

Application of Novel Gamma Alumina Nano Structure for Preparation of Dimethyl ether from Methanol

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(Received: 01 Oct. 2013 and Accepted: 12 Jan. 2014)

Abstract:

In this study, preparation of nano-sized gamma alumina with high specific surface area and high yield by the reaction between aluminum nitrate and sodium carbonate, without using any surfactant is reported. Bohemite (Aluminum oxyhydroxide) was prepared as a precursor by strict control of pH and reaction temperature. The gel produced was purified by washing followed by centrifugation. The specific thermal program was applied for calcination. This resulted in a leaf flower shaped gamma alumina in 91% yield, with 413 m²/g specific surface area and average pore volume 1.624 cm³/g. The flower like micro sheets of gamma alumina contained spherical particles with an average size of about 38 nanometers. Elemental analysis and FTIR spectra showed that sodium and carbonate ion impurities were completely removed from the prepared gamma alumina. X-ray diffraction pattern and TG/DTA analysis confirmed that bohemite and gamma alumina phase were formed. XRD, SEM and BET data of synthesized catalyst were compared with commercial catalyst. Dehydration of methanol was conducted by the synthesized gamma alumina. The catalyst evaluations were performed at different temperatures and different weights hourly space velocities. The commercial catalyst and the synthesized catalyst were compared in this work and the results showed that the performance of nano-sized catalyst was better than the commercial one.

Keywords: Nano sized-gamma alumina, Catalyst, DME, Methanol.

1. INTRODUCTION

Gamma alumina is a long known important catalyst which has been used in various processes. It can be prepared by different methods. Morphology of synthetic gamma alumina can be changed by varying some of the reaction conditions such as: temperature, pressure, reaction time, thermal decomposition routes and methods of preparation, precursors, reactants and so on. The catalytic properties of gamma alumina depend on its physical properties such as surface acidity, porosity, and pore size of particles [1-6].

There are different methods for synthesizing gamma

alumina. One of these methods is hydrometallurgy reaction at high pressures by using alchoxy, various hydroxides or aluminum oxy hydroxides. In liquid phase the reactions can be performed by two methods: a) aluminum alchoxide hydrolysis and b) deposition in aqueous or semi aqueous of inorganic salts which can produce bohemite. The basis of this method is formation of aluminium monohydrate or bohemite from aluminate. Then by calcination of bohemite in a specific condition with controlling temperature, gamma alumina can be produced. Liu *et al.* in 2008 have reported the synthesis of microscale bohemite and gamma nano leaves of alumina by the reaction between sodium

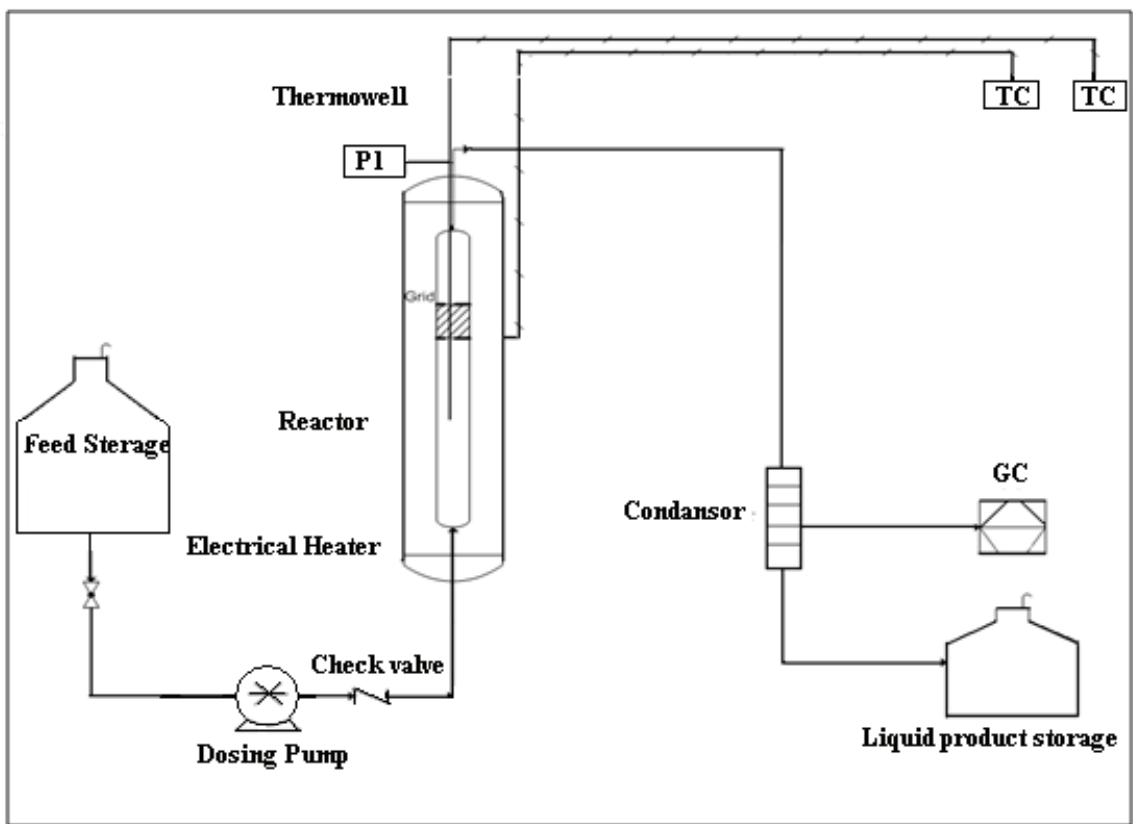


Figure 1: Schematic diagram of the experimental setup.

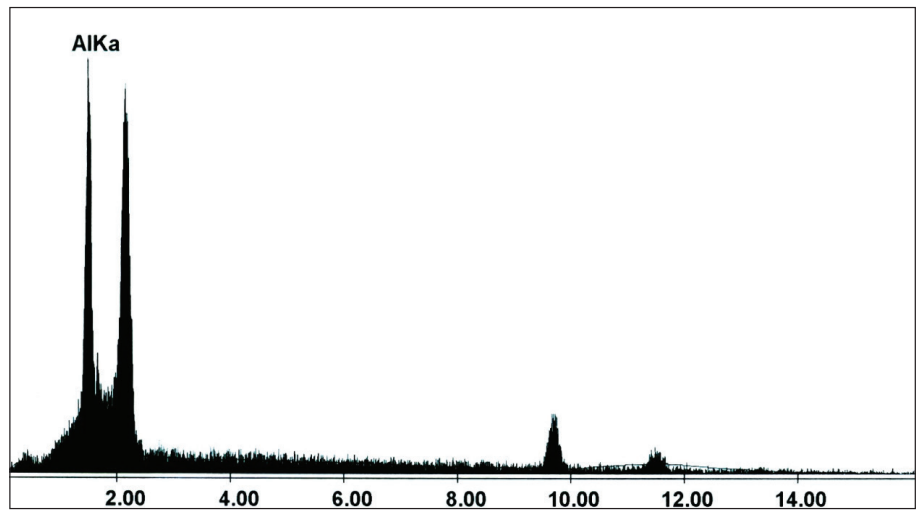


Figure 2: Energy-dispersive X-ray analysis of dried boehmite at 100°C for 16h.

EDAX ZAF Quantification (Standardless)

Oxides

Element	Wt %	At %
Al ₂ O ₃	100.00	100.00
Total	100.00	100.00

Element	Net Inte.	BKgd Inte.	Inte. Error	P/B
AlK	359.05	11.1711	0.94	32.15

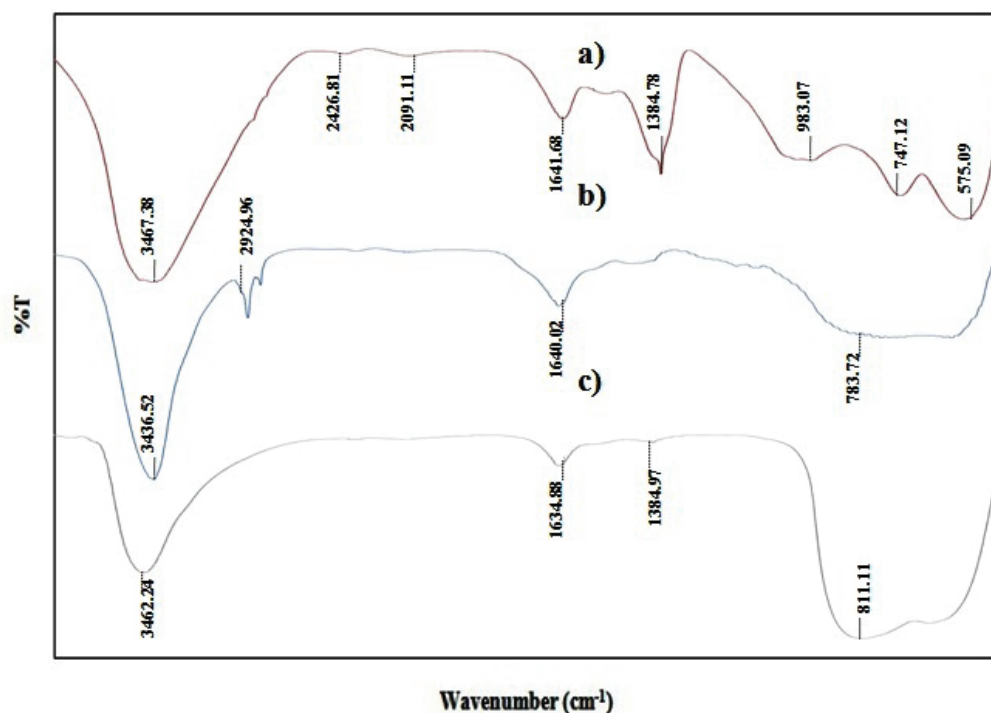


Figure 3: FT-IR Spectra for (a) dried boehmite at 25°C (b) gamma alumina prepared after calcinations in 500 with heating rate 2°C/min and (c) gamma alumina from BASF Co.

hydroxide and aluminium tri chloride. They used Cetyl Trimethyl Ammonium Bromide (CTAB) by the hydrothermal method using an autoclave, for preparation of boehmite nanosheets [7].

Tallinn *et al.* in 2006 synthesized gamma alumina nanopowders by freeze drying technique [8-10] which involved drying amorphous aluminium sulphate powder and then decomposed it at 825°C. By adjusting freezing rate and dispersing conditions they obtained 30 nm and 10 nm gamma alumina. Hosseini *et al.* (2011) could prepare gamma alumina from kaolin. gamma alumina powder was synthesized through extracting alumina from meta-kaolin via H₂SO₄ and subsequent precipitation in ethanol, which led to formation of aluminium sulfate, calcination of which at 900°C yielded gamma alumina [11].

Pride *et al.* (2009) prepared nano gamma alumina by the use of alkalis such as sodium hydrogen carbonate, sodium carbonate and ammonium bicarbonate. With ammonium carbonate they obtained spherical nano-sized particle with a surface area of 190 m²/g and pore volume of nearly

0.467 cm³/g [12]. Boehmite precursor is necessarily used to obtain gamma alumina, whereas aluminum hydroxide usage through precipitation at room temperature, leads to the formation of alfa alumina [13,14]. Other methods such as sol- gel methods and use of aluminium alkoxides are either more expensive proposition or use sensitive starting chemicals.

Keshavarz *et al.* [15] used the sol gel method for preparation of gamma alumina. Due to an extensive number of applications of nano structured gamma alumina in different areas, there is a great amount of interest in producing nano structured gamma alumina in high yield with interesting morphology and high specific surface areas using simpler methods. Potter *et al.* reported synthesis of nanosized gamma alumina via room temperature precipitation/digestion method and subsequent calcination of boehmite at 550°C for 5 hours. They reported that the product surface area and the average pore volume were about 133.90 m²/g and 1.02 cm³/g, respectively[14].

Akarmazyan *et al.* [16] used the sol gel method and

Table 1: Some of experimental conditions for preparing of gamma alumina

Run	Molar ratio Al(NO ₃) ₃ /Na ₂ CO ₃	Temp. (°C)	Flow rate of Al(NO ₃) ₃ (ml/min)	Flow rate of Na ₂ CO ₃ (ml/min)	Na ₂ CO ₃ consumed (ml)	Al(NO ₃) ₃ consumed (ml)	pH	Aging time and temp. (°C)	Drying Temp. and time (°C)	Calcination °C /min heating rate- 1h °C - °C/min cooling rate	AlOOH/ γ-Al ₂ O ₃ g/g- % Yield
I	0.546	60	10	8	173	200	7.5	3h-60	100-16h	5-550-5	3.8/0.6 - 56
II	0.546	60	9/92	8	173	200	7.5	3h-60	100-16h	5-550-5	3.0/0.6 - 56
III	0.546	60	10	8	171	200	7	3h-60	90-16h	5-550-5	3.1/0.6 - 56
IV	0.546	70	10	8	175	200	8	3h-60	80-16h	5-550-5	4.0/0.8 - 75
V	0.546	70	10	6	173	200	7.5	3h-60	100-16h	5-550-5	3.6/0.7 - 66
VI	0.546	70	10	6	173	200	7.5	3h-60	100-16h	5-550-5	3.4/0.7 - 66
VII	0.546	70	10	6	175	200	8	3h-60	100-16h	5-550-5	4.0/0.8 - 75
VIII	0.546	70	10	6	177	200	9.5	3h-60	100-16h	5-550-5	3.5/0.6 - 56
IX	0.546	70	10	6	175	200	8	3h-60	100-16h	5-550-5	3.0/0.7 - 66
X	0.546	70	9	6	349	400	7	3h-70	100-16h	2-500-2	11.99/1.1 - 52
XI	0.546	70	9	6	350.7	400	8	3h-70	25-16h	2-500-2	12/1.8 - 84
XII	0.546	70	9	6	349.7	400	8	3h-70	25-16h	2-500-2	12/1.8 - 84
XIII	0.546	70	9	6	350	400	8.2	3h-70	25-16h	2-500-2	12/1.8 - 84
XIV	0.546	70	9	6	351	400	8.5	3h-70	25-16h	2-500-2	12.2/1.93 - 91
XV	0.546	70	9	6	351	400	8.5	3h-70	25-16h	2-500-2	12.2/1.93 - 91

Table 2: BET analysis results for the synthesized gamma alumina

Average Pore diameter by BJH adsorption method (Å°)	Average pore volume by cumulative BJH adsorption method (ml/g)	Specific surface area measured by cumulative BJH adsorption method (m ² /g)
34.48	1.624	413.8

Table 3: BET analysis results for the BASF gamma alumina catalyst (Kat. D10-10 S4)

Average Pore diameter (Å°)	Average pore volume (ml/g)	Specific surface area (m ² /g)
94.03	0.450	191.5

Table 4: Average pore volume and specific surface area for the nano gamma alumina of Akarmazyan (Akar) et al and Engelhard company (Engel) [16]

Catalyst	Average pore volume (ml/g)	Specific surface area (m ² /g)
Akar	2.13	346
Engel	0.78	202

could prepare nano gamma alumina. The specific surface area of the prepared nano gamma alumina was 346 cm²/g and the average pore volume was about 2.13 cm³/g.

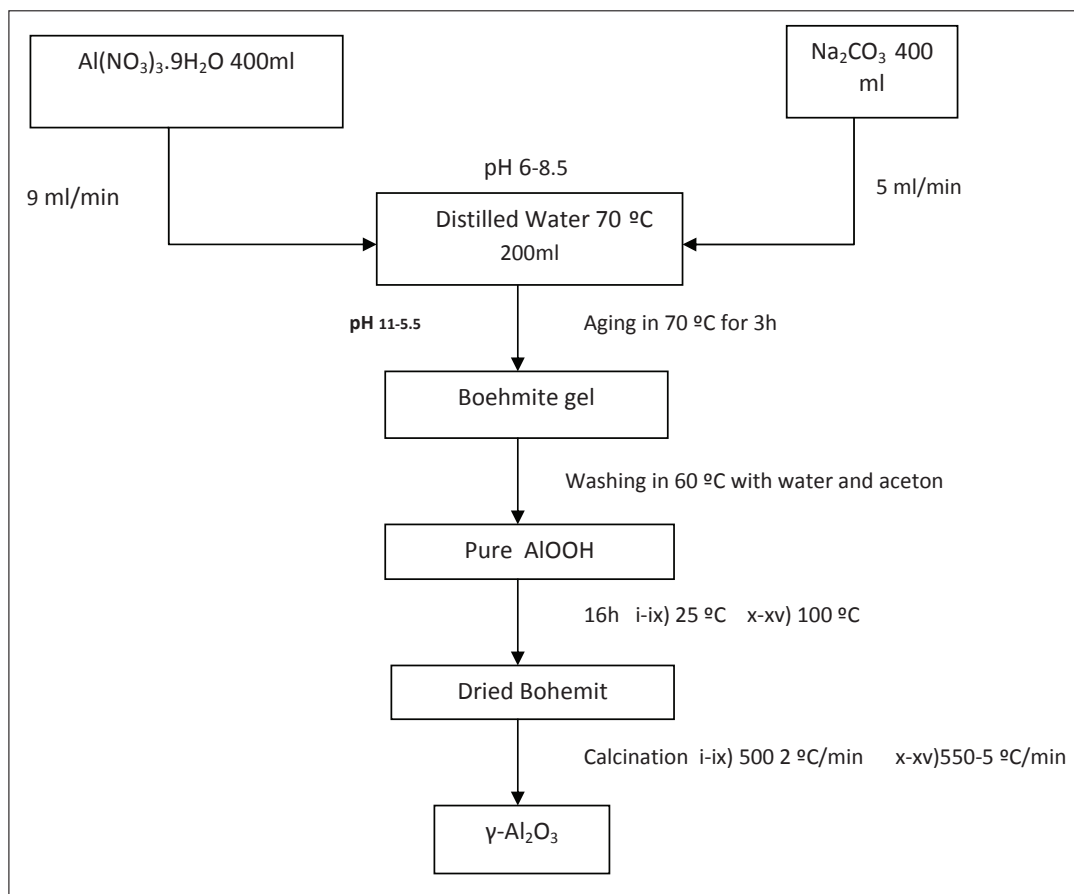
The aim of the current work is to use a simpler and feasible method for preparing nano sized gamma alumina with controlled morphology, in high yield and high specific surface area using low price starting materials without applying any special apparatus and special processes such as freeze drying. Another aim of the present work is to test the performance of nano structured gamma alumina produced by the proposed simpler method in dehydration reaction of methanol to dimethylether (DME). The study also aims to compare chemical properties of synthesized catalysts with a commercial sample which was provided by BASF company.

2. EXPERIMENTAL

All reagents and solvents such as Al(NO₃)₃·9H₂O (Merck, art No. 101063) and Na₂CO₃ (Merck, art No. 106392), were obtained from Merck Chem. Co. and were used without further purification. Commercial gamma alumina from BASF Company was used as reference. FT-IR spectra (400-4000 cm⁻¹) were recorded on a Philips PU 9624 made in Germany in a KBr matrix. Programmable furnace, Nabertherm 1700 made in Germany was used. A Pye-Unicam Spa Philips atomic absorption was used to determine the percentage of Al(III).

X-ray powder diffraction (XRD) measurements were performed with graphite monochromatic CuK_α (λ=1.54056 Å) radiation using a Philips diffractometer manufactured by X'pert. Crystallite

Scheme 1: γ-Alumina preparation flow chart



Scheme 1: Block diagram of boehmite and gamma alumina preparation.

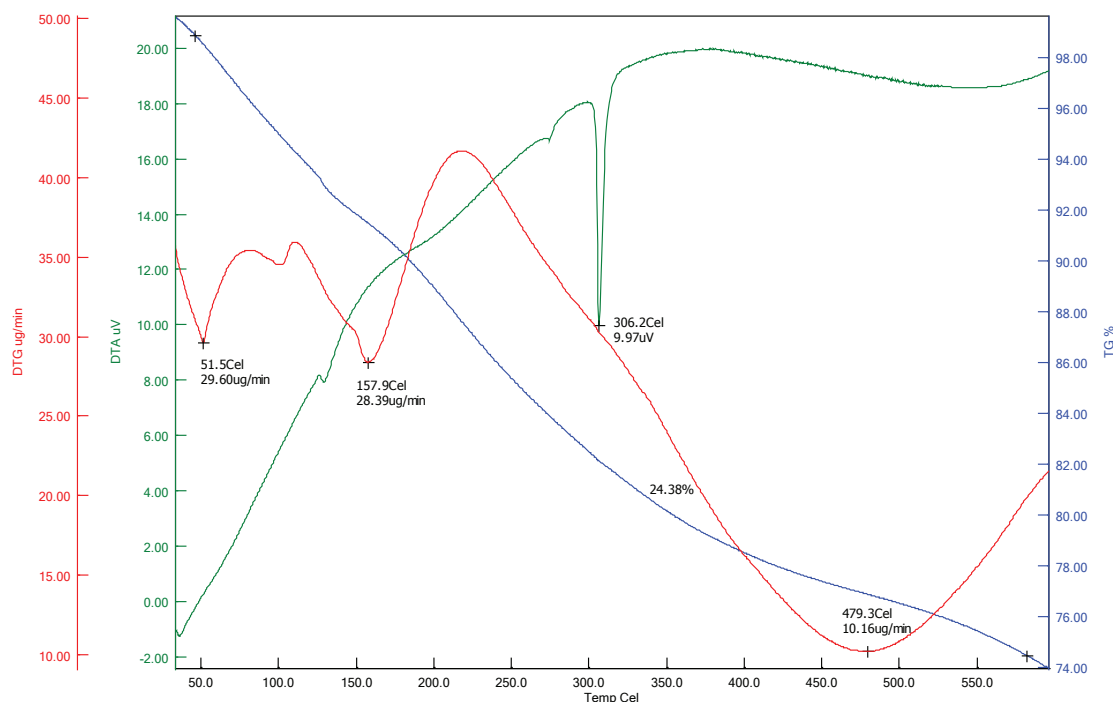


Figure 4: TG/DTA diagrams of dried boehmite at 100°C, 16h.

sizes of selected samples were estimated using the Scherrer method. The samples were gold coated for characterization with a scanning electron microscope. pH measurements were done by a pHmeter Orion 420 A made in Germany. De-ionized water was used for making solutions. Thermo gravimetric diffraction thermal analysis (TG-DTG) was carried out by using a thermal gravimetric analysis instrument (pyres, Diamond Thermo gravimetric).

The compounds were heated in a nitrogen atmosphere from 10-600°C controlling the heating rate of about 10°C/ min. The BET surface areas and pore volumes were estimated from nitrogen adsorption and desorption isotherm data on a Quantachrome Autosorb Automated gas sorption system. The pore volumes were determined at a relative pressure (P/P_0) of 2. The prepared samples of run 14 were degassed at 150°C for 298.2 min before measurements. The pore size distributions in prepared sample from run 14 (Table 1) were verified by a BJH (Barett-Joyner-Halenda) model from the adsorption branch of the nitrogen isotherms [14,16].

2.1. Preparation of gamma alumina

200 ml distilled water was heated to 70°C in a 2 liter round- bottomed double capped flask. Then $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (15.61 g, 0.041 mol) and $\text{Na}_2(\text{CO}_3)$ (7.95 g, 0.075 mol) were each dissolved in 400 ml distilled water separately. The aluminum nitrate solution was added to 200 ml deionized water by burette with a flow rate of 9 ml/min and along with the simultaneous addition of sodium carbonate solution at a flow rate of 6 ml/min.

The mixture was stirred vigorously to form an aluminum hydroxide gel. The temperature was kept at 70°C during the reaction. After precipitation happened, adding sodium carbonate was continued till the mixture attained a pH range of 8- 8.5. In all 350 ml of sodium carbonate was added to the round-bottomed flask. The produced colloidal solution was aged at 70°C while stirring constantly for 3 hours. The obtained gel was separated from the mixture by 4000 rpm centrifugation for 15 min. The pH of filtrate was 11. Then white gel was washed several times (20 min. each time) with de-ionized water at 70°C till pH of the filtrate attained a pH of about 5.5. After that the product was washed with acetone

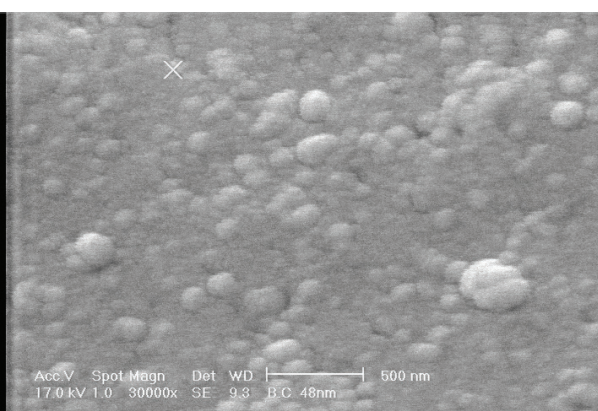
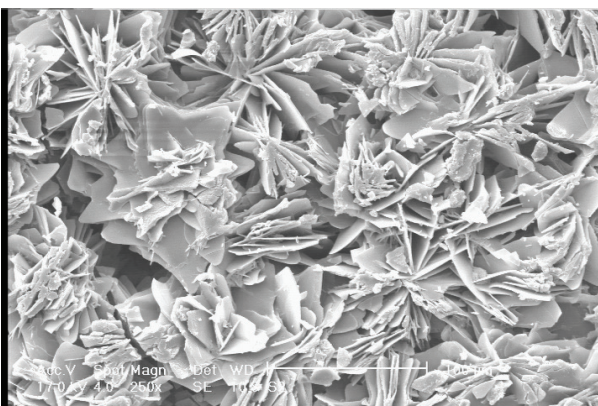
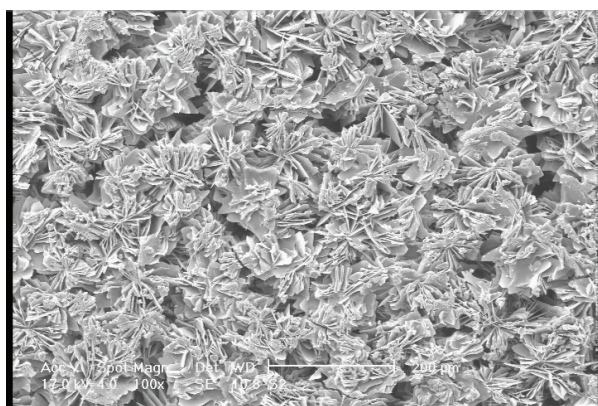


Figure 5: SEM images of boehmite-VII (Table 1) dried in 100°C, 16h.

and then dried in a desiccator at room temperature. The FTIR (KBr) spectrum showed selected bands in the range 400—4000 cm^{-1} for the dried sample as follows: 575.09 (sh), 747.12 (sh), 983.07 (m), 1384.78 (sh), 1641.68 (sh), 2091.11 (w), 2426.81 (w), 3467.38 (b).

The dried product was treated in a furnace by a programmed calcinations. The heating rate was

maintained at 2°C/min from room temperature up to 500°C and maintained at 500°C for 1 hour after which it was cooled to the ambient temperature maintaining a cooling rate of 2°C/min.

The resulting white powder gamma alumina (1.9 g) was prepared in 90% yield. The FTIR (KBr) spectrum selected bands in the range 400—4000 cm^{-1} for this sample were: 3436.52 (sh), 2924.96 (sh), 1640.02 (w), 783.72 (w).

Some of experimental conditions for preparing of nano gamma alumina are reported in Table 1. The reaction was run fifteen times, the molar ratio of boehmite of alumina, temperature reaction, flow rate of starting materials, pH, aging time and temperature, drying time and temperature, calcinations heating rate and cooling rate, boehmite and gamma alumina weight and yield of the reaction are tabulated in Table 1.

2.2. Catalyst testing

The gamma alumina catalysts made by the method mentioned in table 1, were tested for their activity in methanol to DME conversion. Dehydration of methanol for preparation of DME by using the synthesized catalyst was conducted in a stainless steel fixed-bed reactor with inner diameter 19 mm at atmospheric pressure.

A thermocouple was located inside the reactor tube, near the catalyst bed. Methanol and water mixture was pumped into the reactor at a controlled flow rate. Before entering the feed into the reactor, the mixture was preheated up to 150°C. The gases at the outlet of the reactor were taken out intermittently with the aid of a sampler directly connected to the system and analyzed on-line by gas chromatography (Teif Gostar, Iran) with a TCD and a packed column (Molecular Sieve 5A). Reaction data were reported after about 4 h when the steady state conditions were obtained for each temperature. A schematic view of the experimental setup is shown in Figure 1.

3. RESULTS AND DISCUSSION

In the present study boehmite was prepared by the reaction between aluminum nitrate and sodium carbonate at 70°C, followed by aging at 70°C for 3 hours (Scheme 1 shows a block diagram of boehmite

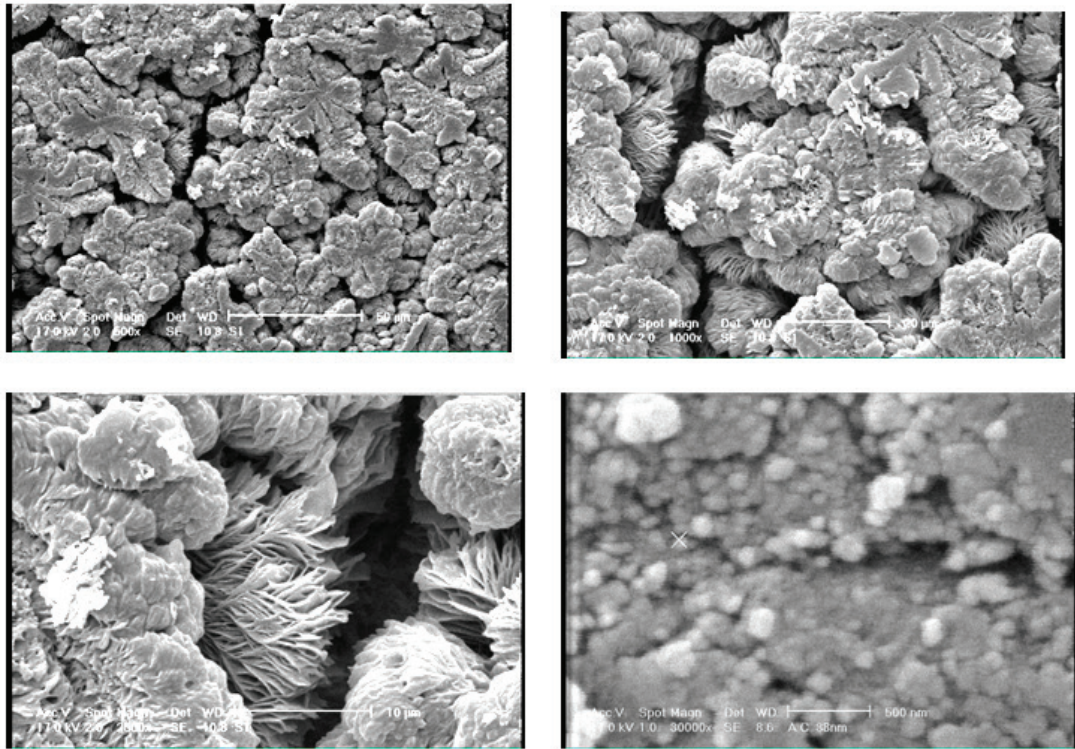


Figure 6: SEM images of gamma alumina-VII (Table 1) calcinated in 550.

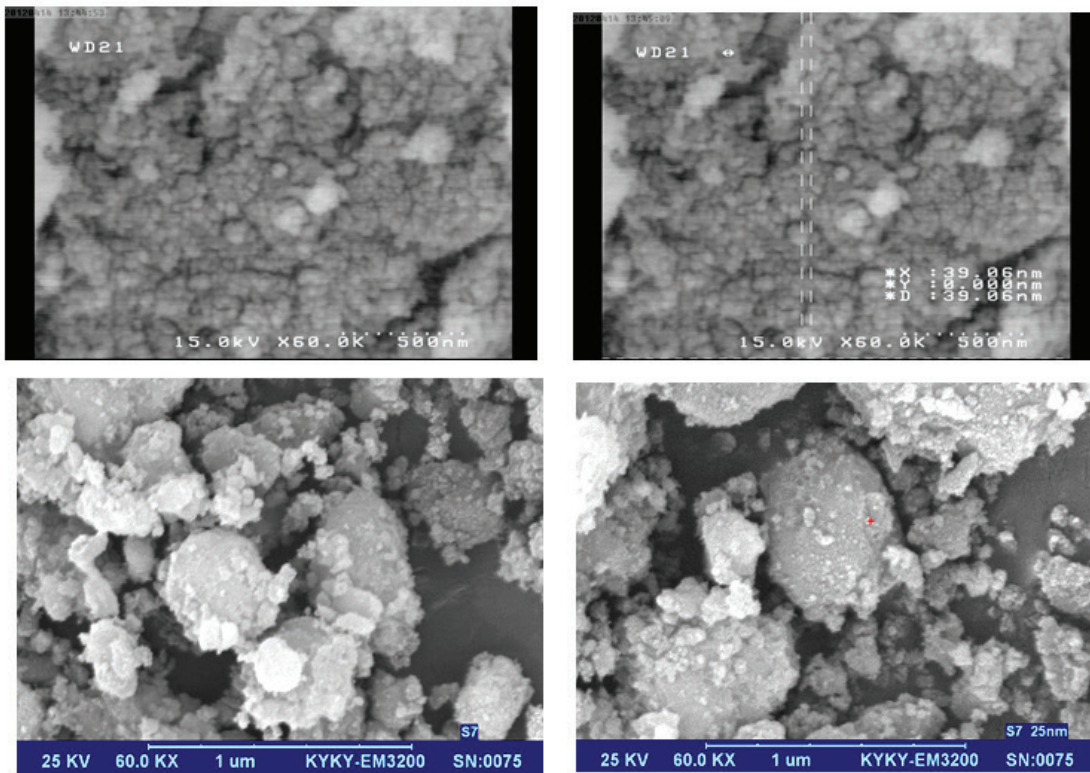


Figure 7: SEM images of (a) gamma alumina-VX (Table 1) calcinated in 500, (b) commercial sample of BASF.

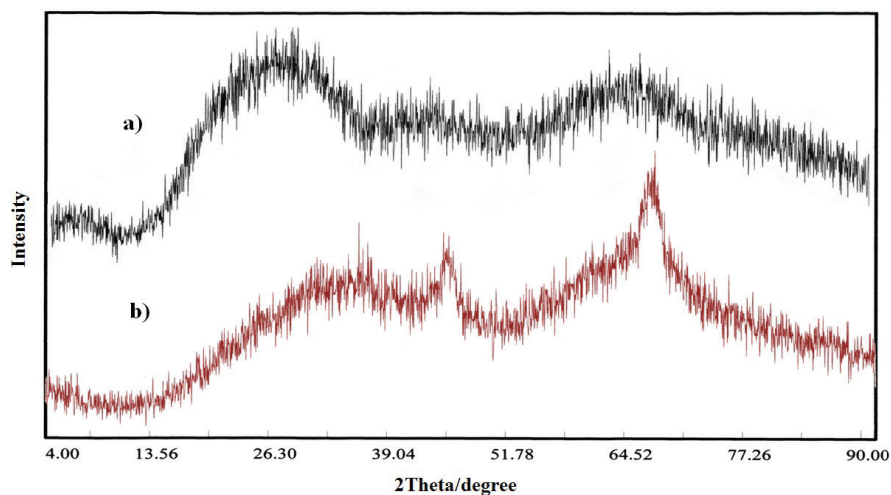


Figure 8: XRD pattern of (a) synthesized boehmit-VII (Table 1) as dried in 100°C, 16h and (b) nano gamma alumina produced by calcinations in 550°C.

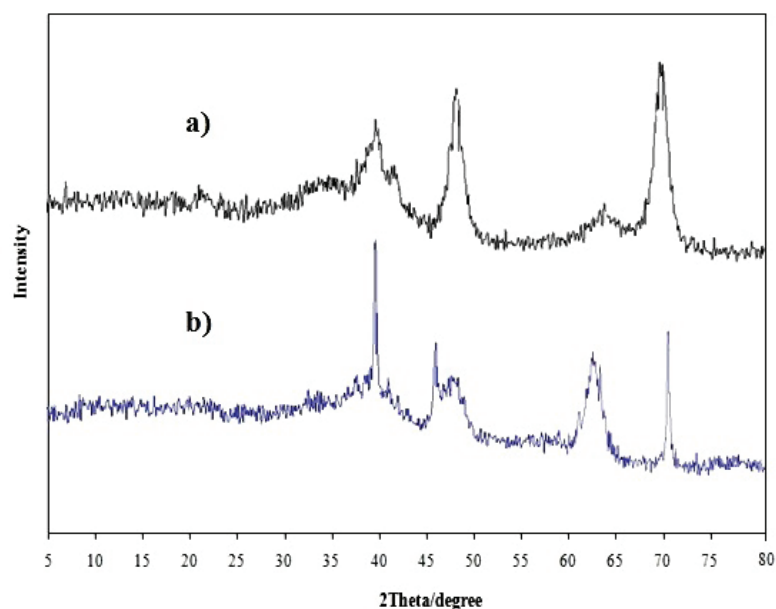


Figure 9: XRD pattern of (a) commercial gamma alumina from BASF and (b) gamma alumina prepared from run VX.

and gamma alumina production). Aluminium hydroxide was precipitated in the 6-8.5 pH range and then digested to obtain boehmite precursor. After washing the resulting white gel with hot water and acetone, it was followed by centrifugation. It was observed that the filtrate solution changed during the process of washing from a pH of 11 to pH of

5.5. Elemental analysis and FTIR studies showed that no sodium and carbonate ions were presented in the product when pH of the filtrate reached 5.5. The results obtained by atomic absorption analysis showed that the Al(III) was in the form of AlOOH. Figure 2 shows energy-dispersive X-ray analysis of dried boehmite after keeping for 16 h at 100°C.

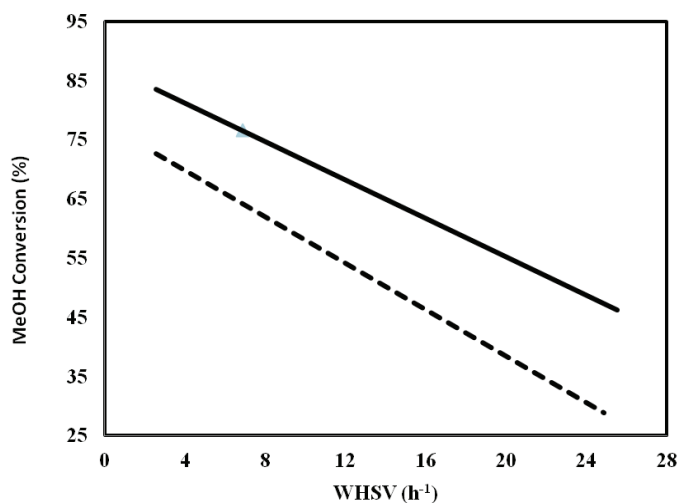


Figure 10: Trend of methanol conversion at 250°C (dashed line) and 300°C (solid line) versus WHSV.

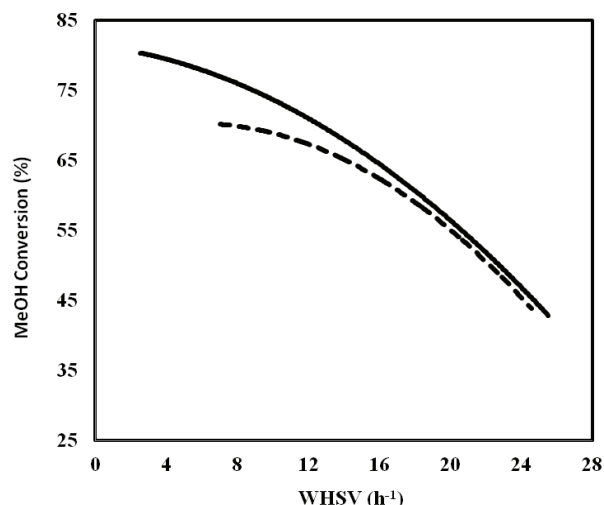


Figure 12: Comparison between the trends of methanol conversion versus WHSV at 300°C for commercial catalyst (dashed line) and the catalyst which is synthesized in this work (solid line).

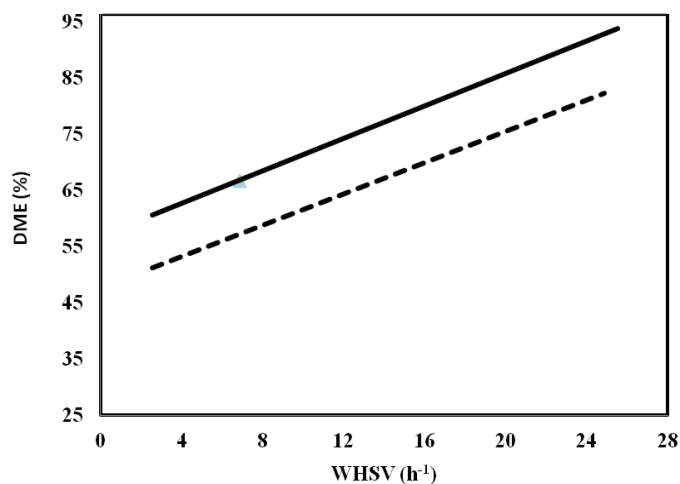


Figure 11: Trend of DME mass percents at gas phase reaction product at 250°C (dashed line) and 300°C (solid line) versus WHSV.

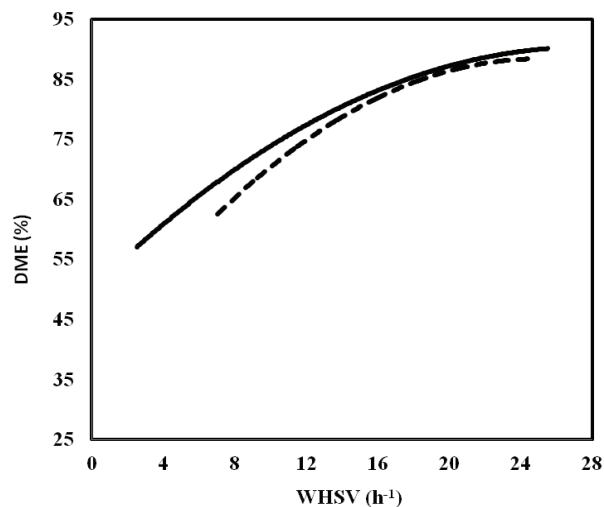


Figure 13: DME percent in gas phase of reaction product by using commercial catalyst (dashed line) and the nano-catalyst of this work (solid line) at 300°C.

It confirms the presence of aluminum and oxygen only. No signal corresponding to sodium atom was present. As shown in Figure 3, a strong and wide band at 3600 to 3400 cm^{-1} and also a weak band at 1641 cm^{-1} may be due to adsorbed water. The peaks in the ranges of 1490-1410 cm^{-1} and 880-860 cm^{-1} were missed, confirming that the product

aluminium oxy hydroxide [14, 17] does not contain any carbonate ions (CO_3^{2-}). Formations of bohemite and gamma alumina were confirmed by the FTIR spectrum of the prepared samples. Figure 3 shows the FTIR spectrum of dried bohemite, new synthesized gamma alumina and commercial gamma alumina from BASF Co. After

the calculation process on boehmite, the vibrational bands due to nitrate or hydroxide ion at 1384 cm^{-1} was removed completely. Appearance of vibration bands in the range of 800 to 890 cm^{-1} shows a phase transition and tetrahedral pore formation in the studied sample, which were not in bohemite sample. The thermal behavior of dried boehmite precursor was studied by TG/DTA analysis which is shown in Figure 4.

There are two small endothermic mass losses at 51.5°C and 157.9°C and a major exothermic mass loss is observed in the DTA curve at 479°C . Two small endothermic weight losses may be due to removal of physically adsorbed water and/or acetone. The broad exothermic curve may be attributed to the crystallization transition of alumina. A total mass loss of 24.38% occurs in three steps, showing that decomposition of aluminium hydroxide to alumina has not occurred, as otherwise total mass loss should be 34.62% . It can be concluded that aluminium oxyhydroxide is decomposed to gamma alumina, as mass loss should be lower than 15% . This additional 9.38% appears to be due to the presence of water/acetone in the precursor.

Figure 5 shows the SEM micrographs for dried boehmite at 100°C . It is showing flower like sheets of boehmite containing spherical particles with sizes of around 48 nm . Figure 6 indicates that gamma alumina has the same morphology as boehmite precursor; it is a flower like sheets and the width of each plane is about 100 - 500 nanometer containing spherical particles about 38 nm .

The images were prepared from the obtained samples before and after calcinations from reaction run VII (see table 1). Figure 7 shows SEM images of gamma alumina produced by the reaction XV (Table 1) in which boehmite was calcinated at 500°C , with a heating rate of $2^\circ\text{C}/\text{minute}$ and commercial sample of BASF. The gamma alumina particles from reaction XV are about 39 nm and spherical in shape. The commercial sample indicated agglomeration of particles with varied sizes. The images show a surface with high porosity.

For studying of impurities in the samples, EDAX spectra were prepared. The data did not indicate the presence of any impurities (specially, sodium ion) in the samples.

Figure 8 (a) shows the X-ray diffraction patterns of powder obtained by reaction VII (see Table 1) as dried boehmite in 100°C and (b) nano gamma alumina produced by calcination in 550°C . The pattern of X-ray diffraction confirms the presence of boehmite and alumina. The patterns indicate the formation of very low crystallinity boehmite and alumina, since broad peaks are observed.

Figure 9 (a) shows XRD pattern of the commercial gamma alumina from BASF, and Figure 9 (b) indicates the XRD patterns of calcined boehmite precursor at 500°C , with heating rate of $2^\circ\text{C}/\text{min}$ in ambient atmosphere (run XV in Table 1). The broadening of the XRD peaks confirms the nano-size nature of gamma alumina particles in the samples. The crystallinity of gamma alumina produced by run XV is more than the one produced by run VII, as the peaks are much sharper in Figure 9.

Recently a commercial nano-sized acidic gamma-alumina catalyst was prepared and 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 [18].

In this work, temperature and space velocity effects were considered on conversion of methanol to DME. Experiments were done at 250 and 300°C and at different weight hourly space velocity (WHSV). Figure 10 shows the obtained results at different WHSV at 250 and 300°C .

On the other hand, the effect of temperature on gas phase product components was investigated. The obtained results show that the percentage of DME in the gas phase increased with increases in the reaction temperature and also WHSV. The obtained results are shown in Figure 11.

The efficiency of the synthesized catalyst was compared with a commercial gamma alumina catalyst, namely gamma alumina which was procured from BASF Company (Kat. D10-10 S4). BET analysis of Kat. D10-10 S4 is reported in Table 3. Also, pore volume and specific surface area of another commercial catalyst from Engelhard company and a nano gamma alumina catalyst which

was prepared by sol gel method by Akarmazayan *et al.* [16] are reported in Table 4. By comparing the results which are reported in Tables 2-4, it can be seen that the specific surface area of gamma alumina which is prepared in this work is more than the three other catalysts.

The comparison between the variations of methanol conversion versus WHSV at 300°C for commercial catalyst and the synthesized catalyst is shown in Figure 12. According to the results tabulated, methanol conversions using nano-sized catalyst of this work is higher than commercial catalyst. But, by increasing WHSV (decreasing residence time) the methanol conversions tend to similar value for both of reactions. On the other hand, DME mass percents in gas phase product of nano-sized catalyst of this work are better than that obtained using commercial catalyst. The obtained data for this result are shown in Figure 13.

5. CONCLUSION

Nano sized gamma alumina was prepared by the reaction between aluminium nitrate and sodium carbonate using the precipitation / digestion method. The results showed that optimum conditions for boehmite and gamma alumina preparation in high yield and with high specific surface area are pH 8.5, reaction temperature 70°C, aging temperature 70°C, removal of impurities by washing and then centrifuging instead of using filter paper, drying boehmit gel at room temperature and then calcination in 500°C with heating rate of 2°C/min, keeping for 1 hour at 500°C and cooling at the rate of 2°C/min.

The yield of gamma alumina recorded using the described method was 91%. The end point step of the purification was obtained by pH measurement. Gamma alumina particles were spherical in shape with about 39 nanometer diameter. FTIR and EDAX analyses show that carbonate and sodium ions were removed completely from the gamma alumina product.

X-ray diffraction pattern confirmed formation of the boehmite and gamma alumina. The average pore diameter of the catalyst was 34.48Å, mean size of

pore volumes was 1.624ml/g and specific surface area of the catalyst was 413.8m²/g.

Process evaluations of the synthesized catalyst at 250 and 300°C show that at higher reaction temperature, more DME component was present in the gas phase. Thus the methanol conversions improved at increased temperature. The synthesized gamma alumina yielded higher DME mass percent in the gas phase in comparison with commercial catalysts of BASF Company.

ACKNOWLEDGMENT

This work is financially supported by Iranian National Science Foundation (INSF). Authors thanks Iranian Research Organization for Science and Technology (IROST) for their helps and special thanks to Mrs. Niloofar Naseri and Mrs. Zeinab Fadavi for doing some of the experiments. Also, the authors thank BASF Co., Germany and Iran, for providing the commercial catalyst.

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