Esterification of Oleic Acid in Biodiesel Synthesis with SO₄²⁻/ZrO₂/MCM-41 as Catalyst

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SO₄²⁻/ZrO₂/MCM-41 was prepared by impregnation method with self-synthesized MCM-41. The investigation of effects on ZrO₂ load ratio and sulphur acid concentration sifted that the catalyst with 40 % ZrO₂ load ratio, 1.5 mol/L sulphur acid performed best. Oleic acid was chosen as a simulation of high-acid-value oil to esterify with methanol. The experimental results showed that SO₄²⁻/ZrO₂/MCM-41 was a high active catalyst in esterification. The optimal condition was as following: the reaction temperature was 80 ºC, the oleic acid/methanol molar ratio was 4:1, the catalyst amount was 5 % (wt. /wt.) of the oleic acid and reaction time was 4 h. Under this condition, the oleic acid conversion could reach 82.6 %. Characterization results of XRD, TEM and SEM showed that SO₄²⁻/ZrO₂/MCM-41 had the typical structure of MCM-41 and SO₄²⁻/ZrO₂. Reusability tests indicated that the load progress largely improved the water tolerance of SO₄²⁻/ZrO₂ and reduced the sulphur leaching rate of it.

Key Words: Biodiesel, MCM-41, Esterification, High-acid-value oil, Sulphated zirconia.

INTRODUCTION

In recent years, biodiesel industry has developed rapidly for the petroleum crisis and its advantages like easily being degradable, lower emission and the most important property-renewable. Biodiesel can be produced from either the trans-esterification of triglycerides (oil or fats) or the esterification of free fatty acids (FFAs) with a short chain alcohol catalyzed by base[1,2,3], acid[4,5] or enzymes[6]. Alkalis are widely industrial used for its fast reaction rate, mild reaction requirements and lower corrosion. Waste oils, such as used frying oil, trap grease, soapstock and acid oil, can't be the feedstock for the production of biodiesel catalyzed by alkalis[4], for only free fatty acids content less than 0.5 wt % can be used in base-catalyzed transesteri-fication. For these feedstocks, the free fatty acids content can be reduced by first esterifying them in the presence of an acid catalyst[7,8]. However, homogeneous acid catalysts cause the extra neutralization process. Therefore, researchers developed solid acid to resolve the questions neutralization caused.

Acid zeolites are common Brønsted-Lowry acid, however, they are not suitable catalysts for biodiesel manufacturing because of their small pores which lead to diffusion limitations of the large fatty acid or triglycerides molecules[9]. Mesoporous silica materials like MCM-41 and SBA-15 have much larger pores than common zeolites, which can minish this limitation and make it possible to catalyze this reaction, but neither of them has sufficiently acidic centre to catalyze esterification or transesterification reactions. As a conventional porous catalyst support, it presents significant advantages, due to its high specific surface areas, large pore size and high thermal stability[10]. Gandia *et al.*[11] prepared a series of catalyst by load NaOH on commercial silica and all the catalyst showed activity but lack of stability. Subramanian *et al.*[12] used phosphoric acid modified mordenite to remove free fatty acids in *Azadirachta indica* (Neem) seed oil by esterification. Farzaneh *et al.*[13] loaded KOH on MCM-41 and Al-MCM-41 and used them to catalyze the transesterification of soybean oil and methanol. They found that they are better support than common silica gel because with same KOH load ratio, oil conversion of catalyst supported by MCM-41 and Al-MCM-41 was much higher than that by silica gel. Wang *et al.*[14] immobilized Al-MCM-41 with concentrated sulphuric acid to obtain SO₃H/Al-MCM-41. This catalyst showed relatively high catalytic activity in the trans-esterification of glycerol triacetate and methanol. Patel and Brahmkhatri[15] used 12-tungstophosphoric acid Anchored MCM-41 catalyzing the esterification of palmitic acid with methanol. The conversion of palmitic acid was nearly 100 % in 4 h. Chen *et al.*[16,17], directly synthesized sulphated zirconia on SBA-15 in one step. And the sulphated zirconia/SBA-15 showed some activity and better tolerance of water. Tropecelo *et al.*[18] tested a series heteropolyacid immobilized SBA-15 in the esterification of palmitic acid with methanol at 60 ºC and found the sort of activity was PW1-SBA-15 > SiW-SBA-15 > PMo-SBA-15. MCM-41 supported WO₃[19] and zirconium sulphate[20] were also showed activity in the esterification or

transesterification. However, most of these cases, catalysts showed their high activity only at very high reaction temperature, which meant autoclave was necessarily used in the production process.

Sulphated zirconia was an effective catalyst in the esterification of oleic acid and methanol[21]. In the present paper, sulphated zirconia has been loaded onto MCM-41 to prepare a mesoporous silica-supported sulphated zirconia. A series of catalysts with different ZrO_2 loadings and SO_4^{2-} loadings has been prepared with impregnation method companied with thermal activation at 600 ℃. The resulting catalysts have been tested in the esterification of oleic acid with methanol under atmosphere. The influence of different experimental parameters such as reaction time, amount of catalyst, methanol/oleic acid molar ratio, heated temperature and catalyst recycle times have been evaluated in order to find the most suitable conditions for this esterification.

EXPERIMENTAL

Synthesis of MCM-41: The MCM-41 used was synthesized by hydrothermal method with cetyltrimethylammonium bromide (CTAB) as template and tetraethoxysilane (TEOS) as silicon resource. At room temperature, 2.5 g CTAB, 9.5 mL ammonium hydroxide and 120 mL ionized water was mixed under stirring until no solid exist. Then 10 g TEOS was dropt slowly in 10 min under violent stirring. After 0.5 h stirring, the mixture was moved into a hydrothermal reactor and kept at 130 ℃ for 72 h. Then the mixture was cooled, flittered and the sediment was washed to neutral and dried at 80 ℃ overnight. The MCM-41 was obtained by calcined the dried powder at 550 ℃ for 5 h.

Synthesis of $SO_4^{2-}/ZrO_2/MCM-41$ solid acid: The ZrO_2/MCM-41 was prepared by the following step: Immersed 1 g MCM-41 into an isopycnic $Zr(NO_3)_2 \cdot 5H_2O$ solution of different concentration which contained ZrO_2 amount ranging between 10 and 50 %. Then the mixture was dried at 110 ℃ and calcined at 300 ℃ for 3 h to obtained ZrO_2/MCM-41. The ZrO_2/MCM-41 was dipped into sulphuric acid solution for 24 h, then filtered and dried. After calcined the powder at 600 ℃ for 3 h, the final solid acid catalyst $SO_4^{2-}/ZrO_2/MCM-41$ was obtained.

Esterification of oleic acid and methanol: Esterification experiments were carried out in a 100 mL four-necked flask, provided with thermostat, mechanical stirring systems. 11.28 g oleic acid (OA) and different amount of methanol and catalyst were added and heated to a given temperature accompanied with stirring. The reaction was taken under certain temperature. After reaction, the reactor was cooled to room temperature and the catalyst was removed from the product mixture by filtration. The excess methanol was distilled with rotary evaporation under subpressure. The conversion of oleic oil was calculated by the following formula:

$$C\,(\%) = \frac{AV_0 - AV}{AV_0} \times 100\,\%$$

where, C % was the conversion of oleic oil. AV_0 and AV was the acid value (mgKOH/g) of the mixture before and after esterification, respectively.

Characterization of catalyst: The catalyst was characterized by powder X-ray diffraction (XRD, X'TRA, ARL), scanning electron microscopy (SEM, XL30, Philips) and transmission electron microscopy (TEM, Tecnai G2, FEI). XRD measurements were performed on a Rigaku D/max-A instrument with a CuK_α radiation at 50 kV and 30 mA and a scan speed of 0.02 º/min.

RESULTS AND DISCUSSION

Esterification reaction

Sifting of catalysts: The active center of the catalyst SO_4^{2-}/ZrO_2 (SZ) was formed by the interactive effect between sulphuric acid and ZrO_2. The amount of ZrO_2 and the concentration of sulphuric acid would largest affect the catalytic ability.

Fig. 1a showed the oleic acid conversion catalyzed by catalysts with different ZrO_2 load ratio but same sulphuric acid concentration. The oleic acid conversion increased with the ZrO_2 load ratio until the conversion of 43.8 % obtained when the ZrO_2 load ratio was 40 %, so raising the ZrO_2 load ratio would enhance the acid center amount and then increase the catalyst's activity. However, when the ZrO_2 load ratio continued increasing beyond 40 %, the oleic acid conversion decreased. The reason of this might be that the excessive ZrO_2 aggregated and blocked some pore of the supporter MCM-41, which largely reduced the specific surface and then the activity of the catalyst. Fig. 1b showed the influence of immersed sulphuric acid concentration on the catalyst activity. When sulphuric acid concentration below 1.5 mol/L, the oleic acid conversion rose as the H_2SO_4 concentration increased. And while the concentration was over 1.5 mol/L, the oleic acid conversion doped apparently. The reason of this phenomenon might be explained as following: below 1.5 mol/L, thicker solution means more sulphuric acid and more active center; over 1.5 mol/L, the too high concentrated sulphuric acid destroyed the second supporter ZrO_2 by the side reaction which formed $ZrSO_4$. Therefore, the $SO_4^{2-}/ZrO_2/MCM-41$ with 40 % ZrO_2 load ratio and 1.5 mol/L was chosen as the best catalyst.

Influence of reaction condition: This esterification reaction could be mainly influenced by the following factors: methanol/acid molar ratio, reaction temperature, mass of catalyst and reaction time.

The effect of catalyst amount ranged between 3 and 7 % was investigated (Fig. 2a). The oleic acid conversion increased when more catalyst amount was added. As this reaction is a multiphase reaction, more catalyst could provide more active center and higher contacting opportunity which would accordingly accelerate the reaction rate. So increase the amount of catalyst can improve yield of product in the same reaction time. However, the oleic acid conversion dropped when the catalyst amount was over 5 % (wt./wt. oleic acid). That was because too much catalyst may also cause slurry and hinder the mass transforming, which slow down the reaction. Therefore, 5 % (wt. / wt. oleic acid) was considered as the best catalyst amount used in the esterification.

Esterification is an equilibrium reaction and excess methanol will push the reaction forward to increase oleic acid conversion. The influence of methanol to oleic acid molar ratio was
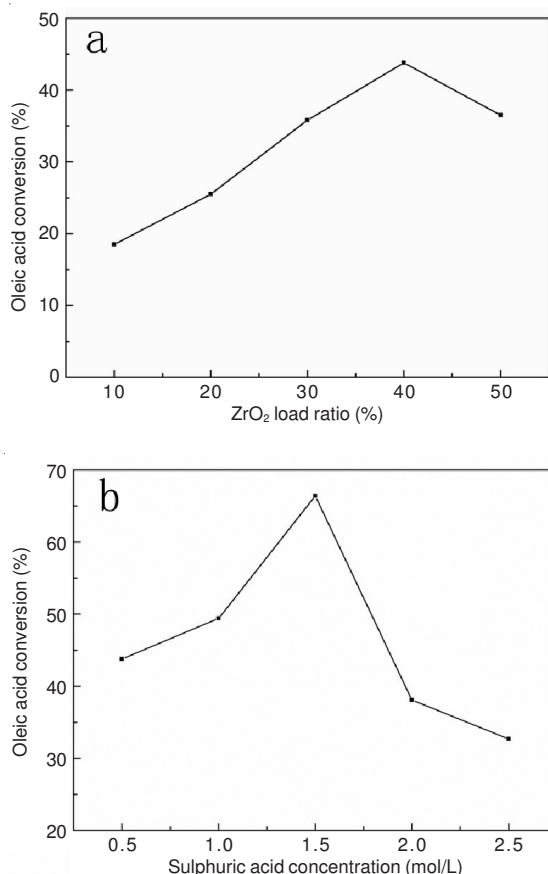
Fig. 1. (a) Effect of ZrO_2 load ratio (sulphuric acid concentration 1.5 mol/ L) reaction condition: methanol/oleic acid molar ratio 4:1; temperature 80 ℃; time 4 h; catalyst amount 5 % (wt/wt oleic acid); (b) effect of sulphuric acid concentration (ZrO_2 load ratio 40 %) reaction condition: methanol/oleic acid molar ratio 4:1; temperature 80 ℃; time 4 h; catalyst amount 5 % (wt/wt oleic acid)
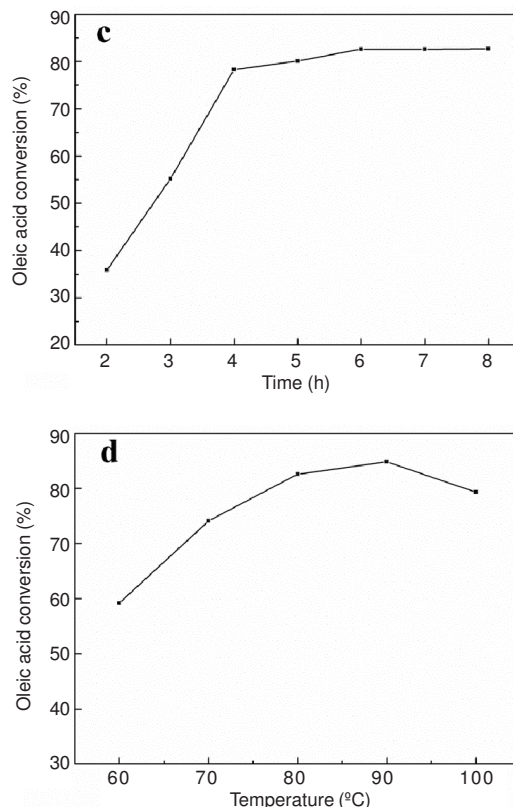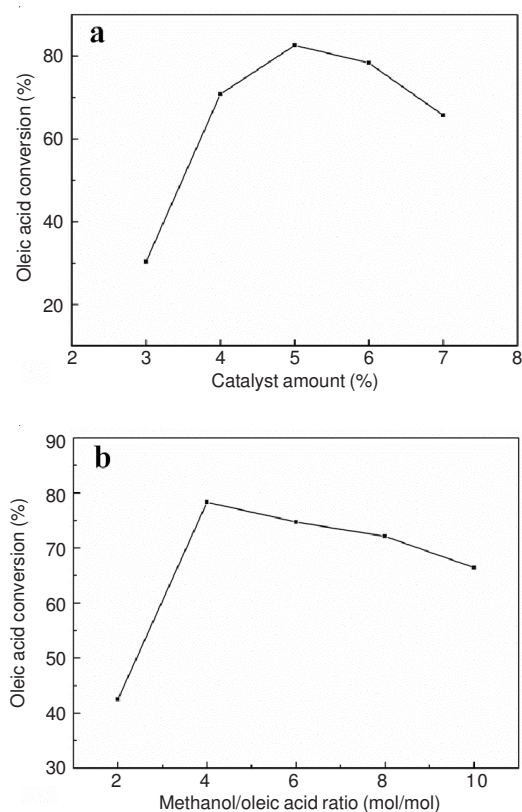

Fig. 2. Effect of different reaction parameter (a) catalyst amount; (b) methanol to oleic acid molar ratio; (c) reaction time; (d) reaction temperature; basic reaction condition: catalyst amount 5 % (wt./ wt. oleic acid), methanol/oleic acid 4:1(mol/mol), time 6 h, temperature 80 ℃)

investigated which can be seen from Fig. 2b. In this figure, oleic acid conversion increased along with the molar ratio of methanol/oleic acid increasing between 2:1 and 4:1. When the molar ratio got over 4:1, the oleic acid conversion dropped slowly (78.3 % with 4:1 and 66.4 % with 10:1). That was because the excess methanol diluted oleic acid, decreased reaction rate and furthermore affects the yield. Moreover, more methanols would make higher cost, therefore, 4:1 was chosen as the optimal methanol/oleic acid molar ratio.

The effect of reaction time from 2-8 h was investigated which can be seen from Fig. 2c. Oleic acid conversion increased (from 35.9-82.7 %) as reaction continued (from 2 to 8 h). Esterification reaction catalyzed by acid needs a long reaction time to accomplish a high conversion under relatively low temperature because of the slow reaction rate. And as the conversion only increased *ca.* 5 % from 4 to 8 h, 4 h should be the optimum reaction time.

The influence of reaction temperature at every 10 ℃ from 60-100 ℃ (heated bath temperature) was investigated, which can be seen in Fig. 2d. Oleic acid conversion rose sharply from 60-80 ℃. Over 80 ℃, it still increased, but not that obviously. Temperature rose could shift the balance to synthesize fatty acid methyl ester and at 80 ℃ this balance comes to a critical point. So when temperature exceeds 80 ℃, this balance may have come to a threshold of thermodynamics. However, when the system was heated over 80 ℃, the conversion dropped, this might be caused by the reason that large amount methanol was vaporizing, which increased the mass transfer resistance

for changing the system from liquid-liquid-solid mass transfer to gas-liquid-liquid-solid mass transfer. Therefore the temperature of 80 ºC was considered as the optimum condition with the oleic acid conversion of 82.6 %.

The catalysts had been repeatedly used for four times (Table-1). In the first three times, the oleic acid conversion did not drop apparently. While in the forth time, only few part of oleic acid conversed into fatty acid methyl ester. Considering that the esterification experiment used no water entrainer, these results means the $SO_4^{2-}/ZrO_2/MCM-41$ improve the water tolerance of SZ. And as known, SZ lose it activity by the reason of sulphur leaching. The $SO_4^{2-}/ZrO_2/MCM-41$ can be used for three times without inactivation, meant the load progress reduced the sulphur leaching rate of the catalyst.

TABLE-1
REUSABILITY OF $SO_4^{2-}/ZrO_2/MCM-41$ (REACTION CONDITION:
CATALYST AMOUNT 5 % (wt./wt. OA), METHANOL/ OA 4:1
(mol/mol), TIME 6 h, TEMPERATURE 80 ºC)

Catalysis	Using times				
	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)
$SO_4^{2-}/ZrO_2/MCM-41$	82.6	80.6	79.3	78.0	50.8
SO_4^{2-}/ZrO_2	93.5	20.1	–	–	–

Catalyst characterization: From the XRD patterns of MCM-41 and $SO_4^{2-}/ZrO_2/MCM-41$ in Fig. 3a, it was clearly presented the characteristic peak of SO_4^{2-}/ZrO_2 and ZrO_2[10], which the original MCM-41 did not have. In Fig. 3b, the strong peak at 2.2º (100) was the characteristic peak of mesoporous materials. The peaks of MCM-41 in this figure showed that the supporter we prepared had a typical mesoporous structure, which also can be seen in the SEM images. And the peaks of $SO_4^{2-}/ZrO_2/MCM-41$ showed that after loaded with SO_4^{2-}/ZrO_2, the mesoporous structure of the supporter did not be destroyed for the peak at 2.2°(100) was still strong. But the peak at 3.7°(110) was weakened and peak at 4.3°(200) disappeared, which means the long-range regularity of MCM-41 had reduced. This might also be the reason that high load ratio decrease the activity of the catalyst.

Fig. 4 showed the TEM images of MCM-41 (a) and $SO_4^{2-}/ZrO_2/MCM-41$(b). In Fig. 4a, there was clearly hexagonal pore structure which is the typical structure of MCM-4 and the diameter of the pore was *ca.* 4.2 nm. From Fig. 4b, it could be seen that the hexagonal pore structures still existed but the pore size had reduced to *ca.* 3.8 nm, which was caused by the load of SO_4^{2-}/ZrO_2.

The SEM image of $SO_4^{2-}/ZrO_2/MCM-41$ was given in Fig. 5. This image illustrated that the $SO_4^{2-}/ZrO_2/MCM-41$ solid acids dispersed uniformity without obvious agglomeration.

Conclusion

As a summary, MCM-41 was prepared and used as the support of solid acid catalyst $SO_4^{2-}/ZrO_2/MCM-41$. The catalyst with 40 % ZrO_2 load ratio, 1.5 mol/L sulphur acid was selected as the best. XRD, TEM and SEM characterization results showed that $SO_4^{2-}/ZrO_2/MCM-41$ had the typical structure of MCM-41 and SO_4^{2-}/ZrO_2. And the load of SO_4^{2-}/ZrO_2 on MCM-41 might slightly destroy the regularity of MCM-41, so too much SO_4^{2-}/ZrO_2 would not increase the activity of the solid
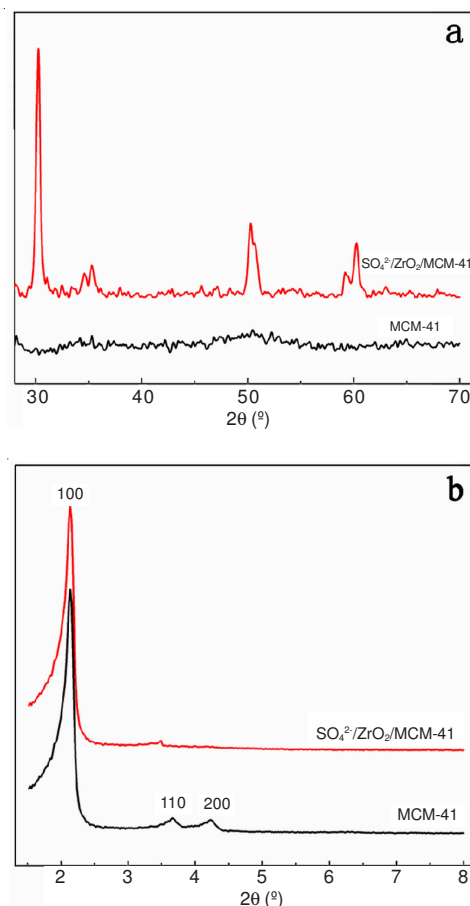

Fig. 3. a-b XRD patterns of MCM-41and $SO_4^{2-}/ZrO_2/MCM-41$ (ZrO_2 load ratio 40 %, sulphuric acid concentrate 1.5 mol/L)

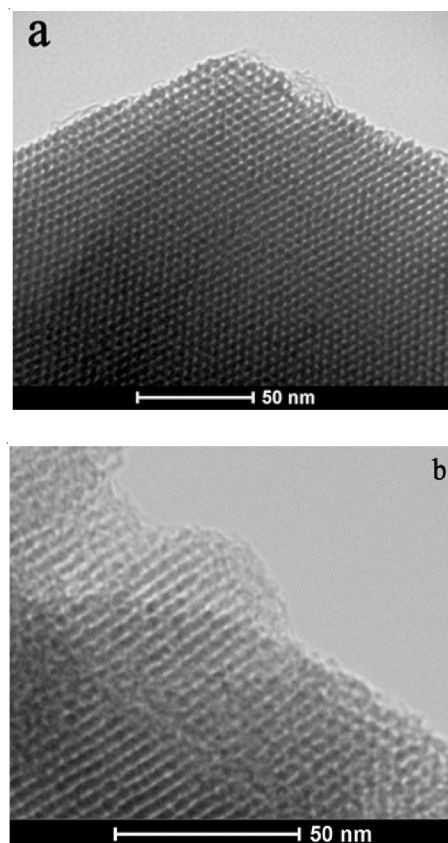Fig. 4. TEM image of MCM-41(a) and $SO_4^{2-}/ZrO_2/MCM-41$ (b)
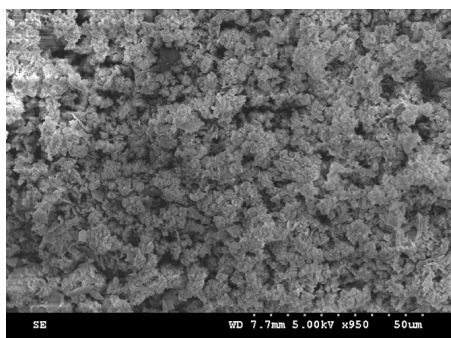
Fig. 5. SEM image of $SO_4^{2-}/ZrO_2/MCM-41$

acid but lowered it. Esterification of oleic acid and methanol was provided as the simulation of high-acid-value oil pre-esterification treatment process. The optimal oleic acid conversion could reach 82.6 %, when the reaction temperature was 80 ºC, oleic acid/methanol molar ratio was 4:1, catalyst amount was 5 % (wt. /wt. oleic acid) and reaction time was 4 h. $SO_4^{2-}/ZrO_2/MCM-41$ can repeatedly use for three times with a slight activity decline without any treatment. This novel catalyst opened the possibility to extend the raw material of biodiesel to high-acid value oil like waste oil without huge productive technology changing but only adding an esterification unit.

ACKNOWLEDGEMENTS

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