Transesterification Catalyzed by Superhydrophobic–Oleophilic Mesoporous Polymeric Solid Acids: An Efficient Route for Production of Biodiesel

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Abstract We report here an efficient mesoporous polymeric solid acid catalyst (p-PDVB-SO$_3$H) with superhydrophobic–oleophilic properties synthesized from copolymerization of divinylbenzene (DVB) with sodium p-styrene sulfonate under solvothermal conditions. N$_2$ isotherm showed that p-PDVB-SO$_3$H has large BET surface area and uniform mesopore. Contact angle tests showed that p-PDVB-SO$_3$H exhibits superhydrophobic–oleophilic property for triolein and methanol, which results in its good miscibility and high exposion degree of active sites for various organic reactants. Catalytic tests showed that p-PDVB-SO$_3$H has much better catalytic activities and recyclability toward transesterification to biodiesel than those of H-form mesoporous ZMS-5 zeolite, carbon solid acid and commercially acidic resin of Amberlyst 15, which will be very important for its wide applications for biodiesel production in industry.

Keywords Solid acids · Transesterification · Biodiesel · Hydrophobic mesoporous polymers · Recyclability

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1 Introduction

Increase in energy demand and environmental concerns coupled with depletion in world petroleum reserves have been the primary drivers for the development of alternative and renewable sources of energy. Biodiesel is a renewable fuel comprising of alkyl esters. It is made from vegetable oil and animal fat and offers advantages of renewability, better lubricity and biodegradability. Additionally, in comparison to petrodiesel, its use results in decreased particulate emission, unburned hydrocarbons and carbon monoxide [1–6].

The production of biodiesel was usually achieved toward transesterification of triolein with short-line alcohol catalyzed by acid or base catalysts [7–10]. Compared with base catalysts, acid catalysts can simultaneously catalyze both esterification and transesterification without forming any soap, unlike base catalysts [7–10]. Thus they can be employed to produce biodiesel from low-quality and low cost feedstock such as waste cooking oil or renewable plants oil [7–10]. Although conventional mineral acids such as H$_2$SO$_4$ or HCl are excellent catalysts for converting crude oils to biodiesel, they are environmentally unfriendly and difficult to recycle in addition to being highly corrosive, which strongly restricts their wide applications [11–16]. On the other hand, solid acids such as sulfated zirconia, heteropolyacids and acidic resins, on the other offer advantages of recyclability and reduced corrosion. Additionally, being environmental friendly, they have been widely used for production of biodiesel at laboratory scale [11–16]. However their poor porosity restricts their catalytic capabilities and largely constrains their application in biodiesel production [11–16]. Mesoporous solid acids, with high BET surface areas, abundant and uniform mesoporosity overcome the disadvantage of porosity limitations [17–19], which exhibit very good catalytic activities in various acid-catalyzed reactions. Typical mesoporous solid acids such as

sulfonic group functional mesoporous silicas (SBA-15-SO_3H), mesoporous sulfated ZrO_2 acidic resins and carbon based solid acids [10, 20, 21] have been studied with good results in esterifications and transesterifications [10, 20, 21]. The limitation on their catalytic activity arises from their inorganic hydrophilic framework and hence low miscibility for various organic substrates [22–24].

Very recently, Liu et al. [24] have successfully synthesized mesoporous polydivinylbenzene (p-PDVB-SO_3H) based solid acids with superhydrophobicity and good oleophilicity, which exhibits excellent catalytic activities in esterification and condensation. The superhydrophobicity and good oleophilicity result in its superior wettability and good miscibility with organic substrates, which were favorable characteristics for the enhancement of its catalytic activity. Thus, synthesis of mesoporous solid acids with good oleophilic polymer network can significantly improve its catalytic activities for biodiesel production toward transesterification. In this work, we demonstrate an efficient route for production of biodiesel by transesterification reaction catalyzed by p-PDVB-SO_3H. The improvement in catalytic efficiency and recyclability have been correlated with surface area, good stability, and excellent hydrophobicity of p-PDVB-SO_3H, which was much better than those of mesoporous ZMS-5 zeolite, carbon based solid acid and commercial Amberlyst 15. The superior catalytic activity and recyclability of p-PDVB-SO_3H in transesterification will be potentially important for its wide applications for biodiesel production in industry.

2 Experimental Section

2.1 Chemicals and Reagents

All chemicals were of analytical grade and used as purchased without further purification. Sodium p-styrene sulfonate, nonionic block copolymer surfactant poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) block copolymer (P123, molecular weight of about 5,800), 3-mercaptopropyltrimethoxysilane (3-MPTS), tetrapropyl ammonium hydroxide (TPAOH) and Amberlyst 15 were purchased from Sigma-Aldrich Company, Ltd. (USA). DVB monomer, initiator of azobisisobutyronitrile (AIBN), tetraethyl orthosilicate (TEOS), sodium aluminate, methanol, triolein and sulfuric acid were obtained from Tianjin Guangfu Chemical Reagent. H-form of Beta zeolite and ultrastable Y zeolite (USY) were supplied by Sinopec Catalyst Co.

2.2 Preparation of p-PDVB-SO_3H

The p-PDVB-SO_3H was synthesized from copolymerization of sodium 4-vinylbenzenesulfonate (SVBS) with DVB by using AIBN initiator under solvothermal conditions. As a typical run, 2.0 g of DVB and 0.5 g of SVBS functional monomer were added to a mixture of 0.065 g of AIBN, 25 mL of THF and 2.5 mL of distilled water, after stirring of the reaction mixture for 2 h at room temperature, the mixture was treated by autoclaving at 100 °C for 1 day and evaporating of the solvents at room temperature. The resultant solid obtained is white in color. Then the resulted sample was ion exchanged by using sulfuric acid as follows: 1.0 g of resulted Na-form solid acid was added into a mixture of 30 mL of distilled water, 10 mL of ethanol and 5 mL of sulfuric acid, vigorously stirred for 24 h, filtered and washed with large amount of water until neutral. The sample was dried at 80 °C for 6 h prior to use, giving the sample of p-PDVB-SO_3H. For comparison, mesoporous ZMS-5 zeolite and carbon solid acid were synthesized according to the literature [25, 26].

The acid-exchange capacity of various catalysts was determined by acid–base titration with standard NaOH solution. As a typical run, 0.1 g of catalyst was added into 25 mL of 2 M aqueous NaCl solution, after stirring for 24 h at room temperature until equilibrium was reached, the resulted suspension was titrated by drop wise addition of standard NaOH solution.

2.3 Characterizations

Nitrogen isotherms were measured using a Micromeritics ASAP 2020 M system. The samples were outgassed for 10 h at 150 °C before the measurements. The Barrett–Joyner–Halenda (BJH) model was used to calculate the pore-size distribution for mesopores. A Bruker 66 V FTIR spectrometer was used for FTIR spectral measurements. Acid–base titration with standard NaOH solution was employed to estimate the acid exchange capabilities of the catalysts. Elemental analyses (C, H, N and S) were performed on a Perkin-Elmer series II CHNS analyzer 2400. Thermogravimetric analysis (TG) were performed on a Perkin-Elmer TGA7 and a DTA-1700 in flowing air, respectively. The heating rate was 20 °C/min.

2.4 Catalytic Reactions

Model transesterification reactions were carried out on triolein with methanol. As a typical run, 2 g (2.26 mmol) of triolein was added into a three-necked round flask equipped with a condenser and a magnetic stirrer, then the temperature was rapidly increased to 65 °C. 10.9 mL of methanol and 0.05 g of catalyst were quickly added under vigorous stirring, the reaction was kept at 65 °C for 16 h. The molar ratio of triolein/methanol was 1:120 and the mass ratio of catalyst/triolein was 0.05. The reaction products were analyzed by gas chromatography (Agilent 5390) with a flame ionization detector (FID).

The recycling experiment of *p*-PDVB-SO$_3$H was performed by separation of *p*-PDVB-SO$_3$H from reaction media by centrifugation, washing with large amount of ethanol for removing of adsorbed reactants or products, and drying at 80 °C for 4 h. The recycled *p*-PDVB-SO$_3$H was activated by 0.1 M H$_2$SO$_4$ at room temperature for 4 h before the next time use.

3 Results and Discussion

3.1 Catalyst Characterization

Figure 1 shows the N$_2$ isotherms and pore size distribution of *p*-PDVB-SO$_3$H. Clearly, *p*-PDVB-SO$_3$H shows a type-IV curve with a sharp capillary condensation step at P/P$_0$ = 0.8–0.95, indicating the formation of obviously mesopores in the sample, which exhibits relative high BET surface area (171 m^2/g) and large pore volume (0.52 cm^3/g), much higher than those of Amberlyst 15 and carbon based solid acid (Table 1). Correspondingly, *p*-PDVB-SO$_3$H shows very uniform pore size centered at 21.2 nm, in good agreement with the results published by us previously [22]. Additionally, the S content and H concentration of *p*-PDVB-SO$_3$H were 1.3 and 1.8 mmol/g respectively, higher than those H form mesoporous ZSM-5 (0.92 mmol/g), lower than those of Amberlyst 15 (4.7 mmol/g) and C–SO$_3$H (2.0 mmol/g). Interestingly, only a little decreasing of S content and H concentration could be observed in *p*-PDVB-SO$_3$H after recycled for five times, which should be attributed to partial deactivation and coverage of active sites during recycling experiment. It should also be noted here that the increasing of the concentration of active sites usually results in the decreasing of BET surface areas of the samples [22].

Fig. 1 N$_2$ isotherms and pore size distribution of *p*-PDVB-SO$_3$H
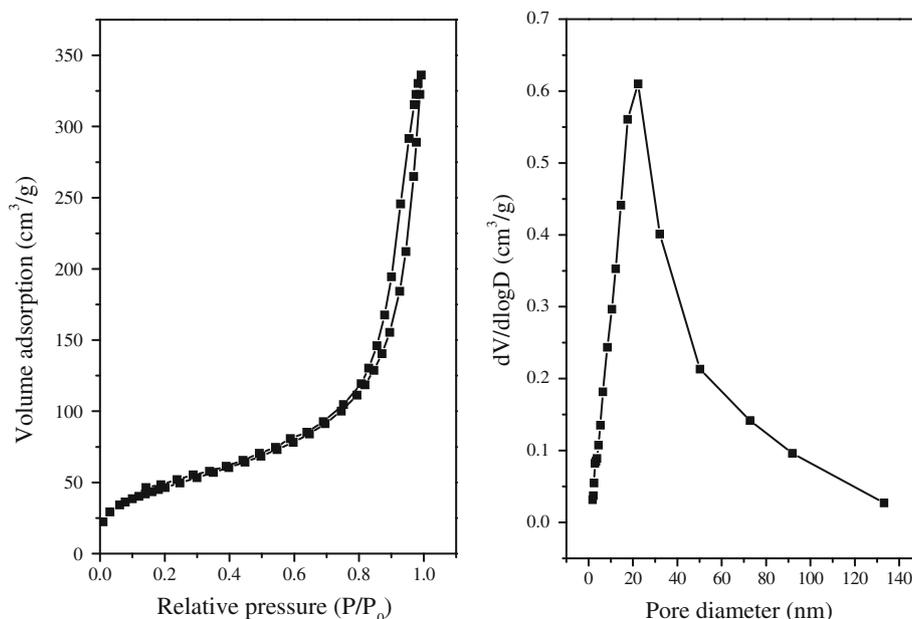
Table 1 The textural and acidic parameters of various solid acid catalysts

| Run	Samples	S content (mmol/g)[a]	Acid sites (mmol/g)[b]	S$_{BET}$ (m^2/g)	V$_p$ (cm^3/g)	D$_p$ (nm)[c]
1	*p*-PDVB-SO$_3$H	1.30	1.8	171	0.52	21.5
2	*p*-PDVB-SO$_3$H[d]	1.26	1.68	165	0.50	22.3
3	Amberlyst 15	4.30	4.70	45	0.31	40
4	C–SO$_3$H	1.91	2.0	10<	–	–
5	Mesoporous ZMS-5[e]	–	0.92	368	0.31	14.5

[a] Measured by CHNS elemental analysis

[b] Measured by acid–base titration

[c] Pore size distribution estimated from BJH model

[d] The sample after being recycled for two times in transesterification of triolein with methanol

[e] Si/Al ratio at 40
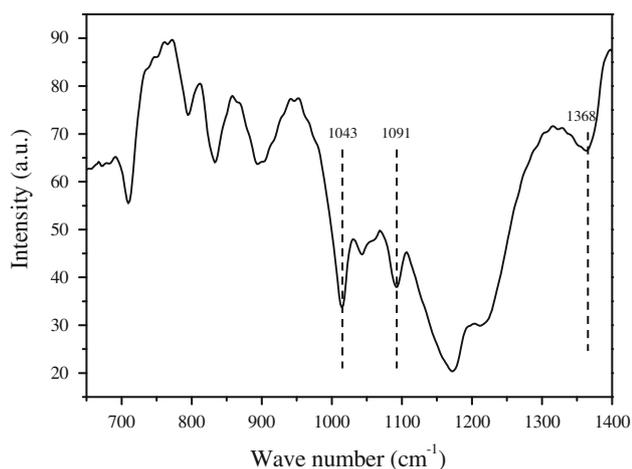
Fig. 2 FT-IR spectrum of *p*-PDVB-SO₃H

Figure 2 shows the FT-IR spectrum of *p*-PDVB-SO₃H. Notably, the peak at 1,042 cm^{-1} associated with C–S bond could also be clearly observed in *p*-PDVB-SO₃H; In the meanwhile, other peaks at around 1,092 and 1,368 cm^{-1} associated with S=O bond could be clearly observed; Above results confirmed that the sulfonic group has been successfully grafted onto the network of *p*-PDVB-SO₃H.

Figure 3 shows the contact angles of *p*-PDVB-SO₃H for water and triolein. Notably, the water droplet contact angle of 150°, on the surface of *p*-PDVB-SO₃H indicates its superhydrophobic nature; On the contrary, the contact angle of soybean oil or methanol droplet on the surface of *p*-PDVB-SO₃H is nearly 0° indicating its super wettability for oil and methanol. Interestingly, the contact angle of 120° for glycerin on the same surface indicates a good anti-wettability for glycerin. The super wettability of *p*-PDVB-SO₃H for oil and good anti-wettability for glycerin and water were favorable for enhancement of its catalytic activities in transesterification of oil with methanol. To the best of our knowledge, solid acids with good hydrophobic and oleophilic properties have not been reported previously.

Figure 4 shows TG curves of *p*-PDVB-SO₃H and Amberlyst 15, both of them demonstrate the weight loss associated with the desorption of adsorbed water, destruction of sulfonic group and polymeric network ranged from 30 to 150, 200 to 440 and 440 to 540 °C; Notably, the weight loss assigned to destruction of sulfonic group and polymeric network were centered at around 364 and 497 °C, which were much higher than those of Amberlyst 15 (295–439 °C), indicating the better thermal stability of *p*-PDVB-SO₃H than that of commercial Amberlyst 15. Similar results have also been reported previously [22, 23].
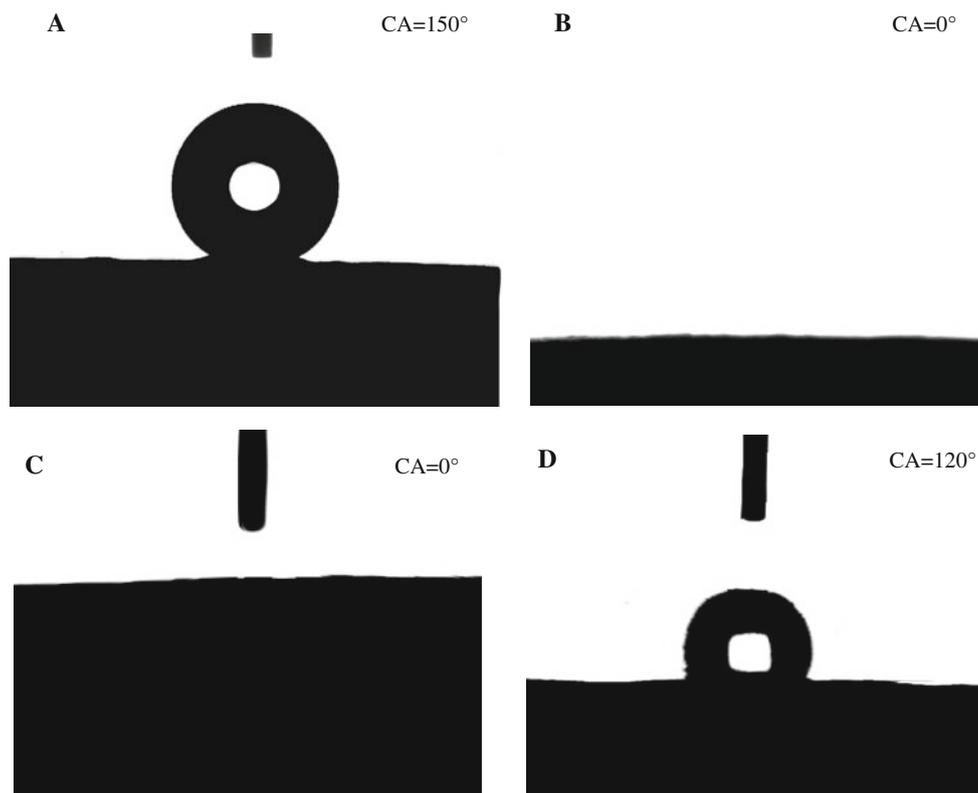

Fig. 3 Contact angles of **a** water droplet, **b** triolein droplet, **c** methanol and **d** glycerin on the surface of *p*-PDVB-SO₃H
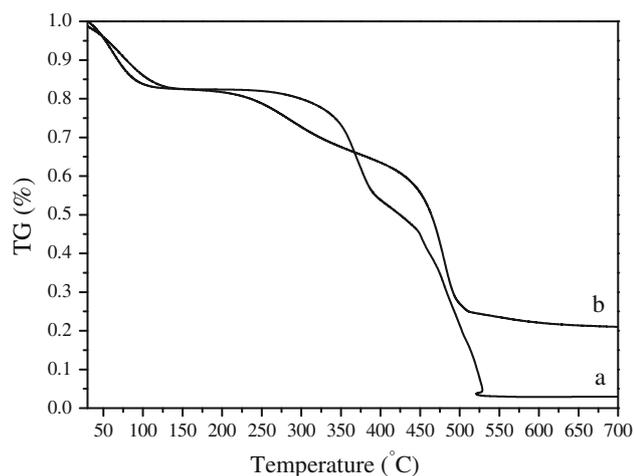
Fig. 4 TG-DTA curves of *a* p-PDVB-SO$_3$H and *b* Amberlyst 15

3.2 Catalytic Reactions

Figure 5 shows the catalytic kinetics curves in transesterification of triolein with methanol catalyzed by various catalysts. Clearly, p-PDVB-SO$_3$H showed very good catalytic activities when compared with those of mesoporous ZMS-5 zeolite, carbon based solid acid and Amberlyst 15. After only 4 h of reaction, the conversion of triolein catalyzed by p-PDVB-SO$_3$H was much higher than those of H-form mesoporous ZSM-5, Amberlyst 15, and carbon based solid acid (Fig. 5). After 16 h of reaction time, the conversion of triolein catalyzed by p-PDVB-SO$_3$H was up to 78.3 %, which was much higher than those of H-form mesoporous ZSM-5, Amberlyst 15 and carbon solid acid (57.32, 43.23 and 40.23 % respectively), suggesting the excellent catalytic activities of p-PDVB-SO$_3$H in transesterification for production of biodiesel. It should be also noted here that the TOF value of p-PDVB-SO$_3$H was 1.71 h^{-1}, much higher than those of Amberlyst 15 (0.28 h^{-1}) and carbon solid acid (0.60 h^{-1}), similar with that of H-form mesoporous ZSM-5 (1.75 h^{-1}), which indicates good activities per sites in p-PDVB-SO$_3$H
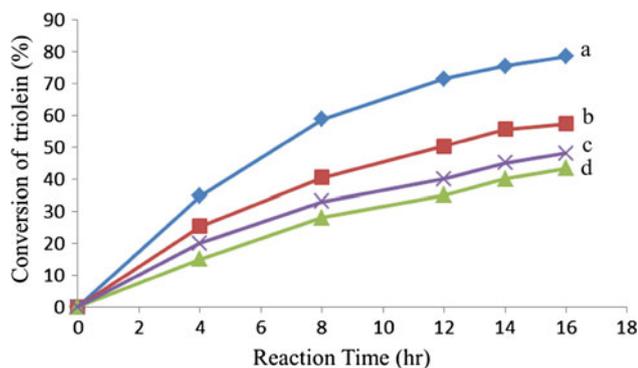
Fig. 5 Catalytic kinetics curves in the transesterification of triolein with methanol catalyzed by *a* p-PDVB-SO$_3$H, *b* H-form mesoporous ZMS-5 zeolite, *c* Amberlyst 15 and *d* carbon solid acid
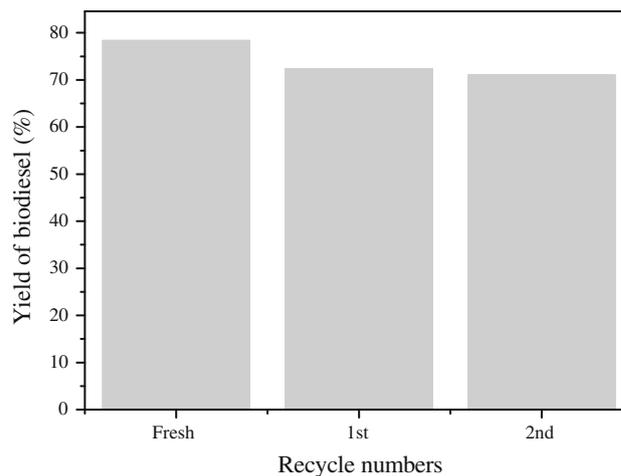
Fig. 6 p-PDVB-SO$_3$H catalyst recyclability for transesterification of triolein with methanol (T = 65 °C, time = 16 h)

when compared with various conventional solid acids. The excellent catalytic performance per sites in p-PDVB-SO$_3$H should be attributed to its unique hydrophobic–oleophilic property. The superhydrophobic network results in the good anti-wettability for the byproduct of glycerin (Fig. 3d), which largely constrains the reverse reaction, further resulting in the high yields of biodiesel [23, 27]. On the other hand, the super-oleophilic property results in the good dispersion of p-PDVB-SO$_3$H in reaction media [24], which leads to the high exposition degree of active sites in p-PDVB-SO$_3$H [28], further resulting in its excellent catalytic activities for biodiesel production.

Figure 6 shows the recyclability of p-PDVB-SO$_3$H in transesterification of triolein with methanol. Compared with fresh p-PDVB-SO$_3$H (conversion at 78.3 %), after recycled for one time, the sample showed the conversion of triolein at 72.3 %, further recycled for two times, the conversion of triolein was still up to 71.0 %. The little decrease in catalytic activities of p-PDVB-SO$_3$H should be attributed to partially coverage of active sites during recycling processes, which confirms that p-PDVB-SO$_3$H do not suffer instant deactivation. The good recyclability of p-PDVB-SO$_3$H comes from its opened and abundant mesoporosity, good thermal stability.

4 Conclusions

In summary, an efficient solid acid of p-PDVB-SO$_3$H with hydrophobic and good oleophilic network was successfully prepared through copolymerization of DVB with sodium 4-vinylbenzenesulfonate. The solid acid exhibited the characteristics of high BET surface area, large pore volume, a stable and hydrophobic network and a high concentration of active sites, which result in their superior

catalytic activities and recyclability in transesterification of triglyceride or plant oil with methanol for production of biodiesel as compared with those of conventional solid acid including H-form mesoporous zeolite, Amberlyst-15 and carbon based solid acid. The successful synthesis of p-PDVB-SO$_3$H will be potentially important for production of biodiesel toward transesterification in industry.

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