Synthesis of Dimethyl Ether over Modified H-Mordenite Zeolites and Bifunctional Catalysts Composed of Cu/ZnO/ZrO$_2$ and Modified H-Mordenite Zeolite in Slurry Phase

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Abstract Synthesis of dimethyl ether (DME) via methanol dehydration were investigated over various catalysts, and via direct CO hydrogenation over hybrid catalysts composed of Al-modified H-Mordenite zeolite and Cu/ZnO/ZrO$_2$. H-Mordenite zeolite exhibited the highest activity in dehydration of methanol. However, its selectivity toward dimethyl ether was rather low. For this reason, the H-Mordenite was modified. Modification of zeolites was performed by wet impregnation method and considered catalysts were characterized by AAS, XRD and NH$_3$-TPD analyses. Results of catalytic tests indicated that H-Mordenite modified with 8 wt% aluminum oxide was the best catalyst for synthesis of dimethyl ether from methanol, in which methanol conversion and DME selectivity were 99.8 and 96.8%, respectively, without noticeable change in catalyst stability. For direct synthesis of dimethyl ether from synthesis gas, hybrid catalysts were prepared by coprecipitation sedimentation method. It was found that optimum ratio of methanol synthesis catalyst to methanol dehydration catalyst is 2:1. In this case, CO conversion and DME selectivity were 64 and 78.8%, respectively, with good catalyst stability. Ultimately, it was concluded that the hybrid catalyst composed of Cu/ZnO/ZrO$_2$ and Al-modified H-Mordenite zeolite is an appropriate catalyst for direct synthesis of dimethyl ether from the synthesis gas.

Abbreviations
HM   H-Mordenite
DME   Dimethyl ether
MeOH   Methanol

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1 Introduction

Dimethyl ether (DME) is a useful chemical intermediate for production of many important chemicals such as dimethyl sulfate, methyl acetate, and light olefins [1, 2]. DME is also used as an aerosol propellant because of its environmentally benign properties and the belief that chlorofluorocarbons (CFCs) destroy the ozone layer of the atmosphere [3]. Moreover, DME has recently been suggested as a clean alternative fuel for diesel engines with much lower NO$_x$ emission, near-zero smoke production, and less engine noise compared with traditional diesel fuels [4].

Several solid acid catalysts have been studied for the title reaction [5–14]. Dehydration of methanol, as shown in Eq. (1), involves a large amount of water as a by-product. During the reaction, both methanol and water compete with each other for the same sites on the catalyst [15–18].

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O + HCs \qquad (1)$$
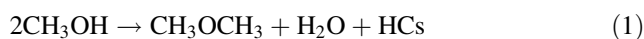
Also, most of these solid-acid catalysts produce undesirable side products such as hydrocarbons (and coke) due to the presence of strong acid sites and the high dehydration temperature [10, 11]. Thus, extensive research has been

focused on finding better catalysts that have higher selectivity for the DME formation and less tendency to generate hydrocarbons (and coke) [19].

Recently, more attention has been directed to the direct synthesis of dimethyl ether from synthesis gas (CO + H₂) over hybrid catalyst including a methanol synthesis catalyst (Cu–Zn–Al) and a methanol dehydration catalyst (zeolites) in one reactor, which is called a ''synthesis gas to dimethyl ether''(STD) process [20–28].

The Cu–Zn oxide-based catalysts have been widely investigated and modified with various metal oxides such as Zr, Cr, Ce, or Ti. It has been reported that the catalytic performance for STD process may be improved through enhancing the dispersion of the two active components [24, 29]. Amongst various metal oxides, zirconia has attracted considerable attention because it shows a good effect for methanol synthesis from both CO and CO_2 hydrogenation [30–34]. It was reported that in addition to dispersion of active sites on catalyst, zirconia enhances reduction of active sites and consequently, CO conversion and DME selectivity [35]. Reference [25] investigated influence of various methods of bifunctional catalyst preparation on reaction of CO hydrogenation. It was indicated that two types of active sites of a bifunctional catalyst prepared by the coprecipitation–sedimentation method maintained a closer contact, and exhibited a higher degree of "synergistic effect", which is responsible for the high activity of CO hydrogenation. Sun and co-workers demonstrated that methanol synthesis catalyst $Cu/ZnO/ZrO_2$ with equal percent of copper and zinc oxide and with 8 wt% zirconium oxide was the optimum catalyst [35].

In previous studies usually Y and ZSM-5 zeolites for production of DME from methanol were utilized [10–12]. However, results of the present research are shown that H-Mordenite zeolite is a better catalyst (than Y and ZSM-5 zeolites) for dehydration of methanol. As such, it was chosen as the dehydration catalyst and then modified with different amounts of aluminum oxide. Ultimately, a new bifunctional catalyst system composed of $Cu–ZnO–ZrO_2$ and Al-modified H-mordenite zeolite (with optimum content of aluminum oxide) was prepared through coprecipitating sedimentation method and its catalytic performance for direct synthesis of DME was investigated in a slurry reactor.

2 Experimental

2.1 Catalyst Preparation

Five different types of zeolites with large, medium and small pore sizes, namely, Y, Mordenite, Beta, ZSM-5 and Ferrierite were investigated. The zeolites were obtained from the Zeolyst Company (USA). The zeolites as received were in Na-form. Alumina and silica were supplied by Merck Chemicals. Na-form zeolite samples were ion exchanged to NH_4^+-form using an aqueous solution of NH_4NO_3. They were subsequently dried at 373 K for 24 h. H^+-form zeolites were prepared by calcination of NH_4^+-form samples 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-Mordenite (HM) modified with aluminum oxide was prepared by wet impregnation of H-Mordenite with aqueous solutions of aluminum nitrate. In detail, the appropriate weights of metal nitrate (e.g., $Cu (NO_3)_2 \cdot 3H_2O$ = 1.21 g) were dissolved in water (15 mL) under moderate stirring (300 rpm). Then, determined amount of zeolite (7.6 g) was added to solution. The solution was stirred under the aforementioned speed for about 1 h and left for 24 h at room temperature. After that, the solution was dried at 110 °C overnight and then calcined at 450 °C for 3 h in an air stream to obtain the modified zeolite (i.e., H-Mordenite modified with 5 wt% CuO).

Bi-functional catalysts ($Cu/ZnO/ZrO_2$: 46/46/8 on Al-modified H-Mordenite zeolite) were prepared by the coprecipitating sedimentation method [25]. In short, the appropriate weights of metal nitrate and sodium carbonate solutions were added to 200 mL of deionized water simultaneously and drop-wise over a period of 30 min at constant pH (ca. 7.0) and temperature (323 K) with continuous stirring. After the mixture had been aged for 2 h under stirring at the same temperature, the resulting precipitates were filtered out and washed. In order to eliminate the effect of residual Na^+ on catalytic activity, the precipitates were washed with hot water (353 K) completely, and then added to the suspension of Al-modified H-Mordenite zeolite. The mixtures were stirred, filtered and dried at 393 K and later calcined in air at 673 K for 3 h.

2.2 Catalyst Characterization

After the aforementioned treatments, catalysts were characterized by standard methods. The atomic ratio of Si to Al (Si/Al) in zeolite samples were determined by MASNMR. The zeolite samples were hydrated in a desiccator with saturated aqueous solution of NH_4Cl at room temperature for 24 h in order to minimize the line width of Al. The MASNMR spectra were recorded at 53.7 and 70.4 MHz (referenced to TMS and Al $(H_2O)_6^{3+}$), for Si and Al; respectively, on a pulsed Fourier transform NMR spectrometer (JNM-GX270, JEOL), which was equipped with a CP/MAS unit (NM-GSH27MU JEOL). All NMR spectra combined with magic angle spinning (MAS) spectra were recorded with H-decoupling during data acquisition. Cross polarization (CP) was not employed, since the protons of

zeolite samples are not directly attached to Si or Al. Each spectrum was recorded with 8 K data points and consisted of 700–1,300 accumulated scans.

The BET specific 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 physicsorbed 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.

X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX-1400 instrument with Cu-Kα radiation, with a scan speed of 15/min and a scan range of 4–70 at 40 kV and 40 mA.

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. The samples adsorbed by NH_3 were subsequently purged with He at the same temperature for 1 h to remove the physisorbed NH_3. The TPD measurements were conducted in flowing He (30 mL/min) from 150 to 550 °C at a heating rate of 10 °C/min.

2.3 Catalytic Reactions

2.3.1 Dehydration of Methanol

Catalyst performance tests were carried out in a 500 ml autoclave. This reactor was equipped with 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 the solid catalyst suspended uniformly in the liquid medium in the form of slurry. The experimental conditions, parameters and their ranges are given in Table 1.

The analysis of the liquid product samples was carried out using a gas chromatograph (Perichrom) equipped with hp pona colon column (length = 50 m, I.D. = 0.2 mm) and FID detector, with helium as the carrier gas. Injector
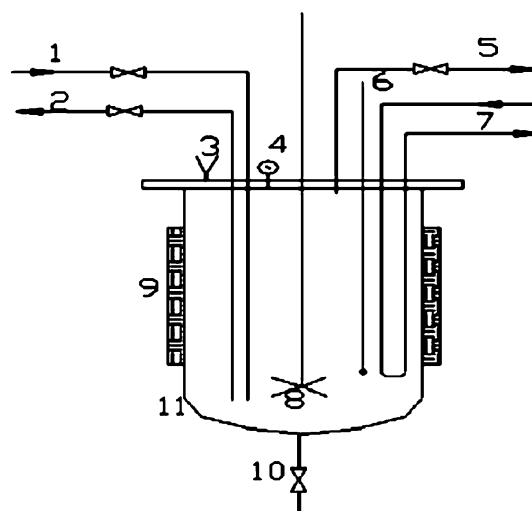

Fig. 1 Schematic of the batch reactor set-up constructed and used in this research; *1* gas inlet, *2* sampling valve, *3* slurry feed inlet, *4* pressure indicator, *5* gas vent, *6* thermocouple, *7* cooling coil; *8* stirrer, *9* reactor heating, *10* discharge valve and *11* reactor body

and detector temperatures were 270 and 300 °C; respectively.

The column temperature program for this analysis was such that, first the column was kept at 35 °C for 5 min. Then it was heated with a rate of 10°/min. (from 35) to 230 °C at which it was kept constant for 30 min.

The material balance was found satisfactory. 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:

MeOH Conversion

$$= \frac{\text{MeOH moles(initial amount)} - \text{MeOH moles(final amount)}}{\text{MEOH moles(initial amount)}} \times 100 \tag{2}$$

DME selectivity

$$= \frac{\text{DME moles produced} \times 2}{\text{MeOH moles(initial amount)} - \text{MeOH moles(final amount)}} \times 100 \tag{3}$$

Table 1 Experimental conditions and reaction parameters

Parameter	Quantity
Temperature(K)	523
Pressure (bar)	30
Catalyst (g)	3
Methanol concentrations (mole/L)	0.962
Agitation (rpm)	1000
Reaction time (h)	3
Solvent (mL)	250

Table 2 Experimental conditions and reaction parameters

Parameter	Quantity
Temperature(K)	523
Pressure (bar)	50
Catalyst (g)	3
The feed rate (mL/min)	300
Agitation (rpm)	1000

2.3.2 Direct Synthesis of Dimethyl Ether from Methanol

The catalyst activity was carried out in a 500 ml autoclave (Fig. 1), in which the catalyst was suspended in liquid paraffin (treated to remove any trace poisons before use) with boiling point of higher than 340 °C. the catalyst was reduced in the autoclave reactor using diluted hydrogen (10% H_2 + 90% N_2) at a programmed temperature, rising from room temperature to 260 °C, and then kept at this temperature for 16 h. After this pre-treatment, the syngas (H2/CO = 2:1) was introduced into the autoclave under 50 bar. The experimental conditions and parameters are given in Table 2.

All of the effluent gaseous products were analyzed by on-line gas chromatographs using carbon molecular sieve column and a thermal conductivity detector (TCD) for hydrogen, carbon monoxide, carbon dioxide and methane, CP-Sil-5 column and a flame ionization detector (FID) for DME, methanol and hydrocarbons.

3 Results and Discussion

3.1 Selection of an Appropriate Dehydration Catalyst

In this research, various types of zeolites were investigated. In addition, two non zeolitic catalysts, namely, amorphous silica and γ-alumina were also evaluated in order to compare their performances with zeolite catalysts. Characterization of these catalysts was given in Table 3.

Table 3 Properties of the studied zeolites (conditions of catalytic tests were according to Table 1)

	Si/Al Ratio	Cation form	Surface area (m^2/g)	Conversion (%)	DME selectivity (%)
ZSM-5	30	H	400	92.46	51.3
Y	80	H	700	91.18	30.22
Mordenite	90	H	500	96.39	68.23
Ferrierite	55	H	400	90.31	22.5
Beta	150	H	850	89.78	20.48
SiO2	–	–	250	82.29	21.31
γ-Al2O3	–	–	290	87.5	25.6

Results of the BET surface area measurements indicate that zeolites, in general, posses higher specific surface area in comparison to other catalysts.

The aforementioned catalysts were evaluated in a slurry reactor and subjected to conditions of Table 1. Results of this part of experiments are provided in Table 3. These have led to following overall conclusions:

1. Zeolites compared to other dehydration catalysts such as silica and alumina possessed higher activity, thus are more suitable for the dehydration process and

2. Amongst investigated catalysts, H-Mordenite zeolite showed the highest conversion and selectivity, thus was selected to be the most suitable for the methanol dehydration process at this stage of the work.

Results obtained from reactor tests shown in Table 3 indicate that in spite of high methanol conversion, the selectivity toward DME production is rather low reaching to 68.23% at best. In order to consider the stability of the selected catalyst, its performance was evaluated. This is shown later in Sect. 3.2.3 where it is observed that the activity of the H-Mordenite is quickly reduced indicating low stability for this catalyst.

It is noteworthy, that methanol and DME molecules could easily diffuse into zeolite cages due to their linear and unbranched structure, therefore, it may be concluded that shape selectivity is negligible. Furthermore, in previous investigations it has been demonstrated that the main reason for catalyst deactivation in the methanol dehydration step is the production of coke over strong acid sites [36, 37].

3.2 Improving of H-Mordenite Performance by Aluminum Oxide

3.2.1 Characterization of Catalysts

The metal oxide contents, determined by AAS are listed in Table 3. The results show that the metal oxide contents were consistent with that added before calcination, suggesting that no noticeable loss of aluminum oxides occurred during calcination.

The XRD spectrum of H-Mordenite and Al-modified H-Mordenite zeolites are shown in Fig. 2. It is found that no diffraction peak of Al could be detected in spectrum of samples. The above results indicate that the Aluminum oxide that is undetectable by XRD might have been highly dispersed on the surface of H-Mordenite.

In order to understand the distribution of surface acidity and strength of acid sites, a systematic study was undertaken. NH3-TPD results of H-Mordenite and Al-modified H-Mordenite are shown in Table 4. these data were calculated from three ammonia desorption peaks detected in the ranges of 100–300 °C (T_1), 300–500 °C (T_2) and 500–700 °C (T_3)
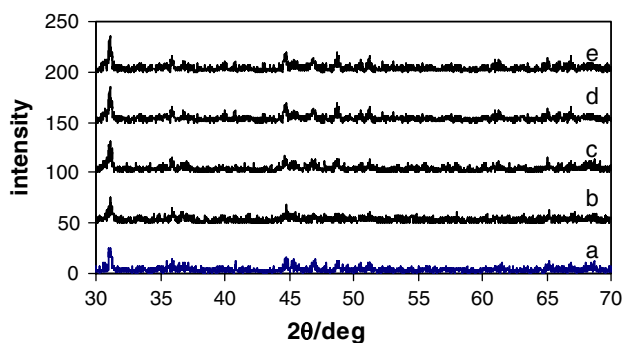
Fig. 2 XRD patterns of the parent and modified zeolites: (*a*) parent, (*b*) Al-modified HM (2 wt%), (*c*) Al-modified HM (5 wt%), (*d*) Al-modified HM (8 wt%) and (*e*) Al-modified HM (10 wt%)

Table 4 Aluminum oxide contents of the H-Mordenite zeolites

Aluminum oxide content (wt%)	
Nominal	Determined
2.00	1.99
5.00	4.92
8.00	7.97
10.00	9.95

according to the desorbed amount of ammonia (Fig. 3). Furthermore, according to the published data [38–40], the first peak (T_1) should be assigned to the desorption of NH_3 on weak acid sites, the second peak (T_2) is due to the desorption of NH_3 on moderate strength acid sites, and the third peak (T_3) is attributed to the desorption of NH_3 on strong acid sites. The area of the third peak (T_3) decreased slightly in all samples, while the areas of the first peak (T_1) and second peak (T_2)
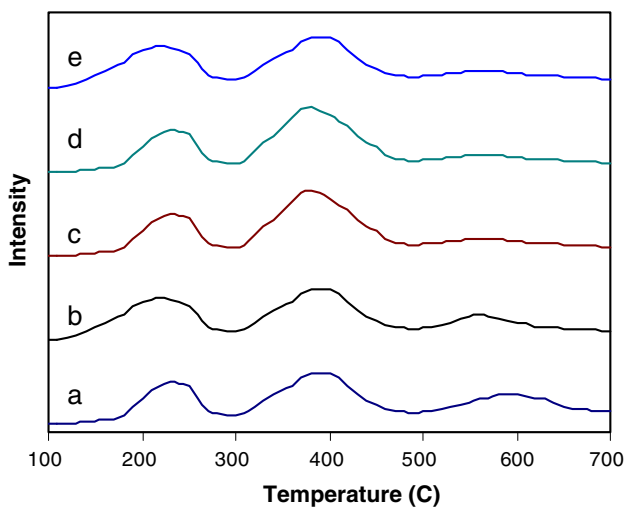

Fig. 3 NH_3-TPD profile of H-Mordenite and of Al-modified H-Mordenite zeolites; (*a*) parent, (*b*) Al-modified HM (2 wt%), (*c*) Al-modified HM (5 wt%), (*d*) Al-modified HM (8wt%) and (*e*) Al-modified HM (10wt%)

increased in all Al-modified zeolites. That is, the amount of weak and medium strength acid sites is increased on the surface of Al-modified H-Mordenite. Also, it was found that total acidity of zeolite is increased with increasing of Al content up to 8 wt% and decreases afterward.

It was displayed that impregnated metal oxides react with the acidic bridging hydroxyl groups and consequently, reduce the number of Bronsted (i.e., strong) acid sites and increase the number of Lewis (i.e., weak and/or medium strength) acid sites [41].

Also, NH_3-TPD data of this research indicates that at low loading of aluminum oxide, a significant decrease in the concentration of the Bronsted acid sites and a remarkable increase in the concentration of the Lewis acid sites occur. A further increase in Al_2O_3 content to 8 wt% results in a slight decrease in the concentration of the Bronsted and a slight increase in the concentration of the Lewis acid sites. Results show that at higher loading, modification process does not occur sufficiently hence the number of acid sites is reduced. This is due to coverage and blocking of the zeolite pores by Aluminum oxide and consequently, unavailability of acidic sites of zeolite.

3.2.2 Methanol Dehydration over H-Mordenite and Al-Modified H-Mordenite

The activity of H-Mordenite and Al-modified H-Mordenite zeolites for methanol dehydration to DME are summarized in Table 5. It is found that H-Mordenite modified with 8 wt% Al_2O_3 is the most active catalyst for methanol dehydration. Through comparison of Tables 4 and 5, it may be concluded that dehydration of methanol depends on the amount of catalyst acidity. This value is the highest in H-Mordenite modified with 8 wt% aluminum oxide.

3.2.3 Stability of Catalysts

Figure 4 compares the stability of H-Mordenite and Al-modified H-Mordenite (8 wt%) for this purpose, each of catalyst was used several times without any treatment. These results (Table 6) indicate that methanol conversion

Table 5 Estimation of acidity from TPD-NH3 on H-Mordenite and Al-modified H-Mordenite catalysts

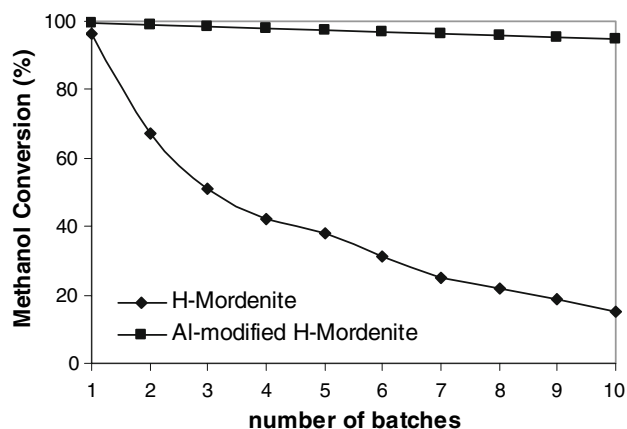| Al content (%)	Acidity (mmole NH_3/g cat.)			
	Weak	Medium	Strong	Total
0	0.271	0.332	0.254	0.857
2	0.296	0.431	0.151	0.878
5	0.321	0.521	0.074	0.916
8	0.338	0.541	0.067	0.946
10	0.314	0.495	0.083	0.892

Fig. 4 Comparison of the stability of applied H-Mordenite and modified H-Mordenite catalysts (condition of catalytic tests was according to Table 1)

Table 6 Results of methanol dehydration over H-Mordenite and modified H-Mordenite (condition of catalytic tests was according to table 1)

Al content (wt%)	Conversion (%)	Selectivity (%)
0	96.39	68.23
2	97.8	89.2
5	99.4	95.2
8	99.8	96.8
10	98.5	93.5

is depleted quickly with increasing of the number of batches in case of H-Mordenite catalyst, while in optimum catalyst (Al-modified H-Mordenite catalyst (8 wt%)), methanol conversion is almost constant. In other words, the stability was improved dramatically by impregnation of Al onto H-Mordenite.

3.3 Direct Synthesis of DME from Synthesis Gas

DME synthesis was carried out using bifunctional catalyst composed of Cu-ZnO-ZrO$_2$ catalyst and the best Al-modified H-Mordenite zeolite. An important parameter in the design of a dual catalytic system is the catalyst loading ratio; that is the amount of methanol dehydration catalyst to the amount of methanol synthesis catalyst. This aspect was studied using five ratio of dehydration to hydrogenation catalyst including; 0:1, 1:3, 1:2, 1:1 and 2:1 and using the same weight of total catalyst in each case.

3.3.1 Characterization of Catalysts

The XRD patterns of Cu–ZnO–ZrO$_2$/Al–H-Mordenite catalysts with different ratios of dehydration to hydrogenation catalysts are shown in Fig. 5. All bi-functional
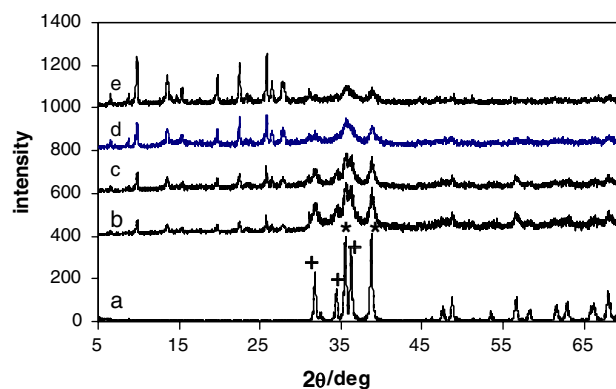

Fig. 5 XRD patterns of the parent and modified zeolites: (a) Cu–ZnO–ZrO$_2$, (b) bifunctional catalyst (1:3 ratio), (c) bifunctional catalyst(1:2 ratio), (d) bifunctional catalyst(1:1 ratio), (e)) bifunctional catalyst(2:1 ratio), (+) ZnO and (*) CuO

catalysts exhibited diffraction lines of CuO and ZnO. Besides the peaks assigned to CuO, ZnO and Zeolite, no other peaks are observed to indicate the formation of new species between components. In higher quantities of dehydration catalyst (e.g., curves d and e), the diffraction peaks of CuO and ZnO overlapped at $34° < 2\theta < 37°$.

3.3.2 Effect of Ratio of Dehydration Catalyst to Hydrogenation Catalyst

The activities of Cu–ZnO–ZrO$_2$ and bifunctional catalysts for direct DME synthesis via CO hydrogenation are shown in Figs. 6 and 7. These results display the followings:

1. CO conversion is increased with the raise of dehydration to hydrogenation catalyst ratio up to 1:2. This is due to the fact that, addition of dehydration catalyst causes the thermodynamic limitation to be removed and, consequently the produced methanol is continuously consumed and converted into other products such as DME. Therefore, methanol concentration is lowered and the methanol synthesis reaction is directed
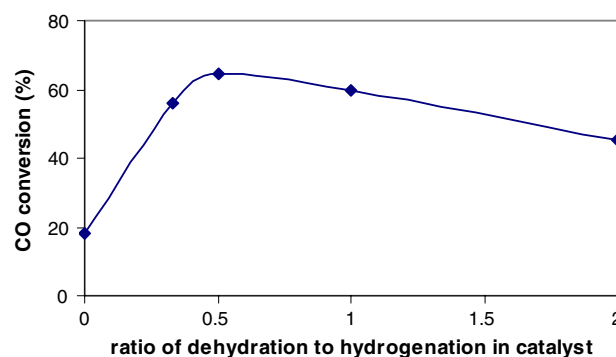

Fig. 6 Variation of CO conversion versus catalyst loading ratio (condition of catalytic tests was according to Table 2)
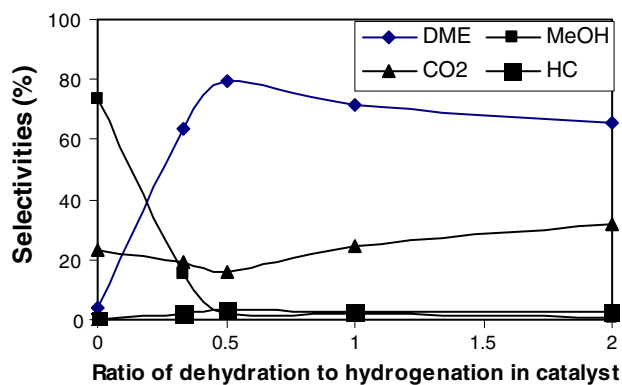
Fig. 7 Variation of selectivities of products versus catalyst loading ratio (condition of catalytic tests was according to Table 2)

Fig. 8 Variation of activity versus reaction time for Cu–ZnO–ZrO$_2$/Al–H-Mordenite bifunctional catalyst (condition of catalytic tests was according to Table 2)

toward production of methanol. CO conversion is decreased in ratio higher than 1:2. In these ratios, quantity of hydrogenation catalyst and consequently, the rate of the methanol synthesis reaction are rather low.

2. DME selectivity is increased with raise of catalysts' ratio up to 1:2 due to increase of rate of dehydration reaction while it is decreased at higher ratio due to decrease of rate of CO$_2$ hydrogenation and consequently decrease of methanol concentration. Reversely, the selectivity of CO$_2$ is first decreased up to 1:2 catalysts' ratio and then increased at higher ratio due to the aforementioned reasons. Furthermore, selectivity of methanol is decreased with raise of the catalysts' ratio due to increase of the rate of methanol dehydration reaction.

3. If dehydration reaction continued, DME might be converted into hydrocarbons. However, in this research selectivity of hydrocarbons is low. This emphasizes that production of HC$_s$ (hydrocarbons) has been restricted by modification of H-Mordenite.

As a result, in order to achieve a higher DME yield in "direct DME synthesis from synthesis gas process", the hydrogenation step (methanol synthesis reaction) and dehydration step (methanol dehydration reaction) should be matched completely. This value in bi-functional catalyst of CuO–ZnO–ZrO$_2$/Al–H-Mordenite is at the ratio of 1:2.

3.3.3 Stability of the Optimum Bifunctional Catalyst

The stability of bifunctional catalyst Cu–ZnO–ZrO$_2$/Al–H-Mordenite was investigated for direct DME synthesis via CO hydrogenation. Result is given in Fig. 8. This figure clearly shows that both the DME selectivity and the CO conversion remained essentially constant for the whole test period, which indicates that no substantial deactivation of the catalyst occurred. This result reveals that the hybrid
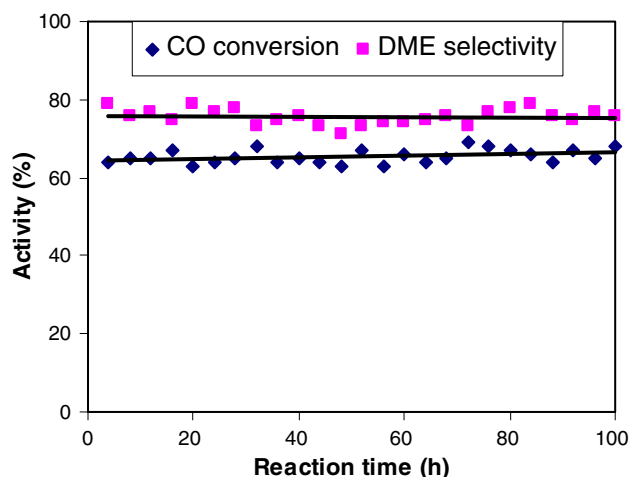
catalyst composed of Cu–ZnO–ZrO$_2$ and Al-modified H-Mordenite with 8 wt% of Aluminum oxide has a good stability for the direct synthesis of DME from synthesis gas.

4 Conclusions

In this study, dehydration of methanol was investigated utilizing various zeolites. Results indicate that zeolites perform satisfactorily in dehydration of methanol to DME. Also, it was found that the mordenite zeolite with H$^+$-form is the most active catalyst for dehydration of methanol. However, this H-mordenite had low selectivity and stability. This study demonstrates that performance of H-Mordenite zeolite is enhanced by modification with Al via wet impregnation method. This material increases activity, selectivity and stability of H-Mordenite for dehydration of methanol to DME. Results of acidity analysis indicate that conversion of the dehydration process is depending upon the total amount of catalyst acidity, while selectivity and stability of catalysts are depending upon the strength of acidic sites of the catalyst. Outcomes of catalytic tests performed using Al-modified H-Mordenite zeolites with different weight content of Aluminum indicate that H-Mordenite zeolite modified with 8 wt% Aluminum oxide is the most appropriate catalyst for dehydration of methanol to DME. Results of catalytic tests with bifunctional catalysts composed of Cu–ZnO–ZrO$_2$ and H-Mordenite modified with 8 wt% aluminum oxide indicated that this hybrid catalyst with dehydration element to hydrogenation component ratio of 1:2 is an appropriate catalyst for direct synthesis of DME from synthesis gas with high activity, selectivity and stability.

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