Structurally Controllable Strong Acid Mesoporous Catalyst SBA-15-TESBS: Synthesis and Application in Biodiesel Production

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Significance and Relevance

By using 4-(Triethoxysilyl)benzenesulfonic acid (TESBS) as a silicon source instead of Tetraethyl orthosilicate (TEOS) in the synthesis of SBA-15, the amount of acid sites and catalytic activity in esterification, transesterification, and isomerization of palm acid oil can be significantly enhanced. When the TESBS ratio reached 30%, the acid content in the catalyst increased to 1.4 mmol/g, effectively improving its catalytic performance. This modification led to a remarkable enhancement in the low-temperature flowability of the resulting product. This study also investigates how the catalyst's structure and acidity change under varying synthesis conditions.

Primary topic:: *Green chemistry and biomass transformation, renewable resources conversion*
Secondary topic: Sustainable and clean energy production and transport
Preferred presentation: ORAL preferred or SHORT ORAL.

Introduction and Motivations

The refining of palm oil results in the production of a byproduct, palm acid oil (PAO), which contains triglycerides (TG <70%) and free fatty acids (FFA >30%) as waste products. In the past, this laboratory has developed a BDF production process using solid acid catalysts to react PAO with methanol. However, the poor low-temperature flowability of the BDF has proved problematic. This may result in fuel filter clogging and poor engine performance in cold climates [1]. To address these problems, studies have shown that isomerization of the product can improve its low-temperature flowability [2]. Research indicates that Brønsted acids have the capability to promote the isomerization of unsaturated fatty acids [3]. SBA-15, a mesoporous catalyst with a large surface area and high-temperature stability, offers significant advantages[4]. However, its low Brønsted acid content limits its effectiveness in skeletal isomerization. Therefore, this study aims to develop a sulfonic acid-modified SBA-15-MPSBS catalyst to enhance esterification, transesterification, and isomerization reactions, thereby addressing the challenge of poor low-temperature flowability in biodiesel fuel (BDF). Additionally, the study explores the structural and acidity variations of the catalyst under different synthesis conditions.

Materials and Methods

TESBS was introduced into SBA-15 surface to synthesize a mesoporous mesopore-SBA-15-benzene sulfonic acid (MPSBS). During the synthesis, TESBS/TEOS ratio, the removal method for P123, and reaction temperature etc. were investigated. The catalysts were characterized by use of BET, XRD, and Boehm acid-base back titration.

The reaction feedstock consisted of a model oil prepared by mixing erucic acid (FFA22:1) and triolein (TG18:1) in a 3:7 ratio. The experiments were conducted using a batch reactor, with a reaction temperature of 260°C and a reaction time of 3 hours. Additionally, the esterification, transesterification, and skeletal isomerization performance of the model compounds were evaluated. The products were analyzed using GC-FID and GC-MS. To assess the low-temperature flowability of the resulting oil, the slip point [5] was measured.

Results and Discussion

1. synthesis of SBA-15-MPSBS

Table 1 lists the results of the amount of acid in prepared SBA-15-MPSBS. With the increase of TESBS, the acid amount of the catalyst rises significantly. Due to TESBS being almost the sole source of acidity, it indicates that even with a TESBS content of up to 30%, TESBS can still be successfully incorporated onto the surface of SBA-15. The acid amount reached 1.4 mmol/g. It could be theorized that increasing the proportion of MPSBS will result in a continuous increase in the acid amount of the catalyst. However, it should be noted that the benzene ring structure of MPSBS will affect the size of the original structure of SBA-15. XRD spectra showed that all catalysts successfully had the structure of SBA-15.

.2. Catalyst activity

In the experiment, a batch reactor was used, the reaction temperature at 220~260 °C for 3 hours. Experiments were conducted to investigate the effects of varying ratios of MPSBS (2% to 30%) on the observed activity. In accordance with the preceding findings, the proportion of MPSBS augmented, concomitant with an increase in the quantity of acid present within the catalyst. The results of the activity experiment are presented below. It can be concluded that an increase in the quantity of acid present in the catalyst results in a notable enhancement in the activity of the esterification, transesterification and isomerization reactions. Using SBA-15-MPSBS (30) at 260°C for 3 hours, the low-temperature flowability of the product is greatly improved.

Conclusion

By using TESBS instead of TEOS as the silicon source for SBA-15, a large amount of acidic substance can be successfully introduced, significantly enhancing the catalytic activity of SBA-15 while maintaining the integrity of its structure. Through the method developed in this study successfully produces BDF with excellent low temperature flowability.

Table 1 Quantified acid sites of the prepared SBA-15-MPSBS

Catylst	TEOS/TESBS(g/g)	pH	Aging temperature (℃)	Aging time (h)	Template (P123, g/100ml)	Acid sites (mmol/g
SBA-15-MPSBS(2)	98/2	<<1	100	48	8	0.53
SBA-15-MPSBS(5)	95/5					0.64
SBA-15-MPSBS(10)	90/10					0.73
SBA-15-MPSBS(20)	80/20					0.97
SBA-15-MPSBS(30)	70/30					1.40
SBA-15-MPSBS(20)	80/20	1				1.01
		2				1.32
		3				1.45
		7				1.11
		<<1	80			0.85
			90			1.00
			110			0.99
			100	24		0.68
				72		0.89
				96		0.95
				48	0.5	0.90
					1	1.01
					10	0.85

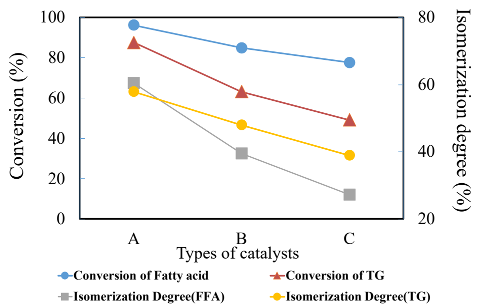

Fig. 1 Results of Conversion of FFA、TG、Selectivity of isomerized Substances and the rate of Isomerization by different temperature. A : SBA-15-MPSBS(10), B : SBA-15-MPSBS(5), C : SBA-15-MPSBS(2)

References

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