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Hollow alumina nanospheres as novel catalyst for the conversion of methanol to dimethyl ether

N. Rostamizadeh[1], **M. S. Sadjadi**[1,*], **S. A. A. Sadjadi**[2]

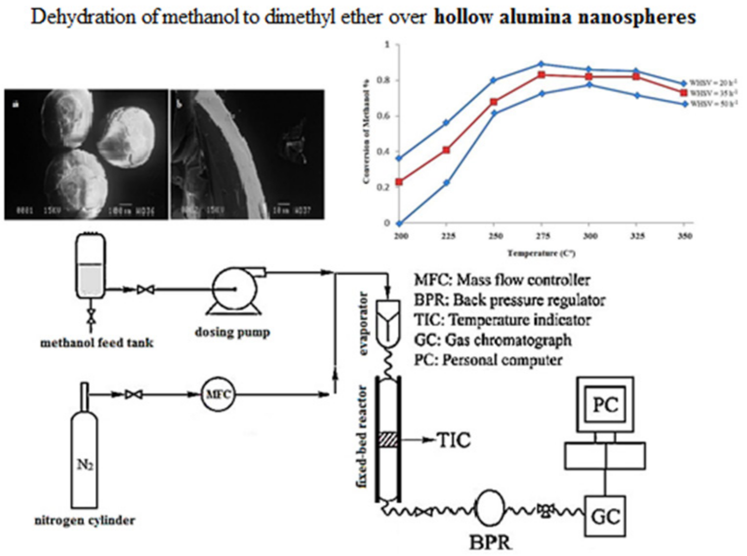
[1] *Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, I. R. Iran*

[2] *Institute of Water and Energy, Sharif University of Technology, P.O. Box 11365-8639, Tehran, I. R. Iran*

HIGHLIGHTS

- Hollow and porous alumina nanospheres were prepared by integrating techniques of microemulsion and templating.
- The prepared samples were used as catalyst for conversion of methanol to DME.
- Effect of acidity, temperature and WHSV on performance of the catalysts wasinvestigated.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper investigates hollow and porous alumina nanospheres that were previously synthesized to be used for the dehydration of methanol to dimethyl ether (DME). As hollow nanostructures possess characteristics such as low density and high surface to volume ratio, their catalytic activity between hollow and porous structure is compared. For this purpose, three most important parameters (acidity, temperature and weight hourly space velocity (WHSV)) affecting the performance of these catalysts were investigated. The catalysts were characterized by scanning electron microscopy (SEM), BET, X-ray diffraction (XRD), and the temperature programmed desorption of ammonia (NH_3-TPD) techniques. Results show that the optimum operating condition for hollow alumina nanosphere can be achieved at temperature of 275 ºC and WHSV of 20 h^{-1} compared with operating condition for porous alumina at temperature of 325 ºC and WHSV of 20 h^{-1}.

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* *Corresponding author. Tel.:+98 2122285032; fax: +98 2122285032*
E-mail address:m.s.sadjad@gmail.com

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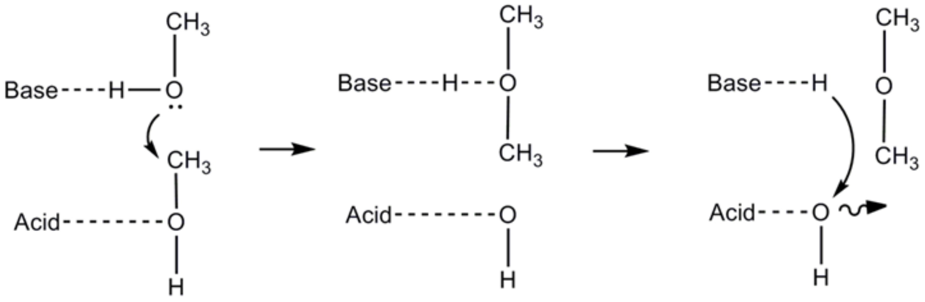
1. Introduction

Application of dimethyl ether (DME) as a fuel and fuel additive for use in diesel engines has been investigated due to its high volatility, high cetane number, lower NOx and smoke emissions and lower engine noise. In addition to alternative fuel, DME can also be used as feed stock to many products such as short olefins (ethylene and propylene), gasoline, hydrogen, acetic acid and dimethyl sulphate [1-4]. It can also be used a substitute for Liquefied Petroleum Gas (LPG) because of having similar properties. Its major technical advantages coupled with its environmentally-friendly nature of the DME have attracted the attention of various planners to design and construct the DME plants [5-9]. DME can either be produced by direct synthesis from syngas ($CO/H_2/CO_2$) in a single step [10-14], or indirect synthesis by conventional bimolecular catalytic dehydration of methanol over various solid acids [15–18]. As conditions of the two consequent reactions are similar, these can be conducted simultaneously in the same reactor over a bifunctional catalyst. The direct method, known as syngas to dimethyl ether (STD) process is a single-step vapour phase having three reactions. The combination of reactions affects the methanol production equilibrium. One of the disadvantage of this process is that high operating conditions cause more by-product synthesis, which in return, requires more complex distillation in order to separate the reactor effluent to achieve high purity DME [19-20]. For these fundamental reasons, more focus has recently been made on methanol dehydration process and dimethyl ether purification.

Dehydration of methanol to DME can be achieved by employing solid-acid catalysts such as γ-alumina and zeolite. The catalytic activity of solid-acid for methanol dehydration is linked to Lewis acid-Lewis base pair formed during calcination [7-11]. A mechanism involving an acid-base pair in methanol dehydration is proposed by Padmanabhan and Eastburn (1972):



Among solid acid catalysts, γ-alumina is commercially preferred due principally to its fine particle size, high surface area, excellent thermal stability, high mechanical resistance and low cost catalyst to mention a few examples [4-6].

Much of the research work in the last decade has been devoted for preparation dense nanoparticles. Hollow nanomaterials have become the focus of investigations because of their great application potentials such as the confined nanoreactors in drug delivery and catalytic purpose [21-23]. Among these category materials, hollow γ-Al_2O_3 nanosphere has been favoured because of its very large specific surface area and low density makes it appropriate for catalytic usage [24-25].

Two samples of alumina nanosphere are used in this study as the catalysts for the dehydration of methanol to DME. The principal effects of preparation method on the morphology, acidic properties and catalytic activity of γ-alumina samples have been investigated.

2. Experimental

2.1. Catalyst preparation and characterization

Two catalyst samples, hollow and porous alumina nanospheres, were prepared by integrating two techniques of microemulsion and templating process. These were based on the procedure described in our previous work [26]. In line with this, the alginate hydrogels was prepared by microemulsion method, and was subsequently used as templates for the formation of core-shell structures of aluminum-alginate. Hollow and porous alumina nanospheres were then obtained in the presence and absence of ammonia referred to here as Al-B and Al-A catalysts respectively.

The powder XRD pattern was recorded on PW1800 Philips Diffractometer using Cu Kα radiation (λ=1.5418Å) to characterize crystalline structure of the prepared samples.

A scanning electron microscope (S-360) was used to show hollow structure, shell thickness and finally surface morphology. The BET technique measures surface area, pore size and pore volume of the products, using Quanta chrome instrument (Model Nova 2000). The analysis of temperature programmed desorption of ammonia (NH_3-TPD) was performed in order to determine the acidic sites on the catalysts using BEL- CAT (type A, Japan) instrument. The methodology involved initially flushing about 0.1 g of the sample with a He under the flow rate of 50 ml/min for 2h at 500 ° C. It was then cooled to 100 ° C and subsequently saturated with NH_3. After exposing NH_3, the sample was purged with He until the initial excess of NH_3 is removed. The sample was then heated under the flow of the carrier gas from 100 °C to 500 °C and the amount of ammonia in effluent was measured via thermal conductivity detector (TCD).

2.2. Catalytic performance tests

The schematic diagram of the used set up is shown in Fig. 1. The gas phase dehydration of methanol was carried out in a stainless steel fixed-bed microreactor (inner diameter = 0.8 cm and length = 20 cm). Prior to experiments, the catalyst was pretreated for 2h at 350 °C under a N_2 flow. The liquid methanol was fed into the reactor using a dosing pump. The reaction was carried out with N_2 as a carrier gas at atmospheric pressure, in the temperature range of 200–350 °C and in the weight hourly space velocity range of 20-50 h^{-1}. Reactor consists of two heating zones. The first is to raise the feed temperature to the desirable level and the second to maintain the reactor surrounding at the proper temperature in order to minimize heat losses and simulate an adiabatic reactor. The effluent of the reactor was analyzed on a gas chromatograph (GC) equipped with a flame ionization detector connected with a capillary column.

3. Results and discussion

3.1. Morphological study

Fig. 2a,b shows SEM images of hollow γ-alumina nanosphere prepared in the alkaline condition (Al-B) and then calcined at 650 °C. The shell thickness image of the sample after nanosphere breaking technics (Fig. 2b) confirms successful formation of hollow γ-alumina nanosphere with ca. 400-500 nm in diameter, and 20 nm in thickness.

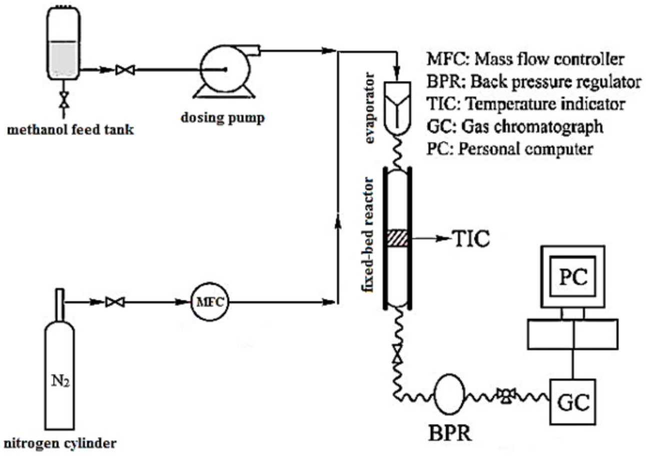


Fig. 1. Schematic view of experimental setup.

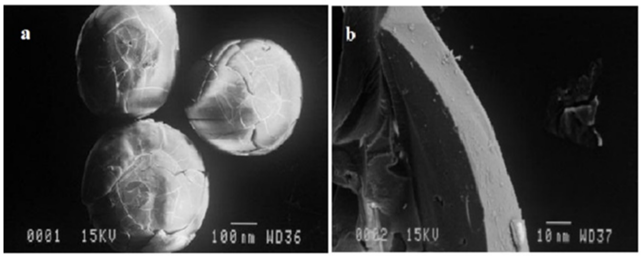


Fig.2. SEM images of hollow γ-alumina nanosphere prepared in alkaline medium, a) after calcination at 650 °C for 3 hours; b) shell thickness image after breaking of nanosphere

Fig. 3c,d represents SEM images of the samples prepared in the aforementioned techniques but in acidic condition (Al-A). The powder obtained after breaking of nanosphere (Fig.3d) indicates formation of γ-alumina nanosphere with ca. 450 nm in diameter. Based on this observation, yielding a large volume nanosphere and powder after breakage suggest that the synthesized sample in acidic condition may not favored formation of hollow γ-alumina nanosphere.

3.2. BET study

From data obtained using BET technique as seen in Table 1, get about surface area, average pore size and total pore volume of the samples. The specific surface area for the samples (Al-B) and (Al-A) was found to be 226.02m^2/g and 196.15m^2/g respectively.

The N_2 adsorption and desorption isotherm is of type IV, as is seen from Fig. 4a,b. According to IUPAC classification [27], the Al-B sample has a hysterics loop of type 1 (H1) that indicates a narrow pore size distribution with uniform size and shape (Fig.

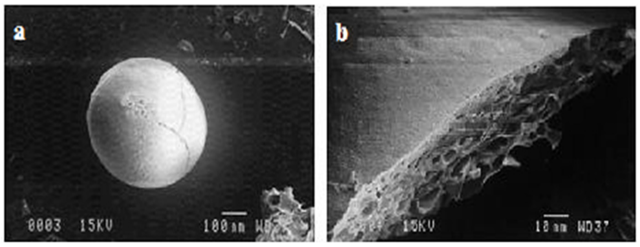


Fig. 3. SEM images of γ-alumina nanosphere prepared in acidic medium , a) after calcination at 650 °C for 3 hours; b) porous powder image after breaking of nanosphere

5a). The Al-A sample has a hysterics loop of type 2 (H2) that suggests a broad pore size distribution (Fig. 5b).

3.3. X-ray structural study

Fig.6. represents the diffraction pattern of as prepared alumina nanosphers obtained after calcination at 650 °C compared with those of standard γ-alumina. The three peaks at $2\Theta=37.8$, $2\Theta=45.7$ and $2\Theta=66.9$ are assigned to (311), (400) and (440) reflection plans of γ-Al_2O_3. JCPDS file number 29-0063 and JCPDS file no.10-0425 can be assigned to cubic γ-Al_2O_3. Cubic γ–alumina has a defect cubic spinel structure in which Al (III) ions occupy both octahedral and tetrahedral positions where the relative partial occupancy in each position is still a matter of dispute [28, 29]. According to the Scherrer equation, the crystalline size of the prepared nanosphere is ca. 14.18 nm.

3.4. Temperature-programmed experiments

NH_3-TPD measurements are performed to determine the acid strength and the amounts of acid sites on the catalyst surface. Desorption peaks in the range of 180−250 °C, 260−330 °C, and 340−500 °C in the NH_3-TPD profiles are commonly attributed to NH_3 that has been chemisorbed on weak, moderate and strong acid sites, respectively [30]. The NH_3-TPD spectra Fig. 7 of the synthesized γ-alumina nanosphere catalysts contain an intense peak in 175°C (I)

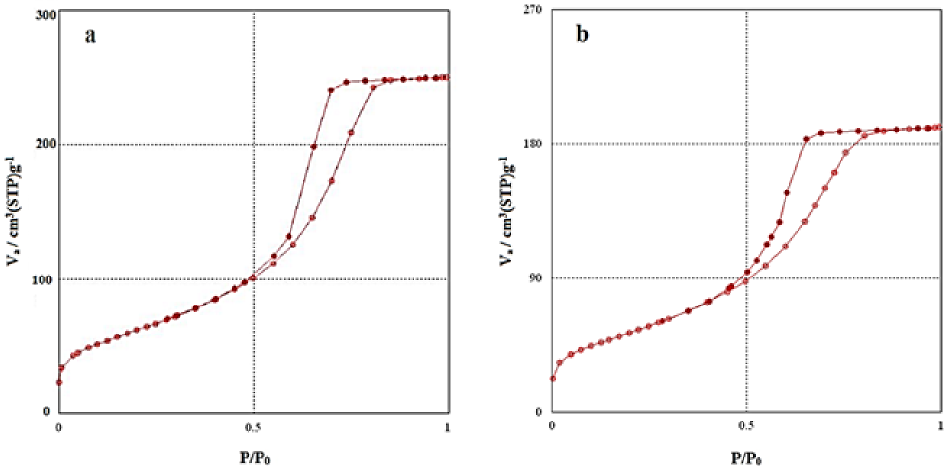


Fig. 4. N_2 adsorption and desorption isotherms, a) Al-B catalyst, b) Al-A catalyst

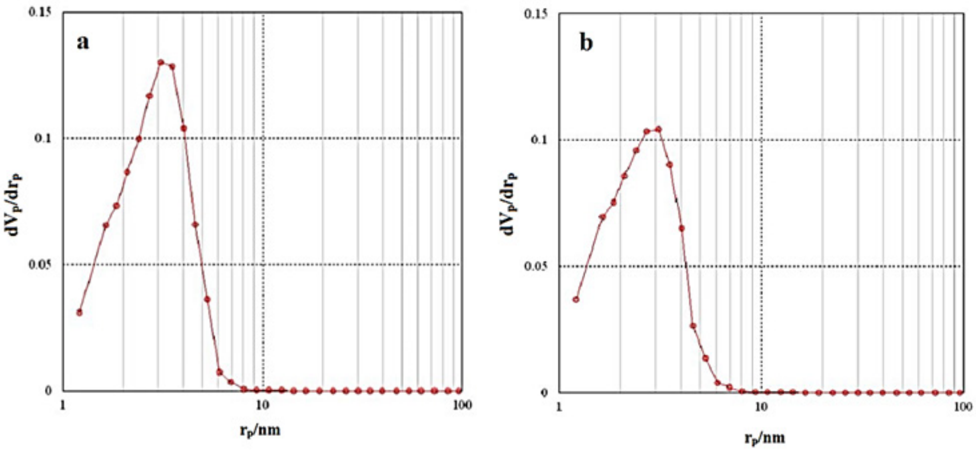


Fig. 5. BJH pore size distribution, a) Al-B catalyst, b) Al-A catalyst

Table.1. BET and NH3-TPD data for catalysts samples

Samples prepared	Specific surface area (m^2/g)	Pore size (nm)	Total Pore volume (cm^3/g)	Totalacidicsite(μmolNH3/g)
(Al-B)	226.25	6.8332	0.3865	741
(Al-A)	196.15	6.184	0.2951	586

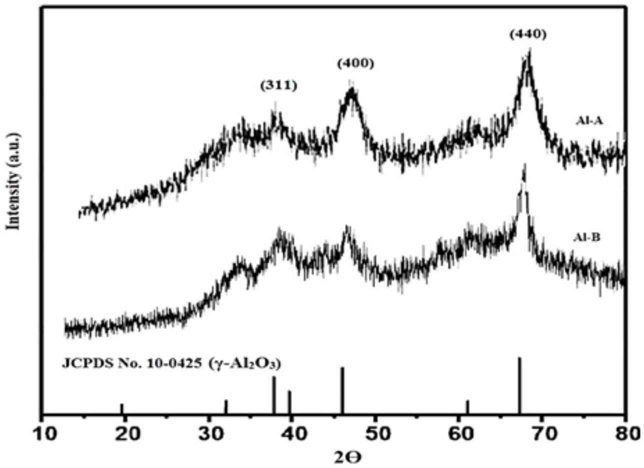


Fig. 6. XRD pattern of the as prepared hollow and porous γ-alumina nanosphere compared with standard γ-alumina

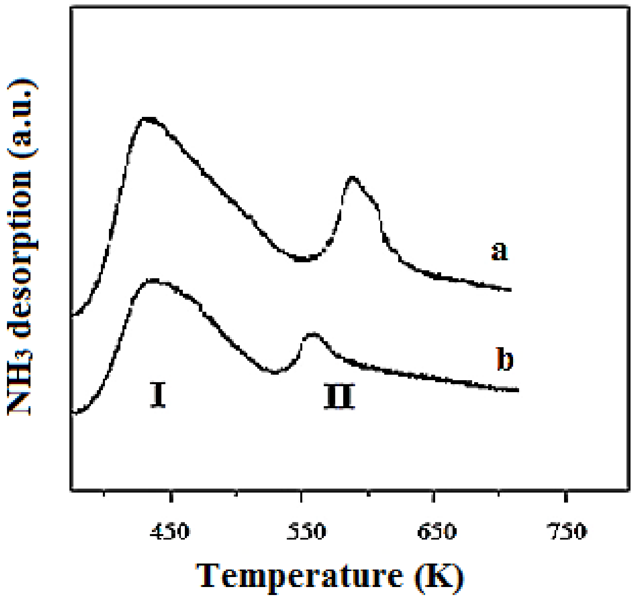


Fig. 7. NH_3-TPD profile a) Al-B catalyst, b) Al-A catalyst

and 325 (II) .This peak was slightly reduced in the temperature range of 200–500 ºC that corresponds weak to medium acid sites. Data obtained using NH_3-TPD technique as seen in Table 1.

3.5. Catalytic activity

Experimental conversions of methanol are depicted in table 2, 3 and figure 8,9. Equation 1 bellow was used to measure the conversion of feed methanol (X, %).

$$X_{MeOH}\% = [\ 1- \frac{\quad}{\quad}\ ] \times 100 \qquad (1)$$

Based on the data shown in the above tables, it was found that the A1-B catalyst has a relatively better performance than Al-A catalyst. This means that the greatest A1-B catalyst conversion has 89% occurred on temperature 275 ºC, while the maximum Al-A catalyst conversion has 81% occurred on temperature 325 ºC.

The performance variation of the two catalysts based on two important parameters of temperature and WHSV are to be discussed later in the paper.

3.5.1. WHSV:

WHSV is an important factor in controlling and optimising the catalyst performance. This is because from one hand the increase in WHSV increases the input feed and decreases feed contact time with the catalyst [31].

Under the circumstances where WHSV decreases the conversion time increases. The most important limitation factor is the catalyst amount. The reaction prior to reaching the equilibrium and at low temperatures is to a great extent depends on WHSV. This dependency tends to decrease on the equilibrium point due to the temperature increment that in turn, compensates the WHSV [32].

The experimental data of this study are clear demonstration of this. The optimum WHSV for both catalysts as the experimental data suggest is 20 h^{-1}.

3.5.2. Temperature

The dehydration reaction from methanol is an exothermic reaction (Equation (2)). Research findings show that temperatures higher than 525 ºC have an undesirable effect on reaction, because ΔG^0 takes positive values [33]. The optimum reaction temperature for the Al-B catalyst was observed to be at 275 ºC which compared with Al-A catalyst having a temperature of 325 ºC has a more appropriate operational condition.

$$2CH_3OH \leftrightarrows CH_3OCH_3 + H_2O \qquad (\Delta H = -24\ kJ/mol) \qquad (2)$$

Table.2. Experimental data for dehydration of methanol over Al-B catalyst

Temperature (ºC)	**WHSV = 20 h^{-1}**	**WHSV = 35 h^{-1}**	**WHSV = 50 h^{-1}**
	Conversion %	Conversion %	Conversion %
200	0.36	0.23	0
225	0.56	0.41	0.23
250	0.80	0.68	0.62
275	0.89	0.83	0.73
300	0.86	0.82	0.78
325	0.85	0.82	0.72
350	0.78	0.73	0.67

Table.3. Experimental data for dehydration of methanol over Al-A catalyst

Temperature (ºC)	**WHSV = 20 h^{-1}**	**WHSV = 35 h^{-1}**	**WHSV = 50 h^{-1}**
	Conversion %	Conversion %	Conversion %
200	0	0	0
225	0.11	0	0
250	0.34	0.18	0.09
275	0.49	0.41	0.29
300	0.66	0.63	0.48
325	0.81	0.82	0.63
350	0.77	0.76	0.62

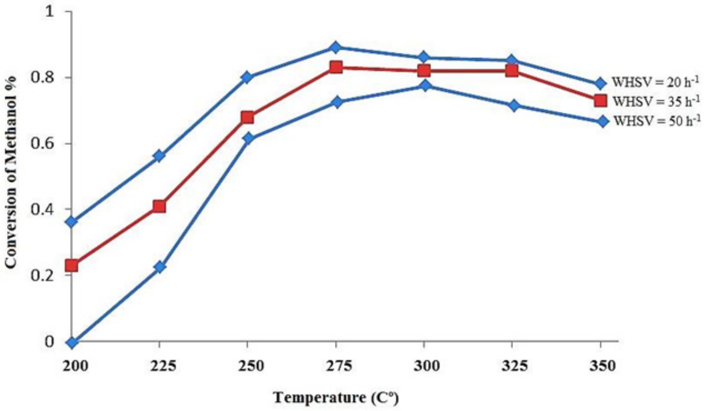


Fig. 8. Conversion of methanol as a function of reaction temperature profile obtained over Al-B catalyst

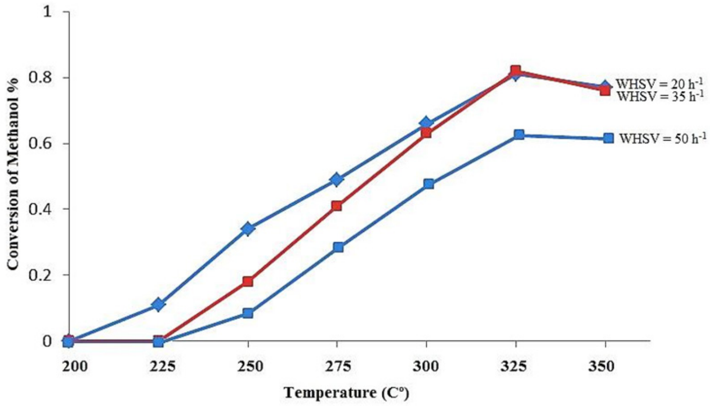


Fig. 9. Conversion of methanol as a function of reaction temperature profile obtained over Al-A catalyst

4. Conclusions

Two synthetic samples, porous and hollow γ-Al_2O_3 nanospheres were applied to successfully synthesize DME from methanol. Quite desirable results were obtained in the process. This was particularly the case for the Al-B which having a higher rate of conversion at the relatively lower temperature compared with the commercial dimethyl ether synthesis samples provided by Engelhand، Sasol and Akzo Nobel as shown in Fig. 10 [34].

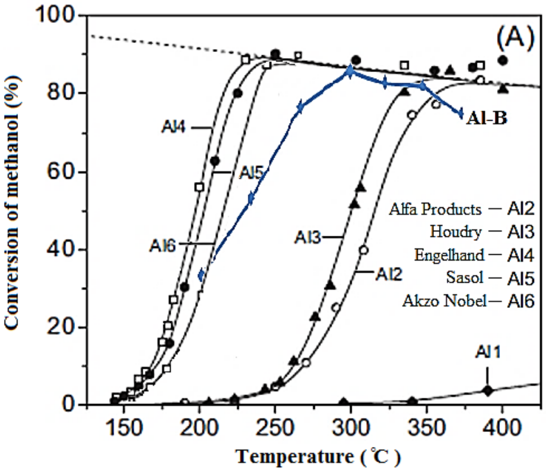


Fig. 10. Optimum conversion of methanol to DME over Al-B catalyst compared with commercial catalysts

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References

[1] G. Cai, Z. Liu, R. Shi, C. He, L. Yang, C. Sun, Y. Chang, Light alkenes from syngas via dimethyl ether, Appl. Catal. A. 125 (1995) 29-38.

[2] M. Xu, J. M. Lunsford, D.W. Goodman, A. Bhattacharya, Synthesis of dimethyl ether (DME) from methanol over solid-acid catalysts, Appl. Catal. A. 149 (1997) 289-301.

[3] T. Takeguchi, K. Yanagisawa, T. Inui, M. Inoue, Effect of the property of solid acid upon syngas-to-dimethyl ether conversion on the hybrid catalysts composed of Cu–Zn–Ga and solid acids Appl. Catal. A: Gen. 192 (2000) 201-209.

[4] A.M. Arkharov, S.D. Glukhov, L. V. Grekhov, A. A. Zherdev, N. A. Ivashchenko, D. N Kalinin, Use of Dimethyl Ether as a Motor Fuel and a Refrigerant, Chem. Petrol. Eng. 39 (2003) 330-336.

[5]. Q. Ge, Y. Huang, F. Qiu, S. Li, Bifunctional catalysts for conversion of synthesis gas to dimethyl ether, Appl. Catal. A. 167 (1998) 23-30.

[6] F. Yaripour, F. Baghaei, I. Schmidt, J. Perregaard. Synthesis of dimethyl ether from methanol over aluminium phosphate and silica–titania catalysts, Catal. Commun. 6 (2005) 542-549.

[7] J. Fei, Z. Hou, B. Zhu, H. Lou, X. Zheng, Synthesis of dimethyl ether (DME) on modified HY zeolite and modified HY zeolite-supported Cu–Mn–Zn catalysts, Appl. Catal. A. 304 (2006) 49-54.

[8] J. Xia, D. Mao, B. Zhang, Q. Chen, Y. Zhang, Y. Tang, Catalytic properties of fluorinated alumina for the production of dimethyl ether, Catal. Commun. 7 (2006) 362-366.

[9] J. Khom-in, P. Praserthdam, J. Panpranot, O. Mekasuwandumrong, Dehydration of methanol to dimethyl ether over nanocrystalline Al_2O_3 with mixed γ- and χ-crystalline phases, Catal. Commun.9 (2008) 1955-1958.

[10] R. Vakili, E. Pourazadi, P. Setoodeh, R. Eslamloueyan, M. R. Rahimpour, Direct dimethyl ether (DME) synthesis through a thermally coupled heat exchanger reactor, Appl. Energ. 88 (2011) 1211–1223.

[11] A. García-Trenco, A. Martínez, Direct synthesis of DME from syngas on hybrid CuZnAl/ZSM-5 catalysts: New insights into the role of zeolite acidity, Appl. Catal. A. 411-412 (2012) 170– 179.

[12] M. H. Zhang, Z. M. Liu, G. D. Lin, H. B. Zhang, Pd/CNT-promoted Cu ZrO_2/HZSM-5 hybrid catalysts for direct synthesis of DME from CO_2/H_2 , Appl. Catal. A. 451 (2013) 28– 35.

[13] Y. Zhang, D. Li, Y. Zhang, Y. Cao, S. Zhang, K. Wang, F. Ding, V-modified CuO–ZnO–ZrO_2/HZSM-5 catalyst for efficient direct synthesis of DME from CO_2 hydrogenation, Catal. Commun. 55 (2014) 49–52.

[14] F. Frusteri, G. Bonuraa, C. Cannilla, G. D. Ferrantea, A. Aloise, E. Catizzone, M. Migliori, G. Giordano, Stepwise tuning of metal-oxide and acid sites of CuZnZr-MFI hybrid catalysts for the direct DME synthesis by CO_2 hydrogenation, Appl. Catal. B 176–177 (2015) 522–531.

[15] Y. J. Lee, J. M. Kim, J. W. Bae, C. H. Shin, K. W. Jun, Phosphorus induced hydrothermal stability and enhanced catalytic activity of ZSM-5 in methanol to DME conversion, Fuel 88 (2009) 1915–1921.

[16]L. Liu, W. Huang, Z. h. Gao, L. h. Yin, Synthesis

of AlOOH slurry catalyst and catalytic activity for methanol dehydration to dimethyl ether, J. Ind. Eng. Chem. 18 (2012) 123–127.

[17] Y. Sang, H. Liu, S. He, H. Li, Q. Jiao, Q. Wu, K. Sun, Catalytic performance of hierarchical H-ZSM-5/MCM-41 for methanol dehydration to dimethyl ether, J. Energ. Chem. 22(2013)769–777.

[18] Z. Zuo, L. Wang, P. Han, W. Huang, Effect of surface hydroxyls on dimethyl ether synthesis over the γ-Al_2O_3 in liquid paraffin: a computational study, J. Mol. Model 19 (2013) 4959–4967.

[19] S. M. Solyman, M. A. Betiha, The performance of chemically and physically modified local kaolinite in methanol dehydration to dimethyl ether, Egyp. J. Petroleum. 23 (2014) 247-254.

[20] F. Yaripour, Z. Shariatinia, S. Sahebdelfar, A. Irandoukht, The effects of synthesis operation conditions on the properties of modified c-alumina nanocatalysts in methanol dehydration to dimethyl ether using factorial experimental design, Fuel. 139 (2015) 40–50.

[21] F. Caruso, X. Shi, R. A. Caruso, A. Susha, Hollow titania spheres from layered precursor deposition on sacrificial colloidal core particles, Adv. Mater. 13(10) (2001) 740-744.

[22] Y. Sun, B. Mayer, Y. Xia, Metal nanostructures with hollow interiors, Adv. Mater. 15 (2003) 641-646.

[23] U. Jeong, Y. Wang, M. Ibisate, Y. Xia, Some new developments in the synthesis, functionalization, and utilization of monodisperse colloidal spheres, Adv. Funct. Mater. 15 (2005) 1907-1921.

[24] Y. Wang, W. J. Tseng, A novel technique for synthesizing nanoshell hollow alumina particles, J. Am. Ceram. Soc. 92 (2009) S32–S37.

[25] R. G. Chaudhuri, S. Paria, Core/Shell nanoparticles: Classes, properties, synthesis mechanisms, characterization and Applications, Chem. Rev. 112 (2012) 2373–2433.

[26] M. S. Sadjadi, N. Rostamizadeh, A new strategy in the synthesis of hollow γ-Al_2O_3 nanosphere using alginate gel casting process, Res J Biotechnol. 11(4) (2016) 30-35.

[27] M. Firoozi, M. Baghalha, M. Asadi, The effect of micro and nano particle sizes of H ZSM-5 on the selectivity of MTP reaction, Catal. Commun. 10 (2009) 1582–1585.

[28] Z. Zeng, J. Yu, Z. Guo, Preparation of functionalized core-shell alumina/polystyrene composite nanoparticles, Macromol. Chem. Phys. 206 (2005) 1558–1567.

[29] T. Shirai, H. Watanabe, M. Fuji, M. Takahashi, Structural properties and surface characteristics on aluminum oxide powders, Annual Report of the Ceramics Research Laboratory Nagoya Institute of Technology. 9 (2009) 23-31.

[30] F. Arena, R. Dario, A. Parmaliana, A characterization study of the surface acidity of solid catalysts by temperature programmed methods, Appl. Catal. A. 170 (1998) 127-137.

[31] G. R. Moradi, R. Ghanei, F.Yaripour, Determination of the optimum operating conditions for direct synthesis of dimethyl ether from Syngas, Int. J. Chem. Reactor Eng. 5 (2007) A14-19.

[32] M. Fazlollahnejad, M. Taghizadeh, A. Eliassi, G. Bakeri, Experimental study and modeling of an adiabatic fixed-bed reactor for methanol dehydration to dimethyl ether, Chin. J. Chem. Eng. 17 (2009) 630-634.

[33] B.T. Diep, M.S. Wainwright, Thermodynamic equilibrium constants for the methanol-dimethyl ether-water system, J. Chem. Eng. Data. 32 (1987)330–333.

[34] S. S. Akarmazyan, P. Panagiotopoulou, A. Kambolis, C. Papadopoulou, D. I. Kondarides, Methanol dehydration to dimethylether over Al_2O_3 catalysts, Appl. Catal. B. 145 (2014) 136– 148.