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Synthesis and characterization of mesoporous silica-supported nano-crystalline sulfated zirconia catalysts prepared by a sol–gel process: Effect of the S/Zr molar ratio

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Abstract

Mesoporous silica-supported nano-crystalline sulfated zirconia catalysts were prepared via the sol–gel process using an in situ sulfation. The parameter studied in this work was the S/Zr molar ratio. The synthesized solids were characterized using XRD, N_2 physisorption, TG-DTA/SM, sulfur chemical analysis and adsorption–desorption of pyridine, and tested in the gas-phase acid-catalysed isomerization of *n*-hexane. The gelation process is highly affected by the sulfate loadings. Two gelation mechanisms were evidenced depending on the S/Zr molar ratio. The first one observed when $0.15 \leq \mathrm{S/Zr} \leq 0.5$, is characterized by a relatively high gelation rate. This mechanism favours the formation of two types of mesopores and a low percentage of retained sulfur. The second gelation mechanism occurs for higher S/Zr ratios: $0.5 \leq \mathrm{S/Zr} \leq 1.2$. In that case, slower gelation rates are observed. This slower gelation process leads to materials with reduced BET surface area but the amount of retained sulfur is increased. Appreciable catalytic properties were observed for the sample prepared with the highest S/Zr ratio, which presents the smallest size of sulfated zirconia crystallites and shows both Brönsted and Lewis acid sites on its surface.

Keywords: Sulfated zirconia; Nano-crystalline; Silica; *n*-Hexane; Acidity

1. Introduction

In recent years, much attention has been paid to solid acid catalyst. Sulfated zirconia based oxides is one class of these solids, used especially to catalyse *n*-alkane isomerization reactions. The relatively small surface area of sulfated zirconia limits its use as a catalyst for several reactions [1]. This disadvantage was overcome by supporting sulfated zirconia on another oxide such as silica [2]. This alternative allowed to combine the acidic properties of sulfated zirconia with the improved textural properties and the enhanced thermal stability of the silica support [1–4]. It is well known that the properties of these catalysts are highly influenced by the preparation method [1,5]. The sol–gel process is a convenient one for the synthesis of these mixed oxides. This method offers not only a good homogeneity of the different precursors but also the possibility of a better control of the grain size and porosity of the final material [5,6]. The catalytic features of sulfated zirconia based samples depend greatly on the preparation procedure [6–10], crystalline phase of zirconia [11], sulfur species [12,13], calcination temperature [14] and textural properties [15].

The objective of this work is to optimize the preparation parameters in order to obtain nano-crystalline materials. Such materials are known to be highly effective catalysts due to a large surface to volume ratio [5,16]. The use of nano-crystallites of sulfated zirconia supported on mesoporous silica as catalysts is then very promising due to the interesting structural properties and good dispersion of the active phase.

One of the important steps in the sol–gel method is solvent elimination after gelation. The easiest way to perform it is the evaporation in an oven at 120 °C. However, in almost all cases this drying mode induces a partial destruction of the solid structure [17]. We have studied in a previous work [18] the effect of the drying mode on the physico-chemical properties of

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this kind of solids. We have demonstrated that, drying in the supercritical conditions of the solvent results in silica-supported sulfated zirconia aerogels with low densities and enhanced textural properties.

The sulfation of these solids is usually achieved via a wet impregnation technique where the mixed oxide is contacted with an aqueous solution of sulfuric acid [3]. In this work, the samples were synthesized via a one-step preparation procedure with in situ sulfation, using sulfuric acid both as sulfating agent and as hydrolysis–polycondensation catalyst, as reported in our earlier work [15,19]. Here the sulfate loadings of the catalysts have been varied, in order to study the effect of the S/Zr molar ratio on the physico-chemical and catalytic properties of these solids evaluated in the *n*-hexane isomerization reaction. Furthermore, the influence of the added amount of sulfate on the gelation process and on the textural properties of silica-supported sulfated zirconia catalysts has been investigated.

2. Experimental

2.1. Catalyst preparation

Tetraethoxysilane (TEOS—Aldrich 98%) and zirconium acetylacetonate ($Zr(acac)_4$) were used as precursors. Sulfation was done in situ with H_2SO_4 used at different concentrations to adjust the molar S/Zr ratio to the desired value, the solvent was propanol. The preparation of these mixed oxides was performed via a single step synthesis by mixing all the reagents before gelation: initially, propanol was combined with the aqueous acidic solution of H_2SO_4. The TEOS was then added dropwise over 30 min prehydrolysis time, under continuous stirring at 60 °C. The amount of $Zr(acac)_4$ necessary to adjust the molar ratio Zr/Si at 0.1 was, then added and the mixture was stirred until gelation. In order to focus only on the effect of the S/Zr molar ratio, the other parameters were held constant ($[TEOS] = 2\ mol\ L^{-1}$, the molar ratio $H_2O/Si = 4$ and $Zr/Si = 0.1$). After gelation, the sample was aged during 20 h, and then dried in an autoclave under supercritical conditions of the solvent ($T = 265$ °C, $P = 51$ bar).

The sulfate-free sample was prepared using HCl instead of H_2SO_4 to insure complete TEOS hydrolysis.

The dried solids were calcined under flowing oxygen at 600 °C for 3 h.

The calcined samples were labelled as S*x*ZSi where x = S/Zr molar ratio.

The non-calcined samples were labelled as S*x*ZSi*nc* where x = S/Zr molar ratio, *nc*: non-calcined.

2.2. Experimental techniques

The effect of the studied parameter on the properties of the resulting solids was examined by nitrogen physisorption at 77 K, X-ray diffraction, mass spectrometry and sulfur chemical analysis.

Surface areas, pore volume and pore size distributions were obtained from the N_2 isotherms determined at 77 K using a Micrometrics ASAP 2000 auto-sorptometer. Surface area was calculated by using BET equation and pore size distribution was calculated by the BJH method using the desorption branch. Prior to N_2 adsorption, the samples were previously outgassed for 6 h at 200 °C.

XRD powder patterns were recorded on Bruker D5005 equipment, using Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å) in the 10–80° 2θ angle range. Crystallite size of zirconia tetragonal phase was determined from the characteristic peak ($2\theta = 30.18°$ for the (1 1 1) reflection) by using the Scherrer's equation $L = K\lambda/\beta \cos\theta$, where $K = 1$, L represents the crystallite size, λ the wavelength of Cu $K\alpha_1$ radiation and β the corrected half width of the diffraction peak.

The bulk sulfur content was determined by heating the samples at 1800 °C under flowing oxygen, with a flowing rate of $50\ L\ h^{-1}$. The amount of SO_2 was determined by IR spectroscopy.

Thermogravimetric analysis were carried out using a SETARAM apparatus. A platinum crucible was used as sample holder. Samples were treated under air flow, with a flow rate of $80\ mL\ min^{-1}$ and heated up to 900 °C with a ramp of $5\ °C\ min^{-1}$. A BALZERS mass spectrometer was used for evolved gas analysis upon the thermal treatment.

The nature and strength of acid sites on silica-supported sulfated zirconia samples were studied by adsorption–desorption of pyridine followed by infrared spectroscopy. The calcined sample was pressed into a self-supported wafer and evacuated at 400 °C for 1 h. After cooling to room temperature, the sample was exposed to pyridine vapour for 15 min. The sample was then outgassed for 1 h at 25, 100 and 200 °C. After each thermal treatment the sample was cooled to room temperature and an IR spectrum was recorded after each stage of thermal treatment.

2.3. Catalytic reaction

Silica-supported sulfated zirconia samples were studied for the gas-phase acid-catalysed isomerization of *n*-hexane. This reaction was carried out over mechanical mixtures obtained by grinding together during 15 min, an equal weight (100 mg) of the synthesized sample with Pt/Al_2O_3 (0.35 wt.% Pt). Promotion with platinum [14] or other transition metals [20] increases the stability of the catalyst towards deactivation in *n*-alkane isomerization and improves the selectivity towards dibranched isomers according to a metal-acid bifunctional mechanism. Prior to use, Pt/Al_2O_3 was reduced at 450 °C for 4 h under H_2. The catalytic test was performed as follows: The mixture Pt/Al_2O_3 + solid acid catalyst was pretreated in a fixed-bed reactor, first under He flow at 400 °C for 2 h and then under H_2 for 30 min at 220 °C. Hydrogen saturated with *n*-hexane at 0 °C was passed over the catalyst during 5 min and results were collected after this contact time. Typical conditions for the reaction were: reaction temperature 220 °C and total flow rate $1.8\ Lh^{-1}$. The reaction products were analysed on line using FID gas chromatography.