Korean J. Chem. Eng., **22**(3), 353-357 (2005)

Transformation of Methanol to Gasoline Range Hydrocarbons Using HZSM-5 Catalysts Impregnated with Copper Oxide

Hasan Akhtar Zaidi and Kamal Kishore Pant[†]

Department of Chemical Engineering, Indian Institute of Technology Delhi-110016, India

(*Received 15 November 2004 • accepted 28 February 2005*)

Abstract−Various CuO/HZSM-5 catalysts were studied in a fixed bed reactor for the conversion of methanol to gasoline range hydrocarbons at 673 K and at one atmospheric pressure. The catalysts were prepared by wet impregnation technique. Copper oxide loading over HZSM-5 (Si/Al=45) catalyst was studied in the range of 0 to 9 wt%. XRD, BET surface area, metal oxide content, scanning electron microscopy (SEM) and thermogravimetric (TGA) techniques were used to characterize the catalysts. Higher yield of gasoline range hydrocarbons (C_5-C_{12}) was obtained with increased weight % of CuO over HZSM. Effect of run time on the hydrocarbon yields and methanol conversion was also investigated. The activity of the catalyst decreased progressively with time on-stream. Hydrocarbon products' yield also decreased with the increase in wt% of CuO. Relatively lower coke deposition over HZSM-5 catalysts was observed compared to CuO impregnated HZSM-5 catalyst.

Key words: HZSM-5, MTG, Catalysis, Impregnation, Gasoline, Deactivation

INTRODUCTION

Methanol is used as a raw material for the production of olefins and other hydrocarbons using zeolite catalysts. Zeolites such as HZSM-5 have attracted many researchers to obtain yield of gasoline range hydrocarbons. Its nature and extent of reaction depends on acid strength, acid site density, catalyst topology, temperature, pressure, space velocity and other process conditions [Alkawaldeh et al., 2003; Cañizares et al., 1998; Marchi and Froment, 1993; Oh et al., 1992]. The influence of metal/metal oxide incorporation over the surface of zeolite enhanced the methanol conversion and hydrocarbons yields [Zaidi and Pant, 2004; Al-Jarallah et al., 1997; Freeman et al., 2002; Kang, 2000; Zhu et al., 2000]. Conversion of methanol to gasoline range hydrocarbons over CuO, ZnO doped HZSM-5 catalyst increases the hydrocarbons yield as compared to unmodified HZSM-5. It has been reported that the long life of zeolite catalysts for methanol conversion to gasoline (MTG) is due to the variation in physicochemical properties of ZnO over CuO/HZSM-5 [Zaidi and Pant, 2004]. Various techniques have been used to characterize zeolite catalysts and the impact of catalytic action with different types of zeolite catalysts [Donk et al., 2003; Cañizares et al., 2003; Gervasini et al., 1999]. It has been reported that channel intersections of HZSM-5 provide enough volume for cyclization reactions and intermolecular hydride transfer reactions by which olefins can be converted into alkane and aromatics [Haw et al., 2003].

The main aim of the present investigation is to study the effect of CuO loading on HZSM-5 support for conversion of methanol to gasoline range hydrocarbons. A series of CuO/HZSM-5 catalysts were prepared, characterized and experimented for their performance on methanol conversion and hydrocarbon yield. The effects of run time on methanol conversion and hydrocarbon yield with various CuO doped HZSM-5 catalysts have been studied.

EXPERIMENTAL

1. Catalyst Preparation

HZSM-5 (Si/Al=45), zeolites used in this study were supplied by the Süd Chemie (Germany). CuO amount ranging from 0-9-wt% was doped on the HZSM-5. All these catalysts were prepared by impregnation technique. For the preparation of these catalysts copper nitrate salt (Merck, Germany) was dissolved in deionized water. The HZSM-5 pellets were dipped in this solution and continuously stirred for 12 hours. Ammonium hydroxide solution was added to maintain the solution pH at 5±0.2. The catalyst slurry was transferred to a rotary vacuum evaporator where excess water was removed. These pellets were then dried in a furnace at 393 K for 12 hours followed by calcination for 5 hours at 833 K to get copper oxide doped HZSM-5 catalyst.

2. Catalyst Characterization

The surface area and pore volume of the catalysts were determined by using ASAP-2010 (Micromeritics, USA) by adsorption with liquid nitrogen at 77 K. Prior to the analysis the catalyst samples were degassed for 6 hours at 423 K under vacuum. Thermogravimetric profiles were recorded on TG/DTA 32 system by (Sieko instruments, Japan). It was used to analyze the coke content over the surface of the catalyst. Flow rate of air was kept at 0.5 ml/s and the catalyst samples were heated from 300 K to 1,223 K in an air stream at heating rate of 0.2 K/s. In the recorded profiles, the weight loss before 533 K is due to desorption of adsorbed water. The decrease in the sample weight from 533-985 K is caused by burning of coke. An X-ray diffraction pattern of catalysts was taken in order to characterize the phases present and also the crystallinities of the catalysts. The samples were analyzed by X-ray diffraction method using a Bruker D 8 advance X-ray diffractometer with monochromatic CuKα radiation and scanning 2θ from 0^0 to 40^0. The wavelength of adsorption was kept at 1.54 A^0. The morphology and structure of the catalysts were studied by using Cambridge 360 scanning electron microscope (SEM). To determine the actual amount

---

[†] To whom correspondence should be addressed.

E-mail: kkpant@chemical.iitd.ac.in

Table 1. Physical properties of the catalysts

Catalyst	Metal content (wt%)	S_{BET} (m^2/g)		Pore volume (cm^3/g)	
	CuO	Fresh*	Coked•	Fresh*	Coked•
HZ (9)	9	204.2	155.7	0.31	0.29
HZ (7)	7	254.6	212.2	0.33	0.32
HZ (5)	5	265.8	237.7	0.36	0.35
HZ (3)	3	274.8	249.1	0.37	0.36
HZ (0)	0	289.8	279.2	0.39	0.38

*Fresh catalyst

•Coked catalyst (Run time 12 hrs)

of CuO doped over HZSM-5, the catalyst samples were digested with nitric acid 363 K for two hours under reflux condition. The digested samples were diluted with deionized water and analyzed. The final weight percent of copper oxide on the catalyst was measured by a metal trace analyzer (Metrohm 757 VA Computrace). The final wt% of CuO on these catalysts is shown in Table 1. The catalyst with 9, 7, 5, 3 and 0 wt% CuO loading were designated as HZ (9), HZ (7), HZ (5), HZ (3) and HZ (0), respectively.

3. Catalyst Performance Testing

The performance of the catalysts for methanol conversion was evaluated by conducting experiments in a fixed bed reactor under identical conditions. The details of the experimental procedure are given elsewhere [Zaidi and Pant, 2004]. The weighed catalyst was placed in the central portion of the reactor where isothermal conditions were maintained. The product stream from the reactor was passed through the condenser maintained at 268 K to remove all the condensable products. The non-condensable were passed through a gas sampler, a gas flow meter, and then vented. The gaseous and liquid products were analyzed by two gas chromatographs--thermal conductivity detector (TCD) and flame ionization detector (FID). The TCD was used for the determination of N_2, CH_4 and any possible CO and CO_2 formed during reaction. The hydrocarbon gases were analyzed by using a Porapak-Q column (i.d. 2 mm, length 1.8 m) using FID. The liquid hydrocarbons were determined by using a capillary column (Petrocol DH, L=60 m, i.d.=0.25 mm fused silica). The oven, injector and detector temperatures were maintained at 353 K, 403 K and 413 K, respectively. The total duration of the run was kept at 12 hours in order to study the catalyst activity with time on-tream. At the end of the run, the reactor was flushed with nitrogen and coked catalyst was removed for further investigation.

RESULTS AND DISCUSSION

1. Catalyst Characterization

The X-ray diffraction patterns for copper oxide doped catalyst samples indicated that there was no new phase formation during heat treatment and CuO doping. The structure of zeolite remained intact after the different treatment procedures. No peak related to copper oxide species was found for these catalysts. This confirms that copper oxide in microporous HZSM-5 can be automatically dispersed. However, the peak intensities differ depending upon CuO contents. The higher intensity was observed for the starting zeolite HZ (0). The decrease in the intensities may be due to higher absorption coefficient of CuO. Similar observations were also reported in published literature [Gervasini et al., 2000]. The morphology of the surface was determined by scanning electron microscopy which indicated that all catalysts particles are spherical.

The surface area and pore volume of the catalyst was determined by BET method. The results are shown in Table 1. The surface area of catalyst decreased on increasing copper oxide loading. Volume of N_2 adsorbed decreased with increasing copper oxide content due to partial coverage of the surface with copper oxide. The decrease in pore radius for the copper exchanged materials as compared to the parent matrix is indicative of copper presence in pores of the lattice. As can be seen from Table 1 the surface area of the CuO catalyst decreased from 290 m^2/g to 204 m^2/g on increasing CuO doping from 0 to 9 wt%. The total pore volume was also reduced from 0.39 to 0.31 cm^3/g with increasing metal content. The reduction in pore volume and surface area of the catalyst could be due to the diffusion of metal solution in the pore of zeolite catalysts. Similar trends have also been reported in literature with other catalysts [Cañizares et al., 1998; Donk et al., 2003].

2. Effect of CuO Loading on Conversion and Products Yield

Methanol conversion and hydrocarbons yield were investigated on HZSM-5 catalysts and compared with HZSM-5 doped with different CuO loading catalyst. For comparison, the total the mass of catalyst placed in the reactor was 3.0 g using quartz beads as inert diluents. Table 2 shows the comparison of product composition with different CuO loading HZSM-5 catalyst. The detailed product distribution with these catalysts is shown in Table 3. There was a significant increase in conversion due to CuO loading. The methanol conversion increased from 38 to 97% as CuO loading was increased from 0 to 7 wt%. The strong acid sites of the zeolites decrease with the increase of the CuO loading over HZSM-5. The observed decrease in acidity may be due to the replacement of some of the protons by copper ions [Gervasini et al., 2000]. Further increase in CuO loading did not improve the activity of the catalyst possibly due to coverage of the active sites and pore blocking. Thus, for better performance in methanol to gasoline conversion there should be a proper

Table 2. Products composition in methanol conversion to hydrocarbons over various catalysts [T=673 K, W/F_{A0} (gm cat*hr/mol methanol fed)=4.14]

Catalysts	Aromatics yield (wt%)	Olefins yield (wt%)	Alkanes yield (wt%)	DME yield (wt%)	C_5+ yield (wt%)
HZ (0)	3.17	4.2	6.23	1.16	0.4
HZ (3)	24.86	1.13	2.84	0.39	5.97
HZ (5)	26.98	2.68	3.5	2.2	3.64
HZ (7)	32.04	1.6	2.25	0.73	5.52
HZ (9)	10.7	4.32	4.84	2.85	9.74

Table 3. Products distribution for the conversion of methanol [T=673 K, W/F_{A0} (gm cat*hr/mol methanol fed)=4.14]

Compound	HZ (9)	HZ (7)	HZ (5)	HZ (3)	HZ (0)
Conversion (%)	75	97	95.7	92.2	38
Yield (wt%)					
CH_4	0.45	0.33	0.60	0.90	1.0
C_2	2.03	0.957	2.1	1.60	1.35
C_3	2.92	0.85	2.13	2.8	3.47
C_4	2.28	0.61	1.49	1.74	1.89
C_5	1.11	0.55	0.87	1.06	2.12
C_5+	10.11	6.1	3.5	4.3	1.0
C_6H_6	0.05	0.1	0.18	0.02	0.27
C_7H_8	0.12	3.34	2.60	1.43	0.72
C_8H_{10}	6.09	12.2	12.26	8.8	1.1
C_9H_{12}	4.09	12.98	9.26	9.96	1.1
$C_{10}H_{14}$	0.17	3.43	2.4	2.75	Tr.•
D.M.E	2.85	0.73	2.16	1.35	1.16
Hydrocarbon products	32.28	42.16	39.7	37.7	15.2
Water (wt%)	29.4	37.20	36.2	35.70	19.38
Others*	13.32	18.80	16.42	18.80	3.42

*Include CO, and CO_2

•Tr.=trace.

balance between acidity and Cu species in the zeolite channel [Adebajo et al., 2004]. From Table 3 it can be concluded that the higher gasoline range of hydrocarbons yield and methanol conversion is obtained with 7 wt% CuO/HZSM-5 under identical conditions. The major products of the reaction were methane, ethylene, propylene, dimethyl ether, pentane, toluene, ethyl benzene, xylene, isopropyl benzene, ethyl toluene, trimethyl benzene and tetra methylbenzene with all these catalysts. All these products were identified from their retention times as obtained by gas chromatography of pure components. Both liquid hydrocarbon and aromatic hydrocarbon yield increased progressively with increase in wt% of CuO upto 7 wt%, but further increase in loading to 9 wt% decreased the aromatic yield possibly due to the coverage of active sites and pore blocking [Gervasini et al., 2000]. A comparison of products obtained with various catalysts is shown in Table 3.

As the CuO loading was increased from 0 to 7 wt%, the total hydrocarbon and aromatic yield in the products significantly increased, while the yield of C_2 and C_3 olefins decreased, indicating those alkenes were intermediates. The product distribution with zeolite catalyst strongly depends on its pore size and acidic sites. It also mainly depends on the structure of zeolites, steric restriction and a secondary process such as hydrogen transfer activity and coking. The increase in the liquid product of higher hydrocarbons with high CuO loading is probably due to the consequence of the diffusion. This could be due to the enhancement of the reactant in the solid porous system, which consequently increases the number of active collisions, resulting in higher hydrocarbon product ions. In the initiation step methanol is activated when it is contacted with CuO/HZSM-5 catalyst and generates the methyl cation (CH_3^+) or carbenes (: CH_2), which are highly reactive intermediates. Mihail et al., 1983 reported that generation of these intermediates depends upon strength of acidic sites over surface of catalyst. Dimethyl ether obtained from dehydration of methanol generates carbenes, and these ions again react with hydrogen and produce methane. Methyl cations react with light olefins to produce higher olefins and these ions again react with higher olefins to form paraffins and dienes. Methanol adsorption may also take place at different acidic and basic sites over the surface of copper impregnated HZSM-5 [Freeman et al., 2002]. The acidic sites help methanol to get converted into DME, olefins and water initially followed by a secondary reactions to form gasoline range hydrocarbons. Incorporation of CuO increases the selectivity to lower olefins from which the aromatic hydrocarbons are formed through cyclization and aromatization. It was also reported by many researchers that 673 K was the optimum temperature for conversion of methanol to hydrocarbons [Haw et al., 2002]. At 673 K the acidic sites become more energetic due to molecule migration from basic sites to acidic sites and get converted to olefins and then finally converted to higher molecular weight hydrocarbons [Freeman et al., 2002; Haw et al., 2003]. The transformation of methanol to various products may be explained by the above reaction mechanisms. Significant amounts of liquid products (C_5-C_{12}) were formed with the CuO doped catalysts in the present study.

3. Effect of Run Time

It was observed that catalyst with higher wt% CuO loses its activity faster as compared to lower wt% of CuO. As can be seen from Table 1, with increase in copper oxide loading there was a decrease in surface area and pore volume due to pore plugging. The surface area and pore volume further reduced during reaction due to coke deposition. The catalyst loses active sites within the micropore of catalyst and finally micropore gets filled with coke. Effect of run time on conversion and products yield was studied for CuO doped HZSM-5 and compared with HZSM-5 catalysts by conducting experiments for a run time of 12 hours. As can be seen from Fig. 1, conversion of methanol decreased progressively with time on-stream. Initial methanol conversion with HZ (7) and HZ (0) catalysts was 97% and 38%, respectively. After 12 hours run the conversion reduced to 76% and 29%, respectively, with these two catalysts. The decrease in methanol conversion was slower for HZSM-5 as com-

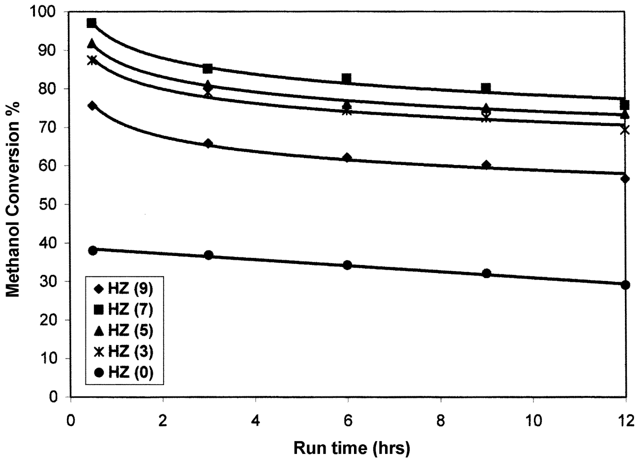

Fig. 1. Effect of run time on conversion of methanol, [T=673 K, P=1 atm, W/F_{A0} (gm cat*hr/mol methanol fed)=4.13].

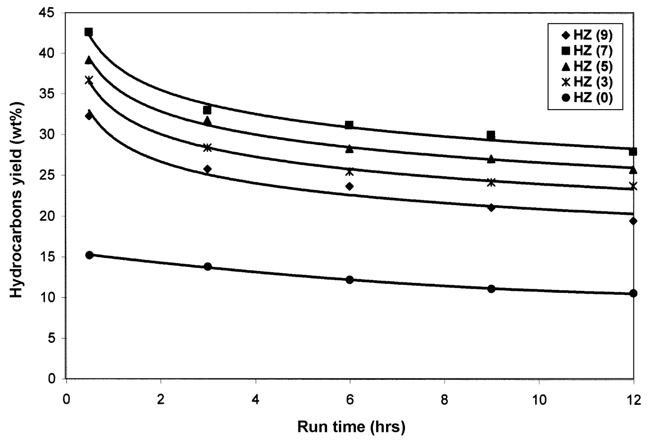

Fig. 2. Effect of run time on the yield of total hydrocarbons, [T= 673 K, P=1 atm, W/F$_{A0}$ (gm cat*hr/mol methanol fed)=4.13].

Table 4. Effect of run time on coke deposited over catalysts

Sample	Run time (hrs)	Coke content (wt%)
HZ (0)	12	2.05
HZ (3)	12	3.7
HZ (5)	12	4.8
HZ (7)	12	5
HZ (9)	12	5.4

pared to CuO/HZSM-5. The relatively slow deactivation for the reaction over HZSM-5 is because of dehydration steps is considerably slower than the deactivation of subsequent steps of reaction [Gayubo et al., 2001]. The total yield of hydrocarbons with respect to time is also shown in Fig. 2. The hydrocarbon product yield also decreased with run time. For a run time of 12 hours the total product yield reduced from 42-wt% to 28 wt% on HZ (7) catalyst. Coke deposition on to HZSM-5 catalyst was higher with the increase in wt% CuO over HZSM-5 as shown in Table 4. A thermogravimetric (TG) analysis was done to estimate the amount of the surface carbon deposited, which was burned off, on heating catalysts in presence of air at 303 K to 1,223 K. increasing the temperature. Table 4 shows the increase in the weight percent of coke on different catalysts with run time. The maximum coke 5.4 wt% was deposited on HZ (9) as compared to other catalysts after the run time of 12 hours. In the methanol to gasoline process on HZSM-5, methanol dehydration take place without its reaction rate being decreased, although the catalyst deactivated faster for the formation of olefins and gasoline [Gayubo et al., 2001]. There was a reduction in conversion and total product yields due to deposition of coke on the catalyst during reaction. The deactivation of catalyst in the transformation of methanol to hydrocarbons is mainly due to coke deposition cover the active sites and decreases the active surface area. The surface area and pore volume also decreased with increase in coke deposition over the surface of catalyst as shown in Table 1. The data confirm that coke deposition leads to significant loss of pore volume and surface area. After 12 hours run under identical conditions, the physical properties of coked catalysts were analysed. The typical surface area decreased from 279 m^2/g to 156 m^2/g and pore volume was reduced from 0.39 cm^3/g to 0.29 cm^3/g with an increase in coke deposition.

CONCLUSIONS

Copper oxide doped HZSM-5 impregnated catalysts resulted in an increased activity for conversion of methanol to hydrocarbons of gasoline range. Compared to HZSM-5 catalyst there was a significant increase in conversion and hydrocarbon yield over CuO impregnated catalysts. The optimal CuO loading was 7 wt% over HZSM-5 produced higher methanol conversion and hydrocarbon yield. There was also a significant deactivation of the HZSM-5 with increasing CuO loading and coke deposition in the pores of catalysts due to coverage of the active sites and pore plugging with increase in run time. The major reaction products were methane, ethylene, propylene, dimethylether, toluene, ethyl benzene, xylene, isopropyl benzene, ethyl toluene, trimethyl benzene and tetra methylbenzene. The reaction mechanism for product formation during the conversion process involves alkylation, isomerization, oligomerization. It is concluded that the new active sites are created on the surface of catalyst due to incorporation of copper oxide, which are highly selective to gasoline range hydrocarbons.

NOMENCLATURE

F_{A0} : molar flowrate of methanol [g mol/hr]
W : weight of catalyst [gm]
T : temperature [K]
id : internal diameter [mm]

Abbreviations

HZ (9) : 9 wt% CuO/HZSM-5
HZ (7) : 7 wt% CuO/HZSM-5
HZ (5) : 5 wt% CuO/HZSM-5
HZ (3) : 3 % CuO/HZSM-5
HZ (0) : HZSM-5

REFERENCES

Adebajo, M. O., Long, M. A. and Frost, R. L., "Further Evidence for Oxidative Methylation of Benzene with Methane over Zeolites Catalysts," *Catal. Comm.*, **5**, 125 (2004).

Al-Jarallah, A. M., El-Nafaty, U. A. and Abdillahi, M. M., "Effect of Metal Impregnation on the Activity, Selectivity and Deactivation of a High Silica MFI Zeolites when Converting Methanol to Light Alkenes," *Appl. Catal. A: Gen.*, **154**, 117 (1997).

Alkhawandeh, A., Wu, X. and Anthony, R. G., "Conversion of Mixtures of Methane and Acetylene or Ethylene in to Higher Molecular Weight Hydrocarbons over Metal-loaded and Unloaded HZSM-5 Zeolite Catalysts," *Catal. Today*, **84**, 43 (2003).

Cañizares, P., Lucas, A. D., Dorado, F., Durán, A. and Asencio, I., "Characterization of Ni and Pd Supported on H-morednite Catalysts: Influence of the Metal Loading Method," *Appl. Catal. A: Gen.*, **169**, 137 (1998).

Chang, C. D., Chu, C. T. and Socha, R. F., "Methanol Conversion to Olefins over ZSM-5," *J. Catal.*, **86**, 289 (1984).

Choudhry, V. R., Mantri, K. and Sivadinarayana, C., "Influence of Zeolitic Acidity on Propane Aromatization Activity and Selectivity of

Ga/HZSM-5," *Microporous and Mesoporous Mater.*, **37**, 1 (2000).

Donk, S. V., Janssen, A. H., Bitter, J. H. and Jong, K. P., "Generation, Characterization, and Impact of Mesopores in Zeolite Catalysts," *Catal. Rev.*, **45**, 297 (2003).

Freeman, D., Wells, R. P. K. and Hutchings, G. J., "Conversion of Methanol to Hydrocarbons over Ga_2O_3/WO_3 Catalysts," *J. Catal.*, **205**, 358 (2002).

Gayubo, A. G., Aguayo, A. T., Castilla, M., Olazar, M. and Bilbao, J., "Catalyst Reactivation Kinetics for Methanol Transformation into Hydrocarbons. Expressions for Designing Reaction-Regeneration Cycles in Isothermal and Adiabatic Fixed Bed Reactor," *Chem. Enging. Scienc.*, **56**, 5059 (2001).

Gervasini, A., Picciau, C. and Auroux, A., "Characterization of Copper Exchanged ZSM-5 and ETS-10 Catalysts with Low and High Degrees of Exchange," *Microporous and Mesoporous Mater.*, **35**, 457 (2000).

Haw, J. F., Song, W., Marcus, D. M. and Nicholas, J. B., "The Mechanism of Methanol to Hydrocarbons Catalysis," *Acc. Chem.*, **36**, 317 (2003).

Kang, M., "Methanol Conversion on Metal-incorporated SAPO-34s (MeAPSO-34s)," *J. Mol. Catal. A: Chem.*, **160**, 437 (2000).

Marchi, A. J. and Froment, G. F., "Catalytic Conversion of Methanol into Light Alkenes on Mordenite like Zeolite," *Appl. Catal. A: Gen.*, **94**, 91 (1993).

Mihail, R. S., Satraja, Maria, G., Musca, G. and Pop, G., "A Kinetic Model for Methanol Conversion to Hydrocarbons," *Chem. Enging. Scienc.*, **38**, 1581 (1983).

Mikkelsen, Ø. and Kolboe, S., "The Conversion of Methanol to Hydrocarbons over Zeolites H-beta," *Microporous and Mesoporous Mater.*, **29**, 173 (1999).

Oh, S. H. and Lee, W. Y., "Characterization of $AlPO_4$-based Molecular Sieves and Methanol Conversion to Light Olefins," *Korean J. Chem. Eng.*, **9**, 37 (1992).

Zaidi, H. A. and Pant, K. K., "Catalytic Conversion of Methanol to Gasoline Range Hydrocarbons," *Catal. Today*, **96**, 155 (2004).

Zhu, Z., Hartmann, M. and Kevan, L., "Catalytic Conversion of Methanol to Olefins on SAPO-n (n=11, 34 and 35), CrAPSO-n and Cr-SAPO-n Molecular Sieves," *Chem. Mater.*, **12**, 2781 (2000).