High selectivity to isopropyl ether over sulfated titania in the isopropanol decomposition

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Abstract

Sulfated titania was prepared by in situ gelling titanium alkoxide with sulfuric acid and by impregnation with ammonium sulfate of titania gels, hi annealing gels at 600 °C, the BET specific surface areas were of 46 and 177 m^2/g for sulfuric and ammonia sulfate preparations, respectively. XRD patterns showed for "in situ" preparation anatase (92%) and rutile phases (8%), while for ammonium sulfate sample only anatase phase was observed. FTIR-pyridine adsorption identified Brönsted (B) and Lewis (L) sites for titania impregnated with ammonium sulfate, however, only Lewis (L) sites were identified in titania prepared with sulfuric acid. In the isopropanol conversion, similar activities were obtained. However, in sulfuric preparation the selectivity was 22 and 78 mol% to propene and isopropyl ether, respectively, while in ammonium sulfated catalyst the selectivity was 70 mol% to propene and 30 mol% to isopropyl ether. The results are discussed with regards to the acidity requirements explaining the role of acid sites in the selectivity.
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1. Introduction

Since the legislation appeared around the world over clean air, fundamental changes in fuels composition were made. These changes restricted the use of heavy metal like tetraethyl lead, lowered permissible levels of light hydrocarbons and benzene in the fuel and raised the minimum fuel oxygenate content. This led to substantial interest in alcohols and ethers which can be used as oxygenated compounds which increase the octane number in gasoline. C_1 to C_3 alcohols, whilst having high octane number and being less expensive than ethers, their disadvantage is that they have a high blending Reid vapor pressure, and that they are very soluble in water. Since 1990, the oxygenate compounds most used have been the methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME) [1]. However, we can considerer as a good option the use the di-isopropyl ether (DIPE), although being scant

literature over their use. The information relates mostly to its blending behavior and the production economics [2–4]. DIPE has a poorer octane number, but a favorable blending Reid vapor pressure. Moreover, it can be produced from iso-propanol.

Decomposition of 2-propanol is frequently used as a test reaction to determine acid–base properties of oxide catalysts in many laboratories [5,6]. It has been reported that the decomposition of 2-propanol occurs by two parallel reactions: (1) the dehydration carried out in acid sites giving the olefin and the ether, in particular propene and isopropyl ether (DIPE) and (2) the dehydrogenation to acetone occurring in basic sites or concerted acid–base pair sites [7–9]. However, the role of acid and basic sites in the formation of propene isopropyl ether and acetone is not well established. Recent reports propose that dehydrogenation and dehydration reactions are not only determined by the surface acidity or by the basic properties, they also depend on the reaction conditions employed, such as reaction temperature, isopropanol partial pressure, the nature of the carrier gas and so forth [5,10–12].

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Isopropanol decomposition has been carried out in several metal oxides with different acid–basic properties, among others MgO, CaO and SrO which are known as basic oxides [13], or ZrO$_2$, Al$_2$O$_3$ and TiO$_2$ with acid properties were studied [14–16]. The results show that the selectivity in this reaction depends on the strength and distribution of the acid and/or basic sites, in particular, the formation of propene and DIPE depends on the acidity present in the catalysts. As a consequence, great efforts have recently been made to design catalysts with controlled acidity.

Sulfated metal oxides are good candidates for this purpose, since they have been tested as catalysts for the isomerization of paraffins [17], acylation of aromatics [18] and dehydration of alcohols [19,20]. Some of them are highly stable in several environmental reactions [21,22]. The most studied sulfated oxides are ZrO$_2$ [23,24] and TiO$_2$ [25–27]. In particular, sulfated titania has been found to be efficient for isomerization [28], alkylation [29], Friedel–Crafts acylation [30], esterification [31], photocatalytic oxidation [32] and reduction of NO$_x$ [33].

With the aim to prepare sulfated oxides with controlled acidity giving high selectivity to isopropyl ether, in the present work sulfated titania was prepared by the sol–gel method and was evaluated in the isopropanol decomposition. The solids were characterized by nitrogen adsorption isotherms, X-ray diffraction (XRD) and FTIR-pyridine adsorption.

2. Experimental

2.1. Sample preparation

2.1.1. TiO$_2$–H$_2$SO$_4$

Deionized water (200 ml) was mixed with 200 ml of *tert*-butanol (Baker, 99%) in a reflux glass system. The mixture was heated at 70 °C, at this temperature concentrated sulfuric acid (Baker 98%) was dropped under constant stirring until pH 3 (0.5 ml) was reached. Thereafter, 85 ml of titanium *n*-butoxide was added to the mixture, maintaining the solution under reflux for 24 h.

2.1.2. TiO$_2$–HNO$_3$

Titania was prepared at pH 3 using nitric acid as hydrolysis catalyst following the same procedure described above.

2.1.3. TiO$_2$–HNO$_3$–(NH$_4$)$_2$SO$_4$

The dried sample, prepared with nitric acid, was impregnated with an aqueous 1N ammonium sulfate solution (5 ml of solution per gram of sample).

All the TiO$_2$–H$_2$SO$_4$, TiO$_2$–HNO$_3$ and TiO$_2$–HNO$_3$–(NH$_4$)$_2$SO$_4$ samples were dried in air at room temperature, thereafter, they were annealed at 600 °C in flowing air for 4 h.

2.2. Characterization

2.2.1. X-ray diffraction

X-ray diffraction patterns of the samples packed in a glass holder were recorded at temperature with Cu Kα radiation in a Bruker Advance D-8 diffractometer that had theta–theta configuration and a graphite secondary-beam monochromator. Diffraction intensity was measured in the 2θ range between 18 and 110°, with a 2θ step of 0.020° for 8 s per point. Crystalline structures were refined with the Rietveld technique by using DBWS-9411CODE [34]; peak profiles modeled with pseudo-Voigt function [35] contained average crystallite size as one of its characteristic parameters [36].

2.2.2. BET specific surface areas

Nitrogen adsorption isotherms were obtained on the samples annealed at 600 °C with an Autosorb-3B Quantachrome equipment. The surface areas were calculated using the BET equation and the mean pore size diameter was calculated using the BJH method.

2.2.3. FTIR-pyridine adsorption

The type and quantity of acid sites (Brönsted and/or Lewis) was determined with a Fourier transform infrared (FTIR) Nicolet 170 SX spectrometer by means of pyridine adsorption. The annealed material was pressed into thin self-supported wafers. Then, they were placed in a glass Pyrex cell with CaF2 windows coupled to a vacuum line, in order to be evacuate (1×10^{-6} Torr) in situ at 400 °C for 30 min. The adsorption was carried out on the cell at 25 °C by breaking a capillary tube, which contains the pyridine. The pyridine excess was desorbed with vacuum from room temperature to 400 °C in 100 °C steps. The quantities of adsorbed pyridine were obtained from the integrated absorbance of the respective bands, following the procedure and coefficient extinction reported elsewhere [37].

2.2.4. Decomposition of 2-propanol

The reaction of 2-propanol was carried out in a tubular glass flow reactor (3 ml) under atmospheric pressure. Prior reaction test, the catalyst (50 mg) was pretreated at 300 °C for 1 h with N$_2$ flow (60 ml/min). To carry out the decomposition, 2-propanol vapor was supplied into the reactor by bubbling nitrogen gas through the alcohol container at 25 °C. The reaction temperature was 150 °C. The products were analyzed with an on-line VARIAN CP-3800 gas chromatograph with WCOT fused silica column.

3. Results and discussion

3.1. X-ray diffraction

XRD patterns of titania and sulfated titania samples annealed at 600 °C are shown in Fig. 1. In the spectrum for TiO$_2$–HNO$_3$ we can see two peaks at 2θ = 25.38 and