



Preparation of fibrous sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) solid acid catalyst using collagen fiber as the template and its application in esterification

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ABSTRACT

A novel fibrous sulfated ZrO_2 ($\text{SO}_4^{2-}/\text{ZrO}_2$) solid acid catalyst was prepared using collagen fiber as the template. The surface morphology of the as-prepared catalyst was observed by scanning electron microscopy (SEM), and the corresponding crystalline properties were determined by X-ray diffraction (XRD). To collect the structural properties of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst, N_2 adsorption/desorption method was carried out. Temperature-programmed decomposition (TPD) of ammonia was conducted to determine the acid strength of the catalyst. It was found that the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst had well-defined fibrous morphology and porous structure, which contained both medium strong acidic sites and strong acidic sites. Subsequently, the esterification of acetic acid with *n*-butanol was carried out to evaluate the catalytic activity and reusability of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst. The $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst exhibited high catalytic activity as compared with other solid acid catalysts. Furthermore, the catalyst can be reused 6 times without significant loss of catalytic activity, suggesting a satisfied reusability.

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1. Introduction

Conventional homogenous acids such as H_2SO_4 , HNO_3 and HF are a class of important catalysts that are traditionally used in petroleum and chemical industries because they are highly active for a variety of organic reactions, including esterification, alkylation and hydration [1–3]. However, use of homogenous acid as catalyst often suffers from the problem of difficult recovery of excessively used acid due to its homogeneous nature. Furthermore, the excessive acid has to be neutralized after the reaction leaving considerable amount of salts to be disposed off into the environment. To overcome the disadvantages of homogenous acid catalyst, many efforts have been devoted to the exploration of heterogeneous acid catalyst [4,5], which offers significant advantages of easy separation, no corrosion, low toxicity and environmental safety.

To date, various heterogeneous acid catalysts have been developed such as heteropolyacids (HPAs), zeolites and the sulfated metal oxides. HPA has high catalytic reactivity while its low thermal stability and low surface area limit its application [6]. As for zeolites, their reactions are often accompanied with side products at higher reaction temperature [7–9]. In contrary, sulfated metal

oxides which provide both high activity and thermal stability, have been recognized as one of the most important classes of heterogeneous acid catalysts [10–14]. Amongst those sulfated metal oxides, sulfated zirconia oxide holds great promise in a number of reactions of industrial importance due to its superior acidity.

Conventionally, zirconia oxides are prepared by the precipitation or hydrolysis of zirconia precursors [15–17]. To ensure high catalytic activities, the formation of high surface area is often claimed, and the corresponding pore size is desirably controlled in mesopores or macropores. However, the texture of zirconia oxides is usually subjected to the influence of precipitation/hydrolysis parameters (solvent, metal precursor and precipitation/hydrolysis rate), which makes it difficult to precisely control the morphology of the as-prepared zirconia oxides. Recently, organic templating technique has been emerged as promising strategy for the effective and convenient fabrication of inorganic porous supports [18,19]. By using organic matrices with ordered shape and pattern as the templates, one can easily synthesize porous supports with sophisticated and highly ordered structure. For example, Xia et al. successfully prepared hierarchical porous cobalt oxide using polystyrene sphere as the template, and the obtained cobalt oxide can be used as effective anode materials due to its highly ordered porous arrangement [20].

Collagen fiber (CF), an abundant natural biomass, is of the highly ordered arrangement of collagen molecules. In collagen fiber, collagen molecules are packed together longitudinally in a ‘quarter stagger’ arrangement, which further forms the holes and overlaps zones in collagen fiber [21]. Therefore, it could be inferred that

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the porous materials with fibrous morphology could be obtained if collagen fiber is used as the template. On the other hand, collagen fiber has abundant functional groups, including $-\text{COOH}$, $-\text{OH}$ and $-\text{NH}_2$ groups, which are highly active with various metal ions such as Zr^{4+} , Cr^{3+} , and Al^{3+} [22]. Consequently in principle, porous zirconia oxide (ZrO_2) with fibrous morphology could be prepared by reacting Zr precursor with CF template, followed by calcination to remove collagen fiber. Accordingly, sulfated porous ZrO_2 fiber can be subsequently synthesized by conventional impregnation treatment using the porous ZrO_2 fiber as the support. In order to evaluate its catalytic activity, sulfated porous ZrO_2 fiber was used as the heterogeneous acid catalyst in catalytic esterification of *n*-butyl alcohol with acetic acid, of which the resultant *n*-butyl acetate is an important organic compound widely used in many fields such as lacquer, artificial perfume and flavouring extraction [23].

2. Experimental

2.1. Materials

Collagen fiber (CF) was prepared from cattle skin according to our previous work [24]. Zirconium sulfate was provided by a commercial supplier (Sichuan Ting Jiang Fine Chemicals Co. Ltd., China). Acetic acid, *n*-butanol, and other chemicals were all analytical grade reagents.

2.2. Catalyst preparation

2.2.1. Preparation of Zr-immobilized collagen fiber and fibrous zirconia oxide (ZrO_2)

15.0 g of collagen fiber was added into 400 mL of deionized water at 25 °C for 1.0 h. The pH of the resultant mixture was adjusted to 1.8–2.0 by using H_2SO_4 – HCOOH solution (H_2SO_4 : HCOOH = 10, v/v). After the mixture was stirred at 25 °C for 4.0 h, a determined amount of $\text{Zr}(\text{SO}_4)_2$ was added, and kept under constant stirring for another 4.0 h. Subsequently, a proper amount of NaHCO_3 solution (15%, w/w) was drop-wise added into the reaction system within 3.0 h in order to increase its pH to 4.0–4.2. When reached the desired pH, the temperature of the system was heated to 40 °C, and the reaction proceeded for 10.0 h. Finally, the Zr-immobilized collagen fiber was collected by filtration, washing and drying at 45 °C.

The prepared Zr-immobilized collagen fiber was treated by temperature-programmed calcination to remove the collagen fiber template. The detailed calcination process was as follows. Zr-immobilized collagen fiber was first kept at 100 °C for 2.0 h in air, and then heated (5 °C/min) to 300 °C and held at this temperature for 2.0 h. After this, the temperature was further increased to 500 °C with a rate of 5 °C/min and held at this temperature for 2.0 h. As a result, fibrous ZrO_2 was obtained. Herein, a series of fibrous ZrO_2 were prepared by varying the final calcination temperature from 500 °C to 800 °C.

2.2.2. Preparation of fibrous $\text{SO}_4^{2-}/\text{ZrO}_2$

0.5 g of fibrous ZrO_2 prepared at 600 °C was impregnated into 20.0 mL of 1.0 M H_2SO_4 solution for 4.0 h, and then collected by filtration, followed by calcination at 300 °C for 4.0 h. The resultant product was sulfated ZrO_2 , which was denoted as $\text{SO}_4^{2-}/\text{ZrO}_2$ in the following text.

2.3. Catalyst characterizations

The surface morphology of $\text{SO}_4^{2-}/\text{ZrO}_2$ was observed by scanning electron microscopy (SEM, JEOL LTD JSM-5900LV). XRD (Philips X'Pert Pro-MPD) characterization was performed to identify the crystalline structures of $\text{SO}_4^{2-}/\text{ZrO}_2$ by using Cu KR

X-radiation ($\lambda = 0.154$ nm). The specific surface areas and the pore size distribution of the $\text{SO}_4^{2-}/\text{ZrO}_2$ were determined by using the N_2 adsorption/desorption approach (Micromeritics TriStar Surface Area and Porosity Analyzer, nitrogen absorption apparatus). The acid strength of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalysts was determined in the CHEMBET-Palsar TPR/TPD (Automated Chemisorption Analyzer) instrument.

2.4. Catalytic reaction

The esterification of acetic acid with *n*-butanol was carried out as a probe reaction to evaluate the catalytic activity of $\text{SO}_4^{2-}/\text{ZrO}_2$ as solid acid catalyst. The reaction was performed in a 50.0 mL autoclave reactor equipped with a temperature controller and stirrer speed controller. A certain amount of the catalyst was added into the mixture of acetic acid and *n*-butanol. Then, a proper amount of dichloromethane was also added into the above mixture as an internal standard. The reaction system was conducted at certain temperature under constant stirring. When the reaction was completed, the catalyst was recovered by filtration and the resultant products were analyzed using gas chromatograph. The reusability of the catalyst was also performed under the same experimental conditions.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. The surface morphology of ZrO_2

Fig. 1a–e shows the surface morphology of un-sulfated ZrO_2 prepared using collagen fiber as the template and calcinated at 600 °C. It was found that the surface morphology of ZrO_2 was highly dependent on the loading amount of Zr on CF. The ZrO_2 prepared from low loading amount of Zr (22.5 mg/g) showed highly packed ZrO_2 crystals instead of fibrous morphology, as shown in Fig. 1a. Possibly, low loading amount of Zr is not sufficiently enough to react with the active sites of collagen fiber ($-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, etc.), which causes the poor distribution of Zr on the surface of collagen fiber. Under such conditions, majority of the un-reacted collagen fiber was burned and released as CO_2 , which further lead to the collapse of fibrous structure of collagen fiber. Due to the structural collapse of collagen fiber, Zr precursor will be gradually aggregated and transformed to ZrO_2 crystal clusters, just like no collagen fiber was used. These are possible explanations that are responsible for the observed highly crystallized ZrO_2 .

When the loading amount of Zr was increased from 22.5 mg/g to 30.3 mg/g, the prepared ZrO_2 has well-defined fibrous morphology, which appears as fiber bundles with a diameter of 2.5 ± 0.5 μm and a length of 0.25 ± 0.05 mm, as shown in Fig. 1b. Similar fibrous morphology can still be observed in those ZrO_2 samples with Zr loading of 40.9 mg/g (Fig. 1c), and their corresponding FE-SEM image is shown in Fig. 1e, in which nanoscaled ZrO_2 fibers are well arranged with defined fiber bundles. These observations suggested that the morphology of the natural collagen fiber was well preserved in ZrO_2 . More importantly, the fibrous morphology of ZrO_2 can still be preserved after the treatment of sulfuric acid impregnation (Fig. 1f). According to the literature [25], fibrous catalysts often exhibited the distinct advantages of high geometrical flexibility and low mass transfer resistance when used in liquid-phase or three-phase reactions. Therefore, the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst is expected to have high catalytic reactivity in the following probe reaction.

However, when further increasing the loading amount of Zr to 48.7 mg/g, the obtained ZrO_2 exhibited irregularly arranged ZrO_2

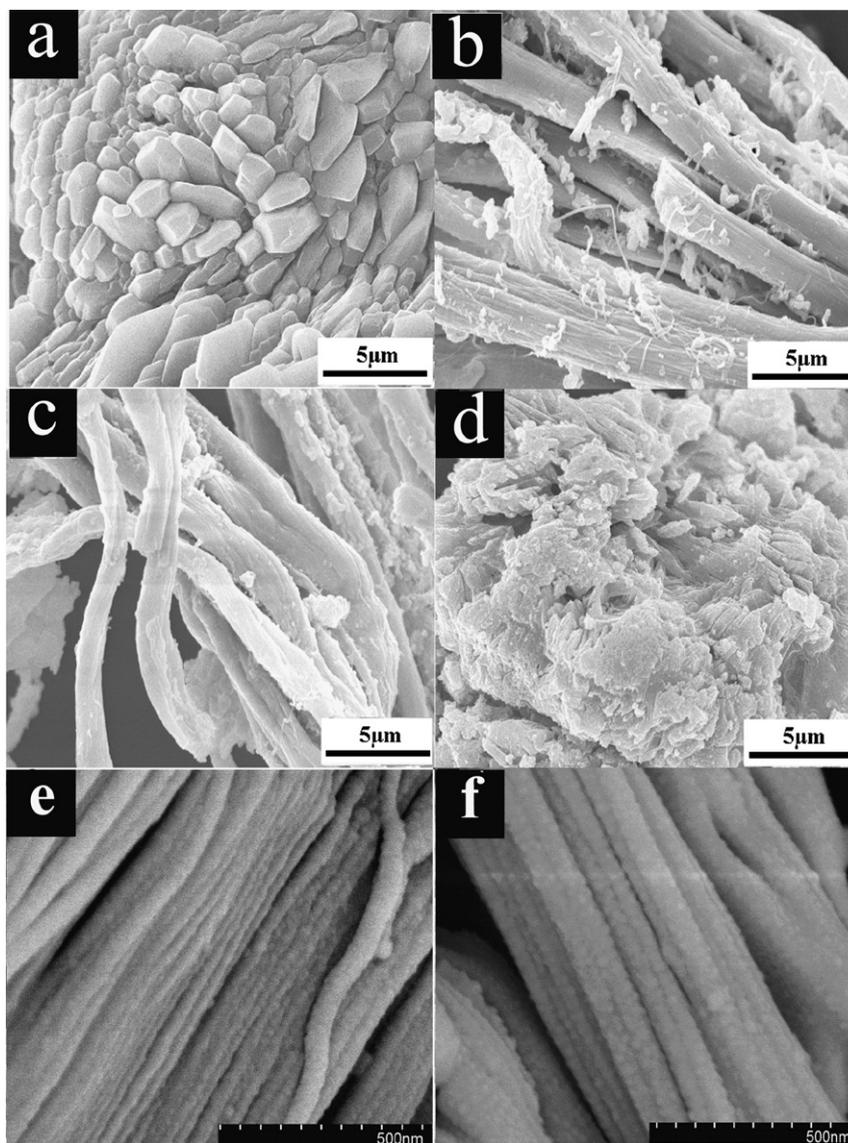


Fig. 1. SEM images of the ZrO_2 prepared using collagen fiber as the template and calcinated at $600^\circ C$.

aggregation, as shown in Fig. 1d. This phenomenon should be due to that excessive amount of Zr precursor cannot be stabilized by the collagen fiber, which leads to the growth and aggregation of ZrO_2 crystals on the surface of collagen fiber. When the used Zr precursor was excessive, the collagen fiber can be completely covered by the serious aggregated ZrO_2 . Obviously, the image observed in Fig. 1d belongs to this phenomenon.

In order to obtain fibrous ZrO_2 , the loading amount of Zr on collagen fiber was fixed at 40.9 mg/g in the following experiments.

3.1.2. XRD characterization of ZrO_2

Fig. 2 shows the XRD patterns of ZrO_2 , which were prepared at different calcination temperatures with a fixed loading amount of Zr (40.9 mg/g). When the calcination temperature was in the range of $500\text{--}600^\circ C$, only tetragonal phase ZrO_2 was prepared. Once the calcination temperature reached $700^\circ C$, the phase transformation of ZrO_2 was observed from tetragonal phase to monoclinic phase, and this phenomenon was more obvious in those ZrO_2 prepared at $800^\circ C$. According to the literature [26], the sulfated zirconia is not stable in the monoclinic phase, and thus ZrO_2 prepared at $500\text{--}600^\circ C$ is much preferred when only considering the effect of crystal phase on the activity of ZrO_2 .

3.1.3. Specific surface area and average pore size of ZrO_2 and SO_4^{2-}/ZrO_2 catalysts

In general, the specific surface area and pore size of the catalyst have significant influence on its catalytic activity. Thus, N_2 adsorption/desorption method was carried out to investigate the structural properties of the fibrous ZrO_2 prepared at different calcination temperatures. The corresponding results are summarized in Table 1. When the calcination temperature was $500^\circ C$, the specific surface area of the prepared ZrO_2 is $27.72 \text{ m}^2/\text{g}$, and its average pore size is about 3.5 nm . Along with the increase of calcination temperature from $500^\circ C$ to $600^\circ C$, the specific surface area of ZrO_2 is increased from 27.72 to $37.14 \text{ m}^2/\text{g}$, and the corresponding average pore size is also expanded to 16.2 nm . However, the further increase of calcination temperature leads to a sharp decrease of specific surface area and average pore size. For example, the specific surface area is only $15.62 \text{ m}^2/\text{g}$ and the average pore size is as small as 3.4 nm when the calcination temperature was $800^\circ C$.

Actually, the color of ZrO_2 prepared at $500^\circ C$ is a little grey, which suggested that the collagen fiber was not completely removed. Therefore, the ZrO_2 prepared at $500^\circ C$ has relatively low specific surface area and narrow pore size. When the calcination temperature was raised to $600^\circ C$, the collected ZrO_2 was

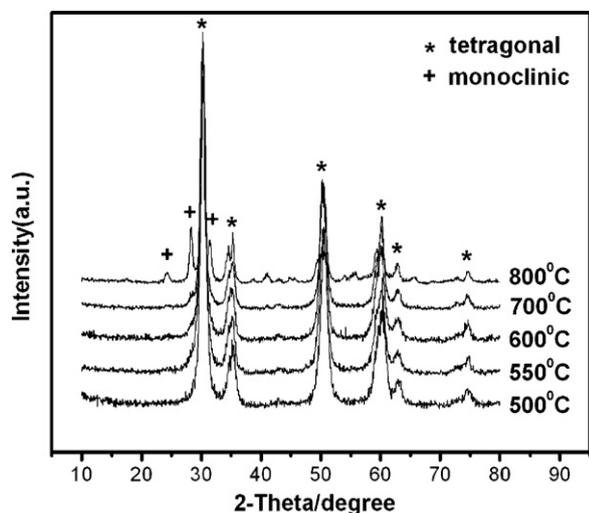


Fig. 2. XRD patterns of the ZrO_2 prepared at different temperatures.

pure white, suggesting the complete removal of collagen fiber template. According to the above SEM analysis, the ZrO_2 prepared at 600°C has well-defined fibrous morphology, and thus, the highest specific surface area and largest pore size were obtained in those fibrous ZrO_2 . Further increasing the calcination temperature will inevitably lead to a partial structural collapse of collagen fiber, which caused a substantial decrease of specific surface area and pore size as observed in those of ZrO_2 prepared at 800°C . The specific surface area of other fibrous ZrO_2 (Zr loading of 30.3 mg/g) was also analyzed by N_2 adsorption/desorption method but its specific surface area ($32.16\text{ m}^2/\text{g}$) was lower than the sample with Zr loading amount of 40.9 mg/g .

Considering that ZrO_2 prepared at 600°C has the highest specific surface area and largest pore size, those ZrO_2 were therefore used for the preparation of $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst, which was further used for the following esterification. Much to our delight, the obtained $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst still preserved the porous structure of ZrO_2 , as shown in Table 1. Although the specific surface area of $\text{SO}_4^{2-}/\text{ZrO}_2$ was not very high ($36.39\text{ m}^2/\text{g}$), its large pore size (8.4 nm) and the fibrous morphology should still be able to ensure a high catalytic activity of the catalyst.

3.1.4. Determination of acid strength of fibrous $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst

Temperature-programmed reduction desorption (TPD) of ammonia is a common method for investigating the strength of acid sites present on the surface of an acidic solid. Therefore, this method was used to determine the acid strength of the as-prepared fibrous $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst. The TPD profile of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst is shown in Fig. 3. Two major desorption peaks are observed at $300\text{--}500^\circ\text{C}$ and $650\text{--}750^\circ\text{C}$, which suggested that the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst contains both medium strong acidic sites and strong acidic sites [27].

Table 1
Specific surface area and average pore size of ZrO_2 at different temperatures.^a

	Temperature				
	500°C	550°C	600°C	700°C	800°C
BET surface area (m^2/g)	27.72	37.38	37.14/36.39 ^b	27.97	15.62
Average pore size (nm)	3.5	9.7	16.2/8.4 ^b	13.1	3.4

^a The ZrO_2 was prepared by calcinating collagen fiber with Zr loading amount of 40.9 mg/g .

^b BET surface area and average pore size of $\text{SO}_4^{2-}/\text{ZrO}_2$.

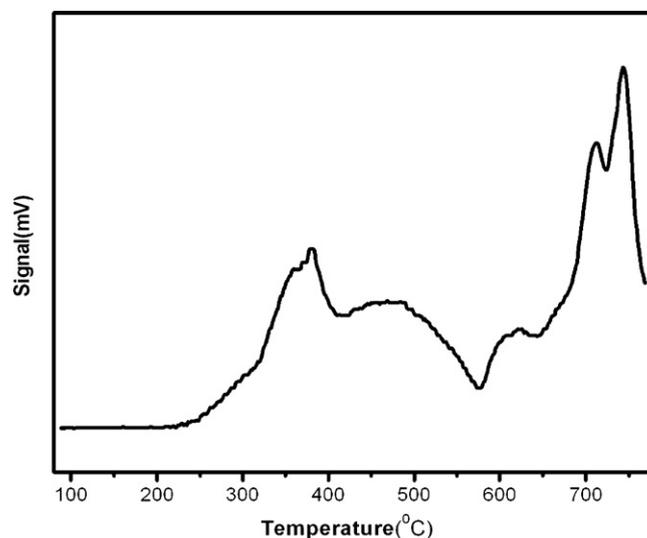


Fig. 3. TPD profile of the fibrous $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst.

3.2. Catalytic activity

3.2.1. Influence of reaction time

The influence of reaction time on the activity of $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst is shown in Fig. 4. A sharp increase of conversion was observed in the first reaction period of 5.0 min, in which the corresponding conversion of acetic acid was as high as 82.45%. This high initial conversion rate is possibly explained by the relatively high concentration of substrates. Then in the following reaction period of 5.0–60.0 min, the conversion is gradually increased along with the reaction proceed. When reacted for 60.0 min, the conversion reaches 99.0%. It should also be noted that the activity of as-prepared $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst is much higher than that of other reported solid ZrO_2 catalysts under the similar experimental conditions [28,29]. This distinct advantage of $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst should be derived from its fibrous morphology and large pores, which favors the mass transfer during the esterification process.

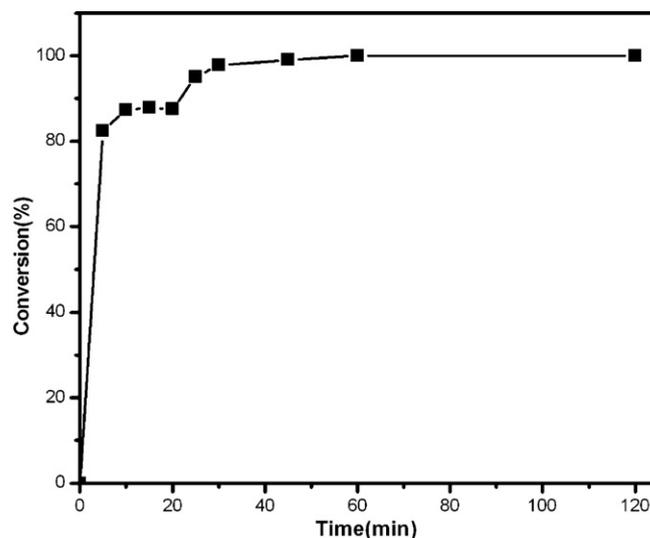


Fig. 4. Effect of reaction time on esterification of reaction temperature 363 K , $n\text{-butanol:acetic acid} = 1.1:1$, $0.2\text{ g SO}_4^{2-}/\text{ZrO}_2$ catalyst.

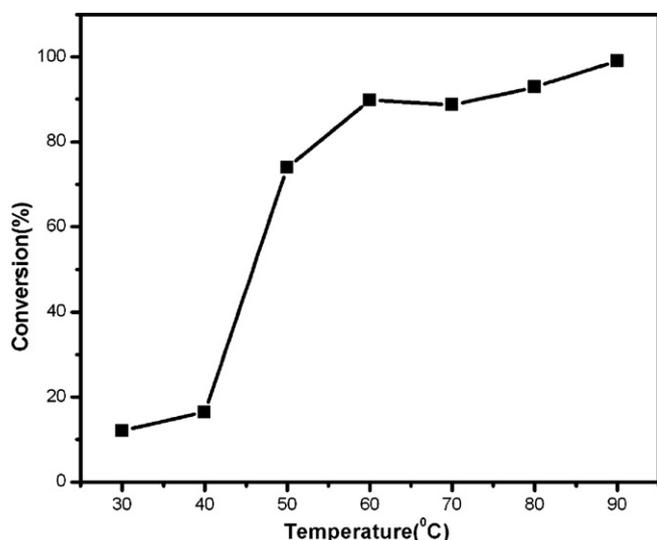


Fig. 5. Effect of reaction temperature on esterification.

3.2.2. Influence of reaction temperature on catalytic activity of fibrous $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst

According to the literature [30], esterification is an endothermic reaction, which can be promoted by the increase of reaction temperature. Thus, it is necessary to investigate the influence of reaction temperature on the esterification of acetic acid with *n*-butanol using $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst as the solid acid catalyst. Fig. 5 shows the effects of reaction temperature on the conversion yield of acetic acid at different reaction temperatures. The conversion yield was found to be dependent on the reaction temperature, increasing with the increase of temperature. In the range of 30–40 °C, the increase of substrate conversion yield is not obvious but a sharp increase was observed when the reaction temperature was beyond 40 °C. In the temperature range of 60–90 °C, the conversion yield of acetic acid is gradually increased along with the increasing temperature. When the reaction temperature reaches 90 °C, the conversion yield of acetic acid reached 99%. Thus the following catalytic experiments were all carried out at 90 °C.

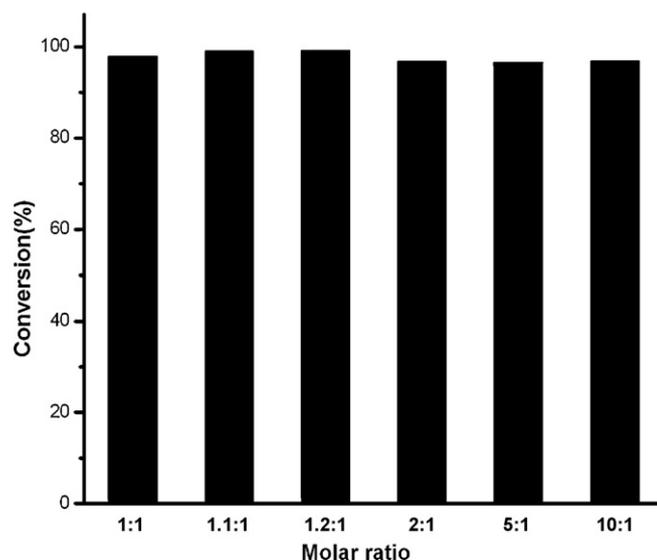


Fig. 6. Effect of molar ratio of *n*-butanol to acetic acid on the conversion yield of acetic acid.

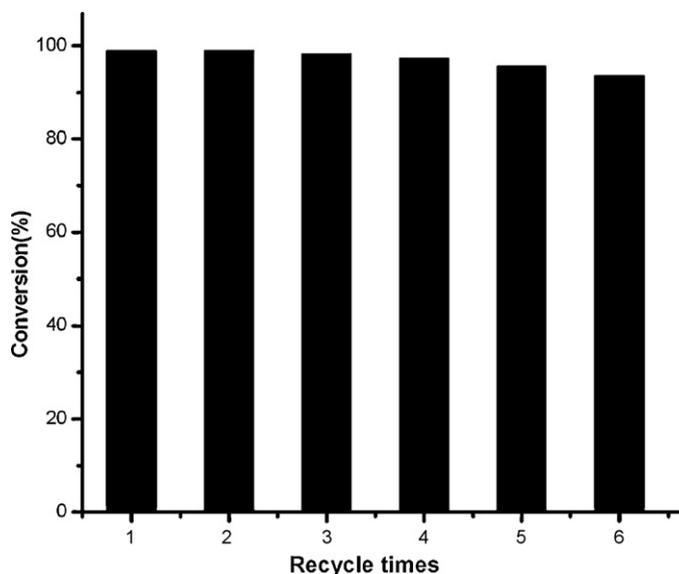


Fig. 7. Reusability of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst.

3.2.3. Influence of molar ratio of reactants

The influence of molar ratio of the reactants on the esterification of *n*-butyl acetate was studied. Various molar ratios of *n*-butanol to acetic acid were used during the esterification, which includes 1:1, 1.1:1, 1.25:1, 2:1, 5:1, and 10:1. The corresponding conversion yields of acetic acid are shown in Fig. 6. We found that the increase of molar ratio of *n*-butanol to acetic acid has no significant influence on the conversion yield of acetic acid, which varied from 93% to 99%. In general [31], a high esterification activity of sulfated ZrO_2 was obtained at high molar ratios of *n*-butanol to acetic acid while our prepared fibrous $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst can exhibit a high activity even when the molar ratio of *n*-butanol to acetic acid was 1:1, which is much preferred in practical application.

3.3. Reusability of the catalyst

Compared with homogenous acid, the superior advantages of heterogeneous solid acid catalyst are their easy recovery and good reusability. Therefore, it is quite necessary to evaluate the reusability of the as-prepared $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst, especially in viewpoint of practical application. After the fresh catalyst was used in esterification for the first time, the used catalyst was recovered by filtration and washed with ethanol, followed by drying. The resultant catalyst was then used for esterification under the same experimental conditions. The reusability of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst is shown in Fig. 7. It can be seen that for the first three cycles, there was a slight decrease in catalytic activity of the catalyst. In the fourth and fifth cycles, the conversion is decreased about 2% and 3%, respectively. In the sixth cycle, the conversion remained as high as 93.5%. All these facts suggested the good reusability of the as-prepared $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst in esterification of acetic acid with *n*-butanol.

4. Conclusion

In summary, a novel sulfated ZrO_2 solid acid catalyst was successfully prepared by using collagen fiber as the template. By adjusting the preparation conditions, including Zr loading and calcination temperature, the structural properties of collagen fiber can be well preserved in the ZrO_2 solid acid catalyst. Due to its unique fibrous morphology and large pores, the as-prepared fibrous sulfated ZrO_2 was highly active in esterification of acetic acid with

n-butanol. Moreover, the catalyst can be reused 6 times without significant loss of catalytic activity.

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