shifted to 334.5 eV, which was probaly due to the inhibition of the electron transformation from palladium to RGO, resulting in the decrease of the interaction between Pd and RGO. TEM image of the recycled catalyst indicates the aggregation of Pd NPs during the recycling process (Fig. 1b). In addtion, the element mappings (Fig. S4) of metallic Pd on Pd/RGO catalyst provide available and visual evidence for the aggregation and loss of Pd after five runs even if those corresponding SEM images have no observed changes. Therefore, the derease of interaction between Pd and RGO and the increasing of Pd particle size were respondibale for the loss of catalytic activity in the fifth runs. Further work should be done to improve the reusability of Pd/RGO catalyst for practical application.

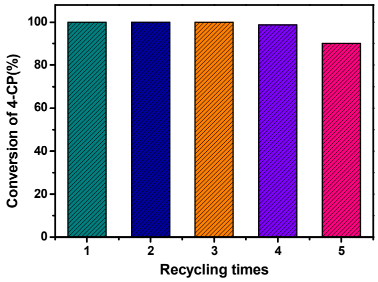

Fig. 6 Recyclability survey of Pd/RGO for the HDC of 4-CP.

3.4 Reactivity of the Pd/RGO for the HDC of various CPs

To evaluate the activity of the as-prepared Pd catalyst for the HDC of different substrates, the catalytic performance of Pd/RGO was screened for the HDC of other five kinds of chlorophenols (Table 1). The observations indicate that the reaction time for the complete conversion of monochlorophenols increases in the order of 3-CP < 2-CP< 4-CP, which probably results from the distinguishable electronic and steric hindrance of these monochlorine-substituted substrates. Additionally, dichlorophenols (2,4-DCP and 2,6-DCP) and trichlorophenol (2,4,6-TCP) can be completely HDC to produce phenol as reaction time was prolonged. In brief, the HDC rates of CPs decrease in the following order: monochlorophenols> dichlorophenols>trichorophenol, which was consistent with a previous study.[20] The increased reaction time with the increase of substituted substrates was probably assigned to the poisoned active sites of Pd/RGO catalyst because of the higher content of HCl generated during the reaction proccess.

Table 1 HDC of different CPs catalyzed by Pd/RGO

Substrates	Product	Conv.(%)	Time(min)
2-CP	Phenol	100	70
3-CP	Phenol	100	60
2,4-DCP	Phenol	100	120
2,6-DCP	Phenol	100	150
2,4,6-TCP	Phenol	100	200

Reaction conditions: temperature: 25 °C, pressure: hydrogen balloon pressure, metal concentration: 1.0 g/L, 4-CP concentration: 2.5 g/L(total volume 5.0 mL).

Conclusions

In summary, Pd/RGO synthesized by a facile one-pot method exhibited excellent reactivity for the HDC of various chlorophenols. Moreover, the as-prepared Pd/RGO could be reused at least four times without significant deactivation. Especially, in environment-friendly water completed converison of 4-chlorophenol was achieved by the Pd/RGO catalyst in 90min under moderate conditions. This advanced composite material provides a kind of effective catalyst with great promise for catalytic HDC of CPs in practical application. What is more, a novel preparation stratage concerning a one-pot co-reduction will attract researchers more attentions.

Acknowledgements

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Graphical Abstract

Convenient Preparation of Pd/RGO Catalyst for the Efficient Hydrodechlorination of Various Chlorophenols

Weidong Jiang, Zhen Xiang, Bin Xu, Xiaojing Li, Fuan Liu and Guangyin Fan

Highly active Pd/RGO (RGO, reduced graphene oxide) was easily prepared by one pot co-reduction of Pd ions and GO using $NaBH_4$. The as-prepared catalyst exhibited excellent reactivity towards the degradation of chlorophenols at mild conditions without additives.