Investigation the Effect of Temperature and Weight Hourly Space Velocity in Dimethyl Ether Synthesis from Methanol over the Nano-Sized Acidic Gamma-Alumina Catalyst

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Abstract: A commercial nano-sized acidic gamma-alumina catalyst was prepared and characterized by XRD, SEM, TEM, NH_3-TPD, and N_2 adsorption-desorption for BET surface area and porosity measurements. Vapor phase dehydration of methanol to dimethyl ether (DME) was investigated over the catalyst in the fixed bed micro reactor. At constant pressure, by changing the weight hourly space velocity (WHSV) from 20 to 50 h^{-1} and operating temperature of the reactor from 250 to 450°C, changes in methanol conversion were monitored. The results showed that the conversion of methanol strongly depended on the reactor operating temperature and WHSV. Finally, a new experimental equation was developed to predict methanol conversion from operating temperature and WHSV.
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1. Introduction

During the past few years, dimethyl ether (DME) has received global attention as a clean-burning fuel for diesel engines due to the increasingly stringent environmental regulations [1, 2]. 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, antiperspirants and room air fresheners. Then there would be a growing requirement to produce large scale of DME to meet the future market [3, 4].

Two processes are used for DME production, indirect [5-10] and direct processes [11, 12]. In indirect process, methanol is converted to DME in a catalytic dehydration reactor over a solid-acid catalyst by the following reaction:

$$2CH_3OH \longleftrightarrow CH_3OCH_3 + H_2O \qquad (1)$$

In the direct process, synthesis gas is used as the feed of the process. In this process, the synthesis gas is primarily converted to methanol and then it is followed by methanol dehydration to DME. The net reaction is as follows:

$$3CO + 3H_2 \longleftrightarrow CH_3OCH_3 + CO_2 \qquad (2)$$

Methanol dehydration to dimethyl ether (indirect process) is a potential process and more favorable in views of thermodynamics and economy [9]. Gamma-alumina is used as a common catalyst for this process because of high surface area, excellent thermal stability and high mechanical resistance [13-15]. In this research, a commercial nano-catalyst was evaluated by different characterization tests in views of textural, morphological and acidic properties. Then, the conversion of methanol to DME was considered by dehydrating process over the catalyst in the fixed bed micro reactor at different conditions. One of the most important problems related to the operation of heterogeneous catalysts is the loss of catalyst activity with time on-stream. In the indirect process to produce DME using γ-alumina, water has the most important effect on catalyst deactivation [16]. To overcome this problem, extra pure methanol (purity> 99.9 wt %) was used for activity tests of catalyst.

2. Experimental

2.1. Catalyst and Feed Preparation

Acidic γ-alumina, 20 nm in particle size, was obtained from Nano Pars Lima Company. Some of the physical and chemical properties of the catalyst are reported in Table 1. Also, methanol was obtained from Fanavaran Petrochemical Company which is a subsidiary of National Iranian Petrochemical Company (NIPC) as the feed to the reactor. Its composition is also given in Table 2.

Table 1. Characteristics and chemical composition of the catalyst

Appearance	Bulk density (g/cm³)	Composition (wt)						
		Al₂O₃	Ca	V	Cl	Na	Mn	Co
White powder	0.90	> 99%	≤ 25[1]	≤ 7[1]	≤ 315[1]	≤ 70[1]	≤ 3[1]	≤ 2[1]

[1] The values are based of ppm.

2.2. Catalyst Characterization

The crystallinity of catalyst, measured by JDX-8030 (40 kV, 30 mA) X-ray diffractometer using Cu Kα radiation source (λ=1.54056 Å) through the range of 2θ = 5° to 90°. 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°C in N_2 flow for 3 h to remove the physically adsorbed water immediately before analysis. The pore size distribution of the catalyst 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. 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°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). Scanning electron microscopy (SEM) was performed with a Seron Technology (model: AIS 2100) scanning electron microscope. Also, the microstructure of catalyst was studied by transmission elecrtron microscope (TEM) image obtained on a ZEISS EM900 instrument operated at 80 kV.

Table 2. Composition of the methanol feed (sp. gr. = 0.786 g/cm^3)

Methanol (wt %)	Water (wt %)	Ethanol (wt %)	Acetone (wt %)
99.975	0.0185	0.0006	0.0001

2.3. Process Test of Catalyst

A schematic diagram of the experimental setup employed in this study is shown in Figure 1. All of the experiments were performed at pressure of 3 bar. Weight hourly space velocity (WHSV) and reactor temperature were changed between 20 to 50 h^{-1} and 250 to 400°C, respectively. Pure methanol was pumped from methanol storage tank to the pre-heater before entering the reactor. Then, the vaporized methanol was conducted to the fixed bed micro reactor (stainless steel tubing, O.D. = 1.27 cm, thickness = 0.9 mm, length = 16.9 cm). The

temperature of catalyst bed was measured by the submerged thermocouple which is placed in middle of the catalyst bed. 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. Also, the product line was heated electrically where necessary in order to avoid unwanted condensation of methanol and water.
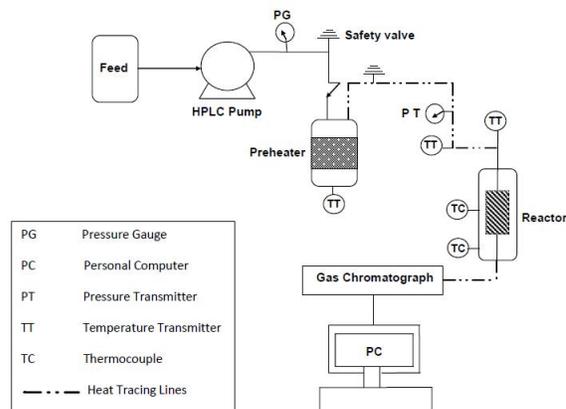

Figure 1. Schematic representation of the experimental setup

3. Results and Discussion
3.1. Catalyst Characterization

The XRD pattern of the sample has been shown in Figure 2. It is clear that the catalyst has highly crystalline structure. All reflections shown in Figure 2 are indexed for the standard reported γ-alumina phase [JCPDS File no. 29-63]. The characteristic peaks of gamma phase of alumina at 2θ = 38.1° for (311) reflection, 2θ = 42.9° for (400) reflection and 2θ = 62.8° for (440) reflection are seen in XRD pattern of the catalyst. Also, it shows nano-size nature as is seen from the broadening of the peaks due to the presence of small crystallite sizes.
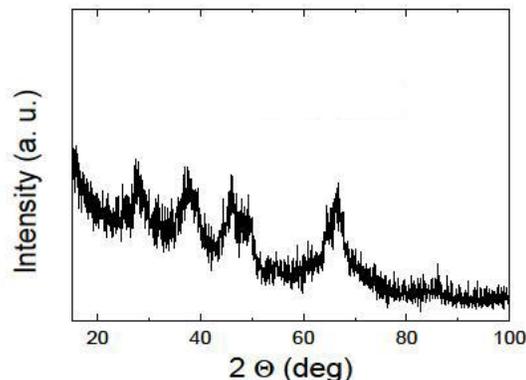

Figure 2. XRD pattern of the catalyst

The surface area, average pore diameter and pore volume data obtained for γ-Al$_2$O$_3$ nano-catalyst have been tabulated in Table 3. From the N$_2$ adsorption-desorption study, changes in hysteresis of the adsorption/desorption isotherm has been shown for γ-Al$_2$O$_3$ powder in Figure 3(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 (2-50 nm) porous solids. The BJH pore size distribution curve is also reproduced in Figure 3(b). It is clear that the pore size distribution is wide and pore size lies between 2 and 78 nm. Most of the pores lie in the meso porous range.

Table 3. Surface area, average pore diameter and total pores volume of the catalyst

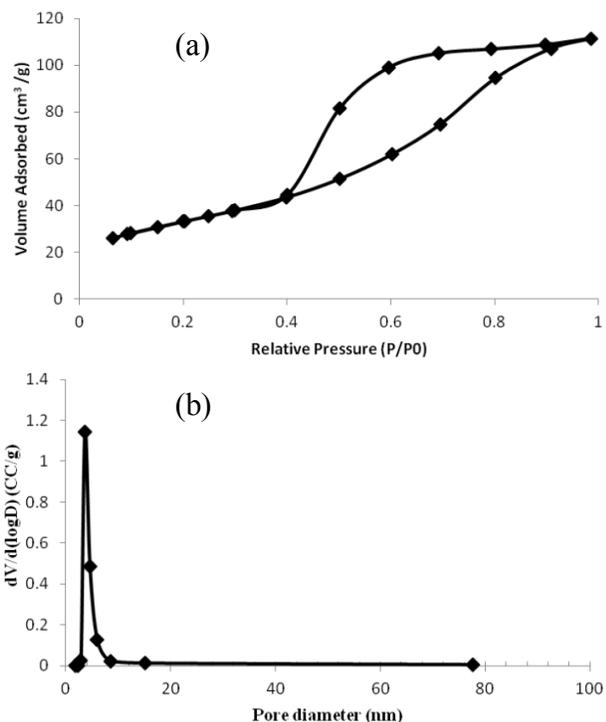| Surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3)
119.0	3.6	0.194

Figure 3. (a) Nitrogen adsorption-desorption isotherm of catalyst, (b) Pore size distribution of catalyst

Figure 4 shows the SEM and TEM micrographs of γ-Al$_2$O$_3$ catalyst. As shown in Figure 4 (a), the SEM micrograph of the sample, the crystals of the catalyst have good dispersion and the morphology of the crystal is regular. Also, it is seen strong agglomeration of the particles with uniform sizes. To get more information of morphological features of catalyst, TEM study was undertaken.

From Figure 4 (b), typical TEM image of powder, it is clear that the γ-alumina particles are spherical in nature, having a narrow size distribution around 20 nm. These particles are aggregated to form pores of varying sizes. This observation is consistent with BJH pore size distribution curve (Figure 3 (b)) where wide pore size distribution is evident.
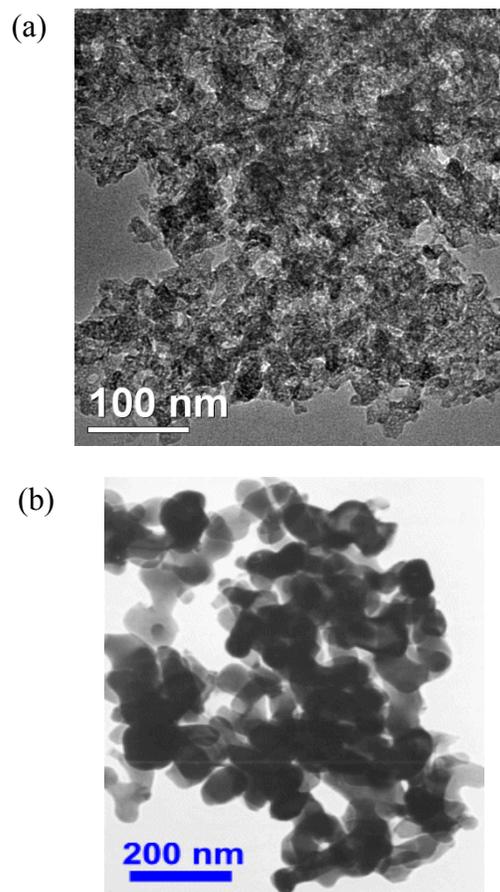

Figure 4. (a) SEM micrograph of catalyst, (b) TEM image of catalyst

Figure 5 shows the NH$_3$-TPD spectrum of the γ-Al$_2$O$_3$ containing a peak in the temperature of 193°C and a broad peak at 307°C. First peak is assigned to the NH$_3$ desorbed from the weak acidic sites and second peak assigned to acidic sites with moderate strength. The total amount of ammonia desorbed from the catalyst is 3.064 mmol NH$_3$/g$_{cat}$ that is significant in comparison with other used acidic catalysts for methanol dehydration reaction. On the other hand, 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 because the strong acid sites on the catalyst, leading to the formation of byproducts (Kumar et al., 2006; Mollavali et al., 2009; Hosseini et al., 2011). It can be concluded that

the commercial catalyst used in present research has high amount of weak and moderate acid sites which are more appropriate for methanol dehydration reaction.
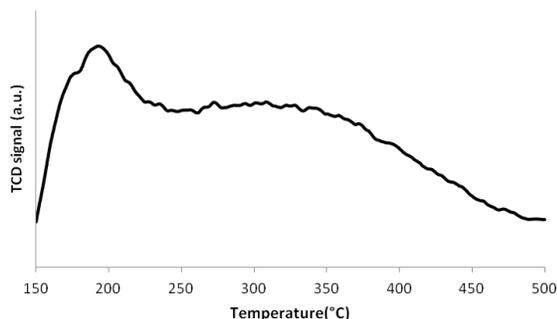

Figure 5. NH$_3$-TPD profile of catalyst

3.2. Catalytic Dehydration of Methanol

Since the methanol dehydration to DME is an equimolar reaction, pressure could not affect on conversion. Therefore, pressure changes have not been studied in this research. The catalyst activity tests were conducted at different operating temperatures of 250, 275, 300, 325, 350, 375, 400, 425 and 450°C under WHSVs of 20, 35 and 50 h^{-1} at pressure of 3 bar to investigate the effect of operating temperature and WHSV on methanol conversion. Figure 6 shows the catalyst performance for methanol dehydration reaction at different operating parameters under steady-state conditions. At all of the operating conditions, the catalyst selectivity to DME was approximately 100%. In general, methanol conversion was not substantial below 350°C in different WHSVs and increased at temperatures up to 425°C. Also, since the methanol dehydration reaction is an exothermic and reversible, conversion decreased beyond 425°C based on the Le Chatelier's principle. Also it could be seen that the conversion decreased at higher WHSVs because of the less residence time. At WHSV of 50 h^{-1}, conversion is very low below 350°C due to the both factors of less residence time and low reaction rate. It can be concluded the temperature and space velocity are two major factors affecting on methanol conversion. From Figure 6, it is clear that the operating temperature of the rector is more effective on methanol conversion compared with WHSV.

A new correlation was developed to predict methanol conversion from temperature and WHSV by using the obtained data at different temperatures and WHSVs. This equation is applicable at temperature range of 250 to 450°C and space velocity range of 20 to 50 h^{-1} with high accuracy and presented below:

$$X = 456.1 - 4.907\,T + 5.385\,W + 0.0173\,T^2$$
$$- 0.02612\,TW - 0.04358\,W^2$$
$$- 1.839 \times 10^{-5}\,T^3 + 3.127$$
$$\times 10^{-5}\,T^2W + 9.156$$
$$\times 10^{-5}\,TW^2$$

In this equation, X is conversion of methanol (%); T is the operating temperature of reactor (°C) and W is the weight hourly space velocity (h^{-1}). Figure 7 presents a comparison between the proposed correlation results and the experimental data. This Figure demonstrates a good consistency between the calculated and experimental results.
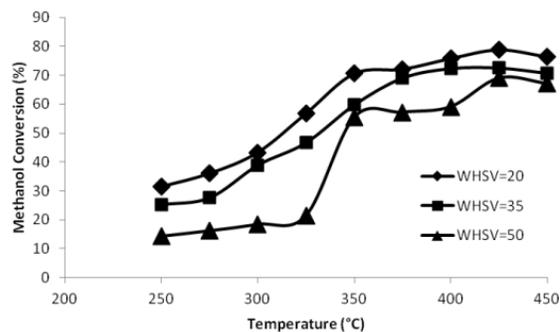

Figure 6. Variations of methanol conversion with operating temperature of the reactor at different WHSVs
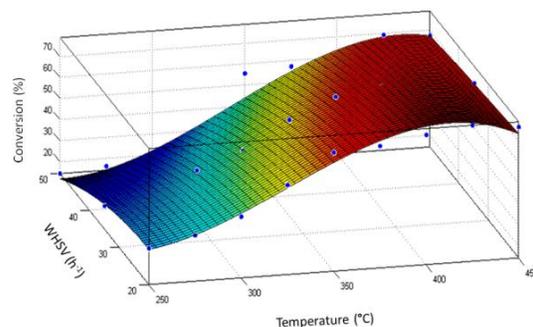

Figure 7. A comparison between the calculated conversions of methanol using the proposed equation (curvilinear surface) and the experimental data (points)

4. Conclusions

A commercial nano-sized acidic γ-alumina was prepared and characterized by different techniques. The results of characterization tests showed suitable characteristics of catalyst for production of DME via dehydrating process. Next, methanol dehydration reaction on γ-alumina catalyst was studied in the fixed bed micro reactor to produce DME over operating temperature and WHSV ranging from 250 to 400°C and 20 to 50 h^{-1}, respectively. This study showed that methanol conversion was not substantial

below 350°C and increased with temperature till 425°C where it decreased with further increase in temperature due to the reversibility principle. Also, conversion decreased by increasing the WHSV due to the less residence time. Finally, a correlation was developed to predict methanol conversion at different temperatures and WHSVs in the ranges mentioned above.

Acknowledgments

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