

Preparation and catalytic use of the solid acid $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-M}_x\text{O}_y$ for the reaction of crotonaldehyde with *n*-butanol

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Abstract

The Mo-promoted the nanosolid acid $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ are characterized by the method of IR, TEM, and B.E.T. The result shows that $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ is superfine solid (<30 nm) belonging to nanocrystal and has high specific surface area. SO_4^{2-} is combined with metal ions of catalysis in a bidentate state. The various metal oxide-promoted nanosolid acid $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$ was investigated in the synthesis of 1,1,3-tributoxy-butane. The reactions were carried out in the liquid phase under atmospheric pressure. The dependencies of conversion, selectivity and the product distribution on the ratio of two metals, the calcining temperature, the immersing concentration of ammonium sulfate solution and the reactant/catalyst ratio were investigated. In this reaction, the selectivity to 1,1,3-tributoxy-butane up to 79.8% at conversions up to 76% have been observed when the $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ was used.

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1. Introduction

Much work had been done, since Hino et al. [1] reported that the surface of Zirconia that treats with sulfuric acid (sd-ZrO_2) showed a dramatic enhancement of its acidic properties, and this enhancement is so large that it was called superacid. It is applied in many reactions [2], for example, the Friedel–Crafts acetylation reaction [2], the activation of the ethane [3] and methane [4], etc. The solid acid has many advantages over liquid Brønsted and Lewis-acid. They are noncorrosive and environmentally benign, presenting fewer disposal problems. The repeated using of this kind of catalyst is possible, and the catalyst separation from liquid products is much easier. Furthermore, they can be designed to give higher activity, selectivity and longer catalysis life. Moreover, catalytic functions have been improved by loading various additional components [5–8]. Recently, a new type of solid superacid catalyst, sulfated ternary oxide containing Fe, Mn and Zr has been developed by Hus et al. [9] and has

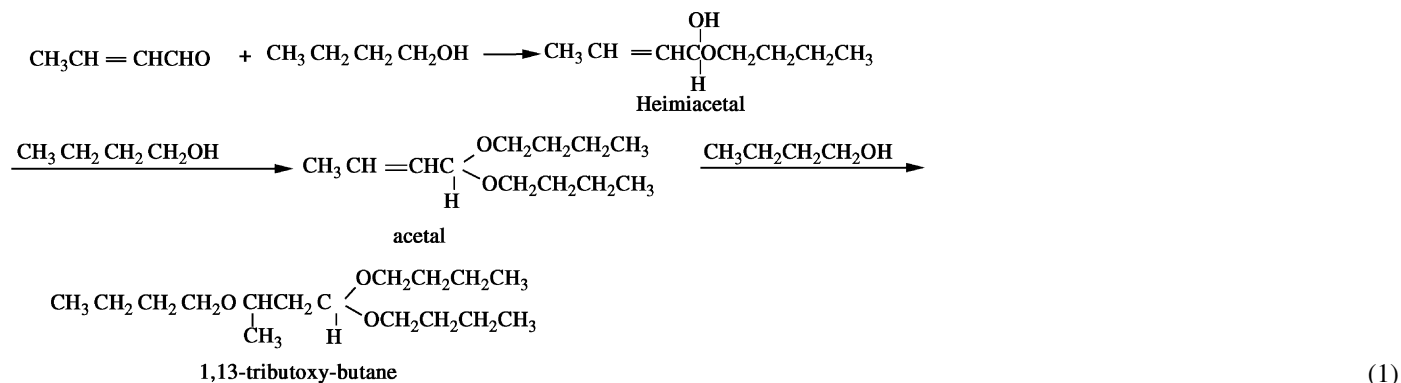
shown higher superacidity than other solid superacid. Miao et al. [10,11] have reported that the doping of sulfated zirconia with various transition metals, such as Cr or V, could enhance the catalytic activity for the *n*-butane isomerization reaction. The researcher [12] have pointed that the Sn or Co promoted sulfated iron oxide, and this kind of catalyst has higher activity in the reaction of esterification. Since the nanometer material has large specific surface area, the nano-catalyst had a helpful application foreground. Recently the researcher [13] has reported the preparation method and characterization of nano-size solid superacid $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-CoO}$, and found that there are a better catalytic reactivity and selectivity for the reaction of esterification than other superacid catalyst.

Acetalation reaction is one of the important reactions in organic synthesis used in the protection of the aldehyde group, which are catalyzed by the dry hydrochloride gas or inorganic acid, and the aldehyde was changed into acetal. At same time, the reaction is applied in many organic compounds synthesizing as well, such as the synthesis of anisaldehyde dimethyl acetal and phenylacetaldehyde dimethyl acetal [14]. The dry hydrochloride gas and inorganic acid are able to catalyze the reaction of elimination and others reactions, which would produce lots of byproducts. Moreover, there was lots of gas or liquid waste to

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be given out as well, which is nocuousness for the environment protection, and these catalysts would acutely erode the equipment. For the reaction of α,β -unsaturated aldehyde, the product would be 1,1,3-alkoxyalkane [15], the reactive process is showed in Eq. (1). In the first step the Hemiacetal is formed; then the *n*-butanol reacts with the Hemiacetal continually. In this process, a molecular water is given off, and the acetal is formed; in the third step, an additive reaction would be carried on between the acetal and *n*-butanol.



The 1,1,3-tributoxy-butane is an important intermediate product in the organic synthesis [16–17], which is synthesized by the reaction of crotonaldehyde and *n*-butanol. In this paper the solid superacid catalysts $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ is applied to the reaction of acetalation reaction and to the synthesis of 1,1,3-tributoxy-butane. The conversion and the selectivity to every product were investigated catalyzed by different catalysts as well.

2. Experiment

2.1. Preparation and characteristic of the catalyst

The different ratios of $\text{Fe}(\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$ and $\text{Zn}(\text{Ac})_2$ or $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in the 80 ml water with citric acid. Then heat this solution at the constant temperature of 60°C in flume, until the water is evaporated to form jello. Bake the jello at the temperature of 80°C in the oven, till the jello is dried completely. Then triturate the material in the mortar. The powder of jello is discomposed at the temperature of 300°C , then immerse them in ammonium sulfate solution for 12 h. The sulfated compound was then filtered, dried at 110°C overnight and calcined at 500°C in static air for 3 h. B.E.T surface areas of the samples were acquired on the Micromeritics ST-08 equipment using N_2 as the adsorbent. Infrared spectra of the samples were recorded on SPECTRWM-ONEFT-IR spectrometer. The samples were pressed into thin self-supported disks with a density of 10 mg, then calcining the disk at different temperature. The TEM investigation was fulfilled on the equipment HIGACHIH-600.

2.2. The reaction

This reaction were carried out under atmospheric pressure in a temperature of 120°C , in a glass batch reactor fitted with a reflux system. About 10 ml *n*-butanol and 2 ml Crotonaldehyde

are put into the reactive vessel with 0.6 g catalysts. The reaction mixture was heated in an oil bath under stirring condenser.

2.3. Analysis of the product

The product analysis was performed in a Shimadzu GC-9A using a 30 m capillary column (OV-101) with nitrogen as carrier gas. The injection volume was $0.4 \mu\text{l}$ and injection temperature

250°C , the temperature program start at 50°C and end at 240°C with a heating rate $6^\circ\text{C}/\text{min}$. GC-MS was also used to identity the reactive products.

3. Result and discussion

3.1. The structure of catalyst

3.1.1. The investigation of TEM and B.E.T

Fig. 1 is a $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ TEM photograph at calcining temperature of 500°C ($n_{\text{Fe}}:n_{\text{Mo}}=6:1$). From the TEM photograph, it is found that the diameter of grain of the sample is very small, and the majority of granules are 20–30 nm, all belong to the nanometer material. At the same time, the B.E.T

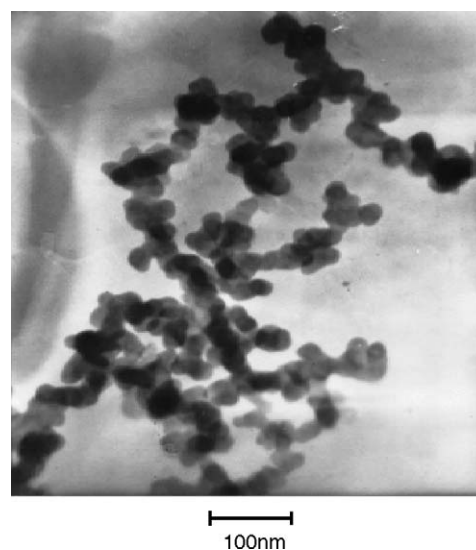


Fig. 1. TEM picture of $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ (Fe:Mo=6:1).

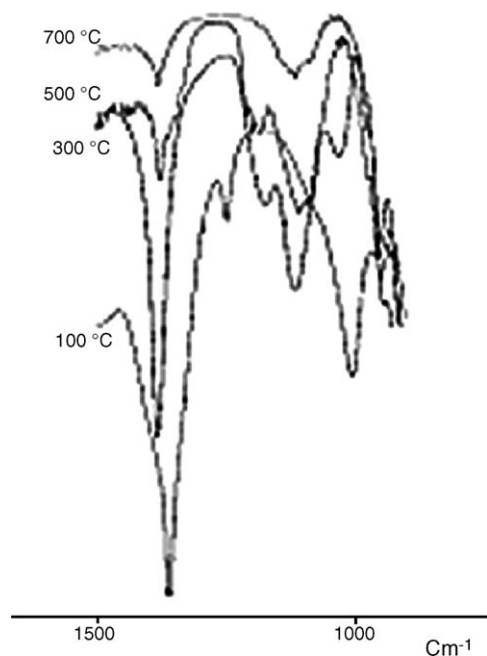
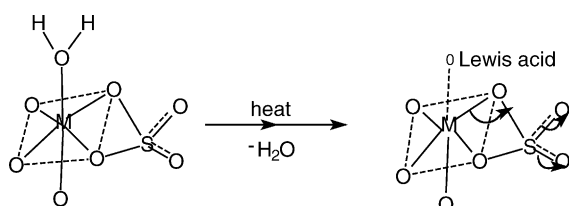


Fig. 2. The FT-IR spectrum of the $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ ($n_{\text{Fe}}:n_{\text{Mo}}=6:1$).

surface of the sample was determined. The result indicates that the B.E.T surface is $163.2 \text{ m}^2/\text{g}$ at the molar Fe/Mo ratio of 6. It indicated that the catalyst has the higher special surface area, and it would be benefit to the enhancement of the catalyst activity.

3.1.2. The investigation of FT-IR

Fig. 2 shows the FT-IR spectrum of the $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ ($n_{\text{Fe}}:n_{\text{Mo}}=6:1$) precalcined at different temperatures. From Fig. 2, it is clearly to find that there are four characteristic bands between 1450 and 800 cm^{-1} at calcining temperature of $300\text{--}700 \text{ }^\circ\text{C}$, namely: 1390 , 1210 , 1128 and 960 cm^{-1} , which indicate that there is sulfate species in these samples [18]. While, at calcining temperature of $100 \text{ }^\circ\text{C}$, there are not any bands at 1390 cm^{-1} in the spectrum, which was shifted to 1350 cm^{-1} . Some papers [19,20] reported that when the sample was heated at high temperature, the sulfate species structure on the surface of the catalyst would be changed in the process of heating dehydrate, namely: forming strong Lewis acid sites (Scheme 1). It is the important factor that the sulfate species must contain strong covalence S=O bond that has strong ability of inducing electron for the formation of the solid superacid, which would enhance Lewis acidity of metal center ion. From Fig. 2, at the calcining temperature of $500 \text{ }^\circ\text{C}$, the band at 1390 and 1128 cm^{-1} can attribute to asymmetry and symmetry stretch and shrink vibration of S=O bond that is similar to the S=O bond in the sulfuric



Scheme 1. The forming process of the catalysts.

ester, and these S=O bonds have the similar character with the covalence bond. So the strong acidic center have been formed on the surface of catalyst as calcining temperature of $500 \text{ }^\circ\text{C}$. According to the report [21], it is easy to find that the surface structure of the sample was a bidentate state from the FT-IR spectrum of the sample at the calcining temperature of $500 \text{ }^\circ\text{C}$.

3.2. Variation of reaction parameters

The selectivity for each product was expressed by the mol% of crotonaldehyde converted to each product in the total crotonaldehyde converted. Crotonaldehyde reacts with *n*-butanol yielding 1,1,3-tributoxy-butane the main product according to Eq. (1). The byproducts are crotonaldehyde *n*-butanol hemiacetal and crotonaldehyde *n*-butanol acetal that are formed by the acetalation reaction of crotonaldehyde and *n*-butanol. The 1,1,3-tributoxy-butane is formed by the additive reaction of crotonaldehyde *n*-butanol acetal and *n*-butanol. The dependence of conversion and selectivity upon the metal atom ratio, reactant/catalyst ratio, the calcining temperature of catalyst and the immersing concentration of ammonium sulfate solution in the catalyst are investigated

3.2.1. Influence of the Fe/Mo ratio

The variations of the activity and selectivity of $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ with different Fe/Mo molar ratios are shown in Table 1. In these experiments, the molar ratio of Fe and Mo has been change from 1 to 8, and the temperature of calcining is $500 \text{ }^\circ\text{C}$. The reactant/catalyst ratio is $0.21 \text{ mol } n\text{-butanol/g catalyst}$; the immersing concentration of ammonium sulfate solution is 1.0 mol/L .

From Table 1, the metal molar ratios of Fe and Mo have strong influence to the conversion of crotonaldehyde as well as selectivity. The use of equimolar ratio of Fe and Mo results in a conversion of 39.5% of crotonaldehyde and a selectivity of 73.1% to 1,1,3-tributoxy-butane. In the interval of 1–6 of Fe/Mo molar ratio, with an increase of Fe molar content, the conversion is increased. The maximum conversion obtained is 76% at a Fe/Mo molar ratio of 6. Then, the conversion of crotonaldehyde would be decreased with the increase of Fe molar ratio. At the same time, the Fe/Mo molar ratio influences strongly the selectivity to 1,1,3-trialkoxyalkanes. There are all good selectivity by using these catalysts, and the selectivity to 1,1,3-tributoxy-butane are all above 60%. The maximum selectivity obtained is 79.9% at a Fe/Mo molar ratio of 6:1.

Table 1
Influence of the metal atom ratio for $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$

$n_{\text{Fe}}/n_{\text{Mo}}$	Conv. (%)	Selectivity (%)		
		Hemiacetal	Acetal	1,1,3-Tributoxy-butane
1	35.9	10.2	16.7	73.1
2	55.8	18.8	20.9	60.3
4	64.2	12.3	17.6	70.1
6	76	7.5	12.6	79.9
8	56.2	16.5	23.3	60.2

Table 2
Influence of immersing concentration of ammonium sulfate solution

Concentration (mol/L)	Conv. (%)	Selectivity (%)		
		Hemiacetal	Acetal	1,1,3-Tributoxy-butane
0.5	50.4	23.4	52.4	24.2
0.75	65.7	19.3	45.2	35.6
1	76	7.8	12.4	79.8
1.25	73.4	13.2	19.6	67.2
1.5	70.3	15.3	23.7	61

In order to optimize the product yield, a Fe/Mo molar ratio of 6:1 was chosen for the following experiments.

3.2.2. Influence of immersing concentration of ammonium sulfate solution

Table 2 shows the influence of immersing concentration of ammonium sulfate solution on the conversion of crotonaldehyde and selectivity to 1,1,3-tributoxy-butane catalyzed by the $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$ at 120 °C for 9 h.

After 9 h reaction time, at an immersing concentration of ammonium sulfate solution from 1.0 to 1.5 mol/L, the conversion of crotonaldehyde are all above 70%, the selectivity to 1,1,3-tributoxy-butane are all above 60%. Especially, at the immersing concentration of 1.0 mol/L, the conversion and the selectivity are the highest. The use of catalyst of the immersing concentration from 0.5 to 0.75 mol/L result in the conversion of 50–66% and the selectivity to 1,1,3-tributoxy-butane of 24–36%, these values are less than that at the immersing concentration from 1.0 to 1.5 mol/L.

From Table 2, when the concentration of $(\text{NH}_4)_2\text{SO}_4$ is less than 1.0 mol/L, the conversion of Crotonaldehyde was enhanced with the increase of the concentration of $(\text{NH}_4)_2\text{SO}_4$. However, as the concentration of $(\text{NH}_4)_2\text{SO}_4$ is larger than 1.0 mol/L, the conversion of 1,1,3-tributoxy-butane would be decreased. At the same time, the change of selectivity to 1,1,3-tributoxy-butane with different concentrations is accord with above law. In fact, the low concentration of $(\text{NH}_4)_2\text{SO}_4$ result in few sum of acidic center of the surface of the catalysts as well as inactive reaction activity. But as the concentration of $(\text{NH}_4)_2\text{SO}_4$ is excess to 1.0 mol/L, the sulfate would be formed over the surface of catalyst [22], which would lay over the acidic center of the surface of the catalyst. And so, it makes the acidity of catalyst would be decreased.

3.2.3. Influence of calcining temperature

In this experiment, the influence of calcining temperature of catalyst has been investigated with the temperature range from 300 to 700 °C (Table 3). From Table 3, it is found that the temperature of calcining has an important effect to the activity of the catalyst. At the calcining temperature of 300 °C, the conversion of crotonaldehyde is only 43.3% and the selectivity to 1,1,3-tributoxy-butane is only 9.1% as well. As the temperature is in the interval of 300–500 °C, the conversion of crotonaldehyde is enhanced with increase of the calcining temperature, and at the calcining temperature of 500 °C, the conversion and selectivity are both the highest. However, as the temperature is higher

Table 3
Influence of calcining temperature

Temperature (°C)	Conv. (%)	Selectivity (%)		
		Hemiacetal	Acetal	1,1,3-Tributoxy-butane
300	43.3	59.4	31.5	9.1
400	61.3	18.6	37.2	42.2
500	76	7.8	12.4	79.8
600	63.2	15.1	26.3	58.9
700	58.1	43.1	12.3	44.7

than 500 °C, the conversion and selectivity would be decrease quickly. According with the report [23], it is necessary that the oxide have a completely crystal changing for the forming of solid acid. The crystal was changed from amorphism to an $\alpha\text{-Fe}_2\text{O}_3$ crystal phase with increasing of the calcining temperature. At the same time, the little crystal particle on the surface of the catalysts was formed. However, when the calcining temperature are above 500 °C, SO_4^{2-} was lost quickly, and so, the acid is weak. The conclusion of this paper is accord with the law.

3.2.4. Influence of the reactant/catalyst ratio

The reaction between the reactant/catalyst ratio (mol *n*-butanol per gram of catalyst) and crotonaldehyde conversion and selectivity to form 1,1,3-tributoxy-butane, respectively, are presented in Table 4. The reactant/catalyst ratio was varied between 0.14 and 0.42 mol *n*-butanol per gram of $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$.

At low values for the reactant/catalyst ratio from 0.14 to 0.16 mol *n*-butanol per gram of $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$, the catalyst shows high activities. The selectivity to 1,1,3-tributoxy-butane of 82% and 83%, respectively, were achieved at conversion of 81–82% after a reaction time of 6 h. With an increase of the reactant/catalyst ratio, the conversion of crotonaldehyde decreases. At a reactant/catalyst ratio of 0.28 mol *n*-butanol per gram of $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-MoO}_3$, a conversion of 76% was obtained, while a reactant/catalyst ratio of 0.42 only led to a conversion of 56.2% with a selectivity to 1,1,3-tributoxy-butane of 18.7%. With decrease of the reactant/catalyst ratio, an increase of the selectivities to 1,1,3-tributoxy-butane could be observed, at the same time the conversion of crotonaldehyde increases with the decrease of the reactant/catalyst ratio.

A reactant/catalyst ratio of 0.21 mol *n*-butanol per gram of catalyst is also suitable for the next experiments in order to compare the other weakly acidic catalyst with strong acidic catalyst.

Table 4
Influence of the reactant/catalyst ratio

Mol <i>n</i> -butanol/g catalyst	Conv. (%)	Selectivity (%)		
		Hemiacetal	Acetal	1,1,3-Tributoxy-butane
0.42	56.2	35.2	46.1	18.7
0.28	76	7.8	12.4	79.8
0.21	78.7	7.3	13.5	79.2
0.16	81.6	6.4	10.9	82.7
0.14	82.2	5.6	11.3	83.1

Table 5
The compare of different catalysts

Catalysts	Conv. (%)	Selectivity (%)		
		Hemiacetal ^a	Acetal ^b	1,1,3-Tributoxy-butane
Blank reaction	39.6	68.5	27.8	3.6
SO ₄ ²⁻ /Fe ₂ O ₃ –MoO ₃ ^c	76	7.8	12.4	79.8
Fe ₂ O ₃	43.2	54.6	39.5	5.9
Fe ₂ O ₃ –MoO ₃ ^d	44.3	56.2	35.6	8.2
SO ₄ ²⁻ /Fe ₂ O ₃	62.7	26.7	51.5	11.8
SO ₄ ²⁻ /Fe ₂ O ₃ –ZnO ^e	74.9	26.1	26.7	47.2
SO ₄ ²⁻ /Fe ₂ O ₃ –NiO ^f	71.2	13.4	14.4	72.2
SO ₄ ²⁻ /Fe ₂ O ₃ –MoO ₃ /La ³⁺	69.6	7.1	13.2	79.7

^a Crotonaldehyde *n*-butanol hemiacetal.

^b Crotonaldehyde *n*-butanol acetal.

^c The ratio of Fe and Mo is 6:1, the concentration of ammonium sulfate solution is 1.0 mol/L.

^d The ratio of Fe and Mo is 6:1.

^e The ratio of Fe and Zn is 2:1, the concentration of ammonium sulfate solution is 1.0 mol/L.

^f The ratio of Fe and Ni is 4:1, the concentration of ammonium sulfate solution is 1.0 mol/L.

3.3. Comparing of different catalysts

The activities and selectivities of different catalysts are given in Table 5. The total conversion and the selectivity to 1,1,3-tributoxy-butane of SO₄²⁻/Fe₂O₃–MoO₃ is the highest among all the catalysts. Comparing this kind of catalyst with Fe₂O₃–MoO₃, the introduction of SO₄²⁻ is able to largely enhance the conversion of crotonaldehyde and selectivity to 1,1,3-trialloxyalkanes in this kind of catalyst. It shows that the existence of sulfate species on the surface of catalysts is the important reason for the forming of superacidity. Comparing the Fe₂O₃–MoO₃ with the blank reaction, the conversion and selectivity to 1,1,3-trialloxyalkane catalyzed by Fe₂O₃–MoO₃ is higher than that of blank reaction. It indicates that the Fe₂O₃–MoO₃ is able to catalyze the reaction, but the activity is dissatisfactory. The same results are observed in the reaction catalyzed by the Fe₂O₃.

At the same time, the results of reaction catalyzed by SO₄²⁻/Fe₂O₃, SO₄²⁻/Fe₂O₃–MoO₃, SO₄²⁻/Fe₂O₃–ZnO, SO₄²⁻/Fe₂O₃–NiO also are given (Table 5). Among the four kinds of catalysts, only the SO₄²⁻/Fe₂O₃ gives the conversion of 62.7%, while, the other three kinds of catalysts give the conversion over 70%. For the selectivity to 1,1,3-trialloxyalkanes, the result is not so. The selectivity to 1,1,3-tributoxy-butane catalyzed by SO₄²⁻/Fe₂O₃ is only 11.8%, while the selectivity to 1,1,3-tributoxy-butane catalyzed by other three kinds of catalysts are all over 70%. So the doping of SO₄²⁻/Fe₂O₃ with Mo, Zn, Ni could enhance the activity of catalysts. The main reason is that the doping of the third component (transition metal) in SO₄²⁻/Fe₂O₃ make the center ion Fe³⁺ exist stronger attracting electron ability, which would enhance the Lewis acidity of the catalysts.

In order to investigate the influence of doping of rare earth element to this kind of catalyst, the La³⁺ is adulterated into the catalyst. It is demonstrated that the doping of La³⁺ is not able to enhance the activity of catalyst. From Table 5, it is concluded that the SO₄²⁻/Fe₂O₃–MoO₃ is the best catalyst for the reaction.

4. Conclusion

A new kind of catalyst SO₄²⁻/Fe₂O₃–MoO₃ has been synthesized and be characterized by the methods of FT-IR, TEM, B.E.T. And find that this kind of catalyst is belong to the nanometer material. The diameter of the granule was 20–30 nm. The special surface of this kind of catalyst is 163.2 m²/g. The surface structure of SO₄²⁻/Fe₂O₃–MoO₃ was bidentate state.

The result shows that the transition metal-promoted the SO₄²⁻/Fe₂O₃ are efficient catalysts in the synthesis of 1,1,3-tributoxy-butane. As the ratio of Fe and Mo was 6:1, the catalyst has the best activity, the conversion of Crotonaldehyde is 76% and the selectivity to 1,1,3-tributoxy-butane is over 79%. The optimal concentration of immersing concentration of (NH₄)₂SO₄ was 1.0 mol/L, and the appropriate calcining temperature for this kind of catalyst is 500 °C.

References

- [1] H. Hino, S. Kobayashi, K. Arata, J. Am. Chem. Soc. 101 (1979) 6439.
- [2] (a) C. Castro, A. Corma, J. Primo, J. Mol. Catal. A: Chem. 177 (2002) 273–280;
(b) J. Deutsch, A. Trunschke, D. Müller, V. Quaschnig, E. Kemnitz, H. Lieske, J. Mol. Catal. A: Chem. 207 (2004) 51–57;
(c) E. Rafiee, F. Shahbazi, M. Joshaghani, F. Tork, J. Mol. Catal. A: Chem. 242 (2005) 129–134.
- [3] K. Cheung, B.C. Gates, J. Catal. 168 (1997) 522.
- [4] T. Kurosaka, H. Matsushashi, K. Arata, J. Catal. 179 (1998) 28.
- [5] R.A. Boyse, E.O. Ko, Catal. Lett. 49 (1997) 17.
- [6] Y.D. Xia, W.M. Hua, Z. Cao, Appl. Catal. A: Gen. 185 (1999) 293.
- [7] F.R. Chem, G. Couderier, J.F. Joly, J. Catal. 143 (1993) 616.
- [8] Z. Gao, J.M. Chen, W.M. Hua, Stud. Surf. Sci. Catal. 90 (1994) 507.
- [9] C.Y. Hus, C.R. Heimbuch, C.T. Armes, J. Chem. Soc. Chem. Commun. (1992) 1645.
- [10] C.X. Miao, W.M. Hua, J.M. Chen, Sci. China (Ser. B) 39 (1996) 406.
- [11] C.X. Miao, W.M. Hua, J.M. Chen, Catal. Lett. 37 (1996) 187.
- [12] S. Wu, L. Li, Chin. Chem. Word 15 (1997) 184.
- [13] D.-J. Lin, S.-F. She, H.-B. Pan, et al., Chin. J. Inorg. Chem. 16 (2000) 757.
- [14] G. Zhang, Handbook of Chemical Products, Publishing House of Chemical Industry, Beijing, 1998.

- [15] T. Kozo, F.H. Wolfgang, *Appl. Catal. A: Gen.* 181 (1999) 399.
- [16] M. Hoepf., EP 0700 889 (05.08.1995) to degussa AG.
- [17] J. Andrade et al., EP 0150 280 (01.02.1984) to degussa AG.
- [18] B. Frederic, C. Gisele, J.C. Vedrine, *J. Catal.* 152 (1995) 341.
- [19] H. Frank, S. Joachim, *J. Am. Chem. Soc.* 120 (1998) 13503.
- [20] F. Babou, B. Bigot, P. Sautet, *J. Phys. Chem.* 97 (1993) 11501.
- [21] T. Yamaguchi, T. Jin, K. Tanabe, *J. Phys. Chem.* 90 (1980) 3148.
- [22] J. Xu, G. Zhou, H. Zheng, *Chin. Chem. Bull.* 10 (2001) 647.
- [23] Z. Cao, J. Cheng, Y. Tan, *Chem. J. Chin. Univ.* 13 (1992) 1498.