The catalytic performance of sulfated zirconia in the dehydration of methanol to dimethyl ether

Abd El-Aziz A. Said*, Mohamed M. Abd El-Wahab, Mohamed Abd El-Aal

Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt

ABSTRACT

Sulfated zirconia catalysts were prepared by wetness impregnation of zirconium hydroxide with an aqueous solution of $(NH_4)_2SO_4$ with SO_4^{2-} loadings (1–30%, w/w) and calcined at 450 °C for 3 h in a static air atmosphere. The catalysts were characterized by FT-IR, XRD, TEM and BET measurements. The surface acidity of the catalysts was investigated by the dehydration of isopropanol and the adsorption of pyridine (PY) and 2,6-dimethyl pyridine (DMPY). The catalysts were tested for dehydration of methanol in a fixed-bed reactor at 230 °C using air as a carrier gas. The results revealed that among different catalysts, 10% SO_4^{2-} supported onto zirconia showed the highest catalytic activity with 83% conversion and 100% selectivity toward dimethyl ether. A good correlation was found between the acidity of the catalysts and their ability to dehydrate methanol.

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1. Introduction

Dimethyl ether (DME) is a well-known building block in the production of valuable chemicals such as methyl acetate and dimethyl sulfate, as well as of petrochemicals (BTX aromatic and light olefins) and conventional fuels by replacing methanol as raw material. Moreover, DME is attracting increasing interest as a potential eco-friendly substitute for petroleum-derived diesel fuel given its high cetane number (55–60), low auto-ignition temperature, and reduced emissions of hazardous compounds such as NO_x, SO_x, and particulate matter [1,2]. DME may also serve as an efficient hydrogen carrier, which could be used to store renewable energy in a chemical form that is easy to handle, distribute, store and use [3]. DME can be produced by methanol dehydration over a solid-acid catalyst or direct synthesis from syngas by employing a hybrid catalyst, comprising a methanol synthesis component and a solid-acid catalyst [4]. The formation of DME from methanol requires a catalyst with optimum acid properties. Usually, strong acid sites favor secondary reactions that lead to undesired hydrocarbons and coke formation, which eventually causes catalyst deactivation [5]. A myriad of solid acid catalysts has been explored for the conversion of methanol into DME, including γ-Al_2O_3, modified alumina with silica, TiO_2–ZrO_2, and zeolite and zeotype materials (HZSM-5, HY, $AlPO_4$, SAPOs, etc.) [6]. Zeolite materials tend to deactivate rapidly because their strong acid sites are responsible for the formation of significant amounts of undesired by-products (hydrocarbons and carbon deposits) [7]. On the other hand, γ-Al_2O_3, which possesses strong Lewis acid sites, exhibits lower methanol dehydration rates compared to zeolites, and thus, could be due to the preferential adsorption of generating H_2O molecules on the Lewis acid sites under the reaction conditions [5]. It is important to develop new catalysts to replace the acids commonly used in this reaction and to overcome the problems take place by using other solid acid catalysts. Sulfated zirconia is the most promising heterogeneous catalyst [8,9]. Its acidity is much higher even than that of concentrated H_2SO_4, with its surface sulfate groups acting as Lewis and Brønsted sites [10]. The high catalytic activity of sulfated zirconia has been attributed to super-acidity. In some cases, super-acids are significantly more active catalysts for reactions than conventional solid catalysts. Super Acid catalysts can offer many advantages: lower loadings, lower reaction temperatures, increased selectivity and fewer by-products, shorter reaction times. Satoshi et al. [11] studied the catalytic action of sulfated tin oxide for etherification and esterification of methanol in comparison with sulfated zirconia. Mohamed et al. [12] used methanol dehydration as a test reaction to compare the acidity of pure and sulfated metal oxides such as ZrO_2, TiO_2-anatase, -rutile and Al_2O_3. However, the catalytic dehydration of methyl alcohol to dimethyl ether on sulfated zirconia systems using air as a carrier gas, to our best knowledge, has not been reported. The objectives of the present study are prepared, characterization and evaluation of sulfated zirconia catalysts, for methanol dehydration to DME. Accordingly, the catalytic

* Corresponding author. Tel.: +20 882412427; fax: +20 882342708.
  E-mail address: aasaid55@yahoo.com (A.E.-A.A. Said).

dehydration of methanol to DME was performed over a series of sulfated zirconia calcined at 450 °C for 3 h. Finally, an attempt has been made to correlate the catalytic activity of these catalysts, during dehydration of methanol, with their structure and the acidity.

2. Experiments

2.1. Materials

Zirconium hydroxide (Aldrich), ammonium sulfate $(NH_4)_2SO_4$, methyl alcohol, isopropyl alcohol, pyridine and 2,6-dimethyl pyridine were obtained as pure reagents and were used without further purification.

2.2. Catalyst preparation

A series of sulfated zirconia samples having different weight percentages of sulfate were synthesized by wetness impregnation of zirconium hydroxide with an aqueous solution of $(NH_4)_2SO_4$. Calculated amounts of ammonium sulfate were dissolved in small amounts of distilled water. The ammonium sulfate solutions were admixed carefully with calculated amounts of zirconium hydroxide till the formation of homogeneous pastes. The samples were dried in an oven at 100 °C for 24 h. The contents of SO_4^{2-} were (1, 3, 5, 10, 20 and 30 wt.%) before being calcined at 450 °C for 3 h in static air atmosphere. Sulfated zirconia catalyst donated by (SZ).

2.3. Catalyst characterization

2.3.1. Fourier transform infrared (FT-IR) spectroscopy
FT-IR spectra of the prepared catalysts calcined at 450 °C for 3 h were recorded using a Shimadzu Spectrophotometer, model (Nicolet 6700), equipped with data station in the range of 4000–400 cm^{-1} with a KBr disc technique.

2.3.2. X-ray diffraction (XRD)
XRD analysis of the test samples was performed with a Philips (The Netherlands) diffractometer (Model PW 2103, $\lambda = 1.5418$ Å, 35 kV and 20 mA) with a source of CuKα radiation (Ni filtered). Patterns were recorded from 4 to 80° (2Θ). Particle size was estimated using Scherrer equation [13]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where D is the mean crystallite diameter (nm), λ is the X-ray wavelength, K is Scherer constant (0.89), β is the observed angular width at half maximum intensity of the peak and was calculated by the following equation [14]:

$$\beta^2 = \beta_s^2 - \beta_o^2$$

where β_s is the full width of a diffraction peak under consideration (radian) in the middle of its height that was considered after computer fit of X-ray data using the Gaussian line shape and θ is the Bragg's angle and β_o is the instrumental broadening, $\beta_o = 0.16$ with the apparatus used.

2.3.3. Transmission electron microscopy (TEM)
The size and morphology of the investigated catalysts were characterized by transmittance electron microscope (TEM) JEOL Model JSM-5400 LV (Joel, Tokyo, Japan). The catalyst powder dispersed in ethanol using ultrasonic radiation for 20 min and a drop of that suspension was placed onto the carbon-coated grids. The degree of magnification of TEM images was the same for all the different investigated catalysts.

2.3.4. Nitrogen gas adsorption
Nitrogen gas adsorption–desorption isotherms were measured at −196 °C using a Nova 3200 instrument (Quantachrom Instrument Corporation, USA). Test samples were thoroughly outgassed for 3 h at 250 °C to a residual pressure of 10^{-5} Torr, and the weight of the outgassed sample was that used in calculations. The specific surface area, S_{BET} was calculated by applying the Brunauer–Emmett–Teller (BET) equation. The porosity of the catalysts was determined from the desorption curves using Nova enhanced data reduction software (Version 2.13). The theoretical particle sizes are also calculated from specific surface area, assuming spherical particles according to the following equation:

$$D_{BET} = \frac{6000}{p \cdot S_{BET}}$$

where D_{BET} is the average particle size (nm), p is the theoretical density of the sample (g cm^{-3}) and S_{BET} is the specific surface area (m^2 g^{-1}).

2.3.5. Acidity determination
The acidity of the catalysts under investigation were determined by studying the dehydration of isopropyl alcohol (IPA), the adsorption of pyridine (PY) and 2,6-dimethyl pyridine (DMPY). The dehydration of IPA was carried out in a conventional fixed-bed flow Pyrex glass tube reactor, at atmospheric pressure using nitrogen as a carrier gas. The reaction conditions were: A 500 mg catalyst, 2% reactant of IPA in the gas feed, 50 ml min^{-1} total flow rate and 200 °C reaction temperature. The measurement of propene yield (%) was made after 1 h to achieve steady-state reaction conditions of the IPA. The chemisorptions of PY and DMPY were carried out by injection of different volumes at steady state conditions. The exit feed was analyzed by direct sampling of the gaseous products into a Unicam ProGC gas chromatograph using a flame ionization detector (FID) with a 10% PEG 400 glass column (2 m). The acidity populations over the surface of catalysts, under investigation, were measured also by thermogravimetric technique (TG) using the adsorption of pyridine as probe molecule. The procedure was 500 mg of calcined sample was preheated at 250 °C for 1 h in the air before saturated with pyridine for 7 days after evacuation. About 15 mg of pyridine-saturated sample was subjected to TG analysis. The TG analysis was recorded heating from room temperature up to 400 °C using at 10 °C min^{-1} and 30 ml min^{-1} flow of N_2, using Computerized Shimadzu Thermal Analyzer TA60 Apparatus (Japan). The mass loss due to desorption of pyridine from the acidic sites, was determined as a function of total surface acidity as sites (g^{-1}$_{cat}$) [15].

2.3.6. Catalytic activity measurements
The catalytic activity of the catalysts under investigation for the vapor – phase dehydration of methyl alcohol was carried out at 230 °C in a conventional fixed bed flow type reactor at atmospheric pressure using air as the carrier gas. The system comprised two reactors. One was used without any catalyst and filled with glass beads (control reactor), to enable a measurement of the 'control' conversion (if any), which was subtracted from that measured in the flow reactor. 500 mg of catalyst was placed in the middle of the second reactor with quartz wool. Space in the reactor pre- and post-heating zone was filled with glass beads to reduce the effect of auto-oxidation of the substrate and products in the gas phase. A methyl alcohol and air were introduced into the reactor after air was bubbled through methyl alcohol saturator. The total flow rate was fixed at 50 ml min^{-1} and used 4% reactant of methanol in the gas feed. The gases after reaction were chromatographically analyzed by FID with a Unicam ProGC using a 2 m DNP glass column for analysis of the reaction products of methyl alcohol on the tested catalysts. Measurements