The zirconium sulfate microcrystal structure in relation to their activity in the esterification

Joon Ching Juan [a,b], Jingchang Zhang [a,*], Yajie Jiang [a],
Weiliang Cao [a], Mohd Ambar Yarmo [b]

[a] *Institute of Modern Catalysis, Beijing University of Chemical Technology, State Key Laboratory of Chemical Resource Engineering, Ministry of Education, Beijing 100029, China*
[b] *Advanced Catalysis Technology Laboratory, School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi 43600, Malaysia*

Abstract

Zirconium sulfate (ZS) varying in crystalline phase from hydrate to anhydrous was prepared at different treatment temperature. The relationship between microcrystal structure at different treatment temperature and activity in esterification was evaluated. The number of acid groups was found to increase with increased of pretreatment temperature, except for the samples treated above 330 °C. For that sample, it is observed that hydration of crystalline water to anhydrous phase is significant at temperature of 330–420 °C, reducing the surface acidity. The reaction was poisoned by the exchange of surface protons on ZS with Cs⁺. Thus, the major effective active sites must be the protons acidity. It was demonstrated that the microcrystal structure and catalytic activity of ZS was affected by thermal treatment due to changes in crystalline water.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Zirconium sulfate; Thermal treatment; Esterification; Acid catalyst

1. Introduction

The use of zirconium sulfate (ZS) or disulfatozirconic acid as catalyst in esterification reaction has received considerable attention. In general, metal sulfate surface possesses acid sites capable of taking part in the catalytic process. Several literatures have studied the influence of treatment temperature [1], ranging from 550 to 750 °C to attain sulfated zirconia [2]. However the information concerning ZS, especially the influence of treatment temperature below 400 °C to catalytic activity is limited. In general, the hydration of ZS from higher hydrate to anhydrous can be obtained by thermal-treatment below 400 °C. It is reported that there is inter-relationship between hydrate water and structure of ZS [3]. The crystalline ZS is an ion exchanger [4], which has a layered structure (Fig. 1). Within the layers, each zirconium (Zr) atom is in contact with four sulfate groups and each sulfate group is in contact with two Zr atom. Also, each Zr atom is in contact with four water molecules, and each water molecule is in contact with one Zr atom. The sulphate oxygen atoms that are not in contact with Zr atoms are linked to water molecules via hydrogen bonds. The interlayer distance, gathered from X-ray diffraction (XRD) of these compounds is around 0.6 nm.

Recently, ZS has been used as a catalyst for esterification of carboxylic acids [5] and redox reaction [6], but the catalyst used was not well characterized. Since the properties of ZS are various with thermal treatment conditions, such as treatment temperature, the reported results must be considered to be preliminary and qualitative. The microcrystal phase of ZS depends on the crystalline water [3]. Therefore, it is probable that the catalytic activity and acidity does also. Thus it is necessary to take all of these factors into account, if meaningful relationships between crystalline water and catalytic behavior are to be uncovered.

In this context, we have correlated the esterification activity with a series of ZS hydrate samples. It is observed that upon heating the ZS samples to 420 °C, they exhibit different catalytic activity. Moreover, the characterization of the samples was performed by mean of XRD, thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) and ammonia FTIR analysis.

2. Experimental

2.1. Catalyst preparation

Zirconium sulfate (Beijing, Shiji Chem. Co) were treated in a muffle furnace at 110, 160, 200, 330 and 420 °C, respectively.

2.2. Characterization

XRD was performed on a Shimadzu HR 6000X. The conditions used were: Cu Kα radiation (λ = 1.54056 Å) at 40 kV and 200 mA, scanning angle (2θ) from 5 to 60° with scan-steps of 0.04°/s.

FTIR spectra of the samples were recorded on a Shimadzu FTIR-8400S by the KBr pellet technique. The sample was ground with spectral grade KBr to form a mixture, which was pelletized using a hydraulic press. This pellet was used to record the infrared spectra, ranging 4000–400 cm^{-1}.

TGA was performed by Mettler Toledo thermal analyzer. All the samples were heated at 10 °C min^{-1} in air up to 900 °C.

Catalyst surface acidity was analyzed by ammonia adsorption followed by FTIR spectroscopy. Finely dried ground catalyst samples were pressed for 2 min into a self-supporting wafer. The wafer was preheated by stepwise heating from 25 to 105 °C under extra-pure nitrogen gas at flow-rate of 30 cm^3 min^{-1} for 30 min. Then, the samples were permeated with ammonia for 30 min at 80 °C. After adsorption of the ammonia vapors on the wafer, the physisorbed ammonia was expelled using nitrogen gas at a flow-rate of 30 cm^3 min^{-1} for 30 min. Sample spectra were recorded at each stage on a Shimadzu FTIR-8400S equipped with a Thermo Spectra-Tech high temperature/vacuum chamber to elucidate the exact acidic nature of the catalyst surfaces. Differences between the spectra of ammonia adsorbed on samples and a reference were obtained by subtraction.

Ion exchanged of ZS sample with cesium chloride (CsCl) solution was conducted to find out whether the surface hydroxyl groups played a role in the catalysis. A known amount of ZS

Fig. 1. Idealized structure of zirconium sulfate (ZS) tetrahydrate.

was treated with 25 ml of 0.05 M CsCl in ethanol solution. After drying at room temperature, the solid obtained was washed and dried before calcined at 420 °C. The thermally treated sample was again mixed with 25 ml of 0.05 M CsCl solution, as stated above. The cesium ion (Cs$^+$) exchanged ZS was tested for its catalytic activity in esterification of oleic acid with a view to determine the poisoning effect of Cs$^+$ and to find out the role of surface hydroxyl groups in the catalysis. It is reported that only the surface protons were exchanged by this procedure [7]. It is possible to exchange only the surface protons of ZS with Cs$^+$ because this ion is too large to exchange into the interior of ZS in the solution.

2.3. Esterification of oleic acid with 1-butanol

Esterification reaction was performed in three-neck flask at atmospheric pressure equipped with a telfon-coated magnetic stirring bar, a thermometer, Dean-Strak receiver and reflux condenser. A typical esterification reactant consists of oleic acid (31.6 ml, 0.10 mol), 1-butanol (11.0 ml, 0.12 mol) and fresh catalyst (1.41 g). The moles ratio for oleic acid to butanol is 1:1.2 and the weight ratio of the catalyst was 5 wt.%, based on oleic acid. No solvent was added to promote more environmental friendly process. The reaction temperature was slowly raised to 110–120 °C and maintained at the desired temperature during the specified reaction periods. The heating was stopped after 4 h to determine the conversion. The product was analyzed by Hewlett Packard Gas Chromatography (GC) 5890 model with flame ionization detector (FID). The column used is MXT-1 Crossbond 100% dimethyl polysiloxane (15 m) and *n*-tetradecane was added as an internal standard.

3. Results and discussion

3.1. XRD

Fig. 2 shows the ZS samples after they have received various thermal treatments. It is obvious that there is phase transformation upon heating the ZS sample to 420 °C. The phase transformation of ZS hydrate to anhydrous upon thermal treatment has also been reported by Bear [8] and Kotsareneko et al. [9]. It is observed that upon heating the sample to 110 °C, its phase remains as the parent ZS. Thus, ZS retained it crystalline water but adsorbed water was removed upon heating up to 110 °C. Further, the tetrahydrate ZS phase was observed upon heating the sample to 160 °C. At 420 °C, tetrahydrate was transformed to anhydrous phase. These findings are in conformity with standard XRD data reported previously [8]. In addition, upon heating the sample to 750 °C, the ZS decomposed to zirconia phase. The strong diffraction lines of ZS treated at 750 °C are corresponded to monoclinic zirconia phase. As shown in Fig. 2, ZS did not decompose to zirconia upon heating up to 420 °C because there is no reflection lines corresponded to zirconia phase was observed. Therefore, it can be assumed that upon heating the ZS to 420 °C, the phase transformations are due the hydration of ZS sample.
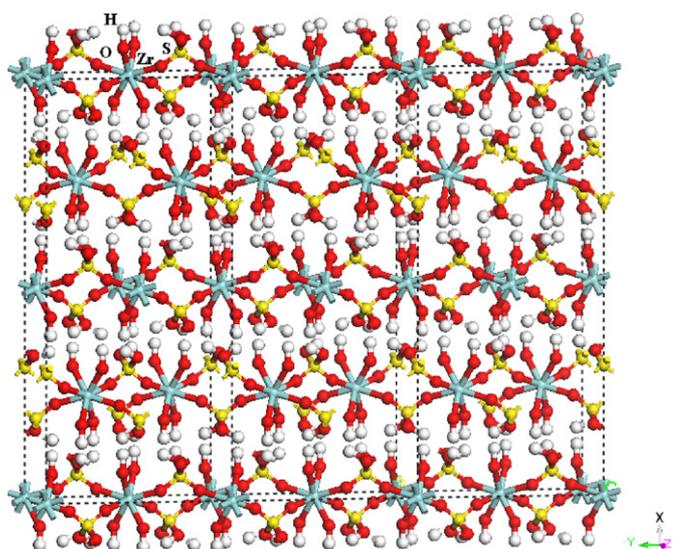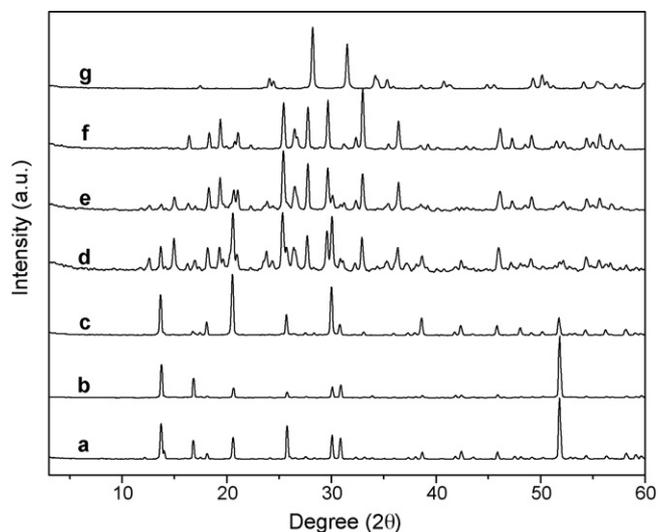
Fig. 2. XRD patterns of ZS. (a) Before heating, and after heating at (b) 110 °C, (c) 160 °C, (d) 200 °C, (e) 330 °C, (f) 420 °C and (g) 750 °C.

3.2. Thermogravimetric analysis

Weight loss curves for the ZS samples are shown in Fig. 3. It is noteworthy that the TGA curves at temperature below 250 °C became shallow upon heating the ZS samples to 420 °C. This would mean that ZS began losing it crystalline water upon heating the ZS to 420 °C. As shown in Fig. 3(a), the parent ZS lose it crystalline water in three steps, around 80, 165 and 220 °C to anhydrous phase before decomposed to zirconia. The weight loss up to 220 °C is corresponded to the removal of 5 moles of crystalline water. Although the ZS brought was labeled as tetrahydrate, it is surprising to observe more than 4 moles of water was removed. The ZS seems to be rather hygroscopic and it is concluded that the starting reactant is ZS with 5 mol of hydrate water attached to it. These finding are also in accordance with those reported by Strydom et al. [10]. Fur-

ther, the weight loss began at 600–730 °C is due to evolution of SO_3 decomposed from zirconium sulfate, following the equation: $Zr(SO_4)_2 \rightarrow ZrO_2 + 2SO_3$. This could be observed from Fig. 3(g) that no weight loss could be observed upon heating to 750 °C.
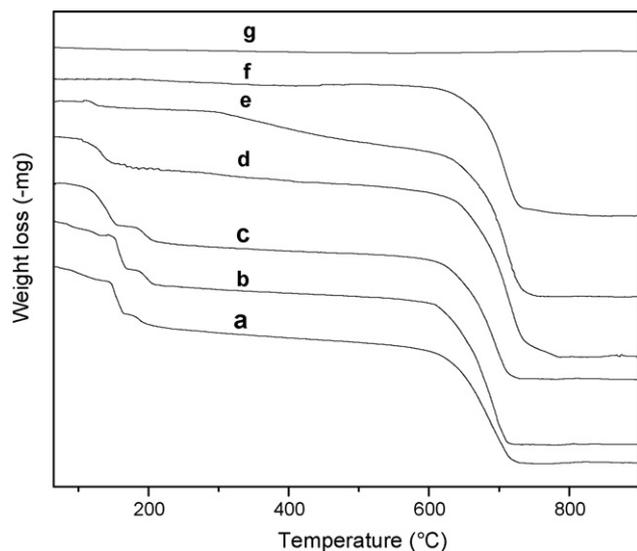
Upon heating the ZS sample to 110, 160, 200, 330 and 420 °C, the calculated weight loss based on TGA curves below 250 °C is corresponded to the removal of 5, 4, 2, 0.5 and 0 mol of crystalline water, respectively. It is noteworthy that the hydration state of ZS at various thermal treatments is parallel to those observed from XRD. For instance, upon heating the ZS sample to 160 °C, 4 mol of crystalline water was calculated from TGA analysis. In addition, upon heating the ZS sample up to 420 °C, a weight loss at 600 °C was still detected. This is clearly indicated that ZS did not decompose to zirconia upon heating up to 420 °C.

3.3. Ammonia adsorption Fourier transform infrared

Fig. 4 shows the FTIR spectra of ammonia adsorbed on ZS sample treated at 110, 160, 200, 330, and 420 °C. The band at 1525 cm^{-1} is the characteristics peaks of ammonium ion, which is formed on the Bronsted acid sites and the adsorption peak at 1700 cm^{-1} is contributed to ammonia coordinately bonded Lewis acid sites, indicating the presence of both Bronsted and Lewis acid sites on the surface of ZS. The Bronsted acidity is due to the Zr–OH groups, while the Lewis acidity is from Zr^{4+}. The peak intensity increased with increasing thermal treatment, meaning that amount of acidity increase with thermal treatment temperature.

With the increasing thermal treatment temperature, the total amount acidity was gradually increased. However, upon heating the ZS sample to above 330 °C, the acidity was slightly reduced. It is observed that ZS treated at 200 °C exhibits higher amount of acidity than other treatment temperatures. Upon heating ZS sample up to 420 °C, the anhydrous ZS still exhibit certain amounts of Bronsted acidity. It is reported that the interaction of Zr^{4+} with

Fig. 3. TGA curves of ZS: (a) Before heating and after heating at (b) 110 °C, (c) 160 °C, (d) 200 °C, (e) 330 °C and (f) 420 °C.
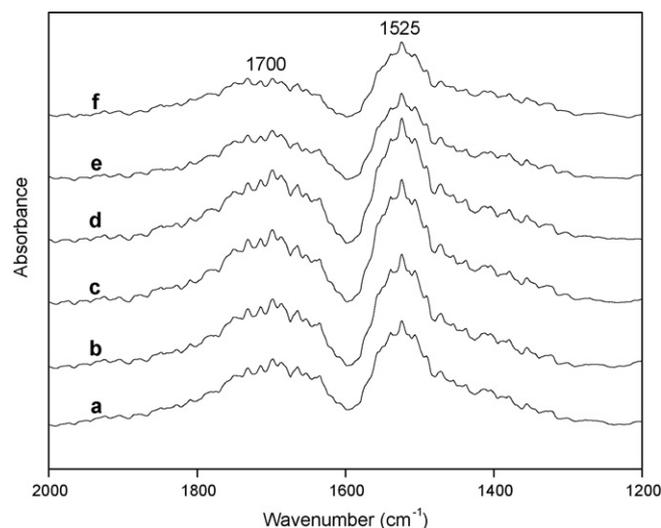
Fig. 4. Infrared spectra of NH3 adsorbed on ZS: (a) before heating and after heating at (b) 110 °C, (c) 160 °C, (d) 200 °C, (e) 330 °C and (f) 420 °C.

sulfate ions in highly active catalysts have a strong tendency to adsorb basic molecules [11], such as water [12]. Perhaps, this is likely to form Bronsted acid sites on anhydrous ZS.

3.4. FTIR spectroscopy

The FTIR spectra of ZS sample treated at different temperature are given in Fig. 5. ZS sample treated up to 420 °C showed absorption bands in the S–O stretching region [12], ranging from 1300 to 850 cm^{-1} provides proof for the presence of several families of surface monosulfates and bidentate sulfate ion coordinated to Zr^{4+} [13]. It is proven that sulfate species was preserved upon heating up to 420 °C. The adsorption bands of lower treatment temperature sample are vague, due to some remaining molecular water complicated the spectrum [12]. The absorption bands around 3300 cm^{-1} systematically changed with thermal treatment. In general, the molecular water in the vapor state found at 3756 and 3652 cm^{-1}, which assigned to OH stretching frequencies, are lowered when the water is bound in a crystal lattice. In addition, stronger hydrogen bonds are characterized by shorter O_w–O distances and lower OH stretching frequencies. Thus, the differences spectra in Fig. 5 are due to the presence of differences bonded water molecules in the present hydrates. It is observed that an absorption maximum occurs near 3200 cm^{-1} in the spectra of ZS samples treated below 160 °C, which due to coordinated water molecules. It is noticeable that upon heating the ZS sample, the OH stretching position shifted to higher frequencies. This would mean that the O_w–O distance became shorter from higher hydrate to anhydrous. Further, it was reported that O_w–O distance is 0.269 and 0.271 nm for ZS tetrahydrate [4] and monohydrate [14], respectively. Therefore, this help us to explain the OH position of ZS sample shifted to higher frequencies is due to transformation of ZS from hydrate to anhydrous. For the ZS sample treated at 420 °C, the maximum absorptions shifted to higher frequencies, substantiates the presence of almost adsorbed water molecules in this compound.
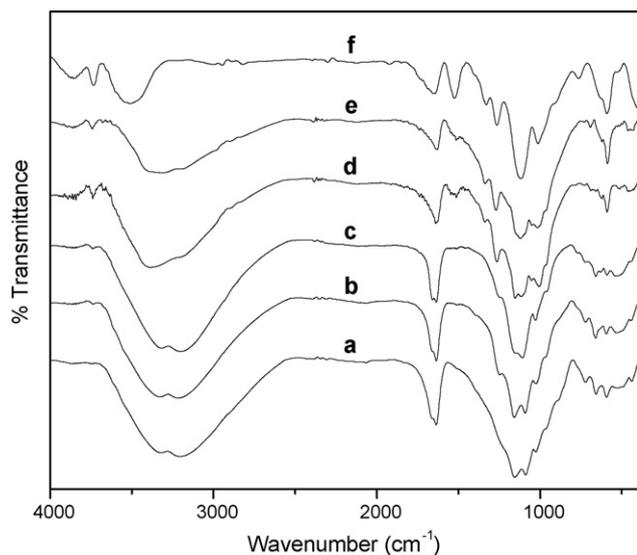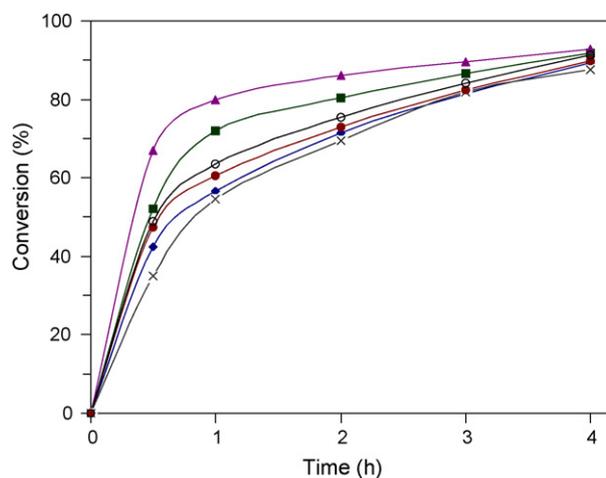
Fig. 6. Catalytic activities of ZS for esterification of oleic acid as a function of treatment temperature (▼) before heating and after heating at (●) 110 °C, (■) 160 °C, (▲) 200 °C, (○) 330 °C and (×) 420 °C.

3.5. Catalyst testing for esterification of oleic acid

The conversion of oleic acid with ZS samples of different treatment temperature is shown in Fig. 6. The reaction condition is mentioned above for esterification of oleic acid with *n*-butanol. It is interesting to observe that the catalytic activity of ZS is influenced by the thermal treatment. The catalytic activity of ZS increased with the temperature but slightly fell after heating above 330 °C. It is presumed that the difference in their activities is closely related to their crystalline water in ZS at elevated temperatures. The catalytic activity of ZS sample treated at 200 °C is most active compared to other samples. During the first hour, a significant catalytic activity change at different treatment temperature was observed. The catalytic activity of ZS sample treated at 200 °C increased rapidly compared with other samples. The conversion of ZS treated at 200 °C is 80% during first hour, which is 32 % more than that of ZS sample treated at 420 °C. The preliminary result from TGA shows that dihydrate is present upon heating the ZS sample to 200 °C. The catalytic activity data show that the entire ZS sample treated at various thermal treatments is selective toward the esterification. The selectivity for esterification of oleic acid to butyl oleate is found to be more than 99%. Very strong acid sites are normally oxidized oleic acid, which are present on sulfuric acid. Our results indicate that this situation these sites are not present on ZS because ZS only exhibit moderate acidity. It is noteworthy that catalytic activity began to decrease upon heating to 330 °C. The decreased of activity for ZS at higher thermal treatment is attributed to the fact that most of its hydroxyl group, which contributed to Bronsted acid sites from hydrate water are condensed out at 420 °C. However, it is seen that ZS sample still having certain amount of acidity after treated at 420 °C.

Therefore, we are interested to determine whether the surface hydroxyl groups were solely responsible for the esterification activity. It may assume that the replacement of the protons by Cs^+ should eliminate this activity. Fig. 7 gives the activity for cesium exchanged ZS samples, from which it is seen that Cs^+ ion exchanged inhibits the reaction considerably. For

Fig. 5. Infrared spectra of ZS: (a) before heating and after heating at (b) 110 °C, (c) 160 °C, (d) 200 °C, (e) 330 °C and (f) 420 °C.
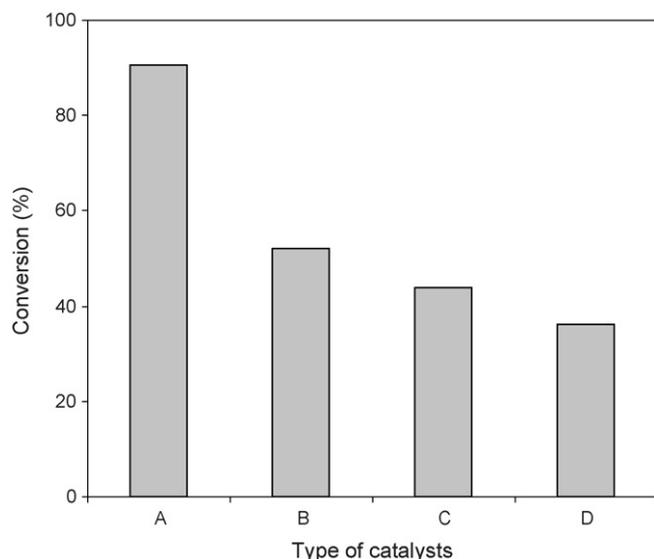
Fig. 7. Effect of Cs$^+$ ion exchanged on the activity of ZS with no Cs$^+$ treated at 420 °C (A), after first treatment with CsCl (B), after second treatment with CsCl (C), and without catalyst (D). The reaction was carried out under the same conditions as stated above for comparison purposes.

comparison purposes, the reaction condition is the same as shown in Fig. 6. The conversion was 52% and second treatment with CsCl yielded a still lower conversion of 44%. Although, the poisoning experiments (Fig. 7) suggest the participation of protons in the chemical reaction, the fact that the catalyst does not get totally indicates that the catalytic activity of ZS is governed not only by the number of protons or acid sites but also certain unknown inherent characteristics or surface defects created by structural modification at elevated temperature. In other words, the present observations suggest the presence of at least two kinds of sites on ZS as mentioned above. One of the sites, which get poisoned by Cs$^+$ ion exchange, should be related to the hydroxyl group (Bronsted acid site). This fact leads us to assume that the second kind of site which does not get poisoned by Cs$^+$ ion or by thermal treatment should be responsible for the residual activity of ZS. This second kind of site should be associated either with the phase transformation to zirconium–oxygen bond stretching or Lewis-type centers formed by removal of protons. Preliminary results show that Lewis-type centers formation is more pronounced. Besides that, it may also assume that Bronsted acid sites are mainly responsible for activity of ZS. The Bronsted acid sites result from the weakening of the –OH bond by the sulfate groups attached to Zr. Meanwhile, the Lewis acid sites are shorts of electrons, at Zr^{4+} centers as the result of electron withdrawing nature of the sulfate groups. These active species

are considered to be the active centers for esterification of fatty acid. Preliminary results show that the esterification may take place through a ligand exchange reaction with fatty acid on the Bronsted acid sites, although we do not have decisive evidence.

4. Conclusions

This paper has shown that there is a correlation between catalytic activity and thermal treatment of ZS for esterification reaction. A close relationship between acidity and catalytic activity could be observed. We can correlate the higher activity exhibited by the ZS at various thermal treatment to its acidity. The different hydrate or phase transformation was obtained upon heating the ZS sample. They give rise to different XRD patterns, FTIR spectra, acidity and catalytic activity. The results show that ZS treated at 200 °C is the most active due to higher amount of acidity. It is demonstrated that upon heating the ZS sample to 420 °C, the crystalline phase and acidity changes are due to hydration of ZS. One of the active sites, which get poisoned by Cs$^+$ ion exchange, should be related to the hydroxyl groups (Bronsted acid sites). This fact leads us to assume that Bronsted acid sites should mainly responsible for activity of ZS.

References

[1] Y. Huang, B. Zhao, Y. Xie, Appl. Catal. A: Gen. 173 (1998) 27.
[2] K. Arata, M. Hino, N. Yamagata, Bull. Chem. Soc. Jpn. 63 (1990) 244.
[3] I.J. Bear, W.G. Mumme, Acta Cryst. B 26 (1970) 1140.
[4] J. Singer, D.T. Cromer, Acta Cryst. 12 (1959) 719.
[5] W. Cao, J. Zhang, Q. Lv, J. Beijing Univ. Chem. Technol. 26 (1999) 72.
[6] W. Cao, J. Zhang, Q. Lv, J. Petrochem. Univ. 13 (2000) 41.
[7] G. Alberti, M.G. Bernasconi, M. Casciola, U. Costantino, Ann. Chim. 68 (1978) 265.
[8] I.J. Bear, Aust. J. Chem. 20 (1967) 415.
[9] N.S. Kotsareneko, V.P. Shmachkova, Kinet. Catal. 43 (2002) 280.
[10] C.A. Strydom, G. Pretorius, Thermochim. Acta 223 (1993) 223.
[11] C. Miao, W. Hua, J. Chen, Z. Gao, Catal. Lett. 37 (1996) 187.
[12] J.R. Sohn, D.H. Seo, Catal. Today 87 (2003) 219.
[13] E.E. Platero, M.P. Mentruit, C.O. Arean, A. Zecchina, J. Catal. 162 (1996) 268.
[14] I.J. Bear, W.G. Mumme, Acta Cryst. B 26 (1970) 1125.