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Clean synthesis of biodiesel over solid acid catalysts of sulfonated mesopolymers

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FDU-15-SO₃H, a solid acid material prepared from the sulfonation of FDU-15 mesoporous polymer, has been demonstrated to serve as an efficient catalyst in the esterification of palmitic acid with methanol as well as in the transesterification of fatty acid-edible oil mixture. FDU-15-SO₃H achieved an acid conversion of 99.0% when the esterification was carried out at 343 K with a methanol/palmitic acid molar ratio of 6:1 and 5 wt% catalyst loading. It was capable of giving 99.0% yield of fatty acid methyl esters (FAME) when the transesterification of soybean oil was performed at 413 K and the methanol/oil weight ratio of 1:1. FDU-15-SO₃H was further applied to the transesterification/esterification of the oil mixtures with a varying ratio of soybean oil to palmitic acid, which simulated the feedstock with a high content of free fatty acids. The yield of FAME reached 95% for the oil mixtures containing 30 wt% palmitic acid. This indicated the sulfonated mesopolymer was a potential catalyst for clean synthesis of fuel alternative of biodiesel from the waste oil without further purification.

mesoporous polymer, sulfonation, esterification, transesterification, biodiesel

1 Introduction

Environmental pollution, fossil resource crisis and frequent economical unbalance have forced human beings to take full advantage of renewable energy. In March 2008 the Chinese government announced that renewable energy will constitute 10% of China's energy consumption by 2010 [1]. Such a big thrust for reducing the reliance on fossil fuels also occurs worldwide. Regenerable biodiesel, derived from bio-grease (plant oil and animal fat) and free fatty acids, becomes more attractive than ever, as it can reduce net carbon dioxide emissions by 70% compared to conventional diesel fuels [2].

Because triglycerides, the main composition of refined bio-grease, have an excessively high viscosity, they are not suitable for direct use through blending with petroleumbased diesel. Four major techniques including dilution, microemulsion, pyrolysis, and transesterification are considered to reduce their viscosity. In particular, the transesterification biodiesel of fatty acids methyl esters (FAME) is considered to be a green fuel free of sulfur and aromatics. The catalytic transesterification with short-chain alcohols is therefore mostly applied to the conversion of triglyceride to FAME. The transesterification catalysts include bases, acids and enzymes [3]. Normally, the transesterification of triglycerides occurs readily under relatively mild conditions with the presence of sodium hydroxide, potassium hydroxide and sodium methoxide. However, using these homogeneous base catalysts inevitably requires troublesome procedures for product purification. Thus, many efforts have been made to develop heterogeneous processes by using zeolite [4-6], salts and metal oxides [4, 5], alumina loaded with alkali metal compounds [7-10], hydrotalcites [5], or anionic ionexchange resin [11].

The utilization of refined greases raises the manufactur-

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ing cost for biodiesel commercialization. The recovered waste oil is naturally favored as a desirable raw material. In addition to triglycerides, the waste oil also contains a relatively large amount of free fatty acids resulted from hydrolysis in the course of utilization or preservation. The presence of free fatty acids would induce saponification and poisoning of base catalysts when using waste oil as the feed stock for the transesterification. The purification procedure required for removing the free fatty acids in waste oil would apparently complicate the biodiesel synthesis process based on the base-catalyzed transesterification.

With the capacity of catalyzing both the esterification of free fatty acids and the transesterification of triglycerides, the acids emerge as more applicable catalysts. Liquid acids, such as H_2SO_4 , HCl, carboxylic salts [12–14] and organic sulfonic acids [15], are reported to work in the aforementioned reactions, but they suffer drawbacks in reuse and product separation. To solve the separation problem, the biodiesel synthesis is thus tried on solid Lewis acids [16–19], sulfonated zirconia [20], organic-inorganic hybrid acid materials [21–23], sugar-SO₃H catalysts [24–27], acidic ion-exchange resins [28, 29] and ionic liquid-type Brönsted acids [30, 31].

An ideal heterogeneous catalyst for biodiesel production should be characteristic of hydrophobic structures, high thermal stability as well as abundant accessible acid sites located within open reaction space. Among the heterogeneous catalysts mentioned above, inorganic solid acids such as niobic acid [16] and zeolites [17] showed a mediocre activity because of poor acidity and narrow microporosity. Although sodium molybdate [18] and Lewis acid/surfactant cerium trisdodecylsulfate [19] are claimed to be efficient, they are not stable enough in oil because of metal ion leaching. With respect to organic-inorganic hybrid acid and sulfonated zirconia, their hydrophilic nature makes them hardly contact with reactants unless at extremely high reaction temperatures. The sugar-SO₃H catalysts exhibit a good potentiality, but their limited reaction space may retard the reaction. The acidic ion-exchange resins face the drawbacks of low thermal stability.

Recently, a series of FDU-type mesoporous polymers have been developed through self-assembly of a resol precursor with a triblock surfactant. These materials have variable mesostructures, highly ordered mesopores, large surface areas, and in particular a thermal stability as high as 623 K [32, 33]. Using a unique vapor-phase sulfonation, we have prepared FDU-SO₃H solid acid, which maintains the mesostructures, contains a large quantity of acid sites, and shows attractive catalytic activities in Beckmann rearrangement and condensation of bulky molecules [34]. We report here the catalytic properties of sulfonated mesopolymers in the esterification of palmitic acid and transesterification of fatty acid-oil mixture. Compared with other acid catalysts, FDU-15-SO₃H manifests its superiority for biodiesel production as a heterogeneous catalyst.

2 Experimental

2.1 Preparation of the catalysts

FDU-15-SO₃H [34] and sugar-SO₃H [24] were prepared according to previously reported methods via sulfonation of mesopolymers and carbon derived from sugar carbonization, respectively. Proton-type zeolites, H-ZSM-5 (Si/Al = 38) and H-Beta (Si/Al = 25) were obtained by conventional hydrothermal synthesis, while the acidic resins, *p*-toluene-sulfonic acid and sulfuric acid were commercially available.

2.2 Characterization methods

The small angle powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 ADVANCE instrument. Nitrogen adsorption-desorption isotherms were measured at 77 K on a Quantachrome Autosorb-3B instrument after the samples were outgassed at 473 K at least for 5 h prior to investigation. HRTEM images were taken on a JEOL-JEM-2010 microscope. FT-IR spectra were recorded on a Nicolet Fourier transform infrared spectrometer (NEXUS 670) using KBr technique. The amount of acid sites was quantified by acid-base titration following previously reported procedures [35]. The amount of Al in the zeolites was quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer.

2.3 Catalytic reactions

In the esterification experiment, 3 mmol palmitic acid (Alfa Aesar, 95%), 90 mmol methanol and 0.038 g catalyst (corresponding to 5 wt% palmitic acid) were mixed in a closed container. The reaction was then carried out under stirring at 343 K for 2 h.

The transesterification was carried out using 2.0 g soybean oil (SBO), 2.0 g methanol and 0.1 g FDU-15-SO₃H catalyst (corresponding to 5 wt% of SBO) at 413 K for 5 h. As for the reaction of fatty acid/oil mixture, the total weight of fatty acid and SBO was kept at 2.0 g while the percentage of fatty acid was varied in the range of 30–70 wt% by blending palmitic acid or stearic acid in SOB. For example, 0.6 g palmitic acid was blended in 1.4 g SBO to obtain the acid/oil mixture of 30% palmitic acid +70% SBO.

The FAME products were identified using authentic chemicals commercially available or determined on a GC-MS spectrometer (Agilent HP6890/5973N). Their amounts were quantified on a Shimadzu 14B gas chromatograph equipped with a capillary column (DM-WAX, 30 m \times 0.25 mm \times 0.25 µm) using *n*-eicosane as an internal standard.

3 Results and discussion

3.1 Catalyst characterizations

The FDU-15 mesoporous polymer and the corresponding

 SO_3H -functionalized sample have been characterized by powder X-ray diffraction, N₂ adsorption, high resolution transmission electron microscopy and FT-IR spectroscopy. The concentration of acid sites of the samples was quantified by acid-base titration.

The low-angle XRD patterns indicated that FDU-15 had a well-ordered 2D hexagonal structure with *p6mm* space group (Figure 1(a)). After sulfonation, the hexagonal mesostructure was still retained although the diffraction peaks of FDU-15-SO₃H slightly shifted to higher angles as a result of shrinkage. These negligible changes indicated that the vaporphase sulfonation by putting mesopolymer powder over fuming sulfuric acid avoided the collapse of the original mesostructure, which occurred easily when FDU-15 mesopolymer was immersed directly in sulfuric acid solution.

The HRTEM images shown in Figure 2 further confirmed that FDU-15-SO₃H still possessed the *P6mm* symmetry. Viewed along both [10] and [11] directions, the array of mesopores in FDU-15-SO₃H suggested a hexagonal structure with ordered channels. The pore diameter estimated from the images was approximately 2–3 nm. The BJH pore distribution given by N₂ adsorption isotherm showed a maximum centered at 2.7 nm (not shown). Thus, the pore size of FDU-15-SO₃H was in good agreement with



Figure 1 XRD patterns of FDU-15 (a), fresh FDU-15-SO₃H (b), FDU-15-SO₃H reused for 3 times (c), and after resulfonation (d).



Figure 2 HRTEM images of FDU-15-SO₃H viewed in the [10] direction (a) and in the [11] direction (b).

the results which we reported previously [34]. In the catalysis of esterification and transesterification, these nanosized pores are expected to decrease the internal mass transfer limitation and to accommodate bulky molecules of triglyceride easily.

FT-IR spectroscopy was adopted to characterize the SO₃H groups grafted onto the benzene rings embedded in the polymer matrix. In comparison to FDU-15 parent, the distinguished feature of FDU-15-SO₃H was the development of a new IR band at 1034 cm⁻¹ in addition to other bands assigned to organic groups (Figures 3(a) and (b)). This band is attributed to the symmetric stretching of S=O bond, and can be taken as the definite evidence that the SO₃H groups have been introduced into the mesoporous polymers. The acid-base titration indicated that the acid site concentration of FDU-15-SO₃H was 1.0 mmol g⁻¹.

3.2 Catalytic activity of FDU-15-SO₃H in the esterification of palmitic acid with methanol

Table 1 first compares the conversions of palmitic acid over FDU-15-SO₃H with those obtained on other acid catalysts such as H-Beta, H-ZSM-5, sugar-SO₃H, acidic resin and liquid acids under the same reaction conditions. The conversion of palmitic acid on FDU-15-SO₃H reached 99% (Table 1, No. 1), which was comparable to the conversions obtained with H₂SO₄ or *p*-toluenesulfonic acid (Table 1, Nos. 2 and 3). However, the absolute amount of acid sites contained in FDU-15-SO₃H was much less at the same catalyst weight. Other solid acids such as microporous zeolites, acidic resins and sugar-SO₃H showed much lower palmitic acid conversion than FDU-15-SO₃H (Table 1, Nos. 4-8). To afford a conversion as high as 96%, the esterification over sugar-SO₃H with an excessively low surface area required more intensified conditions, i.e., increasing the catalyst amount, raising the reaction temperature and prolonging the reaction time as well (Table 1, No. 9).



Figure 3 IR spectra of FDU-15 (a), FDU-15-SO₃H (b), FDU-15-SO₃H reused for 3 times in transesterification (c), and FDU-15-SO₃H used again after sulfonation (d).

No.	Catalyst	Surface area $(m^2 g^{-1})$	Acid amount ^{a)} (mmol g^{-1})	Ester. conv. ^{b)} (mol%)	Transester. yield c) (wt%)
1	FDU-15-SO ₃ H	447	1.0	99.0	99.0
2	H_2SO_4	_	20.4	99.0	99.5
3	p-toluenesulfonic acid	_	5.8	99.0	99.6
4	H-ZSM-5 (Si/Al=38)	420	-	13.3	-
5	H-Beta (Si/Al=25)	330	-	5.7	-
6	Dowex 50*2-100	~10	0.6	26.2	8.0
7	Amberlyst-15	40-50	4.6	56.1	41.6
8	sugar-SO ₃ H	2	1.0	65.0	86.0
9	sugar-SO ₃ H ^{d)}	2	1.0	96.0	-

Table 1 The results of esterification and transesterification catalyzed with various catalysts

a) By acid-base titration. b) Esterfication: 3 mmol palmitic acid; 90 mmol MeOH; 5 wt% catalyst; 343 K; 2 h. c) Transestrification: 2 g SBO; 2 g MeOH; 5 wt% catalyst; 413 K; 5 h. d) 3 mmol palmitic acid; 90 mmol MeOH; 7.5 wt% sugar-SO₃H; 353 K; 5 h.

The advantages of FDU-15-SO₃H are essentially contributed by its abundant acid sites achieved by an efficient gas-solid sulfonation process. In addition, other unique characteristics of it such as high hydrophobicity related to an organic framework, large surface area (447 m² g⁻¹) and nanosized pores (2.7 nm) are also presumed to be beneficial to easy accommodation of bulky molecules. Thus, FDU-15-SO₃H is superior to zeolites, Amberlyst-15 and sugar-SO₃H in the esterification of palmitic acid.

The homogeneous acids of H_2SO_4 and *p*-toluenesulfonic acid worked efficiently for the esterification of palmitic acid at a high acid density (Table 1). However, when the reaction was performed at the same molar amount of acid sites, H_2SO_4 turned to be less effective than FDU-15-SO₃H (Table 2, No. 2). In the two-phase system, the organic framework of FDU-15-SO₃H would be beneficial for adsorption of grease molecules into the pores and then made them protonated easily by the acid sites therein. The H_2SO_4 turned to stay away from the phase of oil. PTSA has the highest hydrophobicity and more easily attacks the hydrophobic triglyceride molecules to give good esterification performance (Table 2, No. 3), but its homogeneous feature causes problems in product separation.

3.3 Catalytic activity of FDU-15-SO₃H for transesterification

In the transesterification of waste oil containing free fatty acids, acid catalysts are capable of simultaneously catalyzing the esterification of fatty acid and the transesterification of triglycerides. According to the natural compositions of soybean oil, four methyl ester products were detected by GC, i.e., methyl palmitate, methyl linoleate, methyl oleate and methyl stearate. Generally, the reaction rate of acidcatalyzed transesterification was extremely slower than that of base-catalyzed reaction. Herein, we first investigated the temperature effect on the transesterification of pure soybean oil (SBO) with methanol. The results obtained with or without FDU-15-SO₃H catalyst are shown in Figure 4. When FDU-15-SO₃H was employed as the catalyst, the ester yield increased sharply with increasing temperature from 373 to 393 K, and finally reached 99% at 413 K. SBO was hardly converted below 473 K in the absence of any catalyst, suggesting a catalytic transesterification was essential for converting SBO to FAME.

Based on the findings above, we have carried out the transesterification of SBO at 413 K over FDU-15-SO₃H, sugar-SO₃H, acidic resins, and liquid acids, separately. The data shown in the right column in Table 1 verified that FDU-15-SO₃H was also an outstanding catalyst in transesterification. The activity given by acidic resins decreased in comparison to that in esterification (Table 1, Nos. 6 and 7), because they were not thermally stable enough to bear a reaction temperature as high as 413 K. From the viewpoint of specific activity, i.e., the catalytic activity per acid site, FDU-15-SO₃H was superior to H_2SO_4 because the transesterification yield dropped from 99.5% to 77.2% when H_2SO_4 was used at the same molar amount as FDU-15-SO₃H

Table 2 The results of esterification and transesterification using the same molar amount of acid sites

No.	Catalyst	Acid amount (mmol g ⁻¹)	Ester conv. ^{a)} (mol%)	Transester yield b) (wt%)
1	FDU-15-SO ₃ H ^{c)}	1.0	99.0	99.0
2	$H_2SO_4^{(d)}$	20.4	90.0	77.2
3	<i>p</i> -Toluenesulfonic acid ^{e)}	5.8	99.0	_

a) Esterification: 3 mmol palm acid; 90 mmol MeOH; 343 K; 2 h. b) Transesterification: 2 g SBO; 2 g MeOH; 413 K; 5 h. c) 5 wt% FDU-15-SO₃H. d) 5 mg H_2SO_4 . e) 6.6 mg *p*-Toluenesulfonic acid.

 Table 3
 The esterification and transesterification of fatty acid-oil mixture catalyzed by FDU-15-SO₃H

No.	Substrate	FAME yield (wt%)
1	palmitic acid ^{a)}	99.5
2	30% Palmitic acid + 70% SBO b)	95.0
3	50% Palmitic acid + 50% SBO	90.0
4	70% Palmitic acid + 30% SBO	91.0
5	30% Stearic acid + 70% SBO	98.2
6	15% Stearic acid + 15% palmitic acid + 70% SBO	96.0
7	SBO	99.0

a) 3 mmol palmitic acid; 90 mmol MeOH; 5wt% catalyst; 343 K; 2 h. b) 2 g (x% palmitic acid or stearic acid + (1–x%)SBO); 2 g MeOH; 5wt% catalyst; 413 K; 5 h.



Figure 4 The temperature effect on the transesterification of SBO with (\bullet) and without (\bullet) FDU-15-SO₃H catalyst. Reaction conditions see Table 1.

(Table 1, Nos. 1 and 2; Table 2, Nos. 1 and 2).

Fatty acid with different amounts was blended in SBO to obtain a series of mixtures, which simulated the compositions of waste oil. The esterification and transesterification were then carried out simultaneously with methanol to investigate the possibility of using FDU-15-SO₃H for biodiesel synthesis from a raw material like waste oil. The reaction slightly retarded in the presence of free fatty acid, but it still proceeded to a large extent depending on the percentage of fatty oil. Even for the mixture of 50% SBO and 50% palmitic acid, the FAME products were formed readily solely with a small amount of palmitic acid unconverted.

As shown in Table 3, the FAME yield was above 95% when the fatty acid amount ratio was no more than 30% (Table 3, Nos. 1 and 2). When the fatty acid amount was increased to 50% or 70%, the yield decreased to about 90% (Table 3, Nos. 3 and 4). This is probably because the presence of a large amount of fatty acid may intensify the competition between esterification and transesterification on the acid sites. The esterification generates water in the reaction system, which not only promoted the hydrolysis of esters

but also restrained the esterification of fatty acid at a reaction temperature as high as 413 K. In this sense, the hydrophobic nature of FDU-15-SO₃H with an organic framework would be advantageous to the reaction in comparison to other hydrophilic solid acid catalysts. In addition, FDU-15-SO₃H also produced the FAME products efficiently when stearic acid was blended in SBO or in the mixture of SBO and palmitic acid (Table 3, Nos. 5 and 6).

3.4 Recycling of the catalyst FDU-15-SO₃H

In order to investigate the reusability of FDU-15-SO₃H, the used catalyst was collected and activated by washing with 10 mL of 5 wt% H₂SO₄ and 200 mL hot deionized water in turn. The regenerated catalyst was then subjected to the transesterification again. The FAME yield slightly decreased but was still over 90% at the third reuse (Figure 5, bars 1-3). XRD investigation showed that the structure of the used catalyst was maintained as before (Figure 1(c)). Nevertheless, the deposition of the oil molecules led to thickening of the pore walls, as a slight shift of [10] the diffraction peak to the low angle region was observed. In the IR spectrum of the spent catalyst, the band at 1034 cm^{-1} due to the stretching of Si=O decreased in intensity (Figure 3(c)), suggesting that the SO₃H groups were leached to a certain extent. The loss of acid sites mainly correspond to partial deactivation of FDU-15-SO₃H in reuse. However, after the used catalyst was recovered by re-sulfonation, the band at 1034 cm⁻¹ was restored (Figure 3(d)), and correspondingly, its transesterification activity was also recovered (Figure 5, bar 4), but not completely, owing to partial collapse of the structure in the second sulfonation process (Figure 1(d)).

4 Conclusions

FDU-15-SO₃H serves as an efficient solid acid catalyst for



Figure 5 The reuse of FDU-15-SO₃H in the transesterification of SBO. Reaction conditions see Table 1.

both fatty acid esterification and oil transesterification. Possessing special properties such as thermally stable organic structures, large surface area, unique mesoporous channels and abundant acid amount, FDU-15-SO₃H is superior to other acid catalysts in the esterification of palmitic acid and particularly in the transesterification of fatty acid-oil mixture. It is durable and easily recycled. Biodiesel is expected to be synthesized from the feed stocks with a high content of free fatty acids without further purification over such solid acid catalyst.

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