Conversion of Methanol on CuO/H-MOR and CuO/H-ZSM-5 Catalysts

Sameh M. K. Aboul-Fotouh* and Marwa M. I. Hassan

Chemistry Department, Faculty of Education, Ain-Shams University, P.O. Box 13, Cairo 11768, Egypt

* Corresponding author: E-mail: saboulfotouh @hotmail.com

Abstract

This paper deals with maximizing dimethyl ether (DME) production from methanol due to its industrial importance as a future diesel fuel. The high acidity and the micro-porous structure of the catalysts encouraged this reaction. Catalysts containg 6% CuO supported on H-ZSM-5 and H-MOR zeolites give high activities for DME production. The 6% CuO/HMOR is more selective for DME production, while the 6% CuO/HZSM-5 is more selective for olefins (ethylene and propylene) formation. The higher acid site strength of CuO/HMOR is the principal factor for DME formation whereas olefins production is more activated on CuO/HZSM-5 due to its narrower pore volume.

Keywords: HZSM-5, H-MOR, Methanol, Catalysts, Conversion.

1. Introduction

Methanol could be one of the main fuels used in future transportation when petroleum resources are depleted. Methanol is used as a raw material for the production of olefins and other hydrocarbons using zeolite catalysts. Catalytic conversion of methanol to hydrocarbons and olefins using zeolites such as HZSM-5 attracted many researchers when the price of fuel started to increase. Its nature and extent of reaction depends on acid strength, acid site density, catalyst topology, temperature, pressure, space velocity and other process conditions.[1–4] The influence of metal/metal oxide incorporation over the surface of zeolite enhanced the methanol conversion and hydrocarbons yields.[5–9] Conversion of methanol to hydrocarbons over 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 conversion of methanol to hydrocarbons is due to the variation in physicochemical properties of ZnO over CuO/HZSM-5.[5] Various techniques have been used to characterize zeolite catalysts and the impact of catalytic action with different types of zeolite catalysts.[2,10,11] The main aim of the present investigation is the evaluation of two kinds of zeolites (H-MOR and H-ZSM-5) and investigation of the effect of CuO loading on these zeolite supports for conversion of methanol to dimethyl ether and olefins. Temperature-programmed desorption of ammonia has been used to study the number and strength of surface acid sites of zeolites. The correlation of activity with surface acid properties of catalysts was also investigated.

2. Experimental

2. 1. Catalyst Preparation
2. 1. 1. H-ZSM-5 and H-MOR Catalyst

These catalysts were prepared via exchanging Na-ZSM-5 and Na-mordenite with 0.6 M NH_4NO_3 solution followed by overnight drying at 110 °C and calcination in air at 550 °C for 3 h. The H- forms (H-ZSM-5 and H-MOR) have a Si/Al ratio of (25 and 6.1), a surface area of (400 and 470 m^2/g), effective pore diameter (5.6 and 7.6 Å) and pore volume (0.16 and 0.27 cm^3/g), respectively.

2. 1. 2. CuO/Zeolite Catalysts

A part of the mother zeolites prepared in Section 2.1.1 was doped with an aqueous solution of copper nitrate containing the requisite quantity for 2.0–8.0 wt% CuO on H-MOR and 6.0 wt% CuO on H-ZSM-5. The

pH of the solution was adjusted to 7.0 with adding concentrated ammonium hydroxide. These catalysts were then dried at 110 °C overnight followed by calcination in air for 3 h at 550 °C to get copper oxide doped zeolite catalysts. The real CuO content was determined by energy dispersive X-ray spectroscopy (EDX). The dispersion of Cu in the catalysts (fraction of metal exposed) was determined by hydrogen chemisorption using a pulse technique similar to that described by Freel.[12] The physical properties of the final wt% CuO loaded catalysts are shown in Table 1.

Table 1 : Physical properties of the current catalysts

Catalyst	Real content of CuO	Surface area, (m^2/g)	Pore volume, (cm^3/g)	Dispersion of Cu
H-MOR	–	470	0.27	–
2 wt% CuO/H-MOR	3.85	446	0.26	–
4 wt% CuO/H-MOR	5.78	431	0.25	64.3
6 wt% CuO/H-MOR	7.82	413	0.23	61.5
8 wt% CuO/H-MOR	–	331	0.21	51.8
H-ZSM-5	–	400	0.16	–
6 wt% CuO/H-ZSM-5	–	352	0.14	–

2. 2. Methanol Conversion Technique and Products Analysis

A silica glass flow-type tubular reactor system packed with 0.1 g of zeolite catalysts was used in all conversion runs. The reactor was heated in an insulated wider silica tube jacket, thermostated to ±1 °C. Argon gas was used as a carrier at a flow rate of 30 cm^3 min^{-1} in all runs. The feed (methanol) was introduced into the reactor via continuous evaporation using the argon flow passing into a closed jar thermostated at a fixed temperature of 26 °C, whereby the quantity of methanol was always of 4.98 × 10^{-2} mole h^{-1}. The reaction temperatures investigated were 100–300 °C, with 25 °C increments. The reaction effluent passing from the reactor was injected in a Perkin–Elmer Autosystem XL gas-chromatograph using a 4 m length, packed with 10% squalane supported on 10% dodecyl phthalate supported on chromosorp W-HP of 80–100 mesh. A flame ionization detector and a Turbochrom Navigator Programme were used.

2. 3. Characterization of Catalysts

2. 3. 1. X-Ray Diffraction Patterns of the Catalysts (XRD)

The X-ray diffraction patterns of the catalysts studied were carried out using a Brucker Axs D8 Advance, Germany. Patterns were run using Ni filter and copper radiation (λ = 1.5404 Å) at 40 kV and 40 mA at a scanning rate of 0.02°/min.

2. 3. 2. Temperature Programmed Desorption (TPD) of Ammonia

The procedure adopted by Aboul-Gheit[13] and Aboul-Fotouh[14] using differential scanning calorimetry (DSC) for detecting the desorption response of presorbed ammonia from the catalyst was used. Ammonia was primarily adsorbed on the catalyst in a silica tube furnace. After evacuation at 1.33 × 10^{-3} Pa whilst heating at 500 °C and subsequent cooling under vacuum to 50 °C, ammonia was introduced through the catalyst at a flow rate of 50 cm^3 min^{-1}. The samples were then measured in a DSC unit (Mettler TA-3000) using standard Al crucibles. Presorbed ammonia was desorbed in the DSC cell in dry nitrogen as the purge gas at a flow rate of 30 cm^3 min^{-1}. The heating rate in the DSC runs was always 10 K min^{-1} and the full-scale range was 25 mW.

2. 3. 3. Infrared Spectroscopy of Pyridine Adsorption (FTIR-Py)

Infrared analyses of H-MOR and CuO-zeolites were performed on a Perkin–Elmer 2000 FTIR spectrometer. The samples were pressed into self-supporting wafers (8–10 mg/cm^2). A well-defined FTIR spectrum in the OH vibration region was obtained after a vacuum treatment at 450 °C for 8 h. Then pyridine was adsorbed at room temperature for at least 2 h and desorbed at 400 °C under vacuum.

3. Results and Discussion

The catalysts listed in Table 1 were prepared to investigate the effect of acidity of different zeolites and the effect of copper oxide loading over zeolite support on the activities of these catalysts. Special interest is focused on the dehydration activity of methanol due to its application in industrial petroleum processes. The conversion of methanol has been investigated in a plug flow-type fixed-bed reactor using argon gas flow of 30 cm^3 min^{-1} throughout a reaction temperature range of 100–300 °C in order to cover all possible exothermic and endothermic reactions. The major products of the reaction under experimental conditions were, ethylene (C''_2), propylene (C''_3) and dimethyl ether (DME).

At low temperatures (50–150 °C), the following reaction takes place:

$$2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad (1)$$
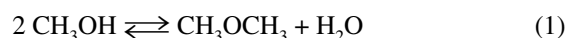
At high temperatures (150–300 °C), the following reactions takes place:

$$CH_3OCH_3 + CH_3OH \rightleftharpoons CH_2=CH_2 \qquad (2)$$

$$CH_2=CH_2 + CH_3OCH_3 \rightleftharpoons CH_2=CH-CH_2 \qquad (3)$$
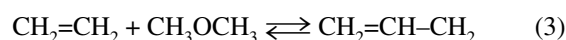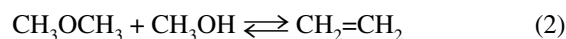
3. 1. Catalyst Characterization

3. 1. 1. X-Ray Diffraction Patterns (XRD)

The X-ray diffraction patterns for copper oxide loaded H-MOR catalysts under study are displayed in Figure 1. The diffractograms indicate that there was no new phase formation during the heat treatment and CuO loading. The structure of zeolite remained intact after the different treatment procedures. No peak related to CuO species was formed for these catalysts. This confirms that CuO in micro pores of zeolites can be automatically dispersed as a result of the exchange of H⁺ by Cu⁺ during the calcination step at 550 °C. However, the peak intensities differ depending upon CuO content and preparation methods. The highest peaks intensities were observed for the starting zeolites. The decrease in the intensities may be due to higher absorption coefficient of CuO. Similar observations were also given in published literature.[11, 15–17]
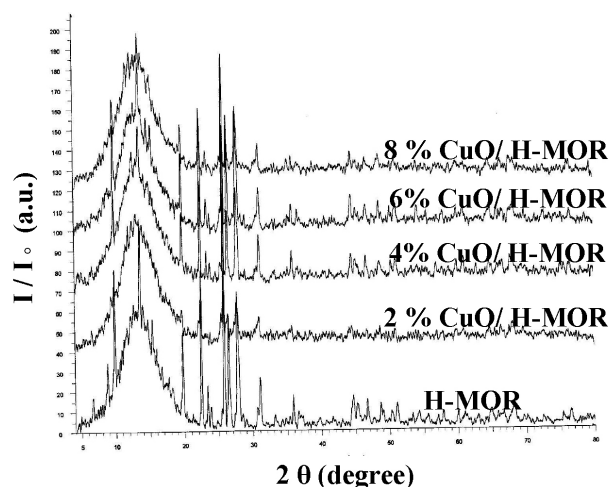

Figure 2: TPD of ammonia from the H- forms of ZSM-5 and mordenite

Table 2: Ammonia desorption enthalpy, HT peak temperature of catalysts

Catalysts	ΔH, J g^{-1}	HT Peak, °C
HZSM-5	123.2	457
H-MOR	98.3	530
2% CuO/HM	90.4	532
4% CuO/HM	87.5	534
6% CuO/HM	85.3	536
8% CuO/HM	80.1	528

Figure 1: XRD diffractograms of copper oxide supported on H-MOR catalysts

3. 1. 2. Surface Acidity of Catalysts

The TPD profiles for H-ZSM-5 and H-MOR zeolites are given in Figure 2. Each profile consists of two endothermic peaks; a low temperature peak (LT) representing desorption of ammonia from the weak acid sites and a high temperature peak (HT) representing desorption of ammonia from the strong acid sites. The latter endothermic DSC effect is of relevance to the catalyst conversion reaction under study; therefore, only values for this effect are given in Table 2. The HT ammonia desorption enthalpy is proportional to the number of strong acid sites in a zeolite, and the HT peak temperatures may compare the strength of these strong acid sites.

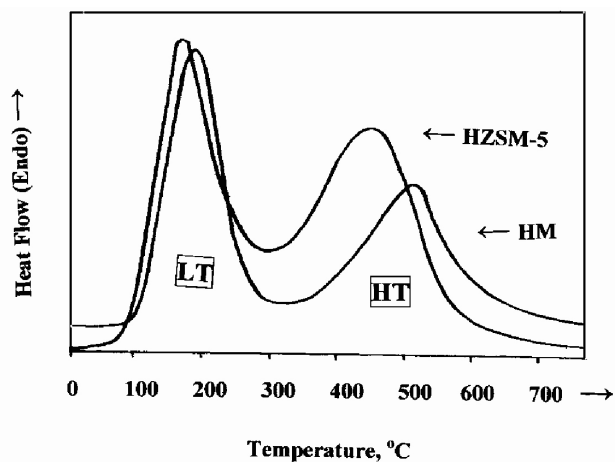Figure 2 and Table 2 show that H-ZSM-5 and H-MOR zeolites possess weak and strong acid sites, however, the former posses large number of strong acid sites (HT peak), whereas the latter posses larger strength of these acid sites. Also, TPD curves that are similar to those shown in Figure 2 were obtained for CuO loaded catalysts and their HT endothermic peak data are given in Table 2. It is indicative that loading the H-MOR zeolite with 2.0%, 4.0% and 6.0% CuO decreases the numbers of strong acid sites; this may be attributed to dilution of protons which are crowded on the surface and cause repulsion between these protons whereby the acid strength increases.[11, 17] A further increase of the CuO loading to 8.0% causes a decrease of the number and strength of acid sites.

FTIR spectra of adsorbed pyridine on H-MOR, 4.0% CuO/H-MOR, 6.0% CuO/H-MOR and 8.0% CuO/H-MOR catalysts (Figure 3) show that all catalysts have acidity in both Brønsted (1545–1550 cm^{-1}) and Lewis acid sites (1450–1460 cm^{-1}) while the number of Lewis sites increased as Brønsted sites decreased upon loading of CuO. It can be seen that Brønsted/Lewis ratio is smaller for the CuO catalysts compared with the parent zeolite (H-MOR), and catalyst with 4.0% CuO/H-MOR present a greater proportion of Lewis sites than 6.0% CuO/H-MOR and 8.0% CuO/H-MOR catalysts.[11, 17]
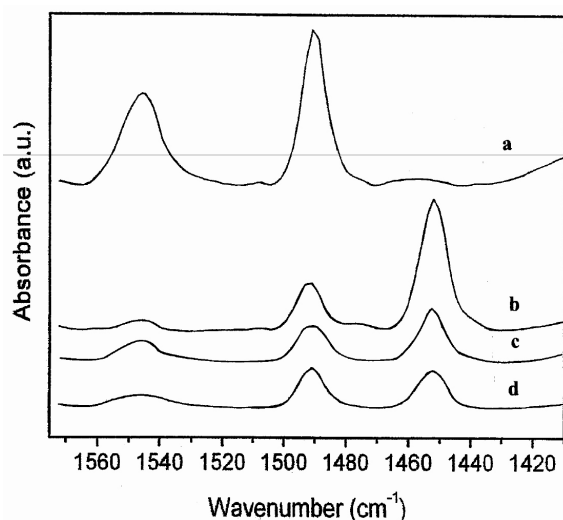
Figure 3: FTIR spectra of adsorbed pyridine on (a) H-MOR, (b) 4.0% CuO/HMOR, (c) 6.0% CuO/HMOR and (d) 8.0% CuO/H-MOR

3. 2. Conversion of Methanol Using the Unloaded H-ZSM-5 and H-MOR Zeolites

The influence of the reaction temperature on the dehydration of methanol to DME over the acid zeolite catalysts, under study, is shown in Figure 4. The data indicate that, briefly, H-ZSM-5 catalyst is significantly more active than H-MOR catalyst for DME formation at the lower reaction temperature range, i.e. at temperatures between 100 and 175 °C, where DME formation is thermodynamically favored. At 175 °C, DME formation achieves a maximum activity of 47.1% using HZSM-5 catalyst; above this temperature DME decreases to 21.0% at 300 °C. On the other hand, a significant achievement is obtained using H-MOR for the current dehydration reaction, since a maximum activity of 32.3% is attained at 225 °C. At higher reaction temperatures, 225–300 °C, the activities of the two current catalysts become almost equal till 300 °C. The decrease of activity for DME formation above 175 °C using HZSM-5 and above 225 °C using H-MOR is attributed to the reaction exothermicity and olefin formation (Figure 5). Since the reaction of methanol dehydration to DME is exothermic, the reaction equilibrium will move to left by further increasing of temperature.[18] In previous publications[19,20] Anderson and Klinowski show that at 150 °C only DME is produced from methanol using HZSM-5 catalyst. These authors also show that using H-ZSM-5 the equilibrium between methanol and DME is approached after heating the sample at 150 °C for 5 min and a much longer period is required when the reaction is carried out over affretite zeolite catalyst. The findings of these authors[19,20] may explain the behaviors of the current HZSM-5 and H-MOR catalysts as shown in Figure 4. The diffe-

rence in activity between HZSM-5 and H-MOR zeolite catalysts towards dehydration of methanol to DME can be explained in terms of the shape and dimension of the channels, as well as the acidities of the zeolites used:

(i) The effective pore opening of these zeolites, which is considered the relevant parameter for diffusion of the reactant molecules along the zeolitic channels, is of intermediate pore size (5.6 Å) in case of H-ZSM-5 and a large pore size (6.7 Å) in H-MOR. It may thus be evident that the order of diffusion restriction along the catalytic pores is in accordance with the order of activities of the catalysts for DME formation.[21] Wei[22] introduced a mathematical model showing that more significantly limited diffusion along the zeolitic channels gives greater opportunity to reactant molecules to come in contact with a larger number of active catalytic sites, and hence, a higher catalytic activity is observed. Shah et al.[23] demonstrated that when methanol is situated in the more open cage regions of zeolites, it appears to be un-protonated and less chemically active. It follows that the medium-sized pores in HZSM-5 should be the most active for the conversion of methanol to DME where methanol appears to be easily protonated.

(ii) Another effect is the difference in the acidities of H-ZSM-5 and H-MOR. Methanol dehydration is considered to occur on the acid sites of the catalyst surface.[24] Hence, from TPD of ammonia (Figure 4, Table 2), the activities of these catalysts for DME production are compatible with the number of strong acid sites, but not with their strengths. So, H-ZSM-5 catalyst exhibits higher catalytic activity for methanol dehydration, compared to that of H-MOR zeolite catalyst. On using H-MOR catalyst the stronger acidity causes the equilibrium to be reversed to the left hand side and hence results in a lower activity of the catalyst.

The activities of the zeolite catalysts under investigation for producing the light olefins (ethylene and propylene) during the conversion of methanol are in the same order of DME production (Figure 5), which can be attributed to the larger number of acid sites in H-ZSM-5.
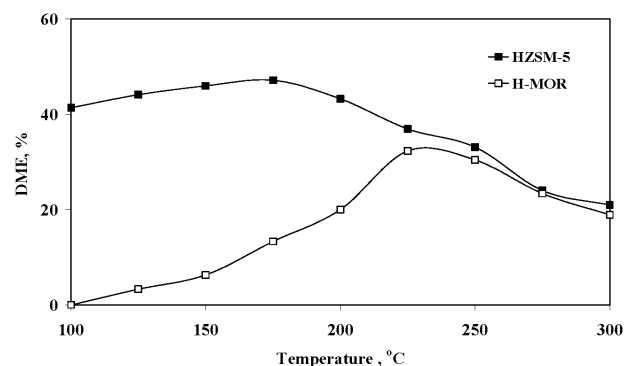

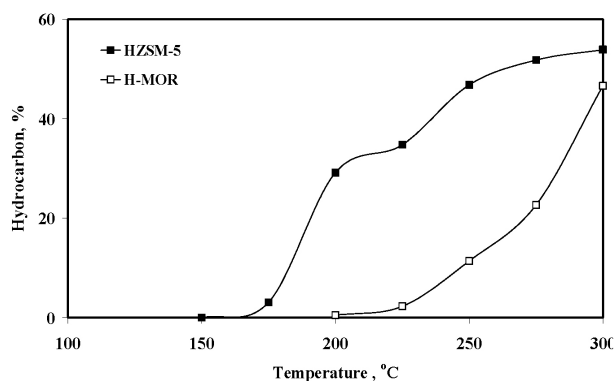**Figure 4:** Dimethyl ether production using H-ZSM-5 and H-MOR catalysts

Figure 5: Hydrocarbons production using H-ZSM-5 and H-MOR catalysts

Figure 6: Dimethyl ether production using CuO supported on H-MOR catalysts

3. 2. Effect of CuO Loading on H-MOR Towards Methanol Conversion

The conversion of methanol to DME and olefins was investigated using H-MOR loaded with 2.0, 4.0, 6.0 and 8.0 wt% CuO, compared to those using the corresponding unloaded zeolite as depicted in Figures 6 and 7. Evidently, CuO loading has enhanced the conversion activities of H-MOR catalyst, so that the activities of the current catalysts can be arranged in the order: 6.0% CuO > 8.0% CuO > 4.0% CuO > 2.0% CuO > 0.0% CuO

The activity of the unloaded H-MOR is found to be lower than those of all CuO-loaded catalysts at almost whole temperature range. Using the unloaded H-MOR zeolite as the catalyst, the methanol conversion to DME amounts to 3.3% at 125 °C and increases by rising the temperature to 32.3% at 225 °C, beyond which DME production declines continually to 18.9% at 300 °C. Loading H-MOR with 2.0 wt% CuO increased DME to attain 12.9% at 100 °C, then increases with reaction temperature to 34.3% at 225 °C beyond which DME decreases to 26.3% at 300 °C. Increasing the CuO loading to 4.0 wt% then to 6.0 wt%, the activity for DME formation continues to increase to a maximum at 200 °C and 175 °C, respectively, then decreases with further increasing the CuO content. Evidently the activity of the 8.0 wt% CuO/H-MOR catalyst has been somewhat lower than using the 6.0 wt% CuO/H-MOR catalyst at all reaction temperatures.

The strong acid sites and Brønsted/Lewis site ratio of the zeolites decrease with the increase of the CuO loading over H-MOR (Table 2 and Figure 3). The observed decrease in acidity may be due to the exchange of some protons by copper ions.[11,15,16] Further increase in CuO loading to 8.0 wt% did not improve the activity of the catalyst; possibly due to coverage of the active sites, pore blocking and decrease of surface area, pore volume, dispersion and acidity of H-MOR zeolite catalyst as shown in Tables 1, 2 and Figure 3. Thus, for better performance in methanol conversion there should be a proper balance between acidity and Cu species in the zeolite channel.[25,26]
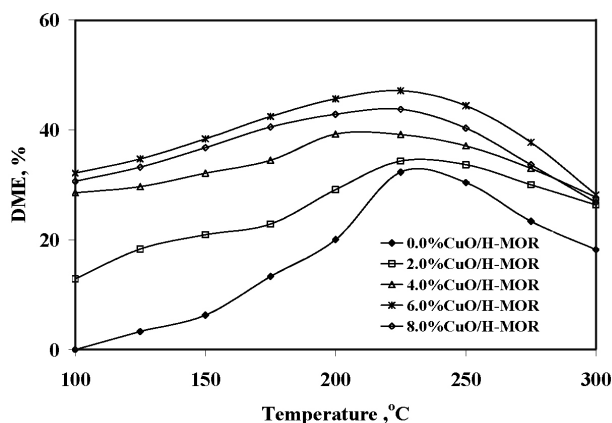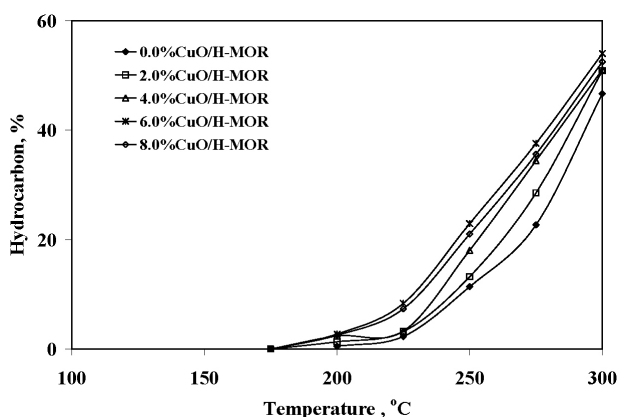

Figure 7: Hydrocarbons production using CuO supported on H-MOR catalysts

The results obtained in this study indicate that the 6.0% CuO supported on H-MOR zeolite catalyst is the most active and selective for dehydration of methanol to DME. Such results can be represented by the so called Waterman's plot (Figure 8) which is important from the
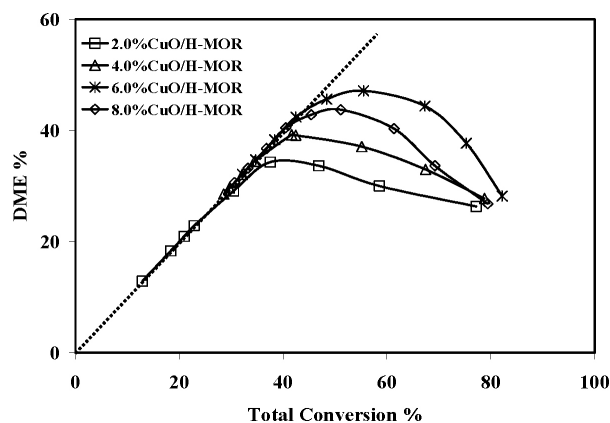

Figure 8: Waterman's plot for DME selectivities using CuO/H-MOR catalysts

industrial point of view to represent the selectivity of fuel production catalysts.

Figure 8 shows the relationship between the yield of DME and the total conversion of methanol. The 2.0% CuO containing catalyst gives 100% selectivity for DME up to 22.9% conversion. This selectivity increases with increasing the metal content so that up to 42.4% conversion on the 6.0% CuO catalyst the selectivity is 100%, beyond which the increase of total conversion results in decreasing the DME selectivity. A further increase of CuO content on the zeolite catalyst to 8.0% the selectivity to DME remains 100% up to 40.5% conversion beyond which the selectivity decreases below 100%.

The selectivity to DME variation as a function of CuO loading at a maximum temperature activity (225 °C) is shown in Figure 9. It is observed that the maximum selectivity toward DME decreases with increasing CuO loading and is comparable with the number of strong acid sites as well as Brønsted/Lewis acid sites ratio, however it is not comparable with the strength of acid sites (Table 2 and Figure 3).
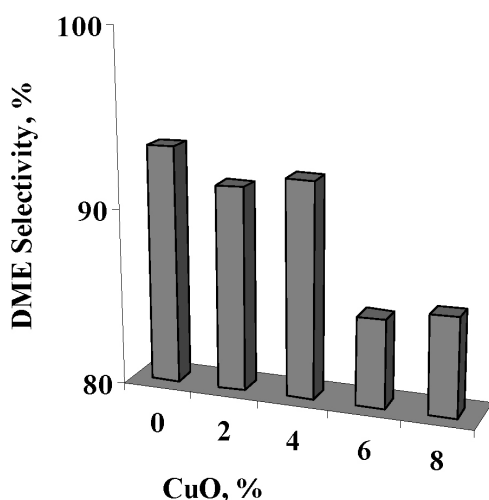

Figure 9: Effect of CuO loading on the maximum DME selectivity at 225 °C

Nunes et al.[27] studied the influence of the acid sites on the methylamine synthesis by methanol amination with different concentrations of Cu on H-ZSM-5 zeolite, and found that catalyst containing 3.7% copper was slightly more selective to monomethylamine (MMA) than the catalysts with other CuO contents. From these results the authors showed that the metal loading present in the catalysts leads to a modification in the nature of the acidic sites, in particular the selectivity depends on the ratio of Brønsted/Lewis acid sites. This modifications would facilitate the amines desorption during the reaction. This reaction resembles our DME formation reaction mechanistically, hence, it can be assumed that the ratio between

Brønsted and Lewis acid sites critically influences our reaction selectivity. Zaidi and Pant[5,15,16] pointed out that the addition of CuO into the zeolite framework usually results in the generation of additional acidic sites and thereby modifies the acidity of the parent material and facilitates the dehydrating activity of the catalyst. New active sites are created on the surface of zeolite catalyst due to incorporation of copper oxide, which are highly selective to methanol conversion to DME and olefins.

3. 3. Effect of 6.0 wt% CuO Loading on H-ZSM-5 Towards Methanol Conversion

We used 6.0 wt% CuO loading on another catalytically active zeolite (ZSM-5) because of its unique zeolitic structure. Figure 10 shows that the unloaded H-ZSM-5 catalyst is more active at lower reaction temperature than the 6.0 wt% CuO loaded catalyst for DME formation. Using the unloaded H-ZSM-5 catalyst, DME comprises 41.4% at 100 °C and rises almost steadily to reach a maximum of 47.1% at 175. However, using the 6.0 wt% CuO loaded HZSM-5 catalyst, DME comprises as low as 24.1% at 100 °C, and activity rises to a maximum of 49.6% at 175 °C. Above this temperature DME formation declines on both catalysts with a further increase of reaction temperature. This indicates that the dehydration-hydration equilibrium shifts beyond 175 °C to the right, due to the endothermicity of the dehydration reaction to produce olefins. At higher reaction temperatures (175–300 °C) the activity of CuO/H-ZSM-5 modestly rises (comparing with the unloaded zeolite) up to 300 °C due to hydrocarbon formation (Figure 11). At low temperature, the unloaded H-ZSM-5 is more active than the CuO loaded one by virtue of its higher acidity. However, at higher temperatures (175–300 °C), the activation of the CuO loaded H-ZSM-5 catalyst over the unloaded one is attributed to the effectiveness of CuO incorporation with zeolite.

The loading of 6.0 wt% CuO on H-ZSM-5 zeolite catalyst resulted in a significant decreases of its DME ac-
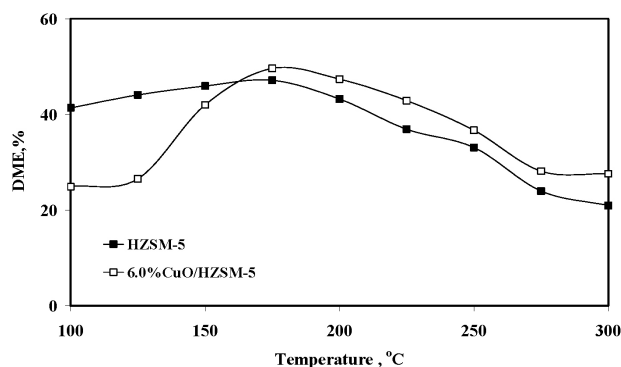

Figure 10: Dimethyl ether production using unloaded H-ZSM-5 and 6.0% CuO/H-ZSM-5 catalysts
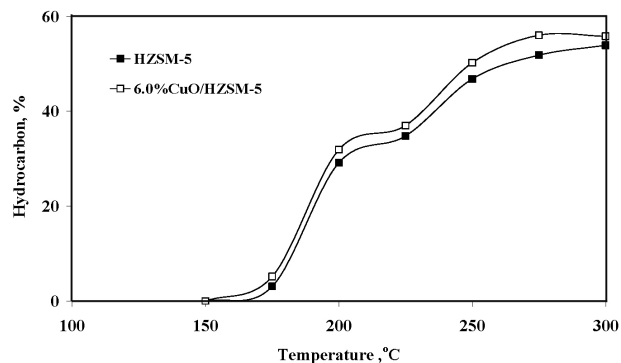
Figure 11: Hydrocarbons production using unloaded H-ZSM-5 and 6.0% CuO/H-ZSM-5 catalysts

Figure 13: Hydrocarbon selectivity using 6.0% CuO supported on H-ZSM-5 and H-MOR catalysts

tivity and selectivity (Figure 12). However, the loading of 6.0 wt% CuO on H-MOR zeolite catalyst resulted in a large enhancement in its DME activity and selectivity on the temperature range investigated (Figure 13). This may be attributed to the acidity strength and acid sites number in CuO/H-MOR that are higher than in CuO/H-ZSM-5, and also the pores in CuO/H-MOR are larger than in CuO/H-ZSM-5. The decrease in pore size of the 6.0% CuO supported H-ZSM-5 zeolite as compared to the 6.0% CuO/H-MOR is indicative of better blocking of the smaller pores of H-ZSM-5 than blocking the larger pores of H-mordenite.[14,27] Moreover, the diffusion of the relatively large product molecule (CH_3–O–CH_3) in the CuO/H-MOR catalyst is easier than in the CuO/HZSM-5 catalyst, since the former catalyst acquires larger pore volume than the latter catalyst. The diffusion of the olefinic molecules produced (CH_2=CH_2 and CH_2=CH–CH_3) in the CuO/zeolites is not significantly effective because these olefins are smaller when compared with CH_3–O–CH_3. Therefore, the principal effect is attributed to the metal dispersion which is higher in CuO/H-ZSM-5 than CuO/H-MOR.[28] The higher activity and selectivity of CuO/H-ZSM-5 than CuO/H-MOR for the formation of olefins can be attributed to the dispersion of Cu in the zeolite (Figure 13).
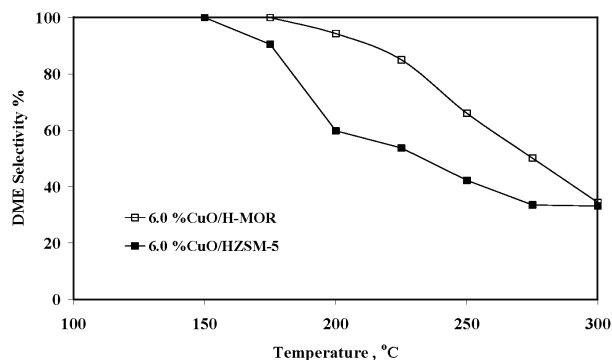
3. 4. Activation Energy for DME Formation

The reaction rate constant (*K*) has been calculated according to the second order reaction kinetics from the data on conversion of methanol to DME.[29] The activation energy (E_a), listed in Table 3, have been conventionally calculated applying the Arrhenius equation from the slope of plot of ln *K* vs. 1/*T*.

The computed E_a values obtained for dehydration of methanol to DME are in general compatible with the activities of the catalysts used. Increasing of CuO loading on H-MOR from 0.0 to 8.0 wt% resulted in a measurable decrease in the value of E_a from 41.2 to 7.2 kJ mol^{-1} due to the higher activity of CuO included. The loading of 6.0 wt% CuO on H-ZSM-5 zeolite resulted in a significant increase of the value of E_a from 3.9 to 20.8 kJ mol^{-1} which can be attributed to the higher activity of the parent zeolite.

Table 3: Activation energies for methanol dehydration to DME on the current catalysts

Catalysts	E_a (kJ mol^{-1})
H-MOR	41.2
2.0 wt% CuO/H-MOR	13.9
4.0 wt% CuO/H-MOR	10.4
6.0 wt% CuO/H-MOR	7.5
8.0 wt% CuO/H-MOR	7.2
H-ZSM-5	3.9
6.0 wt% CuO/H-ZSM-5	20.8

4. Conclusion

(i) The high acidity and small pore opening of zeolites has a marked influence on the conversion of methanol and formation of DME.

(ii) Inclusion of CuO promotes the zeolite catalysts activity towards conversion of methanol and production of DME.

Figure 12: Dimethyl ether selectivity using 6.0% CuO supported on H-ZSM-5 and H-MOR catalysts

(iii) The optimum CuO concentration of 6.0 wt % corresponds to maximum enhancement for catalytic activity and DME yield.

(iv) A decrease in catalytic activity of H-MOR zeolite is observed with increasing CuO loading up to 8.0 wt % which is attributed to coverage of the active sites, pore blocking.

(v) The major reaction products were ethylene, propylene and dimethyl ether. It is concluded that new active sites are created on the surface of catalyst due to incorporation of CuO, which are highly selective to DME formation.

(vi) The higher acid site strength of CuO/HMOR is the principal factor for DME formation whereas olefins production is more activated on CuO/HZSM-5 due to its narrower pore volume.

5. References

1. A. Alkhawandeh, X. Wu, R. G. Anthony, *Catal. Today*, **2003**, *84*, 43–49.

2. P. Cañizares, A. de Lucas, F. Dorado, A. Durán, I. Asencio, *Appl. Catal. A* **1998**, *169*, 137–150.

3. A. J. Marchi, G. F. Froment, *Appl. Catal. A* **1993**, *94*, 91–106.

4. S. H. Oh, W. Y. Lee, *Korean J. Chem. Eng*. **1992**, *9*, 37–44.

5. H. A. Zaidi, K. K. Pant, *Catal. Today* **2004**, *96*, 155–160.

6. A. M. Al-Jarallah, U. A. El-Nafaty, M. M. Abdillahi, *Appl. Catal. A* **1997**, *154*, 117–127.

7. D. Freeman, R. P. K. Wells, G. J. Hutchings, *J. Catal*. **2002**, *205*, 358–365.

8. M. Kang, *J. Mol. Catal. A* **2000**, *160*, 437–444.

9. Z. Zhu, M. Hartmann, L. Kevan, *Chem. Mater*. **2000**, *12(9)*, 2781–2787.

10. S. V. Donk, A. H. Janssen, J. H. Bitter, K. P. Jong, *Catal. Rev.* **2003**, *45*, 297–319.

11. A. Gervasini, C. Picciau, A. Auroux, *Microporous Mesoporous Mater*. **2000**, *35*, 457–469.

12. J. Freel, *J. Catal.* **1972**, *25*, 139–148.

13. A. K. Aboul-Gheit, S. M. Abdel-Hamid, S. A. Ghoneim, A. A. Al-Owais, *Erdol Erdgas Kohle* **1999**, *115*, 90–94.

14. S.M. Aboul-Fotouh, *J. Chinese Chem. Soc.* **2003**, *50*, 1151–1158.

15. H. A. Zaidi, K. K. Pant, *Korean J. Chem. Eng.* **2005**, *22*, 353–357.

16. H. A. Zaidi, K. K. Pant, *Can. J. Chem. Eng.* **2005**, *83*, 970–977.

17. Y. Gong, T. Doua, S. Kang, Q. Li, Y. Hu, *Fuel Process. Technol.* **2009**, *90*, 122–130.

18. Y. Fu, T. Hong, J. Chen, A. Auroux, J. Shen, *Thermochim. Acta* **2005**, *434*, 22–26.

19. M. W. Anderson, J. Klinowski, *Nature* **1989**, *339*, 200–203.

20. M. W. Anderson, J. Klinowski, *J. Am. Chem. Soc.* **1990**, *112*, 10–16.

21. S. M. Aboul-Fotouh, *Acta Chim. Slov.* **2004**, *51*, 293–304.

22. J. Wei, *J. Catal.* **1982**, *76*, 433–439.

23. R. Shah, M. C. Payne, M. H. Liee, J. D. Gale, *Science* **1996**, *271*, 1395–1397.

24. S. Jiang, J.-S. Hwang, T. Jin, T. Cai, W. Cho, Y. S. Baek, S.-E. Park, *Bull. Korean Chem. Soc.* **2004**, *25*, 185–189.

25. M. O. Adebajo, M. A. Long, R. L. Frost, *Catal. Commun.* **2004**, *5*, 125–130.

26. P. Djinović, U. Kocjan, J. Batista, A. Pintar, *Acta Chim. Slov*. **2009**, *56*, 868–877.

27. M. H. O. Nunes, V. T. da Silva, M. Schmal, *Appl. Catal. A* **2005**, *294*, 148–155.

28. N. A. S. Amin, D. D. Anggoro, *J. Natural Gas Chem.* **2003**, *12*, 123–134.

29. P. Mizsey, E. Newson, T.-b. Truong, P. Hottinger, *Appl. Catal. A* **2001**, *213*, 233–237.

Povzetek

Opisujemo metodo maksimiziranja tvorbe dimetil etra (DME) iz metanola, saj DME predstavlja industrijsko pomembno dieselsko gorivo prihodnosti. Velika kislost in mikroporoznost strukture katalizatorja omogoča to reakcijo. Katalizatorja, ki sta vsebovala 6% CuO nanešenega na H-ZSM-5 oz. H-MOR zeolitno osnovno, sta se izkazala z visokimi katalitskimi aktivnostmi za pripravo DME. Katalizator 6% CuO/H-MOR je bil bolj selektiven za pripravo DME, medtem ko je bil katalizator 6% CuO/H-ZSM-5 bolj učinkovit za nastajanje olefinov (etilena in propilena). Večja jakost kisih mest v CuO/H-MOR je glavni faktor, ki olajša nastajanje DME, nastajanje olefinov pa je zlasti pospešeno s CuO/H-ZSM-5, saj ima manjšo razpršitev velikosti por.