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Short communication

Esterification of octanoic acid using SiO_2 doped sulfated aluminum-based solid acid as catalyst

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ABSTRACT

In this paper, SO_4^{2-}/Al_2O_3-SiO_2 (SAS) was prepared and used for the esterification of octanoic acid with methanol. The effect of introduction of SiO_2 was characterized by nitrogen sorption, ICP-AES, XRD, NH_3-TPD, TG, FTIR and FTIR-pyridine adsorption. The results demonstrated that the doping of SiO_2 resulted in the increase of BET surface areas and amount of surface sulfur species which led to an increase of acid sites especially Brönsted acid sites, which consequently boosted the catalytic esterification activity. In addition, the introduction of SiO_2 can also increase the thermal stability of SO_4^{2-} and its interaction with Al_2O_3 support which resulted in the alleviation of catalyst deactivation.

1. Introduction

Bio-oil derived from biomass through pyrolysis process is regarded as an alternative strategy for petroleum [1,2]. However, the bio-oils cannot be directly used as transportation fuels due to their high viscosity, poor thermal and chemical stability, corrosion and immiscibility with hydrocarbon fuels [3,4]. To improve the quality of bio-oil, upgrading is needed. On account of the fact that the bio-oils often contain significant amount of free fatty acids (FFAs), including medium chain length (C_6–C_{12}) aliphatic carboxylic acids especially for raw materials with high acid value [5], a widely used upgrading method is catalytic esterification of the FFAs with methanol (or ethanol) to generate biodiesel [6,7]. Since published works involving the esterification of medium chain length free fatty acids are little available, so, it is necessary to study this issue, such as octanoic acid (defined as OA).

There are several comprehensive studies of the homogeneous acid, mineral acid, and organic sulfonic acid catalysts catalyzed esterification of FFAs in the literatures [8,9]. Yet, the homogeneous acids have some disadvantages, such as pollution, separation and recycling difficulties. Meanwhile, it has been reported that sulfated solid acids SO_4^{2-}/M_xO_y (M = Zr, Ti, Sn, Fe, Al etc.) are highly promising because of their high activity and selectivity for target product, easy separation from the products, reduction of corrosion and environmental problems, recycling and regeneration [10,11]. Among the SO_4^{2-}/M_xO_y catalysts, SO_4^{2-}/ZrO_2 has been most extensively studied because of its strong acidity and ability to catalyze many reactions [12,13]. However, SO_4^{2-}/ZrO_2 is known to suffer significant deactivation due to sulfur leaching or transformation of active tetragonal zirconia phase to monoclinic phase [14].

To develop more active, stable and economic solid catalysts for octanoic acid esterification with methanol, we attempted SO_4^{2-}/Al_2O_3 (SA) which has been little investigated in literatures before. Considering an elimination of the sulfate is sometimes observed [15], and that mixed oxides often show enhanced acidity and thermal stability than their constituent single oxide in literatures [16], we attempted introducing SiO_2 into SO_4^{2-}/Al_2O_3 to generated SO_4^{2-}/Al_2O_3-SiO_2 (SAS) and investigated the effect of introducing SiO_2 on the structure, acidity, stability and activity as well. This work will develop a foundation to industrial production of biodiesel via bio-oil esterification process over inexpensive sulfated aluminum-based solid acids with the economic value and strategic significance.

2. Experimental

The catalysts were prepared through a precipitation method, and the catalytic activity measurements were carried out in a stainless

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autoclave with 50 mL capacity. Detailed procedures are included in the supporting information.

3. Results and discussion

3.1. Optimization of calcination temperature of SA and reaction conditions for esterification

To obtain the super acid sites for the solid acid catalysts, a high temperature is needed to evaporate the H_2O and H_2SO_4 on the surface of samples and promote the transformation from amorphous state to crystal for Al_2O_3 [17,18]. XRD results in Fig. S1 showed that γ-Al_2O_3 structure was detected when the calcination temperature reached 550 °C. From Table 1, it can be concluded that the octanoic acid conversion and methyl octanoate yield increased with the increasing of the calcination temperature of SA, and reached a maximum value of 92.56% and 89.08% respectively when the calcination temperature increased to 550 °C. Besides, from NH_3-TPD profies present in Fig. S2, the SA calcined at 550 °C has the most acidic sites.

The OA conversion and methyl octanoate yield increased with the increase of reaction temperature until the temperature reached 160 °C. With further increase in reaction temperature, the catalytic activity diminished on account of the fact that the esterification is an exothermic reaction in thermodynamics. From Table 1, it can also be observed that the SA showed remarkable activity at the methanol/OA molar ratio of 4.5:1. Continuing increasing the molar ratio, no obviously more OA conversion was obtained. Based on the above results, the optimal temperatures for SA calcination and reaction are 550 °C and 160 °C, and the optimal molar ratio of methanol/OA is 4.5:1.

3.2. Effect of addition SiO_2 to SA on the esterification of octanoic acid with methanol

Though the SA catalyst exhibits excellent catalytic activity for OA esterification with methanol, SA shows no satisfactory thermal stability due to the leaching of surface sulfur species [14]. To enhance acidity and thermal stability of catalyst, we attempted introducing various contents of SiO_2 into SO_4^{2-}/Al_2O_3 to generated SO_4^{2-}/Al_2O_3-SiO_2 with different Al/Si molar ratio of 15:1, 10:1, 5:1 and 1:1, which were designed as SAS-15, SAS-10, SAS-5 and SAS-1. From Fig. 1, the conversion of OA and the yield of methyl octanoate increased with the increasing of the SiO_2 content, and were up to the maximum value of 99.11, 99.07% respectively at the Al/Si molar ratio of 5:1. No by-products were detected.

3.2.1. BET surface areas and SO_4^{2-} contents of catalysts with different Al/Si molar ratio

In order to study the effect of SiO_2 doping to SA in detail, the BET surface areas and SO_4^{2-} contents of SAS with different Al/Si molar ratio were examined and the results were shown in Table 2. When the SiO_2 content increased, the BET surface area increased until the Al/Si molar ratio was up to 5:1, at which the biggest surface area of 38.50 $m^2\ g^{-1}$ was obtained.

The mmol of SO_4^{2-} loaded on per gram of SAS catalyst with different Al/Si molar ratio was calculated by mass fraction of sulfur which was determinated by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES). From Table 2, it can also be concluded that the doping of SiO_2 to SA significantly increased the content of SO_4^{2-} loaded on catalysts as well, and the loading content of SO_4^{2-} reached the maximum value of 7.73 mmol $g^{-1}{}_{cat.}$ when the Al/Si molar ratio increased to 5:1.

In addition, XRD patterns of SA and SAS were present in Fig. S3, which shown that SiO_2 has been highly dispersed in the catalysts, for no independent peaks due to SiO_2 or any compounds formed between Al_2O_3 and SiO_2 were observed [19].

Table 1
Effect of calcination of SA and reaction temperatures, methanol/OA molar ratio on esterification[a].

$T_{calcination}$ (°C)	$T_{reaction}$ (°C)	Methanol/OA molar ratio	Conversion (%)	Yield (%)
No catalyst	160	4.5:1	40.03	36.27
500	160	4.5:1	87.95	79.54
550	160	4.5:1	92.56	89.08
600	160	4.5:1	93.08	86.47
550	140	4.5:1	80.67	74.27
550	150	4.5:1	87.16	83.47
550	170	4.5:1	90.01	87.21
550	180	4.5:1	84.99	80.23
550	160	3:1	88.70	85.02
550	160	6:1	92.87	88.90
550	160	10:1	93.06	89.13

[a] Reaction conditions: octanoic acid 10 g, SA 0.5 g, reaction time 3 h.

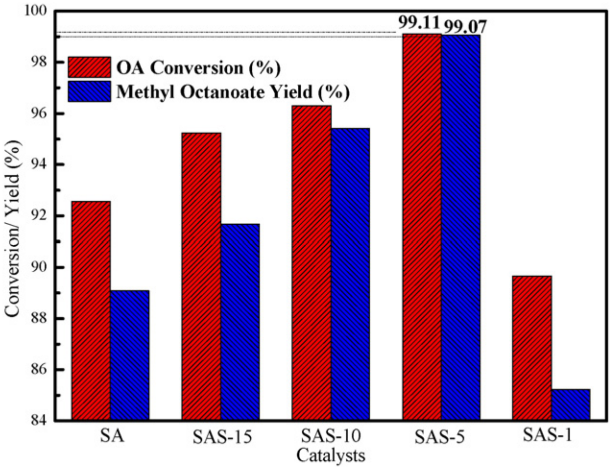

Fig. 1. Effect of SiO_2 content on the esterification (octanoic acid 10 g, methanol/OA molar ratio 4.5:1, catalyst 0.5 g, reaction at 160 °C for 3 h in 50 mL autoclave.)

3.2.2. Analysis of FTIR spectra

The infrared absorption spectra for SA and SAS were shown in Fig. 2. In sulfated metal oxides, it has been assumed that the sulfate ion is covalently bounded to the oxide to form chelate and bridge structures, which show C_{2v} symmetry [20]. Three bands of 1200, 1170, and 1117 cm^{-1} are assigned to $\nu3$ vibrations of bidentate SO_4^{2-} in a C_{2v} symmetry [21], while the bands at 682 and 648 cm^{-1} are attributed to Al-O vibrations. Such results confirm that in our catalysts, SO_4^{2-} appears as sulfate bonded to the metal oxide surface.

After the introduction of SiO_2 to the SA to generate SAS, there appeared two new vibration peaks in 800 and 714 cm^{-1} which belong to Si-O asymmetric stretching vibration and Al-O-Si bending vibration, respectively [22]. Meanwhile, the intensity of the two peaks increased gradually with the increase of SiO_2 doping amount.

It is also shown that the intensity of SO_4^{2-} bands enhanced significantly with the increase of SiO_2 content and reached an optimum value until the Al/Si molar ratio was up to 5:1, which means that the introducing of SiO_2 to SA increases the sulfur species bonded to the aluminum oxide surface and most sulfur species were on the surface of SAS-5, and this is in accordance with the results in Table 2. As it has been proposed that the adsorption of SO_4^{2-} on the surface of metal oxide by coordination bond would induce the deviation of electron cloud of M—O bond, which in consequence generates the Lewis acid sites, and the Brönsted acid is resulted from the cleavage of water adsorbed on the M_xO_y surface by the formation of an $(M—O)_2S(=O)—OH$ group [18], the strong acid property of SO_4^{2-}/M_xO_y solid acid is derived from sulfate ions on the M_xO_y surface. Since the esterification reaction is acid