



Original Research Paper

Synthesis and characterization of superfine pure tetragonal nanocrystalline sulfated zirconia powder by a non-alkoxide sol–gel route

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ABSTRACT

Nanocrystalline sulfated zirconia powder was prepared by a non-alkoxide sol–gel route using acidic condition (pH 1–2). The samples had superfine crystallites and pure tetragonal phase at 700 °C. $Zr(acac)_4$ was used as zirconium precursor due to a better retention of sulfate species and H_2SO_4 0.5 M was used as sulfating agent. Fourier transform infrared (FT-IR) spectra have shown Zr–O–Zr and sulfate bonds. Crystal phase and crystallite size have been determined by X-ray Diffraction (XRD) analysis. Besides, the morphology of the samples has been investigated by field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). The optical properties of the samples have been analyzed using photoluminescence (PL) spectroscopy, too. All the analyses consistently have shown fairly uniform nanoparticles (calcined at 600 and 700 °C) with very small size and pure tetragonal phase with crystallite size between 5 and 10 nm.

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1. Introduction

Solid acids are nowadays among the most important heterogeneous catalysts. Among this class, especial importance can be given to sulfated zirconia having outstanding catalytic properties. So, in many organic reactions (e.g. isomerization, cracking of paraffins, alkylation, oligomerization, and acylation of aromatics), sulfated zirconia can be used as an effective catalyst [1]. Moreover, sulfated zirconia can be used as proton conductor in fuel cell electrodes [2]. Catalytic properties of sulfated zirconia depend on a number of factors such as synthesis method [3–7], zirconia crystal phase [8], sulfur species [9,10], calcination temperature [11], and textural properties [12]. However, the key factor in determining catalytic properties of sulfated zirconia is the content of sulfur in zirconia surface [13]. In 1962, sulfated zirconia was first found by Holm and Bailey [14]. In 1979 and 1980, *n*-butane isomerization was performed by Hino and Arata using sulfated zirconia at room temperature [15,16]. Using Hammett indicators, they showed that sulfated zirconia had distinctive super acidity characteristic.

Common sulfated agents used for zirconia are H_2SO_4 and $(NH_4)_2SO_4$ [1]. However, Sohn and Kim made use of CS_2 , H_2S , and SO_2 [17]. Sulfation process is usually comprised of hydrous zirconia washing in sulfating agent solution [18]. Aiming at the synthesis of sulfated zirconia crystal, sulfation process often takes place before

calcination. In the past, it was believed that if sulfation was carried out before calcination, the catalytic properties of sulfated zirconia would increase [15]. However, it has recently been proved that sulfation of crystallized zirconia can also provide an active catalyst [19]. Doping of sulfated zirconia with some metals like Al [20], Ga [21], Pt [22], Mn and Fe [23] can enhance catalytic properties of sulfated zirconia.

Two different approaches to the problem of the super acidic centre of sulfated zirconia, which is responsible for the catalytic activity, have been reported in the literature. By the first approach, it can be stated that super acidic centers are indeed Lewis sites which are bound with atoms of zirconium [24,25] (Scheme 1a). By the second approach, it can be mentioned that both acidic sites of Bronsted and Lewis exist in sulfated zirconia structure [26] (Scheme 1b).

Zirconia has three phases of tetragonal, monoclinic and cubic. Cubic and tetragonal metastable phases can be stabilized using some dopants like sulfates ion at room temperature [27]. In this case, the crystallite size of sulfated zirconia also decreases to less than 30 nm [28,29]. Cubic and tetragonal phases of sulfated zirconia are active catalysts in isomerization reaction, whereas monoclinic phase is inactive [30]. It should be noted that a combination of tetragonal and monoclinic phases, however, shows less catalytic activity than pure tetragonal [31].

In order to synthesize a catalyst with high level of catalytic activity, it is required that the purity of tetragonal phase in the product increase. Srinivasan et al. [32] suggested that oxygen adsorption by oxygen deficient surface sites could be the cause of

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