

Preparation and properties of sulfated zirconia for hydrolysis of ethyl lactate

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(Received 12 December 2012 • accepted 3 March 2013)

Abstract—Sulfated zirconia catalysts are proposed for the reversible hydrolysis of ethyl lactate instead of liquid acids. Sulfated zirconia catalysts were prepared by precipitation-impregnation method. The zirconium hydroxide was produced from zirconium oxychloride by adding aqueous ammonia and then impregnated in sulfuric acid. The solid samples were obtained by filtration and evaporation of the mixtures, respectively. After the samples were calcined, the sulfated zirconia catalysts were prepared. The results showed that the catalyst prepared by evaporation has higher catalytic activity. The physicochemical characteristics of the sulfated zirconia catalysts were studied by thermal analysis, X-ray powder diffraction (XRD), temperature programmed desorption of ammonia (NH₃-TPD) and N₂ adsorption-desorption, respectively. By the precipitation-impregnation-evaporation method, the optimal sulfated zirconia catalyst of tetragonal phase was prepared under liquid-solid ratio of 5 ml/g, 1 mol/L of H₂SO₄ and calcination at 650 °C for 3 h. The conversion of the ethyl lactate was 87.8% in 3 h at 85 °C with the catalyst loading 2 wt% and initial molar ratio of water to ethyl lactate 20 : 1.

Key words: Sulfated Zirconia, Hydrolysis, Ethyl Lactate, Catalyst, Precipitation-impregnation Method

INTRODUCTION

Lactic acid is an important organic acid used widely in food applications and the raw material of polylactic acid [1]. Esterification-hydrolysis is effective for producing high purity lactic acid for synthesizing polylactic acid [2]. Sulfuric acid is conventionally used as catalyst for esterification and hydrolysis; however, it has some disadvantages, including corrosion, recycling difficulties and pollution [3]. Recently, great efforts have been devoted to search for solid acid catalysts in esterification and hydrolysis [4-6]. Sun et al. reported the cation exchange resin was used as the catalyst for hydrolysis reaction with the hydrolysis yield of butyl lactate of 75% [7]. However, the cation exchange resin exhibited unsatisfactory activity due to the resin particle size, strength and swelling property. Therefore, sulfated zirconia has gained much attention for reactions due to its non-toxicity, high strength of acidity and high activity [8-10]. Sulfated zirconia has been widely used in n-alkanes isomerization [11], acylations [12], esterification [13] and the dehydration of sugars [14], but rarely used in the hydrolysis reaction of ester. In our previous work, we prepared sulfated zirconia by filtration method, and the prepared catalyst had a certain activity for the hydrolysis reaction [15]. Matsushashi et al. [16] did systematic studies on preparation, characterization and application of the sulfated zirconia. It has been reported that the catalytic activity of sulfated zirconia depended on sulfation procedure, sulfating agent, precipitation procedure and calcination temperature [17].

The objective of this paper is to give fundamental insight into the preparation and performance of sulfated zirconia catalyst. The difference between the filtration and evaporation method in prepa-

ration of sulfated zirconia catalysts was to be investigated.

EXPERIMENTAL

1. Preparation of Catalyst

About 10 g of ZrOCl₂·8H₂O (purity ≥99.0 wt% AR) was dissolved in 30 g of ultrapure water (Millipore, 18.2 MΩ). Aqueous ammonia (28 wt%) was added into the solution dropwise from a burette with vigorous stirring at room temperature till the pH of the solution reached 8. The obtained sediment was washed with ultrapure water to remove chloride ions and then dried at 100 °C for 12 h. The obtained hydrous zirconia sample was powdered below 140 mesh and immersed with different concentrations solution (0.5 mol/L, 1 mol/L and 2 mol/L) of sulfuric acid with a liquid-solid ratio of 5 ml/g. This process was performed under magnetic stirring and maintained at ambient temperature for 3 h. The mixture solution was treated by two methods as shown in Fig. 1. One part of the mixture solution was filtered with filter paper and dried at 100 °C for 12 h, then calcined at 650 °C for 3 h in static air atmosphere. The prepared catalysts were labeled as SZ1-0.5, SZ1-1 and SZ1-2 according to the concentration of sulfuric acid solution. The other part of the mixture solution was evaporated on the heat-up magnetic agitator at about 150 °C and ground to fine powder, then calcined at 650 °C for 3 h in static air atmosphere. The prepared catalysts were labeled as SZ2-0.5, SZ2-1 and SZ2-2 according to the concentration of sulfuric acid solution. The SZ2-1 catalysts with different liquid-solid ratios (1 ml/g, 2.5 ml/g, 4 ml/g, 5 ml/g, 10 ml/g and 15 ml/g) were labeled as SZ2-1-1, SZ2-1-2.5, SZ2-1-4, SZ2-1-5, SZ2-1-10 and SZ2-1-15. The SZ2-1-5 catalysts were calcined at different temperatures ranging from 550 °C to 700 °C and different calcination times.

2. Characterization

The physicochemical properties of zirconia and sulfated zirconia

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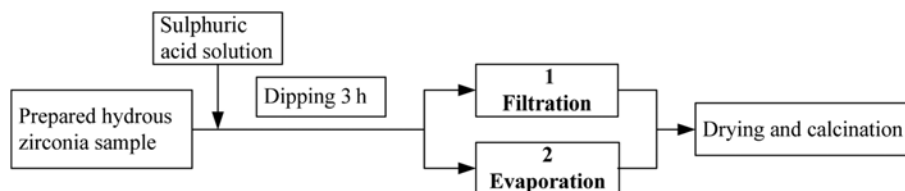


Fig. 1. Preparation process of the SZ catalysts by filtration and evaporation.

catalysts were examined by various techniques: thermal analysis, X-ray diffraction, NH_3 -TPD, BET and particle size analysis. Thermogravimetry and differential scanning calorimetry (TG-DSC) was performed in nitrogen by thermoanalyzer (Sta 449 F3, Netzsch, Germany) in the temperature range 25–1,400 °C with a heating rate of 10 °C/min. For each experiment, 10–15 mg of sample was used. X-ray powder diffraction measurements were performed by (D8 Advance, Bruker AXS, Germany) at the scan speed of 5°/min and scan range 10–80°. The acid strength of the sample was determined by temperature-programmed desorption of ammonia (Belcat-A, BEL, Japan). As for TPD, 200 mg of sample was heated at a rate of 10 °C/min up to 500 °C and kept for 0.5 h in 30 ml/min of He to remove adsorbed impurities on the surface. Then, the sample was cooled to 100 °C in a flow of He and saturated for 1 h using 30 ml/min of NH_3/He (1 : 9). The system was flushed with He (30 ml/min) at 100 °C for 1 h to eliminate physically adsorbed NH_3 . For TPD of the probe molecules, the temperature was increased to 500 °C at a rate of 10 °C/min, and then was kept for 1 h. The TCD detector was used to measure the NH_3 desorption profile. BET surface area was measured on a Micromeritics Tristar II 3020 instrument. Prior to the adsorption measurements, the sample was evacuated overnight at 200 °C to remove adsorbed species on the surface. The particle size was measured by Malvern Mastersizer 2000.

3. Activity Test of Catalytic

The activity of the catalyst for the hydrolysis of ethyl lactate with water was investigated in a three-necked flask with a thermometer reflux condenser and magnetic stirrer. The total volume of solution was 87.6 ml, of which the volume of the ethyl lactate was 21.3 ml. After the reaction, catalyst was separated by 0.22 μm polyethersulfone membrane. The selectivity of the reaction was found to be 100% for hydrolysis of ethyl lactate. The activity of all catalysts was characterized by the hydrolysis reaction of ethyl lactate. The concentration of ethyl lactate was determined with GC (GC-2014C, Shimadzu, Japan) equipped with a flame ionization detector (FID). The capillary column used (30 m \times 0.25 mm \times 0.25 mm, Rtx-1) was held at 80 °C. The injector and detector temperatures were 200 °C. The carrier gas was nitrogen (99.99%). The sample size for GC was 0.2 μl .

RESULTS AND DISCUSSION

1. Thermal Analysis

The temperature stability of the prepared samples was investigated by TG-DSC method. The obtained thermograms of uncalcined zirconia and SZ samples prepared by filtration and evaporation methods are illustrated in Fig. 2 and Fig. 3, respectively. As shown in Fig. 2, the endothermic peaks observed on DSC traces at 100 °C in the four samples are attributed to the desorption of physically adsorbed water with weight loss. As for uncalcined zirconia sample (A), a strong

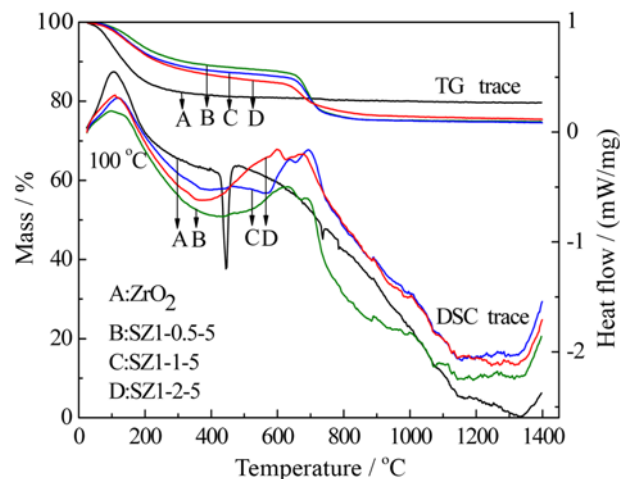


Fig. 2. TG-DSC results of the SZ1 catalysts with different concentration of sulfuric acid.

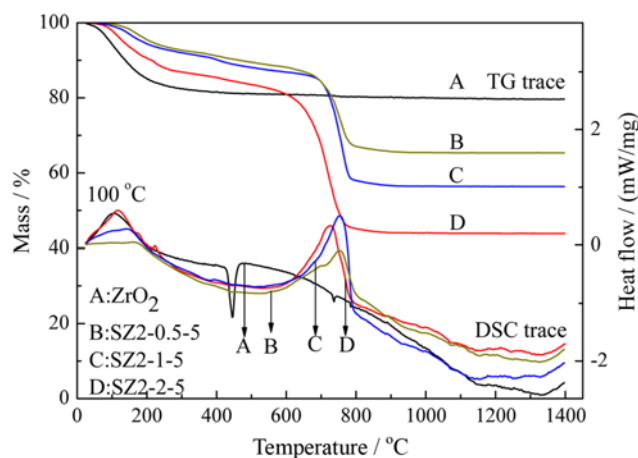


Fig. 3. TG-DSC results of the SZ2 catalysts with different concentration of sulfuric acid.

exothermic peak at 430 °C in the DSC trace could be attributed to the heat effect of the phase transformation from amorphous zirconia to tetragonal zirconia because the mass of sample didn't vary observed from the curve A of the TG trace. Guan et al. [18] also observed the phenomenon of the strong exothermic peak for the uncalcined zirconia sample. However, the sulfated zirconia samples B, C and D had no this specific exothermic peak. The broad endothermic peaks of DSC trace at about 700 °C are attributed to decomposition of surface sulfate groups because mass loss was observed in TG trace for samples B, C and D. And similar phenomena were observed by Reddy [19]. The mass losses of the SZ1 sam-

ples B, C and D at 700 °C from TG traces were 12%, 11% and 8%, respectively. It demonstrated that the quantity of sulfate groups of the three SZ1 samples immersed in different concentration of sulfuric acid solution was almost equal. However, as shown in Fig. 3, the mass loss of the samples B, C and D prepared by the method of evaporation at 700 °C from TG traces was 21%, 30 % and 37%, respectively. The TG results showed that the mass loss of the three catalysts (SZ2-0.5-5, SZ2-1-5, SZ2-2-5) increased with the concentration of dipping solution. It obviously demonstrated that the mass losses of the catalysts prepared by filtration and evaporation methods were different. The catalysts dried by evaporation exhibited higher sulfur content than those by filtration. The phenomenon indicated that the sulfates on the surface of zirconia after immersion ran away by filtration, but evaporation was favorable to the load of SO_4^{2-} . Based on the thermal gravimetry (TG) analysis, the calcination temperature for sulfated zirconia was determined at 650 °C.

2. XRD Patterns

The sulfate zirconia catalysts with tetragonal crystal phase had

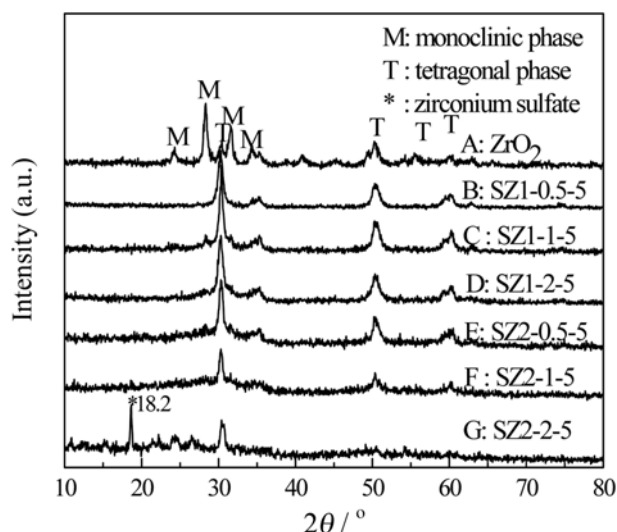


Fig. 4. XRD spectra of SZ1 and SZ2 catalysts with different concentration of sulfuric acid.

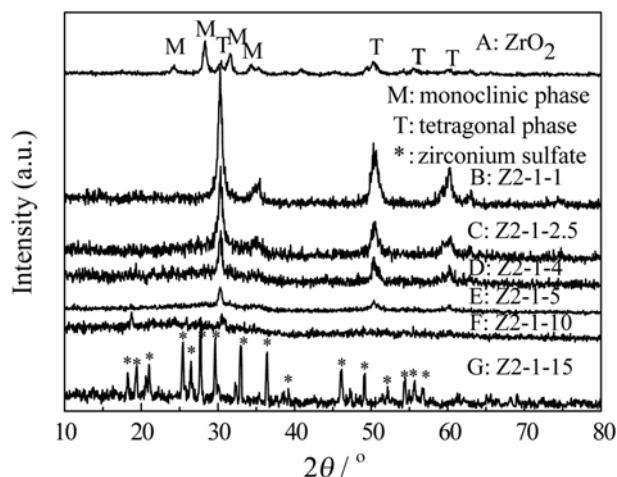


Fig. 5. XRD spectra of SZ2-1 catalysts prepared with different liquid-solid ratios.

good activity for reactions [18]. The XRD patterns of zirconia, SZ1 and SZ2 samples calcined at 650 °C were measured and shown in Fig. 4 and Fig. 5, respectively. The qualitative analyses of the phases present in the catalysts were performed by comparing the observed profile with the profiles reported in the database of the International Centre for Diffraction Data (ICDD). The broad peaks that appear at $2\theta=30.2^\circ$, 35.3° , 50.4° , 55.5° , 59.7° correspond to the tetragonal phase (JCPDS no.88-1007). The broad peaks that appear at $2\theta=28.2^\circ$, 31.5° correspond to the monoclinic phase (JCPDS no.72-1669). The broad peaks that appear at $2\theta=18.2^\circ$, 19.23° , 20.93° , 25.35° , 26.34° , 27.59° , 29.55° , 32.89° , 36.32° , 39.09° , 46.03° , 49.01° , 52.10° , 54.23° and 55.54° correspond to the zirconium sulfate (JCPDS no.24-1492). The zirconia A after calcination at 650 °C has transformed from amorphous to monoclinic phase and tetragonal phase. The sulfated samples B, C, D, E, F and G were in tetragonal phase. It indicated that the impregnated sulfate ions took great influence on the phase modification of zirconia from amorphous to the tetragonal phase. There was no change of the samples B, C and D prepared by the method of filtration. However, as for E, F and G prepared by the method of evaporation, the intensity of tetragonal phase weakened with the increasing concentration of sulfuric acid solution. When the concentration of sulfuric acid solution increased to 2.0 mol/L, the intensity of the tetragonal phase was quite weak and a peak of $\text{Zr}(\text{SO}_4)_2$ at 18.2° appeared in the sample G. It indicated that the sulfate ions could effectively inhibit the phase change of zirconia crystal [20-22].

A suitable liquid-solid ratio (sulfuric acid-hydrous zirconia) was investigated via the method of evaporation. As shown in Fig. 5, with the increasing of the liquid-solid ratio, the strength of the tetragonal phase became weak. When the liquid solid ratio was over 10 ml/g, many peaks of zirconium sulfate appeared in XRD patterns of the samples F and G. The results showed that the addition of sulfuric acid decreased the intensity of the tetragonal phase and a new phase of zirconium sulfate was formed. Therefore, the amount of H_2SO_4 had great effect on the crystallization of the sulfated zirconia catalysts.

The XRD patterns of SZ2-1-5 samples at different calcination temperatures and times are shown in Fig. 6. The samples calcined at 500 and 600 °C were mainly amorphous. For samples calcined

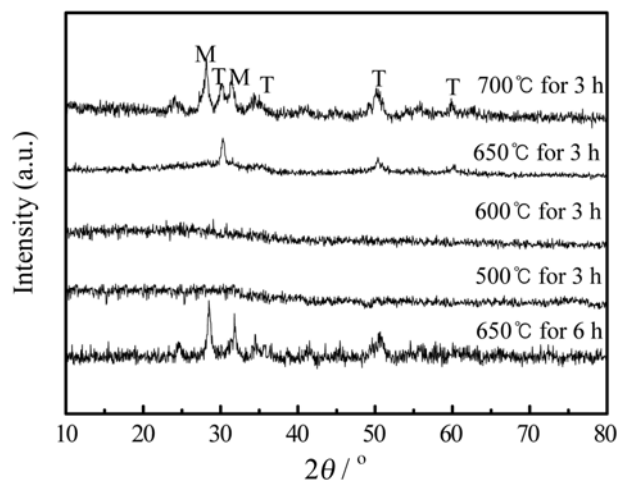


Fig. 6. XRD spectra of SZ2-1-5 catalysts prepared at different calcination temperature and time.

at 650 °C, the predominant phase was the tetragonal phase. When the calcination temperature increased to 700 °C, the intensity of the tetragonal phase enhanced and the monoclinic phase was formed. The intensity of the tetragonal phase also enhanced and the tetragonal phase began to transform to the monoclinic phase for samples whose calcination time was 6 h. Thus, the calcination temperature and time also played a very important role on the crystallization of the sulfated zirconia catalysts.

3. NH₃-TPD

The acidity of the catalyst samples was measured by NH₃-TPD [23]. The NH₃-TPD results of various catalysts calcined at 650 °C are shown in Fig. 7 and Fig. 8. The acid amounts were calculated by the amount of desorbed NH₃ and listed in Table 1 and Table 2. The acid sites on the tested samples were classified as weak (100–200 °C), medium (200–450 °C) and strong (450–500 °C) acid sites [24]. The total amount of acid sites was about 0.08 mmol/g for SZ1 catalysts higher than 0.041 mmol/g for ZrO₂. The distribution of the acid strength of SZ1 catalysts had no obvious change in Fig. 7 and Table 1. This was ascribed to the loss of sulfate ion by filtration. It demonstrated that the effect of the starting concentration of sulfuric acid on acid strength of the SZ1 catalysts was found to be negligible as given in Table 1. These were in good agreement with

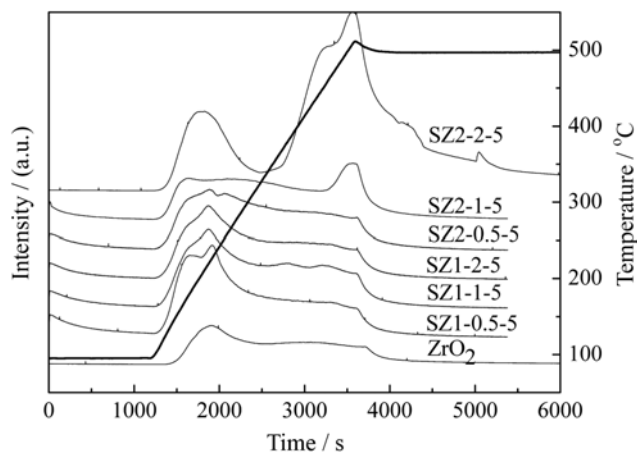


Fig. 7. NH₃-TPD of ZrO₂, SZ1 and SZ2 calcined at 650 °C.

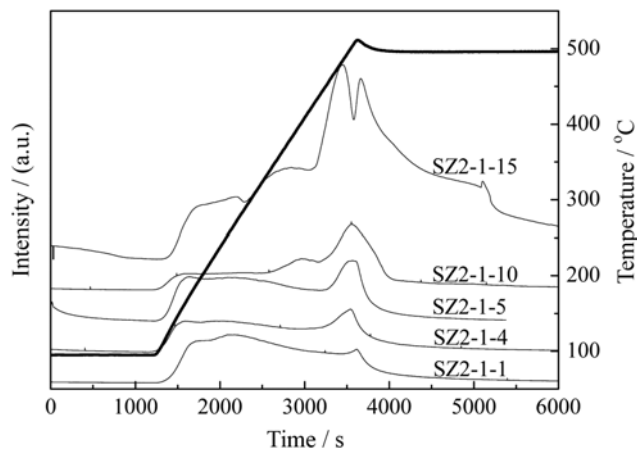


Fig. 8. NH₃-TPD of SZ2-1 at different liquid-solid ratio calcined at 650 °C.

the results of the TG-DSC results. However, the amount of strong acid site increased from 0.014 mmol/g for SZ2-0.5-5 to 0.225 mmol/g for SZ2-2-5 in Table 1, and the amount of strong acid site increased from 0.017 mmol/g for SZ2-1-1 to 0.255 mmol/g for SZ2-1-15 in Table 2. It was clear that the preparation method and the sulfate content played a key role in the formation of the amount of acid site and strong acid site. The acid amount of SZ2-2-5, SZ2-1-10 and SZ2-1-15 was higher than that of other catalysts because the zirconium sulfate was formed from the results of XRD. However, zirconium sulfate could be solved in water and difficult to separate from the reaction mixture. Therefore, the optimum concentration of sulfuric acid was 1 mol/L and the liquid-solid ratio was 5 ml/g.

The NH₃-TPD results of SZ2-1-5 samples at different calcination temperatures and times are shown in Fig. 9 and the amount of

Table 1. The distribution and the strength of acid sites in SZ1 and SZ2 prepared at different concentrations of sulfuric acid

Catalysts	The amount of acid site (mmol/g)			
	Weak	Medium	Strong	Total
ZrO ₂	0.007	0.025	0.009	0.041
SZ1-0.5-5	0.019	0.053	0.012	0.084
SZ1-1-5	0.015	0.055	0.015	0.085
SZ1-2-5	0.015	0.053	0.012	0.080
SZ2-0.5-5	0.012	0.049	0.014	0.075
SZ2-1-5	0.013	0.048	0.030	0.091
SZ2-2-5	0.023	0.098	0.225	0.346

Table 2. The distribution and the strength of acid sites in SZ2-1 prepared at different liquid-solid ratios

Catalysts	The amount of acid site (mmol/g)			
	Weak	Medium	Strong	Total
SZ2-1-1	0.011	0.047	0.017	0.075
SZ2-1-4	0.010	0.044	0.026	0.080
SZ2-1-5	0.013	0.048	0.030	0.091
SZ2-1-10	0.006	0.033	0.056	0.095
SZ2-1-15	0.012	0.101	0.255	0.368

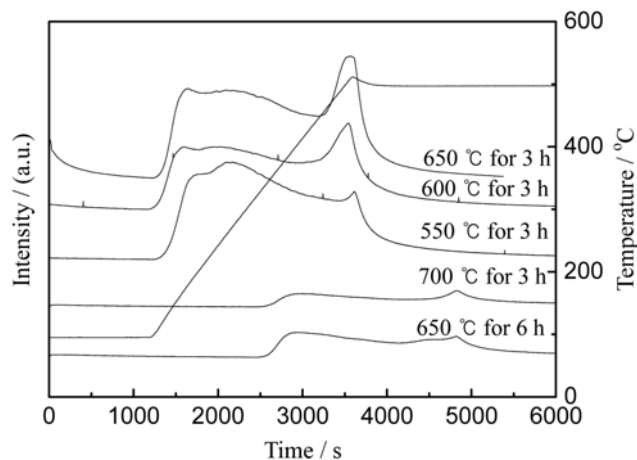
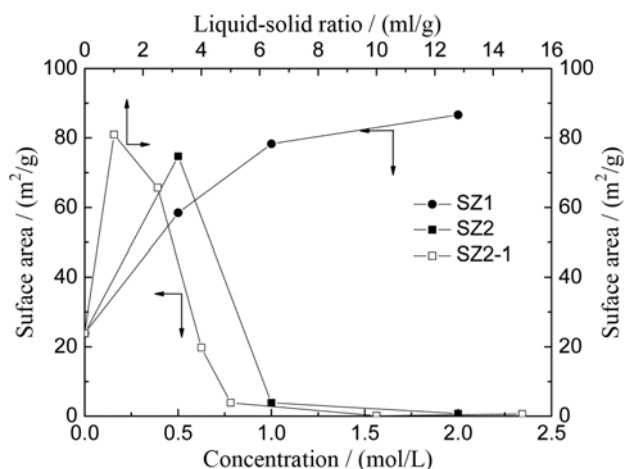


Fig. 9. NH₃-TPD of SZ2-1-5 at different calcination temperatures and times.

Table 3. The distribution and the strength of acid sites of SZ2-1-5 prepared at different calcination temperatures and calcination times

Calcination conditions	The amount of acid site (mmol/g)			
	Weak	Medium	Strong	Total
550 °C (3 h)	0.011	0.043	0.015	0.069
600 °C (3 h)	0.010	0.045	0.016	0.071
650 °C (3 h)	0.013	0.048	0.030	0.091
700 °C (3 h)	0.006	0.025	0.011	0.042
650 °C (6 h)	0.008	0.023	0.013	0.044

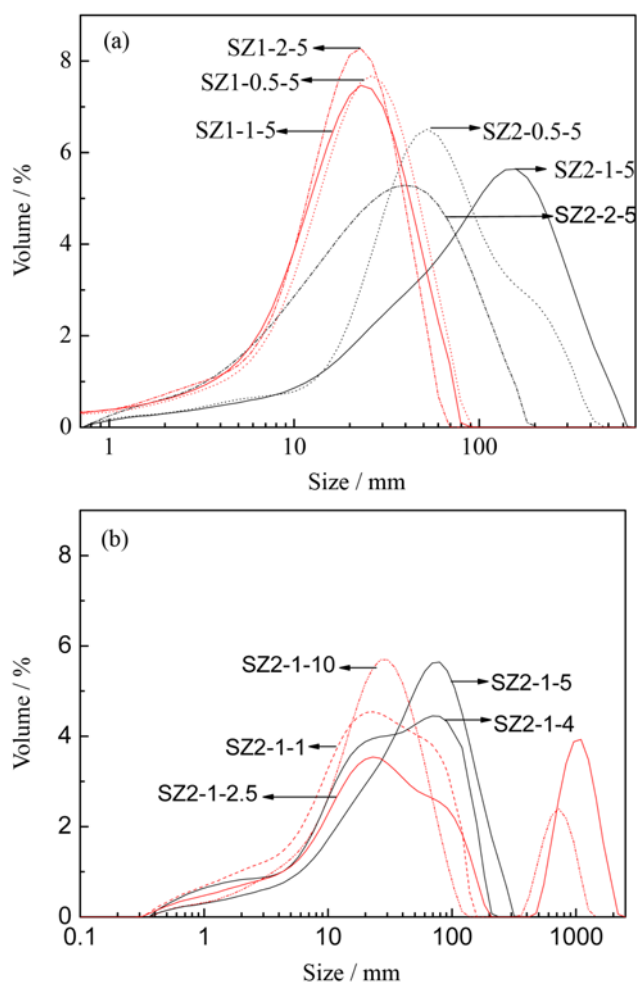
**Fig. 10. The specific surface areas of the prepared catalysts.**

acid site is listed in Table 3. The amount of strong acid site increased from 0.022 mmol/g to 0.030 mmol/g when the calcination temperature increased from 550 °C to 650 °C. Temperature had great influence upon the calcination of catalyst. At a lower calcination temperature the catalyst was amorphous and the acid sites did not completely form. However, when the calcination temperature was increased to 700 °C, the amount of strong acid site decreased because of the decomposition of sulfate groups. Furthermore, the amount of strong acid site with calcination time of 6 h was lower than that of 3 h. We ascribed the decrease to the phase transformation of the catalyst which is shown in Fig. 6. It's obvious that the calcination temperature was crucial for the activity of the prepared catalyst.

4. BET and Particle Size Distribution

The specific surface areas of the catalysts synthesized at different conditions are shown in Fig. 10. Clearly, the specific surface areas of SZ1 catalysts increased with the concentration of sulfuric acid. The specific surface area increased from 58.4 m²/g for SZ1-0.5-5 to 86.7 m²/g for SZ1-2-5. However, the specific surface area decreased from 74.7 m²/g for SZ2-0.5-5 to 0.8 m²/g for SZ2-2-5. As for the SZ1 catalysts, the sulfate amount on the surface of ZrO₂ changed slightly with the concentration of sulfuric acid from Fig. 2. And the sulfate content for SZ1 was less than 15 wt%. Ahmed [25] reported that the specific surface area of sulfated zirconia increased with the quantity of sulfate before 15 wt% and then decreased.

As for the SZ2 catalysts, the sulfate amount on the surface of ZrO₂ changed dramatically with the concentration of sulfuric acid from Fig. 3. And the sulfate content for SZ2 was larger than 15 wt%. Thus,

**Fig. 11. The particle size distributions of the catalysts prepared at different conditions (A: SZ1 and SZ2 prepared at different sulfuric acid concentrations; B: SZ2-1 prepared at different liquid-solid ratios).**

the specific surface area of SZ2 catalysts decreased with the concentration of sulfuric acid. As for the SZ2-1 catalysts, the sulfate amount on the surface of ZrO₂ changed dramatically with the liquid-solid ratio from Fig. 4. The sulfate content for SZ2-1 was also larger than 15 wt%, which resulted in that the specific surface area of SZ2-1 catalysts decreased with the liquid-solid ratio.

Particle size distributions of the catalysts prepared under different conditions are presented in Fig. 11. It shows that average particle sizes were almost the same by filtration method, which was lower than that by evaporation. The reason might be the agglomeration of particles in the process of evaporation.

5. Hydrolysis of Ethyl Lactate with the Prepared Sulfated Zirconia

To detect the activity of catalysts, the conversion of hydrolysis of ethyl lactate using different catalysts was investigated under the same reaction conditions: reaction temperature of 85 °C, water to ethyl lactate molar ratio of 20 : 1, catalyst loading 2.0 wt% and reaction time 3 h.

5-1. Comparison of Various Catalysts (SZ1 and SZ2)

As shown in Fig. 12, the conversion of hydrolysis using the sulfated zirconia catalysts prepared by evaporation was obviously higher

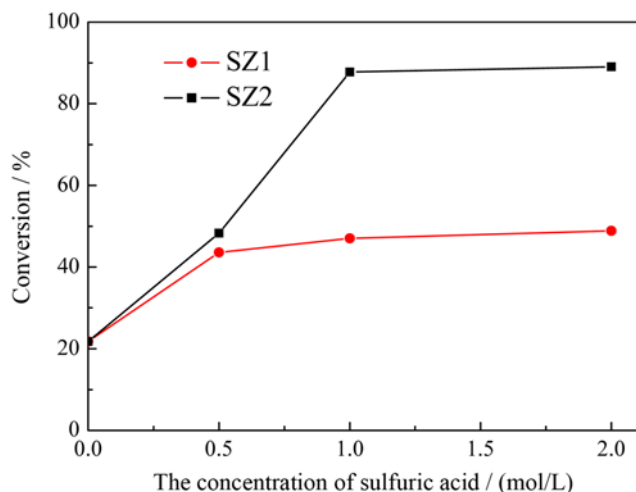


Fig. 12. Conversion of ethyl lactate with catalysts SZ1 and SZ2 prepared with different concentrations of sulfuric acid (reaction temperature of 85 °C, water to ethyl lactate molar ratio of 20 : 1, catalyst loading 2.0 wt% and reaction time 3 h).

than that by filtration. The conversion of the ethyl lactate was only 21.7% with pure zirconia. As for the method of filtration, the catalytic activity of the series of SZ1 catalysts was not satisfactory and below 48.9%. However, as for the method of evaporation, the conversion increased obviously with the concentration of sulfuric acid. The conversion of the ethyl lactate is 48.3%, 87.8% and 89.2% for the sulfuric acid concentration of 0.5, 1.0 and 2.0 mol/L, respectively. As listed in Table 1, it was indicated that the conversion with sulfated zirconia was related to the concentration of strong acid sites on the catalyst. Clearly, the series of SZ2 was better than the series of SZ1 and the optimum concentration of dipping solution was 1 mol/L.

5-2. Effect of Liquid-solid Ratio on Catalytic Activity

Fig. 13 shows the conversion of ethyl lactate in hydrolysis reaction with SZ2-1 at different liquid-solid ratios. The conversion increased with the increasing liquid-solid ratio from 1 ml/g to 5 ml/g

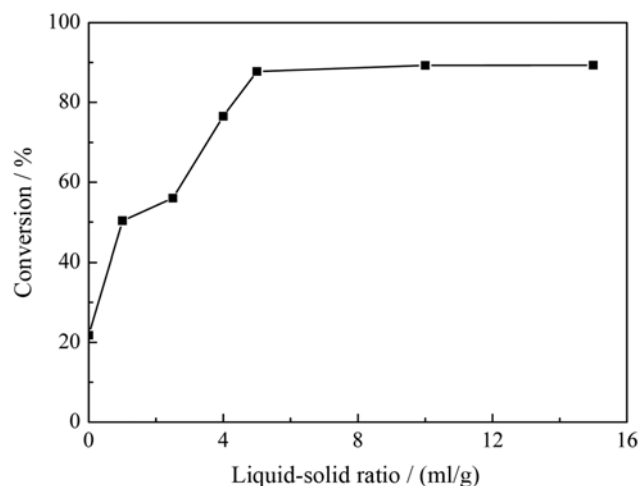


Fig. 13. Conversion of ethyl lactate with catalysts SZ2 prepared with different liquid-solid ratios (reaction temperature of 85 °C, water to ethyl lactate molar ratio of 20 : 1, catalyst loading 2.0 wt% and reaction time 3 h).

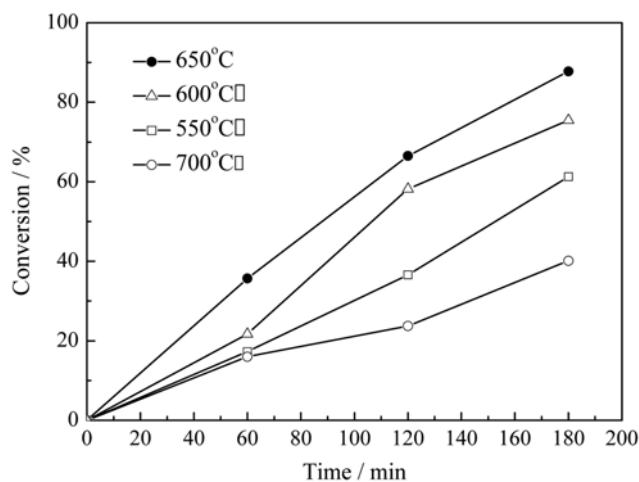


Fig. 14. Conversion of ethyl lactate with catalysts SZ2-1-5 prepared at different calcination temperatures (reaction temperature of 85 °C, water to ethyl lactate molar ratio of 20 : 1, catalyst loading 2.0 wt% and reaction time 3 h).

and then changed slightly. It could also be explained by the strong acid site in Table 2. On the basis of the experimental results, the optimum liquid-solid ratio was 5 ml/g.

5-3. Effect of Calcination Temperature and Calcination Time on Catalytic Activity

The calcination temperature and calcination time greatly affected the performance of sulfated zirconia catalysts SZ2-1-5. To ensure the optimum calcination temperature and time, the catalytic activity of the catalysts calcined at different temperatures and times was investigated and shown in Fig. 14 and Fig. 15. The catalysts calcined at 650 °C for 3 h exhibited maximum activity due to strongest acidity as listed in Table 3. Thus, the optimum calcination temperature and time were 650 °C and 3 h, respectively.

5-4. Effect of Reaction Time on Conversion

The conversion variation of ethyl lactate catalyzed by SZ2-1-5

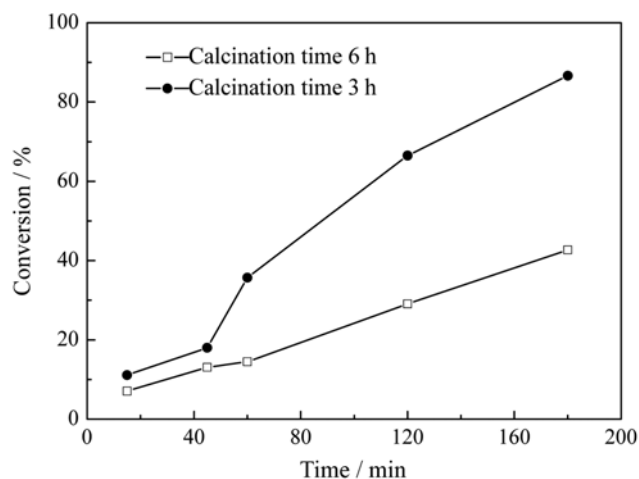


Fig. 15. Conversion of ethyl lactate with catalysts SZ2-1-5 prepared at different calcination times (reaction temperature of 85 °C, water to ethyl lactate molar ratio of 20 : 1, catalyst loading 2.0 wt% and reaction time 3 h).

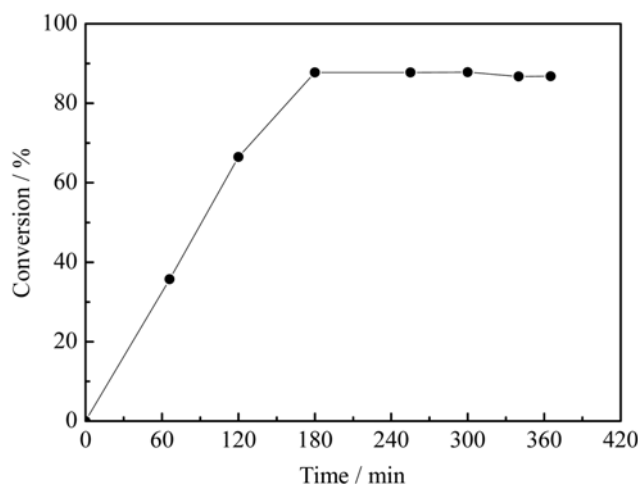


Fig. 16. Conversion of ethyl lactate with SZ2-1-5 varied with time (reaction temperature of 85 °C, water to ethyl lactate molar ratio of 20 : 1, catalyst loading 2.0 wt% and reaction time 3 h).

with time is shown in Fig. 16. It represents that the hydrolysis conversion increased with time before 3 h and then reached the equilibrium 87.8% at 85 °C with the catalyst loading 2 wt% and the initial molar ratio of water to ethyl lactate 20 : 1.

CONCLUSION

Sulfated zirconia catalysts were prepared by precipitation-impregnation method and used for hydrolysis of ethyl lactate. The catalysts prepared by precipitation-impregnation-evaporation had higher catalytic activity than that by precipitation-impregnation-filtration for hydrolysis of ethyl lactate. The optimized parameters were the concentration of sulfuric acid 1 mol/L, the liquid-solid ratio 5 ml/g and calcination temperature 650 °C for 3 h. The experimental results showed that the conversion of ethyl lactate was 87.8% after 3 h at 85 °C with the catalyst loading 2 wt% and the initial molar ratio of water to ethyl lactate 20 : 1.

ACKNOWLEDGEMENTS

This work was financially supported by National Natural Science Foundation of China (No. 20806039), Program from State Key Laboratory of Materials-Oriented Chemical Engineering (No. ZK201005), Jiangsu Province Natural Science Foundation for University of China (No. 11KJB530005) and National Hi-tech Research Development Program of China (No. 2007AA03Z437).

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