

Dehydration of Methanol to Dimethyl Ether Employing Modified H-ZSM-5 Catalysts

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Abstract

Synthesis of Dimethyl ether from methanol was investigated over H-ZSM-5 and promoted H-ZSM-5 catalysts employing Mg, Na, Zr, Al and Zn components. All samples were characterized by AAS, BET, XRD and TPD analyses. Results of TPD analysis indicated that the number of weak strength acid sites increased on the surface of Na, Zn and Mg modified H-ZSM-5, while the number of medium strength acid sites increased on the surface of Zr and Al modified H-ZSM-5. Zr- modified H-ZSM-5 zeolite exhibited higher activity (94%) and selectivity (99%) than other materials while all modified catalysts exhibited good stability.

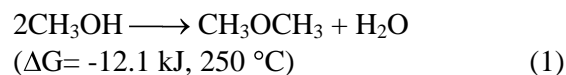
Ultimately, it was concluded that production of dimethyl ether from methanol occurred on acidic sites with medium and/or weak strengths. In this direction, an optimum catalyst for dehydration of methanol to DME with high conversion, selectivity and stability was developed.

Keywords: Dehydration, methanol, dimethyl ether, H-ZSM-5

1. Introduction

Dimethyl ether (DME) has attracted a good deal of attention as a potential clean fuel for diesel engines due to its higher cetane number, lower concentration of particulates and NO_x in emission. DME can be produced from methanol and natural gas. In the former process, methanol is dehydrated into DME. However, in the latter, synthesis gas produced from natural gas is first converted into methanol and the methanol is then

dehydrated into DME [1-5]. Nonetheless, both processes include reaction of methanol to DME (through Eq. (1)) catalyzed by liquid sulfate, phosphate acid or solid acids [6-9]:



Several solid-acid catalysts such as HZSM-5, H-beta, alumina and SAPOs are reported for methanol dehydration in a temperature range

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of 250 – 400°C [10–15]. However, most of these solid-acid catalysts produce undesirable side products such as hydrocarbons and coke due to the presence of strong acid sites and high dehydration temperature [11, 12]. Thus, extensive research has been focused on finding better catalysts which have higher selectivity for the DME formation and less tendency to generate hydrocarbons and coke [9].

Results of previous studies have shown that H-ZSM-5 zeolite was an active catalyst for this reaction [9-12], however, this catalyst without any treatment demonstrated low stability. It is known that impregnation of some of 1A, 2A, 3A and B groups of metals of the periodic table of elements onto zeolites modify the zeolites' acidic property. Furthermore, elements like Zn, Zr, Al, Na and Mg previously displayed good results presented in other studies [4, 5, and 7]. These reasons made them a legitimate choice to be utilized in this research where attempts were made to improve the properties of H-ZSM-5 for production of DME from methanol. In this direction, the effects of some additives such as Zn, Zr, Al, Na and Mg on properties of H-ZSM-5 were investigated. This ultimately led to an optimum catalyst for the aforementioned production.

2. Experimental

2.1. Catalyst preparation

ZSM-5 zeolite was obtained from the Zeolyst Company (USA). The zeolite as received was in Na-form. A Na-form zeolite sample was ion-exchanged to NH_4^+ -form using an aqueous solution of NH_4NO_3 . It was subsequently dried at 373 K for 24 h. H^+ -form zeolite was prepared by calcination of the NH_4^+ -form sample at a constant rate of temperature rise (2 K/min) from 373 to 773 K while keeping the temperature at 773 K for 5 h.

H-ZSM-5 modified with various metal oxides was prepared by wet impregnation

with aqueous solutions of metal salts (i.e.; nitrates of Na, Zn, Al and Mg, and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), followed by drying at 110 °C overnight and then calcined at 450 °C for 3 h in an air stream. For example, HZSM-5 with 5 wt% Zn was prepared by impregnation of the HZSM-5 zeolite (7.6 g) with 1.46 g of $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (> 99%, Merk) dissolved in 15 ml of deionized water. The resulting material was stirred and heated until a paste was formed. The paste was then left at room temperature for several days before drying [11]. Ultimately, it was dried at 110 °C overnight and then calcined at 450 °C for 3h in an air stream.

2.2. Catalyst characterization

After the aforementioned treatments, catalysts were characterized by standard methods. X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX-1400 instrument with $\text{Cu-K}\alpha$ radiation, with a scan speed of 15°/min and a scan range of 4–70° at 40 kV and 40 mA.

The surface area of the samples was measured by a multipoint N_2 adsorption–desorption method at liquid- N_2 temperature (–196 °C) with a Micromeritics TriStar 3000 surface area analyzer. Samples were out-gassed under vacuum to remove the physisorbed water immediately before analysis.

The metal oxide content of the modified zeolites was determined by atomic adsorption spectroscopy (AAS) on a Perkin-Elmer AA 800 instrument.

Acidity measurements were performed by temperature programmed desorption of ammonia (NH_3 -TPD) with a conventional flow apparatus equipped with a thermal conductivity detector (TCD). A given amount of the sample, 0.1 g, was pretreated in flowing helium at 500 °C for 1 h, cooled to 150 °C, and then exposed to NH_3 (20 ml/min) for 30 min. Samples adsorbed by NH_3 were subsequently purged with He at the same

temperature for 1h to remove the physisorbed NH_3 . The TPD measurements were conducted in flowing He (30 ml/min) from 100 to 700°C at a heating rate of 10°C/min.

2.3. Catalytic reactions

Catalyst performance tests were carried out in a 500 ml autoclave. This reactor was equipped with a variable speed stirrer, cooling coil and PID controller. Maximum operational temperature and pressure were 350°C and 100 bar, respectively. The experimental setup is shown in Fig. 1. To operate near isothermal conditions and to minimize catalyst deactivation effects, a known quantity of methanol was dissolved in isooctane (as the solvent) and the mixture was charged into the reactor along with a predetermined quantity of catalyst. The reactor was then flushed several times with nitrogen. Reaction was induced by bringing

the reaction mass to the reaction temperature and turning on the agitation. The reaction was essentially a liquid-phase reaction with a solid catalyst suspended uniformly in the liquid medium in the form of slurry. Experimental parameters and their employed values are given in Table 1.

2.4. Analytical methods

The analysis of the liquid product samples was carried out using a gas chromatograph (Perichrom) equipped with an hp pona colon column and FID detector, with helium as the carrier gas. Injector and detector temperatures were 270 and 300°C, respectively. The material balance was found acceptable. The error in this analysis was in the range of 3-5%. The activity and selectivity for various catalysts were calculated according to the following equations:

$$\text{MeOH Conversion} = \frac{\text{MeOH moles (initial amount)} - \text{MeOH moles (final amount)}}{\text{MeOH moles (initial amount)}} \times 100 \quad (1)$$

$$\text{DME selectivity} = \frac{\text{DME moles produced} \times 2}{\text{MeOH moles (initial amount)} - \text{MeOH moles (final amount)}} \times 100 \quad (2)$$

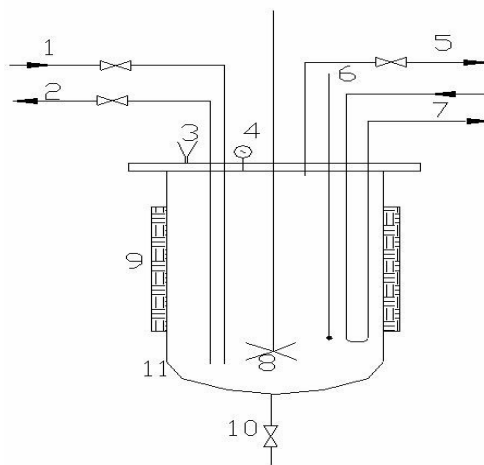


Figure 1. Schematic of the batch reactor set-up constructed and used in this research; 1: gas inlet, 2: sampling valve, 3: slurry feed inlet, 4: pressure indicator, 5: gas vent, 6: thermocouple, 7: cooling coil, 8: stirrer, 9: reactor heating, 10: discharge valve, 11: reactor body

Table 1. Reaction conditions for the present study

Parameter	Value
Temperature (K)	523
Pressure(bar)	20
Agitation speed (rpm)	1000
Reaction time (h)	4
Catalyst loading (g)	5
Methanol concentrations (mole/l)	0.962

3. Results and discussion

3.1. Characterization of modified H-ZSM-5 zeolites

The metal oxide contents determined by the AAS are listed in Table 2. Results show that the metal oxide contents were consistent with those added before calcination, suggesting that no noticeable loss of these materials occurred during calcination.

The BET surface areas, total pore volumes and average pore diameters of the parent and modified H-ZSM-5 zeolites are provided in Table 2. The BET surface areas and total pore volumes have decreased in the modified zeolites which may be attributed to parts of the zeolite pores being filled up with metal oxides. Furthermore, results of the average pore diameter of the zeolites determined indicate that micropores (i.e.; small pores less than 0.4 nm) have been filled up with modifying materials. For example, in the case of the modified H-ZSM-5 zeolite with

Zirconium compared to parent ZSM-5, the BET surface area and pore volumes have respectively reduced from 400 to 254m²/g and 0.2139 to 0.1741cm³/g, whereas the average pore diameter has risen from 2.9154 to 6.8639 nm. Thus, it is concluded that through impregnation, metal oxides are deposited onto the internal (i.e.; inside pores and channels) as well as outer zeolite surfaces.

XRD patterns of the parent and modified zeolites are compared in Fig. 2. It is seen that with the modification, the H-ZSM-5 structure was retained; nevertheless, the relative crystallinity decreased with the impregnation of metal oxides. In addition, no crystalline metal oxide was detected in the XRD spectra. The above results indicate that the metal oxides that are undetectable by XRD may have been highly dispersed on the surface of H-ZSM-5.

Table 2. physical characteristics of catalysts in this study

Modified zeolite	Metal oxide content (wt%)		BET Surface	Total Pore Volume	Mean Pore Diameter (nm)
	Nomina	Determined			
HZSM-5	—	—	400	0.2139	2.9154
Mg-HZSM-5	5.00	4.95	145.87	0.1491	2.4492
Zn-HZSM-5	5.00	4.96	267.10	0.1861	4.8838
Al-HZSM-5	5.00	4.97	286.23	0.1978	5.0918
Zr-HZSM-5	5.00	4.94	254.20	0.1741	6.8639
Na-HZSM-5	5.00	4.92	168.21	0.1511	2.0262

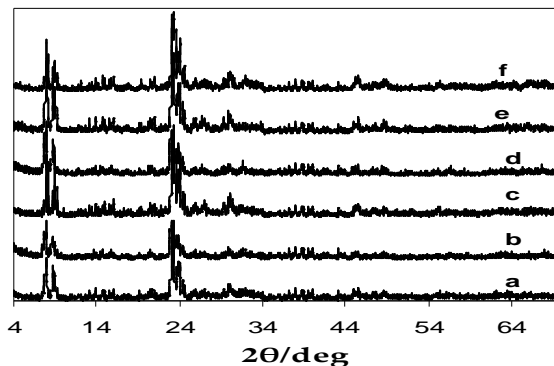


Figure 2. XRD spectra of H-ZSM-5 and modified H-ZSM-5 catalysts; a) H-ZSM-5, b) Mg-H-ZSM-5, c) Zn-H-ZSM-5, d) Al-H-ZSM-5, e) Zr-H-ZSM-5, f) Na-H-ZSM-5

3.2. Surface acidity of H-ZSM-5 and each modified H-ZSM-5:

NH_3 -TPD analyses of H-ZSM-5 and modified H-ZSM-5 catalysts performed in the present investigation showed three NH_3 desorption peaks (Fig. 3), which is consistent with published data [16-18]. Three NH_3 desorption peaks were detected at ranges of 100–300°C (T_1), 300–500°C (T_2) and 500–700°C (T_3). Also, the quantitative estimation of acid sites and their strength distribution, region wise, is shown in Table 3. These peaks should be assigned to the desorption of NH_3 on weak, medium and

strong acid sites, in the same order as they appeared in the TPD curve. In the current study, the area of the third peak decreased slightly in all samples, while the area of the first peak increased in Na, Zn and Mg modified zeolites. Furthermore, the area of the second peak increased in Zr and Al modified samples. That is, the amount of weak strength acid sites increased on the surface of Na, Zn and Mg modified H-ZSM-5, while the amount of medium strength acid sites increased on the surface of Zr and Al modified H-ZSM-5.

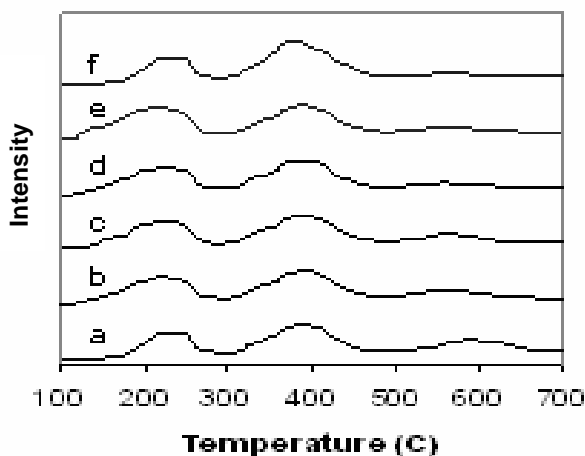


Figure 3. NH_3 -TPD profile of H-ZSM-5 and of modified H-ZSM-5 zeolite; (a) parent, (b) Mg-modified H-ZSM-5, (c) Zn-modified H-ZSM-5, (d) Al-modified H-ZSM-5, (e) Zr-modified H-ZSM-5, (f) Na-modified H-ZSM-5

Table 3. Results of TPD-NH₃ analysis and catalytic tests over H-ZSM-5 and metal-modified H-ZSM-5 catalysts (conditions of catalytic tests are according to Table 1)

Catalyst	Acidity (mmole NH ₃ /g cat.)				Conversion (%)	Selectivity (%)
	Weak	Medium	Strong	Total		
HZSM-5	0.261	0.322	0.264	0.847	78	68
Mg-HZSM-5	0.363	0.353	0.140	0.856	81	85
Zn-HZSM-5	0.413	0.370	0.095	0.878	85	92
Al-HZSM-5	0.311	0.506	0.074	0.891	91	95
Zr-HZSM-5	0.362	0.497	0.064	0.923	94	99
Na-HZSM-5	0.415	0.351	0.098	0.864	82	89

3.3. Methanol dehydration over H-ZSM-5 and modified H-ZSM-5:

The conversion of methanol over H-ZSM-5 and modified H-ZSM-5 zeolites are summarized in Table 3. In order to clearly show the effect of the extent and strength of the acid sites on the catalytic activity; variations of the conversion and selectivity versus the amount and strength of acidity are presented in Figs. 4 to 6, respectively. It is seen in Fig. 4 that as the overall amount of catalyst acidity is increased, the conversion is enhanced as well. In other words, conversion is a direct function of the amount of catalyst acidity. On another issue, the strength effect of acid sites upon selectivity is displayed in Figs. 5 and 6. It is seen in Fig. 5 that selectivity is directly related to the sum of the weak and moderately strong acid sites. Put simply, as this cumulative amount of strength is enhanced, the selectivity toward DME is increased. However, this selectivity trend is reversed regarding strong acid sites where the increase in the number of these types of sites dramatically reduces the selectivity toward the DME production (Fig. 6).

Therefore, it is concluded that conversion depends on the amount of acidity and is enhanced when this parameter is increased. However, selectivity of the DME depends on

the strength of acidic sites, such that it rises when the number of acidic sites having weak and/or medium strength increase, while it lowers as the number of strong acid sites increase. Also, It is found that Zr-modified H-ZSM-5 is the best catalyst for dehydration of methanol.

3.4. Stability of catalysts:

To investigate the stability of catalysts, each one was utilized in several batches without any treatment. Results of catalyst performance are given in Fig. 7. Methanol conversion decreased quickly with increasing of the number of batches in the case of the parent H-ZSM-5 catalyst, and slowly in Mg-modified H-ZSM-5 catalyst, while in all other cases (utilizing Al-, Zr-, Zn and Na-modified H-ZSM-5 catalysts), methanol conversion is almost constant. That is, the stability was clearly improved in cases of Al-, Zr-, Zn and Na- modified H-ZSM-5 catalysts.

These behaviors indicate that through the wet impregnation modifications employed here, the catalyst deactivation process which is in the form of production of long chain hydrocarbons over strong acid sites has been dramatically slowed down [19,20].

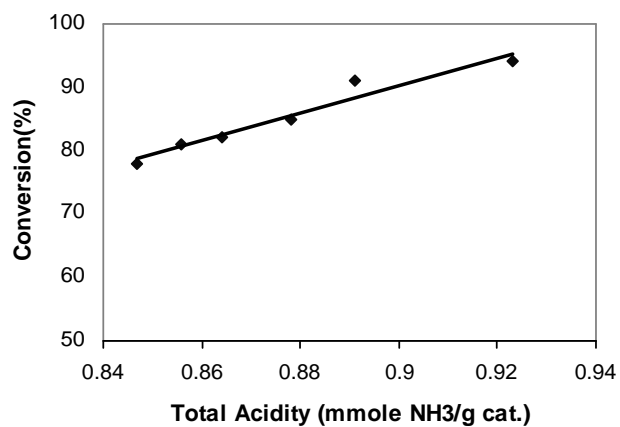


Figure 4. Variation of conversion versus total amount of acidity (according to Table 3)

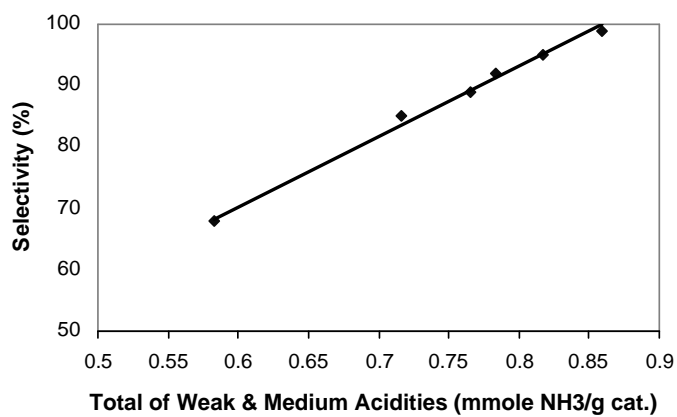


Figure 5. Variation of selectivity versus amount of acidities of weak and medium (according to Table 3)

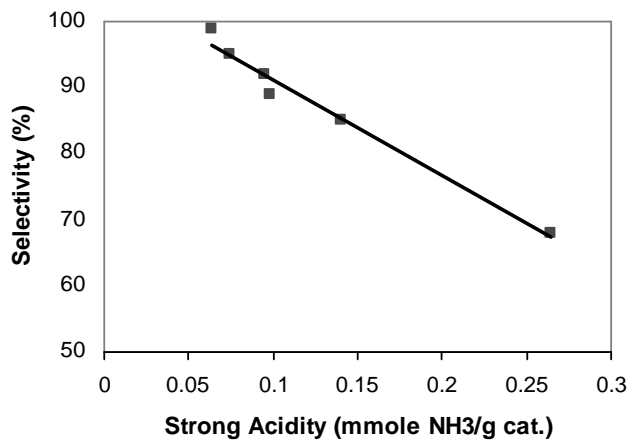


Figure 6. Variation of selectivity versus amount of strong acidity (according to Table 3)

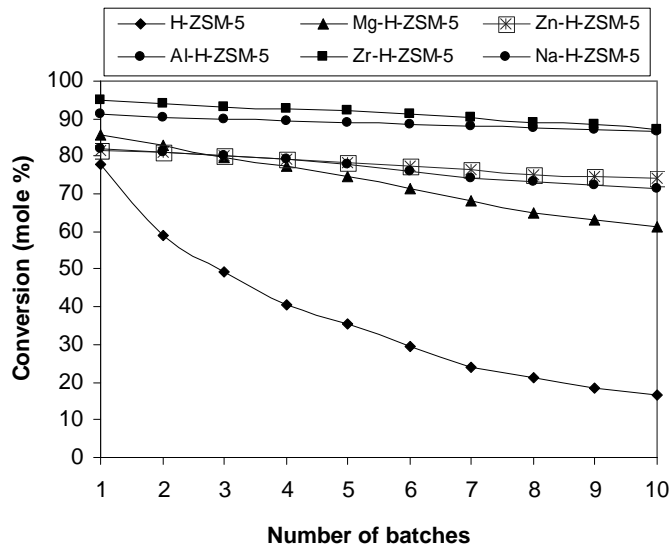


Figure 7. Comparison of stability of applied H-ZSM-5 and modified H-ZSM-5 catalysts

4. Conclusions

It was found that the ZSM-5 zeolite with an H⁺-form is an active catalyst for dehydration of methanol. However, this H-ZSM-5 had low selectivity and stability. To improve these parameters for this catalyst, it was modified with various materials such as Na, Al, Zr, Mg and Zn. Results revealed that the selectivity of DME was improved in all modified zeolites. Also, zeolites modified with Al, Zr, Na and Zn oxides showed high stability.

Comparison of results obtained through TPD analysis and other catalytic tests pointed toward the conclusion that in the methanol conversion reaction to DME, the amount of conversion was related to the extent of acidity, while selectivity toward DME and stability of the catalyst depended upon the strength of the catalytic sites being utilized. In other words, as the numbers of sites with strong acidity were reduced, the catalyst selectivity and stability were improved. Ultimately, it was determined that Zr-modified H-ZSM-5 zeolite is an optimum catalyst for dehydration of methanol to DME with high conversion, selectivity and stability.

5. Acknowledgment

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6. Abbreviations

DME=Dimethyl Ether

H-beta= H form of beta zeolite

MeOH=Methanol

SAPOs=Silica Alumina Phosphates

TPD= Thermal programmed desorption

References

1. Qi, G.X., Zheng, X.M., Fei, J.H. and Hou, Z.Y., "A novel catalyst for DME synthesis from CO hydrogenation 1. Activity, structure and surface properties", *Journal of Molecular Catalysis A: Chemical*, 176, 195 (2001).
2. Sun, K. and Lu, W., "Direct synthesis of DME over bifunctional catalyst: surface properties and catalytic performance", *Applied Catalysis A: General*, 252, 243 (2003).
3. Xu, M., Lunsford, J.H., Goodman, D.W. and Bhattacharyya, A., "Synthesis of dimethyl ether (DME) from methanol over solid acid catalysts", *Applied Catalysis A: General*, 149, 289 (1997).

4. Kim, S.D., Baek, S.C., Lee, Y.J., Jun, K.W., Kim, M.J. and Yoo, I.S., "Effect of g-alumina content on catalytic performance of modified ZSM-5 for dehydration of crude methanol to dimethyl ether", *Applied Catalysis A: General*, 309, 139 (2006).
5. Fei, J., Hou, Z., Zhu, B., Lou, H., and Zheng, X., "Synthesis of dimethyl ether (DME) on modified HY zeolite and modified HY zeolite-supported Cu–Mn–Zn catalysts", *Applied Catalysis A: General*, 304, 49 (2006).
6. Vishwanathan, V., Roh, H.S., Kim, J.W., and Jun, K.W., "Surface properties and catalytic activity of TiO₂–ZrO₂ mixed oxides in dehydration of methanol to dimethyl ether", *Catal. Lett.*, 96, 23 (2004).
7. Vishwanathan, V., Jun, K.W., Kim, J.W., and Roh, H.S., "Vapour phase dehydration of crude methanol to dimethyl ether over Na-modified H-ZSM-5 catalysts", *Applied Catalysis A: General*, 276, 251 (2004).
8. Yaripour, F., Baghaei, F., Schmidt, I., and Perregaard, J., "Catalytic dehydration of methanol to dimethyl ether (DME) over solid-acid catalysts", *Catal. Commun.*, 6, 147 (2005).
9. Yaripour, F., Baghaei, F., Schmidt, I., and Perregaard, J., "Synthesis of dimethyl ether from methanol over aluminium phosphate and silica–titania catalysts", *Catal. Commun.*, 6, 542 (2005).
10. Wang, A.W., Weigel, S. and Muraro, G., "Topical report molecular sieves as catalyst methanol dehydration", *Air Products and Chemicals Inc.*, (2002).
11. Xu, M., Lunsford, J.H., Goodman, D.W. and Bhattacharyya, A., "Synthesis of dimethyl ether (DME) from methanol over solid-acid catalysts", *Applied Catalysis A: General*, 149, 289 (1997).
12. Fu, Y., Hong, T., Chen, J., Auroux, A. and Shen, J., "Surface acidity and the dehydration of methanol to dimethyl ether", *Thermochim. Acta.*, 434, 22 (2005).
13. Jun, K.W., Lee, H.S., Roh, H.S. and Park, S.E., "Highly water-enhanced H-ZSM-5 catalysts for dehydration of methanol to dimethyl ether", *Bull. Korean Chem. Soc.*, 24, 106 (2003).
14. Jiang, S., Hwang, Y.K., Jung, S.H., Chang, J.S., Hwang, J.S. and Cai, T.X., "Zeolite SUZ-4 as selective dehydration catalyst for metanol conversion to dimethyl ether", *Chem. Lett.*, 33, 148 (2004).
15. Jiang, S., Hwang, J.S., Jin, T.H., Cai, T.X., Baek, W.Y.S. and Park, S.E., "Dehydration of methanol to dimethyl ether over ZSM-5 zeolite", *Bull. Korean Chem. Soc.*, 25, 185 (2004).
16. Dumitriu, E. and Hulea, V., "Effects of channel structures of large-pore zeolites on liquid phase t-butylation of phenol", *J. Catal.* 218, 249 (2003).
17. Anand, R., Maheswari, R., Gore, K.U., and Khaire, S.S., "Isopropylation of naphthalene over modified faujasites: effect of steaming temperature on activity and selectivity", *Applied Catalysis A: General*, 249, 265 (2003).
18. Arena, F., Dario, R. and Parmaliana, A., "A characterization study of the surface acidity of solid catalysts by temperature programmed methods", *Applied Catalysis A: General*, 170, 127 (1998).
19. Jin, D., Zhu, B., Hou, Z., Fei, J., Lou, H., and Zheng, X., "Dimethyl ether synthesis via methanol and syngas over rare earth metals modified zeolite Y and dual Cu–Mn–Zn catalysts", *Fuel*, doi:10.1016/j.fuel.2007.03.011 (2007).
20. Arena, F., Dario, R. and Parmaliana, A., "A characterization study of the surface acidity of solid catalysts by temperature programmed methods", *Applied Catalysis A: General*, 170, 127 (1998).