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Synthesis and characterization of a highly active alumina catalyst for methanol dehydration to dimethyl ether

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ABSTRACT

A simple sol–gel method was adopted to synthesize boehmites with high surface area using aluminum *iso*-propoxide (AIP), acetic acid (AA) and 2-propanol, and the effects of surface area and methanol dehydration on activity were investigated. The hydrolysis conditions of AIP in the presence of AA in 2-propanol solvent were systematically varied to observe their effect on phase formation, crystallinity, surface area and pore size distribution of the alumina. The surface area and the number of acidic sites varied considerably with the variation in the molar ratio of AA/AIP. This study revealed that a high surface area boehmite (in the range of 628–717 m^2/g) could be obtained by keeping the molar ratio of AA/AIP as 0.5 and that of H_2O/AIP at ~3. Rod shaped, porous γ-Al_2O_3 powder with a high surface area of 438 m^2/g was obtained after calcination of the boehmite at 500 °C for 5 h in air. The temperature programmed desorption of ammonia (NH_3-TPD) of the γ-Al_2O_3 samples demonstrated higher concentration of acidic sites when acetic acid was used during preparation than when it was not used. The vapor phase dehydration of methanol (containing 20 mol% H_2O) to dimethyl ether (DME) was conducted on the prepared aluminas. With increasing surface area of γ-Al_2O_3, the temperature required to reach 50% conversion of methanol decreased due to the increased number of acidic sites which are favorable for methanol dehydration with low byproduct formation. The catalytic activity for methanol dehydration to DME correlated well with the total number of acidic sites of γ-Al_2O_3, which was controlled by changing the AA/AIP and H_2O/AIP molar ratios.

1. Introduction

Alumina is a low cost material most widely used as a catalyst and catalyst support [1]. In addition, it is also used as the starting material for the preparation of Al_2O_3 based ceramics [2]. A wide variety of these applications are possible because of the fact that alumina exists in the corundum and transition alumina forms [3]. The corundum or α-alumina has excellent mechanical, electrical, thermal and optical properties due to hexagonal close packing of oxygen ions. On the other hand, transition aluminas, including γ-Al_2O_3, have a cubic close packing of oxygen ions resulting in high surface area, mesoporosity and surface acidity [4]. As a result of these important properties, γ-Al_2O_3 is also extensively used as an adsorbent and a membrane [3]. Solid acid catalysts e.g. γ-Al_2O_3, modified γ-Al_2O_3 with silica, phosphorus or B_2O_3 based are widely used, excellent catalysts for the dehydration of methanol to DME [5]. However, systematic study on the effect of various preparation parameters on physical and chemical characteristics of γ-Al_2O_3 affecting DME synthesis is lacking.

In the our previous investigations, the efforts to achieve the preparation of γ-Al_2O_3 powders by using various chemical routes through boehmite precursor have been continued to synthesize a thermally stable γ-Al_2O_3 at fixed preparation conditions [6] and to evaluate the catalytic activity of home-made γ-Al_2O_3 prepared from aluminum nitrate precursor via coprecipitation/digestion routes [7]. An attempt is made in the present investigation to synthesize γ-Al_2O_3 catalysts with different surface areas by varying preparation parameters systematically during sol–gel synthesis and to correlate the catalytic activity with the surface area of γ-Al_2O_3.

In view of the increasing demand for DME as a raw material for the production of dimethyl sulfate, methyl acetate, light olefins and alternative clean fuels [8–10], the importance of a commercially viable catalyst is further enhanced. In order to get a reliable and reproducible alumina for these applications, a stringent control of composition, surface area, porosity (i.e. pore size and its distribution) and surface acidity are essential. Although various chemical routes [4,11,12] have been tried, the sol–gel route offers an excellent opportunity for controlling the physical, chemical and

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textural properties of the aluminum oxide. Sol–gel derived alumina powders are generally prepared through acid- or base-catalyzed hydrolysis and condensation reactions of aluminum alkoxide precursors such as aluminum *iso*-propoxide (AIP) or aluminum *sec*-butoxide [1,2] in organic solvents. In the case of the Yoldas process [13], it is reported that the aging treatment over a period of 24 h at 80 °C yields boehmite [AlO(OH)] whereas aging at room temperature yields bayerite, $Al(OH)_3$. The thermal decomposition of boehmite at 400–500 °C in air produces γ-Al_2O_3.

The catalytic activity of the alumina for methanol dehydration is generally dependent on the surface acidity, which could be varied by adding some promoters or controlling the acidic properties of alumina or zeolites [14,15]. Hence, it is important for the synthesis of γ-Al_2O_3 with controllable and reproducible properties to get the stable catalytic activity. It is also necessary to study the effect of various preparation parameters on the physico-chemical properties of the solid–acid catalyst, with particular attention given to the changes in the acidity. The present investigation focuses on elucidating the effects of acetic acid (AA)/AIP and H_2O/AIP mole ratios on the properties of boehmite and also on the γ-Al_2O_3 obtained by subsequent heat treatment. Detailed investigations have been carried out to correlate the changes in acidity with those of the textural properties of the γ-Al_2O_3 during its transformation.

2. Experimental

2.1. Syntheses

AIP was used as an aluminum precursor, AA as hydrolysis rate controller and 2-propanol as solvent during the synthesis. Initially, AIP was dissolved in 2-propanol under continuous stirring. By controlling the rate of addition of AA and water (H_2O) to the above stirred solution, we could make the hydrolysis occur faster and the condensation occur slower so as to get the precipitates in the form of a fine hydroxide gel. The gel was further aged at 80 °C for 20 h. The molar ratio of AA/AIP was varied from 0 to 0.5, whereas that of H_2O/AIP was varied from 3 to 25. The product was washed several times with 2-propanol and finally dried at 80 °C in vacuum for 12 h. Finally, the material was calcined in a flow of air at 500 °C for 5 h with a heating rate of 2 °C/min.

2.2. Characterization

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the samples were conducted in a TA Instrument (DMA, SDT 2960) in flowing nitrogen atmosphere at a heating rate of 10 °C/min up to 1200 °C using a commercial alumina as the reference material to discover the various decomposition steps occurring in the as-dried precursor as a function of temperature.

In order to identify the various phases present and the crystallinity of as-prepared boehmite and calcined γ-Al_2O_3 powder, we carried out powder X-ray diffraction (XRD) studies with a Rigaku diffractometer using Cu-K_α radiation. The Brunauer–Emmett–Teller (BET) surface areas and pore volumes were determined from nitrogen adsorption and desorption isotherm data obtained at −196 °C on a constant-volume adsorption apparatus (Micromeritics, ASAP-2400). The pore volumes were determined at a relative pressure (P/P_o) of 0.99. The as-prepared samples were degassed at 150 °C for 3 h before measurements. The pore size distributions in as-prepared samples were determined by a Barett–Joyner–Halenda (BJH) model from the adsorption branch of the nitrogen isotherm [16].

The analysis of temperature programmed desorption of ammonia (NH_3-TPD) was performed to determine the total acid sites on the catalyst. About 0.1 g of the sample was initially flushed with a He flow at 500 °C for 5 h, next cooled to 100 °C and then saturated with NH_3. After NH_3 exposure, the sample was purged with He until the initial excess of NH_3 which is not utilized is removed. Then this sample is heated from 100 °C to 700 °C at a heating rate of 10 °C/min. The BEL-CAT (PCI-3135) instrument was employed to monitor the amount of ammonia in the effluent by a thermal conductivity detector (TCD) and the values were recorded as a function of temperature.

The microstructures of both as-prepared and calcined samples were studied by transmission electron microscope (TEM) images obtained on a JEOL JEM 2100F (field emission electron microscope) instrument operated at 200 kV. Fourier transform infrared (FT-IR) spectra of boehmite and γ-Al_2O_3 powder were recorded using a Bio-Rad Digilab FTS-165 FT-IR spectrometer.

2.3. Activity measurement in methanol to DME

The performances of the prepared catalysts with different AA/AIP ratios were compared with that of the γ-Al_2O_3 catalyst prepared from catapal-B (SASOL) boehmite. The vapor phase dehydration of methanol containing 20 mol% H_2O was carried out in a fixed-bed reactor (inner diameter = 0.8 cm and length = 30 cm). Prior to experiments, the catalyst (volume of 1.5 ml and size of the pellet in the range of 20–40 mesh) was pretreated for 1 h at 300 °C under a N_2 flow. The methanol solution was fed into the reactor using a pump. The reaction was performed with N_2 as a carrier gas at 10 atm pressure, in the temperature range of 210–400 °C and at a methanol feed rate of 0.25 ml/min (SV = 10 h^{-1}). The reaction products were analyzed on a gas chromatograph (GC) equipped with a flame ionization detector connected with a capillary column (Porapack Q).

3. Results and discussion

3.1. Physico-chemical properties of the synthesized boehmites

Boehmite is obtained in the present study through hydrolysis of AIP in the presence or the absence of acetic acid, followed by aging at 80 °C for 20 h. In the sol–gel process, two simultaneous reactions, namely hydrolysis and condensation, occur when AIP reacts with water. The amount of water determines the degree of hydrolysis and the type of initial species formed, thus influencing condensation reactions that involve polymerization of hydrolyzed species in alcoholic medium. If the H_2O/AIP ratio is kept $\geq$3, the AIP would get hydrolyzed completely, leading probably to the nucleation of tiny particles of boehmite after the aging process by the following reactions:

$$Al(OR)_3 + 3H_2O \rightarrow Al(OH)_3 + 3ROH \quad (1)$$

$$Al(OH)_3 \rightarrow AlO(OH) + H_2O \quad (2)$$

$$Al(OR)_3 + 2H_2O \rightarrow AlOOH + 3ROH \quad (3)$$

Initially, the amorphous hydroxide gel precipitated by reaction (1) is converted in to boehmite precursor after 20 h of aging at 80 °C by reactions (2) and (3), respectively. To confirm the formation of boehmite by reactions (2) and (3), we undertook DTA/TGA, XRD, and IR studies on the as-dried boehmite precursor. The DTA/TGA curves of the as-dried boehmite using acetic acid during processing are shown in Fig. 1(a). The as-dried boehmite precursor appeared to have undergone three stages of decomposition reaction with a total weight loss of ~35%. The first step corresponds to an endothermic weight loss of ~15% which is attributable to the removal of adsorbed water below 200 °C. The second broad exothermic weight loss is due to the decomposition of associated organics including adsorbed acetic acid, followed by a