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RESEARCH PAPER

Synthesis of tetragonal sulfated zirconia via a novel route for biodiesel production

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Abstract: The sulfated zirconia was prepared by directly impregnating ammonium persulphate on the crystalline zirconia and followed by the calcination temperatures of 300–500°C. The structural properties of the catalysts were characterized by X-ray diffraction (XRD), N_2 adsorption-desorption, ammonia temperature programmed desorption (NH_3-TPD), Fourier transform infrared spectroscopy (FT-IR) and a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS). The experiment results demonstrated that the catalysts presented the tetragonal structure of zirconia and high crystallinity. The catalyst calcined at 500°C possessed the highest sulfur content and acidic sites in the catalysts. The catalyst exhibited high catalytic activity in transesterification of soybean oil with methanol. The yield of biodiesel achieved 84.6% because of the preferable super-acid sites on the surface of the catalyst.

Key words: tetragonal sulfated zirconia; impregnating; crystalline zirconia; transesterification; biodiesel

Inorganic solid acid catalysts have been gained great attention in recent years because of acknowledged environmental-friendly advantages[1]. Among the solid acids, sulfated zirconia exhibits perfectly catalytic activity for the reactions such as hydrocarbon isomerization, alkylation and transesterification[2–4], in which the tetragonal or cubic sulfated zirconia is active, but the monoclinic is inactive[5]. The mixture of tetragonal and monoclinic phases show much lower activity than pure tetragonal phase[6]. Therefore, the great efforts are being devoted to improve tetragonal phase structure of the sulfated zirconia to increase catalytic activity by various methods.

Some research groups reported that the percentage of tetragonal phase in zirconia could be increased with the metals as promoter, such as Pd[7], Pt[8], Al[9], Cu[10], Ga[11], etc. These investigations also indicated that the metal elements supported on sulfated zirconia played an important role to stabilize the tetragonal phase. Song et al[12] reported that the sulfated zirconia promoted by adding simultaneously Pt, Y, and Al, resulted in approximately 80% conversion for *n*-hexane due to pure tetragonal zirconia obtained by water-washing treatment. Gao et al[13] demonstrated that the formation of tetragonal phase resulted from supporting ceria on sulfated zirconia, which exhibited excellent catalytic activity in selective reduction of nitric oxide with ammonia. However, these methods usually were involved in the addition of high cost metal feedstock as promoters and followed by the sulfation of amorphous zirconium hydroxide with sulfating agent to prepare sulfated zirconia catalyst. Recently, the sulfated crystalline zirconia was obtained by calcining zirconium hydroxide without any metal elements, but in which the tetragonal and monoclinic phases coexisted because of the phase transition during the calcinations[14].

Here, we report a novel and efficient method to prepare the sulfated tetragonal zirconia without any additive, and which is applied for the transesterification of soybean oil with methanol. The preparation route by calcining the as-synthesized crystalline zirconia impregnated ammonium persulphate effectively prevents phase transition from tetragonal to monoclinic phase. The prepared catalyst presents the tetragonal structure of zirconia with high crystallinity and superacidity, displays high catalytic activity for the transesterification of soybean oil with methanol.

1 Experimental

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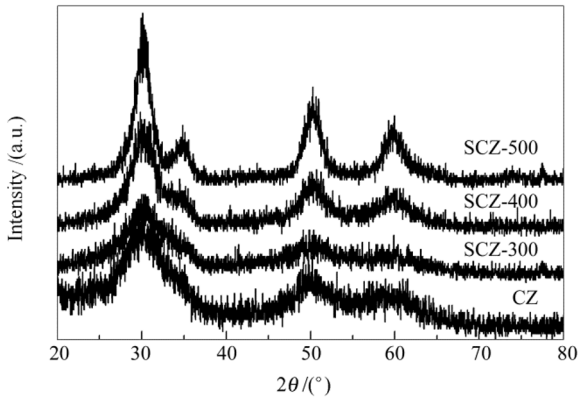

Fig. 1 XRD patterns of all the samples including calcined samples (SCZ-300, SCZ-400, SCZ-500) and as-synthesized sample CZ

1.1 Reagents

Ammonium persulphate $(NH_4)_2S_2O_8$ (98%), used as sulfate species, was purchased from Bodi, Tianjin, China. Methanol (99%) and soybean oil (food grade) were obtained from Kermel and Jiali, Tianjin, China. Zirconium *n*-butoxide ($Zr(OC_4H_9)_4$, 80%) and benzyl alcohol (98%) used in the synthesis procedure were purchased from Sigma-Aldrich, Shanghai and Guangfu, Tianjin, China respectively. All the chemicals in the study were used without further purification.

1.2 Synthesis of the crystalline zirconia

The crystalline zirconia was directly synthesized via vapor phase hydrolysis without high temperature treatment[15]. In a typical procedure, 3.36 g zirconium *n*-butoxide was dissolved into a 40 mL benzyl alcohol and stirred for 10 min. Then the mixed solution was transferred into a Teflon-lined hydrothermal chamber, in which the water was previously placed. To avoid the fierce hydrolysis, the water did not directly contact the zirconium *n*-butoxide. Subsequently, the hydrothermal chamber was sealed into the autoclave for vapor phase reaction at 140°C for 24 h. After cooling to the ambient temperature, the white product was separated by centrifugation and dried at 60°C overnight. The as-synthesized crystalline zirconia was designated as CZ.

1.3 Synthesis of the sulfated zirconia catalysts

The sulfated zirconia catalysts were synthesized by the wet impregnation of 3 g crystalline zirconia (CZ) with 1 mol/L ammonium persulphate solution for 2 h with continuously stirring at 25°C. The resultant mixture was then filtered to remove the excess ammonium persulphate and dried at 60°C overnight in an oven. The obtained solid products were calcined at 300, 400, 500°C in air for 1 h respectively. The resulting sulfated crystalline zirconia (SCZ) samples were labeled as SCZ-300, SCZ-400 and SCZ-500 according to the different calcination temperatures.

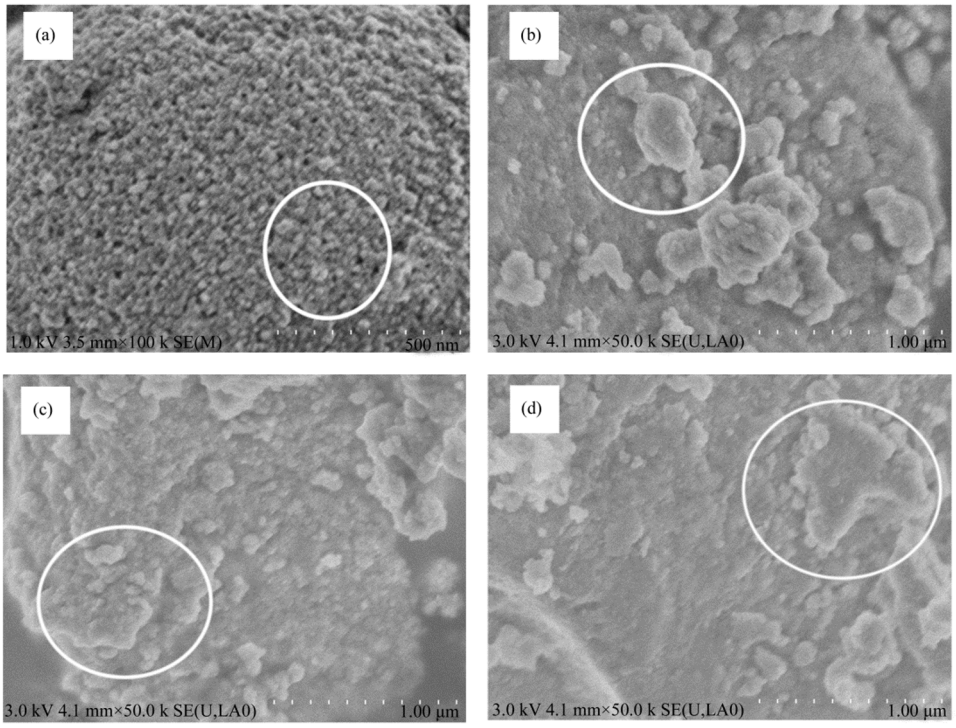

Fig. 2 SEM images of CZ (a), SCZ-300 (b), SCZ-400 (c) and SCZ-500 (d)