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Design and elaboration of new solid acids for the synthesis of butylacetate

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Abstract

New and efficient solid-acid catalysts were designed and prepared by the coprecipitation-impregnation method, for the esterification of acetic acid and butanol synthesizing the butylacetate ester in fine chemical industry, in which the conventional catalyst was sulfuric acid. This work resulted in a cleaner process for acid-catalyzed reaction. The preparation parameters in the precipitation step and in the calcination were improved for a better performance. With the optimized new solid-acid catalyst, a good ester yield of 93.3% was achieved with the selectivity of 96.0%. The samples were characterized by XRD, N_2-adsorption and TGA measurements, the SO_4^{2-} anion was essential in the active structure.

Keywords: Sulfated solid acid; Catalyst; Cleaner process; Precipitation; Calcination; Esterification; Iron–zirconium; Silica

1. Introduction

There are many cases using the acidic catalysts in the modern chemical industries or for the production of fine chemicals [1–6]. The liquid acid like H_2SO_4 was often used, however, there were several disadvantages like the corrosion of equipment and environmental pollution. There were more and more works for developing efficient solid acids for the replacement of H_2SO_4 application [3–8], leading to cleaner processes. Since the primary work of Arata and Hino in 1979 [8], the super acids by sulfated metal oxides have been attracting more and more attention for investigations.

In our previous work [5,9], some good results have been achieved for the synthesis of butylacetate using a cleaner process without sulfuric acid in the catalyst system, over the sulfated solid-acid catalysts. In the present paper, we will focus on how the preparative conditions affect the catalytic performance of the iron oxide enhanced zirconia system, in the cleaner process of esterification.

2. Experimental

2.1. Catalyst preparation

The initial precursor materials were Fe $(SO_4)_3{\cdot}xH_2O$, $ZrO(NO_3)_2{\cdot}2H_2O$, $Na_2SiO_3{\cdot}9H_2O$. The pH value was adjusted by diluted H_2SO_4 or NaOH. The catalysts were prepared by coprecipitation-impregnation [5,10] or stepwise precipitation-impregnation.

The coprecipitation-impregnation method was performed by the following steps: the salt solution of Fe, Zr, Si was mixed to be homogeneous at room temperature, the coprecipitation was done by adjusting the pH value, aging for 2 h, drying at 383 K, pre-calcinated at 573 K for 3 h; then impregnated with diluted H_2SO_4 for 15 min, then dried and calcinated at 873 K for 5 h.

The stepwise precipitation-impregnation method was conducted by the following steps: the precipitation of Fe, Zr, Si was done respectively, at room temperature, then the slurries were mixed together, the pH was adjusted to a certain value, aging for 2 h, the other steps like drying, impregnation and calcination were the same in the coprecipitation-impregnation.

2.2. Synthesis of butylacetate in liquid phase

The reaction apparatus [5,11] was composed of a tri-neck bottle, water-separating device and refrigerant tube, with a

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magnetic stirring, the oil-bath was for maintaining the system temperature. The reaction parameters were: the amount of acetic acid was 125 mmol, the molar ratio of butanol over acetic acid was 1:1, the reaction temperature was 363–387 K (typically 366 K for 2 h), no other solvent was used in the reaction system. The catalyst was separated from the reaction mixture by filtration. The products were analyzed by using gas chromatogram equipped with TCD, the column had a length of 2.5 m, internal diameter of 3 mm, at 428 K.

2.3. Characterization of catalysts

The XRD, N_2-adsorption and TGA techniques were used for the catalyst characterization [12,13]. The surface area was achieved on a Digisorb 2000 type automatic adsorption instrument by BET method (M*icrometics* company). The TGA results were conducted on Perkin-Elmer TGA7 type thermal gravimeter analyzer in air atmosphere at an increment rate of 10 K/min. The analysis of crystal structure of catalyst samples was performed on a Rigaku D/max-X-ray diffractionmeter, with Cu Kα radiation, the working current was 40 mA, the voltage was 50 kV.

3. Results and discussion

3.1. Influence of the amount of catalyst component

In the solid acid systems, the expression SO_4/MeOx means sulfated metal oxide [3] such as sulfated zirconia. The valence of S in the sulfated metal oxide is +6; the expression is based on the image of sulfation together with the neutral charge. The sulfated zirconia (SO_4/ZrO_2) has been investigated in various reactions. It is commercially available and used actually as an acid catalyst for the organic synthesis in industry. In our precious works [5,9], we have studied the sulfated zirconia, sulfated titania and other promoted system in the esterification of acetic acid with butanol, it was found that the promoted systems with iron oxide and/or silica gave better catalytic performance. In the present work, the role of molar content of silica and that of molar ratio of iron over zirconium have been studied in detail.

It was shown in Fig. 1 that the Fe/Zr molar ratio (from 0 to 3.0) influenced the catalytic performance. It was observed that there was an increase of ester yield of butylacetate when the Fe/Zr ratio was raised from 0 to 0.40. A maximum value of 55.1% of ester yield was achieved at a Fe/Zr ratio of 0.25, compared to 38.4% for the system without iron promotion. When the Fe/Zr ratio was equal to 1.0 and higher than 1.0, the ester yield decreased to a lower level. The optimum Fe/Zr ratio was during 0.20–0.40.

The effect of molar content of silica was illustrated in Fig. 2. The Fe/Zr ratio was fixed at 0.33, an ester yield of 53.4% was obtained for 20% of silica content in the catalyst, with a selectivity of 97.1% in butylacetate, a small amount of

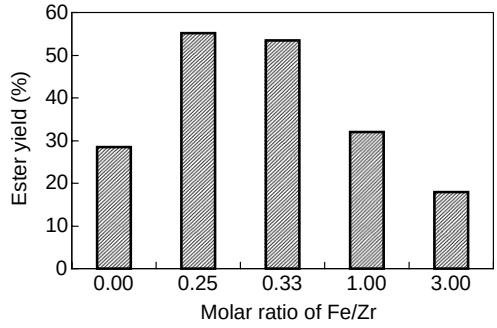

Fig. 1. Ester yield of butylacetate vs. the molar ratio of iron over zirconium in the solid-acid SO_4/Zr–Fe–Si–O.

butyl ether was observed as a by-product (less than 3%). The dependence of catalytic performance on the silica content followed a continuous variation shown in Fig. 2, there was a maximum of ester yield at 91.8% for the sample with 2% molar content of silica in the catalyst. The silica content from 1 to 5% in the sample gave better catalytic performance than the results of the sample with more than 10% silica. For the selectivity of butylacetate, it was very similar, a value about 97% was obtained for all the silica promoted catalysts.

3.2. Effect of preparation condition in the precipitation step

The sulfated solid acids were prepared from their salts by a coprecipitation-impregnation method or a stepwise precipitation-impregnation method, the typical catalyst performance were shown in Table 1. For the system of 20% silica and a Fe/Zr ratio of 0.25, the catalyst prepared by the coprecipitation-impregnation method gave better conversion and ester yield than those of the catalyst prepared by the stepwise precipitation-impregnation method. So did the system with a Fe/Zr ratio of 1.0 by coprecipitation-impregnation method. This method was also simple, compared with the more complexity of the stepwise precipitation method.

In the coprecipitation-impregnation process, different parameters could have important effects on the catalyst structure, surface acidity and catalytic performance [14–16], such

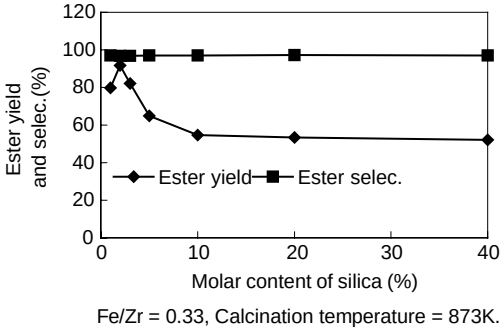

Fig. 2. Ester selectivity and ester yield vs. the molar content (C^*) of silica in the solid-acid SO_4/Zr–Fe–Si–O.

Table 1
Comparison of catalytic performances over solid-acids SO_4/Zr–Fe–Si–O by different preparation method

f_1*	Coprecipitation-impregnation		Stepwise precipitation-impregnation	
	Ester yield (%)	Ester selectivity (%)	Ester yield (%)	Ester selectivity (%)
0.25	55.14	97.16	53.58	96.17
1	32.05	96.75	26.74	96.53

f_1^* = molar ratio of Fe/Zr, silica content = 20%, calcination temperature = 873 K.

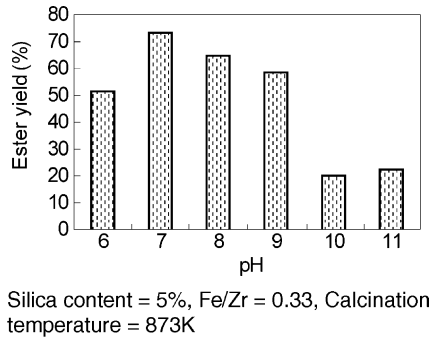

Fig. 3. Ester yield vs. pH value of coprecipitation for the solid-acid SO_4/Zr–Fe–Si–O.

as pH value of precipitation, temperature of precipitation, washing agent, aging time and the concentration of impregnating sulfuric acid. The influence of pH value of precipitation on ester yield was illustrated in Fig. 3. When the pH value was changed from 6.0 to 11.0, the butylacetate yield increased at first then decreased. A maximum value of 73.3% was achieved when pH value was equal to 7.0. When the pH value was equal to 10.0 or more than that, the catalyst activity was very low, while the ester selectivity could maintain a good value about 97%. The explanation was the variation of crystal grain size and the diminution of surface area or the heterogeneity of the catalyst prepared at high pH value.

The influence of aging time of precipitate was shown in Fig. 4, when silica content was 5%, with a pH of 8.0. The ester yield of butylacetate was enhanced with the enlarging of aging time. The good selectivity of ester was kept at 97%. The ester yield without an aging was only 39.0%, it increased to 64.8% with an aging time of 1 h, then the enhancement of

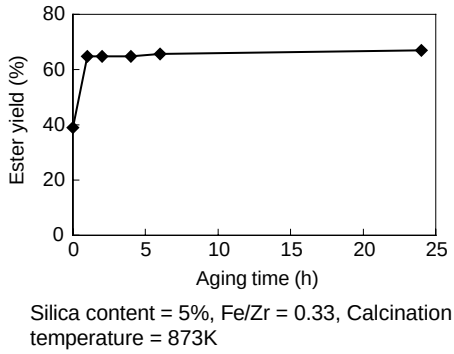

Fig. 4. Role of aging time on the ester yield over the solid-acid SO_4/Zr–Fe–Si–O.

ester yield was slightly varied, to a value of 67.0% with 24 h aging. From the XRD patterns of the samples with different aging time, there were mainly the amorphous phase for the catalyst components.

With the increasing of aging time, a small amount of cubic crystallites of ZrO_2 was appeared ($2\theta = 31^\circ, 51^\circ, 61^\circ$). The reason was that there was an active structure composed of a certain proportion of Fe, Zr, Si and oxygen, which was difficult to be crystallized. This structure was favored with a certain aging time, the rest of ZrO_2 could form a small amount of cubic crystallites of zirconia.

3.3. Influence of calcination parameters

In the reference work, the pre-calcination temperature, calcination atmosphere and temperature could have important effects on the catalyst structure and performance [2,3,17,18]. In some cases, a double calcination on the Pt-added sulfated zirconia was investigated for a better dispersion and a lowered Pt content, achieving an optimum activity [2,3]. The role of pre-calcination temperature was investigated. With a temperature range from 473 to 1073 K, it was between 573 and 773 K that a better performance was observed (64.8–68.7% for ester yield). When the pre-calcination temperature was equal to 873 K or higher, the ester yield became much lower. From the BET results of the catalysts pre-calcination at different temperature, a decreasing tendency of surface area was observed with the rising of temperature. Another reason could be the structure changing of the active phases.

By the coprecipitation-impregnation method, the catalyst precursor was prepared, with a silica content of 5% and Fe/Zr ratio of 0.33. Then it was calcinated at 873 K in different atmosphere such as H_2, N_2, air or oxygen [13]. The results of catalytic performance were grouped in Table 2. The sample calcinated in H_2 atmosphere gave a black color, while the catalysts calcinated in other atmospheres gave a red color.

Table 2
Ester selectivity and ester yield vs. calcination atmosphere for the solid-acid SO_4/Zr–Fe–Si–O

	Calcination atmosphere			
	H_2	N_2	Air	O_2
Ester yield (%)	12.64	61.02	63.31	64.79
Ester selectivity (%)	96.9	96.83	97.1	97.02

Silica content = 5%, Fe/Zr = 0.33, calcination temperature = 873 K.

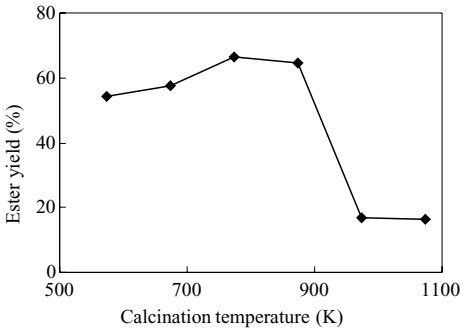

Fig. 5. Effect of calcination temperature on ester yield on the solid-acid SO_4/Zr–Fe–Si–O.

The ester yield of butylacetate in different atmosphere followed the order: oxygen > air > nitrogen ≫ hydrogen. The reason could be that the SO_4^{2-} and other components had been reduced to lower valences in the hydrogen atmosphere, it resulted in the decrease of catalytic activity. The ester selectivity was not affected with different calcination atmosphere. Therefore, the calcination in an oxidative atmosphere gave better results.

The influence of calcination temperature on catalytic performance was demonstrated in Fig. 5. With a temperature range from 573 to 1073 K, it was between 773 and 873 K that a better ester yield was achieved (64.8–66.3%), the maximum was obtained at 773 K. When the calcination temperature reached 973 K or higher, the ester yield decreased dramatically to a much lower value of 16.9%. The thermal analysis (TGA) was operated on the samples calcinated at different temperature, the weight loss of SO_4^{2-} was 11.6% for the catalyst calcinated at 773 K, 2.3% for that at 873 K, and 0.0% for that at 973 K. Comparing the reference works, it was suggested the SO_4^{2-} could be one of the important active components [3,15]. The activity variation with the rise of calcination temperature could be explained: when the calcination temperature increased to higher one than 873 K, there was less amount of SO_4^{2-} in the catalyst sample, then there were less active centers. There was a better formation for the active centers between SO_4^{2-} and other active components when the calcination temperature was about 773 K.

3.4. Effect of reaction cycles on catalytic performance

One of the advantages of solid-acid catalysts is the facility of separation of desired products and catalyst, by a simple filtration method, comparing the complexity of that with sulfuric acid. The influence of recycling our sulfated solid-acid catalyst on catalytic activity was illustrated in Table 3, the reaction was operated at 366 K with 1 g of catalyst. The initial ester yield was 93.3% with a good selectivity of 96.0%. Then, the catalyst was recovered by a filtration from the products, and used again for a second reaction cycle, the ester yield was almost kept, with only a little diminution to a value of 91.4%. The ester yield was 85.7% at the eight-times recycle of the catalyst, with a slightly improved selectivity of 97.3%. Then, the catalyst was regenerated by impregnation and calcination, its ester yield could be recovered to 91.1% with a butylacetate selectivity of 96.6%.

Table 3
Influence of recycle times of catalyst on ester selectivity and ester yield on the solid-acid SO_4/Zr–Fe–Si–O

Recycle times of catalyst	Ester yield (%)	Ester selectivity (%)
1	93.26	96.00
2	91.38	96.87
3	90.02	96.52
4	89.46	96.73
5	88.75	97.25
6	87.98	96.91
7	86.45	96.68
8	85.67	97.34
9[a]	91.07	96.58

$T = 366$ K, catalyst amount = 1 g.
[a] Regenerated after eight times application.

3.5. Structure analysis of catalyst samples

There were often some relations between the performance and catalyst structure, the XRD, N_2-adsorption and thermal analysis (TGA) were applied for the catalyst characterizations [12]. From the XRD results of SO_4/Fe_2O_3–ZrO_2–SiO_2 catalysts, there are mainly the amorphous species for the components, with only a small amount of cubic crystallites of ZrO_2 ($2\theta = 31^\circ, 51^\circ, 61^\circ$). It was suggested that there was a combined structure of Fe, Zr, Si and SO_4^{2-}, which was difficult to be crystallized and acted as the active centers.

The results of N_2-adsorption measurements and TGA tests were listed in Table 4. It was observed that the catalyst surface area (BET) was not affected by the filtration and re-cycles, but the content of SO_4^{2-} anion decreased quite obviously. Thus, the reason for the slight decreasing of activity could be the extracting of SO_4^{2-} on the catalyst surface by the CH_3COOH in reactant materials. If the catalyst sample after eight-times re-cycles was regenerated by impregnation and calcination, the content of SO_4^{2-} anion

Table 4
BET surface area and TGA result of the catalyst after different application-cycle of the solid-acid SO_4/Zr–Fe–Si–O

Application cycle of catalyst	Surface area ($m^2\ g^{-1}$)	Weight loss percentage (%)[a]
0	79.8	12.80
1	79.5	11.80
2	79.6	11.19
3	79.3	10.72
9[b]	74.2	12.86

$T = 366$ K, catalyst amount = 1 g.
[a] Weight loss percentage from TGA results.
[b] Regenerated after eight times application.

could be restored to the initial value, its ester yield could attain nearly its beginning value. Therefore, the SO_4^{2-} anion was the essential component in the active structure of the catalyst, there was an important effect of its content on the catalytic performance.

4. Conclusion

The coprecipitation-impregnation method gave better results in the solid-acid catalyst design than those by the stepwise precipitation-impregnation. In the new and efficient SO_4/Fe_2O_3–ZrO_2–SiO_2 catalyst preparation, the better Fe/Zr molar ratio was 0.25, the better silica molar content was 2%.

The preparation conditions influenced greatly the catalytic performance, the improved parameters were: pH = 7.0, with an aging time of 1 h. The calcination conditions were also optimized: calcinated at 773 K in an oxygen atmosphere.

The characterization results by nitrogen adsorption measurements and TGA tests indicated that the SO_4^{2-} anion was the essential component in the active structure of the catalyst. The novel solid-acid catalyst had a good stability, the ester yield of butylacetate kept a good value of 85.7% after eight-times recycles, it was 92% of the initial value (93.8%). The catalyst could be regenerated with a simple treatment.

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References

[1] M. Hino, K. Arata, J. Chem. Soc., Chem. Commun. (1995) 53.
[2] H. Matsuhashi, T. Tanaka, K. Arata, J. Phys. Chem. B 105 (2001) 969.
[3] K. Arata, H. Matsuhashi, M. Hino, H. Nakamura, Catal. Today 81 (2003) 17.
[4] K.T. Wan, C.B. Khouw, M.E. Davis, J. Catal. 158 (1996) 311.
[5] W. Chu, J.P. Hu, F.L. Qiu, Q.L. Chen, Chinese Invention Patent CN 1323 655A (2001).
[6] A. Corma, A. Martinez, P.A. Arroyo, J.L.F. Monteiro, E.F. Sousaaguiar, Appl. Catal. A 142 (1996) 139.
[7] X. Song, A. Sayari, Catal. Rev.-Sci. Eng. 38 (1996) 329.
[8] (a) M. Hino, K. Arata, Chem. Lett. (1979) 1259;
(b) M. Hino, K. Arata, Chem. Lett. (1979) 477;
(c) M. Hino, K. Arata, J. Chem. Soc., Chem. Commun. (1980) 851;
(d) M. Hino, S. Kabayashi, K. Arata, J. Am. Chem. Soc. 101 (1979) 6439.
[9] W. Chu, J.P. Hu, Q.L. Chen, et al., Chinese Invention Patent CN 1323 780A (2001).
[10] J.P. Hu, W. Chu, F.L. Qiu, Q.L. Chen, Synth. Chem. (Hecheng Huaxue chin.) 8 (4) (2000) 326.
[11] J. Liu, C. Wang, P. Chu, Chin. J. Mol. Catal. 12 (3) (1998) 237.
[12] W. Chu, F.L. Qiu, Top. Catal. 22 (2003) 131.
[13] W. Chu, T. Zhang, C.H. He, Y.T. Wu, Catal. Lett. 79 (2002) 129.
[14] F. Arena, R. Dario, A. Parmaliana, Appl. Catal. A 170 (1998) 127.
[15] F. Garin, D. Andriamasinoro, A. Abdulsamad, J. Sommer, J. Catal. 131 (1991) 199.
[16] W.M. Hua, Z. Gao, Appl. Catal. B 27 (1998) 37.
[17] T. Turosaka, H. Matsuhashi, K. Arata, J. Catal. 179 (1998) 28.
[18] N. Satoh, J. Hayashi, H. Hattori, Appl. Catal. A 202 (2000) 207.