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Short Communication

Well-dispersed sulfated zirconia nanoparticles as high-efficiency catalysts for the synthesis of *bis*(indolyl)methanes and biodiesel

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ABSTRACT

Well-dispersed sulfated zirconia nanoparticles were synthesized with poly(*N*-vinylpyrrolidone) as a surfactant. The resultant sulfated zirconia nanoparticles are characterized by SEM, XRD, FT-IR and XPS. These nanoparticles were directly used as catalysts for the synthesis of *bis*(indolyl)methanes and biodiesel via electrophilic substitution reaction of indole with various aldehydes and the esterification of long-chain free fatty acids and exhibited excellent catalytic activity. The mechanism of the formation of the synthesized zirconia nanoparticles was also proposed.

1. Introduction

As environmentally benign catalysts, inorganic solid acids are gaining much attention in recent years due to recognized advantages of heterogeneous catalysts, like simplified product isolation, mild reaction conditions, high selectivities, ease in recovery and reuse of the catalysts and reduction in the generation of wasteful by-products [1]. Among these solid acids, sulfated zirconia interestingly exhibits excellent activity not only for alkylation, isomerization and cracking reactions [2] but also for a wide range of organic syntheses and transformation reactions [3].

Several different methods have been attempted for the synthesis of sulfated zirconia catalyst. For example, mesoporous sulfated zirconia has been synthesized from various surfactants [4], both monoclinic and tetragonal sulfated zirconia with high surface area have been prepared by a one-step crystallization method [5], and sulfated zirconia has been supported into the pores of ordered mesostructured silica [6]. These preparation methods of sulfated zirconia could be mainly classified into two types. The first one is one-step sol-gel method. Most of the sol-gel methods are based on the hydrolysis of water or organic solvent-soluble zirconia precursor, like zirconium alkoxide, and subsequent condensation to the inorganic framework. Sulfuric acid solution is added during the sol-gel formation of the alcogel in such a way that the sulfate is incorporated into the alcogel network, leading to a zirconium-sulfate cogel. After supercritical drying, the desired sulfated zirconia aerogel was obtained [7]. This approach is a very sensitive one that requires considerable effort to develop convenient size- and shape-controllable processes.

The second approach includes the preparation of zirconium hydroxide in the first step followed by sulfate impregnation in the second step. The type of precursors used for the preparation of zirconium hydroxide play a vital role in the final texture and hence on the performance of the final catalyst. Various zirconium compounds, such as zirconium nitrate, zirconium chloride, zirconium oxychloride and zirconium isopropoxide, are employed to prepare the zirconium hydroxide, and the precipitation is mostly carried out by using the agents, like ammonium hydroxide and urea. In the second step, also the sulfate impregnation is carried out by using various sulfating agents; the most commonly used are H_2SO_4 and $(NH_4)_2SO_4$ [8]. Some sulfur compounds, like H_2S and SO_2, have also been used. However, particle agglomeration usually occurs in the second step for this method.

In this study, a novel two-step precipitation method with poly(*N*-vinylpyrrolidone) (PVP) as a surfactant to synthesize well-dispersed sulfated zirconia nanoparticles was developed. In the first step, zirconium oxychloride is employed to prepare the zirconium hydroxide, and the precipitation is carried out by using ammonium hydroxide. In the second step, the sulfate impregnation is carried out by using the sulfating agent H_2SO_4. To prevent particle agglomeration, the surfactant PVP was added in this step. Subsequent glycothermal processing and calcination induce the formation of nanoparticles. With the help of this method, the products can be synthesized at gram scale. The synthesized sulfated zirconia nanoparticles can be directly used as catalysts to synthesize *bis*(indolyl)methanes and biodiesel, and exhibited excellent catalytic performances.

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2. Experiment

2.1. Synthesis of well-dispersed sulfated zirconia nanoparticles

Improved procedures were adopted to synthesize sulfated zirconia. Typically, 5 g of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 100 mL distilled water. To this clear solution, dilute aqueous ammonia was added dropwise from a burette with vigorous stirring until the pH of the solution reached 8. The obtained precipitate was washed with distilled water until free from chloride ions and dried at 80 °C for 24 h. The obtained zirconium hydroxide sample was ground to fine powder. To a two-necked flask, 40 mL of ethylene glycol and 2 g of PVP were transfered, and the mixture was stirred at 60 °C until the solution was clear. Thereafter, zirconium hydroxide powder (1 g) was added and stirred for 2 h before 3 mL of H_2SO_4 solution (0.2 M) was added. The suspension was continuously stirred for 12 h before loaded into a poly(tetrafluoroethylene) (PTFE)-lined stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 12 h and then cooled down to room temperature. The final products were filtered and washed with distilled water and ethanol several times to remove any impurities. The as-prepared precursors were finally calcined at 650 °C for 5 h.

Detailed catalytic reaction procedure, characterization, and NMR data are provided as supporting information.

3. Results and discussion

3.1. Characterization of the synthesized sulfated zirconia nanoparticles

Scanning electron microscopy (SEM) images show that sulfated zirconia nanoparticles are in a high dispersed state (Fig. 1). Ellipse nanoparticles with the size of 500 to 800 nm were presented with the improved method. Powder X-ray diffraction (XRD) analysis discloses structural information about the phase and the size of the crystalline domains of the sulfated zirconia. The XRD pattern of the synthesized nanoparticles (Fig. 2) exhibits that the tetragonal phase is predominant, which is represented by reflections at $2\theta = 30.18°$ as well as at 31.56°, 34.62°, 35.28°, 50.21°, 59.29°, 60.19°, and 62.72° [9]. The width of the reflections varies slightly, indicating that there is not a substantial change in the crystalline domain size [10]. Fourier transform infrared spectra (FT-IR) exhibits obvious bands at 997, 1045, and 1142 cm^{-1}, which are assigned to typical bands for chelating bidentate sulfate ion coordinated to zirconium cation [11], as showed in Fig. 3. Better resolved bands appeared clearly at 1640 cm^{-1}, characteristic of Brønsted acidic sites [12]. X-ray photoelectron spectroscopy (XPS) was applied to detect the surface chemical component of the sulfated zirconia. Fig. 4 is the XPS survey spectrum of the sample calcined at 650 °C for 1 h. Four elements can be discriminated: zirconium (Zr3d, 183.8 ev), sulfur (S2s, 234.4 ev), oxygen (O1s, 531.7 ev), and carbon (C1s,284.8 ev). The carbon detected by XPS is adventitious carbon, which is typically introduced from carbon compounds existing in the enviroment under testing conditions. The surface atomic mole concentration of sulfur is about 0.32%. Parameters such as the amount of zirconium hydroxide and PVP, H_2SO_4 concentration, glycothermal temperature, etc., significantly influence sulfated zirconia particle size and morphology. Well-dispersed yorlk-like sulfated zirconia nanoparticles with the size of 700–900 nm were obtained under synthesis conditions of 1.0 g of zirconium hydroxide, 2.0 g of PVP, and 1.2 mL of H_2SO_4 (0.2 M) as shown in Fig. 5(b). Interestingly, when the amount of zirconium hydroxide was decreased to 0.5 g, near-spherical sulfated zirconia nanoparticles were obtained, as shown in Fig. 5(a). The diameters of the nanoparticles range between 40 and 70 nm. These in all manifest that well-dispersed sulfated zirconia nanoparticles were obtained.

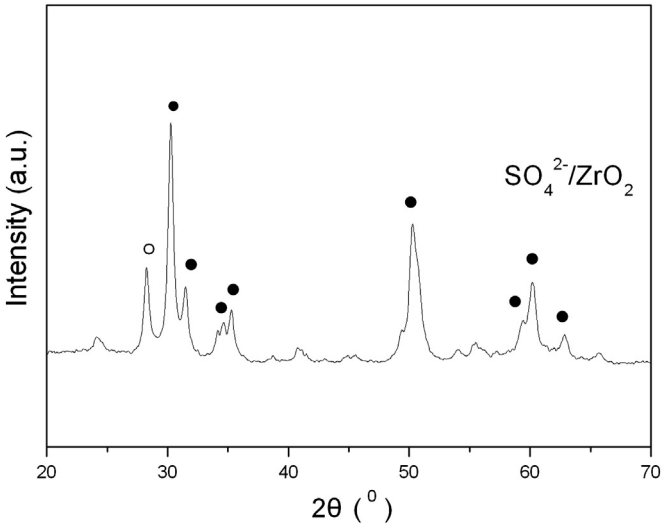

Fig. 2. The XRD patterns of the synthesized sulfated zirconia. (●) Characteristic lines due to tetragonal zirconia; (○) characteristic lines due to monoclinic zirconia.

3.2. Formation mechanism of sulfated zirconia nanoparticles

The combination of glycols and hydrothermal treatment proves itself a successful method for preparing well-dispersed sulfated

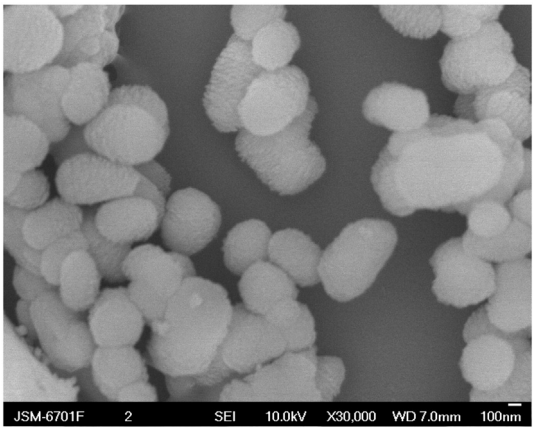

Fig. 1. SEM image of sulfated zirconia nonoparticles.

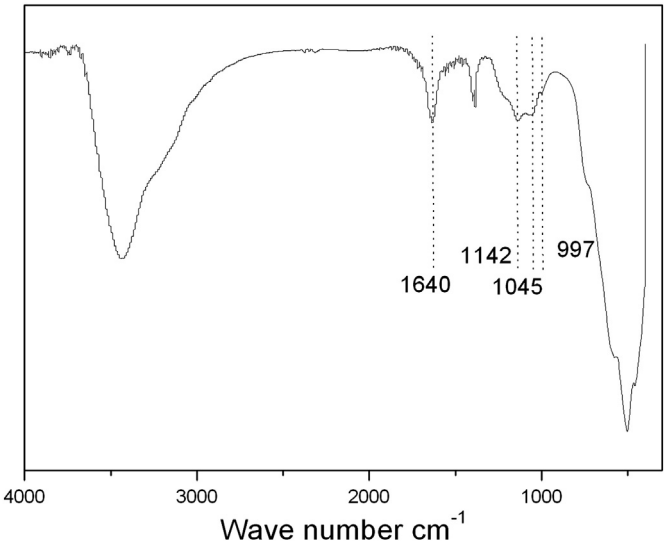

Fig. 3. XPS survey spectrum of the synthesized sulfated zirconia calcined at 650 °C.