Conversion of Methanol Using Modified H-MOR Zeolite Catalysts

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Abstract: The conversion of methanol was carried out over various mordenite zeolite catalysts to evaluate their catalytic performance. A post-preparation treatment of the H-MOR catalyst by halogenation with NH_4Cl or NH_4F and by hydrohalogenation with HCl or HF was carried out and its effect on methanol conversion reactions at 100–300 °C in a continuous flow reactor was investigated. The as-synthesized H-mordenite (H-MOR) is generally more active during dimethyl ether (DME) production than the $\text{NH}_4\text{-MOR}$ and Na-MOR . Fluorinated treatment with HF or NH_4F significantly improved the catalytic activity during methanol conversion and the formation of DME in comparison to chlorinated treatments with HCl or NH_4Cl . This is principally attributed to the higher Si/Al ratio and an increase in the number of acid sites and their strength. Halogenation treatment with the acids of both F^- or Cl^- gave the highest conversion activity for DME production compared to halogenation treatments with the salts of the same halogens. Zeolite dealumination by the acids was more profound than that by the halogen ion salts, which resulted in a decrease in the crystallinity and crystallite sizes of the zeolite.

Key words: methanol; conversion; H-MOR; halogenation; hydrohalogenation

CLC number: O643

Document code: A

Methanol will possibly be one of the main fuels used in future when the petroleum resources are depleted. Methanol is produced from synthesis gas (mixture of CO_2 and H_2), which is formed by the steam reforming of natural gas, the gasification of coal or from biomass. Methanol is abundant and, therefore, it has been used as a raw material for the production of gasoline and olefins. It can be obtained from renewable sources such as biomass. The catalytic conversion of methanol to gasoline and to olefins attracted the attention of many researchers when the price of fuel started to increase. Literature concerning the conversion of methanol to hydrocarbons over zeolite catalysts is extensive [1–12]. Its nature and the extent of the reaction depend on the acid site density and strength as well as the reaction conditions [13–16].

Metal/metal oxide incorporation on to the surfaces of zeolites leads to an increase in methanol conversion and dimethyl ether (DME) yield [17–21]. If the metal is supported on Al_2O_3 [22], the acid sites are of the weak Lewis type where the acid strength is not strong enough to promote methoxonium ion formation and hence the dehydration reaction cannot occur. However, the H-forms of the zeolites possess strong Brönsted acid and Lewis sites that promote methanol conversion to DME and olefins and their reaction schemes are complicated. Nevertheless, treatment of cation-exchanged zeolites with HCl or HF leads to decationation and partial dealumination. The hydroconversion of

cyclohexene over metal/ Al_2O_3 with and without Cl^- and F^- ions has been studied by Aboul-Fotouh and Aboul-Gheit [23]. Introducing Cl^- or F^- ions into aluminate alumina in different ways causes Brönsted acid sites to appear and a drastic increase in both the skeletal isomerization and total conversion. Arena et al. [24] indicated that Cl^- adsorbed on the surface of γ -alumina results in promotion because of a substantial change in the electronic properties of the outermost alumina layer. Ultimately, these effects result in a weakening of the O–H bond, which renders the proton more acidic.

Doping H-ZSM-5 with a low concentration of F^- followed by thermal activation enhances surface acidity by the formation of new Brönsted acid sites and the strengthening of other acid sites on the parent zeolite [25–27]. The aim of our work is to evaluate different mordenite (MOR) zeolites (H-MOR, $\text{NH}_4\text{-MOR}$, and Na-MOR) and study the effect of doping H-MOR with 3.0 wt% HCl , HF , NH_4Cl , and NH_4F to visualize this effect on methanol conversion in a flow reactor that operates in a flow of argon at temperatures of 100–300 °C.

1 Experimental

1.1 Preparation of the catalysts

1.1.1 H-MOR catalyst

Received 19 October 2010. Accepted 23 November 2010.

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English edition available online at ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

The sodium ions in the Na-mordenite zeolite (Zeolon 900-Na, kindly supplied by Norton Co., USA, in the form of 1.59 mm extrudates) were exchanged five times using an NH_4NO_3 solution under reflux. A fresh solution was used each time and the reflux lasted for 8 h at 70 °C. The zeolite was then separated, washed with distilled water until it was free of NO_3^- , dried at 110 °C overnight, and then calcined in air at 550 °C for 3 h. The H-form (H-MOR) had a Si/Al ratio of 6:1, a surface area of 470 m^2/g , an effective pore diameter of 0.67 nm, and a pore volume of 0.27 cm^3/g .

1.1.2 Chlorinated and fluorinated H-MOR catalysts

Some of the batch zeolite prepared in section 1.1.1 was doped with 3.0 wt% aqueous HCl, HF, NH_4Cl , or NH_4F , dried and then calcined as mentioned above.

1.2 Methanol conversion and product analysis

A silica glass flow tubular reactor system packed with 0.1 g of the zeolite catalyst was used in all the conversion runs. The reactor was heated in an insulated wider silica tube jacket, which was kept to within ± 1 °C. Argon gas was used as a carrier at a flow rate of 30 cm^3/min in all the runs. The feed (methanol) was introduced into the reactor by continuous evaporation using the argon flow that passed into a closed jar and that was kept at a fixed temperature of 26 °C. The amount of methanol used was always 49.8 mmol/h. The reaction temperatures investigated ranged from 100–300 °C at 25 °C increments. The reaction effluent that passed from the reactor was injected into a Perkin-Elmer Autosystem XL gas-chromatograph containing a 4 m column packed with 10% squalane on 10% didecyl phthalate on chromosorp W-HP of 80–100 mesh. A flame ionization detector and the Turbochrom Navigator Program were used for analysis.

1.3 Characterization of the catalysts

X-ray diffraction (XRD) patterns of the catalysts were obtained using a Bruker AXS D8 Advance. Patterns were run using a Ni filter and copper radiation ($\lambda = 0.15404$ nm) at 40 kV and 40 mA and at a scan rate of $0.02^\circ/\text{min}$.

For temperature-programmed desorption (TPD) of ammonia experiments, we applied the procedures reported by Aboul-Gheit et al. [28] and Aboul-Fotouh [29] using differential scanning calorimetry (DSC) to detect the desorption response of presorbed ammonia from the catalysts. Ammonia was primarily adsorbed on the catalyst in a silica tube furnace. After evacuation at 1.33×10^{-3} Pa and upon heating at 500 °C and subsequent cooling under vacuum to 50 °C ammonia was introduced to the catalyst at a flow rate of 50 cm^3/min . The samples were then assessed in a DSC unit

(Mettler TA-3000) using standard Al crucibles. Presorbed ammonia was desorbed in the DSC cell using dry nitrogen as a purge gas at a flow rate of 30 cm^3/min . The heating rate in the DSC runs was always 10 °C/min and the full-scale range was 25 mW.

2 Results and discussion

2.1 Characterization of the catalysts

2.1.1 XRD patterns

Figure 1 shows that none of the main diffraction bands in the XRD patterns obtained for the modified H-MOR show a measurable shift in their 2θ positions compared to the stock H-MOR sample. However, the diffraction intensities of all the bands decreased for the halogen-modified zeolites. Moreover, the mordenite samples treated by chlorination with NH_4Cl or hydrochlorination with HCl gave higher diffraction intensities than those treated by fluorination with NH_4F or hydrofluorination with HF and this can be attributed to a greater extent of zeolite dealumination by the F^- ions than by the Cl^- ions [22,27].

Fig. 1. XRD patterns of the halogenated and hydrohalogenated H-MOR catalysts.

Figure 2 shows that treatment of H-MOR by halogenation or hydrohalogenation leads to a decrease in the degree of crystallinity (crystallite size). The as-synthesized H-MOR was found to have the largest crystallite size among the treated samples and the sizes decreased according to: H-MOR > $\text{NH}_4\text{Cl}/\text{H-MOR}$ > $\text{HCl}/\text{H-MOR}$ > $\text{NH}_4\text{F}/\text{H-MOR}$ > $\text{HF}/\text{H-MOR}$.

The stronger attack on the Al in the zeolite framework is

Fig. 2. Crystallite sizes from XRD of the H-MOR zeolite catalysts.

known to be followed by the migration of Si atoms to fill the vacant Al positions. Therefore, the Si–O–Al bonds are partially changed to Si–O–Si bonds to stabilize the zeolitic structure. Since Si–O bonds are shorter than Al–O bonds, the zeolitic crystal units cells shrink while the channels (pores) and the surrounding crystals become narrower. F[−] ions are more reactive than Cl[−] because of their larger inductive effect [30,31].

2.1.2 Surface acidity of the catalysts

TPD of the presorbed ammonia on the acid sites of the catalysts was carried out using DSC with nitrogen as an inert purge gas. TPD profiles for the studied catalysts are given in Fig. 3. Each profile consists of two endothermic peaks, one of which is a low temperature peak (100–300 °C) that is not related to the activation of carbonium ion formation and, therefore, it cannot be correlated with changes in the catalytic activity during DME formation. The higher temperature peak (400–650 °C) that appears in the thermogram is closely related to carbonium ion formation

Fig. 3. TPD of ammonia from the untreated and halogenated H-MOR catalysts.

and, therefore, to the activity of DME production. This figure shows that the number of acid sites decreases whereas the acid site strength increases with the different treatments (Table 1).

Table 1 HT-ammonia desorption enthalpy, HT-peak temperature, and Si/Al ratios for the zeolite catalysts

Catalyst	$\Delta H/(\text{J/g})$	HT-peak temperature (°C)	Si/Al ratio
H-MOR	98.3	530	6.1
HF/H-MOR	82.2	537	8.1
NH ₄ F/H-MOR	79.6	533	7.8
HCl/H-MOR	74.3	535	7.3
NH ₄ Cl/H-MOR	70.5	531	6.5

HT: High temperature.

2.2 Conversion of methanol

The studied catalysts were prepared to investigate the effect of different mordenite zeolite treatments by the above mentioned halogenation and hydrohalogenation processes. The conversion of methanol was investigated in a fixed-bed reactor using an argon flow of 30 cm³/min for a reaction temperature range of 100–300 °C to cover all possible exothermic and endothermic reactions. The major products of the reaction under these experimental conditions were ethylene, propylene, and DME.

2.2.1 Conversion of methanol with the H-, NH₄-, and Na-MOR catalysts

The conversion of methanol was examined over the H-MOR, NH₄-MOR, and Na-MOR catalysts at 100–300 °C in a flow reactor. Figure 4 shows the DME and hydrocarbon products that were produced by methanol conversion. The data shows that the dehydration and alkylation products (DME and olefins, respectively) were obtained using H-MOR and NH₄-MOR whereas only the dehydration product (DME) is produced when using Na-MOR. This is attributed to the absence of strong acid sites, which are capable of promoting olefin formation. Campbell et al. [32] used CH₃OH-TPD for the characterization of the acid properties of the surface zeolite (strength and nature of the acid sites) and concluded that methanol dehydration to DME and the production of light hydrocarbons are related to the type and strength of the acid sites. Brønsted acid sites with moderate to high strengths are responsible for the formation of by-products (e.g. ethylene and propylene) during a reaction between methanol molecules while Lewis acid sites do not show catalytic activity. For the dehydration of methanol to DME, Brønsted and Lewis sites cooperate and the conversion is proportional to the acid strength.

Fig. 4. DME (a) and hydrocarbons (b) in the mordenite catalyst products.

Figure 4 shows the activities of the studied catalysts from 100–300 °C for the conversion of methanol to DME and olefins, respectively. The activity decreases as follows: H-MOR > NH₄-MOR > Na-MOR. This order is compatible with the order of mordenite catalyst acidity [28]. From the acid site desorption of NH₃ in the Na-MOR and H-MOR Aboul-fotouh [29] indicated that the acidity of H-MOR can be attributed to the strong acid sites whereas the acidity of Na-MOR is due to the weaker acid sites. On the other hand, Aboul-Gheit et al. [28] showed that the acidity of NH₄-MOR is lower than that of H-MOR since the acid sites in H-MOR are strong Brönsted sites.

2.2.2 Conversion of methanol using halogenated and hydrohalogenated H-MOR zeolite catalysts

Fluorination and chlorination using NH₄F and NH₄Cl with halogen concentrations from 1.0 to 6.0 wt% has been carried out in previous works [22,23,26,27] and a halogen content of 3.0 wt% was found to be optimum. Hence 3.0 wt% F⁻ or Cl⁻ was used in this study to prepare the halogenated H-MOR zeolite catalysts by NH₄F and NH₄Cl doping. Moreover, hydrohalogenated catalysts were also prepared by doping with 3.0 wt% HCl or 3.0 wt% HF solutions, respectively.

The prepared halogenated and hydrohalogenated H-MOR catalysts were examined for methanol conversion from 100–300 °C. The total methanol conversion activities of the studied H-MOR catalysts doped with 3.0 wt% HF, HCl,

NH₄F, or NH₄Cl, were found to be effective (Fig. 5). Moreover, fluorination and hydrofluorination were found to be more effective than chlorination and hydrochlorination, respectively.

Fig. 5. Total conversion of methanol using the halogenated and hydrohalogenated H-MOR catalysts.

Figure 6 shows that higher activities for methanol conversion to DME were obtained by F⁻ inclusion compared to Cl⁻ inclusion. Moreover, direct acid treatment with HF or HCl results in higher activities than that of the corresponding ammonium salt treatments because of direct halogen liberation in the former treatments. The superiority of F⁻ treatment over Cl⁻ treatment is attributed to its higher electronegativity [30,31]. DME production increases as a func-

Fig. 6. DME (a) and hydrocarbons (b) in the product upon halogenated and hydrohalogenated H-MOR catalysts.

tion of reaction temperature up to 200 °C beyond which DME decreases in the product as the temperature increases further because of hydrocarbon formation (Fig. 6).

The relatively higher activities of all the treated catalysts compared to the H-MOR catalyst are attributed to the higher acid site strengths of the catalysts (Fig. 3 and Table 1). The number of acid sites is expressed by the desorption enthalpy of the pre-adsorbed NH_3 from HF/H-MOR, HCl/H-MOR, and the H-MOR catalysts and amount to 82.2, 74.3, and 98.3 J/g, respectively. The acid site strengths as expressed by the desorption temperature were found to be 537, 535, and 530 °C. Additionally, the desorption enthalpies of the pre-adsorbed NH_3 from NH_4F /H-MOR, NH_4Cl /H-MOR, and H-MOR are 79.6, 70.5, and 98.3 J/g, respectively. The acid site strengths as expressed by the desorption temperature were found to be 533, 531, and 530 °C, respectively. These data indicate that the fluorination of mordenite increases its acid strength, which is evident from the increased HT-peak temperature determined during NH_3 desorption (acid site strength).

Figures 1 and 2 show XRD spectra for the halogenation and hydrohalogenation of the H-MOR catalysts. Evidently, F^- and Cl^- incorporation into the catalyst results in smaller (nanoscale) H-MOR crystallites, which increases catalyst activities. The decrease in H-MOR crystallinity because of the removal of some Al from the framework increases the hydrophobicity of the zeolite and its Si/Al ratio (Table 1). Corma [33–35] found that the dealumination of zeolites increases their hydrophobicity, which results in a higher capacity for hydrocarbon adsorption and a lower capacity for water adsorption and both these factors are favorable for an increase in activity. Since the dehydration reactions are equilibrium-limited and water is continuously removed from the catalyst surface because of its hydrophobic nature, the catalytic activity of the dealuminated zeolite is greatly enhanced.

2.3 Activation energy of methanol conversion to DME

The reaction rate constant was calculated for the different reaction temperatures according to the second-order flow reactor equation (1):

$$k = (F/W)[x/a(a-x)] \quad (1)$$

Where F is the rate of feed injection 49.8 mmol/h, k is the reaction rate constant, W is the catalyst weight (0.1 g), x is the mole fraction of methanol converted to DME, and a is the initial concentration of methanol.

The E_a values for the dehydration of methanol to DME using the studied zeolite catalysts were determined using the Arrhenius equation (2) and the plots are given in Fig. 7.

$$k = A \exp(-E_a/RT) \quad (2)$$

Where A is the pre-exponential factor and T is the absolute

Fig. 7. Arrhenius plot for methanol conversion to DME using treated and untreated mordenite catalysts.

reaction temperature.

The obtained E_a values for methanol dehydration to DME over the studied catalysts are given in Table 2. The E_a values determined for methanol dehydration to DME generally agree with the activities of the catalysts used. Na-MOR showed lower activity particularly at lower temperatures and, therefore, the E_a value for this catalyst is higher than that of the $\text{NH}_4\text{-MOR}$ and H-MOR catalysts since the latter are more acidic. The treatment of H-MOR with HF, HCl, NH_4F , or NH_4Cl results in a decrease in the activation energy (E_a) of the former catalyst from 41.2 kJ/mol before treatment to 21.9, 25.2, 31.4, and 35.6 kJ/mol, respectively, after treatment. This decrease in E_a after halogenation or hydrohalogenation indicates that higher activation results from halogen (F, Cl) inclusion. Moreover, these values indicate that fluorine is more activating than chlorine.

Table 2 Activation energies for methanol conversion to DME based on the studied catalysts

Catalyst	E_a /(kJ/mol)
H-MOR	41.2
$\text{NH}_4\text{-MOR}$	48.7
Na-MOR	56.1
HF/H-MOR	21.9
$\text{NH}_4\text{F/H-MOR}$	31.4
HCl/H-MOR	25.2
$\text{NH}_4\text{Cl/H-MOR}$	35.6

3 Conclusions

Na-MOR was found to be the least active catalyst for DME production among a series of studied mordenite catalysts. It was completely inactive toward olefin production because of the lack of Brönsted acid sites. The increase in methanol conversion and the formation of DME on hydrohalogenated H-MOR compared to the halogenated catalysts

is attributed to the increase in acidity. The higher activity of the halogen treated H-MOR zeolite is attributed to an increase in the Si/Al ratio and a decrease in the crystallinity of the current zeolite catalysts. Hydrofluorination treatment was found to be consistently more effective than hydrochlorination treatment.

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