CONVERSION OF METHANE USING MO-MFI ZEOLITE CATALYST

NOR AISHAH SAIDINA AMIN[1]*, NORZITA NGADI[2], & DIDIK PRASETYOKO[3]

Abstract. HZSM-5 (Si/Al = 30), silicalite and Mo-MFI with different molybdenum concentrations were synthesized by direct synthesis method. The catalyst samples were characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy 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 effects of metal content on methane conversion and products selectivity were investigated. Characterization results revealed that the samples were MFI-zeolite catalysts and the molybdenum metal most probably occluded in the defect sites of the zeolite. Modification of zeolite with metal resulted in the enhancement of catalytic activation. The experimental results using Mo(0.1)-MFI demonstrated a high selectivity of C$_1$-oxygenates. However, Mo-MFI catalyst was found not suitable for gasoline production.

Keywords: Mo-MFI; direct synthesis; XRD; FTIR; TPD-NH$_3$

Abstrak. HZSM-5 (Si/Al = 30), silikalit dan Mo-MFI dengan kepekatan logam molibdenum 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 lapisan terpadat mikro. Kesan kandungan logam dalam mangkin terhadap penukaran metana dan kadar kepilihan terhadap produk dikaji. Hasil pencirian menunjukkan bahawa sampel-sampel tersebut adalah mempunyai struktur seperti MFI-zeolit dan logam molibdenum yang hadir berkemungkinan besar terletak di tapak cacat zeolit. Ubahsuaian zeolit dengan logam memberi kesan kepada peningkatan aktiviti pemangkinan. Keputusan eksperimen yang menggunakan Mo(0.1)-MFI menunjukkan kepilihan C$_1$-oksigenat yang tinggi. Walau bagaimanapun, mangkin Mo-MFI didapati tidak sesuai untuk penghasilan gasolin.

Kata kunci: Mo-MFI; sintesis langsung; XRD; FTIR; TPD-NH$_3$

1.0 INTRODUCTION

The dependencies on liquid petroleum as the main energy resource for various industries and as transportation fuel cannot be denied. Over 80 million barrels of petroleum are processed every day in refineries around the world to meet the demand for liquid transportation fuels such as gasoline, diesel fuel and jet fuel [1]. Natural gas, which comprises of mostly methane (up to 98%), is found abundantly and seems to be the

[1,2&3] Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor Bahru, MALAYSIA
* Corresponding Author. Tel: 07-553-5588; Fax: 607-5581463 Email: noraishah@fkkksa.utm.my

best alternative to replace petroleum. Currently, natural gas is used for home and industrial heating and also for power plants. Natural gas burns cleanly since it does not contain SO_x as in the case with petroleum, coal, and other fossil fuels.

A number of strategies are being explored and developed for the conversion of methane to more useful chemicals and fuels. These include steam and carbon dioxide reforming or partial oxidation of methane to form carbon monoxide and hydrogen, followed by Fischer-Tropsch chemistry, direct oxidation of methane to methanol and formaldehyde, oxidative coupling of methane to ethylene and direct conversion to aromatics and hydrogen in the absence of oxygen [2]. However, most of those processes occurred at high temperature [3] and suffered from severe catalyst deactivation because of carbon formation on the catalyst surface [4,5,6].

High temperature operation for the direct methane conversion led to poor economics associated with a low yield of the desired hydrocarbon products [6,7]. This is because the products formed may be readily oxidized under the conditions required to activate methane, thus limiting selectivity [8]. Zeolites such as ZSM-5 have been found to be active for low temperature conversion to more valuable hydrocarbons with and without oxidants. Higher hydrocarbons, especially C_5-C_{10} liquids, were reported to be produced at temperatures between 440°C and 465°C with 100% conversion of O_2 using zeolite and were believed to be formed via a methane oxidation and methanol-to-gasoline (MTG) pathway [9]. Knops and Goddard [10] claimed that methane can be converted into methanol with α-oxygen that are formed on iron sites of the Fe/ZSM-5 catalyst at room temperature using N_2O as an oxidant.

The highly acidic sites, combined with the high selectivity arising from shape selectivity and large internal surface area makes the ZSM-5 an ideal industrial catalyst for the refining industry. However, its high acidity promotes the formation of CO_x. High selectivity of CO_x suppressed the formation of higher hydrocarbons and hinders the development of the ZSM-5 zeolite for other applications such as the gas to liquid (GTL) process. The acidity of the ZSM-5 can be modified by loading some metals into its framework. Previously, it was reported that modification of catalysts with metals such as Ga, Cu, Co, Na, Zn, Mo and Ni had good potential in obtaining higher hydrocarbon selectivity [7,11-14].

Solymosi and coworkers [15] reported that the formation of ethane, ethylene and benzene were prominent when molybdenum was highly dispersed on the ZSM-5 surface. It was reported that conversion of methane up to 13% was obtained using Mo/ZSM-5 under partial pressure condition [16]. Several recent studies have demonstrated that Mo-loaded zeolite are active and selective for the conversion of methane to aromatics particularly benzene [14,17,18]. The selectivity of higher hydrocarbons can be improved by non-oxidative methane conversion [14,19]. In another study, Tang *et. al.* [20] reported that under non-oxidative conversion of methane, 100% selectivity to benzene with 7.4 % methane conversion were obtained using modified Mo/HZSM-5 catalyst.

In this paper, molybdenum modified MFI zeolites with different Mo concentrations were prepared by direct synthesis method and tested for the conversion of methane under oxidative conditions. The effect of metal (0.1 and 1.0 mole % of Mo) content on methane conversion and products selectivity were investigated and the catalytic performance of the Mo-MFI zeolites were compared with HZSM-5 and silicalite.

2.0 EXPERIMENTAL

2.1 Catalyst Preparation

The catalysts were prepared via direct synthesis method [21]. (Mo,Al)-containing MFI zeolite was prepared by 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), tetrapropylammonium bromide (>98 %, Fluka), ammonium molybdate solution (>98 %, Fluka), 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 the gel formed was stirred thoroughly for 24 hours, followed by autoclaving at 160°C under vacuum pressure for seven days. The powder formed product was filtered, washed with distilled water, and finally dried at 110°C over night. The catalysts were then calcined at 550°C for five hours to remove the template. H-zeolites were formed by treating every one gram of the catalyst with 10 mL of 1.0 M ammonium nitrate solution. The solution then was stirred under reflux at 80°C for six hours and this step was repeated 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 the ammonia. The Mo-MFI samples are denoted as Mo(1)-MFI and Mo(0.1)-MFI for 1 and 0.1 mole % of molybdenum, respectively. 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+MoO_3) : $30SiO_2$: 2.8 tetrapropylammonium bromide : $1071H_2O$.

2.2 Catalyst Characterization

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

Fourier Transform Infrared measurements were performed using a Shimadzu 3000 FTIR spectrometer wiyh a KBr technique, in the framework (v_{T-O}) region. All measurements were performed at ambient temperature to keep the hydration state of zeolites constant and to minimize any spectral changes. The FTIR measurements were carried out in the 400 - 1400 cm^{-1} region (the mid-infrared region). The mid-infrared region of the spectrum 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 nitrogen flow at 400°C for three hours. After the 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 Thermal Conductivity Detector (TCD) detector.

2.3 Catalyst Testing

The catalytic activity test was performed in a continuous flow packed-bed quartz 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 a flow of nitrogen at 700°C for one hour. Pure methane and air with a CH_4/O_2 volume ratio of 10:1 were then 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 using an on-line gas chromatography equipped with thermal conductivity detector (TCD) and analytes separated on a Porapak-N column (GC conditions: He (carrier gas) flow at a rate of 21mL/min, air combustion agent:18mL/min, detector temparature:200°C, final temperature:200°C, total time:30min). Liquid products were analyzed using a gas chromatography was equipped with flame ionization detector (FID) and a HP^{-1} capillary column (GC conditions: 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 at a rate of 20°C/min. Methane conversion and products selectivity were calculated on the basis of carbon number according to eqs (1–2).

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

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

3.0 RESULTS AND DISCUSSION

3.1 Characterization Results

3.1.1 XRD

The diffractograms of the XRD for all catalyst samples are shown in Figure 1. The results indicated that the samples have similar peak patterns like the MFI-zeolites [22]
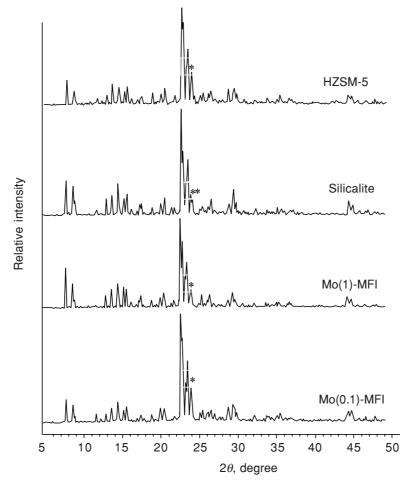
Figure 1 XRD diffractogram of the catalysts

and the structure did not collapse as a result of loading metals into the samples. The XRD diffractograms showed that silicalite is MFI-zeolite with monoclinic phase (the peak split into two at $2\theta = 24.17° – 24.5°$) while H-ZSM-5, Mo(1)-MFI and Mo(0.1)-MFI are MFI-zeolites with orthorhombic phase (the peak did not split at $2\theta = 24.17° - 24.5°$). The related peaks are indicated with the (*) and (**) symbols for orthorhombic and monoclinic, respectively, as shown in Figure 1.

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 Mo(0.1)-MFI since both catalysts have Al in their structures while silicalite is taken as standard for Mo(1)-MFI since both are Al-free catalysts. The results in Table 1 indicated that Mo-MFI catalyst favored the crystalline phase. From the unit cell volume result, Mo(1)-MFI has a higher unit cell volume, 5.389 Å^3, compared to its standard (silicalite) which is 5.226 Å^3. However, from this observation, it cannot be confirmed whether molybdenum metals have been substituted into the zeolite framework although the

Table 1   Crystallinity and unit cell volume of the catalysts

Sample	Crystallinity (%)	Volume (Å^3)
HZSM-5	100.00	5.386
Mo(0.1)-MFI	118.46	5.373
Silicalite	100.00	5.226
Mo(1)-MFI	119.43	5.389

ionic radii of a molybdenum atom (0.55 Å) is similar to the aluminium ionic radii (0.53 Å). The difference in the unit cell volume between Mo(1)-MFI and HZSM-5 is only 0.163 Å^3 and there are many factors which contributed to the difference in the unit cell volume. The other factors may be the water content and the extraframework species in the zeolite [23]. Furthermore, the simulation study by Zhou *et al*. [18] indicated that molybdenum metals stayed preferentially at the channel intersection just as aluminium does. From the recent studies, it is reported that, molybdenum species which is most possibly MoO_2^+ $(MoO5)_2^+$ migrated into the zeolite channel and replaced H^+ position [14,17,19]. Other characterization techniques such as Nuclear Magnetic Resonance (NMR) classified as the short-range order, should be applied in future study to confirm whether the metals are incorporated in the zeolite framework or not.

3.1.2   FTIR Analysis

Table 2 shows that all the samples consisted of asymmetric and symmetric T-O-T modes (1250-1000 cm^{-1} and 800 cm^{-1}, respectively), double ring vibration (540 cm^{-1}) and T-O bending (450 cm^{-1}) [24] typical of the MFI structure. The obtained results indicated that all samples are MFI structure. The main sensitive mode is T-O-T internal asymmetric vibration around 1100 cm^{-1}. The peak will shift to higher frequency as the SiO_2/AlO_3 ratio increased and vice-versa. As can be seen, Mo(1)-MFI sample shows lower frequency compared to silicalite, which is 1082 cm^{-1} and 1096 cm^{-1} respectively. This observation indicated that silicalite sample is more siliceous than Mo(0.1)-MFI. Meanwhile, Mo(0.1)-MFI sample vibrate at higher frequency (1092 cm^{-1}) compared to its standard, HZSM-5 (1087 cm^{-1}), meaning that Mo(0.1)-MFI is more siliceous than HZSM-5. This shows that molybdenum metals are not isomorphously substituted into the framework and took the positions of aluminium because if so, Mo(0.1)-MFI should be shifted to lower frequency compared to HZSM-5.

As can be seen in Figure 2, a new band was observed (at 900 cm^{-1} to 1 000 cm^{-1}) for the sample with high molybdenum content (Mo(1)-MFI) and sample with silicalite structure. These peaks were attributed to T-M (T-O or T-O-M) stretching, implying that the cations interacted with the zeolite framework [25] or associated with the defect centers containing the incorporated metal such as Mo in this case [26-28]. Since FTIR

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

Sample	TO$_4$ Stretching,			T-O Bending		T-O$^-$
	Asymmetric		Symmetric			T-O-M
HZSM-5	1220.9	1087.8	789.8	543.9	453.2	-
Mo(0.1)-MFI	1218.9	1092.6	790.8	545.8	454.2	-
Silicalite	1220.8	1096.4	793.7	548.7	453.2	978.8
Mo(1)-MFI	1223.7	1082.0	796.5	541.0	447.5	997.1

is the long-range order, which only can reveal the molecular vibration, the results in Figure 2 suggest that most probably Mo metals in this study are occluded in the defect sites and not incorporated into the framework of zeolite.

3.1.3 *TPD-NH^3 Analysis*

The TPD-NH$_3$ results in Table 3 indicated Mo(1)-MFI and silicalite samples exhibited desorption peaks at low temperature only. The acidity of Mo(1)-MFI is the lowest at 0.26 mmol/g. In contrast Mo(0.1)-MFI and HZSM-5 zeolites showed desorption peaks at both low and high temperatures. More interesting, the acidities of HZSM-5 zeolite and Mo(0.1)-MFI are almost equal at 7.68 mmol/g and 7.60 mmol/g, respectively. The amount of metal loaded at 0.1 wt % may have been too small for Mo to exert any effects on the acidity of the sample. As the loading of Mo increased, the number of acid sites decreased due to poor dispersion of the molybdenum species at high Mo loading and the possibility of the presence of polymeric species [16]. Low acidity is also expected for silicalite and Mo(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 aluminium 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 [24]. With this observation, it is confirmed that aluminium 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 Mo(0.1)-MFI > Silicalite > Mo(1)-MFI.

3.2 Catalytic Activity Tests

The results for the methane conversion for the reaction between methane and oxygen at 800°C and atmospheric pressure are shown in Figure 3. The conversion of methane
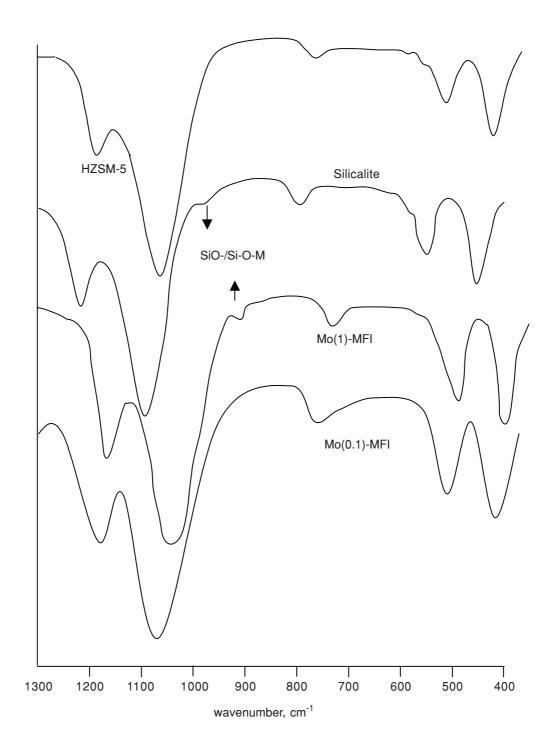
Figure 2   FTIR spectra of the catalysts

Table 3 Temperature programmed data for catalyst samples

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
	-	-	
Mo(1)MFI	147	0.26	0.26
	-	-	
Mo(0.1)-MFI	210	4.68	7.60
	448	2.92	

is 11.8 % over Mo(1)-MFI followed by Mo(0.1)-MFI at 10.4 % , HZSM-5 at 10.2 %, and silicalite at 4.7 %. The results obtained indicated that both Mo(1)-MFI and Mo(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, Mo-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 metal in modified zeolite acted as dehydrogenating component [29]. Consequently, the presence of molybdenum species resulted in the enhancement of methane activation by abstracting hydrogen from methane to form methyl radicals.

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}). Loading of metals onto the catalyst has obviously provided an advantage over the parent zeolite. For example, loading of metals into the zeolite sample led to a decrement in the CO_2 selectivity. However, CO_2 is still dominant for the reaction over all the catalyst samples. Deep oxidation of methane is unavoidable since methane oxidation reaction requires the use of oxygen.

The results in Figure 4 indicated that CO was detected for reactions involving Mo-loaded MFI catalysts only. The trend seems to suggest that the reaction over the Mo-MFI catalysts followed the partial oxidation pathway as most researchers had claimed that Mo loaded catalyst is the most active and selective for partial oxidation reaction [2,30,31]. Only traces of H_2 is detected for all the samples due to low H_2 formation. Since there is no Mo in the HZSM-5 and silicalite samples, complete oxidation of CO to CO_2 occurred. As a result, CO was not observed over the two samples.
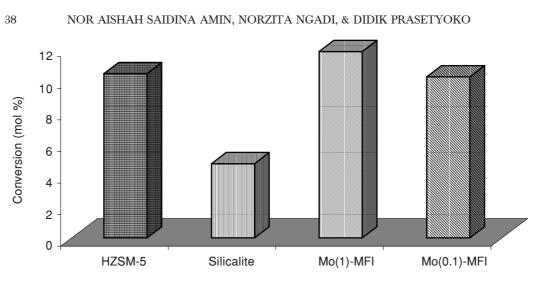
Figure 3   Methane conversion as a function of catalyst

More interesting, C_1-oxygenates were 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 [32-35]. 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 [5]. Another possible mechanism for the C_1-oxygenates is reported by Ono and coworkers [32] who claimed that at low pressure (8 Torr), C_1-oxygenates were formed through the addition of surface hydrogen to methoxide ion on the catalyst rather than the hydrogen abstraction from CH4.

The selectivity for C_1-oxygenates are 12.3 %, 10.8 %, and 10.0 % for Mo(0.1)-MFI, HZSM-5 and Mo(1.0)-MFI catalysts, respectively. The results suggested that too much
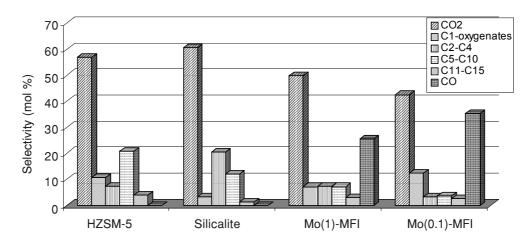

Figure 4   Distribution of the products selectivity

metal loaded into the zeolite framework would reduce the C_1-oxygenates selectivity, and its formation may be correlated to the density of acidic sites. As expected, C_1-oxygenates selectivity over silicalite is the lowest, about 3.20 % as the silicalite is low in activity [10].

Gasoline production could also be formed via the oligomerization of olefins on the zeolite acidic sites [5-7,13]. The results in Figure 4 implied that gasoline selectivity was higher for HZSM-5 and silicalite at 20.9 % and 12.2 %, respectively compared to the 5 % gasoline selectivity using Mo loaded MFI zeolites. The results are different from other literature reports which indicated that modified catalysts are more superior for producing gasoline compared to those which are not modified [7,12]. 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 treatment [13]. The poor catalytic performance of Mo loaded catalyst with respect to gasoline formation in this study may be due to the Mo species blocking the zeolite channels [14,18,19]. Mo species may have deposited in the channels and consequently, blocked the path for the migration of the reactant or the propagation of oligomer chains. From the catalytic performance tests, Mo loaded catalyst demonstrated good selectivity to C_1-oxygenates, which is up to 12 %, but is not a suitable catalyst for gasoline formation. Vu *et al.* [17] had claimed that Mo/MCM-22 was twice more active than Mo/ZSM-5 in aromatization of methane. This suggested that different zeolite catalyst with different pore systems would exhibit different activity and selectivity.

It is also interesting to note that silicalite which is considered low in activity posed gasoline selectivity higher than the Mo modified zeolites. The silicalite are also considered in the MFI zeolite family as revealed by the XRD data. The TPD results indicated the silicalite has a medium strength acidity, which may contribute to the oligomerization of C_2–C_4 hydrocarbons.

4.0 CONCLUSIONS

The MFI-zeolites and Mo modified MFI-zeolites were successfully synthesized. It is suggested that Mo species could probably be occluded in the defect sites of the zeolites. Other characterization techniques such as Nuclear Magnetic Resonance should be used to confirm whether or not the metals are incorporated in the zeolite framework. The modification of zeolite with molybdenum metal seems to increase methane conversion whilst CO_2 selectivity is suppressed. The enhancement of the catalytic activity is due to the bifunctional oxidative-acid catalyst, with zeolite as the acidic component and metal as the dehydrogenating component. However, modification of zeolite with molybdenum is found to be the most effective catalyst for producing C_1-oxygenates and not gasoline. Therefore, the selection of the right catalyst is the important factor for increasing the selectivity of the desired products.

ACKNOWLEDGEMENT

REFERENCES

[1]   Kaufmann, T. G., A. Kaldor, G. F. Stuntz, M. C. Kerby, and L. L. Ansell. 2000. "Catalysis Science and Technology for Cleaner Transportation Fuels". *Catalysis Today*. 62: 77-90.

[2]   Zaman, J. 1999. "Oxidative process in Natural Gas Conversion". *Fuel Processing Technology*. 58: 61-81.

[3]   Hohn, K. L. and L. D. Schmidt. 2001. "Partial Oxidation of Methane to Syngas at High Space Velocities over Rh-Coated Spheres". *Applied Catalysis A: General*. 211: 53-68.

[4]   Shepelev, S. S., and K. G. Ione. 1983. "Preparation of Aromatic Hydrocarbons from Methane in the Presence of O_2". *Reaction Kinetic Catalyst Letter*. 23: 323-325.

[5]   Han, S., D. J. Martenak, R. E. Palermo, and D. E. Walsh. 1994. "Direct Partial Oxidation of Methane over ZSM-5 Catalyst: Metals Effects on Higher Hydrocarbon Formation". *Catalysis*. 148: 134-137.

[6]   Saidina Amin, N. A., and S. Z. Sharif Hussien, 1999. "Screening of Metal Loaded HZSM-5 Zeolites Catalyst for Single Step Conversion of Methane to Liquid Hydrocarbon". Proceedings World Engineering Congress. 1999: 223-227.

[7]   Anggoro, D. D. 1998. "*Single Step Conversion of Methane to Gasoline: Effect of Metal Loaded HZSM-5 Zeolite Catalysts*". Universiti Teknologi Malaysia. MSc. Thesis.

[8]   Choudhary, V. R., V. H. Rane, and S. T. Chaudhari. 2000. "Factors Influencing Activity/Selectivity of La-Promoted MgO Catalyst Prepared from La- and Mg- Acetates for Oxidative Coupling of Methane". *Fuel*. 79: 1487-1491.

[9]   Liu, C. -j., R. Mallinson, and L. Lobban, 1999. "Comparative Investigations on Plasma Catalytic Methane Conversion to Higher Hydrocarbons over Zeolites". *Applied Catalysis A: General*. 178: 17-27.

[10]   Knops-Gerrits, P. P., and W. A. Goddard. 2001. "Methane Partial Oxidation in Iron Zeolites: Theory Versus Experiment". *Molecular Catalysis A: Chemical*.166: 135-145.

[11]   Ji, S. -f., T. -c. Xiao, S. -b. Li, C.-z. Xu, R. -l. Hou, K. S. Coleman, and M. L. H. Green. 2002. "The Relationship Between the Structure and the Performance of Na-W-Mn/SiO_2 Catalysts for the Oxidative Coupling of Methane". *Applied Catalysis A: General*. 225: 271-284.

[12]   Saidina Amin, N. A., and A. Asmadi. 2001. "Characterization of Modified HZSM-5 with Gallium and Its Reactivity in Direct Conversion of Methane to Liquid Hydrocarbons". *Jurnal Teknologi*. 35: 21-30.

[13]   Saidina Amin, N. A., and D. D. Anggoro. 2002. "Dealuminated ZSM-5 Zeolite Catalyst for Ethylene Oligomerization to Liquid Fuels". *Natural Gas Chemistry*. 11: 79-86.

[14]   Wang, J., M. Kang, Z. Zhang, and X. Wang. 2002. "Propane Aromatization over Mo/HZSM-5 Catalysts". *Natural Gas Chemistry*. 11: 43-50

[15]   Solymosi,F., J. Cserenyi, A. Szoke, T. Bansagi, and A. Oszko. 1996. "Aromatization of Methane over Supported and Unsupported Mo-Based Catalysts". *Catalysis*. 165: 150-161.

[16]   Lucas, A., J. L. Valverde, L. Rodriguez, P. Sanchez, and M. T. Garcia. 2000. "Partial Oxidation of Methane to Formaldehyde over Mo/HZSM-5 Catalysts". *Applied Catalysis A:General*. 203: 81-90.

[17]   Vu, T. T., L. V. Tiep, P. Meriaudeau, and C. Naccache. 2002. "Aromatization of Methane over Zeolite Supported Molybdenum: Active Sites and Reaction Mechanism". *Molecular Catalysis A: Chemical*. 181: 283-290.

[18]   Zhou, D., D. Ma, X. Liu, and X. Bao. 2001. "A Simulation Study on the Absorption of Molybdenum Species in the Channels of HZSM-5 Zeolite". *Molecular Catalysis A: Chemical*. 168: 225-232.

[19]   Su, L., Y. Xu, and X. Bao. 2002. "Study on Bifunctionality of Mo/HZSM-5 Catalysts for Methane Dehydro-Aromatization under Non-Oxidative Condition". *Natural Gas Chemistry*. 11: 18-27.

[20]   Tang, S., H. Chen, J. Lin, and K. L. Tan. 2001. "Non-Oxidative Conversion of Methane to Aromatics over Modified Mo/HZSM-5 Catalysts". *Catalysis Communications*. 2: 31-35.

[21]   Plank, C. J., E. J. Rosiniski, and A. B. Schwartz. 1974. "Method for Producing Zeolites". UK Patent 1402981.

[22] Treacy, M. M. J., J. B. Higgins, and R.V. Ballmoos. 1996. *Collection of Simulated XRD Powder Patterns for Zeolites*. 3rd Edition. Elsevier.

[23] Weitkamp, J. 2000. "Zeolite and Catalysis". *Solid State Ionics*. 131: 175-188.

[24] Szostak, R. 1989. *Molecular Sieves Principle of Synthesis and Identification*. New York: Van Nostrand Reinhold. Catalysis Series.

[25] Sobalik, Z., Z. Tvaruzkova, and B. Wichterlova. 1998. "Monitoring of Skeletal T-O-T Vibrations of Metal Ion Exchanged Zeolites: An Attempt at Quantitative Evaluation". *Microporous and Mesoporous Materials*. 25: 225-228.

[26] Raghavan, P. S., V. Ramaswamy, T. T. Upadhya, A. Sudalai, and S. Sivasanker. 1997. "Selective Catalytic Oxidation of Thioethers to Sulfoxides over Mo-Silicalite-1 (MoS-1) Molecular Sieves". *Molecular Catalysis A*: *Chemical*. 122: 75-80.

[27] Aiello, R., F. Crea, E. Nigro, F. Testa, and R. Mostowicz. 1999. "The Influence of Alkali Cations on the Synthesis of ZSM-5 in Fluoride Medium". *Microporous and Mesoporous Materials*. 28: 241-259.

[28] Ke, J. -A, and I. Wang. 2001. "Elucidation of The Role of Potassium Fluoride in the Chemical and Physical Nature of ZSM-5 Zeolite". *Materials Chemistry and Physics*. 68: 157-165.

[29] Trombetta, M. 2001. "Conversion and Hydroconversion of Hydrocarbons on Zeolite-Based Catalysts: An FTIR study". *Catalysis Today*. 65. 285-292.

[30] Aoki, K., M. Ohmae, K. Takeishi, and N. Azuma. 1998. "Direct Conversion of Methane into Methanol over MoO_3/SiO_2 Catalyst in an Excess Amount of Water Vapour". *Catalysis Today*. 29-33.

[31] Shu, Y., and M. Ichikawa. 2001. "Catalytic Dehydrocondensation of Methane Towards Benzene and Naphthalene on Transition Methane Supported Zeolite Catalysts: Templating Role of Zeolite Micropores and Characterization of Active Metallic Sites". *Catalysis Today*. 71: 55-67.

[32] Ono, T., H. Kudo, and M. Anpo. 2000. "Partial Oxidations of CH_4 and C_2H_6 at Low Pressure Over H-and Na-ZSM-5 Catalysts". *Applied Catalysis A: General*. 194/195: 71-79.

[33] Kudo, H., and T. Ono. 1997. "Partial Oxidation of CH_4 Over ZSM-5 Catalysts". *Applied Surface Science*. 121/122: 413-416.

[34] Barbero, J. A., M. A. Banares, M. A. Pena, and J. L. G. Fierro. 2001. "Partial Oxidation of Methane into C1-Oxygenates: Role of Homogeneous Reactions and Catalyst Surface Area". *Catalysis Today*. 71: 11-19.

[35] Otsuka, K., and Y. Wang. 2001. "Direct Conversion of Methane Into Oxygenates". *Applied Catalysis A: General*. 222: 145-161.