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Role of Cu-Mfi Zeolite Catalyst on Direct Conversion of Methane Ethane to Gasoline

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ABSTRACT

HZSM-5 (Si/Al = 30), silicalite and Cu-MFI with different copper concentrations were synthesized by direct synthesis method. The catalyst samples were characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and Temperature Programmed Desorption of Ammonia (TPD-NH_3) techniques. The catalytic performance of the samples was evaluated in a continuous micro packed-bed reactor. The reaction was performed at reaction temperature 800°C under atmospheric pressure. The effects of Cu content on methane conversion and products selectivity were investigated. Characterization results revealed that the samples were MFI-zeolite catalysts and the copper species most probably occluded in the defect sites of the zeolite. Modification of zeolite with copper resulted in the en-hancement of methane conversion up to 15 %. The experimental results using Cu(0.1)-MFI demonstrated a high selectivity to gasoline, which is 29.7%.

Keywords: Direct conversion, methane, gasoline, Cu-MFI, atmospheric pressure

ABSTRAK

HZSM-5 (Si/Al = 30), silikalit dan Cu-MFI dengan kepekatan yang berbeza telah disintesis secara kaedah langsung. Sampel-sampel mangkin ini dicirikan dengan menggunakan teknik pembelauan sinar-X (XRD), spektroskopi inframerah fourier transformasi (FTIR) dan penjerapan suhu teraturcara bagi ammonia (TPD-NH_3). Prestasi pemangkinan sampel-sampel ini dijalankan di dalam reaktor aliran berterusan terpadat mikro. Tindakbalas dikendalikan pada suhu 800°C di bawah tekanan atmosfera. Kesan kandungan kuprum dalam mangkin terhadap penukaran metana dan kadar keterpilihan terhadap produk dikaji. Hasil pencirian menunjukkan bahawa sampel-sampel mempunyai struktur seperti MFI-zeolit dan logam kuprum besar kemungkinan menutupi tapak cacat zeolit. Ubahsuaian zeolit dengan kuprum memberi kesan kepada peningkatan penukaran metana sehingga 15%. Keputusan eksperimen yang menggunakan Cu(0.1)-MFI menunjukkan keterpilihan gasolin yang tinggi iaitu 29.7%.

Kata kunci: Penukaran terus, metana, gasoline, Cu-MFI, tekanan atmosfera

INTRODUCTION

The development of effective catalysts and the selection of reactors of optimal configuration and mode of operation are the challenges for the direct conversion processes. The difficulty in direct methane conversion catalytically and or thermally is the strength and stability of the methane C-H bond,

which is due to their electronic structure with the value for energy dissociation of methane, E_{dissoc} = 440kJ/mol (Banares 1999). High temperature operation required by the direct methane conversion leads to poor economics associated with a low yield of the desired hydrocarbon products. Besides, the process also suffers from high carbon formation (Han et al. 1994; Saidina Amin & Sharif Zein 1999; Shepelev & Ione 1983). From previous studies (Gormley 1996; Han et al. 1994; Rao & Weitkamp 2000), ZSM-5 zeolite catalyst seems to be a promising catalyst since the medium size pore openings (5.5Å) provide shape-selective effect. The highly acidic nature of ZSM-5 helps in oligomerization, cracking, isomerization and aromatization reaction. However, modification of ZSM-5 zeolite with some metals (metal-zeolite) has been reported to be more superior for producing higher hydrocarbon products compared to the ZSM-5 zeolite alone (Anggoro 1998; Saidina Amin & Ali 2001). The use of the bifunctional oxidative-acidic catalyst, with zeolite as the acidic component and metal as the hydrogenating component has resulted in the enhancement of the catalytic activity and the selectivity of the desired products (Trombetta et al. 2001). The metal-loaded catalyst will activate methane by abstracting hydrogen from methane to form methyl radicals. Methyl radicals can be generated in the gas phase and on the catalyst surface. C-H bond activation in methane is the most crucial step hence the generation of methyl radicals is the rate-limiting step (Burch et al. 1999; Shu & Ichikawa 2001). The olefins formed then were oligomerized into higher hydrocarbon on the acid sites provided by zeolite.

Previously, Ni-HZSM-5 and Cu-HZSM-5 catalysts prepared by impregnation method were discovered to be the potential catalysts for oxidation of methane to gasoline, where over these catalysts, the gasoline yield reached to about 21% and 22%, respectively (Anggoro 1998). In this work, modification of ZSM-5 with Cu through direct synthesis was conducted with the same conditions as reported elsewhere (Anggoro 1998). Performance of the Cu-MFI zeolites catalyst on methane conversion and products selectivity were investigated and were compared with HZSM-5 and silicalite.

EXPERIMENTAL PROCEDURE

CATALYSTS PREPARATION

The catalysts were prepared via direct synthesis method (Plank et al. 1974). (Cu, Al)-containing MFI zeolite was prepared by direct crystallization at 160°C in a stainless steel autoclave (capacity: 300 mL) under static conditions for seven days. The first solution was prepared by mixing aluminium sulfate hexadecahydrate (>98%, Fluka chemika), tetrapropylammonium bromide (>98%, Fluka chemika), cupric nitrate trihydrate (>99%, R & M Chemicals), and water. A second solution was prepared by mixing sodium silicate solution (Na_2O = 8%; SiO_2 = 27% w/w; Merck) and water. The two solutions were mixed and stirred thoroughly for 24 hours (gel form), followed by autoclaving under autogeneous pressure for seven days. The powder formed were filtered, washed with distilled water, and finally dried at 110°C over night. Then, the catalysts were calcined at 550°C for five hours to remove the template. H-zeolite was formed by treating every one gram of the catalyst with 10 mL, 1.0 M ammonium nitrate solution. The solution then was stirred under reflux at 80°C for six hours and this step was repeated for

three times. Again, the catalysts were filtered, washed and dried at 110°C over night. Finally, the catalysts were calcined at 550°C for five hours to remove ammonia. As references, silicalite and HZSM-5 were prepared using the same method. The molar ratio of reaction mixture is based on $8.6Na_2O$: (Al_2O_3 + CuO): $30SiO_2$: 2.8TPABr: $1071H_2O$.

CATALYSTS CHARACTERIZATION

Information about the phase, lattice parameters and particle size of the samples were obtained by X-Ray Diffraction. This characterization was performed using a Philips 1840 with CuKα radiation with $\lambda = 1.54056$ Å at 40 kV and 30mA in the range 2θ 2° to 60° at a scanning of 4 degree per minute, with vertical goniometer at room temperature.

Fourier Transform Infrared measurements were performed using Shimadzu 3000 FTIR spectrometer using KBr technique, in the framework (ν_{T-O}) region. All measurements were performed at ambient temperature to keep the hydration state of zeolites constant and to minimize any spectral changes. This characterization has been carried out in the 400 - 1400 cm^{-1} region (the mid-infrared region). The mid-infrared region of the spectum is useful, since it contains the fundamental vibrations of the framework TO_4 (T=Si or Al) tetrahedral.

The acidity measurements were obtained from TPDRO 1100 Thermo Quest CE Instrument. The samples were pre-treated in a flow of nitrogen at 400°C for 3 hours. After cooling step, ammonia adsorption was performed by feeding ammonia at 10 ml/min for one hour. Ammonia was thermally desorbed by raising the temperature with a linear heating rate of approximately 10°C/min from 80°C to 600°C. The amount of NH_3 desorbed was measured by a TCD detector.

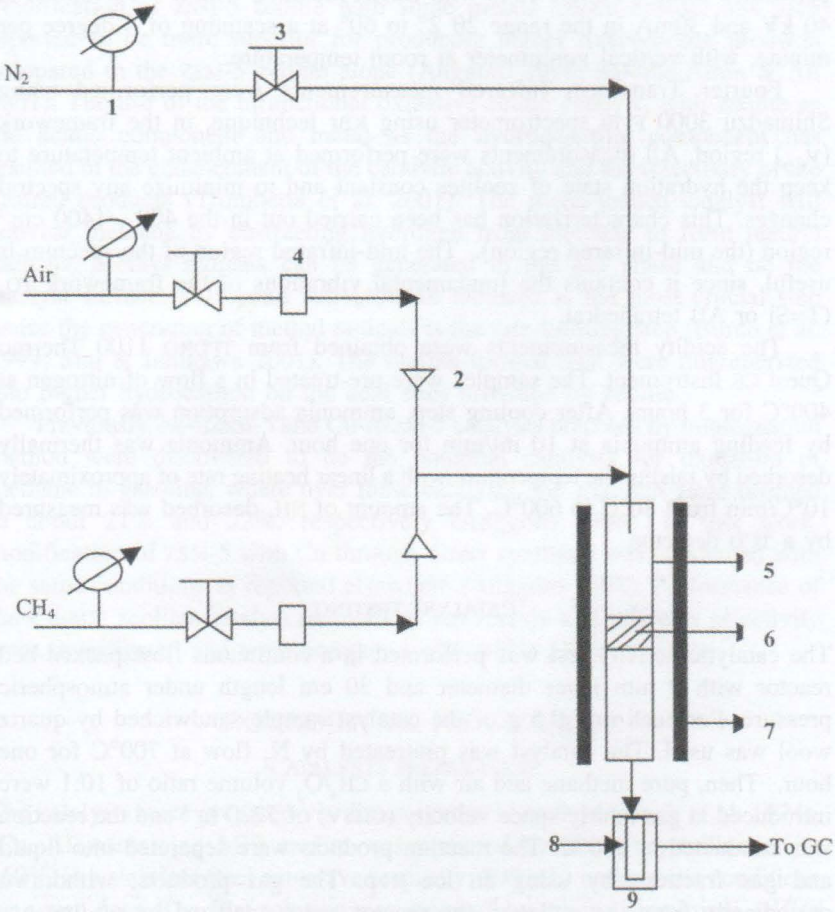
CATALYST TESTING

The catalytic activity test was performed in a continuous flow packed-bed reactor with 9 mm inner diameter and 30 cm length under atmospheric pressure. For each run, 0.5 g of the catalyst sample sandwiched by quartz wool was used. The catalyst was pretreated by N_2 flow at 700°C for one hour. Then, pure methane and air with a CH_4/O_2 volume ratio of 10:1 were introduced at gas hourly space velocity (GHSV) of 5220 hr^{-1} and the reaction was conducted at 800°C. The reaction products were separated into liquid and gas fractions by using an ice trap. The gas products, withdrawn periodically from the outlet of the reactor, were analyzed by on-line gas chromatography equipped with thermal conductivity detector (TCD) and separated using Porapak-N column (GC condition: He (carrier gas) flow rate: 21 mL/min, air combustion agent: 18 mL/min, detector temperature: 200°C, final temperature: 200°C, total time: 30 min). Liquid products were analyzed with gas chromatography equipped with flame ionization detector (FID) and HP-1 capillary column (GC condition: oven temperature: 50°C, carrier gas: 50mL/min, injection temperature: 300°C, detection temperature: 300°C). The amount of coke deposited on the catalysts were determined by using a thermal gravimetric microbalance at 30°C - 900°C in nitrogen stream with 20°C/min rate. Methane conversion and products selectivity were calculated

on the basis of carbon number according to Equations 1 and 2. The schematic diagram of the experimental set-up is shown in Figure 1.

$$\text{Conversion (mol\%)} = \left(\frac{\text{amount of methane reacted (mol)}}{\text{amount of methane input (mol)}}\right)\times 100\% \quad (1)$$

$$\text{Selectivity (mol \%)} = \left(\frac{\text{carbon of desired product (mol)}}{\text{carbon of methane reacted (mol)}}\right)\times 100\% \quad (2)$$



1. Pressure controller; 2. Safety valve; 3. Valve; 4. Digital gas flow meter; 5. Quartz Reactor; 6. Catalysts; 7. Furnace; 8. Bottle of liquid products; 9. Ice Trap

FIGURE 1. Schematic diagram of the experimental set-up apparatus

RESULTS AND DISCUSSION

CATALYSTS PROPERTIES

X-RAY DIFFRACTION

Figure 2 shows the XRD diffractograms for the catalyst samples. The results showed that the samples have similar peak patterns like the MFI-zeolites (Treacy et al. 1996), indicating that all the samples are MFI-zeolite.

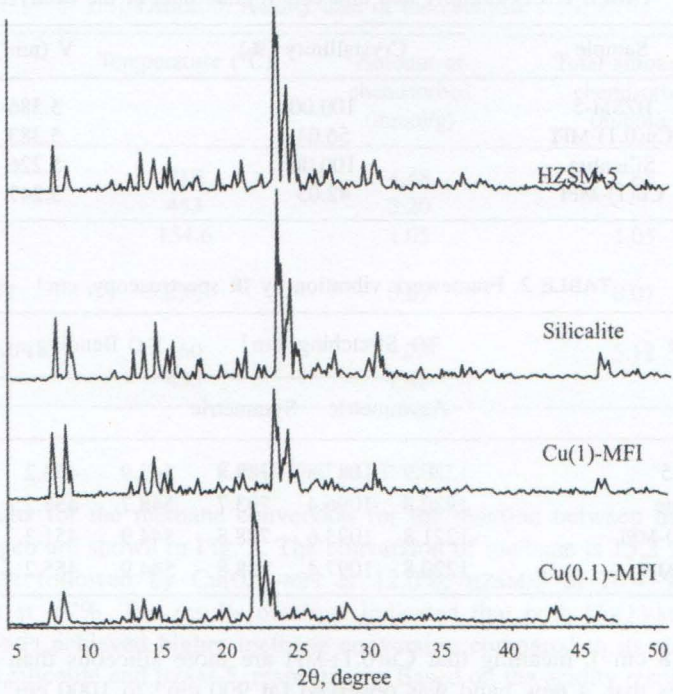


FIGURE 2. XRD diffractograms of the catalysts

As can be seen in Table 1, the presence of metal affected the crystallinity of the standard catalysts. In this study, HZSM-5 is taken as the standard for Cu(0.1)-MFI since both catalysts have Al in their structures while silicalite is taken as standard for Cu(1)-MFI since both are Al-free catalysts. The results in Table 1 indicated that Cu-MFI catalyst did not favor the crystalline phase. From the unit cell volume result, the unit cell volume of HZSM-5 zeolite and Cu(0.1)-MFI are almost equal at 5.386 Å and 5.383 Å, respectively. The amount of metal loaded at 0.1 mole% may have been too small for Cu to exert any effects on the unit cell volume of the sample. By loading the metal up to 1 mole%, the unit cell volume seems to increase compared to its standard as shown by Cu(1)-MFI. However, from this observation, it cannot solely be said that copper metals have been substituted into the zeolite framework. Other characterization techniques such as Nuclear Magnetic Resonance (NMR) classified as the short-range order, should be applied in future study to confirm whether or not the metals are incorporated in the zeolite framework.

FOURIER TRANSFORM INFRARED

Table 2 shows that all FTIR spectra consisted of asymmetric and symmetric T-O-T modes (1250-1000 and 800 cm^{-1}, respectively), double ring vibration (540 cm^{-1}), and T-O bending (450 cm^{-1}) (Szostak 1989). The obtained results confirmed that the structures of all samples are MFI structure. The main sensitive mode is T-O-T internal asymmetric vibration around 1100 cm^{-1}. The peak shifted to higher frequency as the SiO_2/AlO_3 ratio increased as shown by Cu(0.1)- MFI (1093.6 cm^{-1}) when compared to its standard, HZSM-5

TABLE 1. Crystallinity and unit cell volume data of the catalysts

Sample	Crystallinity (%)	V (nm^3)
HZSM-5	100.00	5.386
Cu(0.1)-MFI	56.04	5.383
Silicalite	100.00	5.226
Cu(1)-MFI	42.03	5.247

TABLE 2. Framework vibration by IR spectroscopy, cm^{-1}

Sample	TO_4 Stretching, cm^{-1}			T-O Bending		T-O-
	Asymmetric		Symmetric			T-O-M
HZSM-5	1220.9	1087.8	789.8	543.9	453.2	-
Silicalite	1220.8	1096.4	793.7	548.7	453.2	978.8
Cu(0.1)-MFI	1221.8	1093.6	788.8	544.9	451.3	-
Cu(1)-MFI	1220.8	1097.4	788.8	544.9	455.2	999.1

(1087.8 cm^{-1}), meaning that Cu(0.1)-MFI are more siliceous than HZSM-5. Besides that, a new band was observed (at 900 cm^{-1} to 1000 cm^{-1}) for the sample with high metal content (Cu(1)-MFI) and sample with silicalite structure. These peaks were attributed to T-M (T-O or T-O-M) stretching, implying the cations interacted with the zeolite framework (Sobalik et al. 1998) or associated with the defect centers containing the incorporated metal (Aiello et al. 1999; Ke & Wang 2001; Raghavan et al. 1997). Since, FTIR only can reveal the molecular vibration, so most probably Cu metals in this study are occluded in the defect sites and not incorporated into the framework of zeolite.

TEMPERATURE PROGRAMMED DESORPTION -NH_3

The TPD-NH_3 results in Table 3 indicated Cu(1)-MFI and silicalite samples exhibited desorption peaks at low temperature only. The acidity of Cu(1)-MFI is the lowest at 0.07 mmol/g. In contrast, Cu(0.1)-MFI and HZSM-5 zeolites showed desorption peaks at both low and high temperatures. The total acidity of HZSM-5 zeolite is the highest at 7.68 mmol/g. Low acidity is expected for silicalite and Cu(1)-MFI samples since both catalysts are Al free-catalysts. The acidic sites within the zeolite pores are generated from an imbalance in charge between the silicon and the aluminum ions in the framework. Thus, the number of the acid sites is proportional to the concentration of framework Al since Al is bonded to four oxygen atoms in the tetrahedral directions and has a negative charge (Szostak 1989). With this observation, it is confirmed that aluminum in the framework is responsible for the acidity of the zeolite. The sequence order of acidity from high to low is according to:

HZSM-5 > Cu(0.1)-MFI > Silicalite > Cu(1)-MFI.

TABLE 3. Acidity data of the catalysts

Sample	Temperature (°C)	Amount of chemisorbed (mmol/g)	Total amount of chemisorbed (mmol/g)
HZSM-5	219	4.48	7.68
	453	3.20	
Silicalite	154.6	1.05	1.05
	-	-	
Cu(1)-MFI	230	0.07	0.07
	-	-	
Cu(0.1)-MFI	160	3.72	5.12
	435	1.40	

CATALYTIC ACTIVITY

The results for the methane conversion for the reaction between methane and oxygen are shown in Fig. 3. The conversion of methane is 15.2 % over Cu(1)-MFI followed by Cu(0.1)-MFI at 12.0%, HZSM-5 at 10.4 %, and silicalite at 4.7%. The results obtained indicated that both Cu(1)-MFI and Cu(0.1)-MFI achieved higher methane conversion compared to its standard which is silicalite and HZSM-5, respectively. Based on the acidity result from the TPD data, Cu-MFI catalyst possessed weaker acidity compared to their standards. The addition of metal into the zeolite framework has indeed reduced the acidity of the zeolite. It was reported that the presence of Cu in modified zeolite acted as dehydrogenating component (Trombetta 2001). Consequently, the presence of copper species resulted in the enhancement of methane activation by abstracting hydrogen from methane to form methyl radicals.

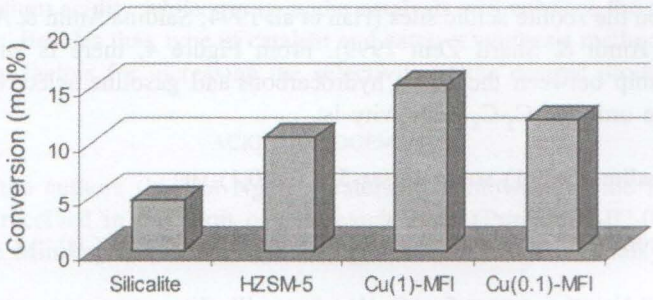


FIGURE 3. Methane conversion of the catalysts

Figure 4 shows the distribution of the products selectivity. The hydrocarbon products from the reaction included light hydrocarbon (C_2-C_4), gasoline (C_5-C_{10}), and kerosene (C_{11}-C_{15}). C_1-oxygenates was detected as a by-product from the reaction for all the samples. The formation of C_1-oxygenates is reported to be formed via partial oxidation of methane (Barbero et al. 2001; Kudo & Ono 1997; Ono et al. 2000; Otsuko & Wang 2001). It was revealed that production of C_1-oxygenates from CH_4 occurred over an oxidation component while the transformation of C_1-oxygenates to

gasoline occurred over acidic sites of zeolite catalyst (S. Han et al.1994). Another possible mechanism for the C_1-oxygenates is reported by Ono and coworkers (Ono et al. 2000) who claimed that at low pressure (8 Torr), C_1-oxygenates was formed through the addition of surface hydrogen to methoxide ion on the catalyst rather than the hydrogen abstraction from CH_4.

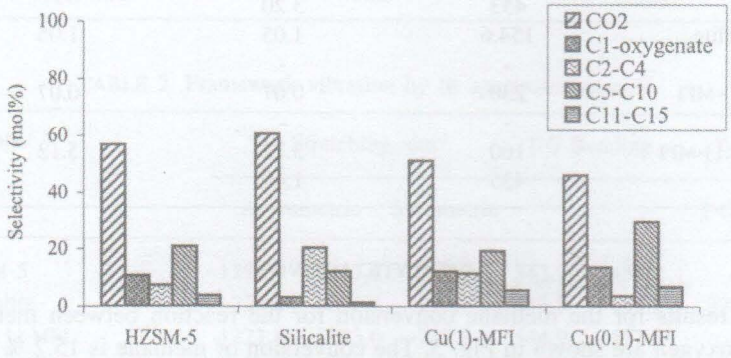


FIGURE 4. Distribution of products selectivity as a function of catalysts

The selectivity of C_1-oxygenates is higher on modified catalyst (Cu-MFI) compared to the HZSM-5 and silicalite catalysts. This would suggest that Cu or oxides play an important role in C_1-oxygenates selectivity. The selectivity of C_1-oxygenates demonstrated by Cu(1)-MFI and Cu(0.1)-MFI, is 12.3% and 13.7%, respectively. The results obtained showed that higher metal content resulted in the decrement of C_1-oxygenates, suggesting that its formation may be correlated to the density of acidic sites. The reaction using silicalite exhibits the lowest selectivity, about 3 %, as the silicalite is low in activity (Knops-Gerrits & Goddard 2001).

Gasoline production was believed be formed via the oligomerization of olefins on the zeolite acidic sites (Han et al. 1994; Saidina Amin & Ali 2001; Saidina Amin & Sharif Zein 1999). From Figure 4, there is an inverse relationship between the C_2-C_4 hydrocarbons and gasoline selectivity. The sequence order of C_2-C_4 selectivity is:

silicalite > Cu(1)-MFI > HZSM-5 > Cu(0.1)-MFI.

In contrast, the sequence order of gasoline selectivity is:

Cu(0.1)-MFI > HZSM-5 > Cu(1)-MFI > silicalite.

As mentioned before, C_2-C_4 is a source for gasoline production. Consequently, low C_2-C_4 is observed over the samples, which gave high gasoline selectivity. However, although the presence of metal is believed to activate methane dissociation, but too much metal resulted in the depletion of gasoline formation as demonstrated by Cu(1)-MFI. From the TPD data, the acidity of the catalyst was reduced as the Cu content was increased. Samples with too strong in acidity, however, created favorable conditions for the oligomers to crack (Anggoro 1998) as indicated by the performance of HZSM-5 catalyst which did not produce the highest gasoline despite its

acidity being the highest. From the catalytic performance tests, Cu(0.1)-MFI which has moderate acidity was found to be the best catalyst to produce the highest gasoline selectivity (29.67%). The result obtained is consistent with the others work (Saidina Amin & Ali 2001) who, reported high gasoline selectivity over catalysts that were moderate in acidity. In another study, the gasoline selectivity over HZSM-5 was reported to be better than the MFI zeolites modified with Cu by the acidic ion-exchange method (Saidina Amin & Anggoro 2002). It is suggested that method of catalyst being prepared affected to the catalytic activity. (Saidina Amin, Ngadi & Prasetyoko 2003) reported that, MFI zeolites modified with Mo gave very low in gasoline selectivity than HZSM-5, 7% and 21%, respectively, even though being synthesized using direct synthesis method. However, they found out that, modification of MFI zeolite with Mo were promising for the C_1-oxygenates formation, which is up to 25% selectivity. Therefore, it is believed that the selection of the right catalyst and preparation method is the important factor for increasing the selectivity of the desired product.

CONCLUSION

The MFI-zeolites and Cu modified MFI-zeolites were successfully synthesized. It is suggested that Cu species most probably occluded in the defect sites of the zeolites. The incorporation of Cu into the zeolite seems to be very beneficial either for better methane conversion or for enhancement of liquid hydrocarbon selectivity. The enhancement of the catalytic activity using Cu modified MFI zeolites is due to the bifunctional oxidative-acid catalyst, with zeolite as the acidic component and Cu as the dehydrogenating component. Dehydrogenating component is responsible in the abstraction of hydrogen from methane compound to form methyl radicals and this is the most crucial step while acidic site is needed for the oligomerization of olefin to form higher hydrocarbon products. The oligomerization reaction favors catalyst with medium acidity while strong acidic catalysts will enhance the cracking reactions. Besides that, type of catalyst and catalyst synthesis method are the important factors for increasing the selectivity of the desired product.

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