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Superhydrophilic mesoporous sulfonated melamine–formaldehyde resin supported palladium nanoparticles as an efficient catalyst for biofuel upgrade†

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Mesoporous sulfonated melamine–formaldehyde resin (MSMF) has been successfully synthesized from the self-assembly of a copolymer surfactant (F127) with a mixture of melamine, formaldehyde and $NaHSO_3$ in an aqueous solution. After removal of the copolymer surfactant (F127) by ethanol extraction, the MSMF exhibits uniform mesopore sizes centered at 10.2 nm. The contact angle (0°) of water on the sample shows that the MSMF is superhydrophilic. After impregnating with a Pd species, a MSMF supported Pd catalyst (Pd/MSMF) is obtained, which shows high activity and excellent recyclability in an important model reaction for biofuel upgrade (hydrodeoxygenation of vanillin), compared with a conventional carbon supported Pd catalyst (Pd/C). The superior catalytic properties of the Pd/MSMF catalyst should be potentially important for biofuel upgrades in the future.

Introduction

As a renewable energy source, biofuel produced from the pyrolysis of biomass, has attracted considerable attention as a substitute for petroleum fuels.[1–23] However, biofuel is not suitable for direct combustion in modern diesel engines due to the presence of a large amount of oxygen components, which require upgrading.[15–23] As an effective approach, hydrodeoxygenation plays an important role to upgrade the biofuel.[24–43] For example, large surface carbon supported Pd nanoparticles (Pd/C) is a good catalyst for biofuel hydrodeoxygenation.[33–39] However, due to the presence of hydrophilic groups such as oxygen components in the raw biofuels, the relatively hydrophobic Pd/C catalyst has a relatively poor wettability to the biofuel in some cases. To solve this problem, scientists have used N-doped carbon as a support to increase the reactant wettability.[40–43]

Recently mesoporous phenol–formaldehyde resins with a very high surface area (as high as 652 $m^2 g^{-1}$) have been successfully synthesized,[44–46] but unfortunately their hydrophobicity significantly influences the wettability[47] of the biofuel as a reactant in biofuel upgrading.

In order to obtain a good wettability of the biofuel on the support, we have designed and synthesized a superhydrophilic mesoporous sulfonated melamine–formaldehyde resin (MSMF) *via* self-assembly of a copolymer surfactant (F127) with a mixture of melamine, formaldehyde and $NaHSO_3$ in an aqueous solution. The superhydrophilicity of the support is helpful for increasing the miscibility of the catalyst with the biofuel reactant. As a typical model for biofuel upgrade, catalytic tests in the hydrodeoxygenation of vanillin to 2-methoxy-4-methylphenol show that the MSMF supported Pd catalyst (Pd/MSMF) is highly active and extremely recyclable, compared with a conventional Pd/C catalyst.

Experimental

Synthesis of MSMF

MSMF was hydrothermally synthesized at the temperature of 150 °C from a mixture and molar ratio of 1.0 melamine : 3.5 HCOH : 1.0 $NaHSO_3$: 0.004 F127 : 0.005 NaOH : 40 H_2O. In a typical run, 10.0 g of melamine, 23 g of formaldehyde solution (37 wt%) and 0.16 g of NaOH were dissolved in 17 mL of deionized water and stirred at 80 °C for 30 min. After the addition of 8.3 g of $NaHSO_3$ with stirring at 80 °C for another 2 h, 25 mL of deionized water containing 4 g of F127 was added, followed by stirring for 1 h at room temperature. After the addition of an aqueous HCl solution (36 wt%) to adjust the pH value to 2–3 and further stirring at 70 °C for 30 min, the mixture was transferred into an autoclave for heating at 150 °C for 24 h. After filtrating, washing and drying, a solid product was finally obtained (Fig. S1 and S2†). F127 surfactant was removed by the extraction with ethanol at 60 °C for 3 h. The synthesis route is outlined in Scheme 1.

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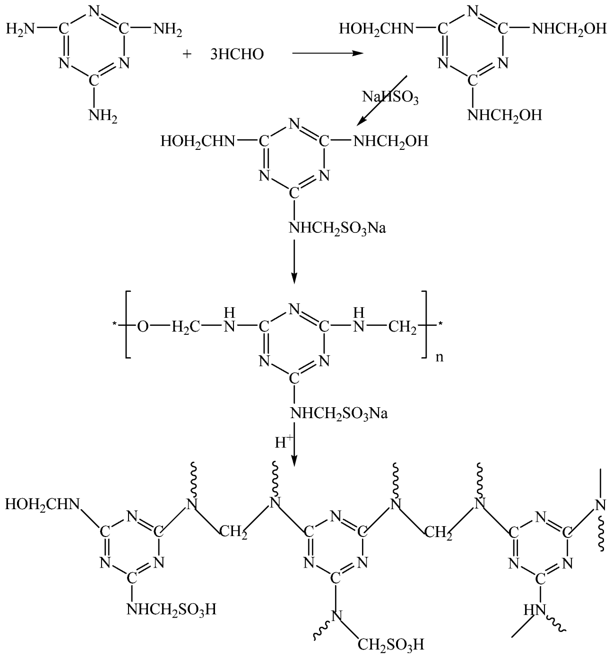

Scheme 1 Proposed route for synthesizing MSMF.

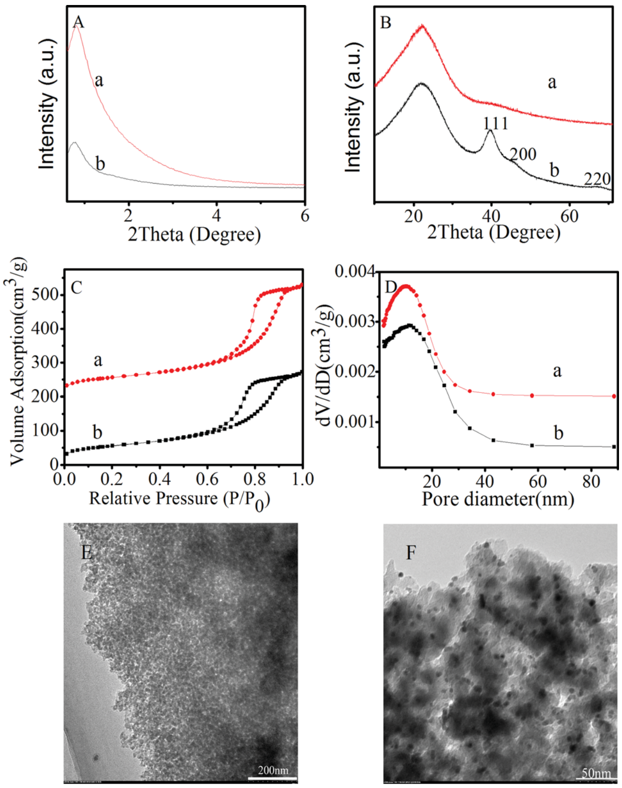

Fig. 1 (A) Small-angle XRD patterns, (B) wide-angle XRD patterns, (C) N_2 sorption isotherms and (D) pore size distribution of (a) MSMF and (b) Pd/MSMF samples. TEM images of (E) MSMF and (F) Pd/MSMF samples. Line a in C and D have been offset by 200 $cm^3 g^{-1}$ and 0.0005 $cm^3 g^{-1}$ respectively, along the vertical axis for clarity.

Preparation of MSMF supported Pd catalyst (Pd/MSMF)

Pd/MSMF catalyst was prepared by a simple impregnation method. Typically, 1 g of MSMF was added to 50 mL of deionized water in a beaker under stirring, followed by the addition of 85 mg of $PdCl_2$ and this was further stirred for 24 h at room temperature. After adjusting the pH value to 8–9 by a NaOH solution, 0.1 g of $NaBH_4$ in 50 mL of deionized water was added followed by further stirring for 30 min. After filtrating, washing and drying, a solid product of Pd/MSMF was finally obtained.

Characterization

X-Ray powder diffraction (XRD) patterns were measured with a Rigaku X-ray diffractometer using Cu Kα ($\lambda = 1.54$ Å) radiation. Nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics Tristar system. The samples were outgassed for 10 h at 100 °C before the measurements. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα irradiation at $\theta = 90°$ for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.6 eV. FTIR spectra were performed on an iS5 (Nicolet) IR spectrometer in the range of 400–4000 cm^{-1}. Transmission electron microscope (TEM) images were obtained using a Hitachi HT-7700. ^{13}C MAS spectra were performed on a Varian Infinityplus-400 spectrometer. The static contact angles were measured with SL200KB at 25 °C. CHNS elemental analyses were performed on a Perkin-Elmer series II CHNS analyzer 2400.

Catalytic tests

As a model reaction for biofuel upgrade, the hydrodeoxygenation of vanillin was chosen. 0.304 g (2 mmol) of vanillin and 0.021 g of Pd/MSMF catalyst were sealed in an autoclave containing 20 mL of deionized water, which was purged with H_2 3 times. The pressure of H_2 was adjusted to the desired value and the autoclave was placed in the preheated oil bath. After the reaction at 110 °C for 2 h, the mixture was extracted with ethyl acetate and the catalyst was taken out from the system by centrifugation before being analyzed by gas chromatography. Dodecane was added as an internal standard.

Results and discussion

Catalyst characterizations

Fig. 1 shows XRD patterns, N_2 sorption isotherms, and TEM images of MSMF and Pd/MSMF samples. The small-angle XRD patterns shows that both MSMF and Pd/MSMF exhibit a broad peak at *ca.* 0.8° (Fig. 1A), which should be assigned to the presence of a worm-like mesostructure in the samples as reported in the previous literature.[48,49] The Pd/MSMF shows peaks at 40.0, 46.6 and 68.1° in the wide-angle XRD patterns (Fig. 1B), which are assigned to the characteristic (111), (200) and (220) planes of the Pd nanoparticles. The N_2 sorption isotherms show that both MSMF and Pd/MSMF have typical type-IV curves with a hysteresis loop at 0.45–0.90, confirming the presence of mesoporosity in the samples.[50] Correspondingly, their pore sizes are distributed at 10.2 and 11.2 nm

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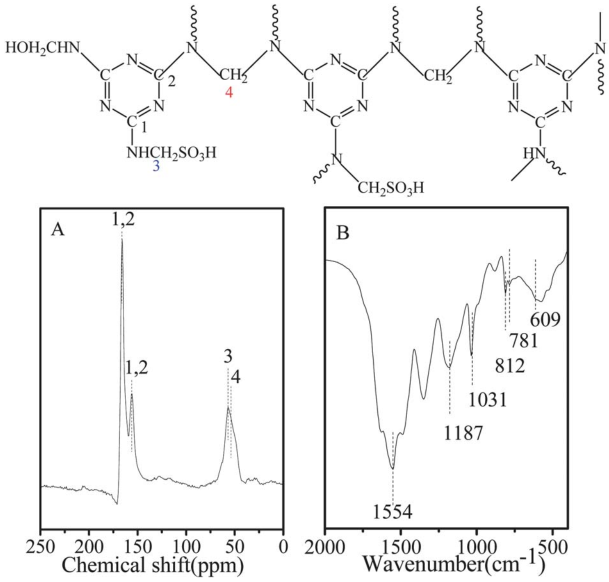

Fig. 2 (A) ^{13}C MAS NMR and (B) IR spectra of the MSMF sample.

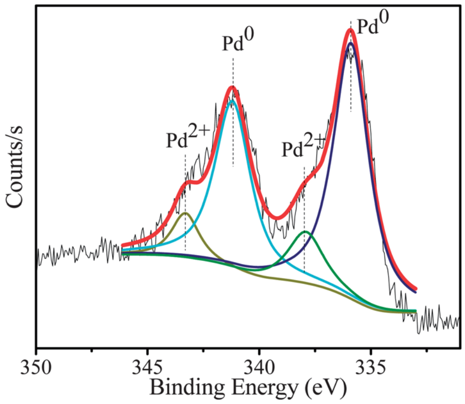

Fig. 3 Pd3d XPS spectrum of the Pd/MSMF sample.

(Fig. 1D), BET surface areas are at 256 and 197 m^2 g^{-1}, and pore volumes are at 0.51 and 0.42 cm^3 g^{-1} (Table S1†), respectively. TEM images show direct evidence that both samples have the worm-like mesostructure (Fig. 1E and F). In addition, the TEM image of Pd/MSMF reveals the dispersion of Pd nanoparticles in MSMF. Particularly, the HRTEM image shows a characteristic Pd lattice fringe (Fig. S3†). The Pd sizes are estimated at 6–8 nm, which are consistent with the results obtained from wide-angle XRD patterns. Very interestingly, the contact angle of a water droplet on the surface of MSMF is zero (Fig. S4†), indicating that the MSMF is superhydrophilic.

Fig. 2 shows ^{13}C NMR and IR spectra of the MSMF sample. The NMR spectrum (Fig. 2A) exhibits peaks at 53, 57, 155, and 165 ppm. The strong peaks at 155 and 165 ppm could be assigned to the triazine rings, while the strong peak at 57 ppm is related to the species of –NH–CH$_2$–SO$_3$–.[51,52] The shoulder peak at 53 ppm is proposed to the species of –NH–CH$_2$–NH–. These assignments are in good agreement with those reported previously.[51] Notably, the signal at 70 ppm assigned to the methylene–ether linkage (CH$_2$–O–) is undetectable, which is consistent with the only methylene linkage in the sample. The methylene linkage is very important in the polymer network because this linkage is more stable than the methylene–ether linkage. The IR spectrum in the region of 500–2000 cm^{-1} of the sample gives bands at 609, 781, 812, 1031, 1187, and 1554 cm^{-1}. The bands at 1554, 812 and 781 cm^{-1} are assigned to characteristic frequencies of triazine, while the bands at 609, 1031, and 1187 cm^{-1} are assigned to the characteristic vibration of sulfonic groups.[53,54] In addition, elemental analysis of MSMF shows that the molar ratio of C/H/N/S is 1/2.13/1.16/0.12 (Table S2†), indicating the presence of a large amount of N element in the sample.

Based on the results of XRD patterns, N$_2$ sorption isotherms, TEM images, NMR and IR spectra, it could be concluded that MSMF with a large surface area and uniform mesopores has been successfully synthesized.

Fig. 3 shows the Pd3d XPS spectrum of the Pd/MSMF sample, giving the peaks of Pd3d$_{5/2}$ and Pd3d$_{3/2}$ at 335.7 and 341.0 eV, respectively. In contrast, the Pd/C sample shows a little higher values at 336.2 and 341.5 eV (Fig. S5†). This shift is possibly related to the nitrogen species in the MSMF acting as strong Lewis base sites, which strongly influences the electronic state of Pd/MSMF, compared with Pd/C. Similar phenomena have been shown in literature.[41] Furthermore, a molar ratio of C/N/O/S in MSMF is also analyzed by XPS, as presented in Table S3.†

Fig. 4 shows the contact angles of water and 2-methoxy-4-methylphenol (product of vanillin hydrodeoxygenation) on the surface of Pd/MSMF and Pd/C catalysts. When a water droplet is contacted with the Pd/MSMF, the water is momentarily adsorbed, giving a swollen surface (Fig. 4A), suggesting very good wettability of water into the Pd/MSMF.[55,56] However, when a water droplet is contacted with the Pd/C, the contact angle is about 9.5° (Fig. 4B). These results indicate that the Pd/MSMF has a much better water wettability than the Pd/C catalyst. In addition, when a 2-methoxy-4-methylphenol droplet is contacted with the surface of Pd/MSMF, the angle is about 19.5° (Fig. 4C). In contrast, when a 2-methoxy-4-methylphenol droplet is contacted with the surface of the Pd/C catalyst, the catalyst quickly adsorbs this droplet, forming a swollen surface. These results suggest that the adsorption of 2-methoxy-4-methylphenol on the Pd/C catalyst is much faster than that on the Pd/MSMF. *i.e.* the desorption of 2-methoxy-4-methylphenol on the Pd/MSMF is much easier than that on the Pd/C catalyst.

Catalytic activities for the hydrodeoxygenation of vanillin

To evaluate the catalytic performance of the superhydrophilic Pd/MSMF, the hydrodeoxygenation of vanillin as a model for biofuel upgrade in the presence of a water solvent has been carefully investigated, as shown in Table 1, Table S4–S6 and Fig. S6 and S7.† Notably, when the temperature is between 110–150 °C, the Pd/MSMF exhibits both full conversion and selective production of 2-methoxy-4-methylphenol (entry 1 and 2, Table 1). Particularly, the formation of pure 2-methoxy-4-methylphenol product at 150 °C takes only 1.0 h (entry 2, Table 1). In contrast, conventional Pd catalysts exhibit relatively low selectivity for 2-methoxy-4-methylphenol (entries 6–9, Table 1), although they have full

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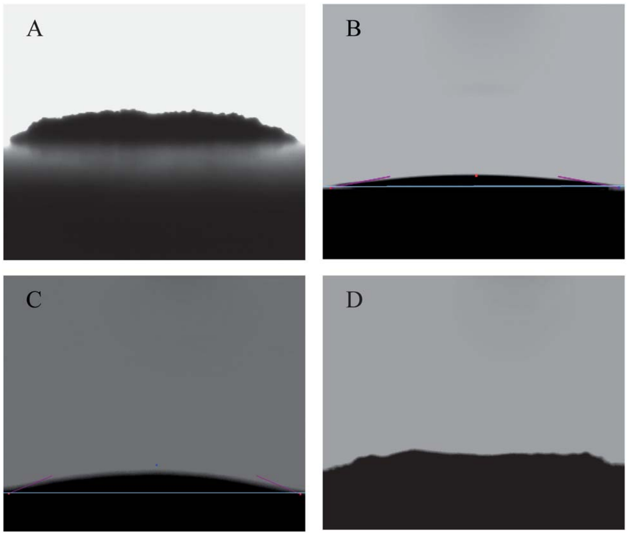
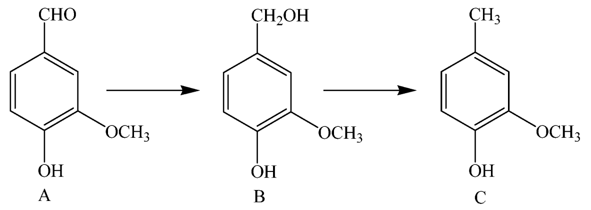


Fig. 4 Contact angles of water droplets on (A) Pd/MSMF and (B) Pd/C and 2-methoxy-4-methylphenol droplets on (C) Pd/MSMF and (D) Pd/C.

Table 1 Catalytic performance in the hydrodeoxygenation of vanillin over various catalysts[a]



			Sel. (%)[b]	
Entry	Catalyst	Conv. (%)[b]	B	C
1	Pd/MSMF	>99.5	—[c]	>99.5
2[d]	Pd/MSMF	>99.5	—[c]	>99.5
3[e]	Pd/MSMF	>99.5	13	87
4[f]	Pd/MSMF	>99.5	—[c]	>99.5
5[g]	Pd/MSMF	>99.5	13	87
6	Pd/C	>99.5	21	79
7	Pd/MMF	>99.5	29	71
8	Pd/TiO_2	>99.5	83	17
9	Pd/γ-Al_2O_3	>99.5	33	67

[a] *Reaction conditions*: the reaction was carried out under a hydrogen pressure of 1 MPa in 20 mL of water containing 2 mmol of vanillin at 110 °C for 2 h. The Pd loading is 4.5 wt%. [b] Determined by GC. [c] Undetectable. [d] Reaction at 150 °C for 1 h. [e] Reaction at 90 °C for 6 h. [f] Reuse at 110 °C for 2 h. [g] Recycles for 6 times at 110 °C for 2 h.

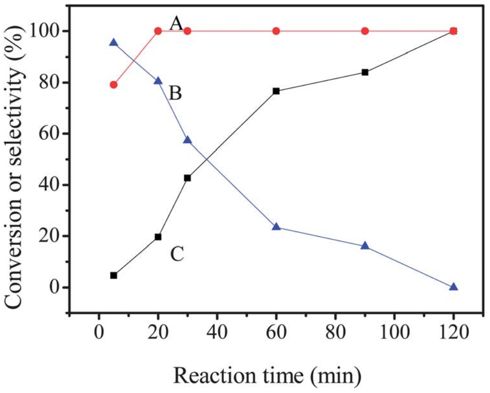


Fig. 5 The dependencies of vanillin conversion (A), vanillin alcohol (B) and 2-methoxy-4-methylphenol selectivities (C) on reaction time over the Pd/MSMF catalyst.

conversion. Considering the similar Pd loadings between the Pd/MSMF with Pd/C and larger Pd nanoparticles (Fig. 1F) of the Pd/MSMF than those of Pd/C (Fig. S8†), the higher activity and better selectivity for the Pd/MSMF catalyst than those over the Pd/C catalyst are mainly attributed to better the wettability of the reactant to the Pd/MSMF catalyst than that to the Pd/C catalyst. The superhydrophilic Pd/MSMF catalyst is favorable for adsorption of oxygen-rich reactants (*e.g.* vanillin) and desorption of the hydrodeoxygenated 2-methoxy-4-methylphenol product. This feature would change the reaction balance, leading to a significant enhancement of the catalytic performance. On the contrary, the Pd/C catalyst with weak hydrophilicity has a low adsorption rate of the vanillin reactant and a low desorption rate of 2-methoxy-4-methylphenol product, resulting in a relatively low catalytic performance in the hydrodeoxygenation of vanillin, compared with the Pd/MSMF catalyst.

Fig. 5 shows dependencies of vanillin conversion and 2-methoxy-4-methylphenol selectivity on reaction time over the Pd/MSMF catalyst. Notably, in only 5 min, 79.1% of vanillin is converted, but 2-methoxy-4-methylphenol selectivity is very low (less than 5%). At this point, the major product is vanillin alcohol. Therefore, the hydrogenation of vanillin alcohol plays an important role for the selective formation of the 2-methoxy-4-methylphenol product.

More importantly, the Pd/MSMF catalyst exhibits excellent recyclability (entries 4 and 5, Table 1, Table S6†). After being recycled for 6 times, the selectivity for methoxy-4-methylphenol is still at 87%. At the same time, Pd species in the liquid phase are still undetectable, indicating that no leaching occurs in the reaction. The excellent recyclability of this catalyst could be potentially important for practical applications in upgrading biofuel in the future.

Conclusions

Superhydrophilic mesoporous sulfonated melamine–formaldehyde resin (MSMF) has been synthesized from a self-assembly route. Very importantly, MSMF supported Pd (Pd/MSMF) catalyst exhibits high activity, good selectivity and excellent recyclability in the hydrodeoxygenation of vanillin as a model for biofuel upgrade, compared with the conventional Pd/C catalyst. The superior catalytic performance is related to the good wettability of the vanillin reactant to the Pd/MSMF. This feature should be important for designing and preparing novel catalysts for biofuel upgrade in the future.

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Notes and references

1 D. Mohan, C. U. Pittman and P. H. Steele, *Energy Fuels*, 2006, **20**, 848.
2 D. Tilman, J. Hill and C. Lehman, *Science*, 2006, **314**, 1598.
3 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484.
4 C. Luo, S. Wang and H. Liu, *Angew. Chem., Int. Ed.*, 2007, **46**, 7636.
5 F. Chen and R. A. Dixon, *Nat. Biotechnol.*, 2007, **25**, 759.
6 G. Stephanopoulos, *Science*, 2007, **315**, 801.
7 E. M. Rubin, *Nature*, 2008, **454**, 14.
8 G. P. Robertson, V. H. Dale, O. C. Doering, S. P. Hamburg, J. M. Melillo, M. M. Wander, W. J. Parton, P. R. Adler, J. N. Barney, R. M. Cruse, C. S. Duke, P. M. Fearnside, R. F. Follett, H. K. Gibbs, J. Goldemberg, D. J. Mladenoff, D. Ojima, M. W. Palmer, A. Sharpley, L. Wallace, K. C. Weathers, J. A. Wiens and W. W. Wilhelm, *Science*, 2008, **322**, 49.
9 P. Kumar, D. M. Barrett, M. J. Delwiche and P. Stroeve, *Ind. Eng. Chem. Res.*, 2009, **48**, 3713.
10 M.-Y. Zheng, A.-Q. Wang, N. Ji, J.-F. Pang, X.-D. Wang and T. Zhang, *ChemSusChem*, 2010, **3**, 63.
11 E. J. Steen, Y. Kang, G. Bokinsky, Z. Hu, A. Schirmer, A. McClure, S. B. del Cardayre and J. D. Keasling, *Nature*, 2010, **463**, 559.
12 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552.
13 J. A. Geboers, S. V. de Vyver, R. Ooms, B. O. Beeck, P. A. Jacobs and B. F. Sels, *Catal. Sci. Technol.*, 2011, **1**, 714.
14 Y. Nakagawa and K. Tomishige, *Catal. Surv. Asia*, 2011, **15**, 111.
15 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044.
16 G. W. Huber and A. Corma, *Angew. Chem., Int. Ed.*, 2007, **46**, 7184.
17 M. E. Himmel, S.-Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady and T. D. Foust, *Science*, 2007, **315**, 804.
18 M. St Öcker, *Angew. Chem., Int. Ed.*, 2008, **47**, 9200.
19 R. Rinaldi and F. Schüth, *Energy Environ. Sci.*, 2009, **2**, 610.
20 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493.
21 R. French and S. Czernik, *Fuel Process. Technol.*, 2010, **91**, 25.
22 P. M. Mortensen, J.-D. Grunwaldt, P. A. Jensen, K. G. Knudsen and A. D. Jensen, *Appl. Catal., A*, 2011, **407**, 1.
23 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 8075.
24 D. C. Elliott and T. R. Hart, *Energy Fuels*, 2009, **23**, 631.
25 N. Yan, Y. Yuan, R. Dykeman, Y. Kou and P. J. Dyson, *Angew. Chem., Int. Ed.*, 2010, **49**, 5549.
26 J. Fu, X. Lu and P. E. Savage, *Energy Environ. Sci.*, 2010, **3**, 311.
27 S. Crossley, J. Faria, M. Shen and D. E. Resasco, *Science*, 2010, **327**, 68.
28 N. Li, G. A. Tompsett, T. Y. Zhang, J. Shi, C. E. Wyman and G. W. Huber, *Green Chem.*, 2011, **13**, 91.
29 T. Nimmanwudipong, R. C. Runnebaum, D. E. Block and B. C. Gates, *Energy Fuels*, 2011, **25**, 3417.
30 T. Nimmanwudipong, C. Aydin, J. Lu, R. C. Runnebaum, K. C. Brodwater, N. D. Browning, D. E. Block and B. C. Gates, *Catal. Lett.*, 2012, **142**, 1190.
31 C. H. Ko, S. H. Park, J.-K. Jeon, D. J. Suh, K.-E. Jeong and Y.-E. Park, *Korean J. Chem. Eng.*, 2012, **29**, 1657.
32 A. J. Foster, P. T. M. Do and R. F. Lobo, *Top. Catal.*, 2012, **55**, 118.
33 A. Mori, T. Mizusaki, T. Ikawa, T. Maegawa, Y. Monguchi and H. Sajiki, *Tetrahedron*, 2007, **63**, 1270.
34 C. Zhao, Y. Kou, A. A. Lemonidou, X. Li and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2009, **48**, 3987.
35 R. J. White, V. Budarin, R. Luque, J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, 2009, **38**, 3401.
36 C. Zhao, J. He, A. A. Lemonidou, X. Li and J. A. Lercher, *J. Catal.*, 2011, **280**, 8.
37 W. Deng, M. Liu, X. Tan, Q. Zhang and Y. Wang, *J. Catal.*, 2010, **271**, 22.
38 C. Zhao and J. A. Lercher, *ChemCatChem*, 2012, **4**, 64.
39 C. Zhao, W. Song and J. A. Lercher, *ACS Catal.*, 2012, **2**, 2714.
40 V. Z. Radkevich, T. L. Senko, K. Wilson, L. M. Grishenko, A. N. Zaderko and V. Y. Diyuk, *Appl. Catal., A*, 2008, **335**, 241.
41 Y. Wang, J. Yao, H. Li, D. Su and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 2362.
42 X. Xu, Y. Li, Y. Gong, P. Zhang, H. Li and Y. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 16987.
43 I. T. Ghampson, C. Sepúlveda, R. Garcia, L. R. Radovic, J. L. G. Fierro, W. J. DeSisto and N. Escalona, *Appl. Catal., A*, 2012, **439–440**, 111.
44 F. Q. Zhang, Y. Meng, D. Gu, Y. Yan, C. Z. Yu, B. Tu and D. Y. Zhao, *J. Am. Chem. Soc.*, 2005, **127**, 13508.
45 Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, H. F. Yang, Z. Li, C. Z. Yu, B. Tu and D. Y. Zhao, *Angew. Chem., Int. Ed.*, 2005, **44**, 7053.
46 Y. Huang, H. Q. Cai, D. Feng, D. Gu, Y. H. Deng, B. Tu, H. T. Wang, P. A. Webley and D. Y. Zhao, *Chem. Commun.*, 2008, 2641.
47 Y. Cui, W. Q. Yuan and Z. J. Pei, *ASME Int. Manuf. Sci. Eng. Conf., Proc.*, 2010, **1**, 525.
48 K. Kailasam, Y.-S. Jun, P. Katekomol, J. D. Epping, W. H. Hong and A. Thomas, *Chem. Mater.*, 2010, **22**, 428.
49 P. Zhang, L. Wang, L. Ren, L. Zhu, Q. Sun, J. Zhang, X. Meng and F.-S. Xiao, *J. Mater. Chem.*, 2011, **21**, 12026.
50 M. Kruk and M. Jaroniec, *Chem. Mater.*, 2003, **15**, 2942.

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51 H. Pasch, G. Hovakeemian and S. Lahalih, *J. Polym. Sci., Part A: Polym. Chem.*, 1991, **29**, 525.

52 M. Rätzsch, H. Bucka, S. Ivanchev, V. Pavlyuchenko, P. Leitner and O. N. Primachenko, *Macromol. Symp.*, 2004, **217**, 431.

53 M. Singh and V. Kumar, *J. Appl. Polym. Sci.*, 2009, **114**, 1870.

54 F. Liu, W. Kong, C. Qi, L. Zhu and F.-S. Xiao, *ACS Catal.*, 2012, **2**, 565.

55 H. Liu, L. Feng, J. Zhai, L. Jiang and D. Zhu, *Langmuir*, 2004, **20**, 5659.

56 L. Xu, W. Chen, A. Mulchandani and Y. Yan, *Angew. Chem., Int. Ed.*, 2005, **44**, 6009.

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