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Accelerated catalytic activity of Pd NPs supported on Amine-Rich Silica Hollow Nanospheres for Quinoline Hydrogenation

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Tuning the catalytic performance of metal nanoparticles (NPs) is very important in nanocatalysis. Herein, we report that amine rich mesoporous silica hollow nanospheres (HS-NH<sub>2</sub>) synthesized by one-pot condensation could efficiently stabilize ultrasmall Pd NPs and also increase the surface electronic density of Pd NPs due to the coordinating and electron donating effect of the amine group. Pd NPs supported on HS-NH<sub>2</sub> afford TOF as high as 5052 h<sup>-1</sup> in quinoline hydrogenation reaction and is much more active than Pd/C with TOF of 960 h<sup>-1</sup> and also most reported solid catalysts. The intrinsic activity of Pd NPs increases as particle size of Pd decreases, revealing that quinoline hydrogenation is a structure sensitive reaction. The results of TEM, XPS, CO adsorption and CO stripping voltammetry indicate that the high activity of Pd NPs supported on HS-NH<sub>2</sub> is mainly attributed to its ultrasmall particle size and high surface electronic density. Our primary results demonstrate that the organo-modified silicas are promising solid supports for modify the electronic property of metal NPs supported and consequently tailoring their catalytic functions.

# Introduction

Metal nanoparticles (NPs) with ultrasmall size (1-3 nm) generally exhibit dramatically different electronic and chemical properties.<sup>1-4</sup> Studies show that downsizing the particle size of metal NPs could dramatically enhance their catalytic activity in most cases owing to the increased low coordination sites and surface vacancies.<sup>5, 6</sup>

Various strategies are used for the synthesis of ultrasmall metal NPs with precise size control.<sup>7-10</sup> Generally, the ultrasmall NPs was prepared by the colloid method and subsequently deposited on the solid material, followed by removing the stabilizer or directly impregnated the precursor of the metal on the oxide support by using the metal support interaction. However, either the aggregation of NPs or the residual cappers will inevitably influence their catalytic activity. Another alternative approach is to encapsulate the metal NPs in the porosity materials, such as zeolites,<sup>11</sup> MOFs,<sup>12</sup> ZIFs,<sup>13</sup> polymers,<sup>14</sup> etc. Yu et al. reported a facile strategy to synthesize Pd NPs with size of 1.8 nm encapsulated within the intersectional channels of nanosized zeolite, which shows superior catalytic activities and excellent recyclability of hydrogen generation from formic acid.<sup>11</sup> However, the very less metal loading and tedious synthesis procedure restrict the application. Recently, N-modified solid

# supports have been widely used for stabilizing ultrasmall metal NPs. For example, Li and co-workers demonstrated that N-functionalized ordered mesoporous carbons could be used for stabilizing ultrasmall Pd NPs.<sup>15</sup>

Compared with the N-doped carbon materials and functionalized porous polymers, the organo-modified silica nanomaterials with tunable structure and morphology and easy functionalization would be more desirable support materials for obtaining the ultrasmall metal NPs. Considering the coordination ability and electron donating properties of NH<sub>2</sub>,<sup>16</sup>, <sup>17</sup> herein, we choose amine modified mesoporous silica hollow nanospheres as support materials to tune the particle size and surface electronic density of Pd NPs. With quinoline hydrogenation as model reaction, the relation of the catalytic performance of Pd NPs with particle size and surface electronic density was investigated. Our preliminary results suggest that ultrasmall Pd NPs with electron-rich surface afford high catalytic activity.

# **Experimental section**

# Chemicals and reagents

All materials were of analytical grade. Tetraethoxysilane (TEOS) was obtained from Sinopharm Chemical Reagent Co., Ltd (China). 3-Aminepropyltriethoxysilane (APTES), cetyltrimethyl ammonium bromide (CTAB) were purchased from Sigma-Aldrich Company Ltd. (USA). Commercial Pd/C (5 wt%) was obtained from TCI (Shanghai) Development Co., Ltd. Quinoline compounds were purchased from TCI, Admas or Ark Chemicals. Other reagents were purchased from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group.

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#### Synthesis of amine-rich silica hollow nanospheres (HS-NH<sub>2</sub>).

0.16 g of CTAB and 0.5 mL of  $NH_3 \cdot H_2O$  (25-28 %) were dissolved in 40 mL of  $H_2O$  and 10 mL of EtOH solution at 50 °C, followed by the addition of 0.16 ml of TEOS (in 1 mL EtOH). After stirring for 2 min, the clear solution turned milky white. Then, 0.1 mL of APTES (in 1 mL EtOH) was added and the mixture was stirred for another 2 h at 50 °C. Then the temperature was raised to 80 °C and the mixture was stirred at this temperature for 2 h. After cooling down to room temperature, the powder product was isolated by filtration, washed with distilled water and air-dried. The surfactant was extracted by dispersing as-synthesized materials (1 g) in 120 mL of ethanol (95%) containing 80 mg of ammonium nitrate and the mixture was heated at 60 °C for 30 min. The process was repeated for three times. After filtration and drying, the powder product obtained was denoted as HS-NH<sub>2</sub>.

For comparison,  $SiO_2$  HS with particle size of 110 nm was prepared with a modified method according to our previous report (details see SI).<sup>18</sup>

#### Preparation of Pd/HS-NH<sub>2</sub> (X%).

The Pd/HS-NH<sub>2</sub> (X%) was synthesized by conventional impregnation-reduction method. Typically, 400 mg of HS-NH<sub>2</sub> was dispersed in 5 mL of deionized water in a centrifuge tube under ultrasound. Then desired amount of Na<sub>2</sub>PdCl<sub>4</sub> aqueous solution (0.01 g mL<sup>-1</sup>) was added into the tube. After ultrasound treatment for 10 min, a freshly prepared NaBH<sub>4</sub> aqueous solution (7.5 mg mL<sup>-1</sup>) was added slowly. The brownish red colour transformed into gray black. After ultrasound treatment for another 30 min, the mixture was filtered and the black powder product was washed with deionized water and EtOH for several times. After drying in an oven at 60 °C overnight, Pd/HS-NH<sub>2</sub> (X%) was obtained, where X refers to the weight percent of Pd.

We also tried to prepare Pd/HS (5 wt%) in a similar method to Pd/HS-NH<sub>2</sub> (5 wt%). However, reduction with NaBH<sub>4</sub> solution cannot disperse Pd NPs well on HS possibly due to the weak interaction of Pd and SiO<sub>2</sub>. Thus, the reduction was performed at 200 °C with H<sub>2</sub>.

#### Hydrogenation of quinoline.

In a typically process, a desired amount of solid catalyst  $(5 \times 10^{-3} \text{ mmol Pd})$  was added in an ampoule tube, followed by the addition of quinoline (1 mmol) (S/C = 200) and 2 mL of solvent. The ampoule tube was loaded into a stainless steel autoclave (300 mL) with a thermocouple probed detector. After purging with hydrogen for six times, the final pressure was adjusted to 1 MPa and the reactor was heated to 50 °C with vigorous stirring. After reaction, the solid catalyst was separated by centrifugation and the filtrate was collected, diluted with ethanol and analyzed by an Agilent 7890B GC equipped with an Agilent J&W GC HP-5 capillary column (30 m × 0.32 mm × 0.25 µm) and n-decane as internal standard.

For recycling the catalyst, the liquid was decanted after centrifugation, and the catalyst was thoroughly washed with EtOH and dried under vacuum at room temperature and used directly for the next run.

#### Characterization.

N<sub>2</sub> sorption isotherms were carried out on a Micromeritics ASAP2020 volumetric adsorption analyzer. Samples prepared

in this work and commercial Pd/C (5 wt%) were degassed at 120 °C and 250 °C for 6 h prior to the measurement, respectively. X-ray photoelectron spectroscopy (XPS) was recorded on VG ESCALAB MK2 apparatus using Al K $\alpha$  (h $_{\lambda}$  = 1486.6 eV) as the excitation light source. The peaks in the spectra were fitted by using the shareware program XPS-PEAK with Gaussian-Lorentzian peak shapes and a Shirley background. High-resolution transmission electron microscopy (HR-TEM) was performed on a JEOL JEM-2100 at an acceleration voltage of 200 kV. Transmission electron microscopy (TEM) was performed using a HITACHI HT7700 at an acceleration voltage of 100 kV. Scanning electron microscopy (SEM) was undertaken by using a FEI Quanta 200F operating at an acceleration voltage of 1-30 kV. FT-IR spectra were performed on a Nicolet Nexus 470 IR spectrometer. The IR spectra were collected in KBr pellets with the range of 400-4000 cm<sup>-1</sup>. The Pd content was determined by PLASAM-SPEC-II inductively coupled plasma atomic emission spectrometry (ICP-AES). The solid-state NMR spectra were obtained on a Bruker DRX 400 spectrometer equipped with a MAS probe by using a 4 mm  $ZrO_2$  rotor. <sup>13</sup>C and <sup>29</sup>Si signals were referenced to tetramethylsilane (TMS). The experimental parameters were as follows: 8 kHz spin rate, 3 s pulse delay, 4 min contact time, and 1000 scans. The thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449F3 analyzer from 30 to 900 °C with a heating rate of 10 °C min-1 under air atmosphere. CO chemisorption measurement was performed at 40 °C on a Quantachrome Autosorb-1/C chemisorb apparatus. Samples were treated in H<sub>2</sub> atmosphere at 200 °C for 2 h before measurement. The metal dispersion and particle size were estimated on the basis of the assumption of a spherical geometry of Pd particles, assuming a chemisorption stoichiometry of Pd/CO = 2. The average Pd particle size was calculated by using the classical equation  $d_{CO} \cdot S =$  $(1/Q_{CO}) \cdot (6\rho_{site}/N\rho_m)$ , where d<sub>CO</sub> is the Pd particle size, S is average ratio between Pd surface atoms and chemisorbed CO molecules (S=2),  $Q_{CO}$  is the CO monolayer uptake (mmol g<sup>-1</sup>),  $\rho_{\rm site}$  is the Pd surface site density (for Pd: 12.7 atoms nm<sup>-2</sup>),  $\rho_{\rm m}$ is the metal density (for Pd: 11.9 g cm<sup>-3</sup>), and N is the Avogadro number  $(6.022 \times 1023 \text{ mol}^{-1})$ .<sup>19, 20</sup>

Electrochemical measurements.<sup>21</sup> To prepare a working electrode, an ethanol dispersion of catalysts (7.5  $\mu$ g) was deposited on a glassy carbon electrode (3 mm). After the ethanol was dried, 3  $\mu$ L of 2.5 V% Nafion solution was dropped on the electrode surface to stabilize the catalysts on the electrode surface. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrode, respectively. For CO stripping, pure CO (99.999%) gas was purged through the catalyst surface in the cell filled with 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte for 30 min while holding the working electrode at 0.2 V (versus SCE). After transferring the electrodes to another cell filled with  $N_2$  for 15 min, the CO stripping was performed in the potential range of 0.2-1.2 V (versus SCE) at a scan rate of 5 mV s<sup>-1</sup>.

# **Results and discussion**

Synthesis and characterization of amine-rich silica.



The synthesis procedure for amine-rich silica hollow nanospheres is outlined in Scheme 1. The process for the synthesis of hollow nanospheres involves the hydrolysis of TEOS in basic water-ethanol solution with CTAB as the surfactant, and then APTES was added to the above mixture. The hydrothermal treatment of the mixture at 80 °C gives final hollow nanospheres. Based on the results of morphology transformation with reaction time (Figure S1), the formation of hollow nanospheres possibly related with the etching effect of APTES.<sup>22-24</sup>

The morphology and structure of  $HS-NH_2$  were characterized with SEM and TEM (Figure 1). The SEM shows that  $HS-NH_2$ is mainly composed of nanospheres with particle size of ~ 110 nm though some oval spheres co-exist. Oval spheres have smaller diameter of ca. 110 nm and larger diameter varying in the range of 80 to 150 nm. The TEM image clearly shows that all spheres have hollow structure with shell thickness of 20 nm. Based on the TEM image, hollow spheres have mesoporous channels aligning perpendicular to the cores in the shell, which would benefit the diffusion of reactants and products during the catalytic process. The SEM and TEM characterizations confirm that HS-NH<sub>2</sub> has hollow spherical morphology with mesoporous structure in the shell.

 $N_2$  adsorption-desorption isotherm of HS-NH<sub>2</sub> is of type IV, with a sharp capillary condensation step and an H<sub>3</sub> hysteresis loop starting from the relative pressure P/P<sub>0</sub> of 0.40 (Figure 2A), showing that HS-NH<sub>2</sub> has mesoporous structure. The H<sub>3</sub> hysteresis loop is from the inner void space. HS-NH<sub>2</sub> has large



Figure 1. (A) SEM and (B) TEM image of HS-NH<sub>2</sub>.



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pore volume (0.54 cm<sup>3</sup> g<sup>-1</sup>) and high BET surface area (301 m<sup>2</sup>  $g^{-1}$ ), which will benefit the diffusion of guest molecules during the catalytic process. The FT-IR spectrum of HS-NH<sub>2</sub> clearly displayed the vibrations at 2942 cm<sup>-1</sup> ( $\upsilon$  <sub>C-H</sub>), 1385 cm<sup>-1</sup> ( $\delta$  <sub>C-H</sub>), 3441 cm<sup>-1</sup> ( $\upsilon$ <sub>N-H</sub>) and 1558 cm<sup>-1</sup> ( $\delta$ <sub>N-H</sub>) (Figure 2B). The solidstate <sup>13</sup>C CP/MAS NMR spectrum displays the chemical shifts at 9.3 ppm, 21 ppm and 42.3 ppm, which could be assigned to  $C^1$ ,  $C^2$  and  $C^3$  of  $-C^3H_2C^2H_2C^1H_2NH_2$  (Figure 2C). The results of FT-IR and <sup>13</sup>C CP/MAS NMR suggest the successful incorporation of amine groups. <sup>29</sup>Si NMR spectrum exhibits both T site (-66.7 ppm for T<sub>3</sub>,  $T_n = R\text{-}Si(OSi)_n(OH)_{3-n}$ ) and Q site (-102.6 ppm for  $Q_3$  and -110.7 ppm for  $Q_4$ ,  $Q_n$  =  $Si(OSi)_n(OH)_{4-n}$  with T / (Q + T) ratio of 31 %, showing the integration of high content of amine groups in HS-NH<sub>2</sub> (Figure 2D). Based on TG analysis (Figure S2), the weight loss of 21.7 wt% in the range of 240 to 700 °C could be assigned to the content of amine groups, which corresponds to amine amount of 3.74 mmol g<sup>-1</sup>. The C, H, N elemental analysis affords N content of 5.18 wt%, corresponding to amine content of 3.70 mmol g<sup>-1</sup> (Table S1). The above results confirm that HS-NH<sub>2</sub>



Figure 3. (A) TEM images, (B) HAADF-STEM images and (C) Pd particle size distribution estimated by STEM of (a) Pd/HS-NH<sub>2</sub> (1 wt%), (b) Pd/HS-NH<sub>2</sub> (3 wt%), (c) Pd/HS-NH<sub>2</sub> (5 wt%), (d) Pd/HS-NH<sub>2</sub> (10 wt%) and (e) Pd/HS-NH<sub>2</sub> (15 wt%) (scale bar: 20 nm).

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## has amine rich character. Characterization of Pd/HS-NH<sub>2</sub> (X%).

Pd/HS-NH<sub>2</sub> (X%) was prepared by a simple impregnationreduction method. The HS-NH2 with amine rich character could easily adsorb Pd<sup>2+</sup> because nitrogen atom has a high affinity for binding metal cations. Pd<sup>2+</sup> was successfully reduced to Pd NPs with NaBH<sub>4</sub>. Figure 3 shows the TEM images of Pd/HS-NH<sub>2</sub> (X%) with different Pd loading (1-15 wt%). Based on the TEM results, Pd NPs with particle size of 1.6 nm, 1.9 nm and 2.1 nm are uniformly distributed in the shell region of HS-NH<sub>2</sub> with Pd loading of 1 wt%, 3 wt% and 5 wt%, respectively. For Pd/HS-NH<sub>2</sub> (10 wt%) and Pd/HS-NH<sub>2</sub> (15 wt%), the particle size distribution of Pd is very broad. It should be noted that the ultrasmall Pd NPs of 2.1 nm could be maintained nicely when the metal loading as high as 5 wt%. This could be ascribed to the amine-rich character of HS-NH<sub>2</sub>. Recent work suggested that metal NPs would be highly dispersed inside the confined mesoporous, 25-27 thus, the "confinement effect" of the mesoporous structure to prevent the growth of Pd NPs also contributes to the formation of ultrasmall Pd NPs, especially for the low Pd loading catalyst (≤5 wt%). The HR-TEM image of Pd/HS-NH<sub>2</sub> (5 wt%) is shown in Figure 4A. It is notably observed that Pd NPs were uniformly dispersed in the shell of HS-NH<sub>2</sub>, and the plane spacing measured is about 0.228 nm, which is in agreement with the (111) crystal plane of Pd. The

**Table 1**. Dispersion and particle size of Pd NPs for Pd/HS- $NH_2$ , Pd/HS (5 wt%) and Pd/C (5 wt%).

E		•	
Samples	Pd (wt%) <sup>a</sup>	Particle size (nm) <sup>b</sup>	Dispersion (%) <sup>b</sup>
Pd/HS-NH <sub>2</sub> (1 wt%)	1.0	3.0	36.2
$Pd/HS-NH_2$ (3 wt%)	3.0	3.4	32.5
Pd/HS-NH <sub>2</sub> (5 wt%)	4.7	4.0	27.7
Pd/HS-NH <sub>2</sub> (10 wt%)	9.4	5.6	20.1
Pd/HS-NH <sub>2</sub> (15 wt%)	14.1	8.2	13.6
Pd/HS (5 wt%)	4.5	5.8	19.3
Pd/C (5 wt%)	5.0	3.2	35.1

 $^{\rm a}$  Pd content determined by ICP-AES analysis;  $^{\rm b}$  data calculated from CO chemisorption results.



HR-SEM image further shows that  $Pd/HS-NH_2$  (5 wt%) is composed of uniformly distributed nanoparticles with particle size of 80-150 nm (Figure 4B).

Taken 1 wt%, 5 wt% and 15 wt% samples as examples, the results of BET surface area and pore size distribution are shown in Figure S3. With Pd content increasing from 1 wt% to 15 wt%, the BET surface area of Pd/HS-NH<sub>2</sub> decreases from 289 to 241 m<sup>2</sup> g<sup>-1</sup>, slight lower than HS-NH<sub>2</sub> with BET surface area of 301 m<sup>2</sup> g<sup>-1</sup>. The pore size of all Pd/HS-NH<sub>2</sub> samples is almost the same and distributed at ca. 2.2 nm. The FT-IR spectra show that the N-H vibration of HS-NH<sub>2</sub> shifts from 1558 cm<sup>-1</sup> to 1543 cm<sup>-1</sup> after Pd loading, suggesting the formation of interactions between Pd and amine groups (Figure S5).<sup>28, 29</sup>

The CO chemisorption was used to give further information of the particle size and dispersion of Pd NPs (Table 1). The results clearly show that average particle size of Pd increases gradually from 3.0 to 8.2 nm along with the metal content from 1 wt% to 15 wt%. It shows a similar trend with the TEM results although larger value was obtained. Through increasing Pd loading, the size of Pd NPs could be adjusted. It is observed that the metal dispersion of Pd/HS-NH<sub>2</sub> (5 wt%) is better than Pd/HS (5 wt%), suggesting the amine group has good coordination and dispersion ability with metal cations.

Figure 5 shows the XPS spectra in the Pd 3d binding energy region of Pd/HS-NH<sub>2</sub> (5 wt%) and Pd/C (5 wt%). The peaks that appear at 335.1 eV and 336.7 eV could be attributed to the Pd<sup>0</sup> and Pd<sup>2+</sup>, respectively. Pd<sup>0</sup>/Pd<sup>2+</sup> ratio calculated from the relative peak areas for Pd/HS-NH<sub>2</sub> (5 wt%) and Pd/C (5 wt%)



Figure 6. CO stripping voltammetry of Pd/HS-NH<sub>2</sub> (5 wt%), Pd/HS (5 wt%) and Pd/C (5 wt%).

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are 68/32 and 43/57, showing that Pd/HS-NH<sub>2</sub> (5 wt%) has more  $Pd^0$  than Pd/C (5 wt%).  $Pd^0/Pd^{2+}$  ratio (73/27) of Pd/HS (5 wt%) is a little higher than Pd/HS-NH<sub>2</sub> (5 wt%), suggesting amine group or reduction method has a little influence on the oxidation state of Pd NPs. HS-NH2 with a high nitrogen content of 3.70 mmol g<sup>-1</sup> (Table S1) could be suitable for stabilizing highly dispersed Pd<sup>0</sup> particles and preventing their reoxidation.<sup>30, 31</sup> This could explain higher Pd<sup>0</sup> ratio for Pd/HS-NH<sub>2</sub> (5 wt%). The XPS result also shows that Pd 3d binding energy of Pd/HS-NH<sub>2</sub> has a downshift of  $\sim 0.1$  eV and  $\sim 0.2$  eV in comparison with Pd/HS and Pd/C, suggesting that Pd on HS-NH<sub>2</sub> has more electron-rich character than that on SiO<sub>2</sub> and C (Figure S6). This is possibly due to the electron denoting property of amine group. The N 1s core level for Pd/HS-NH<sub>2</sub> (5 wt%) and HS-NH<sub>2</sub> could also verify the electron donating character of nitrogen atom although small remnant -NH<sub>3</sub><sup>+</sup> coexist in the amine-functionalized silicas (Figure S7).<sup>32, 33</sup> The surface Pd contents of Pd/HS-NH<sub>2</sub> (5 wt%) calculated from the XPS results is 4.0 wt%, similar to the ICP results (4.7 wt%), suggesting that Pd NPs are uniformly distributed on the shell of HS-NH<sub>2</sub>.

The CO stripping voltammetry is an effective technique to measure the surface electronic structure of noble metals.<sup>21, 34</sup> As shown in Figure 6, the CO stripping potential for Pd/HS-NH<sub>2</sub> (5 wt%), Pd/HS (5 wt%) and Pd/C (5 wt%) is 0.84 V, 0.77 V and 0.72 V, respectively. Amine in HS-NH2 acts as an electrondonating ligand that increases the electronic density of Pd NPs, thereby favouring the back-donation of electrons to the  $2\pi$ \* antibonding orbitals of CO, which accounts for the  $C \equiv O$  bond weakening (high potential to oxide CO).35 Therefore, higher CO stripping potential indicates higher electronic density on metal NPs surface. This suggests that Pd/HS-NH<sub>2</sub> (5 wt%) is more electron rich than Pd/C (5 wt%), which is consistent with XPS results. The CO stripping potential of Pd/HS (5 wt%) is higher than Pd/C (5 wt%) because of the -OH group in silica electron donation effect to the Pd NPs.34 The strong, background oxidized electric current of commercial Pd/C (5 wt%) is possibly due to high conductivity of carbon support.

#### Catalytic performance of Pd NPs catalysts.

1, 2, 3, 4-Tetrahydroquinoline framework is a common structural motif and is found in numerous biologically active natural products and pharmacologically relevant therapeutic agents.<sup>36, 37</sup> The quinoline hydrogenation reaction represents one of the efficient method for the production of 1, 2, 3, 4tetrahydroquinoline (Scheme 2). The catalytic performance of Pd/HS-NH<sub>2</sub> was tested in quinolines hydrogenation to produce tetrahydroquinolines. Considering the important role of solvent plays in catalytic activity and selectivity, solvent effect was investigated firstly (Table S2). The product selectivity is > 99% for all solvents investigated. However, the type of solvent greatly affects the catalytic activity of Pd/HS-NH2. The quinoline conversion in aprotic solvents is much higher than that in protic solvents. This is possibility relative to the hydrogen bonding effect between protic solvent and quinoline or amine in Pd/HS-NH2. Considering the volatility, toxicity and activity, cyclohexane was selected as the reaction solvent. We

Table 2 The catalytic performance of Pd/HS-NH <sub>2</sub> ,	Pd/HS (5
wt%) and Pd/C (5 wt%) in quinoline hydrogenation	ı.

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Catal.	Conv. (%)	Sel. (%)	TOF $(h^{-1})$
Pd/HS-NH <sub>2</sub> (1 wt%)	95	>99	121
Pd/HS-NH <sub>2</sub> (3 wt%)	94	>99	128
Pd/HS-NH <sub>2</sub> (5 wt%)	96	>99	135
Pd/HS-NH <sub>2</sub> (10 wt%)	63	>99	85
Pd/HS-NH <sub>2</sub> (15 wt%)	29	>99	28
Pd/HS-NH <sub>2</sub> (5 wt%) <sup>b</sup>	98	>99	1084
$Pd/HS-NH_2$ (5 wt%) <sup>c</sup>	90	>99	5052
Pd/HS (5 wt%)	59	>99	81
Pd/C (5 wt%)	36	>99	58
Pd/C (5 wt%) <sup>c</sup>	42	>99	960

Reaction conditions: quinoline 1 mmol. S/C = 200. solvent 2 mL cyclohexane. H<sub>2</sub> pressure (1 MPa), 50 °C; <sup>a</sup> Apparent TOF is calculated as moles of converted guinoline per mol of Pd per hour based on the slope of the conversion with the conversion less than 30%; <sup>b</sup> S/C=1000, solvent 1 mL cyclohexane, 3 MPa H<sub>2</sub>, 80 °C; <sup>c</sup> S/C = 4000, solvent 1 mL cyclohexane, 3 MPa H<sub>2</sub>, 100 °C

also optimized the H<sub>2</sub> pressure using cyclohexane as solvent (Figure S8). It was found that Pd/HS-NH2 was very active and could catalyse the reaction even with H<sub>2</sub> pressure as low as 0.1 MPa. In the following reaction, H<sub>2</sub> pressure of 1 MPa was employed.

Under the optimized reaction conditions, the catalytic performance of Pd/HS-NH2 with different Pd loading was tested in quinoline hydrogenation (Table 2). All Pd/HS-NH<sub>2</sub> shows excellent selectivity to 1, 2, 3, 4-tetrahydroquinoline, which is consistent with the literature results.38 The kinetic curves for quinoline hydrogenation of Pd/HS-NH2 with different Pd loadings are displayed in Figure S9. The quinoline conversion increases almost linearly with reaction time. It seems that all the catalysts afford zero-order reaction curves when the conversion is less than 80 %, indicating a near saturation coverage of active sites by quinoline species at the initial stage.<sup>39</sup> The apparent TOF increases slightly from 121 to 135 h<sup>-1</sup> as the increment of Pd content from 1 wt% to 5 wt%. Further increasing Pd loading causes sharp decrease in TOF. The influence of Pd loading on the catalytic activity of Pd/HS-NH<sub>2</sub> is related with the particle size of Pd. Due to the broad particle size distribution for Pd/HS-NH<sub>2</sub> with high Pd loading,



Scheme 2. Possible products of the quinoline hydrogenation.

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the particle size measured with CO chemisorption method was used for the following discussion. Pd NPs with average particle size of in the range of 3.4 to 4.0 nm affords highest TOF and with particle size larger than 4.0 nm give low activity, suggesting that quinoline hydrogenation is a size sensitive reaction (Figure S10). Recently, Yin and co-workers also reported the size dependent property of quinoline hydrogenation with Pt NPs stabilized by resorcinolformaldehyde resin as catalysts.<sup>40</sup>

Under similar reaction conditions, the apparent TOF of Pd/HS-NH<sub>2</sub> (5 wt%) is almost 1.6 times and 2.3 times as high as the control sample, Pd/HS (5 wt%, TOF of 81 h<sup>-1</sup>) and the benchmark catalyst, commercial Pd/C (5 wt%, TOF of 58 h<sup>-1</sup>). This shows superior catalytic performance of Pd/HS-NH<sub>2</sub> (5 wt%). The adsorption and desorption of substrates and products play an important role in a catalytic reaction. Generally, the electron-rich metal surface can result in a strong repulsive interaction with electron-rich reactants during reaction, which may enhance the activity or selectivity.<sup>34</sup> Recently, Zheng and co-workers have revealed that the activity and selectivity of nitrobenzene hydrogenation to N-hydroxyaniline is improved greatly on electron-rich platinum nanowires.<sup>21</sup> Earlier work demonstrated that guinoline is electron-deficient in nature.<sup>41</sup> The nature charge of nitrogen atom is -0.494 and -0.681 for quinoline and 1, 2, 3, 4-tetrahydroquinoline, respectively (Figure S11). Consequently, Pd NPs with electron-rich surface would prefer the adsorption of substrates over products, which

<b>Table</b> hetero		<b>3</b> cycli	Hydrogenatio c rings.	on of	quinolines	and	other
	Sub	trate	es Products	S/C	Conv. (%)	Sel. (%	6)

		200	97	>99
$\bigcup_{i=1}^{n}$		25	99	96
	$\bigcirc$	50	99	98
		60	84	99
		400	92	>99
$\square$	$\bigcirc$	200	>99	>99
$\bigcirc$	$\bigcirc$	25	>99	>99

Reaction conditions: subtrate 1 mmol, solvent 2 mL cyclohexane,  $H_2$  pressure 1 MPa, 50 °C, time 2h; <sup>a</sup> S/C=1000, solvent 1 mL cyclohexane, 1 bar  $H_2$ , 25 °C, time 1 min.



Figure 7. Recycling stability of the  $Pd/HS-NH_2$  (5 wt%) in the hydrogenation of quinoline.

may enhance the catalytic activity. Based on the above discussion, the high activity of  $Pd/HS-NH_2$  than Pd/HS and Pd/C is possibly due to the electron rich surface of Pd NPs on HS-NH<sub>2</sub>.

The catalytic performance of model Pd/HS-NH<sub>2</sub> (5 wt%) was tested under different conditions (Table 2). The selectivity to 1, 2, 3, 4-tetrahydroquinoline is >99% under all conditions employed. The apparent TOF of Pd/HS-NH<sub>2</sub> (5 wt%) could reach 1084 h<sup>-1</sup> at 80 °C and 3 MPa H<sub>2</sub> and 5052 h<sup>-1</sup> at 100 °C and 3 MPa H<sub>2</sub>. Pd/C (5 wt%) shows apparent TOF of 960 h<sup>-1</sup> at 3 MPa H<sub>2</sub> and 100 °C. Pd/MgO affords TOF of 300 h<sup>-1</sup> at 4 MPa H<sub>2</sub> and 150 °C.<sup>42</sup> Rh/PEG gives TOF of 762 h<sup>-1</sup> at 3 MPa H<sub>2</sub> and 100 °C.<sup>43</sup> As far as we know, Pd/HS-NH<sub>2</sub> (5 wt%) is the most active solid catalyst ever reported for quinoline hydrogenation (Table S3).

The applicability of Pd/HS-NH<sub>2</sub> (5 wt%) to other heterocyclic compounds were investigated, and the results are summarized in Table 3. Pd/HS-NH<sub>2</sub> (5 wt%) could efficiently catalyse the hydrogenation of 8-methylquinoline, 4-methylquinoline, 2-methylquinoline, quinoxaline, pyridine, furan, and benzofuran to corresponding hydrogenated products with conversion ranging from 84% to >99% and selectivity ranging from 96 % to >99%. For methyl substituted quinoline, 8-methylquinoline shows the highest reactivity and 4-methylquinoline affords the lowest reactivity. This is possibly due to the fact that 4-methylquinoline with substitution at pyridine ring is difficult to be adsorbed on Pd NPs. The wide substrate scope denmostrates the excellent catalytic performance of Pd/HS-NH<sub>2</sub> (5 wt%) for the hydrogenation of heterocyclic compounds.

We tested the recycle stability of Pd/HS-NH<sub>2</sub> (5 wt%) with quinoline hydrogenation as model reaction. After the first reaction cycle, the catalyst could be recovered by centrifugation. After being washed with ethanol thoroughly and dried under vacuum, the recovered catalyst was directly used for the next run. Pd/HS-NH<sub>2</sub> (5 wt%) could be stably recycled for 6 cycles without obvious loss in catalytic activity and selectivity. After the sixth cycle, the catalyst was characterized by TEM as shown in Figure S12. No aggregation of Pd NPs could be observed in the TEM image. This also demonstrate the stability of Pd/HS-NH<sub>2</sub> (5 wt%).

## Conclusions

In summary, Pd/HS-NH<sub>2</sub> with tunable particle size of Pd was synthesized by impregnation-reduction method with amine-rich mesoporous silica hollow nanospheres as the supports. The results of CO stripping voltammetry and XPS show that Pd NPs on HS-NH<sub>2</sub> have electron rich property due to the electron donating effect of amine. The catalytic activity of Pd/HS-NH<sub>2</sub> strongly depends on the size of Pd NPs in quinoline hydrogenation, showing that this reaction is size sensitive. Pd/HS-NH<sub>2</sub> (5 wt%) shows the apparent TOF of 5052 h<sup>-1</sup>, which is the highest value ever reported for solid catalysts. The high activity of Pd/HS-NH<sub>2</sub> (5 wt%) is mainly attributed to ultrasmall size and the electron-rich surface of Pd NPs.

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# Notes and references

- 1 O. Wilson, M. Knecht, J. Garcia-Martinez and R. Crooks, J. Am. Chem. Soc., 2006, **128**, 4510.
- 2 B. Kim, M. Hackett, J. Park and T. Hyeon, *Chem. Mater.*, 2013, **26**, 59.
- 3 R. Jeff, M. Yun, B. Ramalingam, B. Lee, V. Misra, G. Triplett and S. Gangopadhyay, *Appl. Phys. Lett.*, 2011, **99**, 072104.
- 4 R. Jin, C. Zeng, M. Zhou, Y. Chen. Chem. Rev., 2016, 116, 10346.
- 5 R. Van Santen, Acc. Chem. Res., 2009, 42, 57.
- S. Vajda, M. Pellin, J. Greeley, C. Marshall, L. Curtiss, G. Ballentine, J. Elam, S. Mucherie, P. Redfern, F. Mehmood and P. Zapol, *Nature Mater.*, 2009, 8, 213.
- 7 J. Lu, J. Elam and P. Stair, Acc. Chem. Res., 2013, 46, 1806.
- 8 C. Bock, C. Paquet, M. Couillard, B. Gianluigi and M. Barry, J. Am. Chem. Soc., 2004, **126**, 8028.
- 9 L. Chen, H. Chen, R. Luque and Y. Li, *Chem. Sci.*, 2014, **5**, 3708.
- C. Li, S. Zhang, B. Zhang, D. Su, S. He, Y. Zhao, J. Liu, F. Wang, M. Wei, D. Evansa and X. Duan, *J. Mater. Chem. A*, 2013, 1, 2461.
- 11 N. Wang, Q. Sun, R. Bai, X. Li, G. Guo and J. Yu, *J. Am. Chem. Soc.*, 2016, **138**, 7484.
- 12 K. Choi, K. Na, G. Somorjai, and O. Yaghi, *J. Am. Chem. Soc.*, 2015, **137**, 7810.
- 13 P. Wang, J. Zhao, X. Li, Y. Yang, Q. Yang and C. Li, Chem. Commun., 2013, 49, 3330.
- 14 Y. Wang, H. Zhong, L. Li and R. Wang, *ChemCatChem*, 2015, 8, 2234.
- 15 Z. Li, J. Liu, C. Xia, and F. Li, ACS catal., 2013, 3, 2440.
- 16 K. Mori, M. Dojo and H. Yamashita, ACS Catal., 2013, 3, 1114.
- 17 H. Wei, X. Wei, X. Yang, G. Yin, A. Wang, X. Liu, Y. Huang and T. Zhang, *Chin. J. Catal.*, 2015, **36**, 160.
- 18 Y. Yao, X. Zhang, J. Peng and Q. Yang, Chem. Commun., 2015, 51, 3750.
- 19 G. Fagherazzi, P. Canton, P. Riello, N. Pernicone, F. Pinna and M. Battagliarin, *Langmuir*, 2000, **16**, 4539.
- 20 P. Canton, G. Fagherazzi, M. Battagliarin, F. Menegazzo, F. Pinna and N. Pernicone, *Langmuir*, 2002, 8, 6530.

- 21 G. Chen, C. Xu, X. Huang, J. Ye, L. Gu, G. Li, Z. Tang, B. Wu, H. Yang, Z. Zhao, Z. Zhou, G. Fu and N. Zheng, *Nature Mater.*, 2016, **15**, 564.
- 22 Y. Chen, H. Chen and J. Shi, Acc. Chem. Res., 2014, 47, 125.
- 23 Y. Chen, H. Chen, L. Guo, Q. He, F. Chen, J. Zhou, J. Feng and
- J. Shi, ACS Nano, 2010, 4, 529.
  24 Y. Yang, J. Liu, X. Li, X. Liu and Q. Yang, Chem. Mater., 2011, 23, 3676.
- 25 C. Parlett, D. Bruce, N. Hondow, N. Hondow, A. Lee, and Karen Wilson, ACS Catal., 2011, 1, 636.
- 26 C. Yang, M. Zhou and Q. Xu, *Nanoscale*, 2014, **6**, 11863.
- 27 C. Galeano, J. Meier, V. Peinecke, H. Bongard, L. Katsounaros, A. Topalov, A. Lu, K. Mayrhofer and F. Schüth, J. Am. Chem. Soc., 2012, 134, 20457.
- 28 P. Babykutty, C. Prabhakaran, R. Anantaraman and C. Nair, J. Inorg, Nucl. Chem., 1974, **36**. 3685.
- 29 Y. Zhang, X. He, J. Ouyang and H. Yang, *Sci. Rep.*, 2013, **3**, 2948.
- 30 V. Radkevich, T. Senko, K. Wilson, L. Grishenko, A. Zaderko and V. Diyuk, Appl. Catal. A: Gen., 2008, 335, 241.
- 31 Y. Gong, P. Zhang, X. Xu, Y. Li, H. Li and Y. Wang, J. Catal., 2013, 297, 272.
- 32 L. Zhang, J. Liu, J. Yang, Q. Yang and C. Li, *Micropor. Mesopor. Mat.*, 2008, **109**, 172.
- 33 B. Zhmud, J. Sonnefeld, J. Non-Cryst. Solids, 1996, 185, 16.
- 34 P. Luksirikul, K. Tedsree, M. Moloney, M. Green and S. Tsang, Angew. Chem. Int. Ed., 2012, 51, 6998.
- 35 T. Ye, J. Li, M. Kitano, M. Sasase and H. Hosono, *Chem. Sci.*, 2016, **7**, 5969.
- 36 B. Trost and I. Fleming, Comprehensive organic synthesis: reduction, Elsevier, 1991.
- 37 V. Sridharan, P. Suryavanshi and J. Menéndez, Chem. Rev., 2011, 111, 7157.
- 38 N. Hashimoto, Y. Takahashi, T. Hara, S. Shimazu, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Lett.*, 2010, **39**, 832.
- 39 M. Guo, G. Lan, J. Peng, M. Li, Q. Yang and C. Li, J. Mater. Chem. A, 2016, 4, 10956.
- 40 L. Bai, X. Wang, Q. Chen, Y. Ye, H. Zheng, J. Guo Y. Yin and C. Gao, *Angew. Chem. Int. Ed.*, 2016, **55**, 15656.
- 41 A. Sahin, O. Cakmak, I. Demirtas, S. Okten and A. Tutar, *Tetrahedron*, 2008, **64**, 10068.
- 42 R. Rahi, M. Fang, A. Ahmed and R. Sánchez-Delgado, *Dalton Trans.*, 2012, **41**, 14490.
- 43 M. Niu, Y. Wang, P. Chen, D. Du, J. Jiang and Z. Jin, *Catal. Sci. Technol.*, 2015, **5**, 4746.

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An amine-rich silica hollow nanospheres were prepared by using a one-pot condensation method. The ultralsmall Pd NPs stabilized by the material with TOF as high as  $5052 \text{ h}^{-1}$  is among the most active solid catalyst for quinoline hydrogenation. The high catalytic activity could be mainly attributed to the ultrasmall particle size and high surface electronic density of Pd NPs.

