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# AuPd@Mesoporous SiO<sub>2</sub>: Synthesis and Selectivity in Catalytic Hydrogenation/Hydrodechlorination of *p*-Chloronitrobenzene

Guangming Yang<sup>1, 2</sup>, Hongbo Yu<sup>1</sup>, Jianfeng Zhang<sup>2</sup>, Hongfeng Yin<sup>1</sup>, Zhen Ma<sup>3, \*</sup>, and Shenghu Zhou<sup>1, 4, \*</sup>

<sup>1</sup> Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, P. R. China <sup>2</sup> Department of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang 315211, P. R. China <sup>3</sup> Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, P. R. China

<sup>4</sup> School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

AuPd nanoparticles (NPs) protected by tetradecyl trimethyl ammonium bromide (TTAB) were coated with SiO<sub>2</sub> through hydrolysis of tetraethylorthosilicate (TEOS). The as-synthesized AuPd@SiO<sub>2</sub> core–shell NPs were calcined in air at 500 °C to remove TTAB and open up mesopores within the SiO<sub>2</sub> shells. The obtained Au–PdO@m-SiO<sub>2</sub> NPs were reduced by H<sub>2</sub> at 300 °C to obtain AuPd@m-SiO<sub>2</sub> NPs with AuPd NP cores (diameter: ~3 nm) and SiO<sub>2</sub> shells (thickness: ~18 nm). Results from relevant characterization indicated that these SiO<sub>2</sub>-protected core–shell NPs were highly stable during calcination and subsequent reduction. Au@m-SiO<sub>2</sub>, Au<sub>10</sub>Pd@m-SiO<sub>2</sub>, Au<sub>5</sub>Pd@m-SiO<sub>2</sub>, AuPd<sub>5</sub>@m-SiO<sub>2</sub>, AuPd<sub>10</sub>@m-SiO<sub>2</sub>, and Pd@m-SiO<sub>2</sub> NPs with similar core sizes and shell thicknesses were also synthesized. These samples were tested in the catalytic hydrogenation of *p*-chloronitrobenzene. The activity and selectivity were found to be tunable, depending on the composition of the bimetallic alloys. AuPd@m-SiO<sub>2</sub> NPs with a 1/1 molar ratio of Au/Pd showed the highest selectivity for the hydrodechlorination of *p*-chloronitrobenzene.

Keywords: AuPd Alloy, Core–Shell, Mesoporous SiO<sub>2</sub>, Nanoparticles, Thermal Stability.

## **1. INTRODUCTION**

Conventional supported catalysts are prepared by supporting active components (e.g., metals, metal oxides) onto solid supports via methods such as impregnation, colloidal deposition, and deposition-precipitation. These catalysts are easy to prepare and have many choices of active components and supports, thus they can be tailored to satisfy the specific needs in different reactions. However, the thermal stability of supported noble metal catalysts remains to be an issue because metal nanoparticles (NPs) tend to agglomerate/sinter under elevated temperatures. To tackle this problem, metal@oxide core-shell catalysts have been developed.<sup>1-8</sup> A core-shell particle can be regarded as a nanoreactor in which the metal NP within the shell can provide catalytically active centers and the oxide shell can not only host the metal NP but also protect it against thermal sintering.9-14 The oxide shell should be porous, otherwise the reactants cannot diffuse into the "nanoreactor"

for a reaction to take place. Usually the oxide shell is  $SiO_2$  because the sol–gel chemistry of  $SiO_2$  is well established and  $SiO_2$  has better thermal stability than  $TiO_2$  and  $ZrO_2$ .<sup>15</sup>

Although some papers have reported the preparation and catalytic application of metal@oxide core-shell NPs, it would be desirable to prepare alloy@oxide coreshell NPs. Bimetallic NPs have attracted much attention because of their unique optical,<sup>16-18</sup> magnetic,<sup>19,20</sup> and catalytic properties.<sup>21-23</sup> In particular, supported AuPd NPs are useful for catalyzing many reactions such as CO oxidation,<sup>24,25</sup> combustion of methane,<sup>26</sup> combustion of tolune,<sup>27,28</sup> photocatalytic degradation of antibiotic levofloxacin,<sup>29</sup> direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>,<sup>30,31</sup> selective oxidation of alcohols,<sup>32-34</sup> aerobic oxidation of clclohexane,<sup>35</sup> H<sub>2</sub> generation from formic acid,<sup>36</sup> and partial reduction of organic substrates.<sup>37-42</sup> However, the synthesis and catalytic application of AuPd@oxide core–shell NPs have been barely reported. In a recent work, Torimoto et al. developed a new method to coat AuPd NPs with In<sub>2</sub>O<sub>3</sub> coatings, and studied the

<sup>\*</sup>Authors to whom correspondence should be addressed.

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performance of the catalysts in electrocatalytic oxidation of ethanol.<sup>43</sup>

We previously developed PdNi@m-SiO2,44 Pd-NiO@m-SiO<sub>2</sub>,<sup>44</sup> PtNi@m-SiO<sub>2</sub>,<sup>45</sup> and Pt-NiO@m-SiO<sub>2</sub>,<sup>45</sup> and tested their catalytic performance in the hydrogenation of *p*-chloronitrobenzene. The hydrogenation of p-chloronitrobenzene (p-CNB) may yield p-chloroaniline (p-CAN), p-aminophenol (p-AP), and aniline (AN), depending on the nature of catalysts and reaction conditions (Fig. 1).44 Most references report the partial hydrogenation of p-CNB to p-CAN,44-53 because p-CAN is a useful chemical intermediate, whereas a few references focus on the hydrodechlorination of p-CNB to AN,<sup>54</sup> because hydrodechlorination is an important topic in environmental catalysis. The influence of support on the selectivity of Pd catalysts in gas-phase hydrogenation of p-CNB was also reported.55 It was found that while Pd/ZnO favored the formation of p-CAN, Pd/SiO<sub>2</sub> favored the formation of *p*-AN.

In the present work, a series of AuPd@m-SiO<sub>2</sub> NPs with different Au/Pd ratios were synthesized using a sol–gel method, and were tested in the hydrogenation of *p*-CNB. It was found that Au@m-SiO<sub>2</sub>, Au<sub>10</sub>Pd@m-SiO<sub>2</sub>, and Au<sub>5</sub>Pd@m-SiO<sub>2</sub> showed no activity or low activity for this reaction, whereas AuPd@m-SiO<sub>2</sub>, AuPd<sub>5</sub>@m-SiO<sub>2</sub>, AuPd<sub>10</sub>@m-SiO<sub>2</sub>, and Pd@m-SiO<sub>2</sub> showed 100% conversion under the reaction condition. Pd@m-SiO<sub>2</sub> showed 55.0% selectivity to AN and 42.0% selectivity to *p*-CAN, whereas AuPd@m-SiO<sub>2</sub> with a 1/1 Au/Pd ratio favored dechlorination, showing 94.7% selectivity to AN. The data indicate that the activity and selectivity are tunable in this bimetallic catalyst system.

 $NH_2$ 

Figure 1. Reaction network for the catalytic hydrogenation of *p*-CNB. Reproduced with permission from [44], X. J. Zhang, et al., *Catal. Lett.* 145, 784 (2015). © 2015, Springer.

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## 2. EXPERIMENTAL DETAILS

## 2.1. Chemicals

Potassium tetrachloropalladate(II) ( $K_2PdCl_4$ ), gold chloride solution (23.5–23.8%), sodium borohydride (NaBH<sub>4</sub>, 98%), aqueous ammonia solution (25–28%), tetraethylorthosilicate (TEOS, AR), and tetradecyl trimethyl ammonium bromide (TTAB, AR) were purchased from Aladdin. *p*-Chloronitrobenzene (*p*-CNB, AR) was purchased from Shanghai Chemical Reagent Company.

## 2.2. Synthesis of TTAB-Capped AuPd NPs and AuPd@SiO<sub>2</sub> NPs

In a typical synthesis, an aqueous solution of K<sub>2</sub>PdCl<sub>4</sub> (0.183 mL, 153.2 mM) and an aqueous solution of HAuCl<sub>4</sub> (0.280 mL, 100 mM) were mixed with 90 ml of deionized water in a 250 mL three-neck round-bottomed flask with magnetic stirring at room temperature, and then 0.840 g TTAB was added. The mixture was stirred for  $\sim 10$  min to fully dissolve TTAB. An ice-cooled NaBH4 aqueous solution (5 mL, 0.53 M) was then injected using a syringe. The tip of the syringe was maintained in the system to release the gas generated during the reaction, and was then removed to make a closed system. The solution was further stirred at low speeds for 15 h at room temperature to obtain AuPd NP colloids. The as-synthesized AuPd colloids (24 mL) were mixed with 120 mL of deionized water in a 250 mL three-neck round-bottomed flask at room temperature with magnetic stirring. A few drops of ammonia solution (25-28 wt.%) were added to adjust the pH value to 10.7, and then TEOS (600  $\mu$ L, 2.69 mmol) was added. The resultant solution was stirred at low speeds for 2 h at room temperature to obtain AuPd@SiO<sub>2</sub> NP colloids. The mixture was centrifuged, washed with ethanol twice and water twice, and then dried at 100 °C for 3 h.

# 2.3. Synthesis of Au-PdO@m-SiO<sub>2</sub> and AuPd@m-SiO<sub>2</sub> NPs

The dried AuPd@SiO<sub>2</sub> NPs were grounded and calcined in a muffle furnace at 500 °C for 2 h to remove TTAB. The resultant Au–PdO@m-SiO<sub>2</sub> powders were reduced by high-purity H<sub>2</sub> (30 mL/min) in a fixed bed reactor at 300 °C for 2 h to obtain AuPd@m-SiO<sub>2</sub> NPs.

### 2.4. Synthesis of Other Core–Shell NPs

Au@m-SiO<sub>2</sub>, Au<sub>10</sub>Pd@m-SiO<sub>2</sub>, Au<sub>5</sub>Pd@m-SiO<sub>2</sub>, AuPd<sub>5</sub>@m-SiO<sub>2</sub>, AuPd<sub>10</sub>@m-SiO<sub>2</sub>, and Pd@m-SiO<sub>2</sub> NPs were prepared by the similar method mentioned above. In each synthesis with different ratios of Au/Pd, the total molar number of the metal(s) was equal to that of AuPd@m-SiO<sub>2</sub>.

#### 2.5. Characterization

XRD patterns of samples were collected by a Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation in the



 $2\theta$  range from 10° to 90°. Transition electron microscopy (TEM) images were obtained by JEOL 2100 transmission electron microscope. The samples were made as follows: a certain amount of catalysts was dispersed in ethanol by ultrasonic treatment, and a drop of the solution was dropped onto a carbon-coated copper grid that was subsequently dried in air at room temperature. The actual metal contents of the catalysts were obtained by a PE Optima 2100DV inductive coupled plasma optical emission spectrometer (ICP-OES). Infrared (IR) spectra of the NPs before and after treatments were recorded in the transmission mode by a Bruker Tensor 27 spectrophotometer. The thermal degradation property of the sample before treatment was measured by a Pyris Diamond thermo gravimetric analyzer (TGA). The sample was heated from 50 to 500 °C at a heating rate of 10 °C/min under flowing air (50 mL/min). Brunauer-Emmett-Teller (BET) surface areas, pore size distributions, and the adsorption/desorption isotherms of the samples were measured by N<sub>2</sub> adsorption at 77 K, using a Micrometrics ASAP-2020 M automatic specific surface area and porous physical adsorption analyzer.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the TEM images of various as-synthesized NPs. The average particle size of TTAB-capped AuPd NPs with a 1/1 ratio of Au/Pd is  $\sim 2.5$  nm, and the lattice spacing is 0.302 nm (Fig. 2(a)), consistent with the of Au@SiO<sub>2</sub>, Au<sub>10</sub>Pd@SiO<sub>2</sub>, Au<sub>5</sub>Pd@SiO<sub>2</sub>, AuPd@SiO<sub>2</sub>, AuPd<sub>5</sub>@SiO<sub>2</sub>, AuPd<sub>10</sub>@SiO<sub>2</sub>, and Pd@SiO<sub>2</sub> are shown in Figures 2(b-h), respectively. AuPd@SiO<sub>2</sub> in Figure 2(e)shows an average particle size of 2.5 nm for AuPd cores

and a thickness of  $\sim 18$  nm for SiO<sub>2</sub> shells. Empty SiO<sub>2</sub> NPs are rarely seen in Figures 2(b-h), but a few core-shell NPs with multiple cores are found. In this study, the optimal hydrolysis condition is found at a pH value of 10.7 and a TEOS/total metal molar ratio of 192/1. Empty SiO<sub>2</sub> NPs are observed at lower pH values, and a large percentage of NPs with multiple cores are observed at higher pH values. Moreover, higher TEOS/total metal ratios result in thicker silica shells.

Figure 3 shows the TEM images of mesoporous coreshell NPs obtained by removing the TTAB at 500 °C followed by reduction in H<sub>2</sub> at 300 °C. The average particle size of the metal cores and thickness of silica shells of metal@m-SiO<sub>2</sub> structures are nearly the same as those of metal@SiO<sub>2</sub> NPs (Fig. 4), demonstrating the high thermal stability for these core-shell catalysts. The presence of mesopores is illustrated in Figure 3(f) showing one AuPd<sub>5</sub>@m-SiO<sub>2</sub> NP.

Figure 5 shows the N<sub>2</sub> adsorption-desorption isotherms and pore size distribution of various metal@m-SiO<sub>2</sub> NPs with different Au/Pd ratios. Table I shows the BET surface areas, pore volumes, and pore sizes of these samples. These mesoporous core-shell NPs exhibit large BET surface areas higher than 1000 m<sup>2</sup>/g and the average pore sizes are identical (2.1 nm).

The creation of mesopores through calcination is due to the removal of TTAB. The TGA curve of AuPd@SiO<sub>2</sub> in Figure 6 suggests that the calcination at 500 °C in air can completely remove TTAB, and FT-IR spectra for lattice spacing of AuPd (111) plane. The TEM imagesd by AuPd@SiO2 and AuPd@m-SiO2 in Figure 7 further confirm the removal of TTAB upon calcination in air.

> Figure 8 shows the XRD patterns of various core-shell NPs. The broad feature in the  $2\theta$  range of  $20^{\circ}$  and  $30^{\circ}$ corresponds to amorphous SiO<sub>2</sub>. PdO@m-SiO<sub>2</sub> prepared



Figure 2. TEM images of core-shell NPs synthesized at the condition of a pH value of 10.7 and a TEOS/total metal molar ratio of 192/1. (a) TTABcapped AuPd NPs, and insert is HRTEM image of one NP showing a lattice spacing of 0.302 nm; (b) Au@SiO<sub>2</sub>; (c) Au<sub>10</sub>Pd@SiO<sub>2</sub>; (d) Au<sub>5</sub>Pd@SiO<sub>5</sub>; (e)  $AuPd@SiO_2$ ; (f)  $AuPd_5@SiO_2$ ; (g)  $AuPd_{10}@SiO_2$ ; (h)  $Pd@SiO_2$ .

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Figure 3. TEM images of NPs synthesized at the condition of a pH value of 10.7 and a TEOS/total metal molar ratio of 192/1 after 500 °C calcination and following 300 °C H<sub>2</sub> reduction. (a) Au@m-SiO<sub>2</sub>; (b) Au<sub>10</sub>Pd@m-SiO<sub>2</sub>; (c) Au<sub>5</sub>Pd@m-SiO<sub>2</sub>; (d) AuPd@m-SiO<sub>2</sub>; (e) AuPd<sub>5</sub>@m-SiO<sub>2</sub>; (f) details of AuPd<sub>5</sub>@m-SiO<sub>2</sub>; (g) AuPd<sub>10</sub>@m-SiO<sub>2</sub>; (h) Pd@m-SiO<sub>2</sub>.



Figure 4. Size distribution of AuPd and AuPd<sub>5</sub> NPs in different systems. (a) AuPd NPs capped with TTAB; (b) AuPd@SiO<sub>2</sub>; (c) AuPd@m-SiO<sub>2</sub>; (d) AuPd<sub>5</sub> NPs capped with TTAB; (e) AuPd<sub>5</sub>@SiO<sub>2</sub>; (f) AuPd<sub>5</sub>@m-SiO<sub>2</sub>.



Figure 5.  $N_2$  adsorption-desorption isotherms (left panel) and pore size distribution (right panel). (a) Au@m-SiO<sub>2</sub>; (b) Au<sub>10</sub>Pd@m-SiO<sub>2</sub>; (c) Au<sub>5</sub>Pd@m-SiO<sub>2</sub>; (d) AuPd@m-SiO<sub>2</sub>; (e) AuPd<sub>5</sub>@m-SiO<sub>2</sub>; (f) AuPd<sub>10</sub>@m-SiO<sub>2</sub>; (g) Pd@m-SiO<sub>2</sub>.

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shell NPs.						
Samples	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)			
Au@m-SiO <sub>2</sub>	1527	2.0	2.1			
Au <sub>10</sub> Pd@m-SiO <sub>2</sub>	1308	1.6	2.1			
Au <sub>5</sub> Pd@m-SiO <sub>2</sub>	1209	1.5	2.1			
AuPd@m-SiO <sub>2</sub>	1153	1.5	2.1			
AuPd <sub>5</sub> @m-SiO <sub>2</sub>	1199	1.5	2.1			
AuPd <sub>10</sub> @m-SiO <sub>2</sub>	1178	1.4	2.1			
Pd@m-SiO <sub>2</sub>	1147	1.4	2.1			

Table I. BET surface areas, pore volumes, and pore sizes of core-shell NPs.

by calcining Pd@m-SiO<sub>2</sub> at 500 °C shows a diffraction peak at  $2\theta = 33.8^\circ$ , corresponding to the (101) plane of PdO (Fig. 8(a)). PdO@m-SiO<sub>2</sub> can be reduced in H<sub>2</sub> at 300 °C to form Pd@m-SiO<sub>2</sub>, as seen from a peak at  $2\theta =$ 40.1° corresponding to the (111) plane of metallic Pd (Fig. 8(b)). Au@m-SiO<sub>2</sub> obtained by calcining Au@SiO<sub>2</sub> at 500 °C contains metallic Au, as seen from a peak at  $2\theta = 38.2^{\circ}$  corresponding to the (111) plane of Au (Fig. 8(c)). Figure 8(d) shows the XRD pattern of assynthesized AuPd@SiO<sub>2</sub> (without calcination to remove TTAB and open up mesopores). A very weak diffraction at  $2\theta = 39.1^{\circ}$  of (111) plane of AuPd is present. The XRD pattern of AuPd@m-SiO<sub>2</sub> (prepared by calcining AuPd@SiO<sub>2</sub> in air at 500 °C followed by reduction in H<sub>2</sub> at 300 °C) is shown in Figure 8(e). The AuPd alloy phase is maintained after calcination and reduction.

Catalytic hydrogenation of *p*-chloronitrobenzene with  $H_2$  using mesoporous core–shell NPs as catalysts was tested using ethanol solvent with vigorous stirring at 50 °C and atmospheric pressure. Table II shows the actual loadings of Au and Pd in various mesoporous core–shell NPs, as obtained by ICP. The weight of catalysts was adjusted according to the actual metal loadings to keep the total molar number of Au and Pd constant. Figure 1 shows the reaction network,<sup>44</sup> and Table III shows the catalytic results. It is clear that Au@m-SiO<sub>2</sub> and Au<sub>10</sub>Pd@m-SiO<sub>2</sub> are not active at all. Au<sub>5</sub>Pd@m-SiO<sub>2</sub> shows a low conversion of 6.5%. The null activity of Au@m-SiO<sub>2</sub> in the







**Figure 7.** FT-IR spectra. (a) AuPd@m-SiO<sub>2</sub>; (b) AuPd@SiO<sub>2</sub>. The 2853 and 2923 cm<sup>-1</sup> peaks in spectrum b are ascribed to methylene group in TTAB, which disappears in the calcined sample in spectrum a.

hydrogenation of *p*-chloronitrobenzene is in line with the finding that Au/C showed no activity in the hydrogenation of 2-chloronitrobenzene.<sup>56</sup>

On the other hand, AuPd@m-SiO<sub>2</sub>, AuPd<sub>5</sub>@m-SiO<sub>2</sub>, AuPd<sub>10</sub>@m-SiO<sub>2</sub>, and Pd@m-SiO<sub>2</sub> show 100% conversion under the reaction conditions. The selectivity to AN obtained using different catalysts follows the sequence of AuPd@m-SiO<sub>2</sub> (94.7%) > AuPd<sub>5</sub>@m- $SiO_2$  (77.8%) > AuPd<sub>10</sub>@m-SiO<sub>2</sub> (51.3%)~Pd@m-SiO<sub>2</sub> (55.0%). The selectivity to p-CAN obtained using different catalysts follows the sequence of AuPd@m-SiO<sub>2</sub>  $(3.3\%) < AuPd_5@m-SiO_2$  (20.2%) > AuPd<sub>10</sub>@m-SiO<sub>2</sub> (44.0%)~Pd@m-SiO<sub>2</sub> (42.0%). The data indicate that the selectivity is tunable and AuPd@m-SiO<sub>2</sub> favors dechlorination. Corbos and co-workers developed several PdAu/C catalysts with Pd/Au weight percentage ratios of 10/90, 50/50, 75/25, and 100/0, respectively, and tested the catalysts in the hydrogenation of 2-chloronitrobenzene.<sup>56</sup> The authors found that the selectivity to 2-CAN increased when the Pd content of the catalyst was increased. The trend is consistent with the trend seen in our current work. Additional theoretical work is still needed to understand the



**Figure 8.** XRD patterns of NPs. (a) PdO@m-SiO<sub>2</sub>; (b) Pd@m-SiO<sub>2</sub>; (c) Au@m-SiO<sub>2</sub>; (d) as-synthesized AuPd@SiO<sub>2</sub>; (e) AuPd@m-SiO<sub>2</sub>.

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Table II. The real metal loadings of core-shell NPs as analyzed by ICP-OES.

Sample	Au content (wt.%)	Pd content (wt.%)	
Au@m-SiO <sub>2</sub>	1.876	N/A	
Au <sub>10</sub> Pd@m-SiO <sub>2</sub>	1.737	0.0875	
Au <sub>5</sub> Pd@m-SiO <sub>2</sub>	1.6235	0.1625	
AuPd@m-SiO <sub>2</sub>	0.9615	0.496	
AuPd <sub>5</sub> @m-SiO <sub>2</sub>	0.321	0.757	
AuPd <sub>10</sub> @m-SiO <sub>2</sub>	0.174	0.872	
Pd@m-SiO <sub>2</sub>	N/A	1.009	

**Table III.** Hydrogenation of *p*-CNB with  $H_2$  catalyzed by core–shell MPs. The products are aniline (AN), *p*-chloroaniline (*p*-CAN), and *p*-aminophenol (*p*-AP).

		Selectivity (%)		
Catalysts	Conv. (%)	AN	<i>p</i> -CAN	p-AP
Au@m-SiO <sub>2</sub>	0.0	0.0	0.0	0.0
Au <sub>10</sub> Pd@m-SiO <sub>2</sub>	0.0	0.0	0.0	0.0
Au <sub>5</sub> Pd@m-SiO <sub>2</sub>	6.5	3.5	49.4	47.1
AuPd@m-SiO <sub>2</sub>	100	94.7	3.3	2.0
AuPd <sub>5</sub> @m-SiO <sub>2</sub>	100	77.8	20.2	2.0
AuPd <sub>10</sub> @m-SiO <sub>2</sub>	100	51.3	44.0	3.7
Pd@m-SiO <sub>2</sub>	100	55.0	42.0	3.0

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reasons for the change of selectivity as a function of Pd/Audratios.

The recyclability of representative catalysts was also studied. There was slight loss of catalysts after the separation of catalysts and the products, so the amount of reactant (*p*-CNB) and solvent (ethanol) were adjusted to make sure that the ratios of ethanol/*p*-CNB and catalyst/*p*-CNB in the following cycles were kept the same as those in the first cycle. As shown in Table IV, AuPd@m-SiO<sub>2</sub> shows

**Table IV.** Recyclability of typical catalysts in hydrogenation of p-CNB with  $H_2$ . The products are aniline (AN), p-chloroaniline (p-CAN), and p-aminophenol (p-AP).

Cycle	Weight (g)	p-CNB (g)	Conversion (%)	AN (%)	p-CAN (%)	p-AP (%)
			AuPd@m	-SiO <sub>2</sub>		
1	2.000	1.000	100	95.2	3.1	1.7
2	1.786	0.893	99.8	85.6	10.3	4.1
3	1.542	0.771	99.0	84.7	10.8	4.5
			Pd@m-S	SiO <sub>2</sub>		
1	2.008	1.00	100	55.6	43.2	1.2
2	1.806	0.899	99.6	54.9	43.8	1.3
3	1.578	0.786	98.2	56.7	42.7	0.6

*Note*: Reaction conditions: atmospheric  $H_2$  pressure; reaction time (2.5 h); speed of agitation (600 rpm); 30 ml of ethanol was used as solvent in the first cycle, and the ratios of ethanol/*p*-CNB and catalyst/*p*-CNB in the following cycles were kept the same as those in the first cycle.

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100% conversion and the selectivity to AN is 95.2%. In the second cycle, the conversion is 99.8%, and the selectivity to AN somehow decreases to 85.6%. In the third cycle, the conversion is 99%, and the selectivity to AN remains 84.7%. For Pd@m-SiO<sub>2</sub>, the conversion is 100% and the selectivity to AN is 55.6% under the reaction condition. Both the conversion and selectivity to AN are constant in three cycles. These data indicate that both catalysts are recyclable.

### 4. CONCLUSIONS

Various AuPd@m-SiO<sub>2</sub> mesoporous core-shell NPs were synthesized by a sol-gel method. They exhibited high surface areas (>1000  $m^2/g$ ) and mesopores (average pore sizes  $\sim 2.1$  nm) due to the removal of TTAB template by calcination. These materials were tested in the hydrogenation of *p*-chloronitrobenzene. Au@m-SiO<sub>2</sub> and Au<sub>10</sub>Pd@m-SiO<sub>2</sub> are not active at all under the reaction condition. Au<sub>5</sub>Pd@m-SiO<sub>2</sub> shows a low conversion of 6.5%. AuPd@m-SiO2, AuPd5@m-SiO2, AuPd10@m-SiO<sub>2</sub>, and Pd@m-SiO<sub>2</sub> show 100% conversion. The selectivity to aniline obtained using different catalysts follows the sequence of AuPd@m-SiO<sub>2</sub> (94.7%) > AuPd<sub>5</sub>@m- $SiO_2$  (77.8%) > AuPd<sub>10</sub>@m-SiO<sub>2</sub> (51.3%)~Pd@m-SiO<sub>2</sub> (55.0%). In particular, AuPd@m-SiO<sub>2</sub> with a 1/1 ratio of Au/Pd exhibited enhanced hydrodechlorination selectivity. This kind of materials could be potentially used in high temperature reactions due to the high thermal stability. In addition, they may be tested in other hydrogenation and hydrodechlorination reactions because the selectivity can be tuned as a function of alloy compositions.

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