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ARTICLE TYPE

Hydrodeoxygenation of vanillin as bio-oil model over carbonaceous microspheres-supported Pd catalysts in 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 hydrodeoxygenation of vanillin have been investigated in both pure aqueous phase and water/oil biphasic systems. The wettability of the 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. In aqueous-phase reactions, the more hydrophilic of catalysts, the more active for hydrodeoxygenation of vanillin. And the wettability of the support affect the activity through the interaction between the catalysts and substrates/products. In the case of water/oil biphasic, the wettability of the supports played key roles in forming Pickering emulsions. It was found that the selectivity of the hydrodeoxygenation reactions was determined by the type of the Pickering emulsions and high selectivity of p-cresol 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 upgrading process is necessitated to reduce the oxygen content, 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 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 substrates and the active metal sites.¹⁵⁻¹⁷ For example, a series of support materials for Pd nanoparticles, including traditional TiO₂, MgO, CeO₂, γ -Al₂O₃ and a novel N-doped carbon had 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 resulted in excellent activity and selectivity due to the hydrophilic property of the support. In order to obtain a 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 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 HDO of vanillin efficiently. Moreover, the water/oil biphasic system could facilitate separation of water-insoluble organic products. All the above studies indicate that the wettability of the catalyst plays important role in 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 solvents²² 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 applications in 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 aqueous phase and water/oil-biphasic conditions. The role of the wettability of the

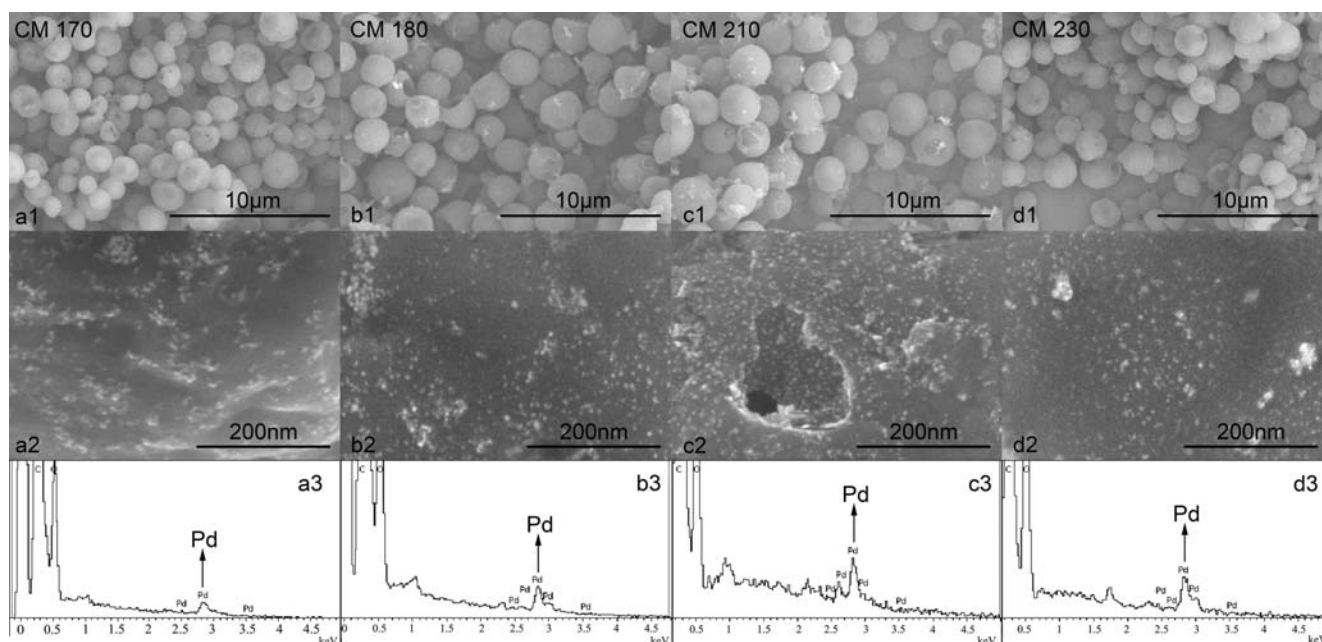


Fig. 1. (a1-d1) SEM images of CM170, CM180, CM210 and CM230; (a2-d2) SEM images of Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230, and (a3-d3) the corresponding EDX spectra.

Pd/CM catalysts in their catalytic performances had 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 of 1.5-2.5 μm. Some cracked microspheres reveal that they are hollow, which are 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 PdCl₂ with NaBH₄ as 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 4.9wt. % 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 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 Other four diffraction peaks at 39.7, 46.1, 67.6 and 81.1° can be assigned to the diffractions of (111), (200), (220) and (311)

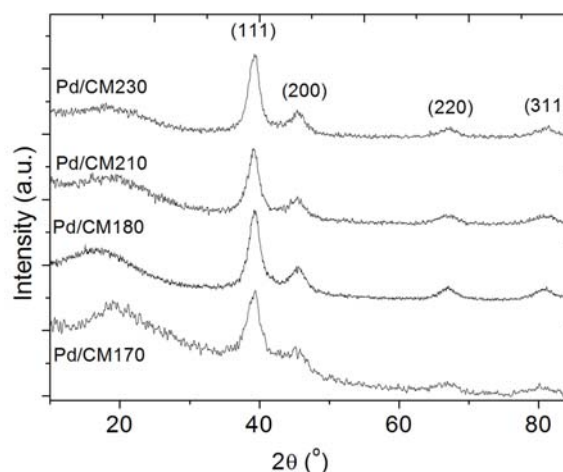


Fig. 2 XRD patterns of Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230 catalysts.

planes of Pd nanoparticles. The size of Pd nanoparticles was estimated to be about 6 nm from the diffraction peak of (111) lattice plane according to 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 a $\Delta = 5.27$ eV, indicating the presence of metallic Pd (0) species. And the shoulders at 342.49 and 336.99 eV ($\Delta = 5.5$) can be assigned to 3d_{3/2} and 3d_{5/2} of Pd (II), respectively. All the XPS spectra show that the peaks of Pd (II) are much weaker than those of Pd (0), indicating metallic Pd is the dominant state in all of the Pd/CM catalysts (Table S1).

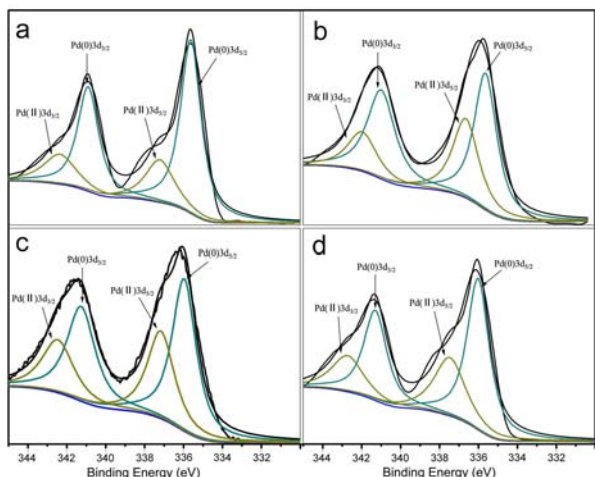


Fig. 3 Pd3d XPS spectra for (a) Pd/CM170, (b) Pd/CM180, (c) Pd/CM210 and (d) Pd/CM230 catalysts.

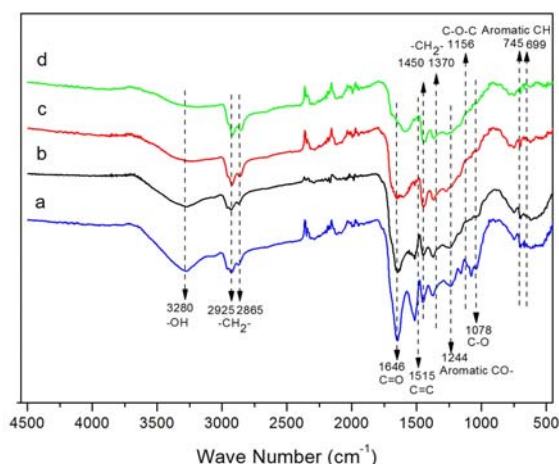


Fig. 4 FTIR spectra for (a) Pd/CM170, (b) Pd/CM180, (c) Pd/CM210 and (d) Pd/CM230 catalysts.

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 -CH₂- 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 hydrophilic groups decrease and those of hydrophobic groups increase remarkably in order of Pd/CM170, Pd/CM180, Pd/CM210 and Pd/CM230, indicating 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 C1s XPS spectra (Fig. S2) further demonstrated the effects of the hydrothermal synthesis temperature on surface chemistry of the catalysts. There were four kinds of carbon components with the binding energy of

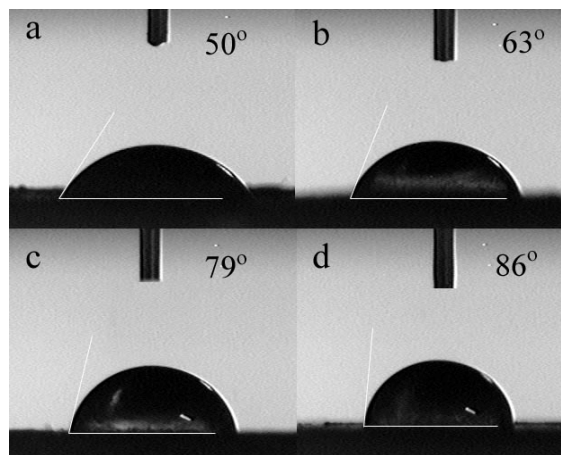


Fig. 5 Air-water contact angles for (a) Pd/CM170, (b) Pd/CM180, (c) Pd/CM210 and (d) Pd/CM230 catalysts. The photos were immediately captured after a drop of water was deposited on the surface of the self-supporting pressed sample disc.

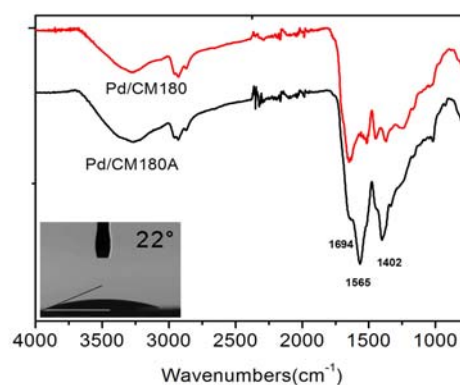


Fig. 6 FTIR spectra for Pd/CM180 and Pd/CM180A catalysts. Insert shows the water contact angles for Pd/CM180A.

284.5, 285.6, 286.6 and 287.8 eV, respectively. 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 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 transformation of surface function groups of carbonaceous microspheres lead to the decrease of hydrophilicity as the synthesis temperature of the carbonaceous microspheres increased.

In fact, there are many carboxyl groups on 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 catalysts were further treated with 0.05 mol/L NaOH aqueous solutions under ultrasound for 15 min, washed with distilled water, dried and the obtained samples were signed 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 Pd/CM180A catalysts, confirming ionization of 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 indeed 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 facily 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 of 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 hydrodeoxygenation of vanillin under mild conditions; and the transformation of vanillin into 2-methoxy-4-methylphenol (p-cresol) 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 possibility of the Pd/CM catalysts for 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, H₂ 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 the reaction time in the presence of Pd/CM180. Within the first 1 h, vanillin alcohol is the main products and p-cresol can also be formed. As the reaction proceeds, the content of vanillin alcohol begins to decrease with the increase of p-cresol. After 3 hours, vanillin was consumed completely and p-cresol selectivity of 49% can be achieved. Compared with vanillin alcohol, p-cresol is more valuable as biofuel. In order to improve the yield of p-cresol, reaction conditions were optimized and the results are shown in Fig. 7b. It was found that under higher H₂ pressure (200 psi), 100% vanillin conversion could be achieved with p-cresol 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.

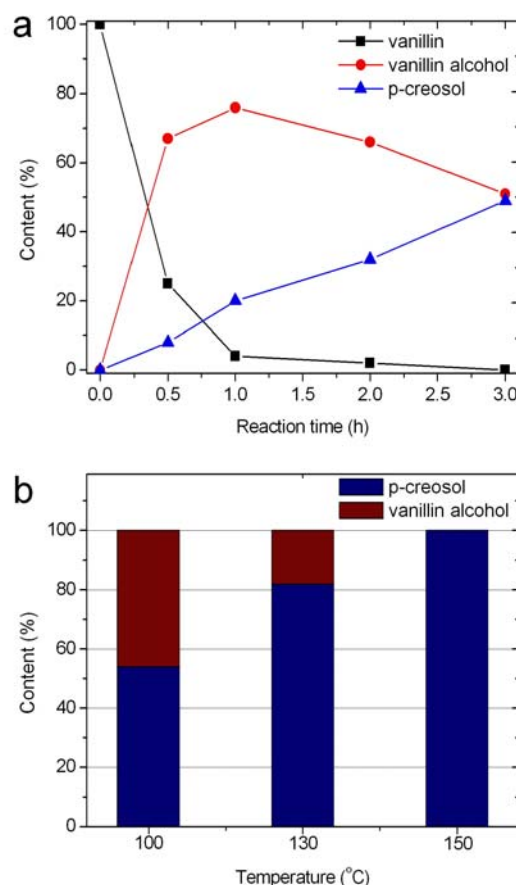


Fig. 7 (a) Trend of reactant and product proportion with reaction time during aqueous-phase hydrodeoxygenation of vanillin by Pd/CM180. Reaction conditions: vanillin/Pd molar ratio (S/C) = 200, H₂ pressure of 50 psi, temperature of 90 °C. (b) Product distribution at different temperatures during aqueous-phase hydrodeoxygenation of vanillin by Pd/CM180. Reaction conditions: S/C = 100, H₂ 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-cresol. Conditions: vanillin/Pd molar ratio (S/C) = 100, H₂ pressure of 145 psi, temperature of 100°C and time of 1 h.

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 H₂ 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-cresol 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

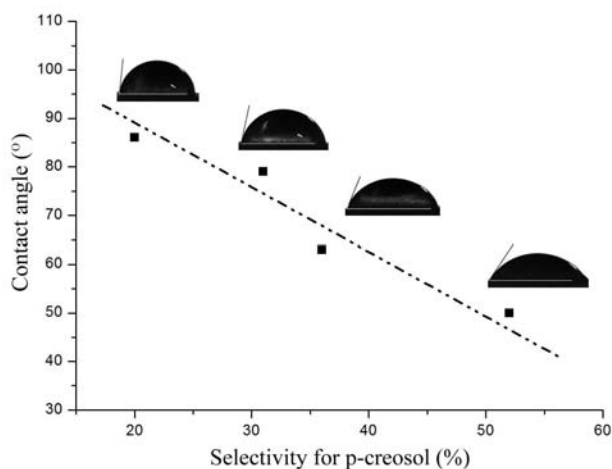


Fig. 8 Effect of the catalyst wettability on the selectivity for p-cresol.

To further prove the role of the wettability, a comparative study of 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-cresol selectivity of 23% is achieved at 80 °C, which can be further enhanced to 55% and 100% at 100 and 130 °C, respectively. However, the counterpart Pd/CM180 catalyst only obtain a 98% conversion of vanillin at 80 °C, and lower p-cresol selectivities at all the 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.

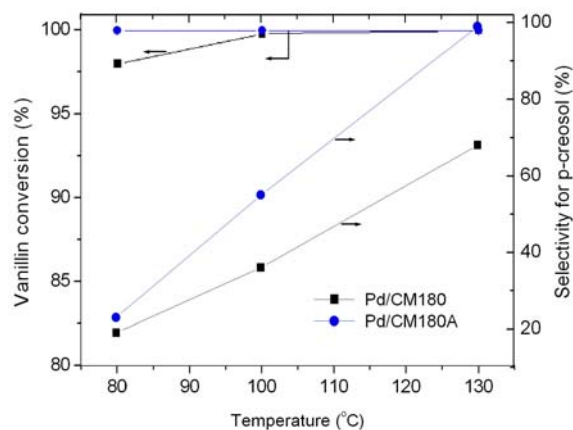


Fig. 9 Comparison of catalytic performances for aqueous-phase HDO of vanillin between Pd/CM180 and Pd/CM180A at different temperatures. Reaction conditions: vanillin/Pd molar ratio (S/C) = 100, H₂ pressure of 145 psi and time of 1 h.

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 the better activity for hydrodeoxygenation. One reason for this wettability-dependent behaviour should be due to 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 contact intimately 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-cresol, on the surface of the Pd/CM catalysts. It is known that although vanillin and vanillin alcohol can be dissolved in water, p-cresol is hydrocarbon-solvent soluble. Once p-cresol was formed during the reaction, some hydrophobic surface areas of the Pd/CM catalysts would tend to be covered by the products via the well-known hydrophobic effect, resulting in ill contact with the substrates and suppression of the catalytic activity. Combined with the above analysis, it is reasonable that the wettability of support affect the activity through the interaction between the catalysts and substrates/products.

The HDO activity in 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 aqueous-phase HDO of vanillin has been tested over the Pd/CM180A catalyst. After the completion of the first cycle, it afforded the vanillin conversion of 97% and p-cresol selectivity of 32% at 100 °C under 50 psi H₂ in water. And no obvious decrease in the catalytic activity were 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 Pd3d XPS spectra (Fig. S4) of the used catalysts showed that both Pd(0) and Pd (II) were present and metallic Pd was the dominated state, which was similar to the results of 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 the 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, HDO reaction in water/oil biphasic systems is more desirable from a practical view.²¹ Therefore, HDO of vanillin in the Pd/CM-water-decalin Pickering emulsions was carried out. To check the ability of the the Pd/CM catalysts in formation of Pickering emulsions, the oil-water contact angles were measured (Fig. S6). The contact angles are 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 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 interface of water-

decalin. After ultrasonic stirring of the mixture of water, decalin and Pd/CM180, a emulsion layer was immediately formed, resulting in a water-emulsion-decalin three-layer system. Since it was not favourable to forming Pickering emulsions if the Pd/CM is too hydrophilic or hydrophobic, Pd/CM180 with the moderate wettability was employed in the following studies.

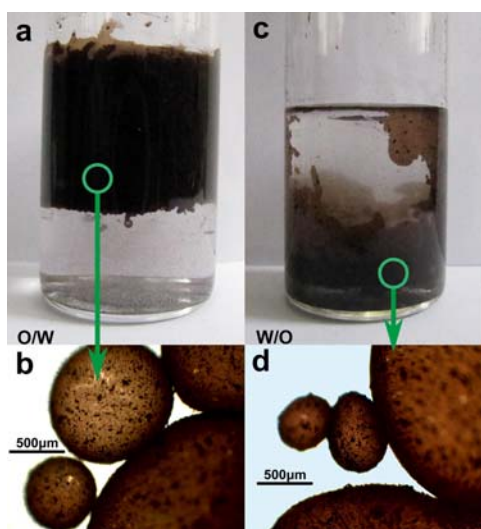


Fig. 10 Photos of Pd/CM180 stabilized (a) O/W and (c) W/O Pickering emulsions. Optical microscopy images of the (b) O/W and (d) W/O emulsions.

It was found that the type of the 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 (10mL:20mL) mixture of decalin and water in the presence of Pd/CM180 catalysts. 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 could proceed well in both the W/O and the O/W Pickering emulsions. After 1 h reaction at 100°C with H₂ pressure of 145 psi, about 96 % conversions of vanillin were achieved in both emulsions. The activities in 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 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-cresol were quite different with the types of the emulsion. In the case of O/W emulsions, the selectivity of p-cresol was 38% after 1 h reaction, which should be compared favourably with the results in aqueous-phase reactions under the same conditions. Interestingly, a remarkable enhancement of p-

cresol selectivity was observed in the W/O emulsions. The selectivity of p-cresol 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.

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-cresol. Conditions: vanillin/Pd molar ratio (S/C) = 100, H₂ pressure of 145 psi and temperature of 100°C.

Since the conversion rates of vanillin were almost the same in the W/O and O/W emulsions, we speculated the origin of difference in the product selectivity should be resulted mainly from the p-cresol 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 water/catalyst would contribute mainly to the whole catalytic performances 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 later. 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 of catalysts, the more active for hydrodeoxygenation of vanillin. In the case of water/oil biphasic, 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 their feasible applications in HDO of the 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 hydrothermal treatment of yeast cells using the methods described in our previous study.²² Especially, in order to tuning the wettability, hydrothermal treatment 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 PdCl₂ (20 mg) were added to H₂O (30 mL) and stirred at room temperature for 1 h; Then 4 mL of NaBH₄ (2.5 g/L) aqueous solution was added into the above slurry; after stirring for 1 h, the mixture was centrifugated, 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. % of 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 catalysts were obtained by using Philips EM 400. Histograms of Pd particle size were calculated from 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 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 Bruker VERTEX 70. The water droplets contact angles were measured at ambient temperature on the 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 reaction, the products and substrate were extracted by ethyl acetate (3 \times 10 mL), and then were determined by GC-FID and identified by MS. A typical GC spectrum of the ethyl acetate extracts was 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 were used in the next several catalysis cycles.

In a 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, H₂ pressure of 145 psi, temperature

80 °C and time of 1 h.

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 added 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 reaction, the products and substrate were extracted by ethyl acetate (3 \times 10 mL), and then were determined by GC-FID and identified by MS. For a oil/water HDO reaction process, the only difference was that the volumes of decalin and water were 10 and 20 mL, respectively.

Acknowledgements

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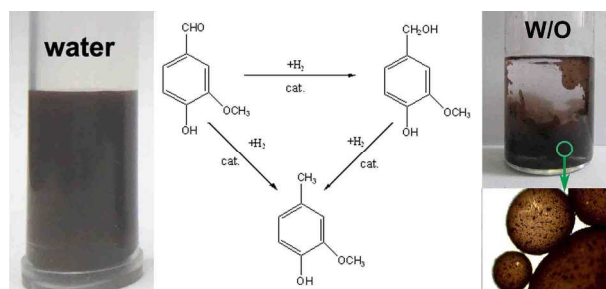
Notes and references

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TOC for: Hydrodeoxygenation of vanillin as bio-oil model over carbonaceous microspheres-supported Pd catalysts in aqueous phase and Pickering emulsions

Colour graphic:



Text:

Amphiphilic carbonaceous microspheres-supported Pd catalysts are effective in hydrodeoxygenation of vanillin in aqueous phase and Pickering emulsions.