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Transesterification to Biodiesel with Superhydrophobic Porous Solid Base Catalysts

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The production of biodiesel from renewable resources has attracted much attention due to the increasing demand for energy.[1] One of the most important routes for producing biodiesel involves the transesterification of triglycerides with short-chain alcohols, normally catalyzed by acids and bases.[2–3] Liquid acids (e.g., H_2SO_4) exhibit good catalytic activities but their environmentally unfriendly properties, such as strong corrosion and difficult recyclability, severely hinder their application.[4] Solid acids (e.g., sulfated zirconia or supported heteropolyacids) offer advantages such as catalyst recycling and a high stability towards CO_2 (a catalyst poison) in air, but applying these catalysts in industrial processes is difficult owing to the relatively low activities, low degree of exposure for active sites, and leaching of active sites.[4a,5] Base catalysts are very active compared to acids.[3,6] Homogeneous base catalysts, such as NaOH and KOH, are preferred in industry because of their widespread availability and low cost, but environmental concerns and the lack of an option to regenerate the catalysts strongly limit their applications.[3c,6a] Solid bases have activities similar to homogeneous base catalysts, but their sensitive active sites, which can be poisoned by molecules such as H_2O, CO_2, and fatty acids (FFAs) in crude vegetable oils, still pose a great challenge.[6a] In these solid catalysts many factors, such as textural parameters, wettability, and adsorption features, strongly influence catalytic properties.[2b,3a,7] Superhydrophobicity is a particularly useful catalyst property when seeking to significantly enhance activity in transesterifications of triglycerides with methanol.[7,8]

Many superhydrophobic materials, with varying compositions, have been fabricated rationally, but the search for solid base catalysts with superhydrophobic features has so far been unsuccessful. Herein, we demonstrate a superhydrophobic and porous solid base, PDVB-VI, obtained by co-polymerization of divinylbenzene and 1-vinylimidazolate. Catalytic tests in the transesterification of tripalmitin as well as virgin plant oil with methanol show that the PDVB-VI catalyst exhibits unprecedentedly high activities, excellent stability, and an extraordinary ability for regeneration compared to conventional bases and vinylimidazolate mono- and polymers.

Samples of porous PDVB-VI-*n* (where *n* is the molar ratio of 1-vinylimidazolate with divinylbenzene) were obtained by a hydrothermal route, at 100 °C for 24 h in the presence of ethyl acetate, methyl acetate, or THF as solvent. Nitrogen adsorption–desorption isotherms of these samples showed type IV curves with hysteresis loops in the relative pressure region 0.7–0.9 (Figure S1, Table 1), indicating mesoporosity. Correspondingly, the pore sizes were found to be in the range 20–40 nm. Interestingly, the samples have high Brunauer–Emmett–Teller (BET) surface areas (513–680 m^2g^{-1}) and large pore volumes (0.45–1.24 cm^3g^{-1}), as shown in Table 1. X-ray photoelectron spectroscopy (XPS) (Figure S2) and IR (Figure S3) spectra indicated the presence of 1-vinylimidazolate groups in the sample. Transmission electron microscopy (TEM) images clearly confirmed the presence of hierarchical mesopores in the size range 20–40 nm (Figure S4), and scanning electron microscopy (SEM) images showed the rough surface of the samples (Figure S5).

When a water droplet was dropped to contact the surface of PDVB-VI-0.5, the contact angle was 152° (Figure 1 a), indicating that the PDVB-VI-0.5 sample is superhydrophobic. This feature is possibly related to its surface roughness, unique mesostructure, and organic framework; similar phenomena have been reported previously.[9] In contrast, when a droplet of salad oil was brought into contact with the same sample, the angle was 15.7° (Figure 1 b), indicating its oleophilic features. When a methanol droplet was dropped onto the surface the angle was 0° (Figure 1 c), indicating superwettability for methanol. After making contact with methanol the volume of the sample expanded significantly, indicating that PDVB-VI-0.5 has excellent swelling properties (Figure S6). As a result of these features PDVB-VI-0.5 has a very large adsorption capacity for methanol (10.3 gg^{-1}) and plant oil (ESG oil 10.8 gg^{-1}, Figure S7). This implies excellent miscibility of methanol with plant oil in PDVB-VI samples, which is a helpful feature for the conversion of plant oil to biodiesel.[10] When a glycerol droplet was to make contact with the surface of the PDVB-VI-0.5 sample the angle was 135° (Figure 1 d), indicating that PDVB-VI-0.5 has good anti-wetting properties for glycerol. This feature is helpful for repelling glycerol from PDVB-VI in the transesterification of tripalmitin with methanol. After quaternary ammonization of PDVB-VI-0.5 by treatment with CH_3I (sample PDVB-VI-0.5-Q), the sample exhibited a lower contact angle for water (126°, Figure S8), less swelling (Figure S6), a lower adsorption capacity for organic compounds, and higher adsorp-

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Table 1. Textural parameters of various solid base catalysts, and catalytic data on their use in the transesterification of tripalmitin with methanol and other alcohols.[a]

Entry	Sample	Alkaline content [mmol g^{-1}]	Textural parameters S_{BET}[b] [m^2 g^{-1}]	V_p[b] [cm^3 g^{-1}]	D_p[c] [nm]	Alcohol	Alkyl palmitate yield [%] $t=1$ h	$t=3$ h
1	PDVB-VI-0.2	0.953[d]	670	1.13	24.2	methanol	99.5	99.7
2	PDVB-VI-0.33	2.063[d]	594	1.241	38.1	methanol	99.3	99.9
3	PDVB-VI-0.5	2.822[d]	513	0.815	19.2	methanol	99.7	99.6
4	M-PDVB-VI-0.5[e]	2.822[d]	486	0.915	26.3	methanol	99.8	99.2
5	T-PDVB-VI-0.12[f]	0.953[d]	576	0.454	6.83	methanol	–	–
6	PDVB-VI-0.5-Q	2.063[d]	680	1.0	29.1	methanol	63.1	89.3
7	PDVB-VI-0.5[g]	2.822[d]	521	0.813	24.6	methanol	99.2	99.7
8	PDVB-VI-0.5[h]	2.822[d]	510	0.811	26.8	methanol	98.9	99.3
9	PDVB-VI-0.5	2.822[d]	513	0.815	19.2	ethanol[i]	30.1	64.3
10	PDVB-VI-0.5	2.822[d]	513	0.815	19.2	1-butanol[j]	24.6	55.1
11	Amberlite 400	5.18	0.28	–	–	methanol	57.5	79.8
12	Hydrotalcite [$Mg_6Al_2(OH)_{16}CO_3$]	30.2	103	0.85	33	methanol	61.6	80.7
13	PVI	10.625	–	–	–	methanol	59.3	85.5
14	VI	10.625	–	–	–	methanol	67.2	97.3
15	CaO	17.86	–	–	–	methanol	55.8	82.4
16	KOH	17.86	–	–	–	methanol	99.6	99.9
17	KOH[k]	17.86	–	–	–	methanol	94.6	98.1
18	NaOH	25.0	–	–	–	methanol	38.1	85.2
19	DVB	0	–	–	–	methanol	0	0

[a] For each run, 0.05 g catalyst, 0.84 g tripalmitin, and 3.76 mL alcohol were used. [b] BET surface area and pore volume estimated from N_2 adsorption results. [c] Pore size distribution estimated from BJH model. [d] Calculated from the imidazole content of the starting composition. [e] Mesoporous PDVB-PVI synthesized from using methyl acetate as solvent. [f] Mesoporous PDVB-PVI synthesized from using THF as solvent. [g] Catalyst recycled three times. [h] Catalyst recycled five times. [i] $T=78$ °C. [j] $T=115$ °C. [k] Catalyst exposed to air for 7 days.

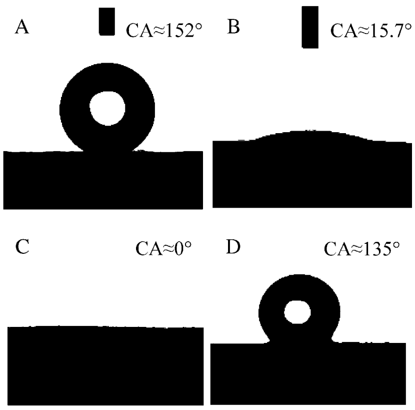

Figure 1. Contact angles of (A) a water droplet, (B) a salad oil droplet, (C) a methanol droplet, and (D) a glycerol droplet on PDVB-PVI-0.5, at a contact time of ca. 0.5 s.

tion capacities for glycerol and water (Figure S7). Interestingly, when a droplet of ethanol or 1-butanol was dropped onto the surface of PDVB-VI-0.5 the angles were ca. 10° or 15°, respectively (Figure S9), indicating that an increased chain length of the alcohols reduces the wettability compared with methanol. This might be due to the larger molecular diameters of ethanol and 1-butanol, leading to slower diffusion rates into the nanoporous PDVB-VI-0.5 sample.

Figure 2a shows water adsorption isotherms for the PDVB-VI-0.5, PDVB-VI-0.5-Q, and hydrotalcite samples. Hydrotalcite has a high adsorption capacity for water, while PDVB-VI-0.5 has a very low adsorption capacity at different humidity levels. The PDVB-VI-0.5-Q sample shows a higher water adsorption capacity, which is the result of a change in hydrophobicity. In contrast, the methanol adsorption isotherms (Figure 2b) reveal a much larger adsorption capacity for PDVB-VI-0.5 compared to hydrotalcite, in good agreement with the superwettability of PDVB-VI-0.5 for methanol. Furthermore, tests for CO_2 adsorption in air show that PDVB-VI-*n* samples cannot adsorb CO_2 while PDVB-VI-0.5-Q can adsorb small amounts of CO_2 (Table S1).

Catalytic data on the transesterification of tripalmitin over various catalysts is presented in Table 1. Conventional solid bases, such as Amberlite 400, hydrotalcite, CaO, NaOH, and KOH, are active for this reaction. Among these catalysts Amberlite 400, hydrotalcite, CaO, and NaOH show relatively low yields (79.8–85.2% in 3 h, entries 11, 12, 15, and 18), while KOH is very active (99.6% in 1 h, entry 16). However, after exposure to air the activity of KOH is reduced (94.6% in 1 h, entry 17) due to its sensitivity to CO_2. 1-vinylimidazolate monomer (VI) shows a high yield (97.3% in 3 h, entry 14), indicating that imidazole sites are very active towards the transesterification. After polymerization, the PVI sample shows a lower conversion than VI, which is due to the better dispersion of catalytic basic sites in the (liquid) monomer compared to the polymer. Interestingly, the solid base catalysts co-polymerized from DVB and VI (PDVB-VI-*n*, $n=0.2$–0.5) exhibited much higher activities than VI monomer, considering that the number of catalytically active sites in the PDVB-VI-*n* samples is much lower than that of the VI monomer. For example, after 1 h, PDVB-VI-0.5 gave a yield of 99.3%, while VI monomer gave a yield of 67.2%. However, after quaternary ammonization, PDVB-VI-0.5-Q sample shows lower activity, giving the yield of 63.1%. Compared with VI monomer, it is clear that PDVB-VI-*n* samples have superhydrophobic property. Apparently, the superhydrophobicity plays a critical role in enhancing catalytic activity in the transesterification. The significant reduction in yield over PDVB-VI-0.5-Q compared to PDVB-VI-0.5 can be reasonably attributed to the change in the hydrophobicity, because both samples have a similar composition and similar textural parameters. Possibly, superhydrophobicity and good oleophilicity of PDVB-VI-*n* are very favorable for the miscibility of methanol with tripalmitin.[10] Once a hydrophilic glycerol by-product is formed the molecules quickly leave the hydrophobic catalysts, promoting

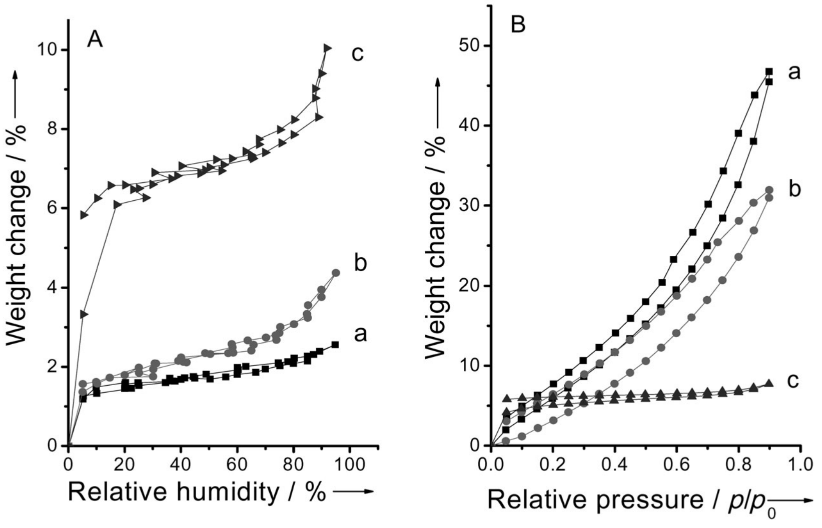

Figure 2. (A) Adsorption curves for water at different humidities, and (B) adsorption curves for methanol at different relative pressures, over: (a) PDVB-VI-0.5, (b) PDVB-VI-0.5-Q, and (c) hydrotalcite.

the transesterification reaction,[11] in good agreement with the high contact angle of glycerol on PDVB-VI-0.5 (Figure 1 d).

Figure 3 shows the dependencies of the catalytic activities of PDVB-VI-0.5, KOH, and CaO in the transesterification of tripalmitin with methanol versus time, giving more insight into catalytic kinetics. For example, at $t=10$ min PDVB-VI-0.5 and KOH exhibited yields of 53.8 and 46.5 %, respectively. Since the same mass (0.05 g) of KOH has more alkaline sites (0.89 mmol) than PDVB-VI-0.5 (0.14 mmol), these results suggest that PDVB-VI-0.5 is a more active catalyst than KOH.

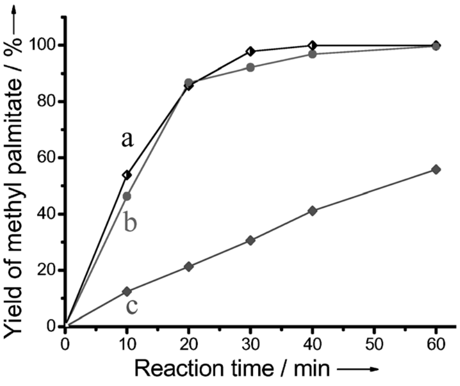

Figure 3. Catalytic activity versus time in the transesterification of tripalmitin with methanol over (a) PDVB-VI-0.5, (b) KOH, and (c) CaO. Conditions: 0.05 g catalyst, 0.84 g tripalmitin, 3.76 mL methanol, 65 °C.

In addition, the PDVB-VI samples have superior recycling properties. For example, after recycling 3 and 5 times in air under atmospheric pressure, PDVB-VI-0.5 still gave yields of 99.2 and 98.9 %, respectively (Table 1, Figure S10). This is due to the stable imidazole transesterification sites in the solid catalysts. Particularly, imidazole sites cannot be poisoned by CO_2 in air, which is confirmed by the adsorption of CO_2 on PDVB-VI samples (Table S1). In contrast, conventional solid base catalysts are very sensitive to CO_2.[6a] Moreover, the superhydrophobicity of the PDVB-VI samples strongly reduces the effect of water on recyclability.[10b]

The catalyst activity was lowered when methanol was replaced with ethanol or 1-butanol, giving yields of 64.3 % ethyl palmitate and 55.1 % butyl palmitate after 3 h (Table 1, entries 9 and 10). Besides intrinsic catalytic behavior, this phenomenon might be attributable to the lower wettability of the PDVB-VI-0.5 sample for ethanol and 1-butanol than for methanol, as shown in Figure S9.

Eruca Sativa Gars (ESG) is a low-cost plant oil ($0.15 kg in China)[12] that has been used as a feedstock for biodiesel production. ESG oil normally contains both free fatty acids (3.6 %) and water (0.08 %) as impurities,[12] which easily poison conventional basic catalysts.[11a] However, after transesterification of ESG oil with methanol for 2 h over PDVB-VI-0.5 the major products (Table S2) were fatty acid methyl esters (yield 88.1 %), including methyl palmitate ($C_{16:0}$, 6.9 %), methyl stearate ($C_{18:0}$, 4.1 %), methyl oleate ($C_{18:1}$, 25.8 %), methyl linoleate ($C_{18:2}$, 49.2 %), and methyl γ-linolenate ($C_{18:3}$, 2.1 %). These catalytic data indicate that the PDVB-VI-0.5 catalyst is very active towards transesterification of plant oil with methanol; even more active than a solid acid-catalyzed procedure reported earlier (SO_4^{2-}/ZrO_2-SiO_2-Et hybrid catalyst, yield 63.1 % in 24 h).[13] Importantly, the imidazole sites in the PDVB-VI-0.5 catalyst are not sensitive to free fatty acids and water, and saponification does not appear to take place. Free fatty acids usually consume conventional base catalysts, such as NaOH, due to saponification. Additionally, the transesterification of ESG oil with methanol was carried out under very mild conditions (65 °C and 1 atm), which is potentially important for the large-scale industrial production of biodiesel. In contrast, conventional base catalysts are generally performed at higher temperatures (130–150 °C) and pressures (1.7 MPa).[10a]

In summary, superhydrophobic and porous solid base catalysts are successfully synthesized by co-polymerization of divinylbenzene and 1-vinylimidazolate for the first time. Catalytic tests in the methanol transesterification of both tripalmitin and ESG oil show that the solid base catalysts are much more active and stable than conventional base catalysts such as basic resin, hydrotalcite, CaO, and NaOH, which is of great importance for production of clean biodiesel from low-cost renewable feedstocks.

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