

Preparation and activity of the catalysts for the synthesis of carboxylic ester with high boiling point

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Abstract

A series of rare earth sulfates catalysts were prepared by hot-impregnation method from rare earth oxides and sulfuric acid, followed by calcination and activation at 470–500°C. Using the synthesis of dibutyl phthalate as test reaction, the catalytic activities of samples were examined in detail, especially about the activities of ceric sulfate containing hydrate water and its composite with transition metal sulfates. The results indicated that $\text{Ce}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x = 4$) exhibited considerably high activity. Catalyzed by ceric sulfates prepared and at the optimal reaction conditions, the conversion of carboxylic acid with high boiling point (b.p.) were 77.1%, which was remarkably higher than that catalyzed by sulfuric acid. Moreover, the reaction could be carried out at relatively lower temperature. Meanwhile, taking into account the orbital structure of sufficient energy-level of rare earth ions and based on Brönsted's acid–base theory, the catalytic activity results of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ were analyzed in detail. Also, the surface acidity properties of various samples were characterized by the adsorption of pyridine as probe molecule studied by IR spectroscopy. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Rare earth; Esterification; Acidity properties; Catalytic activity

1. Introduction

Carboxylic ester, as a kind of important essential materials in chemical industry, has been widely used as organic solvent, internal plasticizer, intermediate for perfume and organic synthesis in the fields of paints, foods, pharmaceuticals and organic synthesis. Up to now, the synthesis processes of carboxylic ester in industry are still catalyzed by sulfuric acid. The disadvantages of this method are: long reaction period, low conversion rate, formation of by-products, after-treatment difficulties, corrosion

of reaction vessels, etc. [1]. There are more disadvantages in the synthesis of carboxylic ester of high boiling point. Thus, the study of novel esterification catalyst with high catalytic activity to substitute sulfuric acid has long been paid considerable attentions by researchers at home and abroad.

The study of non-homogeneous solid catalyst for esterification has started since 1960s [2]. Several effective esterification catalysts such as ZnO and SnO have long been used in industrial production [3]. Recently, more and more studies have been devoted to the novel solid catalysts for ester formation and many new kinds of catalysts are examined and used continuously. The activity and behavior of these catalysts such

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as rare earth oxides, rare earth salts and transition metal salts are studied [4,5].

In recent years, many papers have been reported on the catalytic abilities of rare earth [6], and most of these studies are focused on rare earth oxides, used as catalysts for such reaction as esterification of carboxylic acid, oxidation and dehydrogenation of hydrocarbons, isomerization of alkenes, dehydration and dehydrogenation of alcohol, conversion of nitrogen oxides and cracking reaction of alkanes [7]. Sulfates with water of hydration as catalysts have also been reported [8]. Although the activities are not very satisfactory compared with sulfuric acid catalyst, this kind of catalysts can overcome such disadvantages as low selectivities, corrosion of reaction vessels and environmental pollution caused by sulfuric acid. These sulfates can also lower the reaction temperature [9]. For example, in the reaction of phthalic anhydride with pentanol, catalyzed by metal oxides (ZnO, SnO) or rare earth oxides (Sm_2O_3 , Eu_2O_3), the temperature needed is above 470 K, whereas catalyzed by transition metal sulfates, below 470 K. Besides, these sulfates are more stable and easy to be regenerated.

In the present work, various rare earth sulfates and correspondent composites have been prepared and used in the synthesis of dibutyl phthalate in order to examine the catalytic activity of these samples. Also, the activity results are analyzed in detail.

2. Experimental

2.1. Catalyst preparation

The catalyst powders were obtained via hot-impregnation of appropriate amounts of rare earth oxides and sulfuric acid at room temperature and stirring vigorously. The slurry was heated slowly to evaporate the excess water, then dried at 110°C for 8 h, followed by calcinating at 470–500°C in air for 4–5 h, powdered, milled and equilibrated at room temper-

ature for 24 h. Thus, various sulfates such as $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{La}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Tb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were obtained. The X-ray diffraction were used to determine the structure of catalysts. The formula of catalysts prepared are in agreement with that of in the literature [10].

The composite sulfates were prepared by dispersing the powders in organic solvent for a few minutes then evaporated the solvent and dried at 70–80°C.

2.2. IR spectra detection

The surface acidity type and acid strength were detected by means of IR spectra using pyridine adsorption under vacuum condition [11–14]. After being dried under IR cell, the catalysts were powdered and pressed into disks, calcinated at 393 K for 2 h, cooled at room temperature, then pyridine were introduced from vacuum tube, equilibrated for 2 min and followed by evacuation at the same temperature (373 K).

2.3. Catalytic activity test

Under the reaction conditions of various amount of added catalysts, various compositions and ratio of acid to alcohol, the conversion can be calculated by detecting the acid value of the reaction system with increasing reaction time, then the activity data of the catalyst can be obtained.

3. Results and discussion

3.1. Infrared results and analysis

Fig. 1 shows the IR spectra of pyridine adsorbed on various transition metal sulfates (A) and rare earth sulfates (B).

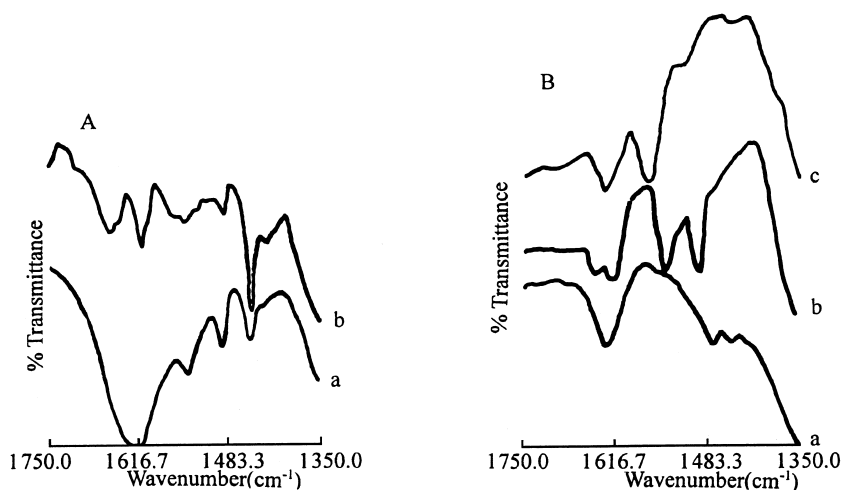


Fig. 1. IR spectra of pyridine adsorbed on: (A) (a) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; (B) (a) $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$; (b) $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (c) $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.

In the present study, pyridine was used as probe molecule, then the surface acidity properties of different catalysts were examined. The infrared spectra of these selected samples show that a few characteristic bands appear near 1540 cm^{-1} and other wavenumbers in relation to acidity properties of catalyst. The bands at 1544 cm^{-1} and 1448 cm^{-1} are considered to be sensitive to the strength of Brönsted acidity and Lewis acidity, respectively. Whereas the band near 1489 cm^{-1} characterizes that of acidity brought by both Lewis and Bronsted acid [15].

Generally, the adsorption parameter for pyridine near 1450 cm^{-1} are apparently larger than that of near 1540 cm^{-1} . So if the peak area at 1544 and 1448 cm^{-1} are almost the same, it means that the sample detected has relatively more Brönsted acidity sites. The more of such sites, the stronger the acidity property of the catalyst. The latter also means the high activity of the catalyst for esterification. Of all the sulfates detected, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ presents a maximum of Lewis acid sites. Other transition metal sulfates either have both Brönsted acid and Lewis acid on the surface or have too weak acidity to be observed. Nevertheless, among the rare earth sulfates detected, only $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ possess large peak area near the band of

1540 cm^{-1} , which shows the large amount of Brönsted acid sites.

The results allow us to deduce that the strength on the surface of ceric sulfates should be stronger than that of other sulfates, and should also have higher catalytic activity. In addition, the number of hydration water in the same catalyst can also affect the surface acidity. In the case of catalyst of Brönsted acid type, the more number of the hydrate water, the stronger the Brönsted acidity. As for ceric sulfates, the maximum number could be 4, so $\text{Ce}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x = 4$) should exhibit much higher activity than that of $x = 0-3$.

3.2. Activity results and analysis

To testify the deduction mentioned above, the activities of catalysts prepared are examined practically in our study in the esterification of phthalic anhydride with butanol

The mole ratio of acid to alcohol, the amount of catalyst added, the ratio of compositions and the reaction time are 1:1.3, 0.0008 mol/mol acid, 1:1 (wt.), 3.5 h, respectively.

The results are shown in Figs. 2 and 3.

As shown in Figs. 2 and 3, all of the samples have catalytic activity. Whereas the activities

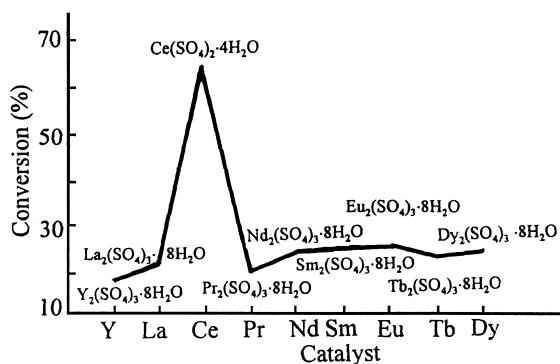


Fig. 2. The catalytic activity of rare earth sulfate.

are quite different with different samples. Only ceric sulfate shows high activity even its composites with various transition metal sulfates. Under the same reaction conditions, only after 3.5 h did the conversion reach 63.6%. The reaction results are in good agreement with that obtained from infrared spectra.

Furthermore, the effects of the number of hydration water on catalytic activities are also studied. The results are shown in Figs. 4 and 5.

As shown in Figs. 4 and 5, the number of hydration water can change samples' activities. It is clear that the activity of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is obviously higher than other ceric sulfates containing less number of hydrate water.

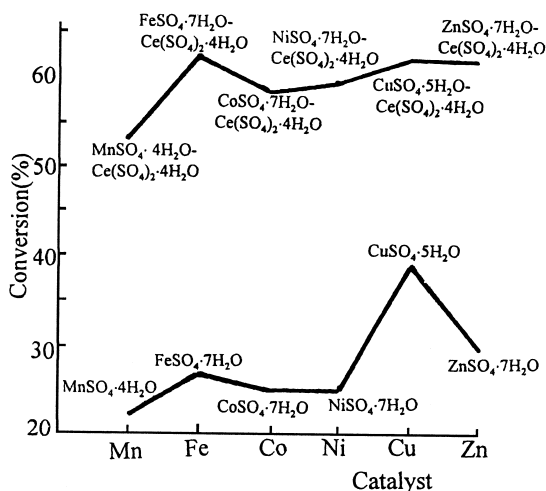


Fig. 3. The catalytic activity of transition metal sulfate and correspondent composite with ceric sulfate.

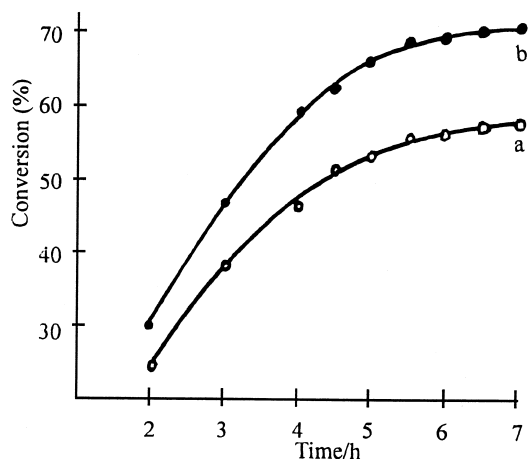


Fig. 4. Effect of number of hydration water on conversion (a) $\text{Ce}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O} / \text{CuSO}_4 \cdot \text{H}_2\text{O}$ ($x \neq 4$); (b) $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} / \text{CuSO}_4 \cdot \text{H}_2\text{O}$.

Catalytic activity results of ceric sulfate can be analyzed as follows.

Among the rare earth, the out-shell electronic configuration of Ce and Ce^{4+} are $4f^2 6s^2$ and $4f^0$, respectively. The latter is in stable state and thus, it should have poor activity. Indeed, its oxides do not have activities in esterification. But the activity results of its sulfates are positive as shown in our experiments. It is thought that since esterification is the typical reaction catalyzed by proton, and protonation can improve ester formation. Hence, although the sul-

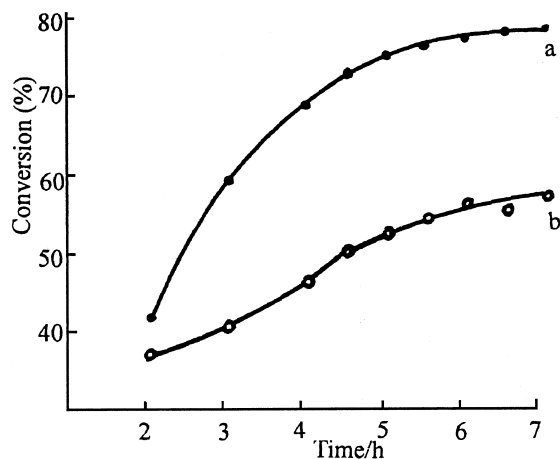


Fig. 5. Effect of hydration water on conversion (a) $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (b) $\text{Ce}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x \neq 4$).

fates have no instinct surface acidity, after proper treatment by physical ways (pre-heating or calcination), they can generate acid sites and show activity as solid catalyst with acid strength. All these have been proven by IR spectra results.

For ceric sulfate, which possessing only Brönsted acid sites, the existence of water of hydration increases the acid sites, which leads to the highest activity of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ than that of $\text{Ce}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x = 0-3$).

Moreover, besides the existence of catalytic action of proton acid, there might have complex catalysis in coordination since rare earth ions belong to hard acid and transition metal ions (II) are between the hard and soft acid. Whereas, the complex of water belongs to hard base. Based on the rule of hard and soft acid/base, the ceric complex must be stable than other metal sulfate complexes. In addition, the stability of combined hard metal ions and hard basic complex increases with that of electronegativity of metal ions. So the ceric complex should be more stable than other rare earth complex. Thus, ceric complex containing hydrate water should be the most stable one. The activity of catalyst increases with the stability. All of these mentioned above lead to the highest activity of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The results are also confirmed by catalytic reaction.

4. Conclusion

(1) Both transition metal sulfates and rare earth sulfates have relatively high catalytic activities for esterification, especially in the case

of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Under the optimal reaction conditions, the conversion is 63.4% after 3.5 h and is up to 77.1% after 6 h. The catalysts in heterogeneous systems, are easy to be separated, recovered and regenerated.

(2) The temperature of treatment can influence the catalytic activities. The higher the temperature of rare earth sulfates treated, the lesser the number of water of hydration contained, so the lower the activities will be.

(3) The IR spectra analysis of pyridine absorbed on the catalysts indicate that the major part of acid on the surface of ceric sulfates is Brönsted acid. Its catalytic action in the synthesis of carboxylic ester is considered to be the acid catalysis and complex catalysis in coordination.

References

- [1] S. Yamaguchi, Appl. Catal. 61 (1) (1990) 1.
- [2] M. W. Fewlass, Brit. Pat. 1,076,702 (1967).
- [3] D.B. Pantall, Brit. Pat. 999,947 (1965).
- [4] L. Chen, L. Ding, W. Qu, H. Tongbao, Chemistry 4 (1998) 52, Chineses.
- [5] T.A. Pecoraro, R.R. Chianelli, J. Catal. 67 (1981) 430.
- [6] M.P. Rosynek, Catal. Rev.-Sci. Eng. 16 (1997) 111.
- [7] Q. Chen, M. Luo, Chin. J. Catal. 12 (1991) 494.
- [8] B. Li, Chin. J. Catal. 10 (1989) 331.
- [9] Z. Jiao, Chin. J. Catal. 8 (2) (1987) 221.
- [10] Chemical Society of Japan, Handbook of Preparation of Inorganic Compound, Publisher of Chinese Chemical Industry, 1984.
- [11] A. Corma, J. Catal. 88 (1984) 374.
- [12] M.R. Basila, Phys. Chem. 71 (1967) 468.
- [13] V.R. Choudhary, J. Catal. 130 (1991) 411.
- [14] M.M. Ramirez de Agudelo, L. González Reyes, N. Do Campo, Appl. Catal. 31 (1987) 1.
- [15] L. Li, S. Ma, J. Hui, Chem. J. Chin. Univ. 16 (1995) 1164.