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# Fabrication of Highly Dispersed/Active Ultrafine Pd Nanoparticles Supported Catalyst: a Facile Solvent-free In-situ Dispersion/Reduction Method

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Development of sustainable routes for synthesis of noble metal supported catalysts is of high importance because of their wide applications at large scale in catalysis field. Herein we report a facile solvent-free solid-state dispersion route to fabricate highly dispersed ultrafine palladium nanoparticles supported catalyst. In the first step, noble metal precursor Pd(acac)<sub>2</sub> was dispersed spontaneously by treating the physical mixture of Pd(acac)<sub>2</sub> and catalyst support hydroxyapatite (HAP) at 120 °C in a flow of N<sub>2</sub>. SubsequentH<sub>2</sub> reduction results in the formation of two kinds of Pd particles. *In-situ* reduction at 120 °C is essential for preparing highly dispersed Pd nanoparticles (~1.2 nm, <sup>a</sup>1Pd/HAP-SSD) and cooling-down reduction leads to the formation of larger Pd nanoparticles (~4 nm, <sup>b</sup>1Pd/HAP-SSD). The as-prepared <sup>a</sup>1Pd/HAP-SSD exhibits higher activity for phenol hydrogenation than <sup>b</sup>1Pd/HAP-SSD and that obtained by traditional wet impregnation method, due to the highly dispersed ultrafine Pd<sup>0</sup> nanoparticles obtained by *in-situ* dispersion/reduction. Compared with conventional wet chemistry-based methods, the synthesis route in this work simplifies the synthesis process, avoids producing large polluted wastes, and enhances the dispersion of noble metals. This may open a new way to prepare highly dispersed/active noble metal supported catalysts and is also potentially of high importance for green production of noble metal supported catalysts at large scale in the future.

## Introduction

Metal supported catalysts have received considerable attention for decades based on their potential applications in energy conversion, environmental remediation, and catalysis.<sup>1</sup> Numerous studies find that properties of these kinds of supported catalysts are strongly dependent on the metal particle size, degree of dispersion, and interaction between metal and support, etc.<sup>2-6</sup> Ultrafine metal nanoparticles (<2 nm) with high dispersion usually exhibit exceptional catalytic performance for their unique properties distinct from those in large-size and bulk counterparts, probably due to their increased surface areas and number of edge and corner atoms. To prepare supported catalysts with ultrafine metal particle size, various routes have been explored including, wet deposition precipitation technique,<sup>7</sup> photo-deposition,<sup>8,9</sup> colloidal method,<sup>10</sup> ion exchange,<sup>11</sup> atomic layer deposition,<sup>12</sup> and so on. Usually, the synthesis of metal nanoparticle supported catalysts is performed under solution conditions, where plenty of solvents such as water are necessary. The use of the water solvent leads to a large amount of polluted wastes, and the forced condensation during the following drying procedure usually results in undesirable dispersion of metal precursors.<sup>13</sup> The synthesis of ultrafine, uniform, highdispersed and catalytically active noble metal nanoparticles in a controllable manner still remains an unmet challenge, despite recent developments in the dispersion and stabilization of noble metal nanoparticles.

Solid state dispersion (SSD) is a solvent-free technique based on spontaneous monolayer-dispersion principle, which suggests that salts can disperse spontaneously onto the surfaces of supports to form a thermodynamically stable monolayer or sub-monolayar structure.<sup>14</sup> Compared with the above-mentioned solution-based methods, no solvents are involved in this procedure therefore circumventing drying steps normally involved in preparing such catalysts. Thus, it is not only a time-saving and energy-saving process without the removal of solvent, but also provides a better dispersion of metal precursors due to the avoidance of forced condensation during drying procedure. Up to now, many transition metal oxides or transition metals, such as CuO, NiO and Co, have been successfully dispersed onto various supports by SSD method,  $^{\rm 15\text{-}17}$  and this technique was also extended to a few organic compounds.<sup>18,19</sup> To the best of our knowledge, the preparation and catalytic performance of noble metal

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supported catalysts by using this solid state dispersion method are far less investigated.

Herein, we explore the solvent-free solid state dispersion route to synthesize highly dispersed ultrafine Pd nanoparticles on hydroxyapatite (HAP). TEM, H<sub>2</sub>-TPR, in-situ XPS with H<sub>2</sub> treatment and IR spectra of chemisorbed CO are used to investigated the dispersion/particle size and the chemical nature of Pd/HAP. Both dispersion and reduction conditions strongly affect the size of Pd nanoparticles, and in-situ dispersion/reduction leads to the highly dispersed ultrafine ~1.2 nm Pd nanoparticles (<sup>a</sup>1Pd/HAP-SSD). Together with Pd/HAP obtained from traditional wet impregnation method (WI), all Pd/HAP samples were evaluated in phenol hydrogenation reaction with a view to correlate with Pd nanostructures. Remarkably enhanced activities for phenol hydrogenation were observed for Pd/HAPs obtained from SSD method (73.5%, <sup>a</sup>1Pd/HAP-SSD; 20.45%, <sup>b</sup>1Pd/HAP-SSD; 3.8%, 1Pd/HAP-WI), especially that with smaller Pd particle size obtained by in-situ dispersion/reduction.

### Experimental

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### Synthesis of Pd/HAP catalyst

HAP is utilized as metal support and synthesized according to the previous report by our group, which presents nanorod morphology with several micrometers in length and ca. 8-50 nm in diameter (Fig. S1<sup>†</sup>, PDF#09-0432).<sup>20</sup> The hydroxyapatite (HAP) was first dried in an oven at 120 °C for 12 h to remove the adsorbed water or gas on the surface. Then, it was physically mixed with the palladium salt Pd(acac)<sub>2</sub> (97%) by grinding to have a nominal content of 1 wt. % of Pd (denoted as  $1Pd(acac)_2/HAP$ ). Then, it was thermally treated at 120 °C for 4 h in a flow of N2. Before cooling to the room temperature, N<sub>2</sub> was switched to H<sub>2</sub>, and catalysts denoted as <sup>a</sup>1Pd-HAP-SSD was obtained by being *in-situ* reduced for 30 min at 120 °C. For comparison, the catalyst was also reduced after cooling down to room temperature in  $N_2$  flow and catalysts denoted as <sup>b</sup>1Pd-HAP-SSD was obtained by being heated at 5  $^{\circ}$ C min<sup>-1</sup> up to 120  $^{\circ}$ C in a H<sub>2</sub> flow for 30 min.

1Pd-HAP-WI was prepared by conventional wet impregnation route as follows: 0.4g HAP were placed in 80 ml ethanol solution containing 0.0115g  $Pd(acac)_2$  in order to have 1 wt. % of Pd in the final solid. The suspension was stirred at room temperature for 12 h and then heated at 60  $^{\circ}$ C in a vacuum evaporator to remove excess ethanol. Finally, the sample was reduced following a similar procedure for the sample <sup>b</sup>1Pd-HAP-SSD.

### Characterization

X-ray diffraction patterns (XRD) were recorded on a Philips X'Pert X-ray diffractometer with a Cu Ka radiation (40 kV, 40 mA). The TEM images were taken on a JEOL JEM-1010 electron microscope operated at 100 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) studies were carried out on an FEI Titan 80-300 electron microscope (200 kV). N<sub>2</sub> sorption isotherms were measured using a Micromeritics ASAP2020 analyzer at 77 K and the Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The

Pd loading of catalyst was analyzed by an Optima 5300 DV ICP-OES.

Temperature-programmed desorption of hydrogen (H<sub>2</sub>-TPR): The catalysts was performed on Tianjin XQ TP-5080 chemisorption instrument. First, the sample was calcined at 100 °C for 30min with a 10 °C min<sup>-1</sup> heating rate in  $N_2$  in order to remove any adsorbed gas. Then, the sample was cooled to 30 °C and the temperature was raised from room temperature to 500 °C with a 10 °C/min heating rate. The profile was continuously registered with a TCD.

Temperature-programmed desorption of hydrogen (H<sub>2</sub>-TPD) of the catalysts was performed on Tianjin XQ TP-5080 chemisorption instrument. First, the sample was calcined at 100 °C for 30min with a 10 °C min<sup>-1</sup> heating rate in Ar in order to remove any adsorbed gas. Then, the sample was cooled to 30 °C and exposed to H<sub>2</sub> flow (20 mL min<sup>-1</sup>) for 1 h. Hydrogen flow was stopped and the sample was flushed with Ar for 1 h to remove any physically adsorbed hydrogen. Finally, the temperature was raised from room temperature to 600 °C with a 10 °C/min heating rate and the hydrogen desorption profile was continuously registered with a TCD.

X-ray photoelectron spectra (XPS): The X-ray photoelectron spectroscopy (XPS) measurements were performed in a commercial XPS system (PHI 5000 VersaProbe) equipped with a hemispherical electron analyzer and monochromatic Al Ka Xray exciting source. The sample was first evacuated at 298 K for 1h and the spectra was measured. Then the sample was reduced at 85  $^{\circ}$ C in a 5 vol. % H<sub>2</sub>/N<sub>2</sub> (30 mL/min) for 1h, after the sample was cooled to room temperature the spectra was measured. All binding energies (BEs) were referenced to the C1s peak at 284.6 eV.

In situ FT-IR: Diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed on a Bruker Tensor 27 spectrophotometer. The catalysts were first activated at 100 °C in ultrahigh-purity N<sub>2</sub> (99.9%, 4 mL/min) for 30 min to remove the adsorbed water or gas on the surface. After the DRIFTS cell was cooled to 25 °C, 10 vol% CO in He with a flow rate of 10 mL/min was introduced into the cell for 30 min to saturate the Pd surface. After the CO saturation, another 20 min N<sub>2</sub> purge at a flow rate of 4 mL/min was performed to remove gas-phase CO from the DRIFTS cell. Finally, the spectrum was recorded.

### **Catalytic Tests**

Catalytic tests were conducted in a 25 mL round flask with a magnetic bar. Heterogeneous Pd catalyst powder (5 mol % relative to phenol), 0.05 mmol phenol, and 3 ml water were introduced into the round flask, and then it was vacuumed and purged with H<sub>2</sub> three times before it was finally pressurized with 1.0 atm of  $\mathsf{H}_2$  gas. Subsequently, the reaction mixture was heated and stirred to 85 °C (10 °C/min) for a certain time. After cooling to room temperature, excess H<sub>2</sub> was carefully released, and the internal standard (toluene) was added. The resultant product mixtures were analyzed by an Agilent gas chromatograph (GC-9860).

### **Results and discussion**

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**Fig. 1** Schematic diagram for the preparation of Pd/HAP with a) solid state dispersion and b) wet impregnation methods.

The schematic diagram for the preparation of Pd/HAP using SSD method is shown in Fig. 1a. Pd(acac)<sub>2</sub> with characteristic of low melting point (116 °C measured with melting point apparatus) and high decomposition temperature (206  $^{\circ}$ C) is selected as metal precursor. In a typical synthesis process (for details see experimental section), Pd(acac)<sub>2</sub> with loading quantity below its monolayer dispersion capacity was first thoroughly ground with HAP to form a physical mixture and then put into a quartz tube under  $N_2$  flow. With the increase of the temperature, Pd(acac)<sub>2</sub> turned into a liquid phase before decomposition and was dispersed onto the surface of HAP to form a thermodynamically stable monolayer, similar to the dispersion behavior of transition metal salts on the surface of silica.<sup>15,16,21</sup> Due to the decrease of Gibbs free energy of the whole system, this procedure can be assumed to be a spontaneous process.<sup>13,22</sup> Besides, driven by the energy of elastic stresses induced by grinding, virtual melting of Pd(acac)<sub>2</sub> on the surface can be occurred at a lower temperature than its standard melting point.<sup>14,23</sup> Finally, 1Pd/HAP-SSD are obtained after being *in-situ* reduced in H<sub>2</sub> with temperature keeping (<sup>a</sup>1Pd/HAP-SSD) or being reduced after cooling down (<sup>b</sup>1Pd/HAP-SSD). As a comparison, 1Pd/HAP-WI is also prepared via conventional wet impregnation method and subsequently H<sub>2</sub> reduction (Fig. 1b).



Obtaining a monolayer dispersed Pd(acac)<sub>2</sub> on HAP is critical for the preparation of ultrafine Pd nanoparticles. So measuring the dispersion capacity of supported Pd(acac)<sub>2</sub> is of obvious significance. Fig. 2a depicts the XRD patterns of Pd(acac)<sub>2</sub>/HAP with different Pd contents (x, denoted as  $xPd(acac)_2/HAP$ ). No Pd(acac)<sub>2</sub> crystalline phase in the XRD patterns was observed on 1Pd(acac)<sub>2</sub>/HAP, indicating that Pd(acac)<sub>2</sub> species were highly dispersed on the HAP support without the formation of any highly crystalline Pd(acac)<sub>2</sub> species or the Pd(acac)<sub>2</sub> content was below the detection of the XRD instrument. At the Pd loading of 5 wt. %, the weak diffraction peak of crystalline Pd(acac)<sub>2</sub> was detected. The intensity of crystalline Pd(acac)<sub>2</sub> diffraction peak increases proportionally with Pd(acac)<sub>2</sub> loading. Since the disappearance of XRD patterns might not a strong criterion for monolayer spreading, its be uncertainty can be further alleviated by employing an extrapolation procedure.<sup>24,25</sup> The dispersion capacity of Pd(acac)<sub>2</sub> on HAP was determined by the amount of residual crystalline Pd(acac)<sub>2</sub>. As a function of Pd(acac)<sub>2</sub> loadings, the intensity ratios of  $I_{Pd(acac)2}/I_{HAP}$  are plotted in Fig. 2b, in which the highest intensity peaks of  $Pd(acac)_2$  (12.3°) and HAP (31°) were chosen for the calculation. The intercept of X-axis corresponds to the utmost monolayer dispersion capacity of Pd(acac)<sub>2</sub> on the surface of HAP and was determined to be  $0.0552 \text{ g Pd}(\text{acac})_2 / \text{ g HAP}$ , which corresponds to 1.9 wt. % Pd. If the Pd(acac)<sub>2</sub> content in the mixture exceeds this critical dispersion capacity, there will be an aggregation of Pd(acac)<sub>2</sub> and formation of crystalline phase after heat treatment, probably leading to form larger Pd particles after reduction. Besides, we found that the dispersion threshold of Pd(acac)<sub>2</sub>/HAP-SSD was much higher than that of Pd(acac)<sub>2</sub>/HAP-WI (less than 1 wt. % Pd, Fig. S2<sup>†</sup>). Such behavior can be rationalized by taking into consideration that competitive adsorption of solvent ethanol molecules will disturb the guest-host interaction and hinder the anchoring of the Pd(acac)<sub>2</sub> species on the surfaces.<sup>14</sup> More importantly, the



forced condensation of Pd(acac)<sub>2</sub> during drying process

**Fig. 2** a) XRD patterns of  $Pd(acac)_2/HAP$  with different Pd loadings treated at 120 °C for 4 h; b) dispersion capacity of  $Pd(acac)_2$  on HAP measured by XRD.

**Fig. 3** Wide and enlarged XRD patterns of Pd(acac)<sub>2</sub>/HAP treated in different temperatures (a) and for different periods (b).

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Suitable temperature is also desirable for monolayer dispersion. Fig. 3a shows the X-ray diffraction (XRD) patterns of 1Pd(acac)<sub>2</sub>/HAP with a nominal content of 1 wt. % Pd thermally treated at different temperatures. With Pd(acac)<sub>2</sub> loading below its monolayer dispersion capacity, Pd(acac)<sub>2</sub> was first physically mixed with HAP and a small diffraction peak of Pd(acac)<sub>2</sub> appeared at the low angle of 12.3° compared with the pure HAP. Then thermal treatment at different temperatures for 24 h, the diffraction peak of crystalline phase Pd(acac)<sub>2</sub> still appeared until the temperature reached 100 °C, and it disappeared at 120 °C, indicative of the well-dispersion of Pd(acac)<sub>2</sub>. If thermal treatment temperature was kept at 120 °C for different times (Fig. 3b), 4 h was enough to allow for the occurrence of Pd(acac)<sub>2</sub> monolayer dispersion. Based on these results, we speculated that the critical dispersion temperature of Pd(acac)<sub>2</sub> is higher than 100  $^{\circ}$ C, which is in agreement with the actual melting temperature of Pd(acac)<sub>2</sub> at 116 °C observed in melting point apparatus. Obviously, at the lower temperature, the solid dispersion would not proceed fast enough to overcome kinetic resistance and require a longer heating time. At 120 °C, slightly above the actual melting temperature of Pd(acac)<sub>2</sub>, Pd(acac)<sub>2</sub> powder will melt and spread on the surface of HAP quickly, forming a uniform layer of coating on it. High temperature treatment (150 °C) will decompose the Pd(acac)<sub>2</sub> and change the color of mixture from light yellow to gray. In this synthesis, 120 °C is the appropriate treatment temperature. Besides, the smaller the particles, the more thorough the mixing, then the more readily this process proceeds and the less time it takes to reach its limit.26

In contrast,  $1Pd(acac)_2/HAP-WI$  clearly gave rise to the peak of the crystalline  $Pd(acac)_2$  species (Fig. S2<sup>†</sup>), suggesting the failure of wet impregnation method to highly dispersed  $Pd(acac)_2$ . This may be caused by the forced condensation of metal precursors during drying procedure.<sup>27</sup> This phenomenon is also confirmed by H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) analysis in Fig. S3<sup>†</sup>, which shows that  $1Pd(acac)_2/HAP-$ WI with large  $Pd(acac)_2$  particle size is much easier to be reduced than  $1Pd(acac)_2/HAP-SSD$  in highly dispersed state.



**Fig. 4** TEM images of a) <sup>a</sup>1Pd/HAP-SSD, c) <sup>b</sup>1Pd/HAP-SSD and d) 1Pd/HAP-WI; b) HAADF-STEM image of <sup>a</sup>1Pd/HAP-SSD. Insets in a) and c) are the corresponding particle size distributions.

Based on the above results, the optimal experimental conditions are determined. With the  $Pd(acac)_2$  loading under its dispersion capacity, physically mixed  $Pd(acac)_2$  and HAP are first thermally treated at 120 °C for 4 h in a flow of N<sub>2</sub>. Subsequently, Pd/HAP was obtained after H<sub>2</sub> treatment and here two reduction methods are compared. All the samples exhibited high similarity between XRD patterns of HAP and Pd/HAP (Fig. S4<sup>†</sup>), indicating that Pd was highly dispersed on the HAP support without the formation of any large Pd particles. The little variation of nitrogen adsorption-desorption isotherm curves and the surface areas (Fig. S5<sup>†</sup> and Table S1<sup>†</sup>) between HAP and Pd/HAP also suggests the retaining of HAP structures, which is in agreement with XRD patterns.

TEM and HAADF-STEM are used to investigate the morphology and distribution of the supported Pd nanoparticles on HAP. In-situ reduction with temperature keeping at 120 °C leads to the formation of ultrafine nanoparticles (black dots) with an average size approximately at 1.2 nm and the Pd loading at 1.08 wt.% determined by emission spectrometer (ICP-AES) (Fig. 4a), in agreement with the amount of raw material added. HAADF-STEM image further confirms that Pd nanoparticles (white dots, Fig. 4b) are uniformly anchored on the surface of HAP and no agglomerations are observed. However, reduction after cooling down leads to the formation of much larger Pd nanoparticles (~4.0 nm, Fig. 4c). We speculate that due to the weak interaction between Pd(acac)<sub>2</sub> and HAP, cooling down might cause the reaggregating of already monolayer dispersed precursor to form larger stable Pd(acac)<sub>2</sub> particles. Therefore, in-situ dispersion/reduction is essential for preparing ultrafine Pd nanoparticles. As a comparison, Pd nanoparticles up to 10 nm are observed for sample 1Pd/HAP-WI (Fig. 4d), which may be attributed to the forced condensation of Pd(acac)<sub>2</sub> during drying (Fig. S2<sup>†</sup>and Fig. S3<sup>†</sup>). Thus, the SSD method can be considered as an alternative to traditional wet impregnation and drying procedures, which provides a better dispersion for metal supported catalysts.

The particle size variation and the chemical nature of Pd/HAP were further investigated by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 5. Samples are first treated in vacuum at 298 K to remove the volatile impurities weakly adsorbed on the surface and the Pd 3d spectra all present two sets of doublet peaks corresponding to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> (Fig. 5A). In the case of <sup>a</sup>1Pd/HAP-SSD (Fig. 5A-a), peaks of <sup>a</sup>1Pd/HAP-SSD centered at Pd 3d<sub>5/2</sub> (336.1 eV) and Pd  $3d_{3/2}$  (341.5 eV) are attributed to Pd<sup>0</sup> species, while the peaks at Pd  $3d_{5/2}$  (336.8 eV) and Pd  $3d_{5/2}$  (341.9 eV) are related to Pd<sup>2+</sup> species.<sup>28,29,30</sup> It is well known that binding energies of small Pd clusters generally increased with the reduced cluster size.<sup>31</sup> In detail, for Pd<sup>0</sup> 3d<sub>5/2</sub> peak, the characteristic value of bulk Pd at >4 nm are approximately 335.0-335.2 eV, and that of the supported Pd clusters at approximately 1 nm is increased to 335.9-336.9 eV.32

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Fig. 5 XPS spectra of a) <sup>a</sup>1Pd/HAP-SSD, b) <sup>b</sup>1Pd/HAP-SSD and c) 1Pd/HAP-WI experienced *in-situ* H<sub>2</sub> treatment.

Thus, compared with Pd 3d signal of <sup>b</sup>1Pd/HAP-SSD and 1Pd/HAP-WI, the shift towards a higher binding energy could be an indication of the decreased Pd cluster size for <sup>a</sup>1Pd/HAP-SSD. Besides, the Pd nanoparticles of <sup>a</sup>1Pd/HAP-SSD at approximately 1.2 nm revealed 336.1 eV for  $Pd^0 3d_{5/2}$  peak, which is consistent with the reported ones. Further, according to XPS data, Pd<sup>0</sup> percentage of <sup>a</sup>1Pd/HAP-SSD is calculated to be 47.1% which is lower than that of <sup>b</sup>1Pd/HAP-SSD (58.1%). The main reason is that smaller Pd particles with more surface metal atoms are inclined to be oxidized in the air.<sup>33</sup> However, after treated at 85 °C (the temperature of following phenol hydrogenation reaction) in the  $H_2$ , the Pd<sup>0</sup> percentage (72.5%) of <sup>a</sup>1Pd/HAP-SSD reaches the highest of all the samples and Pd<sup>0</sup> is formed as the major phase of Pd (Fig. 5B-a). This indicates that smaller Pd particles on <sup>a</sup>1Pd/HAP-SSD are also likely to be reduced in H<sub>2</sub> and with more Pd<sup>0</sup> species, which benefit the hydrogenation reactions.<sup>34</sup>

As a sensitive probe to identify the nature and the exposed sites of the metal particles, IR spectra of CO chemisorption has been extensively used.<sup>35</sup> As shown in Fig. 6a, <sup>a</sup>1Pd/HAP-SSD exhibits two peaks at 2090 and 1920 cm<sup>-1</sup>, which can be assigned to the linear and bridged adsorption of CO on Pd, respectively.<sup>36</sup> It should be noted that the intensity of the linear adsorption band was higher than that of the bridged one, indicating that the linear adsorption of CO is dominant on this catalyst. For <sup>b</sup>1Pd/HAP-SSD and 1Pd/HAP-WI, the low band centred at 2057  $\text{cm}^{-1}$  could also be ascribed to liner CO adsorption.<sup>37</sup> However, its intensity is much lower than their bridged adsorption peaks at 1920 and 1868 cm<sup>-1</sup>. Previous studies have found that the liner adsorption is attributed to CO adsorbed on Pd atoms at edges and corners with single atom or small clusters, whereas bridged adsorption corresponds to CO adsorbed on Pd planes of larger particles.<sup>38-40</sup>



Fig. 6 IR spectra of chemisorbed CO on samples: a) <sup>a</sup>1Pd/HAP-SSD, b) <sup>b</sup>1Pd/HAP-SSD and c) 1Pd/HAP-WI

Thus, in conjunction with the preceding TEM and XPS analysis, the dominant CO liner adsorption for <sup>a</sup>1Pd/HAP-SSD further confirms the decrease of Pd nanoparticle size.

The catalytic performances of Pd/HAP were investigated in the selective hydrogenation of phenol, which is a fundamentally important reaction to produce cyclohexanone as intermediates for chemical industry.41-43 All catalysts are tested and the results are shown in Table 1. Catalyst <sup>a</sup>1Pd/HAP-SSD showed an excellent phenol conversion of 73.5% within only 1 h, while under the same reaction <sup>b</sup>1Pd/HAP-SSD condition, and 1Pd/HAP-WI showed conversions of 20.4% and 3.8%, respectively. According to the analysis using TEM, XPS and IR spectra of chemisorbed CO, the Pd particle sizes in <sup>a</sup>1Pd/HAP-SSD are much smaller than that of <sup>b</sup>1Pd/HAP-SSD and 1Pd/HAP-WI, which is in favor of catalytic hydrogenation reactions. The higher performance of catalyst <sup>a</sup>1Pd/HAP-SSD can also be attributed to the higher Pd<sup>0</sup> percentage, which has

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Catalyst	Time	Conversion	Selectivity /	
	/h	/%	C=O	С-ОН
<sup>a</sup> 1Pd/HAP-SSD	1	73.5	>99	n.d
<sup>b</sup> 1Pd/HAP-SSD	1	20.4	>99	n.d.
1Pd/HAP-WI	1	3.8	>99	n.d.

Reaction condition: phenol (0.05 mmol), Pd (5 mol % relative to phenol), water solvent (2 mL), 85  $^{\circ}C$ , 0.1Mpa of H<sub>2</sub>, stirring at 1000 rpm, unless otherwise noted.



**Fig. 7** Phenol conversion and cyclohexanone selectivity of <sup>a</sup>1Pd/HAP-SSD varied with time.

been supposed as the active sites for hydrogenation reactions.<sup>34,44,45</sup> Besides, higher hydrogen adsorption capacity/ability (higher hydrogen desorption temperature) of <sup>a</sup>1Pd/HAP-SSD exhibited by H<sub>2</sub>-TPD (Fig. S6<sup>†</sup>) may also account for the enhancement of activity.<sup>46</sup> It is particularly remarkable that the selectivity values remain very close to 100% until conversion values exceed 90% (Fig. 7). This specific selectivity is supposed to be related with the abundant basic sites on HAP support.<sup>11</sup> When the reaction time was prolonged to 5 h the final 96.5% selectivity together with 97.9% conversion on <sup>a</sup>1Pd/HAP-SSD was achieved, which satisfied the task of attainment of high selectivity (>95%) at elevated conversion (>80%) simultaneously,<sup>41,42,47</sup> indicating that the highly dispersed ultrafine Pd nanoparticles on hydroxyapatite prepared via the present green solvent-free route hold great potential for the further application in hydrogenation of phenol to cyclohexanone.

### Conclusions

In conclusion, a facile solvent-free solid state dispersion route was reported to prepare highly dispersed Pd clusters onto hydroxyapatite (HAP) support. With Pd(acac)<sub>2</sub> loading below its monolayer dispersion capacity, physically mixed Pd(acac)<sub>2</sub> and HAP were first thermally treated at a temperature slightly higher than its melting temperature for a short time and Pd(acac)<sub>2</sub> were monolayer dispersed spontaneously. After *insitu* H<sub>2</sub> reduction of monolayer dispersed Pd(acac)<sub>2</sub>, highly dispersed Pd nanoparticles with ultrafine sizes were obtained (~1.2 nm, <sup>a</sup>1Pd/HAP-SSD). However, due to the weak

interaction between Pd(acac)<sub>2</sub> and HAP, cooling down might cause the reaggreagting of monolayer dispersed liquid Pd(acac)<sub>2</sub>, leading to the formation of larger Pd nanoparticles (~4 nm, <sup>b</sup>1Pd/HAP-SSD). By contrast, traditional wet impregnation method results in the forced condensation of Pd(acac)<sub>2</sub> during drying procedure. Larger and uneven aggregated Pd particles were obtained (~10 nm). The asprepared <sup>a</sup>1Pd/HAP-SSD catalyst exhibited a higher catalytic activity than those of <sup>b</sup>1Pd/HAP-SSD and their counterparts prepared by wet impregnation method for phenol hydrogenation, which can be attributed to the decrease of Pd cluster size with more edge and corner atoms, the higher active Pd<sup>0</sup> percentage and the enhanced hydrogen adsorption capacity. With this method, no solvents are involved, circumventing drying steps normally involved in preparing such noble metal supported catalysts, which further avoids the forced condensation of metal precursor. This methodology may provide an alternative to classical solution-based preparation methods and open a new green way to prepare highly dispersed ultrafine metal supported catalysts with higher activity.

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