### Accepted Manuscript

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PII:	S1381-1169(15)00200-9
DOI:	http://dx.doi.org/doi:10.1016/j.molcata.2015.05.016
Reference:	MOLCAA 9502
To appear in:	Journal of Molecular Catalysis A: Chemical
Received date:	1-3-2015
Revised date:	21-5-2015
Accepted date:	23-5-2015

Please cite this article as: Yansheng Liu, Bo Qiao, Xinlin Li, Xuanduong Le, Wei Zhang, Jiantai Ma, Hydrodechlorination of chlorophenols catalyzed by SiO2/Pd@m-SiO2 core-shell structured catalyst, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2015.05.016

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Hydrodechlorination of chlorophenols catalyzed by SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> core-shell structured catalyst

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**Graphical abstract** 



### Highlight

- 1. SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> catalyst with encapsulated Pd nanoparticles has been synthesis.
- 2. Which good catalytic activity has been establish in HDC of 4-CP
- 3. The mesoporous shell can solve two major challenges to widespread technology adoption.
- 4.  $SiO_2/Pd@m-SiO_2$  catalyst exhibited good recycle character.

#### Abstract

Palladium metal nanoparticles have been applied to hydrodechlorination of chlorophenols in contaminated water using  $H_2$  as a clean and sustainable reductant. However, there are two major challenges to widespread technology adoption which are the activity loss caused by nanoparticle aggregation and the difficulty of nanoparticle recovery. In this study, a synthesis of a core-shell structured catalyst with encapsulated Pd nanoparticles has been given and whose catalytic activity has been tested in hydrodechlorination of chlorophenols under 1 atm  $H_2$  at room temperature. The catalyst material consists of a nonporous silica core decorated with Pd nanoparticles that are further encapsulated within an ordered mesoporous silica shell. Well-defined mesopores (2.4 nm) provide a physical barrier to prevent Pd

nanoparticle (~10 nm) movement, aggregation and detachment from the support into

water. Compared with some supported Pd catalysts such as Pd/AC and Pd/Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> exhibits higher catalytic performance. After 5 times of recycling, catalytic activity of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> reduces slightly and this result confirms the good recyclability of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>. The function of the mesoporous shell, preventing aggregation of active nanoparticles, suggests a promising general strategy

of using metal nanoparticle catalysts for water purification and related aqueous-phase applications.

### Keywords

 $SiO_2/Pd@m\text{-}SiO_2$  nanocatalyst, metal nanoparticles , HDC reaction, 4-CP

### 1. Introduction

Nowadays, the environmental pollution caused by organic wastes has become an un-ignorable issue. With the staggering growth of industrialization, large numbers of organic compounds, such as the aryl chlorides, have been produced and employed. During the application of aryl chlorides severe environmental pollutions have been produced. Among the most harmful organic contaminants, aryl chlorides are considered as hazardous pollutants because of their acute toxicity and strong potential bioaccumulation.<sup>1</sup> Special attentions have been paid to chlorophenols (CPs) for their widespread availability in important industrial processes, such as the production of germicides, algaecides, fungicides, herbicides, dyes, wood protectors and plant growth regulators.<sup>2</sup> So how to deal with pollutions caused by CPs has become increasingly important and has no time to delay. Up to now, many reported traditional methods including thermal combustion, reduction dechlorination,<sup>3, 4</sup> oxidation dechlorination,<sup>5</sup> biodegradation and photocatalytic degradation have been employed in disposing the wastewater containing CPs. Among the treatment methods mentioned above, thermal combustion and chemical oxidation have been largely employed in the treatment of CPs. Although there are some advantages, it must be noticed that these methods cannot decompose 4-CP completely into simple inorganic compounds such as CO<sub>2</sub>, H<sub>2</sub>O and HCl. In addition, toxic chlorinated chemicals such as dioxins, phosgene and chlorine could generate in these treatments processes.<sup>6</sup> These

accompanied chemicals can result in secondary pollutions and especially do harm to the health of human beings and atmospheric ecosystem. Therefore, removal of these compounds through a cost-effective and environmentally-friendly way has attracted many researchers' attentions. Compared with traditional treatments of 4-CP mentioned above, hydrodechlorination (HDC) possesses some advantages. By using efficient catalysts, the reaction can be run under a mild condition and the energy consumption can be reduced. In addition, it can reduce the formation of by-products and can be suitable for the treatment of a wide range of chlorinated compounds.<sup>7</sup> Both from the economic point of view and for achieving the greatest degradation of 4-CP, catalytic HDC can be considered as an effective and promising method.

In the 1960s, the study of HDC of CPs was initiated, however the first comprehensive report of the liquid phase exhaustive HDC of CPs to phenol over Pd/C only appeared in 1992.<sup>8</sup> From that moment on, the liquid phase catalytic HDC has been studied by many researchers.<sup>7, 9, 10</sup> Many influence factors of 4-CP HDC have been studied, such as active phase, supports, sources of hydrogen and reaction media.<sup>11, 12</sup> By summarizing the experiences of pioneers, the HDC treatment of CPs using noble metal as activity phase and molecular hydrogen as hydrogen source has been proved to be an efficient method.<sup>13</sup> Till now, large numbers of catalysts using metal nanoparticles (NPs) like Pd<sup>12, 14-17</sup>, Pt<sup>18, 19</sup>, Rh<sup>20</sup> and Ni<sup>15</sup> as active phases have been researched greatly. Among them, Pd based catalysts show an excellent catalytic activity for the treatment of CPs at room temperature and atmospheric pressure.

According to the studies of L. Calvo<sup>21</sup> and F. J. Urbano1,<sup>22</sup> it seems that HDC may be a structure-sensitive reaction. The effect factors of supports in HDC reactions had been extensively studied. Recent researches have demonstrated that the supports are significant influences on the dispersion and electronic properties of the NPs. Many supports, such as activated carbon (AC),<sup>23-25</sup> Al<sub>2</sub>O<sub>3</sub><sup>26</sup> or zeolites<sup>27, 28</sup> have been employed to prepare catalysts for HDC of 4-CP. The studies show that Al<sub>2</sub>O<sub>3</sub> as support can improve the stability of active species of the catalyst. Nevertheless, this metal oxide support is more sensitive to HCl produced during the HDC process. Compared with Al<sub>2</sub>O<sub>3</sub>, AC seems more suitable as a support because of its large surface area and particular physical and chemical properties.<sup>13</sup> However, the strong adsorption properties based on surface area, pore size distribution, and surface composition limit the applications of AC. During the HDC process, bare NPs can be directly connected with the reactant molecules which can accelerate reaction velocity. However, the bare NPs can easily drop off the support and result in a loss of noble metal. This situation can reduce the recycling value and catalytic activity of catalyst.

In this study, active phase focuses on Pd NPs because of the excellent catalytic activity of Pd NPs in HDC of 4-CP. Based on the considerations of catalytic activity affected by surface area, large size  $SiO_2$  with ~500 nm is used as a core that can make Pd NPs well dispersed. In order to solve the noble metal loss problem, a sandwich-like structure with large size of NPs and small size of pore has been

designed in this research and its catalytic performance for HDC of CPs has also been studied.

### 2. Experimental

#### 2.1 Materials

Tetraethoxysilane (TOES), Pd(II) acetate, (3-aminopropyl)triethoxysilane (APTES) and Hexadecyl trimethyl ammonium Bromide (CTAB) are purchased from Aladdin Chemical Co., Ltd. 4-Chlorphenol (4-CP), 2-Chlorphenol (2-CP), 2,4-Dichlorophenol (2,4-DCP) and concentrated ammonia aqueous solution are purchased from Lanzhou Aihua Chemical Company. NaBH<sub>4</sub> is supplied by Sinophrm Chemical Reagent Co., Ltd. Oganic solvents used are of analytical grade and do not require further purification.

### 2.2 Preparation of SiO<sub>2</sub> microsphere

The Silica nanospheres is synthesized by a modified Stöber protocol.<sup>29</sup> In a typical synthesis, 2.7 mL of TEOS is added dropwise into a mixture solution of 180 mL of ethanol, 30 mL of concentrated ammonia aqueous solution and 9 mL of distilled water by stirring it at room temperature. After additional stirring for 12 h, the SiO<sub>2</sub> microspheres are collected by centrifugation (8000 rpm, 3 min) and washed with distilled water and ethanol for several times. Then the collected microspheres are dried at 40 °C in a vacuum drying oven over night for further use.

### 2.3 Preparation of APTES modified SiO<sub>2</sub> microsphere

300 mg of SiO<sub>2</sub> microspheres are added in 30 mL of methylbenzene under ultrasonic dispersion for 15 min. Then 150 mg of APTES is added and refluxed at 90 °C for 12 h. The modified SiO<sub>2</sub> microspheres are collected by centrifugation (8000 rpm, 3 min) and washed with distilled water and ethanol for several times. Then the collected nanospheres are dried at 40 °C in a vacuum drying oven over night for further use.

#### 2.4 Preparation of SiO<sub>2</sub>/Pd NPs

300 mg of APTES modified SiO<sub>2</sub> is added in 30 mL of distilled water under ultrasonic dispersion for 15 min. Then 60 mL of Pd acetate acetonitrile solution (2.11 mg mL<sup>-1</sup>) is added under strong stirring for 12 h. After this step, 30 mL of 0.3 M NaBH<sub>4</sub> aqueous solution is added in the solution drop by drop. The products are collected by centrifugation (8000 rpm, 3 min) and washed with distilled water and ethanol for several times. Then the collected nanospheres are dried at 40 °C in a vacuum drying oven over night for further use.

#### 2.5 Preparation of SiO<sub>2</sub>/Pd@mesoporous-SiO<sub>2</sub>

To grow a mesoporous silica shell on the SiO<sub>2</sub>@Pd microspheres, the as-made SiO<sub>2</sub>/Pd nanosphere (300 mg) is redispersed in a mixed solution containing CTAB (0.45 g, 1.2 mmol), distilled water (100 mL), concentrated ammonia solution (2.0 mL, 28 wt %), and ethanol (150 mL). The resultant mixed solution is ultrasonic dispersed for 5 min and then stirred for 30 min to form a uniform dispersion. Subsequently, 0.8 mL of TEOS is added drop-wise to the dispersion under continuous stirring. After

magnetic stirring for 6 h, the product is collected by centrifugation (8000 rpm, 3 min) and washed with distilled water and ethanol for several times. Finally, the purified microsphere is re-dispersed in 100 mL of ethanol and 1 mL of concentrated hydrochloric acid at room temperature for 24 h to remove the template CTAB. The as-prepared catalyst is dried at 40 °C in a vacuum drying oven over night.

### 2.6 General procedures for the hydrodechlorination of CPs

HDC experiments are performed in a three-necked jacketed glass reactor connected with hydrogen balloon by a three-way valve. Firstly, a certain quantity/amount of catalyst is placed into the mixed solution of 30 mL of solvent (H<sub>2</sub>O, ethyl acetate, ethyl alcohol), 1 mmol of reactant and 1 mmol base (Na<sub>2</sub>CO<sub>3</sub>, NaAc, triethyl amine, Na<sub>2</sub>OH). Secondly, use a circulating water vacuum pump to extract the air in the reactor for 5 - 10 sconds. Then open the three-way valve and make the hydrogen get into reactor. Repeating the gases replacement process three times and starting the clock. The reaction maintains for 2 h under vigorous stirring at room temperature. The results of the experiments are analysed by gas chromatograph-mass spectrometer (GC-MS).

### 2.6 Reusability experiment

The reusability experiments are performed in a centrifuge tube (in order to reduce catalyst losing) with supplied  $H_2$ . The catalyst is recovered by centrifugation and simple decantation of liquid products. The catalyst is then washed with deionized water and used directly for the next cycle of the reaction without further purification.

### 2.7 General methods

Transmission electron microscopy (TEM) images are obtained on a Tecnai G2 F30, FEI, USA. The Brunauer–Emmett–Teller (BET) surface area and pore-size distribution are obtained by measuring N<sub>2</sub> adsorption isotherms at 77 K with using a TriStar 3020 (Micromeritics). Powder x-ray diffraction (XRD) spectra are obtained by a Rigaku D/max-2400 diffractometer with using Cu-K $\alpha$  radiation in the 2 $\theta$  range of 0°-80°. X-ray photoelectron spectroscopy (XPS) is recorded on a PHI-5702 and the C1S line at 284.6 eV is used as the binding energy reference. The reaction conversion is estimated by using GC-MS (P.E. AutoSystem XL).

### **3.** Results and Discussion

#### **3.1 Characterization**

Figure 1 shows the FT-IR spectra of the SiO<sub>2</sub> sphere and SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> nanocatalyst. The FTIR bands at 1091 cm<sup>-1</sup> and 804 cm<sup>-1</sup>, corresponding to the antisymmetric and symmetric stretching vibration of Si–O–Si bond in oxygen-silica tetrahedron, respectively. The bands at 461 correspond to Si–O stretching. The band at 3420 cm<sup>-1</sup> shows the large number of Si–OH groups which are proved to be advantageous to the modification of APTES on the SiO<sub>2</sub> surface by hydrogen bonds. The band at 2923 cm<sup>-1</sup> corresponds to -CH stretching. In the FT-IR spectrum of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>, the band around 3400 cm<sup>-1</sup> represents the adsorption of –OH and

 $-NH_2$  groups. The nitrogen, hydrogen, and carbon contents are 0.9%, 1.65%, and 3.92%, which are measured by the elementary analysis, respectively. The FT-IR spectra and elementary analysis results reveal that the APTES is successfully grafted on the surface of SiO<sub>2</sub><sup>30</sup>, thus enabling them to act as robust anchors for metal NPs.<sup>31</sup>, <sup>32</sup>

The synthesis procedures of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> nanaocatalyst are represented in Scheme 1 and described in detail in the experimental section. TEM and SEM images of SiO2/Pd@m-SiO2 with 7.0% metal loading which calculated by inductive coupled measurement are shown in Figure 2. Figure 2b shows a typical SEM image of prepared SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> core-shell structured NPs. From Figure 2a and Figure 2d, it can be seen that mesoporous SiO<sub>2</sub> is capped on the surface of SiO<sub>2</sub>/Pd and it also can be measured that average diameter of SiO<sub>2</sub> core, the thicknesses of m-SiO<sub>2</sub> shell and pore size of m-SiO<sub>2</sub> shell are about ~500 nm, 100 nm and 2.35 nm, respectively. From figure 2c, it can be clearly seen that the Pd NPs with a dimater of 10 nm are located between the SiO<sub>2</sub> core and m-SiO<sub>2</sub> shell. This core-shell structure matches our original intention.

 $N_2$  adsorption-desorption isotherms for the SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> are given in Figure 3. According to the IUPAC classification, the curves of as-prepared sample is type IV isotherms with a very sharp capillary condensation step at P/P<sub>0</sub> = 0.10–0.30 and H<sub>4</sub>-type

hysteresis loop characterizing small-pore mesoporous materials. The pore size of as-prepared catalyst derived from the BJH analysis on the desorption branch is 2.4 nm. The calculated BET surface area and pore volume of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> are 560 m<sup>2</sup> g<sup>-1</sup> and 0.34 cm<sup>3</sup> g<sup>-1</sup>, respectively.

The small-angle and wide-angle XRD patterns of nanaocatalyst are obtained in Figure 4. There is an intense characteristic peak at  $2\theta = 2.3^{\circ}$ , which corresponds to the plane (211) of mesoporous material. From the Figure 3b, SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> possesses three peaks, which correspond to planes (111), (200), (220) of Pd. Within the approximation of the Scherrer equation, one would expect a FWHM of 2. 3° 2theta for the (111) reflection of Pd with an average crystal size of 9.8 nm that matches with the particles size of Pd NPs calculated by using TEM images.

The electronic state of Pd species on the SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> is measured with XPS. The pattern of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> catalyst is exhibited in Figure 5. The Pd<sub>3d</sub> peaks in XPS spectra show that the binding energy values of 335.8 eV and 341.2 eV are attributed to the  $3d_{5/2}$  and  $3d_{3/2}$  peaks of Pd. Because the Pd NPs is encapsulated within an ordered mesoporous silica shell, the intensity of XPS peak of Pd is weak. In addition, no evidence proves the presence of palladium oxide, which indicates that Pd(OAc)<sub>2</sub> is completely reduced to Pd NPs.

#### 3.2 HDC of 4-CP

The catalytic activity of nanocatalyst is established in the HDC of CPs at room temperature and atmospheric pressure. The HDC of 4-CP is negligible without catalyst at the same conditions, which shows that the presence of metal NPs is indispensable for high catalytic activity. In some researchers' studies, three products such as phenol, cyclohexanol and cyclohexanone are generated in the process of HDC of 4-CP.<sup>22</sup> Compared with the reactant 4-CP, the three products are detected of low toxicity and useful as intermediates in the production of high value-added chemicals. The low selectivity of HDC of 4-CP performs in fixed bed reactor<sup>33, 34</sup> or under a high H<sub>2</sub> pressure condition.<sup>18</sup> In the study of L. Calvo, the conversion of 93% and the selectivity of 85% are reported by using Pd/C as catalyst and formic acid as hydrogen source in continuous stirred-tank reactor.<sup>2</sup> Pd/Al<sub>2</sub>O<sub>3</sub> as HDC catalyst are also studied by E. Diaz.<sup>33</sup> in fixed bed reactor with the conversion of 87% and the selectivity of 62%, respectively.<sup>33</sup> However, only high selective product phenol is detected as product and less than 0.1% of CYC is detected after 120 min reaction in presente reaction system. These differences may be caused by using different reaction systems. Also this result agrees with the study that uses the same reaction system in which phenol as major product is detected.<sup>13, 32, 35-38</sup>

The HDC reaction pathway is described as below:  $H_2$  adsorbed on the active site of the nanocatalyst is activated in two hydrogen atoms, in which 4-CP is also adsorbed on the surface of the Pd NPs. The C-Cl bond of 4-CP is attacked by the active hydrogen atoms to form phenol.<sup>36</sup> Simultaneously, in the process of HDC of 4-CP, HCl formes as

by-product which can poison catalysts. In order to reduce the inhibition of generated HCl, four kinds of bases have been studied. By comparing the HDC results, it can be easiliy summarized that NaOH is the best choice.<sup>36</sup> With the addition of base, catalyst deactivation is largely governed by HCl solubility/transport and the nature of the basic species in the catalyst matrix have reported higher HDC rates and enhanced catalyst stability.<sup>39</sup> In addition, organic and inorganc solvent are also tested and water could be consider as the best choice. The results of HDC of 2-CP, 3-CP, 4-CP and 2,4-DCP using SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> catalyst are carried out and exhibited in Table 1. At the same catalyst dosage (15 mg), after 90 min of reaction, 4-CP completely convertes and the convertion of 3-CP and 2-CP are 89.4% and 81.6%, respectively.

The concentration of  $H_2$  can be considered constant since all the reactions are carried out with a high excess  $H_2$ . Therefore, the reaction follows pseudo-first-order reaction kinetics:

$$R_{4-CP} = \frac{dC_{4-CP}}{dt} = -r = -kC_{4-CP}$$
(1)

$$\int_{c_{o'}}^{c_{t}} \frac{1}{c_{t}} dc_{t} = -k \int_{0}^{t} dt$$
(2)

$$\ln \frac{C_t}{C_{0'}} = -kt \tag{3}$$

$$X_{t} = \frac{C_{t}}{C_{0'}} \qquad (4) \qquad C_{0'} = C_{0} - C_{1} \qquad (5)$$

$$\ln \frac{C_t}{C_{0'}} = \ln \frac{C_t}{C_0 - C_1} = \ln X_t - \ln(1 - \frac{C_1}{C_0}) = -kt$$
(6)

$$\ln X_{t} = -kt + \ln(1 - \frac{C_{1}}{C_{0}})$$
(7)

In the practical experiments process, nearly 30s required to make the system stable. So the at the time zero point, some amount of reactant has been converted and the initial concentration changes from  $C_0$  to  $C_0$  which make the fitted curve do not cross original point.

According to the concentration value related to the reaction time, and the plotted logarithm of 4-CP concentration versus reaction time, the linear fittings are drew in Figure 6. The average reaction rate constant per unit mass k = k/MPd is calculated to be 39.2 min<sup>-1</sup> g<sup>-1</sup>. The kinetic reaction rate of HDC catalyzed by Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/pillared clays, Pd/MCM-48 catalyst are 3.33 min<sup>-1</sup> g<sup>-1</sup>, 7.6 min<sup>-1</sup> g<sup>-1</sup> and 42.9 min min<sup>-1</sup> g<sup>-1</sup>, respectively.<sup>18 34 35</sup> Compared with these Pd based catalysts which had been reported, the catalyst activity of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> is at a middle position. On one hand, the catalyst of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> performs higher than low surface area catalyst Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/pillared clays. On the other hand, catalytic activity of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> is smaller than Pd/MCM-48 catalyst which Pd NPs is bare. This indicates that the m-SiO<sub>2</sub> shell can restrain the combination between the reactant molecules and activity phase, which results in the activity reduction of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>.

The recoverability and reusability are investigated by the HDC reaction of 4-CP and the results are summarized in Figure 7. After 5 times of recycling, the metal loading of catalyst is 6.9% instead of 7.0% and catalytic activity of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>

is reduced slightly. These results confirm the good recyclability of the Pd NPs in SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> catalyst.

#### 4. Conclusion

In summary, SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> core-shell structured nanocatalyst has been synthesised successfully and the catalytic property is investigated in HDC process in which 4-CP is used as target compound under the condition of sodium hydroxide aqueous solution and at atmospheric H<sub>2</sub> pressure, fairly mild conditions. According to the characters of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>, large size of Pd NPs are located between SiO<sub>2</sub> core and m-SiO<sub>2</sub> shell. The SiO<sub>2</sub> layer is used as a barrier to prevent the shedding of Pd NPs from support and the small pores in mesoporous SiO<sub>2</sub> allow the molecules to pass through. This structure can reduce the metal losing and increase utilization of catalyst. By analysing the HDC result, SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> nanocatalyst shows a good catalytic activity for HDC of 4-CP, with the reaction rate constant per unit mass  $\mathbf{k}^{'}$ =  $k/M_{Pd}$  is 39.2 min<sup>-1</sup> g<sup>-1</sup>. The SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> nanocatalyst can be recycled for at least five times in the corresponding reactions without significant deactivation and metal loss. In this study, SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> nanocatalyst acts as a relatively mild, economical, and environmental friendly catalyst, and could be regarded as a promising candidate for various Pd based catalytic applications.

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#### **Scheme and Figure captions**

Scheme 1. The schematic synthesis of the SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> catalyst

Figure 1. FT-IR spectra of SiO<sub>2</sub> and SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>

Figure 2. TEM image(a), SEM image(b) and partial enlarged drawing (c,d) of

 $SiO_2/Pd@m-SiO_2$ 

Figure 3. Nitrogen adsorption-desorption isotherms and pore size distribution (inset)

of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>

Figure 4. Small-angle (a) and Wide-angle (b) XRD patterns of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>

Figure 5. XPS spectra of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> (inset: high resolution spectrum of Pd 3d)

Figure 6. Fitted kinetic rate constants of HDC 4-CP to phenol under the catalyst dosage of 10mg (a), 15mg (b), 20mg (c)

Figure 7. The reusability SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> of nanocatalyst for the HDC of 4-CP

### Tables

Table 1. The yield of HDC of 4-CP catalysed by $SiO_2/Pd@m-SiO_2$					
OH SiO₂/Pd@m-SiO₂ ►					

	x ~ _ //				
reactant	Base	Solvent	catalyst dosage	Time(min)/Yield%	
<sup>a</sup> 4-CP	Na <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	15mg	90/82%	
<sup>a</sup> 4-CP	NaAc	H <sub>2</sub> O	15mg	90/72%	
<sup>a</sup> 4-CP	triethyl amine	H <sub>2</sub> O	15mg	90/47%	
<sup>a</sup> 4-CP	NaOH	ethyl acetate	15mg	90/5%	
<sup>a</sup> 4-CP	NaOH	ethyl alcohol	15mg	90/4%	
<sup>a</sup> 4-CP	NaOH	H <sub>2</sub> O	15mg	90/100%	
<sup>a</sup> 4-CP	NaOH	H <sub>2</sub> O	20mg	50/100%	
<sup>a</sup> 4-CP	NaOH	H <sub>2</sub> O	10mg	120/90%	
<sup>a</sup> 2-CP	NaOH	H <sub>2</sub> O	15mg	90/82%	
<sup>a</sup> 3-CP	NaOH	H <sub>2</sub> O	15mg	90/89%	
<sup>b</sup> 2,4-DCP	NaOH	H <sub>2</sub> O	15mg	90/50%	
Reaction conditions: solvent (30 mL), CPs (0.5 mmol); <sup>a</sup> 0.5 mmol base, <sup>b</sup> 1 mmol base					

Figures



Scheme 1. The schematic synthesis of the SiO\_2/Pd@m-SiO\_2 catalyst



Figure 1. FT-IR spectra of SiO<sub>2</sub> and SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>



Figure 2. TEM image(a), SEM image(b) and partial enlarged drawing (c,d) of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>



Figure 3. Nitrogen adsorption-desorption isotherms and pore size distribution (*inset*) of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>



Figure 4. Small-angle (a) and Wide-angle (b) XRD patterns of SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub>



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Figure 6. Fitted kinetic rate constants of HDC 4-CP to phenol under the catalyst dosage of 10mg (a), 15mg (b), 20mg (c)



Figure 7. The reusability SiO<sub>2</sub>/Pd@m-SiO<sub>2</sub> of nanocatalyst for the HDC of 4-CP