

# New Method for Synthesis Nano Size $\gamma$ - $\text{Al}_2\text{O}_3$ Catalyst for Dehydration of Methanol to Dimethyl Ether

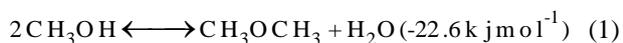
Omid Rahmanpour, Ahmad Shariati, and Mohammad Reza Khosravi Nikou

**Abstract**—Nowadays the importance of nano-particles and their uses in different industries have attracted many researches. The materials in nano-scale show different characteristics in comparison with their bulk state. Nano-materials have potential applications in optoelectronics, catalysis, and membranes. In this paper Nano-size porous  $\gamma$ -alumina was successfully synthesized by precipitation method under ultrasonic vibration mixing. Sonochemistry help the nano particles to synthesis regular form. The synthesized catalyst was characterized by SEM, XRD, BET, and TPD techniques. The effect of two most important operating conditions (i.e. Temperature and WHSV) on performance of this catalyst was investigated for dehydration of methanol to dimethyl ether (DME). The optimum operating condition was at temperature of 320 °C and WHSV of 15 h<sup>-1</sup>.

**Index Terms**—Dimethyl ether (DME),  $\gamma$ -alumina catalyst, Sonochemistry, Nano sized catalyst, operating conditions.

## I. INTRODUCTION

Dimethyl ether (DME) is an important chemical for the production of gasoline, ethylene, aromatics and other chemicals [1]-[5]. Its applications as a fuel or a fuel additive for vehicles and family cooking have been studied [6], [7]. In view of the environmental protection, the substitution of DME for Freon as an aerosol spray and a refrigerant is being considered [8]-[10]. From the literatures, it can be concluded, almost all commercial DME were produced by the dehydration of methanol using different solid-acid catalysts such as zeolites, silica-alumina, alumina,  $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ , etc. by following reaction (Equation (1)): [11].



In recent years, increasing attention has been focused on the development of nano-sized alumina powders for advanced engineering materials [12], [13]. Conventional processes for synthesizing ceramic nano powder involve mechanical synthesis, vapor phase reaction, precipitation, and combustion and sol-gel methods [14]-[16]. Catalytic dehydration of methanol over solid-acid catalysts offers a potential process for dimethyl ether synthesis. Several catalysts having activity and selectivity for the catalytic conversion of methanol to DME are known, the so called acidic dehydration catalysts [17]-[19]. Commercially  $\gamma$ - $\text{Al}_2\text{O}_3$  is used to a large extent for this reaction at a temperature range of 270 to 380 °C.

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The authors are with the Petroleum University of Technology, Ahwaz, Iran (e-mail: orahmanpour@gmail.com; Shariati@put.ac.ir; mr.khosravi@put.ac.ir).

The sonochemical synthesis of nanophase materials has the advantage that various classes of materials can be generated simply by changing the reaction medium. So it is worthwhile to overview the different applications, where cavitations can be used efficient. Preparation of metal and metal oxide nanoparticles immobilized on various materials is one of the key researches in nanoscience and nanotechnology, because an excellent synergy and

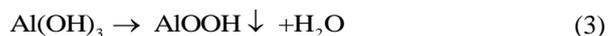
Bifunctional effect would be expected [20]. It is well known that the alternative method for generating stabilized metal nanoparticles involves synthesizing them in or on nanoporous supports, which help define particle size and serve to immobilize the resulting particles [21].

The aim of the present study is to find effect of sonochemistry in particles structure and the optimum operating condition of new nano size synthesized  $\gamma$ - $\text{Al}_2\text{O}_3$ . Dehydration of methanol to dimethyl ether was carried out in the fixed bed micro reactor and the structure of solid-acid catalysts was also studied by SEM, XRD, BET, and TPD techniques.

## II. EXPERIMENTAL

### A. Catalyst Synthesis

Aluminum nitrate  $\{\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 99.5% (Merck), Ammonia  $\{\text{NH}_4\text{OH}$ , 32% (Merck) and deionized water were used as starting chemicals. A transparent gel-like precursor containing Al cations is precipitated at  $\text{pH} \sim 7.5$ - $8.5$  when ammonia (3.2%) and Al nitrate salt solutions (0.26 M) are mixed together in 400 ml deionized water. The solution was mixing under ultrasonic vibration and maintained at a temperature 70 °C for 2 h. The following chemical reactions occurred during preparation:



The precipitate obtained by reaction (2) was aged at a temperature  $\sim 70$  °C helped to homogenize the gel due. The ageing step is essential to convert  $\text{Al}(\text{OH})_3$  to crystalline boehmite precursor by reaction (3). The precipitate is further processed by washing in deionized water. Then was added 300 ml ethanol to the filtered  $\text{Al}(\text{OH})_3$  under ultrasonic vibration for 1 h then dried in oven at  $\sim 70$  °C for 18 h.

$\gamma$ - $\text{Al}_2\text{O}_3$  is produced by calcinations of dried boehmite ( $\text{AlOOH}$ ) at 550 °C for 4 h by reaction (4).

### B. Characterization Tests of Catalyst

The crystallinity of catalyst, measured by PW1840 (40 Kv, 30 Ma) X-Ray diffract meter using  $Cu K\alpha$  radiation source ( $\lambda=1.54056 \text{ \AA}$ ) through the range of  $2\theta=5^\circ$  to  $90^\circ$ . BET surface area, total pore volume and average pore diameter were determined by  $N_2$  adsorption-desorption isotherm at 77 K 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, the sample was degassed at  $200^\circ\text{C}$  in  $N_2$  flow for 3h to remove the physically adsorbed water immediately before analysis. The pore size distribution of the catalyst was verified by a BJH (Barett-Joyner- Helenda) 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  $500^\circ\text{C}$  under The 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  $100^\circ\text{C}$  and saturated with 5%  $NH_3/He$  for 30 min. The sample was then purged with the 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 of  $10^\circ\text{C}/\text{min}$  under the flow of the carrier gas (30 ml/min) from  $100^\circ\text{C}$  to  $700^\circ\text{C}$  and the amount of ammonia in effluent was measured via thermal conductivity detector (TCD).

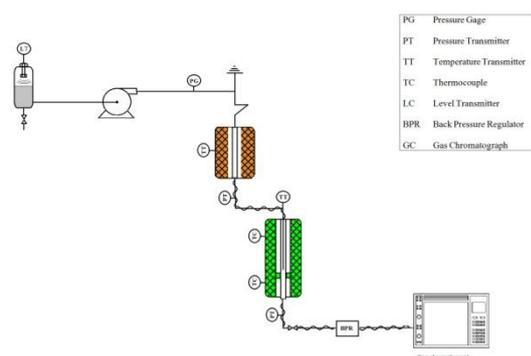


Fig. 1. Schematic view of experimental setup

### C. Methanol Dehydration Process

A schematic representation of the experimental set-up is shown in figure 1. Vapor phase dehydration of methanol to dimethyl ether was carried out in the fixed bed micro reactor (stainless steel, O.D=0.75 in, length=10 in). Liquid methanol (grade AA, 99.9% purity) was injected to the pre heater by means of HPLC (metering) pump (working range of 0.01 to 9.99 ml/min), then evaporated in the pre heater that kept at the constant temperature of  $300^\circ\text{C}$ . After pre-heater, the vaporized methanol is conducted to the fix bed flow reactor. Reactor consists of two heating zones. First zone is to raise the feed temperature to the desirable level and the other one to maintain the reactor surrounding at the proper temperature to minimize heat losses and simulate an adiabatic reactor. The down line effluent was constantly kept at temperatures above  $160^\circ\text{C}$ , to prevent condensation of the reactant and products. The reaction temperature is changed between  $270^\circ\text{C}$  to  $380^\circ\text{C}$  and for each test 1 gr of the catalyst was loaded to the reactor. Methanol was pumped to the pre-heater before entering the reactor. The effluent of the reactor was analyzed

with a gas chromatograph (ACME 6100, Younglin Instrument Korea) which is equipped with nonpolar capillary column TRB-5(95% dimethyl-5% diphenyl polysiloxane) and a flame ionization detector (FID).

## III. RESULT AND DISCUSSION

### A. Phase Analysis

The XRD patterns of the new nano size synthesized  $\gamma$ -alumina are shown in Figure 2 that the three peaks at  $2\theta=37.8^\circ$ ,  $2\theta=45.7^\circ$  and  $2\theta=66.9^\circ$  are assigned to (311), (4 0 0) and (4 4 0) reflections of  $\gamma$ - $Al_2O_3$ . The crystallite sizes were also calculated using the Scherrer (Eq. (5)):

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (5)$$

where,  $K$  is a constant generally taken as  $\sim 0.9$ ,  $\lambda$  is the wavelength of the incident radiation,  $\beta$  is the full width of diffraction peak at half maximum intensity (FWHM) and  $\theta$  is the diffraction angle. The calculated crystallite sizes were found to be in the range of 1-2 nm for nano size synthesized  $\gamma$ -Alumina. Crystal structures were very close in synthesized  $\gamma$ -Alumina catalyst that can be good effect in reaction. These close crystal layers was made under ultrasonic waves.

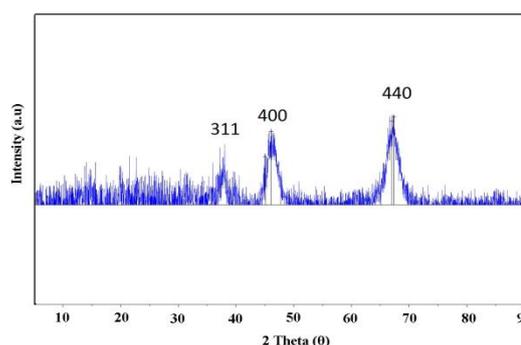


Fig. 2. XRD patterns of synthesized  $\gamma$ - $Al_2O_3$

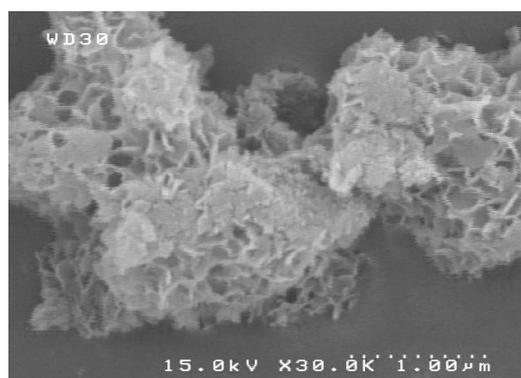


Fig. 3. Scan electron microscopy images of  $\gamma$ - $Al_2O_3$  catalyst

### B. SEM

Fig. 3 shows the SEM image of the synthesized  $\gamma$ - $Al_2O_3$  sample after calcination. The crystals of the sample reached a porous and spongy form, and the morphology of the crystals were regular pores and present enough volume for reaction and increase surface area. SEM of synthesized catalyst shows low bulk density and high bulk pores which these structures

made from evaporation of ethanol under ultrasonic vibration mixing.

### C. Acidity Measurements

The TPD spectra Fig. 4 of the synthesized  $\gamma$ -alumina catalyst contain an intense peak in 160 °C and 320 this peak reduced slightly in the temperature range of 200–500 °C that corresponds weak to medium acid sites which is attributable to the removal of adsorbed  $\text{NH}_3$  on the catalyst surface with low strengths and the temperature of the desorption maxima and the acid content of the catalysts are summarized in Table I. TCD signal shows the synthesized catalyst have medium acid site and this peak was presented in 320 °C and strong acid site was not seen in this signal. TCD signal shows the synthesized catalyst have medium acid site and this peak was presented in 320 °C and strong acid site was not seen in this signal.

TABLE I: SUMMARY OF ACIDIC SITE MEASURED BY  $\text{NH}_3$ -TPD OF SYNTHESIZED  $\gamma\text{-Al}_2\text{O}_3$  CATALYST

	Weak acid sites (mmol/g)	Medium acid sites (mmol/g)	Total
Nano size $\gamma\text{-Al}_2\text{O}_3$	0.883	0.187	1.07
Temperature (°C)	170	320	

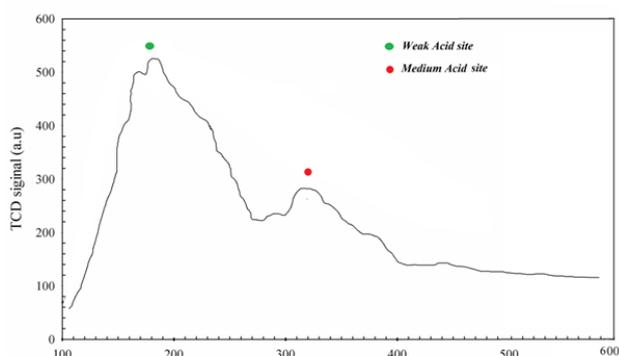


Fig. 4.  $\text{NH}_3$ -TPD profile of  $\gamma$ -alumina

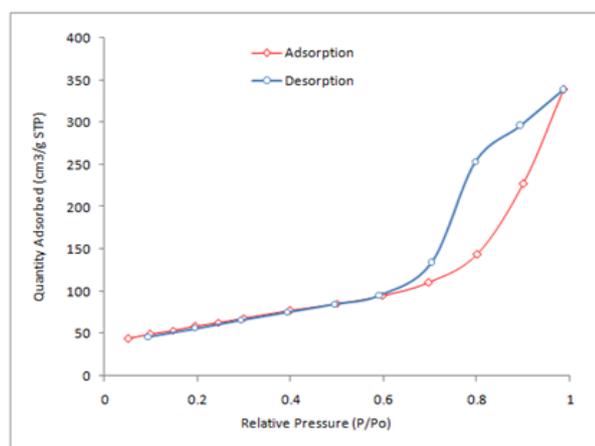


Fig. 5.  $\text{N}_2$  adsorption and desorption isotherms of  $\gamma\text{-Al}_2\text{O}_3$  catalyst

### D. $\text{N}_2$ Adsorption-Desorption (BET)

The  $\text{N}_2$  adsorption and desorption isotherm remains type IV, as is seen from Fig. 5. According to IUPAC classification [22], the hysteresis loop (type *H1*) occurs at a relative pressure range of  $p/p_0 = 0.6\text{--}0.95$ , indicating a broad pore size distribution with uniform size and shape. As it can be seen,

synthesized nano  $\gamma\text{-Al}_2\text{O}_3$  catalyst show a mesoporous structure with different pore size distributions. The surface area, pore size distribution and pore volume data obtained for nano size synthesized  $\gamma\text{-Al}_2\text{O}_3$  catalyst using ammonia agent obtained by its calcination at 550 °C for 4 h in air are tabulated in Table II. The BJH pore size distribution curves are reproduced in Fig. 6. The pore size distribution is wide and pore size lies between 1 and 20 nm.

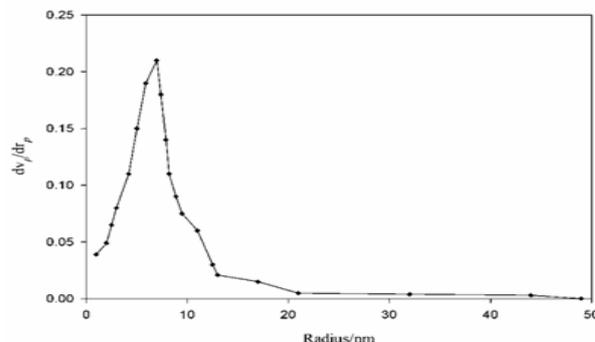


Fig. 6. BJH pore size distribution of  $\gamma\text{-Al}_2\text{O}_3$  catalyst

TABLE II: SUMMARY OF SURFACE AREA AND PORE VOLUME OF SYNTHESIZED  $\gamma\text{-Al}_2\text{O}_3$  CATALYST

	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Average pore diameter (nm)	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
Nano size $\gamma\text{-Al}_2\text{O}_3$	216	9.646	0.5212

### E. Catalytic Activity

The reaction performance results, including methanol conversion calculated according to (Eq. (6)) [23].

$$X_{\text{MeOH}} \% = \frac{n_{\text{initial MeOH}} - (n_{\text{final MeOH}} + 2n_{\text{final DME}})}{n_{\text{initial MeOH}}} \times 100 \quad (6)$$

The conversion variation trend with temperature was investigated for different weight hourly space velocities at range of 15 to 45  $\text{hr}^{-1}$  at a constant pressure of 100 kPa gauge. As depicted in figure 7 the trend is nearly similar for different WHSVs but the amount of methanol conversion is reduced with increasing space velocity in the temperature range of 270 to 380 °C for synthesized  $\gamma$ -Alumina.

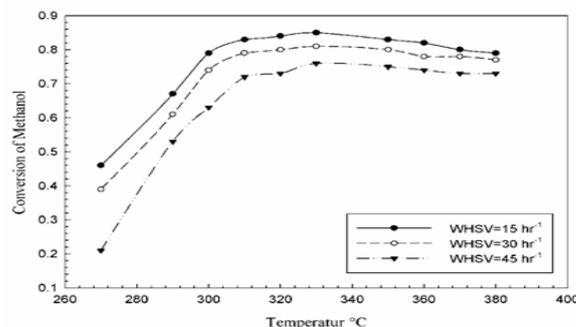


Fig. 7. Catalyst bed temperature profile over different weight hourly space velocity

It is clear from the figure that the system reached to the equilibrium conversion at temperature range of 310 to 340 °C under WHSV of 15  $\text{hr}^{-1}$  and by increasing WHSV, the reaction could not meet the equilibrium conditions. The

highest conversion was resulted in temperature range of 310-340 °C. Equilibrium conversion shows acceptable result for this nano sized catalyst.

#### IV. CONCLUSION

Nano-sized porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was successfully synthesized via a series of synthetic pathways. The calculated crystallite sizes were 1-2 nm with surface area ~216 m<sup>2</sup>/g, average pore diameter of 9.646 nm, and pore volume ~ 0.5212cm<sup>3</sup>/g. According to the hysteric loop (type H1) the synthesized nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst show a mesoporous structure.

The results showed the maximum conversion of reaction was observed at a temperatures range of 310 to 340 °C and WHSV of 15 hr<sup>-1</sup> with methanol conversion of 84% for synthesized. All of results showed that sonochemistry is a new method for synthesized catalysts and have competitive potential with commercial catalysts. Sonochemistry can play major role in formation of particles and crystals structure.

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**Omid Rahmanpour** was born in Marand on March 14<sup>th</sup> 1985. He received her bachelor degree in Chemical Engineering from Babol Noshirvani University of Technology, Mazandaran, Iran, in 2009. Now, he is studying for MS degree in Gas Engineering Department, Petroleum University of Technology, Ahwaz, Iran. Currently his main efforts are taken to synthesis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/CNTs catalyst for dehydration of methanol and other acidic catalysts.