

Effects of Precipitation/aging Temperature on Catalytic Activity of γ -Al₂O₃ Nanocatalysts for Dehydration of Methanol to Dimethyl Ether

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Abstract: This research includes synthesis of nano-sized γ -Al₂O₃ catalysts via precipitation method at different precipitation/aging temperatures comprising 65 °C and room temperature. The catalysts were characterized using XRD, FTIR, NH₃-TPD, SEM, TEM and N₂ adsorption-desorption techniques. The results of characterization tests showed serious effects of precipitation/aging temperature on physical/chemical characteristics of catalyst. Dehydration of methanol to dimethyl ether (DME) on synthesized catalysts was studied in a fixed bed micro reactor at different operating temperatures and WHSVs. It was found that γ -Al₂O₃ catalyst prepared at 65 °C exhibited higher yield of DME at all operating conditions.

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1. Introduction

Dimethyl ether (DME) has been used as a propellant and coolant, but great interest has currently been aroused regarding its use as a fuel, either for diesel engines or a substitute for liquefied petroleum gas (LPG) as a household fuel in rural areas. Furthermore, easy transportation and handling make it a suitable hydrogen source for fuel cells [1-5]. DME can be produced by methanol dehydration over a solid acid catalyst or direct synthesis from syngas by employing a bi-functional catalyst [6]. Methanol dehydration to dimethyl ether is a potentially important process and more favorable in views of thermodynamics and economy [7]. Commercially, γ -Al₂O₃ is used as the catalyst for this reaction. It has high surface area, excellent thermal stability, high mechanical resistance and catalytic activity for DME formation due to its surface acidity [8, 9]. γ -Al₂O₃ can be synthesized by different chemical routes such as precipitation, sol-gel, hydrolysis of aluminum alkoxide and thermal decomposition of aluminum sulfate. Precipitation is a simple method with low cost of the starting chemicals. In this method for γ -Al₂O₃ synthesis, a substance is used as the source of aluminum ions that are precipitated in the form of hydroxide by the other materials with inherent basic properties. The obtained aluminum hydroxide is converted to γ -Al₂O₃ after a series of treatments such as aging, drying and calcination [10]. Although it has been extensively studied as a catalyst for the dehydration of methanol to DME, there is still a deficiency in systematic studies that address the effect of various parameters related to the catalysts' textural properties and some reaction conditions. For the first time, we examine

the effect of precipitation/aging temperature on the morphological, textural and acidic properties of obtained γ -Al₂O₃ catalysts and accordingly their catalytic activity in methanol dehydration to DME.

2. Experimental

2.1. Catalyst Synthesis

Aluminum nitrate nonahydrate {Al(NO₃)₃·9H₂O, 98.5%, [Merck]}, ammonium hydroxide {NH₄OH, 32%, [Merck]} and deionized water were used as starting chemicals. Initially, aluminum nitrate (0.272 M) solution is made by dissolving 35.78 g in 350 ml of water. 175 milliliters of water is taken in a 2 l capacity glass beaker and stirred well using magnetic stirrer. Then ammonium hydroxide and aluminum nitrate solutions are added to 175 ml of water (from separate burettes) drop by drop to precipitate Al cations in the form of hydroxides. The temperature was maintained at 65 °C and pH was controlled between 7.5 and 8.5 during the mixing. Then, the sample was aged overnight at 65 °C for 20 hours. The aged precipitates were filtered and re-dispersed in hot water, filtered and finally washed with ethanol first followed by acetone to avoid contamination of impurities; and air dried at room temperature for 3 days. The as-dried precipitate was calcined in the furnace at 580 °C for 5 hours through atmospheric air by heating rate of 2.2 °C/min to produce γ -Al₂O₃ powder. To compare the effect of precipitation/aging temperature on physical/chemical characteristics of as-prepared γ -Al₂O₃ powders and their effect in methanol to DME conversion, we carried out precipitation/aging experiments at room temperature keeping similar conditions. The prepared

samples at 65 °C and room temperature were coded as γ -65 and γ -RT, respectively.

2.2. Catalyst Characterization

The crystallinity of calcined samples, measured by PW1840 (40 kV, 30 mA) X-ray diffractometer using Copper radiation source ($\lambda=1.54056 \text{ \AA}$) through the range of $2\theta = 5^\circ$ to 90° . BET (Brunauer-Emmett-Teller) surface area, total pore volume and average pore diameter were determined by N_2 adsorption-desorption isotherm at -196°C using NOVA 2000 instrument (Quantachrome, USA). The pore volumes were determined at a relative pressure (P/P_0) of 0.99. The FTIR study of the catalysts was carried out on Bruker (Verteex 89, Germany) FTIR spectrometer using KCl powder as sample matrix and reference material. The acidity of the samples was measured by temperature programmed desorption of ammonia (NH_3 -TPD) 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 $10^\circ\text{C}/\text{min}$. Then, the sample was cooled to 100°C and 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 that, the sample was heated at rate of $10^\circ\text{C}/\text{min}$ 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) 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 catalysts was studied by transmission electron microscope (TEM) images 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, O.D. = 1.27 cm, thickness = 0.9 mm, length = 16.9 cm). In each tests, 2.0 g of the catalyst was loaded to the reactor. Methanol was transferred from methanol storage tank to the pre-heater by the HPLC pump before entering the reactor. Then, the vaporized methanol was conducted to the fixed bed micro reactor. The reaction products were analyzed through 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.

3. Results and Discussion

3.1. Catalyst Characterization

The XRD patterns of the synthesized samples in Figure 1 clearly indicate that the catalysts exhibit the typical γ -phase of alumina [JCPDS File no. 29-63]. Also, they show nano-size nature as is seen from the broadening of the peaks due to the presence of small crystallite sizes. The crystallite size of samples was calculated using Debye-Scherrer equation:

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

Where $k \sim 0.9$ is the Scherrer constant related to the shape and index (hkl) of the crystals, λ is the wavelength of the X-ray, β is the corrected full width of diffraction peak at half maximum intensity (in radian) and θ is the diffraction angle. The calculated crystallite size (D_{XRD}) of the catalysts has been presented in Table 1. It is clear that precipitation/aging at room temperature resulted smaller crystallite size. Also, by the exact control of temperature, pH and other synthesis conditions, production of nano-sized γ - Al_2O_3 is obtainable.

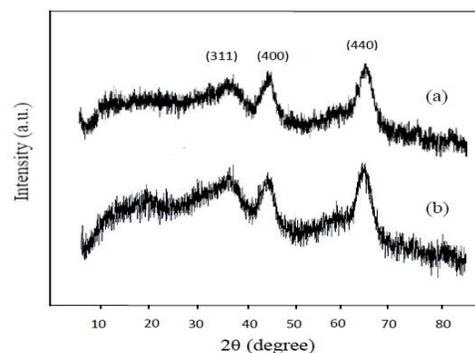


Figure 1. XRD patterns of (a) γ -65, (b) γ -RT

To support our argument, that calcination of as-dried precipitates produces well crystallized γ - Al_2O_3 powders, the systematic FT-IR studies were carried out on calcined materials (Figure 2). A major band centered around 1639 cm^{-1} is assigned to stretching and bending modes of adsorbed water due to high tendency of γ - Al_2O_3 for adsorbing water. The peak corresponding to 1108 cm^{-1} is assigned to Al-O-Al symmetric bending stretching vibrations. The weak band at 2093 cm^{-1} is assigned to a combination band and the peak at 1418 cm^{-1} corresponds to NO_3^{-1} ion or OH stretching due to presence of adsorbed ethanol. A peak corresponding to 1522 cm^{-1} is due to the NH_4^+ formed by the interaction of NH_3 with Bronsted acid sites on γ - Al_2O_3 [11]. Also, the peak at 862 cm^{-1} is assigned to ν - AlO_4 vibrations [12]. So, these catalysts contain both tetrahedral and

octahedral coordinations.

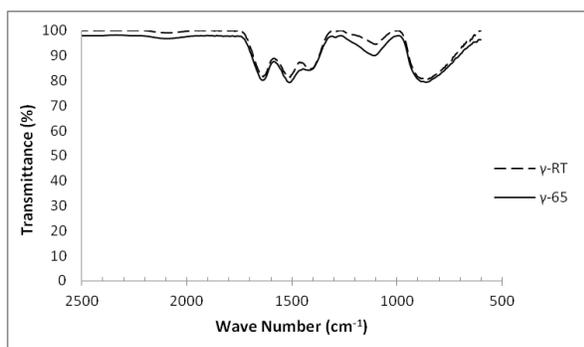


Figure 2. FTIR spectra of synthesized γ -Al₂O₃ catalysts

The surface area (S_{BET}), average pore diameter ($\langle d_p \rangle$) and total pore volume (V_p) data obtained for synthesized γ -Al₂O₃ catalysts have been tabulated in Table 2 for the comparison. The catalyst formed by precipitation/aging at room temperature possesses higher surface area and pore volume compared with other one.

Table 1. Calculated crystallite size, particle size and sintering factor

Sample	D_{XRD} (nm) ^a	D_{BET} (nm) ^b	Ψ ^c
γ -65	6.7	7.7	1.52
γ -RT	4.3	7.3	4.89

^a Crystallite size: determined by XRD results;

^b Particle size: determined by BET surface area;

^c Partial sintering factor

Also, the theoretical particle sizes are also calculated from specific surface area, assuming spherical particles according to the following equation:

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

Where, D_{BET} is the average particle size (nm), ρ is the theoretical density ($\text{g}\cdot\text{cm}^{-3}$) and S_{BET} is the specific surface area ($\text{m}^2\cdot\text{g}^{-1}$). The calculated particle size (D_{BET}) of catalysts has been also presented in Table 1. The ψ as a factor is used to reflect the partial sintering extent of the primary crystallites and it is calculated by the following equation:

$$\psi = \left(\frac{D_{BET}}{D_{XRD}} \right)^3$$

The experimental data showed that ψ is higher for the sample prepared at room temperature. This is due to severe sintering of primary crystals in aforementioned catalyst.

Table 2. Physical properties of γ -Al₂O₃ catalysts

Sample	Surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3)
γ -65	210	6.1	0.382
γ -RT	222	6.1	0.738

The surface acidic properties of the γ -Al₂O₃ samples were determined by NH₃-TPD; the results are depicted in Figure 3. Figure 3 (a) contains two peaks at 191 and 345 °C for γ -65 which are indicative acidic sites with low and moderate strengths, respectively. The catalyst prepared at room temperature contains only one peak at 176 °C corresponding to weak acidic sites. The amount of acid sites of samples is shown in Table 3. The results of NH₃-TPD measurement suggest that both the amount and strength of the acid sites of γ -Al₂O₃ were increased by precipitation/aging at 65 °C.

Table 3. NH₃-TPD data of γ -Al₂O₃ catalysts

Sample	Acidity ($\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{Cat}}$)
γ -65	15.38
γ -RT	5.26

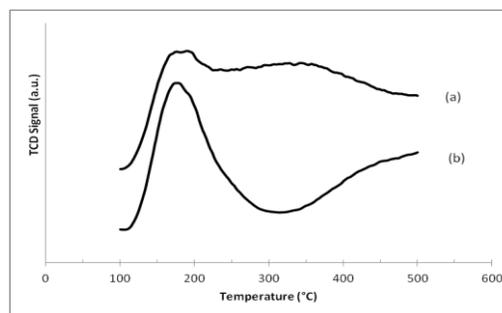
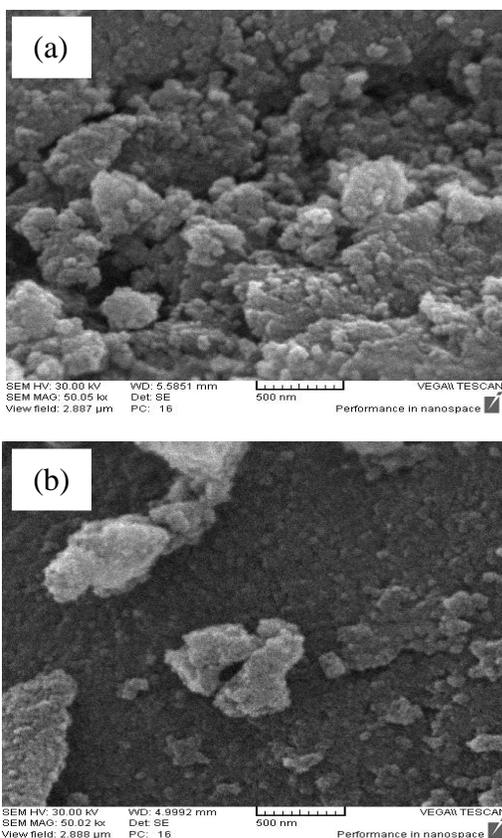
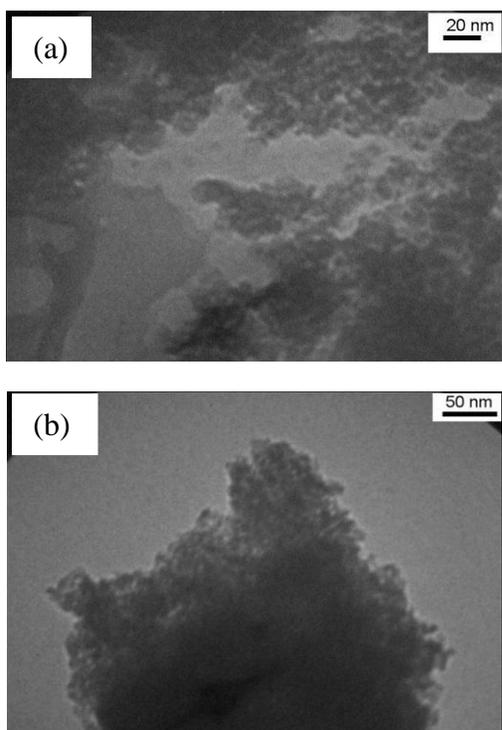


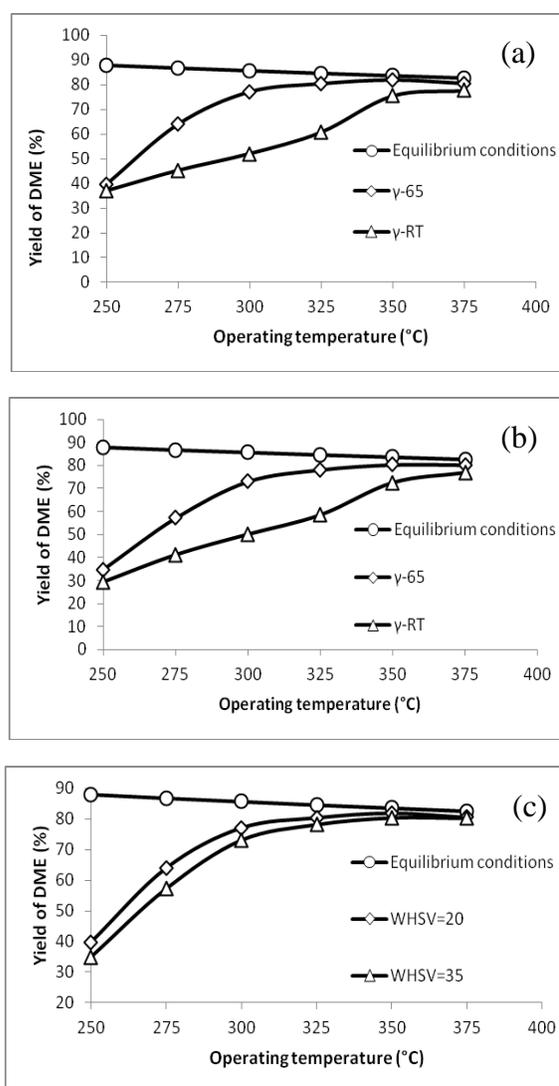
Figure 3. NH₃-TPD profiles of (a) γ -65, (b) γ -RT

Figure 4 shows the SEM image of catalysts prepared at 65 °C and room temperature. Figure 4 shows that the crystals had reached a clod-core form, and the morphology of the crystals became irregular. It is clear that catalyst prepared at room temperature indicated strong agglomeration of particles with varied sizes. This observation is consistent with results of calculated sintering factor for two samples where γ -RT has higher sintering factor. Figure 5 shows the TEM images of synthesized γ -Al₂O₃ nanocatalysts. The TEM images showed good dispersity of particles. Also, the images clearly indicated that the size of particles was below 20 nm.

Figure 4. SEM photographs of (a) γ -65, (b) γ -RTFigure 5. TEM images of (a) γ -65, (b) γ -RT

3.2. Catalyst Activity

The catalyst activity tests were conducted at different temperatures comprising 250, 275, 300, 325, 350 and 375 °C under pressure of 1.0 bar and WHSVs of 20 and 35 h⁻¹ over the synthesized γ -Al₂O₃ catalysts. The results of activity tests are depicted in Figure 6 for different operational temperatures and WHSVs. Since the methanol dehydration reaction in the gas phase is an equimolar reaction, the effect of pressure is not significant in this process and variations of pressure were not investigated in the present research. As measure of the catalytic activity and for purpose of quantitative comparison, yield of DME was used.

Figure 6. Results of activity test of synthesized γ -Al₂O₃ catalysts at pressure of 1 bar: (a) WHSV=20 h⁻¹, (b) WHSV=35 h⁻¹, (c) γ -65 at WHSVs of 20 and 35 h⁻¹

From the results, it is clear that yield increases with temperature in each of the catalysts because of higher reaction rate at high temperatures. From Figure 6 (a, b), γ -RT showed lower yield of DME compared with other catalyst despite having the higher surface area and pores volume. This can be assigned to higher acidity and lower sintering factor of γ -65 catalyst. Also, the results of activity tests of γ -65 catalyst at WHSVs of 20 and 35 h⁻¹ have been depicted in Figure 6 (c) for comparison purposes. It is clear that higher WHSV resulted lower yield of DME due to the less residence time during the reaction. At constant pressure of 1 bar, the highest yield of DME was 81.9% at temperature of 350 °C and WHSV of 20 h⁻¹ for γ -65 catalyst.

4. Conclusions

A simple precipitation method was successfully utilized at different precipitation/aging temperatures comprising 65 °C and room temperature to produce nano-sized γ -Al₂O₃ catalysts for methanol dehydration to dimethyl ether. The results of characterization tests showed that precipitation/aging temperature had significant effects on textural, acidic and morphological properties of obtained nanocatalysts. The γ -Al₂O₃ catalyst prepared at 65 °C showed higher activity in methanol dehydration to DME due to the desirable acidic properties and lower sintering factor.

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