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Hydrodeoxygenation of vanillin as a bio-oil model over carbonaceous microspheres-supported Pd catalysts in the aqueous phase and Pickering emulsions†

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A series of amphiphilic carbonaceous microspheres-supported Pd catalysts have been prepared and their performances for the hydrodeoxygenation of vanillin have been investigated in both a pure aqueous phase and in water−oil biphasic systems. The wettability of the catalyst could be facilely tuned by adjusting the hydrothermal treatment temperature during the synthesis of the carbonaceous microspheres or by a post-treatment process in alkaline solution. In the aqueous phase reactions, the more hydrophilic the catalyst, the more active it was for the hydrodeoxygenation of vanillin. And the wettability of the support affects the activity through the interaction between the catalysts and substrates/products. In the case of a water−oil biphase, the wettability of the support played a key role in forming Pickering emulsions. It was found that the selectivity of the hydrodeoxygenation reactions was determined by the type of Pickering emulsion and high selectivity of *p*-creosol could be achieved in the water-in-oil emulsion systems.

Introduction

Lignocellulosic biomass-related bio-oil has attracted significant attention in the last decade due to the increasing energy demand and environmental concerns.[1–4] Derived from pyrolysis of renewable biomass, bio-oil usually contains up to 60 wt% oxygen and an upgrading process is necessary to reduce the oxygen content, and improve the heating value and the stability.[5–7] Among several strategies, catalytic hydrodeoxygenation (HDO) has been considered as a very promising route.[8,9] Recently, special efforts have been focused on water phase-involved HDO reactions because bio-oil contains a large amount of water (15–30 wt%) and water soluble components.[10,11] It has been reported that a wide range of biomass compounds such as phenol, sorbitol and anisole can be hydrodeoxygenated selectively in water over supported noble metal (like Ru, Pt and Pd) catalysts and the features of both the metals and the supports are believed to be responsible to the catalytic performance.[12–14]

One challenge with water phase-involved HDO reactions is that the dispersion of the supported catalysts in the medium needs to be enhanced to ensure good contact between the

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substrates and the active metal sites.[15–17] For example, a series of support materials for Pd nanoparticles, including traditional TiO$_2$, MgO, CeO$_2$, γ-Al$_2$O$_3$ and a novel N-doped carbon have been investigated in Wang's group for aqueous phase HDO of vanillin (4-hydroxy-3-methoxy-benzaldehyde, a typical model compound of lignin).[18] They found that the traditional solid catalysts tended to be highly aggregated in water, while the N-doped carbon-supported Pd catalyst could be well-dispersed and resulting in excellent activity and selectivity due to the hydrophilic property of the support. In order to obtain good wettability of the substrate on the support, Xiao and co-workers designed and synthesized superhydrophilic mesoporous sulfonated melamine–formaldehyde resin (MSMF).[19] It was found that the MSMF-supported Pd catalyst was highly active for the HDO of vanillin in water.

Besides aqueous phase reactions, water–oil biphasic systems have also gained special attention because there are many hydrocarbon solvent-soluble components in the real bio-oils. Recently, Resasco and co-workers deposited Pd nanoparticles onto hydrophobic carbon nanotube–hydrophilic inorganic oxide hybrid composites for water–oil biphasic HDO of vanillin.[20,21] They found that Pickering emulsions could be formed when the hybrid nanoparticles were dispersed in water–organic biphasic systems, and the emulsions could catalyze the HDO of vanillin efficiently. Moreover, the water–oil biphasic system could facilitate the separation of water-insoluble organic products. All the above studies indicate that the wettability of the catalyst plays an important role in the HDO of

bio-oil and it should be carefully designed to obtain desirable catalytic performances.

In our previous works,[22–24] we reported the synthesis of carbonaceous microspheres (CM) by facile hydrothermal treatment of yeast cells. Interestingly, there were both hydrophobic and hydrophilic functional groups on the surface of the CM, which enabled them to be well-dispersed in either water or organic solvents[22] and Pickering emulsions could be assembled when they dispersed in water–oil-biphasic systems.[24] Herein, a series of Pd nanoparticles supported on the amphiphilic carbonaceous microspheres were prepared and their application in the HDO of vanillin as a model bio-oil upgrading reaction were investigated. It was found that the novel Pd/CM catalysts could catalyze the HDO reaction efficiently in both the aqueous phase and water–oil-biphasic conditions. The role of the wettability of the Pd/CM catalysts in their catalytic performances has been revealed.

Results and discussion

Catalyst characterization

Four groups of carbonaceous microspheres (CM) were synthesized *via* mild hydrothermal treatment of yeast cells at 170, 180, 210 and 230 °C, and denoted as CM170, CM180, CM210 and CM230, respectively. Typical scanning electron microscopy (SEM) images of the as-prepared carbonaceous microspheres are shown in Fig. 1 (a1–d1). It can be seen that all the carbonaceous microspheres are uniform oval microspheres in the size range of 1.5–2.5 μm. Some cracked microspheres reveal that they are hollow, which is consistent with our previous results.[22] The carbonaceous microspheres were then used as supports to synthesize Pd/CM catalysts, which were realized by

reduction of $PdCl_2$ with $NaBH_4$ as the reducing agent. The loading amounts of Pd for all the Pd/CM catalysts were measured by ICP-OES. The results were 5.1, 5.3, 4.5 and 4.9 wt% for Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230, respectively. Fig. 1 (a2–d2) show that the Pd nanoparticles are uniformly dispersed on the surfaces of the carbonaceous microspheres (the size of the Pd nanoparticles is about 4–9 nm) and there is no obvious difference in Pd particle morphology (both size and shape) for all of the Pd/CM catalysts. The morphology of the Pd/CM catalysts and the uniform size distributions of the Pd nanoparticles were also verified by transmission electron microscopy (TEM), as shown in Fig. S1.†

Fig. 2 shows the X-ray diffraction (XRD) patterns of the Pd/CM catalysts. The broad diffraction peaks with 2θ from 10 to 35° are attributed to the carbonaceous microspheres support.[24] The additional four diffraction peaks at 39.7, 46.1, 67.6 and 81.1° can be assigned to diffraction from the (111), (200), (220) and (311) planes of the Pd nanoparticles. The size of the Pd nanoparticles was estimated to be about 6 nm from the diffraction peak of the (111) lattice plane according to the Scherrer equation, which is in line with the results of SEM and TEM analysis.

X-ray photoelectron spectroscopy (XPS) analysis (Fig. 3) was performed in order to test the valence state of palladium. According to Putta *et al.*,[25] a peak-fitting procedure was employed to analyze the XPS data. The XPS spectra show Pd $3d_{3/2}$ and $3d_{5/2}$ binding energies at 340.94 and 335.67 eV, respectively, with $\Delta = 5.27$ eV, indicating the presence of metallic Pd(0) species. And the shoulders at 342.49 and 336.99 eV ($\Delta = 5.5$ eV) can be assigned to the $3d_{3/2}$ and $3d_{5/2}$ levels of Pd(ɪɪ), respectively. All the XPS spectra show that the peaks of Pd(ɪɪ) are much weaker than those of Pd(0), indicating metallic
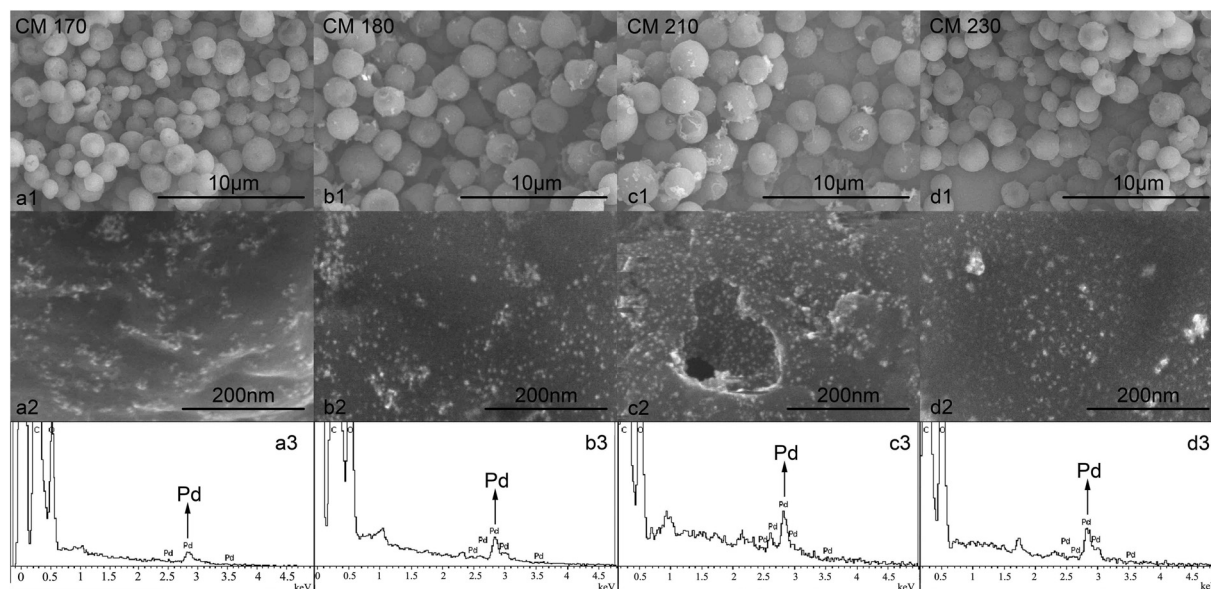

Fig. 1 (a1–d1) SEM images of CM170, CM180, CM210 and CM230; (a2–d2) SEM images of Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230, and (a3–d3) the corresponding EDX spectra.
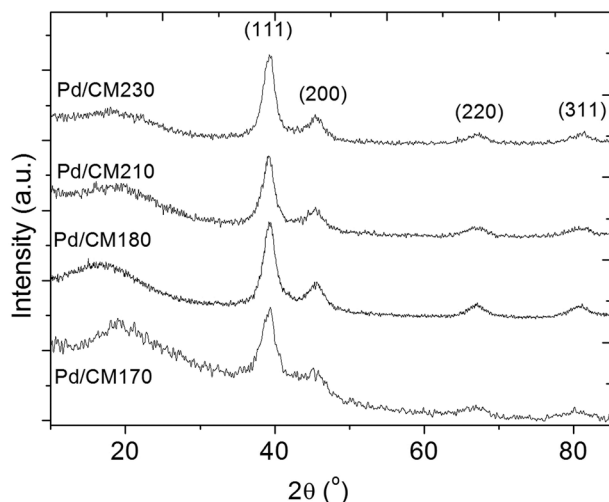
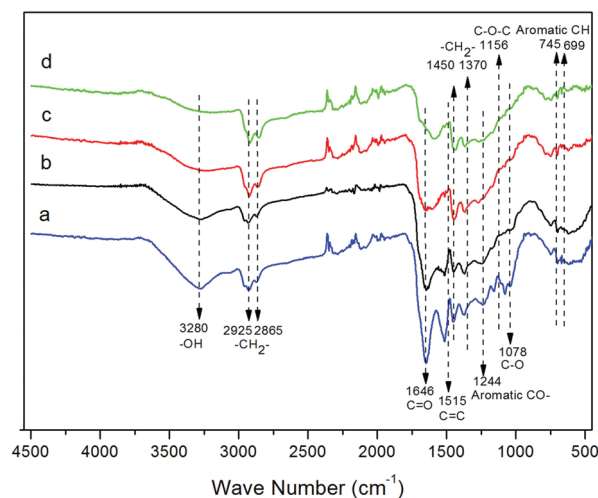**Fig. 2** XRD patterns of Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230 catalysts.

Fig. 4 FTIR spectra for (a) Pd/CM170, (b) Pd/CM180, (c) Pd/CM210 and (d) Pd/CM230 catalysts.
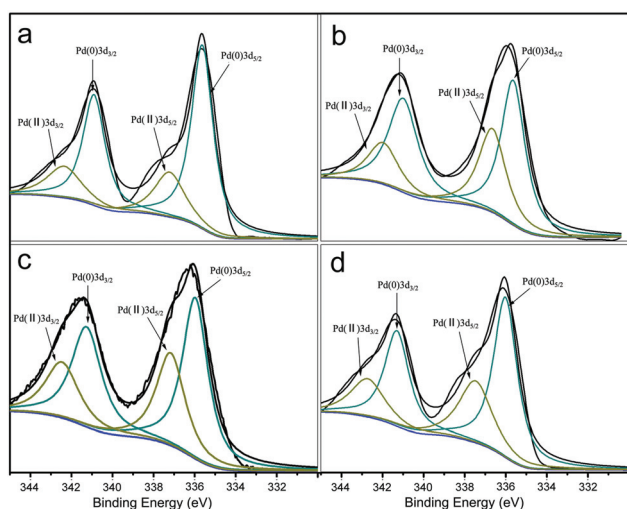

Fig. 3 Pd 3d XPS spectra for (a) Pd/CM170, (b) Pd/CM180, (c) Pd/CM210 and (d) Pd/CM230 catalysts.

Pd is the dominant state in all of the Pd/CM catalysts (Table S1†).

Fourier transform infrared (FTIR) spectra were used to characterize the Pd/CM catalysts and the results are shown in Fig. 4. For all the samples, broad absorption bands at 3280 cm^{-1} are observed which can be assigned to O–H stretching vibrations. The absorption bands at 745 and 699 cm^{-1} are ascribed to the aromatic CH out-of-plane deformation and those at 2925, 2865, 1450, 1370 cm^{-1} to –CH$_2$– units. The bands at 1646 and 1156 cm^{-1} can be assigned to C=O and C–O stretching vibrations, respectively.[26] The FTIR spectra reveal that both hydrophilic (such as O–H stretching vibrations) and hydrophobic (such as aromatic and aliphatic ones) groups are present on the surface of the carbonaceous microspheres.[22] Moreover, the band intensities of the hydrophilic groups decrease and those of the hydrophobic groups

increase remarkably in the order of Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230, indicating that the hydrophilic–hydrophobic balance of the Pd/CM catalysts can be tuned by adjusting the synthesis temperature of the carbonaceous microspheres.

The data obtained from C 1s XPS spectra (Fig. S2†) further demonstrated the effects of the hydrothermal synthesis temperature on the surface chemistry of the catalysts. There were four kinds of carbon components with binding energies of 284.5, 285.6, 286.6 and 287.8 eV. According to our previous study,[22] the component at 284.5 eV could be attributed to C=C, CH$_x$ and C–C species. And those at 285.6, 286.6 and 287.8 eV could be assigned to –C–O, >C=O and –COOR, respectively. As the hydrothermal synthesis temperature increased, the intensity of the components due to hydrophilic groups (such as >C=O and –COOR) gradually decreased or disappeared, indicating that the surface of the carbonaceous microspheres became more and more hydrophobic.

To investigate the wettability of Pd/CM catalysts, the contact angles of water on the surface of the catalysts were measured and the results are shown in Fig. 5. The Pd/CM170 presents a minimum contact angle of 50°, indicating a very hydrophilic character. And the contact angles are 63, 79 and 86° for Pd/CM180, Pd/CM210 and Pd/CM230, respectively. Combined with the FTIR and XPS analysis, it can be concluded that the transformation of surface functional groups of carbonaceous microspheres leads to the decrease of hydrophilicity as the synthesis temperature of the carbonaceous microspheres increased.

In fact, there are many carboxyl groups on the surface of the carbonaceous microspheres, which can be ionized under alkaline conditions.[27,28] Once the ionized species were formed, the hydrophilicity of the catalysts could also be enhanced.[24] Therefore, the Pd/CM180 catalyst was further treated with 0.05 mol L^{-1} NaOH aqueous solution under ultrasound for 15 min, washed with distilled water, dried and the
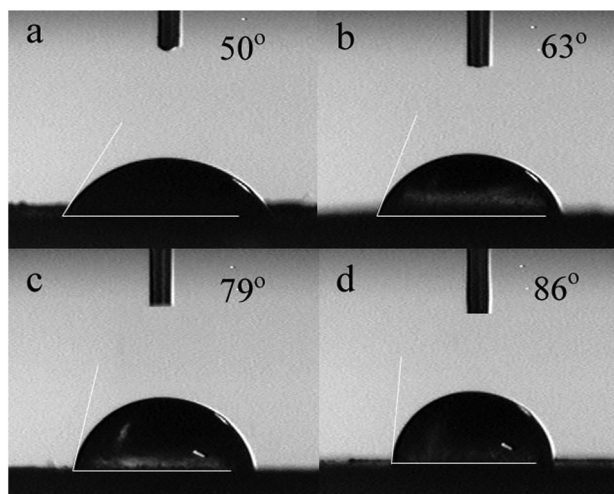
Fig. 5 Air–water contact angles for (a) Pd/CM170, (b) Pd/CM180, (c) Pd/CM210 and (d) Pd/CM230 catalysts. The photos were immediately captured after a drop of water was deposited on the surface of the self-supporting pressed sample disc.
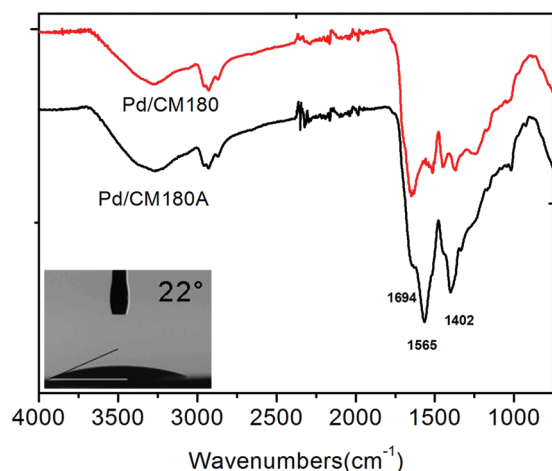

Fig. 6 FTIR spectra for Pd/CM180 and Pd/CM180A catalysts. Inset shows the water contact angle for Pd/CM180A.

obtained sample was denoted as Pd/CM180A. FTIR analysis (Fig. 6) revealed that two absorption bands for carboxylate at 1565 and 1402 cm^{-1} appeared in the spectrum of the Pd/CM180A catalyst, confirming ionization of the carboxyl species.[29] The contact angle of water on the surface of the Pd/CM180A catalysts was 22°, which was smaller than that (63°) of the counterpart Pd/CM180, suggesting an enhancement of hydrophilicity after alkaline-treatment. Other characterizations such as XRD, SEM and XPS revealed that the alkaline-treatment mainly led to the change of wettability of the support with negligible modification of the nature of the active Pd species.

These results show that the wettability of the Pd/CM catalyst could be facilely tuned by adjusting the hydrothermal treatment temperature during synthesis of the carbonaceous microspheres or by a post-treatment process in alkaline solution. As

expected, the difference in the wettability causes different dispersibility of the Pd/CM catalysts. It was found that the more hydrophilic Pd/CM catalysts could be well-dispersed in water, while the more hydrophobic ones tended to be aggregated.

Catalytic performance of aqueous phase HDO of vanillin

It is well known that two products, *i.e.* vanillin alcohol and 2-methoxy-4-methylphenol can be formed during the hydro-deoxygenation of vanillin under mild conditions, and the transformation of vanillin into 2-methoxy-4-methylphenol (*p*-creosol) can proceed through (i) intermediate hydrogenation to vanillin alcohol and further hydrogenolysis and/or (ii) direct hydrogenolysis of the C═O bond.[18,21] To check the ability of the Pd/CM catalysts for the aqueous phase HDO of vanillin, Pd/CM180 with the moderate wettability was tested firstly. The experiments were carried out under the following conditions: 90 °C, H$_2$ pressure of 50 psi and vanillin/Pd molar ratio (S/C) of 200. Two control experiments, with the presence of the support only and without any catalyst, were carried out for comparison. And no conversion of vanillin could be observed after 3 hours reaction at 150 °C in both cases. Fig. 7a shows the trend of substrate and product proportion with reaction time in the presence of Pd/CM180. Within the first hour, vanillin alcohol is the main product and *p*-creosol is also formed. As the reaction proceeds, the content of vanillin alcohol begins to decrease with a corresponding increase in *p*-creosol. After 3 hours, vanillin was consumed completely and a *p*-creosol selectivity of 49% was achieved. Compared with vanillin alcohol, *p*-creosol is more valuable as a biofuel. In order to improve the yield of *p*-creosol, the reaction conditions were optimized and the results are shown in Fig. 7b. It was found that under higher H$_2$ pressure (200 psi), 100% vanillin conversion could be achieved with *p*-creosol selectivity of 54% after 1 h reaction at 100 °C, which can be further enhanced to 100% at 150 °C. The turnover frequency measured at 100 °C was about 0.26 s^{-1}, which is of similar magnitude to that observed by others.[21] These results demonstrate that Pd/CM may be effective catalysts for the hydrodeoxygenation of vanillin in water under mild conditions.

The role of the wettability in the activity for aqueous phase HDO of vanillin was then investigated and the results are summarized in Table 1. At 100 °C with H$_2$ pressure of 145 psi, complete conversion of vanillin can be achieved over Pd supported on CM170, CM180 and CM210 after 1 h reaction, while a conversion of 95% is obtained on the most hydrophobic catalyst, Pd/CM230. The wettability of the catalysts also has a profound effect on the product selectivity. The selectivities of *p*-creosol are 52%, 36%, 31% and 20% for Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230, respectively, which is in line with the decreasing hydrophilicity trend of these catalysts (Fig. 8). Clearly, among the four Pd/CM catalysts, the most hydrophilic Pd/CM170 performs best, while the most hydrophobic Pd/CM230 exhibits poor activity and selectivity.
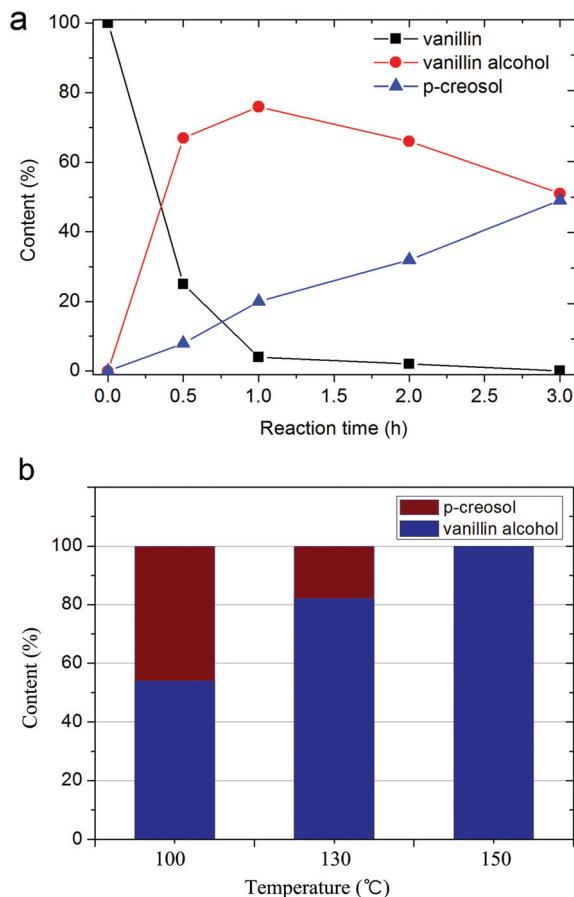
Fig. 7 (a) Trend of reactant and product proportion with reaction time during aqueous phase hydrodeoxygenation of vanillin by Pd/CM180. Reaction conditions: vanillin/Pd molar ratio (S/C) = 200, H_2 pressure of 50 psi, temperature of 90 °C. (b) Product distribution at different temperatures during aqueous phase hydrodeoxygenation of vanillin by Pd/CM180. Reaction conditions: S/C = 100, H_2 pressure of 200 psi; reaction time of 1 h.

Table 1 Catalytic results for aqueous phase HDO of vanillin over different catalysts

Entry	Catalyst	Conv. (%)	Sel. (%) of B[a]	Sel. (%) of C[a]
1	Pd/CM170	>99	48	52
2	Pd/CM180	>99	64	36
3	Pd/CM210	>99	69	31
4	Pd/CM230	95	80	20

[a] B is vanillin alcohol, and C is p-creosol. Conditions: vanillin/Pd molar ratio (S/C) = 100, H_2 pressure of 145 psi, temperature of 100 °C and time of 1 h.

To further prove the role of the wettability, a comparative study of the aqueous phase HDO of vanillin over Pd/CM180 and Pd/CM180A was carried out. The reaction was performed at three different temperatures (80, 100, and 130 °C) and the results are displayed in Fig. 9. In the case of the more hydrophilic Pd/CM180A catalyst, vanillin conversion of 100% and p-creosol selectivity of 23% is achieved at 80 °C, which can be
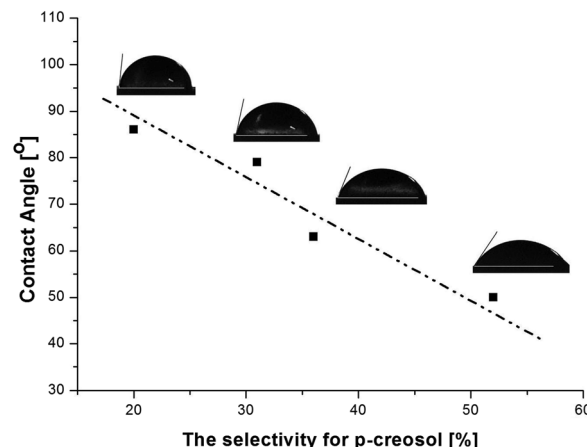

Fig. 8 Effect of the catalyst wettability on the selectivity for p-creosol.
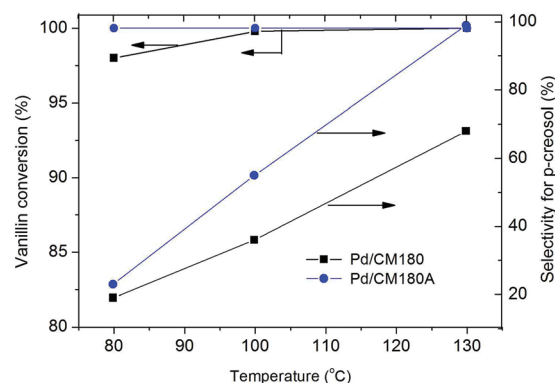

Fig. 9 Comparison of catalytic performances for aqueous phase HDO of vanillin between Pd/CM180 and Pd/CM180A at different temperatures. Reaction conditions: vanillin/Pd molar ratio (S/C) = 100, H_2 pressure of 145 psi and time of 1 h.

further enhanced to 55% and 100% at 100 and 130 °C, respectively. However, the counterpart Pd/CM180 catalyst only obtained a 98% conversion of vanillin at 80 °C, and lower p-creosol selectivities at all three temperatures under the same conditions. These results indicated that compared with Pd/CM180, the activity of Pd/CM180A is improved remarkably with the enhancement of hydrophilicity of the catalyst.

All the above results show that the wettability of the support plays a key role in aqueous phase HDO of vanillin, and the more hydrophilic catalysts exhibit better activity for hydrodeoxygenation. One reason for this wettability-dependent behaviour should be the different dispersibility of the Pd/CM catalysts in water. As mentioned above, the more hydrophilic Pd/CM catalysts can be well-dispersed in water, while the more hydrophobic ones tend to be aggregated. Therefore, the more hydrophilic Pd/CM catalysts have more opportunities to have intimate contact with both the substrate (vanillin) and the intermediate (vanillin alcohol) during the reactions. Another reason may be related to the accumulation of the final

product, *p*-creosol, on the surface of the Pd/CM catalysts. It is known that although vanillin and vanillin alcohol can be dissolved in water, *p*-creosol is hydrocarbon-solvent soluble. Once *p*-creosol is formed during the reaction, some of the hydrophobic surface area of the Pd/CM catalysts would tend to be covered by the products *via* the well-known hydrophobic effect,[30,31] resulting in poor contact with the substrates and suppression of the catalytic activity. Combined with the above analysis, it is reasonable that the wettability of the support affects the activity through the interaction between the catalysts and substrates/products.

The HDO activity in a pure oil was also tested by employing the Pd/CM180A catalyst. It was found that only 31% conversion of vanillin could be achieved after 1 hour reaction at 80 °C when water was replaced by decalin. Compared with the reaction in water, the poor activity in decalin may be mainly due to the lower solubility of vanillin in the solvent.

The reusability of catalysts in the aqueous phase HDO of vanillin has been tested over the Pd/CM180A catalyst. After the completion of the first cycle, it afforded a vanillin conversion of 97% and *p*-creosol selectivity of 32% at 100 °C under 50 psi H$_2$ in water. And no obvious decrease in the catalytic activity was observed during the next four cycles. The loading amounts of Pd for Pd/CM180A were measured after the catalytic tests and no obvious loss of Pd could be found. The Pd 3d XPS spectra (Fig. S4†) of the used catalysts showed that both Pd(0) and Pd(II) were present and metallic Pd was the dominate state, which was similar to the results for the fresh catalysts. TEM images (Fig. S5†) of the used Pd/CM180A catalyst showed that no aggregation of Pd nanoparticles could be observed. These results showed that the Pd/CM catalysts are stable in successive runs.

Catalytic performance of HDO of vanillin in Pickering emulsions

Since the biomass-derived bio-oil is a complex that is partially soluble either in water or hydrocarbon solvents, the HDO reaction in water–oil biphasic systems is more desirable from a practical view.[21] Therefore, HDO of vanillin in Pd/CM–water–decalin Pickering emulsions was carried out. To check the ability of the Pd/CM catalysts in the formation of Pickering emulsions, the oil–water contact angles were measured (Fig. S6†). The contact angles were 76, 93, 127 and 151° for Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230, respectively. Once the Pd/CM catalysts were added into the water–decalin biphasic system, it was found that the more hydrophilic Pd/CM170 was mainly present in the water, while the more hydrophobic Pd/CM230 tended to be dispersed in the oil phase. However, the Pd/CM180 with the moderate wettability was found to be located at the water–decalin interface. After ultrasonic stirring of the mixture of water, decalin and Pd/CM180, an emulsion layer was immediately formed, resulting in a water–emulsion–decalin three-layer system. Since it is not favourable for the formation of Pickering emulsions if the
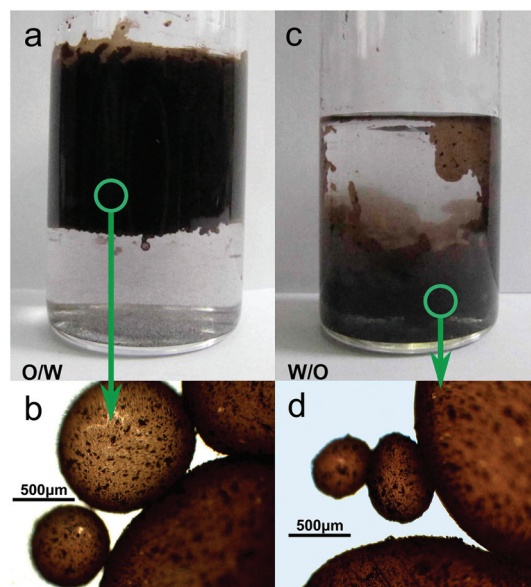

Fig. 10 Photos of Pd/CM180 stabilized (a) O/W and (c) W/O Pickering emulsions. Optical microscopy images of the (b) O/W and (d) W/O emulsions.

Pd/CM is too hydrophilic or hydrophobic, Pd/CM180 with the moderate wettability was employed in the following studies.

It was found that the type of emulsion (water-in-oil or oil-in-water emulsions) and the size of the emulsion droplets were strongly dependent on both the amounts of the Pd/CM180 and the oil to water ratio. Oil-in-water (O/W) emulsions could be assembled by sonicating a 1 : 2 (10 mL : 20 mL) mixture of decalin and water in the presence of Pd/CM180 catalyst. The optical microscopy images (Fig. 10a and b) show that the size of the emulsion droplets is about 0.5–3 mm and the Pd/CM180 steadily straddled the water–decalin interface. When the oil to water ratio was 2 : 1, Pickering emulsions of water-in-oil (W/O) could be obtained (Fig. 10c and d).

Subsequently, the effectiveness of the Pickering emulsions for HDO of vanillin was tested and the results are shown in Table 2. The reactions proceeded well in both the W/O and the O/W Pickering emulsions. After 1 h reaction at 100 °C with H$_2$ pressure of 145 psi, about 96% conversion of vanillin was achieved in both emulsions. The activities in the emulsions were slightly lower than that in the aqueous phase reaction, where a full conversion was obtained under the same conditions. This may be caused by the different locations of the catalysts in the media.[30] In the pure aqueous phase, the Pd/CM catalyst dispersed freely in water, ensuring intimate contact of substrates and the active sites. On the other hand, the catalysts tended to stay at the interfaces of the water–oil in the emulsions, which would suppress the mass transport rate between the medium and the active sites.[20]

Although similar conversions of vanillin were achieved, the selectivities of *p*-creosol were quite different depending on the type of emulsion. In the case of O/W emulsions, the selectivity

Table 2 Catalytic performances for HDO of vanillin over Pd/CM180 in Pickering emulsions

Entry	Emulsion	Time (h)	Conv. (%)	Sel. (%) of B[a]	Sel. (%) of C[a]
1	O/W	1	96	62	38
2	O/W	2	>99	43	57
3	O/W	3	>99	21	79
4	W/O	1	96	40	60
5	W/O	2	>99	25	75
6	W/O	3	>99	6	94

[a] B is vanillin alcohol, and C is *p*-creosol. Conditions: vanillin/Pd molar ratio (S/C) = 100, H_2 pressure of 145 psi and temperature of 100 °C.

of *p*-creosol was 38% after 1 h reaction, which compares favourably with the results of the aqueous phase reaction under the same conditions. Interestingly, a remarkable enhancement of *p*-creosol selectivity was observed in the W/O emulsions. The selectivity of *p*-creosol amounted to 60% after 1 h reaction; and it further increased to 94% when the reaction was extended to 3 h, while it was only 79% in the case of the O/W one.

Since the conversion rates of vanillin were almost the same in the W/O and O/W emulsions, we speculated that the origin of the difference in the product selectivity should mainly have resulted from the *p*-creosol formation reactions *via* hydrogenolysis of vanillin alcohol. According to Jimaré *et al.*,[20] vanillin alcohol is more soluble in water than in decalin and the partition ratios of vanillin alcohol between the individual aqueous and organic phases is about 8:2. Thus the reaction taking place on the water–catalyst would contribute mainly to the whole catalytic performance although hydrogenolysis of vanillin alcohol could proceed on the interfaces of both water–catalyst and decalin–catalyst. Since there was a smaller amount of water in the W/O system (10 mL) than the O/W one (20 mL), vanillin alcohol (once formed) was more concentrated in the former than the latter. Accordingly, the hydrogenolysis would be accelerated in the W/O emulsions.

Conclusions

In conclusion, the effects of the wettability of the carbonaceous microspheres-supported Pd catalysts on the performances of water phase-involved HDO of vanillin have been investigated. It was found that in aqueous phase reactions, the more hydrophilic catalysts were more active for the hydrodeoxygenation of vanillin. In the case of a water–oil biphase, the wettability of the supports played key roles in forming Pickering emulsions and desirable catalytic efficiency could be achieved by the water-in-oil system. All these results indicate that the Pd/CM catalysts with tunable wettability may find feasible applications in HDO of bio-oil as well as other water phase-involved organic reactions.

Experimental

Materials

All the chemical substrates were obtained from commercial sources (Sinopharm, Alfa or Beijing Chemical Company). Yeast cells were purchased from Angel Yeast Co., Ltd.

Preparation of carbonaceous microspheres (CM) and CM-supported Pd catalysts

CM was synthesized *via* the hydrothermal treatment of yeast cells using the methods described in our previous study.[22] In order to tuning the wettability, hydrothermal treatments were carried out at 170, 180, 210 and 230 °C, obtaining CM170, CM180, CM210 and CM230, respectively. CM-supported Pd catalysts were synthesized as follows: CM (100 mg) and $PdCl_2$ (20 mg) were added to H_2O (30 mL) and stirred at room temperature for 1 h, then 4 mL of $NaBH_4$ (2.5 g L^{-1}) aqueous solution was added into the above slurry. After stirring for 1 h, the mixture was centrifuged, washed with distilled water, and dried at 45 °C for 12 h. The Pd loadings were about 5.0 wt% for all the catalysts according to the ICP-OES analysis (Varian Vista MPX). In the case of Pd/CM180, a 1.0 wt% Pd loading sample was also prepared for comparison and for biphasic HDO reactions.

Characterization

Scanning electron microscopy (SEM) analysis was carried out by Tescan XM 5136. Transmission electron microscopy (TEM) images of the catalysts were obtained by using a Philips EM 400. Histograms of Pd particle size were calculated from the TEM images. 40 particles were counted in each case. The power X-ray diffraction (XRD) patterns were collected on MSAL-XD2 using Cu K_α radiation. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCALAB 250Xi using Al K_α radiation. The loading amount of the Pd nanoparticles was measured by using a Varian Vista MPX Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Fourier Transform Infrared Spectroscopy (FTIR) was performed on a Bruker VERTEX 70. The water droplet contact angles were measured at ambient temperature on a self-supporting pressed sample disc by a contact angle measuring system JC2000C1.[17] Once a drop of water was deposited on the surface of the sample disc, the contact angle was determined from pictures immediately captured using a charge-coupled-device camera. The oil–water contact angles were obtained by placing the catalyst discs under a solution of vanillin in decalin, then a drop of water was deposited on the discs and the pictures immediately captured.

Catalytic performance test

The hydrodeoxygenation of vanillin reaction was performed in a SLF-50 autoclave reactor. A typical aqueous phase HDO reaction process is as follows: 155 mg of vanillin and a certain amount of Pd/CM180 catalyst were put into the reactor, and 30 mL of deionized water was added as solvent. The air in the

reactor was replaced by purging with nitrogen gas for 5 min. Then the autoclave was pressurized with hydrogen at a pressure of 145 psi. The hydrogenation of vanillin was carried out at a temperature of 100 °C with magnetic stirring at a speed of 650 rpm. After the reaction, the products and substrate were extracted by ethyl acetate (3 × 10 mL), and then were determined by GC-FID and identified by MS. A typical GC spectrum of the ethyl acetate extracts is shown in Fig. S7.† The reusability of the catalysts was tested as follows: the first-run test was carried out as described above. Then the catalysts were recovered by centrifugation and washed several times with water and ethanol, dried overnight at 45 °C, and subsequently used in the next several catalysis cycles.

In an oil phase HDO reaction process: 155 mg of vanillin and a certain amount of Pd/CM180A (catalyst vanillin/Pd molar ratio (S/C) = 100), 30 mL decalin, H_2 pressure of 145 psi, temperature 80 °C and time of 1 h were used.

In a water–oil HDO reaction process: 155 mg of vanillin and a certain amount of Pd/CM180 catalyst was dispersed in 20 mL of decalin and combined with 10 mL of water. The system was treated by ultrasonic stirring until an obvious layer of emulsion formed. Then the slurry was transferred into the reactor. The air in the reactor was replaced by purging with nitrogen gas for 5 min. Then the autoclave was pressurized with hydrogen at a pressure of 145 psi. The hydrogenation of vanillin was carried out at a temperature of 100 °C with magnetic stirring at a speed of 650 rpm. After the reaction, the products and substrate were extracted by ethyl acetate (3 × 10 mL), and then determined by GC-FID and identified by MS. For an oil–water HDO reaction process, the only difference was that the volumes of decalin and water were 10 and 20 mL, respectively.

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Notes and references

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