# Hydrothermal Synthesis of Nanosized Sulfated Zirconia as an Efficient and Reusable Catalyst for Esterification of Acetic Acid with *n*-Butanol

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A kind of nanosized sulfated zirconia was prepared by a hydrothermal method, and full characterized by XRD, TEM, BET, TGA, and FTIR. Its catalytic activity was evaluated in the esterification reactions, including the testing of the catalytic reusability and the optimization of reaction conditions. The obtained catalyst was revealed to be highly efficient solid catalyst for the esterification of acetic acid with n-butanol, presenting the advantages of high conversion and selectivity, easy recovery, and steady reusability.

Key Words : Sulfated zirconia, Esterification, Hydrothermal

## Introduction

Commonly, esters are prepared by direct esterification of carboxylic acids with alcohols in the presence of acid catalysts. Mineral liquid acids, such as sulfuric acid and ptoluenesulphonic acid are widely used in industrial esterification reactions, owing to their low price and high activity. However the drawbacks they suffered are obvious, such as their corrosive nature, the existence of side reactions, and the difficulty for the separation of the catalyst from the reaction mixture.<sup>1,2</sup> All these problems could be solved thoroughly with the solid acid catalysts, which could eliminate the corrosive nature and the side reactions to achieve higher purity of the products. In addition, the solid acid catalysts can be easily reused by decantation or filtration from the reaction mixture.<sup>2</sup> A variety of materials such as clays, zeolites, sulfated metal oxides, heteropolyacides, etc.<sup>3-5</sup> have been used as solid acid catalysts for esterification reactions. Zirconia has been wildly used as catalyst or catalyst support for acidic catalytic reactions, such as hydrocarbon isomerization, alkylation, and esterification.<sup>6-9</sup>

It is well-known that the catalytic properties of sulfated zirconia are strongly influenced by the preparation methods, which may affect structural and textural features. Nanosized sulfated zirconia has been synthesized by a traditional precipitation method and the sol-gel technique,<sup>10,11</sup> which suffer from overlong reaction time, uncontrollable crystal and complicated processing. Hydrothermal synthesis has been proved to be propitious to nanoparticle formation. Ultrafine particles are produced; particle sizes can be controlled by the operation conditions. And a very short reaction time can suppress the crystal growth. Thus the rapid and continuous synthesis method affords relatively narrow particle size distribution of metal oxides nanoparticles<sup>12</sup>.

In the present study, a kind of nanosized sulfated zirconia was synthesized by the hydrothermal method. The nanosized catalyst is proved to be a highly active and selective catalyst for esterification of acetic acid with *n*-butanol,

together with the advantages of easy recovery and a steady reusability.

## Experimental

Catalysts Preparation. The catalysts of nanosized sulfated zirconia were prepared by a hydrothermal incorporation method: first, the zirconium hydroxide was obtained by the hydrothermal method. 60 mL ethanol was mixed with the same volume of ZrOCl<sub>2</sub>·8H<sub>2</sub>O solution (0.4 mol/L), and 2 molar ratio of urea was added into the above mixture. The mixture was placed in a 160 mL autoclave, and then heated to 120 °C held constantly for 12 h. After the reaction, the obtained zirconium hydroxide sol was washed with distilled water until without the detection of chloride ions with silver nitrate (AgNO<sub>3</sub>), then dried at 120 °C for 24 h. Second, the zirconium hydroxide and ammonium sulfate with a molar ratio of 1:6 were ground in a carnelian mortar for 20 min, and after placement for 18 h at room temperature, the sample was calcined for 4 h at 400-800 °C. The catalysts were denominated as NSZ-T, where T refered to the calcination temperature.

**Esterification Reactions.** The esterification reactions of acetic acid with *n*-butanol were performed in a 250 mL three-neck flask with a condenser and a water separator. The above assembly was heated using a heating jacket. In a typical experiment, it was carried out at 110 °C with 0.2 mol acetic acid and 0.6 mol *n*-butanol. The required quantity of the solid acid catalyst was added and the reaction mixture was refluxed with constant stirring. The reaction was carried out for 30-240 min and the conversion degree of acetic acid was estimated by measuring the acid value of the product. After completion of the reaction, the solid catalyst was separated by filtration and dried in an oven at 120 °C overnight.

**Characterization of Catalysts.** The compositions and phases of the products were identified by powder X-ray diffraction (XRD) on an D8 X-ray diffractometer (Bruker

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AXS, German) using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The angle (2 $\theta$ ) was measured in steps of 0.02° with a dwell time of 1s, between 10° and 85°. The morphologies and sizes of the products were examined by transmission electron microscopy (TEM) with a JEM-2100 (JEOL, Japan) transmission electron microscope at an accelerating voltage of 200 kV. The specic surface area of the catalyst samples was measured according to the Brunauer Emmet Teller (BET) method with nitrogen adsorption at 77.4 K on a ASAP 2020 instrument (Micromeritics, USA), and the degas conditions was 250 °C for 2 h. The thermogravimetric analysis (TGA) of precursor samples was determined with TGA/DSC1/ 1100 SF thermal-analysis instrumentation (Mettler Toledo, Switzerland). The infrared spectra were recorded on an ABB Bomem FTLA2000-104 spectrometer. The samples were prepared as thin films on KBr salt plates. The number of acid sites was also estimated by using a method involving an aqueous ion-exchange step of the catalyst H<sup>+</sup> ions with Na<sup>+</sup> ions, followed by titration of the resulting solution.<sup>13,14</sup>

## **Results and Discussion**

Influence of Calcination Temperature for the Activity of the Sulfated Zirconia Catalyst. The Physic-chemical properties of the catalysts of different calcination temperature ranging from 400 to 800 °C are shown in Table 1. The total acidities of the catalysts were expressed as the total number of acid sites per gram of catalyst. It can be observed that the catalysts calcined at 500 °C showed the highest acidity. With the increasing of the calcination temperature, the acidity decreased clearly. This is match with the thermogravimetric analysis data, the content of sulfate group was decreased with the increasing of calcination temperature, and the active sulfur species were decomposed before the temperature rising to 730 °C. But the BET surface area was increased with the increasing calcination temperature, and got the maximum when the temperature achieved 700 °C. The influence of the calcination temperature on the activity of the NSZ-T catalysts in the esterification of acetic acid with *n*-butanol is displayed in Table 2. The catalysts subjected to calcination at 500 °C, showed the highest activity. With the increasing calcination temperature, the reaction rate of acetic acid decreased clearly, but the conversion of acetic acid at 120 min of NSZ-400, NSZ-500 and NSZ-600 reached almost the same value, which fits the high total acidity of the NSZ-T catalysts. Compare with NSZ-700 and NSZ-800's low activity, they contains more acidic sites. So

 Table 2. Relation between the calcination temperature and the conversion of acetic acid

Calcination temperature (°C)	Reaction time (min)	Conversion (%)	Selectivity (%)
400	30	65.57	100
	60	84.74	100
	90	92.91	100
	120	96.60	100
500	30	91.91	100
	60	97.21	100
	90	97.96	100
	120	98.26	100
600	30	59.57	100
	60	82.07	100
	90	91.90	100
	120	95.97	100
700	30	48.65	100
	60	65.38	100
	90	69.77	100
	120	75.68	100
800	30	23.79	100
	60	32.62	100
	90	40.59	100
	120	46.62	100

Reaction conditions: molar ratio acetic acid: n-butanol = 1:3, reaction temperature 110 °C, 1 wt % catalyst.

at the highest temperature of calcination, *i.e.*, about 800 °C the activity is almost negligible. Obviously, the activity of the sulfated zirconia catalyst was arranged in order of the increasing of the total acidity of the catalyst contain, and the active sulfur species are responsible for the total acidity which depends on the calcination temperature.

Influence of Reaction Time. The influence of reaction time was studied in the following reaction conditions: 0.6 mol *n*-butanol, 0.2 mol acetic acid and the NSZ-500 catalyst represents 1% of the mass of mixture charge in the reaction; the reaction temperature was kept at 110 °C. The results are presented in Figure 1. With the increasing reaction time, the conversion of acetic acid increased remarkably. The NSZ-500 catalyst showed considerable conversion of 92.73% even with a reaction time of 30 min. The high activity at short reaction time shows that the heterogeneous catalyst is comparable with the homogeneous catalyst system (H<sub>2</sub>SO<sub>4</sub>) where the reaction proceeds rapidly.

For comparison, the conversion of acetic acid measured in

Table 1. Physic-chemical properties of the catalysts of different calcination temperature

Catalyst calcination temperature (°C)	BET surface area (m <sup>2</sup> /g)	Total acidity (mmol/g)	Content of sulfated group (%)	ZrO <sub>2</sub> : Sulfate group (mass ratio)
400	-	22.56	_	_
500	2.90	25.88	14.52	5.9
600	20.17	19.37	9.32	9.7
700	85.70	3.16	1.65	59.6
800	34.34	2.27	0.24	415.7



**Figure 1.** Conversion of acetic acid as a function of the reaction time in catalytic and non-catalytic reaction. Reaction conditions: molar ratio acetic acid: *n*-butanol = 1:3, reaction temperature 110 °C, 1 wt % catalyst. ( $\blacksquare$ : non-catalytic reaction,  $\square$ : ZrO<sub>2</sub>,  $\blacklozenge$ : (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, O: H<sub>2</sub>SO<sub>4</sub>, and  $\blacklozenge$ : NSZ-500).

the above reaction conditions as a function of the reaction time over H<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, ZrO<sub>2</sub> and NSZ-500 catalysts were investigated; the results are presented in Figure 1. As expected, the conversion of acetic acid was higher in the presence of a catalyst than without a catalyst. The activities at 60 min of reaction time are compared in the following: NSZ-500 > H<sub>2</sub>SO<sub>4</sub> > (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> > ZrO<sub>2</sub>. NSZ-500 shows the highest conversion of acetic acid, which was probably due to the high acidity of the catalyst. As esterification is a typical acid catalyzed reaction and reversible reaction, the acidity of catalyst attributed greatly to the catalytic activity.

Influence of the Mass Fraction of the Catalyst. The effect of the mass fraction of the catalyst on the esterification was investigated with the NSZ-500 catalysts at 30 and 60 min and the result is shown in Figure 2. The mass fraction of the catalyst was 0.2, 0.5, 0.8 and 1.0% of the total reaction



Figure 2. Effect of catalyst concentration on esterification of acetic acid with *n*-butanol using NSZ-500 catalysts. Reaction conditions: molar ratio acetic acid: *n*-butanol = 1:3, reaction temperature 110 °C. ( $\blacksquare$ : 30 min,  $\bullet$ : 60 min).

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**Table 3.** Reusability of the NSZ-500 and  $(NH_4)_2SO_4$  catalyst in esterification of acetic acid

Cycle	Reaction time (min)	Conversion (%) by NSZ-500	Conversion (%) by (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
1	120	98.26	95.97
2	120	97.51	56.68
3	120	97.05	40.71
4	120	97.11	36.31
5	120	96.96	34.42

Reaction conditions: molar ratio acetic acid: n-butanol = 1:3, reaction temperature 110 °C, 1 wt % catalyst, reaction time 120 min.

mixture. As shown in Figure 2, the conversion of acetic acid increased with the increasing mass fraction of the catalyst from 0.2 to 0.8%. And the conversion of acetic acid decreased lightly with increasing of the mass fraction of the catalyst from 0.8 to 1.0%. That mainly because esterification is reversible reaction, the increasing the mass fraction of the catalyst also accelerate the negative reaction. So it can be concluded that the optimal mass fraction of the catalyst in the reaction medium is around 0.8%.

**Reusability of the Catalyst.** Recycling of the catalyst is an important aspect of any industrial process. For this purpose, the used NSZ-500 catalysts in the first cycle of the reaction was separated by filtration and dried in oven at 120 °C overnight. It was then used as the catalyst for the esterification of acetic acid with *n*-butanol with a fresh reaction mixture under the same conditions. To compare with the traditional heterogeneous catalyst, the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> catalyst was also studied. The results obtained are presented in Table 3. As is shown, the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> catalyst has high activity at the first reaction, and then reduces obviously. But the NSZ-500 catalyst remains high activity during the five cycles. From these results, it can be concluded that the NSZ-500 catalyst can be reused as there is no loss in catalytic activity during the five cycles.

X-ray Diffraction (XRD). Figure 3 shows XRD patterns



Figure 3. XRD patterns of NSZ-T catalysts and ZrO<sub>2</sub>-500; (■) tetragonal phase of zirconia and (□) monoclinic phase of zirconia.

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of the NSZ-T catalysts with different calcination temperatures and ZrO<sub>2</sub>-500 sample. The ZrO<sub>2</sub>-500 sample was made by ZrOCl<sub>2</sub>·8H<sub>2</sub>O calcined at 500 °C for 4 h. The XRD patterns show peaks assigned to both monoclinic phase and tetragonal phase. But NSZ-500 and NSZ-600 catalysts do not exhibit any peak, displaying the amorphous phase of zirconia, which indicates that the join of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> restrains the crystal of zirconia both monoclinic phase and tetragonal phase. It can be also explained in terms of the presence of SO<sub>4</sub><sup>2-</sup> ions, which necessitates into higher thermal energy requirement for the removal of OH<sup>-</sup> ions.<sup>15</sup> The increasing in calcination temperature transforms tetragonal phase to stable monoclinic phase, which can be seen in the XRD patterns of NSZ-700 and NSZ-800 catalysts. Those due to the hydroxide ions stabilize the tetragonal phase and the loss of -OH ions during dehydroxylation at higher temperature leads to increased formation of the tetragonal phase to the monoclinic phase. And the NSZ-400 catalyst shows characteristic peaks are belong to ammonium sulfate hasn't decomposed. This coincides with the thermogravimetric analysis data, ammonium sulfate decomposes completely while the temperature reaches above 425 °C.

**Transmission Electron Microscopy (TEM).** Figure 4 gives TEM images of NSZ-500 and NSZ-700. As is seen in picture (a) and (b), the sample displays a disordered structure with a number of wormhole-like and interconnected channels. The amorphous phase of zirconia is in good agreement with the XRD investigation. Picture (c) shows clearly nanocrystallines of ZrO<sub>2</sub> in NSZ-700, the diameters of particles were 15-30 nm. Because of small size of ZrO<sub>2</sub> brings strong adsorption force, most of these products have been aggregated with each other, it makes the particles generated in forms of conglomeration easily.

**Thermogravimetric Analysis (TGA).** As is shown in Figure 5, The TG-DTA results of the precursor sample of



Figure 4. TEM images of NSZ-500 (a), (b) and NSZ-700 (c).



Figure 5. TG-DTG curve of the precursor sample of NSZ-T catalysts.

nanosized sulfated zirconia catalysts are displayed. The complicated composition results in several weight loss stages. The sample presented a lightly weight loss about 2% from room temperature to 250 °C, mainly due to the loss of crystal water attached to the sample, which mainly attributes to the catalysts preparation method. Incorporation preparation of nanosized sulfated zirconia avoids water presenting. Pure ammonium sulfate decomposes by heating in two stages<sup>16</sup> that can be summarized as:

$$2(\mathrm{NH}_{4})_{2}\mathrm{SO}_{4}(\mathrm{s}) \xrightarrow{260 \,^{\circ}\mathrm{C} \rightarrow 315 \,^{\circ}\mathrm{C}} \longrightarrow (\mathrm{NH}_{4})_{2}\mathrm{S}_{2}\mathrm{O}_{7} + 2\mathrm{NH}_{3}(\mathrm{g}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{g})$$
(1)

$$3(NH_4)_2S_2O_7 \xrightarrow{315 \,^{\circ}C \to 410 \,^{\circ}C} \longrightarrow$$
  
 $2NH_3(g) + 6SO_2(g) + 2N_2(g) + 9H_2O(g)$  (2)

Because the precursor sample contains considerable amount of ammonium sulfate, two significant weight loss separately located at 302 °C and 425 °C amounts to almost 60% corresponded to the decomposition of ammonium sulfate. The weight loss stage at 475 °C is probably attributable to the decomposition of surface SO<sub>x</sub> to SO<sub>3</sub>. Two lightly weight loss stage at 635 °C and 692 °C can be assigned to the structure change of sulfated zirconia and decomposition of sulfate. The activity of the catalysts is extraordinary related to them. So the NSZ-700 and NSZ-800 catalysts have low activity.

Infrared (IR) Spectroscopy. IR spectra of the catalysts prepared by different calcination temperatures are shown in Figure 6. A broad peak observed at around 3400 cm<sup>-1</sup> is attributed to the  $\sigma_{O-H}$  stretching mode of water related with zirconia, the broadness of which is due to a hydrogen bonding effect. Because of the ammonium sulfate hasn't decomposed completely, the peak shift toward lower wavenumber at 3150 cm<sup>-1</sup> and was overlapped with the peak of  $\sigma_{N-H}$  stretching mode of amino. An intense peak around 1630 cm<sup>-1</sup> is attributed to  $\delta_{O-H}$  bending mode of water associated with the sulfate group. The catalysts calcined at 400 °C and 500 °C show the IR bands of the SO<sub>4</sub><sup>2-</sup> group in the region of



Figure 6. FTIR spectra of catalysts of calcination temperature.

1200-900 cm<sup>-1</sup> obvious, with the peaks at about 995, 1058, 1148, 1236 cm<sup>-1</sup> assign to typical bands for inorganic chelating bidentate sulfate ion coordinated to zirconium cation.<sup>17</sup> A middle peak at approximately 1400 cm<sup>-1</sup> is observed in the spectra assigned to asymmetric stretching of covalent  $\sigma_{S=0}$  band. As the calcination temperature increase to 700 °C, the IR bands of the SO<sub>4</sub><sup>2-</sup> group formed a broad and intense peak indicates the formation of the sulfated zirconia has changed. Compare with catalysts calcined at 700 °C and 800 °C, the peak turn to weak and narrow, the peak around 610 cm<sup>-1</sup> which may be another bending mode the SO<sub>4</sub><sup>2-</sup> group is disappeared, and a peak at about 750 cm<sup>-1</sup> is formed which assign to typical bands of Zr-O.

#### Conclusions

Hydrothermal synthesis method for preparing nanosized sulfated zirconia with high activity in esterification reactions was present. The NSZ-T catalysts were acted as efficient stable solid acid catalysts for the esterification of acetic acid with *n*-butanol. The high activity with short reaction time shows that the heterogeneous catalyst is comparable with the homogeneous catalyst system ( $H_2SO_4$ ) where the reaction proceeds rapidly. And the catalytic properties of NSZ-T catalyst are maintained after five successive reactions. The results of XRD and TEM reveal that the NSZ-T catalysts having a low crystallite size about 15-30 nm with tetragonal as a predominant phase. Other characterizations prove the high catalytic activity highly depending on the calcination temperature, which is attributed to the structure change of sulfated zirconia and decomposition of sulfate.

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## References

- Peters, T. A.; Benes, N. E.; Holmen, A.; Keurentjes, J. T. F. Appl. Catal. A-Gen. 2006, 297, 182.
- 2. Altiokka, M. R.; Citak, A. Appl. Catal. A-Gen. 2003, 239, 141.
- Elings, J. A.; Downing, R. S.; Sheldon, R. A. Eur. J. Org. Chem. 1999, 837.
- 4. Patel, S.; Purohit, N.; Patel, A. J. Mol. Catal. A-Chem. 2003, 192, 195.
- 5. Furuta, S.; Matsuhashi, H.; Arata, K. Catal. Commun. 2004, 5, 721.
- Hino, M.; Takasaki, S.; Furuta, S.; Matsuhashi, H.; Arata, K. *Appl. Catal. A-Gen.* 2007, *321*, 147.
- 7. Yadav, G. D.; Kundu, B. Can. J. Chem. Eng. 2001, 79, 805.
- Hu, X. T.; Zhou, Z.; Sun, D. F.; Wang, Y. T., Zhang, Z. B. Catal Lett 2009, 133, 90.
- Garg, S.; Soni, K.; Kumaran, G. M.; Bal, R.; Gora-Marek, K.; Gupta, J. K.; Sharma, L. D.; Dhar, G. M. *Catal Today* **2009**, *141*, 125.
- Wang, J. A.; Valenzuela, M. A.; Salmones, J.; Vazquez, A.; Garcia-Ruiz, A.; Bokhimi, X. *Catal Today* 2001, 68, 21.
- Busto, M.; Shimizu, K.; Vera, C. R.; Grau, J. M.; Pieck, C. L.; D'Amato, M. A.; Causa, M. T.; Tovar, M. *Appl. Catal. A-Gen.* 2008, 348, 173.
- Hayashi, H.; Ueda, A.; Suino, A.; Hiro, Y.; Hakuta, Y. J Solid State Chem. 2009, 182, 2985.
- 13. Meng. Z. Y.; Zhou, R. Chinese J. Catal. 1980.
- Melero, J. A.; van Grieken, R.; Morales, G.; Nuno, V. Catal. Commun. 2004, 5, 131.
- Mishra, M. K.; Tyagi, B.; Jasra, R. V. Ind. Eng. Chem. Res. 2003, 42, 5727.
- Perez, J.; Perez, E.; del Vas, B.; Garcia, L.; Serrano, J. L. *Thermochim Acta* 2006, 443, 231.
- 17. Song, X.; Sayari, A. Catalysis Reviews 1996, 38, 329.