Ethylene Conversion to Higher Hydrocarbon over Copper Loaded BZSM-5 in The Presence of Oxygen

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Abstract

The successful production of higher hydrocarbons from methane depends on the stability or the oxidation rate of the intermediate products. The performance of the BZSM-5 and modified BZSM-5 catalyst were tested for ethylene conversion into higher hydrocarbons. The catalytic experiments were carried out in a fixed-bed micro reactor at atmospheric pressure. The catalysts were characterized using XRD, NH_3-TPD and IR for their structure and acidity. The result suggests that BZSM-5 is considered a weak acid. The introduction of copper into BZSM-5 improved the acidity of BZSM-5. The conversion of ethylene toward higher hydrocarbon is dependent on the acidity of the catalyst. Only weaker acid site is needed to convert the ethylene to higher hydrocarbons. Loading of Cu on BZSM-5 improved the selectivity of higher hydrocarbons especially at lower percentage. The reactivity of ethylene is dependent on the number of acidity as well as the presence of metal on the catalyst surface. Cu 1%BZSM-5 is capable of converting ethylene to higher hydrocarbons. Balances between metal and acid sites influence the performance of ethylene conversion and higher hydrocarbon selectivity. Higher loading of Cu leads to the formation of CO_x.

Keywords: Ethylene conversion, BZSM-5 Zeolite, Acidity, higher hydrocarbon.

1.0   Introduction

The conversion of methane to higher hydrocarbons has been studied in detail and the initial formation of ethylene and its subsequent conversion to long chain hydrocarbons is considered a possible mechanism. The conversion of methane to ethylene followed by processing of ethylene over ZSM-5 is an efficient and flexible route for production of synthetic hydrocarbons from either natural gas. Depending on process conditions, products can be produced ranging from gasoline to distillate fuels [1,2]. The transformation of light alkenes over zeolites catalyst is important in the various petrochemical processes such as Methane-Olefin-Gasoline-Distillate (MOGD) and methane to gasoline (MTG).

The mechanism of the reaction between methane and oxygen to produce higher hydrocarbons over zeolite is postulated to start from the formation of methyl radical from CH_4 [3,4]. The methyl radicals combined to form ethane, which dehydrogenated to ethylene. Oligomerization and aromatization of ethylene will produce higher hydrocarbons such as aromatics or liquid fuels. However ethylene may easily oxidized to CO_x. Therefore, the successful production of higher hydrocarbons depends on the stability or the oxidation rate of

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the intermediate products. The catalysts selected must have the ability to control the oxidation and able to oligomerize the intermediate products.

Acidity is one of the most important characteristics of zeolites, and the one that makes them extremely important materials in catalytic applications. The acidity of zeolites is known to depend on several factors: structure, preparation method, chemical composition, impurities, Si/Al ratio, additives and poisons. A lot of attention has been given to the relationship between the acidity of zeolites and their catalytic activity. Successful production of C_2^+ from methane is depended on the zeolite acidity [5,6]. As previously observed, the synthesized BZSM-5 and modified BZSM-5 present very different acidity and consequently different catalytic properties [7-9]. Thus, it is of considerable interest to compare the catalytic behaviors of BZSM-5 and copper loaded BZSM-5 zeolites for the transformation of ethylene. Ethylene, which is the intermediate product of methane activation, undergoes subsequent oligomerization and aromatization on Brönsted acid sites of zeolites to form higher hydrocarbons. Thus, the higher reactivity of O_2 with C_2H_4 as compared to CH_4 has been a major problem of achieving higher selectivity of higher hydrocarbons. In this context, the possible inhibition of the oxidation of C_2^+ is of special interest. With the aim of identifying the importance of the ethylene as an intermediate species for the oxidative dehydrogenation of methane to higher hydrocarbons, ethylene has been used as a probe performing several catalytic tests. Ethylene was used as it is assumed to play the intermediate role in methane conversion to higher hydrocarbons. This study provides information of C_2^+ stability over these catalysts. These data are relevant to the design of catalyst for direct methane conversion to higher hydrocarbons, since it is crucial that the catalyst are identified that do not decompose C_2^+ to CO_x. Clearly, it is important that C_2^+ should be stable over any potential catalyst, under appropriate conditions.

2.0 Materials & Method

2.1 Catalyst Preparation

BZSM-5 was first synthesized by Taramasso *et al.*, [10] using organic compounds of silicon and tetrapropylammonium cation as a template. Recently, some publications in the open as well as in the patent literature have dealt with boron-containing pentasil type zeolite. The BZSM-5 was prepared following the procedure described by Plank *et al.* [12]. Generally, a gel was prepared by mixing: 69 g of sodium silicate (Merck: 25.5-28.5% SiO_2, 7.5-8.5 %Na_2O), 0.53 g boric acid (Merck), 7.53 g Tetra propyl-ammonium bromide (TPA-Br) as a template (Fluka) and 160 g distilled water to form a reaction mixture with the following molar composition B_2O_3: $20Na_2O$: $70SiO_2$: $7TPABr$: $2200H_2O$. The pH of the reaction mixture was maintained around 10-12 by the addition of sulfuric acid. The gel was stirred at room temperature for 3 hours in a one-liter stainless steel autoclave (PARR reactor). The gel was then heated in the oven at $160^\circ C$ for 5 days without stirring. The TPA ion, present in the solution, was the key reagent favoring the formation of the tetrahedral units, which in turn played a key role in determining the characteristic structure of the BZSM-5. The template was removed through calcination to yield the template-free product.

Once the zeolite was formed (crystalline white solid), it settled at the bottom of the autoclaves, leaving a clear supernatant liquid. The crystalline white solid product was filtered, washed thoroughly with deionized water, dried at $120^\circ C$ for 12 hours. The resultant

material was calcined at 550ᴼC for five hours to remove the organic material and to obtain the sodium form of the BZSM-5, Na-BZSM-5. The Na-form so obtained was converted into the NH_4-form by ion exchange using 1M solution of ammonium nitrate, NH_4NO_3. For every 1 gm of NaBZSM-5, it was treated with 25 ml of 1M NH4NO3 solution, stirred under reflux for three hours at 80oC. The procedure was repeated three times, ending with refluxing the solution for 12 hours. Finally, the catalyst was dried and calcined at 550oC for five hours.

Recently, it has been found that the introduction of copper can remarkably increase the activity of catalyst in methane conversion [6]. Therefore, the effect of copper will be investigated. The incorporation of copper into the calcined BZSM-5 was carried out through impregnation method. BZSM-5 obtained was impregnated with copper nitrate solution to give 1,4, and 9wt% of copper and labeled as Cu1%BZSM-5, Cu4%BZSM-5 and Cu9%BZSM-5 respectively. Then, the solid were calcined in the furnace at 550ᴼC for five hours.

2.2 Catalyst Characterization

There were 3 different types of characterizations being performed in this study, which are, (i) X-Ray Diffraction (XRD), (ii) Infrared spectroscopy (IR) and (iii) Acidity measurement. XRD patterns were acquired on a Siemens D5000 goniometer using CuKα radiation in the range of 2θ from 2° to 60° at a scanning speed of 3° per minute. IR spectra were examined with Shimadzu 3000 FTIR spectrometer using KBr wafer technique. Samples (0.25mg of zeolite powder) were mixed with 300mg KBr powder and finely ground. These mixtures were placed onto a dye and pressed up to make a transparent thin pellet. The IR spectra of the sample were taken between 2400-400 cm^{-1} at room temperature.

For acidity measurement, it is necessary to determine the amount, strength and type of acid sites. In this study, three types of technique: Temperature Programmed Desorption (TPD) of ammonia, IR spectroscopy for hydroxyl region, IR spectroscopy of adsorbed pyridine were used to evaluate the acidic properties of the catalyst. The amount and its strength were determined using Temperature Programmed Desorption (TPD) of ammonia while the type of acid site information were obtained using IR spectroscopy for hydroxyl region and IR spectroscopy of adsorbed pyridine

2.3 Catalyst Testing

The performance of the BZSM-5 and modified BZSM-5 catalyst was tested for ethylene conversion into higher hydrocarbons. The catalytic experiments were carried out in a fixed-bed micro reactor at atmospheric pressure.

Gases of ethylene, compressed air and nitrogen were supplied from individual gas cylinder. The reactor was preheated at the reaction temperature of 800ᵒC under nitrogen flow for two hours to activate the catalyst. Ethylene (purity 99.9%) and compressed air were then fed into the reactor with 9% volume of oxygen in the feed. Total feed flow rate was 200ml/min. The catalyst weight used in this study was one gram. The reaction products were analyzed by an on-line gas chromatography. The GC analysis was carried out using Thermal Conductivity Detector (TCD) equipped with Porapak packed column.

The conversion of ethylene and the selectivity of higher hydrocarbons was determined according to the following equations:

$$\text{Conversion of ethylene} = \frac{\text{moles of } C_2H_4 \text{ reacted} \times 100}{\text{moles of } C_2H_4 \text{ in feed}}$$

$$\text{Selectivity of products} = \frac{\text{moles of hydrocarbon gas produced other than } C_2H_4 \times 100\%}{\text{moles of } C_2H_4 \text{ reacted}}$$

3.0   Results and Discussion

3.1   Catalyst Characterization

Figure 1 shows the diffractogram of the BZSM-5 impregnated with different loading of copper ranging from 1wt% to 9wt%. No significant difference was found between the diffractograms of the parent zeolite (BZSM-5) and the catalysts after impregnation with copper. All the samples show similar pattern and highly crystalline. However, one peak at $2\theta = 38.6^\circ$, which is characteristic of CuO, was detected for the higher loading of Cu (above 4%). This results were consistent with the finding by Torre-Abreu *et al.* [12], where CuO peak were observed when HZSM-5 were loaded with 5.5wt% Cu. They reported that HZSM-5 with low copper loading, the copper was mainly present in the form of isolated Cu^{2+} ions. On the other hand, in catalyst with high copper loading, CuO, isolated Cu^{2+} ions and also Cu^+ ions were detected by using H_2-TPR and ESR. More ever, it was verified that the concentration of CuO species increases when the catalyst copper loading increases, which probably results in the formation of CuO aggregates. Nunes *et al.* [13] reported similar finding in their study on the effect of copper loading on the acidity of Cu/HZSM-5 catalyst.
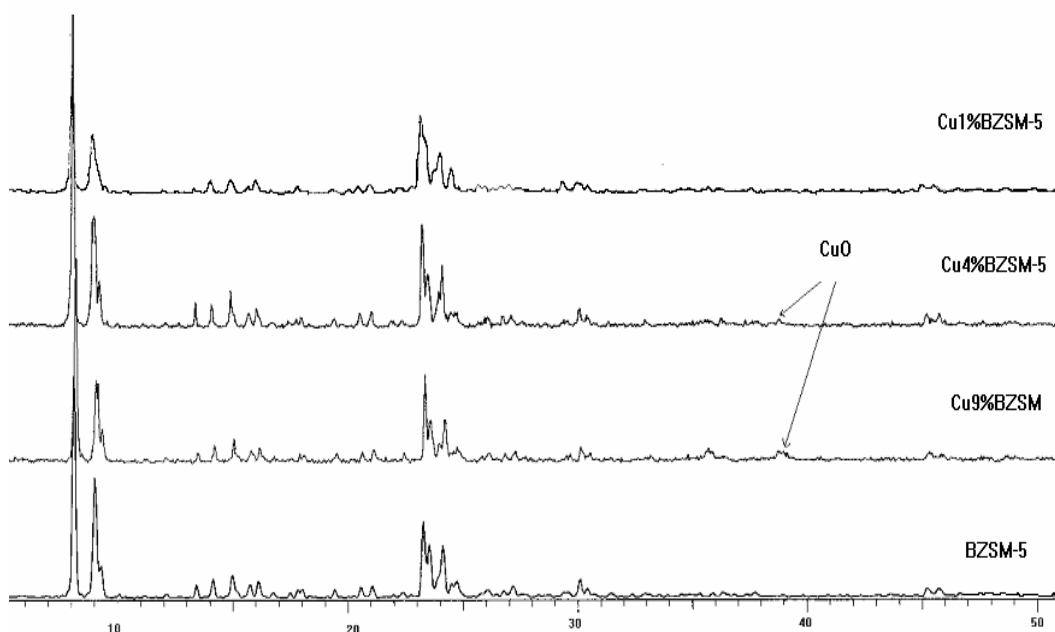

Figure 1   The effect of XRD pattern on different of copper loading on BZSM-5. CuO peak was observed at higher Cu loading

The NH_3-TPD results are shown in Table 1. The addition of 1wt% copper into BZSM-5 has resulted in the increase of acidity however, the acidity decreased about 30% in Cu4%BZSM-5 and Cu9%BZSM-5 catalysts, compared to the BZSM-5. This could be due to the charge imbalance imposed by copper as proposed by Tanabe [14]. A similar observation was reported by Ismail *et al.*, [15] and Anggoro [16] in their study of Cu loaded into HZSM-5. When Cu was loaded into the HZSM-5, it produced additional acid sites. However, when Cu was further loaded (i.e. 4% and 9%), the total amount of acid seemed to diminish from the catalyst surfaces as tabulated in Table 1. There was a possibility that some acid sites were lost during further loading of metal due to the blockage of the zeolite pore and formation of Cu cluster as can be seen using XRD [13,17].

Table 1: The results of the NH_3-TPD experiments

Sample	Total amount of chemisorbed (mmol/g)
BZSM-5	2.302
Cu1%BZSM-5	7.867
Cu4%BZSM-5	1.619
Cu9%BZSM-5	1.426

For a complete characterization of zeolite acidity, it is necessary to determine the nature and the concentration of both Brönsted and Lewis acid sites. This can be carried out by examine hydroxyl group region (3500-3750 cm^{-1}) and pyridine adsorption of IR spectroscopy. The infrared spectra of the samples taken at 303 K in the range of OH stretching vibrations are shown in Figure 2. For HZSM-5 sample, the bands are observed at 3740, 3660, and 3610 cm^{-1}. The band at 3740 cm^{-1} is attributed to the stretching of the terminal silanol (SiOH) groups located at the boundaries of the zeolite crystal. In spite of being terminal, at least part of them are significantly acidic too. The band at 3660 cm^{-1} has been assigned to OH groups associated with extraframework Al while the band at 3610 cm^{-1} is due to the stretching vibration of the bridging hydroxyl groups affiliated with tetrahedrally coordinated aluminium (Si-OH-Al). This band is normally more acidic. This hydroxyl group has acidic properties since the band was not observed when pyridine was adsorbed on the zeolite.

In the case of BZSM-5 sample, the stretching vibration band at 3610cm^{-1} due to the bridging hydroxyl groups having lower intensity. Furthermore, the band area for silanol groups was larger for BZSM-5 compared to HZSM-5. The result clearly shows in the Table 2. This result suggests that BZSM-5 has more terminal silanol groups or silanal at the defect site. The silanol groups are recognized as neutral or very weak acid. The silanol group existing on the external zeolites is considered a weak acid, however, it showed a catalytic role on Beckmann rearrangement and also some reaction with olefin as reported [18,19].

For copper loaded on BZSM-5, the intensity of the hydroxyl band at 3610 cm^{-1} was slightly higher but was still lower than that of HZSM-5. Thus, it can be suggested that the acidity of the BZSM-5 was improved with the introduction of copper into BZSM-5. This result supports the earlier data from the NH_3-TPD analysis, which indicate that adding Cu species on BZSM-5 improved the acidity of BZSM-5.

Table 2: The position of some characteristics OH vibration bands and integrated band area.

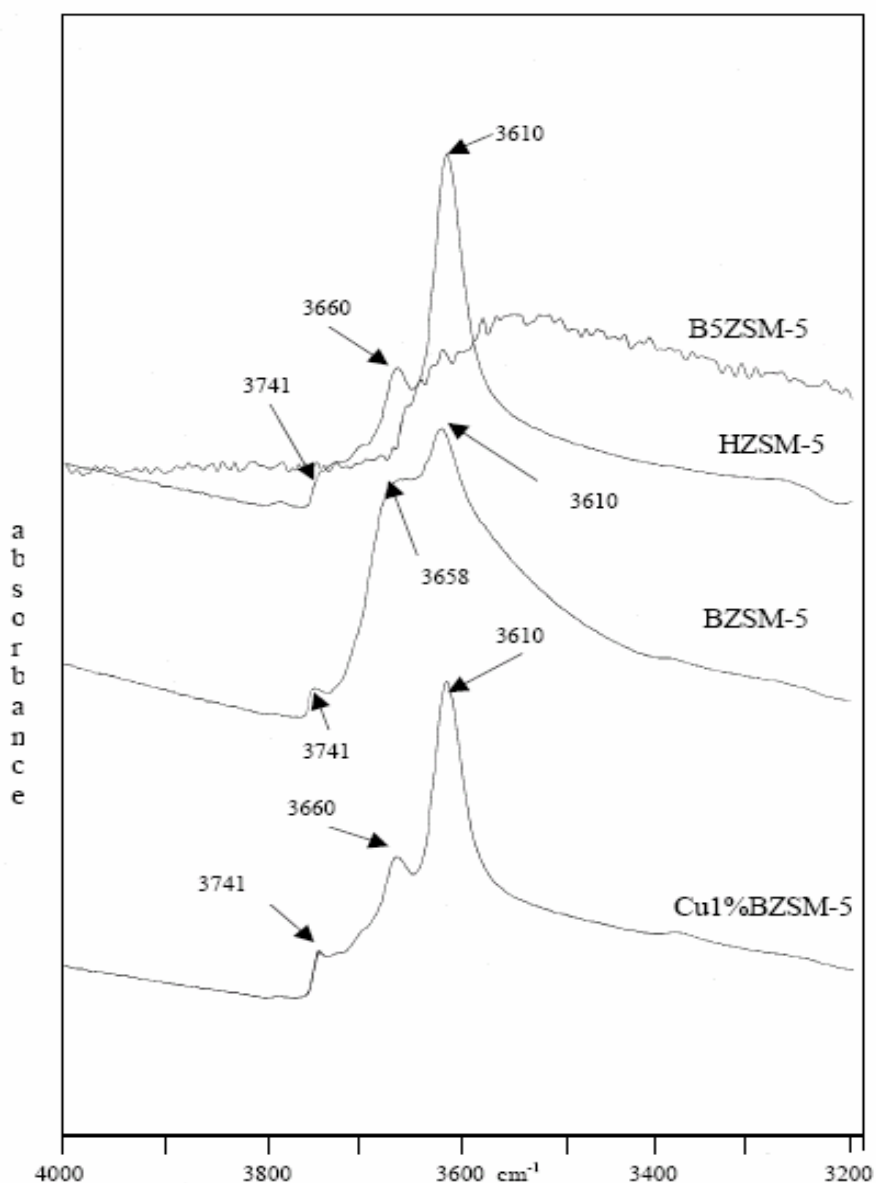| Sample	Wave Number		
	Al-Framework	Al-Non framework	Silanol
HZSM-5	3610	3661	3741
(Integrated area)	(7.21)	(0.55)	(0.09)
B5ZSM-5	Not observed	Not observed	Not observed
(Integrated area)			
BZSM-5	3611	3658	3741
(Integrated area)	(1.95)	(0.65)	(0.21)
Cu1%BZSM-5	3610	3661	3741
(Integrated area)	(5.89)	(0.64)	(0.19)

Figure 2   IR spectra in hydroxyl region of the samples after dehydration at 400 °C, 10-5 bar for 2 hours

The types of acid that were present in the zeolite sample were further characterized using pyridine adsorption method. Pyridinium ion signals (pyridine on Brönsted acid sites) appeared at wave numbers of 1638 and 1546 cm^{-1} and pyridine on Lewis acid sites appeared at 1450cm^{-1} [20]. The concentration of the Brönsted acid sites and the Lewis acid sites were calculated from the integrated area of the 1540 and 1450 cm^{-1} bands according to the formula proposed by Hughes *et al.* [21]. The results are tabulated in Table 3. The acidity increased when BZSM-5 was loaded with copper. More Lewis acid sites were generated when more copper was loaded on BZSM-5. The ratio of Brönsted to Lewis acid site was much reduced at higher loading of copper. There are two factors that explain this result. First, at higher copper loading, the Brönsted acid sites were covered partly by CuO. Second, part of the Cu species had exchanged with those Brönsted acid sites that were capable of transforming into Lewis acid sites. Similar results were reported by Wang *et al.* [22] on their studies of different Mo loading on HZSM-5. They claimed that from IR and NH_3-TPD studies indicated that the number of Brönsted acid centers decreased and the Lewis acid centers increased after more Mo loading into the HZSM-5 zeolite.

Table 3: Concentration of Brönsted and Lewis acidity of the samples.

Sample	Acidity (μmol/g)		
	Brönsted(B) (at 1545 cm^{-1})	Lewis(L) (at 1450 cm^{-1})	Ratio B/L
BZSM-5	5	0	-
Cu1%BZSM-5	105	8	13
Cu4%BZSM-5	6	40	0.15

3.2   Catalyst Testing

The results of the various catalytic performances for the reaction of ethylene and oxygen at 800°C and atmospheric pressure are given in Figure 3. This figure shows that the ethylene conversion and the carbon selectivity towards CO_x, C_2-C_4 (exclude C_2H_4), and C_5^+ for the catalyst tested. BZSM-5 was slightly less effective for ethylene conversion as compared to Cu1%BZSM-5. The acidity of BZSM-5 is lower than Cu1%BZSM-5. Thus, the slightly lower activity of BZSM-5 might be due to lower acidity as explained by Sohn *et al.* [2]. Furthermore, copper loaded in zeolite may act as a bifunctional catalyst and widely used in hydrocarbon conversion. On this catalyst, the transformation of hydrocarbons involved both the hydrogenation and dehydrogenation step on metal sites and the rearrangement and/or cracking step on acid sites. Indeed it has been shown very clearly that the balance between metal sites and acid sites influenced remarkably the performance of the bifunctional catalysts in hydrocarbon conversion [23,24].

The results show that copper loading at low concentration promotes ethylene conversion. However at higher concentrations of copper loading, the ethylene conversion decrease. The difference could be interpreted in terms of copper deposited over BZSM-5 zeolite. At 1 wt% of copper loading, copper oxide may not be totally deposited over the surface of BZSM-5 zeolite. Many active sites of BZSM-5 zeolite remained vacant and were responsible for

ethylene activation. At high copper loading, ethylene conversion decreased due to the deposition of the metal species over the acid sites together with the blocking of the channels.
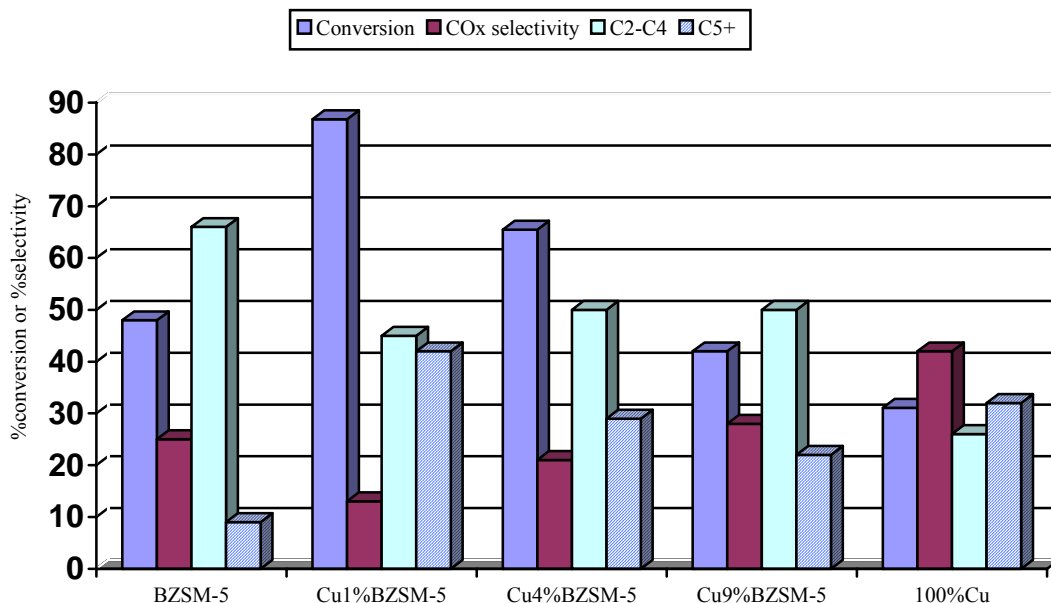

Figure 3   The catalytic performance of the ethylene reaction with 9 vol % of oxygen over BZSM-5 and modified BZSM-5 with copper catalyst at reaction temperature of 800°C and gas hourly space velocity (GHSV) of 8000hr-1 under atmospheric pressure.

BZSM-5 is shown to have reasonable activity but slightly lower selectivity towards higher hydrocarbons as mainly carbon oxides are formed. The selectivity towards C_2-C_4 for all the catalyst was between 45% up to 66%, where BZSM-5 shows the highest C_2^+ selectivity. On the other hand, Cu1%BZSM-5 gives the lowest C_2^+ selectivity. Furthermore, Cu1%BZSM-5 gives the lowest selectivity toward carbon oxides compared to higher loading of copper on BZSM-5 and pure copper itself. These results were consistent with the result obtained by Min *et al*. [25] in their study on the effects of copper additives on the selective oxidation of light alkanes. Min *et al*. [25] demonstrated that the addition of copper enhanced the catalytic performance for oxidation light alkanes under oxygen-poor condition to COx.

Referring to the results discussed above, the only way to relate activity with acidity of zeolite is by considering the amount of acid of the catalyst. Figure 4 shows the effect of acidity on the C_5^+ selectivity for ethylene conversion. Cu1%BZSM-5, which has more acid sites were observed to give a higher conversion of ethylene and higher hydrocarbon selectivity than the other catalyst. Following this observation, the amount of acid can be used to explain the activity of the catalyst. The finding is in-line with the result reported by Guisnet *et al*. [4, 26,27], where oligomerization process was dependent on the zeolite acidity. Nor Aishah and Anggoro [4] reported that oligomerization of ethylene were dependent on the zeolite acidity. As the number of the acid sites increased, the oligomerization reaction increased and thus more C_5^+ were produced.   However, the amount of acid itself is not the only cause of the catalyst being active, rather the presence of copper ions might also affect its activity as in case of Cu4%BZSM-5. From the Figure 4, it can be seen that the acidity of Cu4%BZSM-5 is lower that BZSM-5, however its selectivity toward C_5^+ was higher. Only weak acid site is required to activate ethylene or olefin to gasoline range hydrocarbon [28]. Kitigawa *et al*.

[29] studied the requirement of acid site in C-H bond activation on weakly acidic borosilicates with ZSM-5 structures. They reported that Zn exchanged borosilicates did not catalyze propane dehydrocyclodimerization but these catalysts were able to convert propene to aromatics at a significant rate.

Introducing metal into the zeolite resulted in increase of the conversion and selectivity. This finding was in agreement with the finding by Nishi *et al*. [30], Liu *et al*. [31], and Biscardi *et al*. [32]. They claimed that introducing the metal component to the zeolite catalyst, will improve the product selectivity. Biscardi *et al*. [32] reported that the introduction of Ga, Zn or Pt species into zeolites increased the rate and selectivity of aromatization reactions and inhibited cracking side reactions that led to the loss of carbons to undesirable products. They explained that the oligomerization and cracking of light alkenes occurred readily on acid sites. Light alkenes can be converted to a mixture of higher molecular weight alkenes via sequence of acid-catalyzed shape-selective oligomerization reaction over zeolites. Furthermore, aromatization of the product formed required a concerted reaction between acid and metal cation sites.
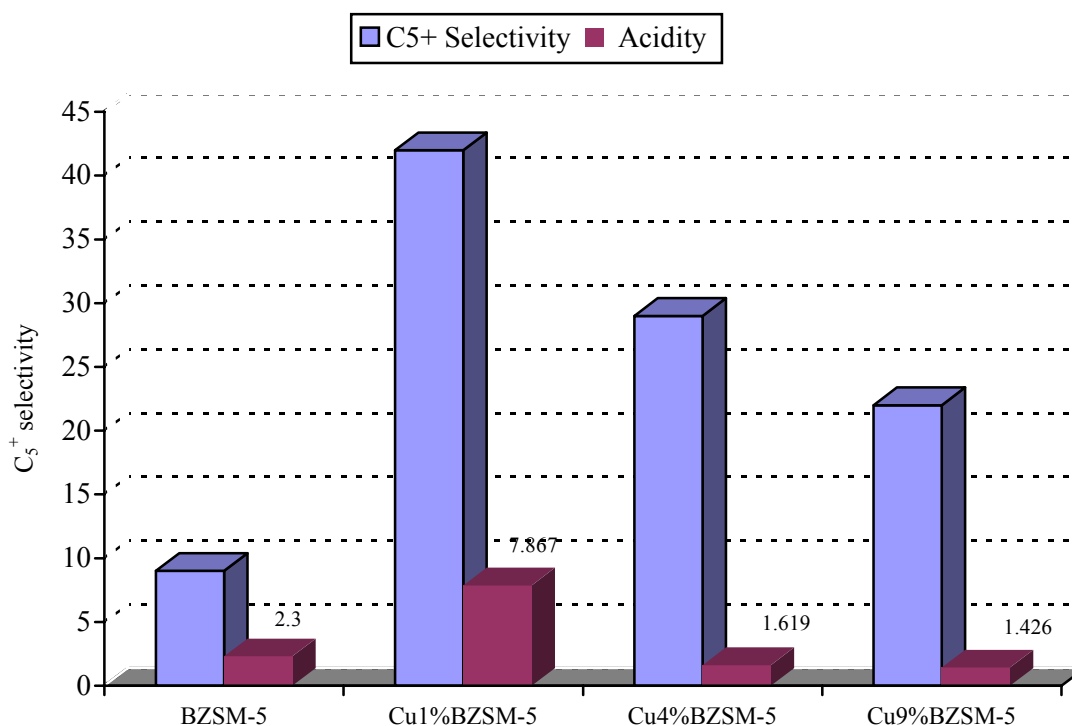

Figure 4   Effect of number of acid (mmol/g) on C_5^+ selectivity for ethylene conversion
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4.0   Conclusion

The conversion of ethylene toward higher hydrocarbon is dependent on the acidity of the catalyst. Only weaker acid site is needed to convert the ethylene to higher hydrocarbons. Loading of Cu on BZSM-5 improved the selectivity of higher hydrocarbons especially at lower percentage. The reactivity of ethylene is dependent on the number of acidity as well as the presence of metal on the catalyst surface. Cu1%BZSM-5 is capable of converting ethylene to higher hydrocarbons. Balances between metal and acid sites influence the

performance of ethylene conversion and higher hydrocarbon selectivity. Higher loading of Cu leads to the formation of CO_x

References

[1] Hevelling, J., Nicolaides, C.P., Scurrell, M.S. (1998) Catalysts and Conditions for the Highly Efficient, Selective and Stable Heterogeneous Oligomerisation of Ethylene. *Applied Catalysis A: General.* 173:1-9

[2] Sohn, J.R., Park, W.C., (2002) Characterization and Catalytic Activity for Ethylene Dimerization of Nickel Sulfate Supported on Zirconia, *Applied Catalysis A: General.* 230:11-18

[3] Han, S., Maternak, D.J., Palermo, R.E., Pearson, J.A., Walsh, D.E., (1994), Direct Partial Oxidation of Methane Over ZSM-5 Catalyst, *Journal of catalysis.* 148: 134-137

[4] Nor Aishah Saidina Amin and Didi Dwi Anggoro. (2002) Dealuminated ZSM-5 Zeolite Catalyst for Ethylene Conversion to Liquid Fuels. *J. of Natural Gas Chemistry*, 11:79-86.

[5] Ernst, S., Weitkamp, J., (1989). Oxidative Coupling of Methane Using Zeolite-Based Catalyst, In: Imarisio, G., Frias, M., Bemtgen, J.M. (eds.) *Hydrocarbons Source of Energy*, 461-469

[6] Nor Aishah Saidina Amin and Didi Dwi Anggoro. (2003) Characterization and Activity of Cr, Cu, Ga Modified ZSM-5 for Direct Conversion of Methane to Liquid Hydrocarbons. *J. of Natural Gas Chemistry*, 12:123-134.

[7] Liu, H., Ernst, H., Freude, D., Scheffler, F., Schwieger, W. (2002) In situ ^{11}B MAS NMR study of the synthesis of a boron-containing MFI type zeolite, *Microporous and Mesoporous Materials,* 54:319-330.

[8] Beyer H.K., Borbely, G., (1986) In: Murakami, Y., Iijima, A., Ward J.W., (eds). *New Developments in Zeolite Science and Technology*. Elsevier, Amsterdam. 867-876

[9] Ratnasamy, P., Hedge, S.G., Chandwadkar, A.J., (1986). The Acidity and Catalytic Activity of Alumino- and Borosilicate Pentasil Zeolites: A Comparison, *Journal of Catalysis.*102:467-470

[10] Taramasso, M, Perego, G., B. Notari, , (1980). Synthesis and Characterization of BZSM-5 Zeolite. In: Rees, L.V., (ed.) *Proc. 5ᵗʰ Intern. Conf. Zeolites.*, Heyden & Son, London, 40-49

[11] Plank, C.J., Rosinski, E.J., Schwartz, A.B., (1974) (U.K Patent 1402981)

[12] Porre-Abreu, C., Ribeiro, M.F., Henriques C., Delahay, G., (1997) Characterization of Cu-MFI Catalyst by TPD of NO; Effect of the Si/Al Ratio and Copper Loading. *Applied Catalysis B: Environmental.* 12:249-262.

[13] Nunes, M.H.O., Teixeira, V., Schmal, M., (2005). The Effect of Copper Loading on the Acidity of Cu/HZSM-5 Catalysts: IR of Ammonia and Methanol for Methylamines Synthesis, *Applied Catalysis A: General*, 294:148-155

[14] Tanabe, K., (1970) *Solid Acids and Bases: Their Catalytic Properties*, Kodansha and Academic Press, Tokyo, New York, London.

[15] Ismail Mohd Said, Abdul Rahman Mohamed, Bhatia, S.(2002) Activity and Characterization of Bimetallic ZSM-5 for Selective Catalytic Reduction of NOx. *J. of Molecular Catalysis A: Chemical*, 189:241-250

[16] Anggoro, D.D, (2003) *Modified Oxidative Coupling Process of Methane to Liquid Fuels Over Metal Loaded ZSM-5 Catalyst*, Universiti Teknologi Malaysia: Ph.D Thesis.

[17] Choudary V.R, Mantri, K., Sivadinarayana, C. (2000) Influence of Zeolite Factors Affecting Zeolite Acidity on Propane Aromatization Activity and Selectivity of Ga/HZSM-5. *Microporous and Mesoporous Materials*, 37:1-8

[18] Roseler, J., Heitmann, G., Holderich, W.F. (1996), Vapour-phase Beckmann Rearrangement Using B-MFI Zeolites,. *Appl. Catal.* 114:319-333

[19] Kondo, J.N, Yoda, E., Ishikawa, H., Wakabayashi, F., Domen, K., (2000) Acid Property of Silanol on Zeolites Assesed by Reaction Probe IR study, *Journal of Catalysis.* 191, 275-281

[20] Tynjala, P., Pakkanen, T.T., (1996) Acidic Properties of ZSM-5 Zeolites Modified with Ba^{2+}, Al^{3+} and La^{3+} Ion Exchanges, *J. of Molecular Catalyst*, 110: 153-159

[21] Hughes, T.R., White, H.M., (1967) A Study of the Surface Structure of Decationized Y Zeolite by Quantitative Infrared Spectroscopy. *Journal Of Physical Chemistry.* 71: 2192-2201

[22] Wang, J. Kang M., Zhang, Z., Wang, X., (2002) Propane Aromatization over Mo/HZM-5 Catalysts, *J. of Natural Gas Chemistry*, 11:43-50.

[23] Wang, J.,Li, Q., Yao, J., (1999) The Effect of Metal-acid Balance in Pt-loading Dealuminated Y Zeolite Catalysts on the Hydrogenation of Benzene, *Applied Catalysis A: General,* 184:181-188.

[24] Girgis, M.J., Tsao, Y.P., (1996) Impact of Catalyst Metal-acid Balance in n-Hexadecane Hydroisomerization and Hydrocracking, *Ind. Eng. Chem. Res.* 35: 386-394.

[25] Min J.S., Mizuno N., (2001), The Effects of Additives on Catalytic Performance of Heteropoly Compounds for Selective Oxidation of Light Alkanes, *Catalysis Today.* 71: 89-96.

[26] Guisnet, M., Gnep, N.S., Vasques, H., and Ribeiro, F.R., (1991). Zn-Doped HZSM-5 Catalysts for Propane Aromatization. In: Jacobs, P.A., Jaeger, N.I., Kabelkova, L., and Wichterlova, B., *Zeolite Chemistry and Catalysis*. Amsterdam: Elsevier 321-329.

[27] O'Connor, C.T., and Kojima, M., (1990) Alkene Oligomerization, *Catalysis Today*. 6: 329-349.

[28] Wang, D.Z., Lu, X.D., Dou, X.Y., Li, W.B., (1990). Effect of Acidity of HZSM-5 Type Zeolite on Conversion of Alkene and Alkanes to Gasoline and Aromatics, *Applied Catalysis*. 59: 75-88.

[29] Kitigawa, H., Sendoda, Y., Ono, Y., (1986) Transformation of Propane into Aromatics Hydrocarbons over ZSM-5 Zeolites. *Journal of Catalysis*. 101: 12-18.

[30] Nishi, K., Komai, S., Inagaki, K., Satsuma, A., and Hattori, T., (2002). Structure and Catalytic Properties of Ga-MFI in Propane Aromatization. *Applied Catalysis A: General*. 223:187-193.

[31] Liu, B., Yang, Y. and Sayari A.H., (2001). Non-oxidative Dehydroaromatization of Methane Over Ga-promoted Mo/HZSM-5 Based Catalyst. *Applied Catalysis A: General*. 214: 95-102.

[32] Biscardi, J.A., and Iglesia, E., (1996) Structure and Function of Metal Cations in Light Alkene Reactions Catalyzed by Modified HZSM-5. *Catalysis Today*. 31: 207-231.