Journal of American Science

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Preparation of γ-Al_2O_3 Using Sodium Bicarbonate as Precipitating Agent for Methanol Dehydration to DME

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Abstract: Nano-sized crystalline γ-Al_2O_3 was synthesized by co-precipitation method as a suitable catalyst for production of DME from methanol. In this method, aqueous solution of aluminum nitrate and sodium bicarbonate were added simultaneously drop by drop to a well-stirred 75 ml volume of distilled water (taken in a beaker) at 70°C to precipitate aluminum cations in the form of hydroxides in the pH range of 7.5-8.5. Then, aging was carried out at the same temperature for 18 h. The aged precipitate was further washed with water and then by ethanol and acetone to remove sodium contaminations and then dried at room temperature. Finally, the calcination of precipitates at 560°C/5h in air produced porous nano-sized γ-Al_2O_3 powder particles. The synthesized catalyst was characterized by XRD, NH_3-TPD and N_2 adsorption-desorption techniques. Finally, methanol dehydration reaction over the synthesized catalyst was successfully carried out in a fixed bed micro reactor to produce DME.

[Seyyed Ya'ghoob Hosseini, Mohammad Reza Khosravi Nikou. **Preparation of γ-Al_2O_3 Using Sodium Bicarbonate as Precipitating Agent for Methanol Dehydration to DME.** J *Am Sci* 2022;18(1):69-73]. ISSN 1545-1003 (print); ISSN 2375-7264 (online). http://www.jofamericanscience.org. 8. doi:10.7537/marsjas180122.08.

Keywords: Co-precipitation**;** Dimethyl ether; γ-Al_2O_3; Methanol dehydration; Sodium bicarbonate.

1. Introduction

During the past few years, DME has received global attention as a clean-burning alternative fuel for diesel engines due to the increasingly stringent environmental regulations [1]. DME can also be used as an aerosol propellant in the cosmetic industry to replace CFC and LPG. Aerosol-based household products include hair sprays, dyes, personal care mousses, antiperspirants, and room air fresheners. Then there would be a growing requirement to produce large scale of DME to meet the future market.

Nowadays, DME is made by the catalytic dehydration of methanol, a method which is industrially important for the production of dimethyl ether. Conventionally, the preparation is performed over a solid-acid catalyst at temperatures between 250 to 400°C [2, 3].

The solid-acid catalysts used for dehydration of methanol are HZSM-5, H-Y zeolite, γ-Al_2O_3 and modified γ-alumina with silica, phosphorus, etc [4, 5]. Commercially, γ-Al_2O_3 is used as the catalyst for this reaction because it has high surface area, excellent thermal stability, high mechanical resistance and catalytic activity for DME formation due to its surface acidity. Recently, many methods have been applied to synthesize alumina with a higher specific surface area and activity for DME synthesis [6].

In the present work, the catalytic dehydration of methanol to DME has been studied over nanocrystalline γ-alumina prepared by co-precipitation method. The textural and acidic properties and catalytic activity of synthesized γ-Al_2O_3 catalyst have been investigated.

2. Experimental

2.1. Catalyst Preparation

Aluminum nitrate nonahydrate {Al $(NO_3)_3.9H_2O$, 98.5% (Merck)}, sodium bicarbonate {$NaHCO_3$, (Merck)} and distilled water used starting materials. Aluminum nitrate solution (0.283 M) and sodium bicarbonate solution (0.639 M) were prepared by dissolving 15.90g Al $(NO_3)_3.9H_2O$ and 8.05 g $NaHCO_3$ in 150 ml of distilled water, separately. Al^{+3} in the form of hydroxides were precipitated through adding aluminum nitrate and sodium bicarbonate solutions in a well stirred beaker containing 75 ml of water. During the mixing, the temperature was maintained at 70°C and pH was controlled between 7.5 and 8.5. The resulting mixture was aged for 18 hours at the same temperature. The aged precipitate was washed and filtered by ethanol and acetone thoroughly. When washing was completed, it was dried by atmospheric air at room temperature. The as-dried precipitate was calcined in the furnace at 565°C for 5 hours through atmospheric air by heating rate of 3.8°C/ min to produce γ-Al_2O_3 powder.

2.2. Catalyst Characterization

To identify phases and their crystallinity in calcined samples, the XRD pattern of them was recorded on a PW1840 (40 kV, 30 mA) diffractometer using Cu radiation source (λ=1.54056 Å) in the range of 2θ= 5° to 90°.

BET surface area, total pore volume and average pore diameter were measured by N_2 adsorption-desorption isotherm at liquid nitrogen temperature (-196°C) using NOVA 2000 instrument (Quantachrome, USA). The pore volumes were determined at a relative pressure (P/P_0) of 0.99. Prior to the adsorption-desorption measurements, sample was degassed at 200°C in N_2 flow for 3 h. The pore size distribution in as-prepared samples was verified by a BJH (Barett-Joyner-Halenda) model from the adsorption branch of the nitrogen isotherms.

The acidity of the sample was measured by temperature programmed desorption of ammonia using BEL-CAT (type A, Japan) instrument with a conventional flow apparatus. A 0.1 g sample was initially degassed at 500°C under He flow rate of 50 ml/min for 60 min at a heating rate of 10°C/min. Next, the sample was cooled down to 100°C and then saturated with 5% NH_3/He for 30 min. The sample was then purged with He flow for 15 min to remove weakly and physically adsorbed NH_3 on the surface of the catalyst. After these operations, the sample was heated at 10°C/min under the flow of He carrier gas (30 ml/min) from 100°C to 610°C and the amount of ammonia in effluent was measured via thermal conductivity detector (TCD) and recorded as a function of temperature.

The surface morphology of catalyst particles was evaluated by Scanning electron microscopy (SEM) with a TESCAN-VEGA scanning electron microscope, operating at 30 kV. Also, the microstructure of catalyst was studied by transmission elecrtron microscope (TEM) image obtained on a ZEISS EM900 instrument operated at 50 kV.

2.3. Activity Test

Vapor phase dehydration of methanol to dimethyl ether was carried out in the vertical fixed bed micro reactor (stainless steel tubing, outlet diameter = 1.27 cm, thickness = 0.9 mm, length = 16.9 cm). Using the synthesized catalyst, the catalytic test was performed at pressure of 2 bar, weight hourly space velocity (WHSV) of 20 h^{-1} and temperature of 300°C. Prior to activity test of catalyst, the sample was crushed and sieved. 2.0 g of the catalyst was loaded to the reactor. Methanol (purity>99.9%) was pumped from methanol storage tank at the rate of 0.84 ml/min to the preheater before entering the reactor. Then, the vaporized methanol was conducted to the fixed bed reactor. The temperature of catalyst bed was measured by a submerged thermocouple which is placed in middle of the catalyst bed. The outer shell of the reactor was insulated by glass wool layer to reduce heat losses and divided into two zones: a high temperature zone (up zone) which tubular reactor was placed and a low temperature zone (down zone) which is downstream of the high temperature zone to maintain almost zero temperature gradient in the shell. The reaction products were analyzed by the online gas chromatograph (Young Lin ACME 6000, FID detector) which was equipped with TRB-5 column (95% dimethyl- 5% diphenyl polysiloxane) and helium as the carrier gas. The product line was heated electrically where necessary in order to avoid unwanted condensation of methanol and water.

3. Results and Discussion

The XRD pattern of the synthesized sample has been shown in Figure 1. It is clear that the resulted catalyst has highly crystalline nature. The characteristics peaks of gamma phase of alumina at 2θ = 36.4° for (311) reflection, 2θ = 46.0° for (400) reflection and 2θ = 67.3° for (440) reflection are seen in XRD pattern of the calcined material. Also, it shows nano-size nature as is seen from the broadening of the peaks due to the presence of small crystallite sizes. The crystallite size is calculated using Scherrer equation:

$$D_{XRD} = \frac{k\lambda}{\beta \cos\theta}$$

Where k is a constant ~ 0.9, λ is the wavelength of the X-rays, β is the full width of diffraction peak at half maximum intensity and θ is the Bragg angle. The calculated crystallite size is found in the average size of 4.77 nm. Therefore, by the exact control of temperature, pH and other synthesis conditions, nano-sized γ-Al_2O_3 is obtained.

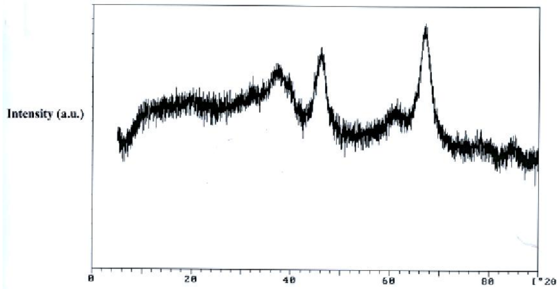


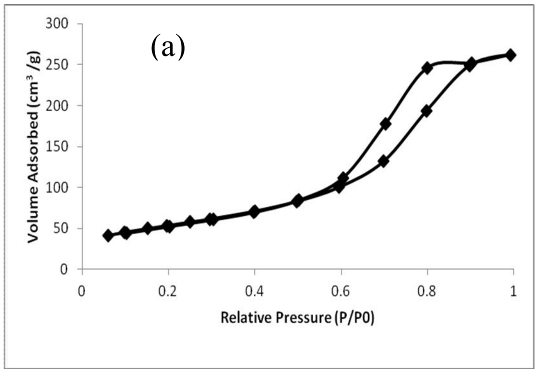
Figure 1. XRD pattern of the synthesized catalyst

The surface area, pore size distribution and pore volume data obtained for synthesized γ-Al_2O_3, industrial catalyst from Engelhard Company and other similar experimental work are tabulated in

Table 1 for the sake of comparison. It is clear that the catalyst in the present investigation has high surface area and pore volume. Higher value of pore volumes may be attributable to direct precipitation/digestion reaction at 70°C and in situ generation of OH ions. Thus, the condition required for fast nucleation and controlled growth is achieved by maintaining a slight alkaline pH of 7.5-8.5 and in situ generation of OH^- produced by $NaHCO_3$ as precipitant. From the N_2 adsorption-desorption study, changes in hysteresis of the adsorption/desorption isotherm has been shown for γ-Al_2O_3 powder in Figure 2 (a), thereby indicating changes in pore structure in this material. It shows the classical shape of type IV isotherm according to the IUPAC classification, typical for meso porous solids. A hysteresis loop (type H_1) occurs at a relative pressure range (P/P_0 = 0.5-0.9) suggesting a broad pore size distribution with uniform size and shape. The BJH pore size distribution curve is also reproduced in Figure 2 (b). It is clear that the pore size distribution is wide and pore size lies between 3 and 128 nm for synthesized catalyst. Most of the pores lie in the meso porous range.

Table 1. Surface area, average pore diameter and pore volume data

	Surface area (m^2/g)	**Average pore diameter (nm)**	**Total pore volume (cm^3/g)**
Present work	194	6.2	0.424
Engelhard Company	183	10.7	0.493
Parida et al. [10]	185	3.8	0.420



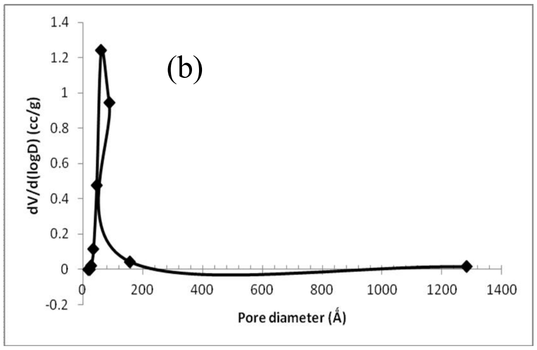


Figure 2. (a) N_2 adsorption-desorption isotherm for synthesized γ-Al_2O_3 catalyst (b) Pore size distribution of synthesized γ-Al_2O_3 catalyst

Figure 3 shows the NH_3-TPD spectrum of the γ-Al_2O_3 containing two peaks in the temperatures of 168 and 189°C. Commonly, TPD patterns of acidic catalysts have desorption peaks with maxima in the range of 100-300, 300-500 and 500-700°C which can be ascribed to the NH_3 desorbed from acid sites with low, medium and high strengths, respectively [7]. These peaks can be assigned to the NH_3 desorbed from the weak acidic sites. The total amount of ammonia desorbed from the acidic sites of synthesized γ-Al_2O_3 catalyst is summarized in Table 2. This amount is considerable in the present work compared to other researches. Also, Kumar et al. [8] and Mollavali et al. [9] found that the catalysts with highest portion of weak and/or moderate acidic sites exhibit the best catalytic performance and stability in methanol dehydration to dimethyl ether. From Figure 3 and Table 2, it can be concluded that the catalyst in present research has high amount of weak acid sites which are more appropriate for methanol dehydration reaction.

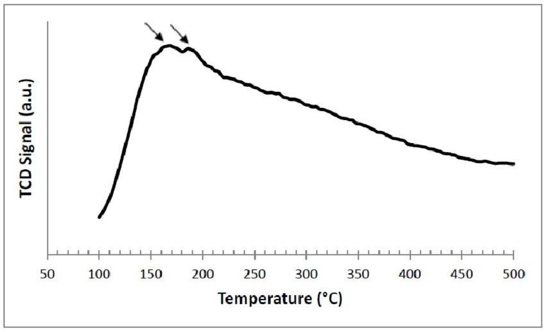


Figure 3. NH_3-TPD profile of synthesized γ-Al_2O_3 catalyst

Table 2. NH_3-TPD data on γ-Al_2O_3 catalyst

Peak 1 (mmol/g)	Peak 2 (mmol/g)	Total amount of acid sites (mmol/g)
0.234	0.859	1.093

Figure 4 (a) shows the SEM micrograph for synthesized γ-Al_2O_3 catalyst. The SEM image indicated strong agglomeration of particles with varied spherical sizes and reached clod-core form. To get more information of morphological features of synthesized γ-Al_2O_3 powders, TEM studies were undertaken. Figure 4 (b) represents typical TEM image of calcined sample. The TEM images showed a narrow size distribution of particles with good dispersity and uniform shape. These particles are aggregated to form pores of varying sizes.

The catalyst activity tests were conducted at four different operating temperatures from of 250, 300, 350 and 400°C under similar reaction conditions for γ-Al_2O_3 catalyst to investigate the effect of operating temperature on methanol conversion and yield of reaction. Table 3 shows the catalytic performance of synthesized γ-Al_2O_3 nano-catalyst for methanol dehydration reaction at 2 bar, WHSV of 20 h^{-1} and different operational temperatures under steady-state conditions. It is clear that methanol conversion was increased with temperature to the maximum amount of 80.1% at 400°C. It was found that the selectivity to DME was nearly 100% at all temperatures. Thus, as is seen from Table 3, the yield of reaction is found to be substantially increased with temperature due to increasing the reaction rate at higher temperatures.

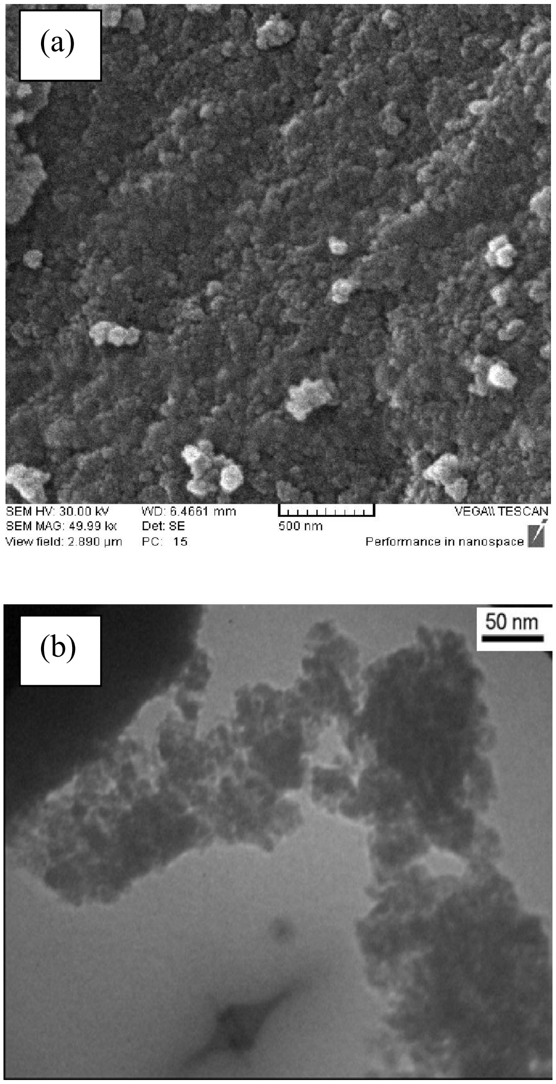


Figure 4. (a) SEM photograph of catalyst (b) TEM image of catalyst

Table 3. Performance of catalyst in fixed bed reaction

Temperature (°C)	Conversion (%)	Selectivity (%)	Yield (%)
250	43.4	100	43.4
300	52.2	100	52.2
350	60.8	100	60.8
400	80.1	100	80.1

4. Conclusions

A co-precipitation method was successfully utilized to produce γ-Al_2O_3 as dehydration catalyst having nano-sized crystallites of size 4.77 nm with surface area ~ 194 m^2/g, average pore diameter of 6.2 nm and total pore volume ~ 0.424 cm^3/g. The acidic properties of the catalyst were suitable for production of DME from methanol without formation of any by-products. Also, methanol dehydration over synthesized acidic γ-Al_2O_3 in the fixed bed reactor was studied over temperature ranging from 250 to 400°C. This study showed that the methanol conversion to DME increased with temperature to the limit of 80% at 400°C.

Acknowledgments

The financially support to this work by Iranian Nanotechnology Initiative Council is gratefully acknowledged.

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11/12/2021