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Synthesis of stearic acid triethanolamine ester over solid acid catalysts

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Abstract

The synthesis of stearic acid triethanolamine ester over solid acid catalysts was investigated. The results showed that the catalytic activity and selectivity of zirconium sulfate supported on SBA-15(6) (pore diameter 6 nm) is better than that of commonly used hypophosphorous acid, zirconium sulfate supported on MCM-41 and zirconium sulfate supported on SBA-15(9) (pore diameter 9 nm).

Keywords: Zirconium sulfate; SBA-15; Stearic acid; Triethanolamine

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Esterquats as a new generation of fabric softening agents combines a good environmental profile with the structural features required for an effective fabric conditioner [1,2]. The synthesis of stearic acid triethanolamine ester (EA) as the intermediate is the key step in the preparation of esterquat. The EA based on triethanolamine (TEA) is the mixtures of mono-, di- and tri-esteramine. The ultimate performance of these products is related to the mono- and di-esterquat content, so the content of mono- and di-esteramine should be increased [3].

In the conventional process, the homogeneous catalysts such as hypophosphorous acid, sodium methoxide, para-toluenesulfonic acid and so on are employed in the synthesis of EA, which produces a series of environmental impacts and applied problems. Thus, solid acid catalysts are desirable for environmentally friendly process. It was reported that the supported zirconium sulfate (ZS) on HZSM-5 used in the esterification of acrylic acid showed high conversion [4], but the pore diameter of HZSM-5 was too small to be used in the esterification of stearic acid with TEA. In recent years, significant interests have been generated in mesoporous molecular sieve materials SBA-15 owing to its larger pores, thicker walls, large surface area and high hydro-thermal stability. The study reported in this paper centered on the synthesis of EA over ZS supported on SBA-15 (ZS/SBA-15) as catalyst was researched.

1. Experimental

SBA-15 was synthesized according to the procedure described by Yang *et al.* [5,6]. MCM-41 was purchased from Tianjin Chemist Scientific Ltd. The SBA-15 support was treated under vacuum at room temperature for 2 h, followed

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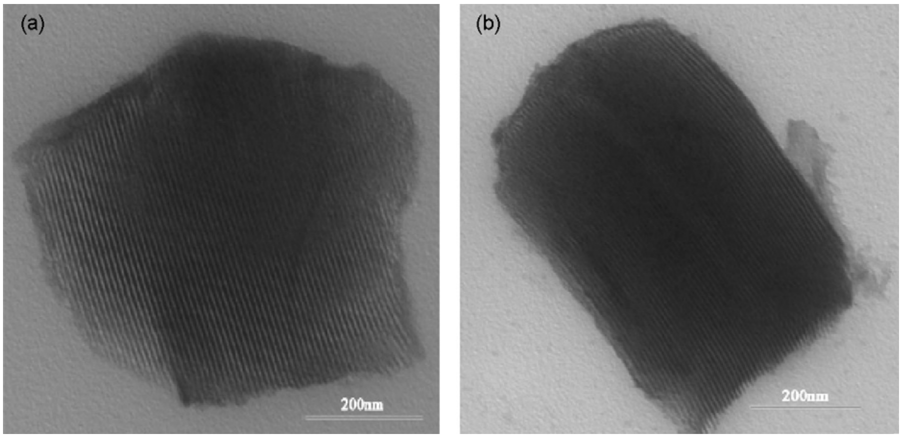

Fig. 1. TEM images of the SBA-15(6) (a) and 20%ZS/SBA-15(6) (b).

by impregnating a required amount of ZS aqueous solution for 24 h. After drying, the catalysts were calcined at 473 K for 2 h. Preparation of 20%ZS/MCM-41 was the same as 20%ZS/SBA-15. XRD (Rigaku D/2500), TEM (JEOL JEM-1011) and nitrogen gas adsorption–desorption isotherm tests (Micromeritics ASAP 2010) were conducted to investigate the pore-structural changes for SBA-15 and the supported samples.

The synthesis of EA was carried out in a four-necked flask equipped with mechanical stirrer under nitrogen atmosphere with the temperature of 190 °C. Water formed during the reaction was removed constantly with the nitrogen flow. After 6 h of reaction, the mixture was cooled down to 70 °C, then the catalyst was filtered from the mixture and collected for the reuse in next batch. The structure of product was characterized with ^{1}H NMR (Bruker, DRX300), and the composition of product was analyzed by RP-HPLC (Elite P230), using Corona electron spray detector (ESA, America) and C18 silica-bonded column (DIKMA Diamonsil, 250 × 4.6 mm 5 μm).

2. Results and discussion

TEM images of SBA-15(6) and ZS/SBA-15(6) are presented in Fig. 1. From the images it could be observed that ZS/SBA-15(6) preserved the straight, parallel and uniform channels of SBA-15(6) and ZS dispersed well on the surface of it. Fig. 2 shows the XRD patterns of samples. It was clear that the crystal structure of ZS/SBA-15 was not destroyed, and the peak intensity decreased with the increase of ZS loading.

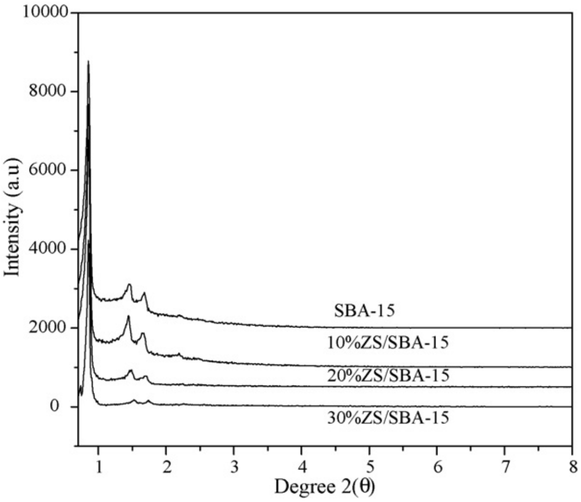

Fig. 2. XRD patterns of samples.

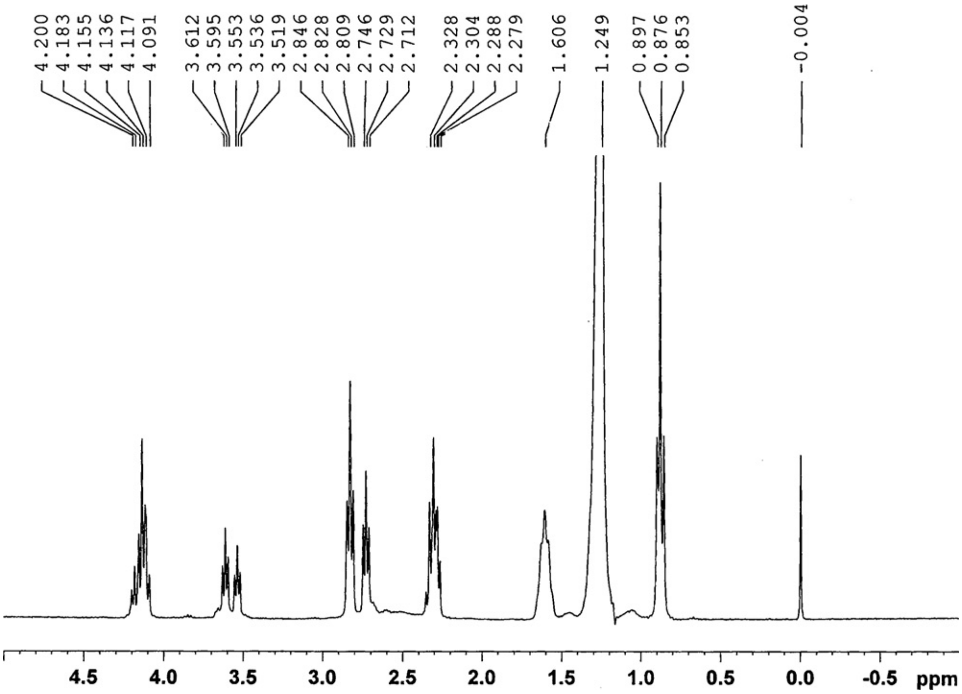

Fig. 3. ^{1}H NMR spectrum of the EA.

The ^{1}H NMR spectrum of product is shown in Fig. 3. According to Fig. 3, the spectrum of product was in good agreement with the ^{1}H NMR spectrum of EA in previous literature [7], and from this it could be concluded that the EA was synthesized successfully. Several kinds of solid acids were used as the catalysts for the synthesis of EA. The data from Table 1 showed that when 20%ZS/SBA-15(6) was used as a catalyst, the acid value of EA was the minimum and the content of mono- and di-esteramine was the maximum. This indicated the catalytic activity and selectivity of 20%ZS/SBA-15(6) was the best for these types of catalysts. Compared with other solid acid catalysts, 20%ZS/SBA-15(6) had proper acid content, the large surface area and appropriate pore diameter. The proper acid content could promote reaction proceed fast. The large surface area could make the reactants contact the active sites effectively and improve the catalytic activity. The appropriate pore diameter could improve the selectivity of catalyst. The selectivity for mono-plus di-esteramine of 20%ZS/MCM-41 and 20%ZS/SBA-15(9) was lower than that of 20%ZS/SBA-15(6), as the pore diameter of 20%ZS/MCM-41 was smaller than the geometric size of di-esteramine molecules (about

Table 1
N_2 adsorption and desorption data, acid value and composition of the EA.

Samples	BSA (m^2/g)	V_p (cm^3/g)	BPD (Å)	AV of EA (mgKOH/g)	The composition of EA		
					Mono-EA	Di-EA	Others
SBA-15(6)	745.43	1.12	60.81	–	–	–	–
10%ZS/SBA-15(6)	615.39	0.88	59.47	2.27	22.30	58.77	18.93
20%ZS/SBA-15(6)	500.93	0.76	57.73	1.68	16.61	67.45	15.94
30%ZS/SBA-15(6)	315.34	0.54	56.56	2.35	20.10	62.02	17.88
SBA-15(9)	452.23	1.06	90.91	–	–	–	–
20%ZS/SBA-15(9)	366.63	0.84	90.19	2.45	21.43	60.31	18.26
MCM-41	1023.83	0.91	29.90	–	–	–	–
20%ZS/MCM-41	656.86	0.57	29.19	2.08	19.99	59.61	20.40
H_3PO_3	–	–	–	2.29	19.11	57.02	23.87

Notes: BSA represents BET surface area, V_p represents volume of pores, BPD represents BJH pore diameter, AV represents acid value. Reaction conditions: 190 °C, n(stearic acid):n(TEA) = 1.8, solid acid catalyst dosage (based on mass of raw material) 1%, H_3PO_3 dosage 0.2%.

Table 2
Impact of catalyst amount on the reaction rate.

Catalyst amount	AV of 4 h (mgKOH/g)	AV of 5 h (mgKOH/g)	AV of 6 h (mgKOH/g)	AV of filtered (mgKOH/g)
1%	2.91	2.28	1.96	1.68
0.75%	2.91	2.12	1.89	1.62
0.5%	3.07	2.02	1.81	1.55
0.25%	2.90	2.12	1.75	1.58

Notes: Reaction conditions: 190 °C, *n*(stearic acid):*n*(triethanolamine) = 1.8. Preparation conditions of ZS/SBA-15(6): ZS loading 20%, calcined at 200°C for 2 h.

Table 3
The re-use of the 20%ZS/SBA-15(6).

Recycling times	AV of 4 h (mgKOH/g)	AV of 5 h (mgKOH/g)	AV of 6 h (mgKOH/g)	AV of filtered (mgKOH/g)
1	2.90	2.12	1.75	1.58
2	2.91	2.12	1.72	1.60
3	3.07	2.02	1.75	1.64
4	2.90	2.12	1.79	1.65
5	3.23	2.68	1.89	1.73

Notes: Reaction conditions: 190 °C, *n*(stearic acid):*n*(triethanolamine) = 1.8, catalyst dosage (based on mass of raw material) 0.25%. Preparation conditions of ZS/SBA-15(6): ZS loading 20%, calcined at 200 °C for 2 h.

4 nm), and the pore diameter of 20%ZS/SBA-15(9) was larger than the size of tri-esteramine molecules (about 7 nm). Compared with the commonly used H_3PO_3, 20%ZS/SBA-15(6) not only can improve the conversion of stearic acid, but also makes the total content of mono- and di-esteramine increase by 8%.

The effect of catalyst amount on the esterification was studied. As shown in Table 2, the reaction rate did not decrease along with the reduction of the catalyst amount. This indicated that a small amount of the catalyst in the esterification reaction could have a good catalytic activity. Therefore, the catalyst amount should be reduced to 0.25%.

At present process of EA, hypophosphorous acid was commonly used as a catalyst. However, the catalyst was difficult to separate from the product and could not be used repeatedly. In addition, the residue of catalyst in the product would impact its application. The 20%ZS/SBA-15(6) could be removed by filtration and could be reused. According to Table 3, when 20%ZS/SBA-15(6) was reused for five times, the catalytic activity of the catalyst did not decrease obviously. This illustrated that 20%ZS/SBA-15(6) had good stability and was an efficient catalyst for the esterification of stearic acid and TEA.

3. Conclusion

Solid acid catalyst ZS/SBA-15(6) not only could speed up the reaction rate and increase the content of mono- and di-esteramine in comparison with hypophosphorous acid, but also had good stability and could be reused for at least five times. Therefore, it could be used as catalyst to replace conventional hypophosphorous acid for the synthesis of EA. In addition, high catalytic activity and selectivity of ZS/SBA-15(6) could be achieved by adjusting the surface area, pore diameter and ZS loading.

Acknowledgments

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