A green and efficient route for preparation of supported metal colloidal nanoparticles in $scCO_2$†

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An efficient method for dispersing active metal colloidal nanoparticles onto supports uniformly is revealed in this paper. The critical feature of this method is to separate the stabilizer simply with the phase-switch function of $scCO_2$; with it the highly dispersed Pd colloidal catalysts were prepared, and the forming procedure is analyzed and discussed in detail. The present work not only overcame the common difficulties of removing the stabilizers in the preparation of supported colloidal particles, but also provided a facile and green process for preparing supported metal colloidal nanoparticles with using the environmentally benign solvent of $scCO_2$.

Introduction

The controllable preparation of heterogeneous catalysts is a gentle art, and various procedures are at the disposal of chemists to efficiently elaborate supported catalysts for improving reaction rate and selectivity.[1] Much attention has been paid recently to metal colloid catalyst preparation because of the wide application of colloidal particles with controllable size, shape and composition.[2] Supported colloidal metal nanocatalysts are generally prepared by adsorption of colloidal nanoparticles, grafting of colloids on solid support,[3] evaporation deposition method[4] and electroless deposition method.[5] However, in these procedures a complex step of support modification is necessary and some modifiers poison the catalyst. It was found that the use of surfactants to disperse the nanoparticles hinders nanoparticle deposition and immobilizing colloidal metal nanoparticles on a solid support lowers their activity due to geometrical restriction of stabilizer.[6] Therefore, in the preparation of supported metal colloid catalysts, removing the stabilizer or without use of any stabilizer initially is advantageous.

Recently, some achievements have been gained in removing stabilizer. Lee *et al.* reported that a stabilizer of poly(*N*-vinyl-2-pyrrolidone) (PVP) could be removed with calcination in air at high temperature,[7] but the morphology of nanoparticles was changed and conglomeration occurred. Besides, PVP stabilizer was removed from the nanoparticles by washing with acetone and/or water solution sufficiently.[8] Although the washing procedure is simple, sedimentation and separation of nanoparticles are very difficult to handle and large amount of organic solvents are required. In addition, the metal clusters may run off and/or conglomerate during the centrifugation. More recently, great progress in the preparation of supported nanoparticle catalysts without stabilizers was reported by Finke *et al.*;[9] the preparation process is, however, sensitive to water, all the substrate and solvent should be anhydrous or dehydrated and carried out in a drybox. Supercritical CO_2 ($scCO_2$) is a unique and effective medium and it can dissolve in some organic solvents at high pressure to form a CO_2-expanded liquid, which is beneficial to separation and deposition processes and other applications.[10] By varying the CO_2 composition,[11] a continuum neat organic liquid phase could change to CO_2-expanded liquid and finally forming a single homogeneous phase. Recently, it was reported that high-density Pd, Ru and Rh nanoparticles could be deposited successfully on functionalized carbon nanotubes (CNTs) in $scCO_2$,[12] in which the metal precursors with CNTs were reduced by hydrogen in $scCO_2$, and the metal particles could be well dispersed on the outer surface of the CNTs, but the function of $scCO_2$ and the particle forming and controlling mechanism are rarely discussed. Herein, we will give an obvious image for the formation of metal colloidal nanoparticles in the presence of dense CO_2, and the forming process as well as the possible mechanism will be given also. In this work, the metal precursor like H_2PdCl_4 was reduced *in situ* in ethylene glycol (EG) without hydrogen as described in literature.[13] PVP was used as a stabilizer to protect the Pd colloidal nanoparticles from aggregation, and it could be partially removed in the presence of dense CO_2 by using the phase-switch function of $scCO_2$. Meanwhile, controllable Pd colloidal nanoparticles were dispersed uniformly onto the catalytic supports SiO_2 or C as illustrated in Fig. 1.

Experimental

Phase behavior observation

Since phase behavior plays an important role in understanding the formation or reaction mechanism in $scCO_2$, it is crucial to observe the phase behavior changes during the material preparation and chemical reaction in $scCO_2$. An 80 ml

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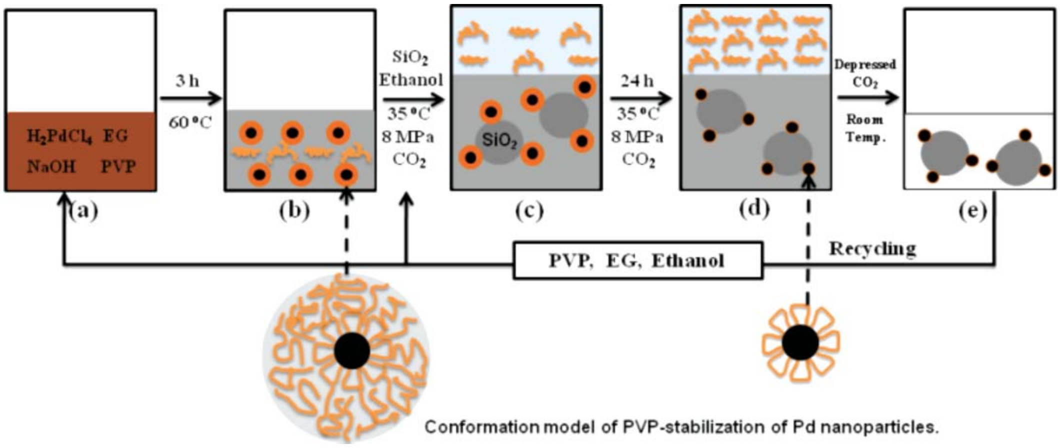


Fig. 1 The forming process of Pd-SiO_2 in EG/ethanol in the presence of $scCO_2$.

high-pressure sapphire-windowed reactor was used to examine the phase behavior. The colloidal solutions, organic solvents and support were added into the reactor and then the reactor was sealed and flushed three times with 1 MPa N_2. After the reactor was heated to 35 °C, CO_2 was introduced into the reactor with desired total pressure, ranging from 0 to 20 MPa. The mixture was maintained at a certain pressure for several minutes while stirring, then the stirring was stopped and the state of mixture was observed by the naked eye from the window.

Preparation of PVP-stabilized Pd nanoparticles in EG system

H_2PdCl_4 was first prepared by converting 0.0175 g of $PdCl_2$ with 0.05 ml of concentrated HCl. The prepared H_2PdCl_4, together with 0.03 g PVP (K-30, 40 000 g mol^{-1}), was dissolved in 10 ml of EG containing 0.15 M NaOH. The solutions were stirred for 30 min in air at room temperature. The pH of solution is about 12. Subsequently, the prepared solvents heated to 60 °C for 3 h and then cooled in air. Dark brown solutions containing the PVP-stabilized Pd colloids were formed in this manner and are referred to as colloidal solutions in this work.

Preparation of supported Pd/PVP colloidal nanoparticles

10 ml PVP-stabilized Pd colloidal solutions, 20 ml ethanol and desired amounts SiO_2 or C were added into a 50 ml stainless steel batch reactor. Then the mixture was stirred continuously with a Teflon-coated magnetic stir bar with a stirring speed around 1300 rpm for 72 h at 35 °C. Upon completion of the process, the reactor was cooled to room temperature. The SiO_2 or C supported Pd catalysts were then filtered and washed extensively with ethanol and water. The SiO_2 or C supported Pd catalysts with PVP were generally dried in vacuum at 60 °C overnight.

Preparation of supported Pd colloidal nanoparticles in $scCO_2$

10 ml PVP-stabilized Pd colloidal solutions, 20 ml ethanol and desired amounts SiO_2 or C were added into a 50 ml stainless steel batch reactor. After the reactor was heated up to 35 °C and then CO_2 were introduced into the reactor to the desired pressure using a high-pressure liquid pump. The mixture was stirred continuously with a Teflon-coated magnetic stir bar with a stirring speed around 1300 rpm for 24 h. Upon completion of the process, the reactor was cooled to room temperature and depressurized carefully with a back-pressure regulator. The supported Pd catalysts were then filtered and extensively washed with ethanol and water. The supported Pd catalysts were generally dried in vacuum at 60 °C overnight. The prepared catalyst was homogeneously ground before use.

Catalyst characterization

Pd loading on the catalysts was measured by ICP-MS (Thermo Scientific ICAP6000, USA) and the physical properties of catalysts were examined by BET (Micromeritics ASAP 2020 V3.01 H). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were performed using JEM-2010EX and JEM-2100F. The powder of catalysts was suspended in ethanol with an ultrasonic dispersion for 5–10 min and then the resulted solution was dropped on a carbon film of copper grid. Thermogravimetric analysis (TGA) was carried out on a TGA/DSC 1/1100 LF (Mettler-Toledo) Thermal Analysis System with a heating rate of 10 °C min^{-1} in nitrogen with a flow rate of 20 ml min^{-1}.

Catalytic activity test

The hydrogenation of MAH was selected as target reaction for evaluation of the catalytic activity of the supported Pd colloidal nanoparticles. The hydrogenation was carried out in a 50 ml stainless steel batch reactor. Catalyst (Pd/SiO_2 or Pd/C) and MAH were loaded into the reactor, and then the reactor was sealed and flushed three times with 1 MPa N_2. After the reactor was heated to the reaction temperature, first H_2 and then CO_2 were introduced into the reactor to the desired pressure using a high-pressure liquid pump. The reaction mixture was stirred continuously with a Teflon-coated magnetic stir bar with a stirring speed around 1300 rpm. Upon completion of the reaction the reactor was cooled to room temperature and depressurized carefully with a back-pressure regulator. The liquid mixture was diluted with acetone. The products were analyzed by gas chromatography (GC-Shimadza-14C, FID, Capillary column, Rtx-Wax 30 m × 0.53 mm × 0.25 μm) and gas chromatography/mass spectrometry (GC-MS, Agilent 5890).

Results and discussion

It is clear that Pd nanoparticles could be dispersed onto the SiO_2 surface with an average particle size around 2 nm as characterized with TEM and HRTEM in Fig. 2.

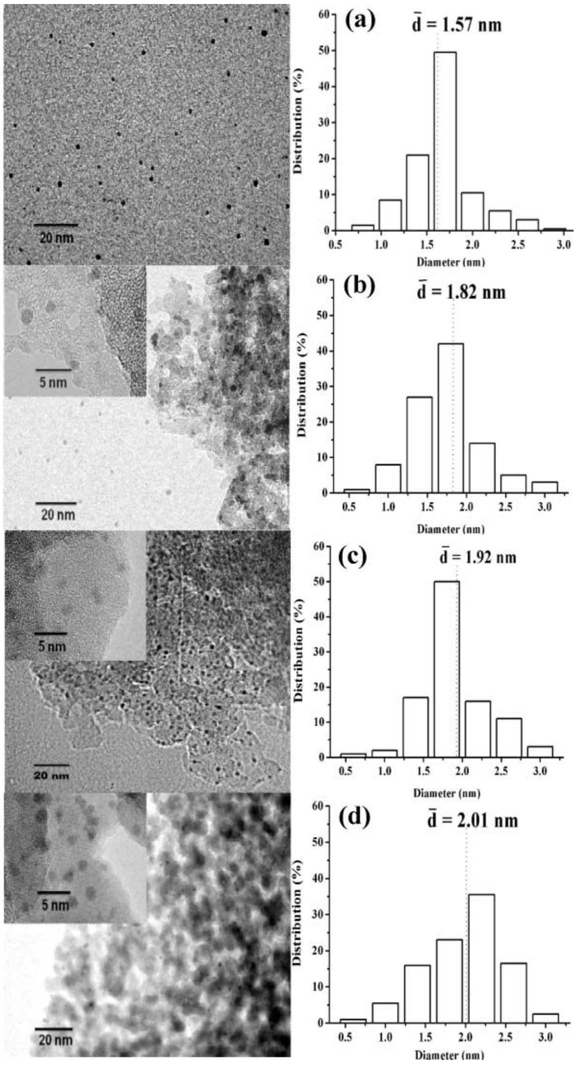


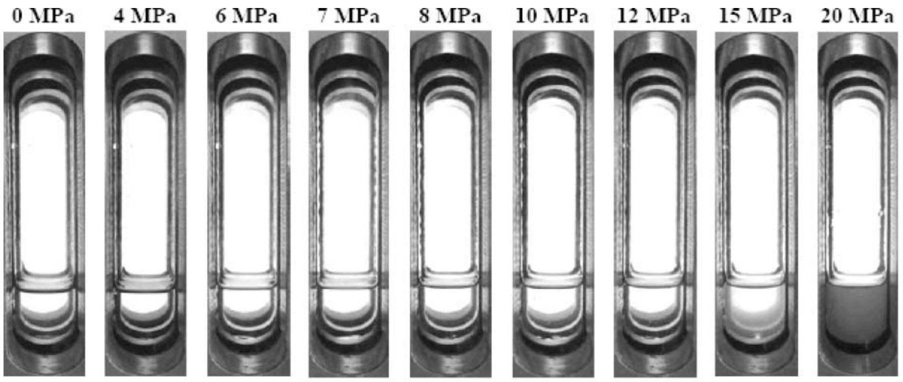
Fig. 2 TEM, HRTEM images and particle size distributions of (a) colloid of Pd-PVP, (b) Pd-PVP/SiO_2 prepared in EG system, (c) Pd/SiO_2 (8 MPa) prepared in $scCO_2$ at 8 MPa and (d) after used for the catalytic reaction.

The size of the free colloidal Pd particles protected with PVP (Pd-PVP) is about 1.57 nm (Fig. 2(a)), and the Pd particle on the surface of SiO_2 is about 1.87 nm (Fig. 2(b)) but there were some unsupported Pd nanoparticles. When the PVP was removed by the interference of CO_2, the particle size on the surface of Pd/SiO_2 (8 MPa) is about 1.92 nm, similar to these Pd particles with the protection of PVP. It indicates that the Pd nanoparticles could be dispersed uniformly onto the supports without any particle conglomeration even if the stabilizer of PVP was removed, and it is independent of the metal content at Pd loading. The advantage of the present method is that it resolved the problem of particle conglomeration in removing the stabilizer PVP by the thermal treating process,[7] which has been puzzling the researchers for many years.

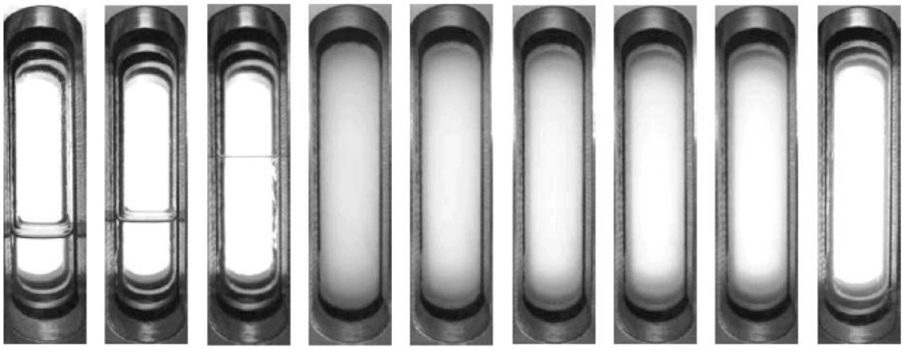
The forming process and a possible mechanism are given and discussed by using the phase behavior (Fig. 3 and Fig. 4) and TGA analysis (Fig. 5). The solution of EG with dissolved PVP (3 g l^{-1}) did not show any change in the presence of dense CO_2 at pressures lower than 15 MPa, while the solution became cloudy at the elevated CO_2 pressures of 15 and 20 MPa as shown in Fig. 3 (a), indicating that the solubility of PVP in EG decreased and it precipitated out at CO_2 pressures above 15 MPa. Compared with EG, the solution of ethanol with dissolved PVP (1.5 g l^{-1}) was expanded in the presence of dense CO_2, and the solution volume increased about two times at a CO_2 pressure of 6 MPa, then with increasing of CO_2 pressure to 7.0 MPa around critical point the solution filled up all the volume of vessel and formed a dark cloudy phase because of the precipitation of PVP as shown in Fig. 3 (b), similar to the literature,[10] (d) which suggested that the solubility of PVP in EG is larger than in ethanol in the presence of dense CO_2. With further increase in CO_2 pressure to above 8 MPa, the expanded ethanol solution changed from dark cloudy to bright because the precipitated PVP could gradually dissolve again at high pressures of 8–20 MPa. Based on the above results, the dense phase CO_2 could act as a phase-switch to distribute the stabilizer PVP between EG and ethanol by adjusting CO_2 pressure simply. As can be seen in Fig. 3 (c), the liquid solution of EG and ethanol was expanded and split into two phases and then filled the vessel fully as increasing CO_2 pressures up to 8 MPa. The up phase of EG-PVP was gradually cloudy and the bottom phase of CO_2 expended ethanol was transparent at CO_2 pressures of 8–20 MPa. So that the PVP was extracted into EG phase from ethanol at CO_2 pressure above 8 MPa. But, it was noted that the PVP could dissolve again into the expended ethanol phase as increasing the pressure further.

Based on the above phase transfer at the different CO_2 pressures, SiO_2-supported Pd colloidal nanoparticles were prepared. The Pd colloidal nanoparticles and SiO_2 supports as well as the Pd/SiO_2 formed finally were dispersed in the bottom expended ethanol phase (Fig. 4 (a)), and PVP precipitated in the up EG phase at 8 MPa (Fig. 4 (b)). After the mixture was cooled to room temperature and decompressed, the phase layer disappeared forming a single transparent solution again (Fig. 4 (c) and (d)), in which PVP was dissolved into the solution of EG/ethanol and could be separated from Pd/SiO_2 samples easily by filtration. The solution of PVP-EG-ethanol was collected and reused for the next preparation. It is confirmed that the PVP was removed mostly in the presence of dense CO_2, and it depends on the CO_2 pressure and treating time. From the results of TGA (Fig. 5), a little amount of PVP was still left on the surface of catalyst for the Pd/SiO_2 catalyst prepared in dense CO_2 at 8 and 15 MPa, but more than 80% PVP was removed compared with Pd-PVP/SiO_2 prepared in EG, while, when Pd-PVP/SiO_2 was treated with 8 MPa for 12 h (Pd-PVP/SiO_2 (8 MPa)-12h) in $scCO_2$, about 40% PVP was removed. Therefore, the PVP was effectively transferred from ethanol to EG and it could be removed mostly from the surface of the Pd nanoparticles in the presence of CO_2.

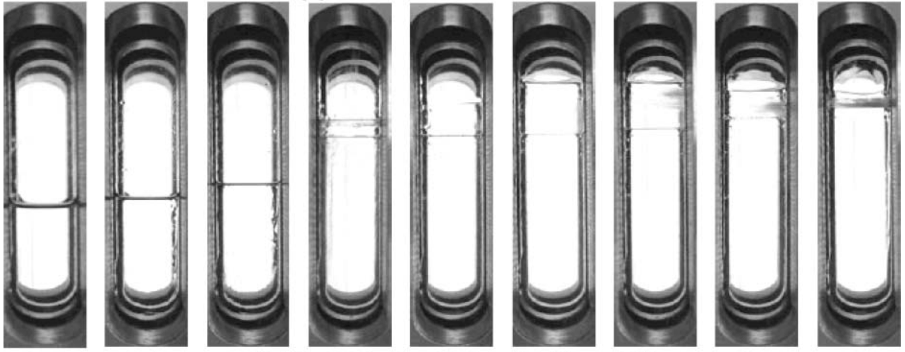
The probable forming process of Pd nanoparticles adsorbed the supports (Fig. 1) showed that the phase behavior could be varied by adjusting the CO_2 pressure, and thus the substrate distribution in different phases was changed. First of all, when CO_2 was introduced into the reactor, the ethanol was expanded and separated from EG, leading to large amount of PVP moved



(a) 10 ml EG + 30 mg PVP



(b) 20 ml Ethanol + 30 mg PVP



(c) 10 ml EG +20 ml Ethanol + 30 mg PVP

Fig. 3 The phase behavior of the mixtures of EG, ethanol and PVP upon pressurization with CO_2 at 35 °C.

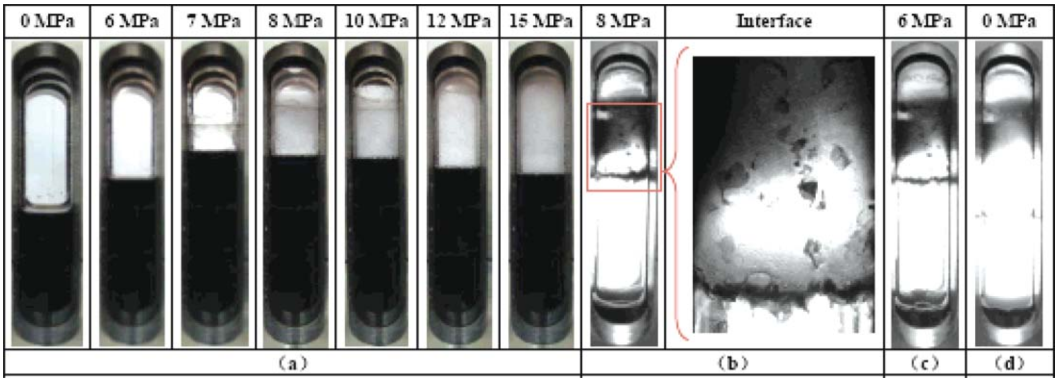


Fig. 4 The phase behaviors of Pd colloid depositing on SiO_2 upon pressurization with CO_2. (a) Deposition at a range of CO_2 pressures of 0–15 MPa at 35 °C. (b) After deposition for 24 h at 8 MPa, 35 °C, (c) the vessel was cooled to room temperature and (d) released of CO_2.

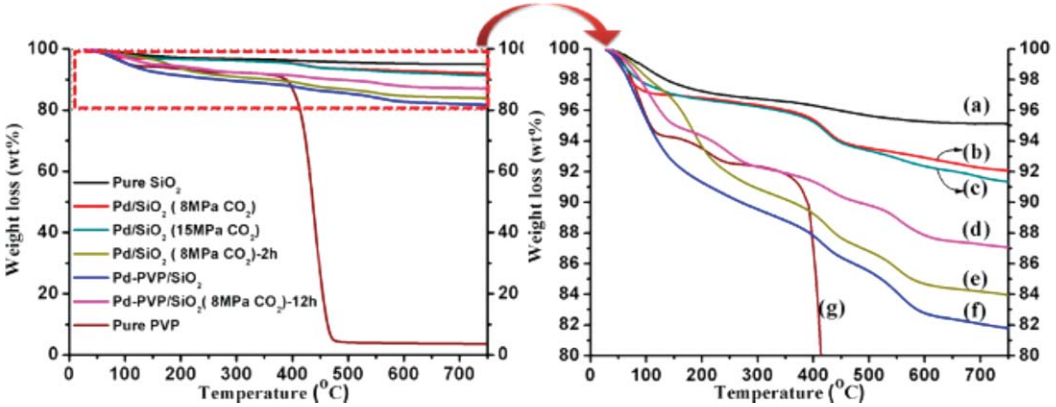


Fig. 5 TGA curves for the samples: (a) pure SiO_2, (b) Pd/SiO_2 (8MPa CO_2), (c) Pd/SiO_2 (15MPa CO_2), (d) Pd-PVP/SiO_2 (8MPa CO_2)-12h, Pd-PVP/SiO_2 samples were treated by a mixture of EG, ethanol and 8 MPa for 12 h at 35 °C, (e) Pd/SiO_2 (8MPa CO_2)-2h, the preparation time was shortened to 2 h, others are the same to the procedure described in the part of experimental, (f) Pd-PVP/SiO_2, (g) pure PVP.

Table 1 Physical properties of SiO_2, Pd-PVP/SiO_2, Pd/SiO_2 (15 MPa), Pd/SiO_2 (8 MPa)

Samples	Surface area/ m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Pore size/ nm
SiO_2	477.23	0.81	6.82
Pd-PVP/SiO_2	413.42	0.70	6.84
Pd/SiO_2 (15 MPa)	339.69	0.61	7.26
Pd/SiO_2 (8 MPa)	328.24	0.60	7.29

Table 2 Comparison the activity of the supported Pd catalysts in the hydrogenation of maleic anhydride (MAH) to succinic anhydride (SAH)

Entry	Catalyst	Conv. (%)	TON
1[a]	Pd/C (8 MPa)	78.8	1003
2[a]	Pd-PVP/C	61.5	847
3[a]	Pd/C (Wako)	59.5	506
4[b]	Pd/C (8 MPa)	93.3	1187
5[b]	Pd-PVP/C	77.5	1067
6[b]	Pd/C (Wako)	79.0	672
7[c]	Pd/SiO_2 (8 MPa)	86.0	9410
8[c]	Pd-PVP/SiO_2	71.8	7509
10[d]	Pd/SiO_2 (8 MPa)	87.2	14313
11[d]	Pd-PVP/SiO_2	67.3	10558

Reaction conditions: H_2 2 MPa, time 1 h, catalyst 5 mg, Pd/SiO_2 (8 MPa) and Pd/C (8 MPa) prepared at 8 MPa CO_2, Pd/C (Wako, 5 wt%) was purchased from Wako. TON (turnover number) was calculated as moles conversion of MAH/moles of Pd used. During the reaction SAH was produced as the sole product. Pd-PVP/SiO_2 and Pd/SiO_2 (8 MPa): Pd-loading is 0.814% and 0.778%. Pd-PVP/C and Pd/C (8 MPa): Pd-loading is 3.089% and 3.345%. [a] MAH 2 mmol, CO_2 8 MPa, temperature 35 °C. [b] MAH 2 mmol, CO_2 12 MPa, temperature 60 °C. [c] MAH 4 mmol, CO_2 8 MPa, temperature 35 °C. [d] MAH 6 mmol, CO_2 12 MPa, Temperature 60 °C.

into EG phase at CO_2 pressure of 8 MPa. Meanwhile, the colloidal Pd-PVP nanoparticles were adsorbed onto the surface of supports. Some particles adhered to the inner surface from the BET results in Table 1, Fig. S1 and Fig. S2 (ESI†), both the surface area and pore volume decreased largely after Pd particles adsorbed on to the supports at 8 and 15 MPa CO_2. This should ascribe to the unique properties like low viscosity, high diffusivity, near zero surface tension of CO_2-expanded liquid.[10,12] Furthermore, excess CO_2 could weaken the interactions between PVP and Pd particles,[14] remaining a single layer of PVP to coordinate with Pd particles. This is in agreement to the results of TGA (Pd/SiO_2 (8 MPa)-2h and Pd/SiO_2 (8 MPa) in Fig. 5). Pd/SiO_2 (8MPa CO_2)-2h (Fig. 5 (e)), the preparation time was shortened to 2 h, others are the same to the procedure of Pd/SiO_2 (8 MPa) described in the part of experimental. It was found more PVP was left on the surface of Pd/SiO_2 (8MPa CO_2)-2h compared to Pd/SiO_2 (8 MPa) prepared in 8 MPa CO_2 for 24 h. Therefore, the duration of preparation or treatment in dense CO_2 is most important for releasing PVP from the surface of catalyst.

Moreover, carbon-supported Pd colloidal nano-catalyst, Pd/C (8 MPa), was also prepared by the method described above. It was produced with a quantitative yield successfully, indicating that the present method could utilize extensively in the preparation of supported transition metal nanoparticles. In addition, the hydrogenation of MAH was selected as a target reaction to compare the activities of several catalysts. As shown in Table 2, the activity of Pd/C (8.0 MPa) prepared in the presence of CO_2 was much higher than the Pd-PVP/C and the commercial Pd/C catalysts. It is because the Pd particles were highly dispersed on the surface of Pd/C (8.0 MPa) compared with the commercial 5% Pd/C catalyst, and only a thin monolayer PVP contacted the Pd particles compared to Pd-PVP/C in which large amount of PVP around Pd particles preventing the adsorption of the substrate.[4] The same results were also obtained with the Pd/SiO_2 (8 MPa) and Pd-PVP/SiO_2 catalysts irrespective to the reaction conditions. Furthermore, the Pd/SiO_2 (8 MPa) catalyst still presented high dispersion without aggregation after reaction, indicating the present process is an effective and facile method for preparing the supported Pd catalyst with high dispersion. To our best knowledge, this is the first time to disperse colloidal Pd particles on the supports with such a small particle size around 1–2 nm.

Conclusions

The advantages of using CO_2 in this work was (1) CO_2 acted as a phase-switch: the EG was separated from expanded ethanol with increasing of CO_2 pressure and PVP was extracted and precipitated in EG phase. This is a very important step for removing PVP from the colloidal Pd nanoparticles. (2) The use of CO_2 benefits the Pd colloidal particles to infuse into the pores and adsorb onto the inner surface due to the low viscosity, high diffusivity and near zero surface tension of CO_2-expanded ethanol. (3) The use of CO_2 could weaken the complexation interactions to break the colloids and remove PVP partially by controlling CO_2 pressure. In summary, a novel method for dispersing active Pd colloidal nanoparticles onto supports uniformly was developed in the present work, in which CO_2 was used as phase-switch to remove PVP successfully from metal nanoparticles by adjusting pressure. The present method overcomes the difficulties associated with the conventional methods and offers both process and environmental advantages. It is expected to extend it to the preparation of various metal colloidal nanoparticles materials.

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