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Article

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 performances of the BZSM-5 and the modified BZSM-5 catalysts 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, NH₃-TPD, and IR for their structure and acidity. The result suggests that BZSM-5 is a weak acid. The introduction of copper into BZSM-5 improved the acidity of BZSM-5. The conversion of ethylene toward higher hydrocarbons is dependent on the acidity of the catalyst. Only weaker acid site is required to convert ethylene to higher hydrocarbons. The loading of Cu on BZSM-5 improved the selectivity for higher hydrocarbons especially at low percentage. The reactivity of ethylene is dependent on the amount of acidity as well as the presence of metal on the catalyst surface. Cu1%BZSM-5 is capable of converting ethylene to higher hydrocarbons. The balances between the 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.

Key words: ethylene conversion; BZSM-5 zeolite; acidity; higher hydrocarbon

1. Introduction

The conversion of methane to higher hydrocarbons has been studied in detail; 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 the processing of ethylene over ZSM-5 is an efficient and flexible route for the production of synthetic hydrocarbons from either natural gas. Depending on the process conditions, the products can be produced ranging from gasoline to distillate fuels [1,2]. The transformation of light alkenes over zeolites catalysts is of importance 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 CH₄ [3,4]. The methyl radicals combine to form ethane, which dehydrogenate to ethylene. Oligomerization and aromatization of ethylene will produce higher hydrocarbons such as aromatics or liquid fuels. However, ethylene may easily oxidize to CO_x. Therefore, the successful production of higher hydrocarbons depends on the stability or the oxidation rate of the intermediate products. The catalysts selected must have the ability to control the oxidation and must be able to oligomerize the intermediate products.

Acidity is one of the most important characteristics of zeolites, which makes these extremely important materials in catalytic applications. The acidity of zeolites is known to depend on several factors: struc-

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ture, preparation method, chemical composition, impurities, Si/Al ratio, additives, and poisons. Considerable attention has been given to the relationship between the acidity of zeolites and their catalytic activity. Successful production of C_{2+} from methane is dependent on the zeolite acidity [5,6]. The synthesized BZSM-5 and the modified BZSM-5 present very different acidity properties and consequently different catalytic properties as reported in refs [7–9]. Thus, it is of considerable interest to compare the catalytic behaviors of the BZSM-5 and the 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 while achieving higher selectivity for 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 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 on C_{2+} stability over these catalysts. These data are relevant to the design of the catalyst for direct methane conversion to higher hydrocarbons, since it is crucial that the catalyst identified does not catalyze the decomposition of C_{2+} to CO_x . Obviously, it is important that C_{2+} must be stable over any potential catalyst, under appropriate conditions.

2. Experimental

2.1. Catalyst preparation

BZSM-5 was first synthesized by Taramasso *et al.*, [10] using organic compounds of silicon and tetrapropylammonium cation as the 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 of boric acid (Merck), 7.53 g of Tetra propyl-ammonium bromide (TPA-Br) as the template (Fluka) and 160 g of 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 h in a one-liter stainless steel autoclave (PARR reactor). The gel was then heated in the oven at 160 °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, and dried at 120 °C for 12 h. The resultant material was calcined at 550 °C for five hours to remove the organic material and to obtain the sodium form of the BZSM-5, Na-BZSM-5. The Na-form obtained was converted into the NH_4 -form by ion exchange using 1M solution of ammonium nitrate, NH_4NO_3 . For every 1 g of NaBZSM-5, it was treated with 25 ml of 1M NH_4NO_3 solution, and was stirred under reflux for three hours at 80 °C. The procedure was repeated thrice, ending with refluxing the solution for 12 h. Finally, the catalyst was dried and calcined at 550 °C 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 needs to be investigated. The incorporation of copper into the calcined BZSM-5 was carried out through the impregnation method. The BZSM-5 obtained was impregnated with copper nitrate solution to provide 1wt% , 4wt% , and 9wt% of copper and was labeled as Cu1%BZSM-5, Cu4%BZSM-5, and Cu9%BZSM-5, respectively. The solid was then calcined in the furnace at 550 °C for five hours.

2.2. Catalyst characterization

Three different types of characterizations were performed in this study, namely, (i) X-ray diffraction (XRD), (ii) infrared spectroscopy (IR), and (iii) acidity measurement. The XRD patterns were acquired on a Siemens D5000 goniometer using CuK_α radiation in the range of 2θ from 2° to 60° at a scanning speed of 3° *per* minute. The IR spectra were examined with a Shimadzu 3000 FT-IR spectrometer using

the KBr wafer technique. The samples (0.25 mg of zeolite powder) were mixed with 300 mg of KBr powder and were finely ground. These mixtures were placed on a die and were pressed to make a transparent thin pellet. The IR spectra in the range of 2400–400 cm^{-1} were recorded at room temperature.

For the acidity measurement, it is necessary to determine the amount, strength, and type of the acid sites. In this study, three types of techniques, namely, temperature programmed desorption (TPD) of ammonia, IR spectroscopy for the hydroxyl region, and IR spectroscopy of adsorbed pyridine, were used to evaluate the acidic properties of the catalyst. The amount and strength were determined using temperature programmed desorption (TPD) of ammonia, while the type of acid site information was obtained using IR spectroscopy for the hydroxyl region and IR spectroscopy of adsorbed pyridine.

2.3. Catalyst testing

$$\begin{aligned} \text{Conversion of ethylene} &= \frac{\text{moles of C}_2\text{H}_4 \text{ reacted} \times 100\%}{\text{moles of C}_2\text{H}_4 \text{ in feed}} \\ \text{Selectivity for C}_2\text{-C}_4 &= \frac{\text{moles of hydrocarbon gas produced other than C}_2\text{H}_4 \times 100\%}{\text{moles of C}_2\text{H}_4 \text{ reacted}} \\ \text{Selectivity for CO}_x &= \frac{\text{moles of CO and CO}_2 \text{ gas produced} \times 100\%}{\text{moles of C}_2\text{H}_4 \text{ reacted}} \end{aligned}$$

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the diffractogram of the BZSM-5 impregnated with different loadings 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 samples showed similar pattern and were 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%). These results were consistent with the findings by Torre-Abreu *et al.* [12], where the CuO peak was observed when the HZSM-5 was loaded with 5.5wt% Cu. They reported that in the HZSM-5 with low copper loading, the copper was mainly present in the form of isolated Cu^{2+} ions. On the other hand, in the catalyst with high copper loading, CuO, isolated Cu^{2+} ions and also Cu^+ ions were detected using H_2 -TPR and ESR. It was also verified that the concentration of the CuO species increases when the catalyst copper

The performances of the BZSM-5 and the 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.

Gases of ethylene, compressed air and nitrogen were supplied from individual gas cylinders. The reactor was preheated at a reaction temperature of 800 $^\circ\text{C}$ 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. The total feed flow rate was 200 ml/min. The catalyst weight used in this study was 1 g. The reaction products were analyzed using an on-line gas chromatograph. The GC analysis was carried out using the thermal conductivity detector (TCD) equipped with Porapak packed column.

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

loading increases, which probably results in the formation of CuO aggregates. Nunes *et al.* [13] reported similar findings in their study on the effect of copper loading on the acidity of the Cu/HZSM-5 catalyst.

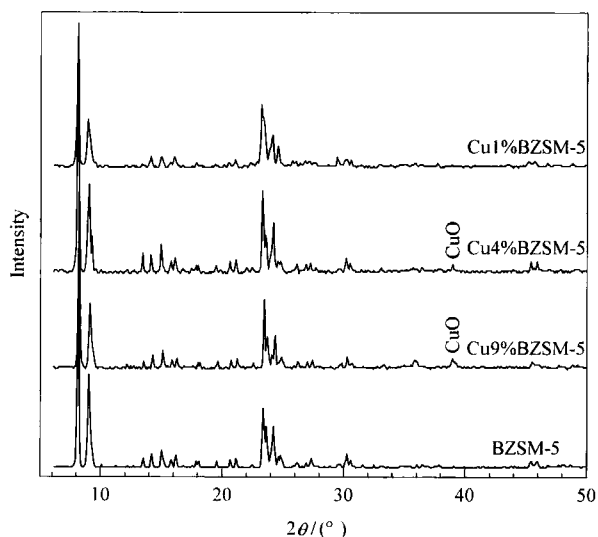


Figure 1. Effect of the XRD pattern on the different copper loadings on BZSM-5. CuO peak was observed at higher Cu loading

The NH_3 -TPD results are shown in Table 1. The addition of 1wt% copper into BZSM-5 resulted in the increase of acidity; however, the acidity decreased by about 30% in Cu4%BZSM-5 and Cu9%BZSM-5 catalysts as compared to the BZSM-5. This may 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 is a possibility that some acid sites were lost during further loading of metal because of the blockage of the zeolite pore and the formation of the Cu cluster as 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 the zeolite acidity, it is necessary to determine the nature and the concentration of both Brønsted and Lewis acid sites. This can be carried out by examining the hydroxyl group region ($3500\text{--}3750\text{ cm}^{-1}$) and the pyridine adsorption of IR spectroscopy. The infrared spectra of the samples recorded at 303 K in the range of OH stretching vibrations are shown in Figure 2. For the 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. The silanol groups are considered a weak acid. The band at 3660 cm^{-1} is assigned to OH groups associated with extraframework Al, while the band at 3610 cm^{-1} is attributed to the stretching vibration of the bridging hydroxyl groups associated with framework aluminium (Si-OH-Al). This band is normally more acidic; this hydroxyl group has acidic properties since the band is not observed when pyridine is adsorbed on the zeolite.

In the case of the BZSM-5 sample, the stretching vibration band at 3610 cm^{-1} is due to the bridging hydroxyl groups having lower intensity. Furthermore, the band area for silanol groups was larger for BZSM-5 when compared to that of HZSM-5. The result is

clearly shown in Table 2; this result suggests that BZSM-5 has more terminal silanol groups or silanol 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 in the refs [18,19].

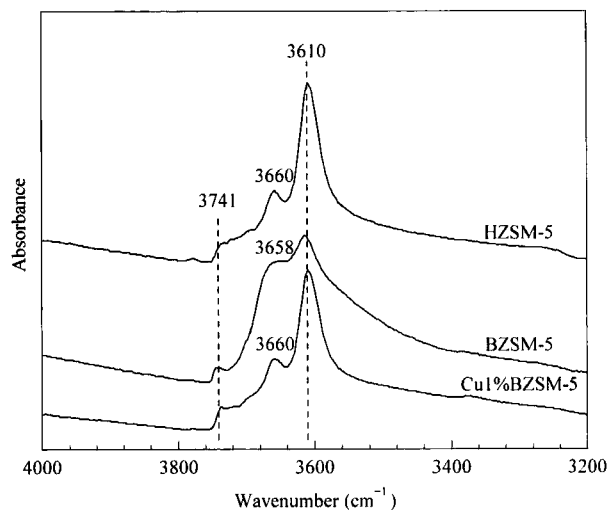


Figure 2. IR spectra in the hydroxyl region of the samples after dehydration at $400\text{ }^\circ\text{C}$, 10^{-6} MPa for 2 h

Table 2. Position of some characteristic OH vibration bands and the integrated band area

Sample	Wavenumber (cm^{-1})		
	Al-framework	Al-non framework	Silanol
HZSM-5	3610	3661	3741
(Integrated area)	(7.21)	(0.55)	(0.09)
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)

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 BZSM-5 improved with the introduction of copper into BZSM-5. This result supports the earlier data from the NH_3 -TPD analysis, which indicates that adding Cu species on BZSM-5 improved the acidity of BZSM-5.

The types of acid that were present in the zeolite sample were further characterized using the pyridine adsorption method. Pyridinium ion signals (pyridine on Brønsted acid sites) appeared at wave numbers of 1638 and 1546 cm^{-1} and pyridine on Lewis acid sites

appeared at 1450 cm^{-1} [20]. The concentration of the Brönsted acid sites and the Lewis acid sites were calculated from the integrated area of the bands at 1540 and 1450 cm^{-1} according to the formula proposed by Hughes and White [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 the Brönsted to Lewis acid site considerably reduced at higher loading of copper. Two factors can explain this result: First, at higher copper loading, the Brönsted acid sites were partly covered by CuO. Second, part of the Cu species were exchanged with the Brönsted acid sites that were capable of transforming into Lewis acid sites. Similar results were reported by Wang *et al.* [22] in their studies of different Mo loading on HZSM-5. They claimed based on the IR and NH_3 -TPD studies 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 the Brönsted and Lewis acidity of the samples

Sample	Acidity ($\mu\text{mol/g}$)		Ratio B/L
	Brönsted(B) (at 1545 cm^{-1})	Lewis(L) (at 1450 cm^{-1})	
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 $800\text{ }^\circ\text{C}$ and atmospheric pressure are given in Figure 3. This figure shows the ethylene conversion and the carbon selectivity towards CO_x , $\text{C}_2\text{--C}_4$ (exclude C_2H_4), and C_5+ (C_5 hydrocarbon and above) 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 may be due to the lower acidity as explained by Sohn and Park [2]. Furthermore, the copper loaded in zeolite may act as a bifunctional catalyst and is widely used in hydrocarbon conversion. On this catalyst, the transformation of hydrocarbons involves both of the hydrogenation and the dehydrogenation step on metal sites and the rearrangement and/or the cracking step on acid sites. Indeed, it has been shown very clearly that the balance between metal sites and acid sites remarkably

influenced the performance of the bifunctional catalysts in hydrocarbon conversion [23,24].

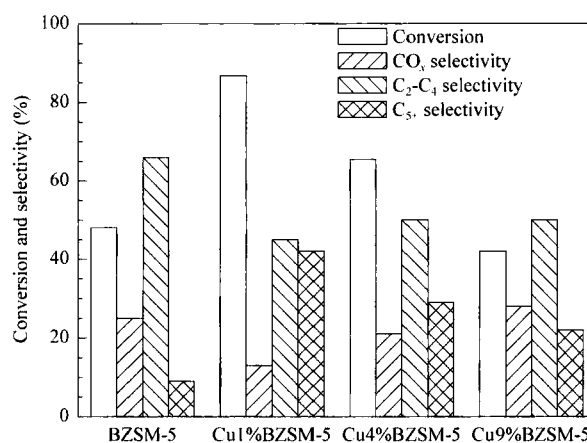


Figure 3. Catalytic performance of the ethylene reaction with 9 vol% of oxygen over BZSM-5 and modified BZSM-5 with copper catalyst at reaction temperature of $800\text{ }^\circ\text{C}$ and gas hourly space velocity (GHSV) of 8000 h^{-1} under atmospheric pressure

The results show that copper loading at low concentration promotes ethylene conversion; however, at higher copper loading, the ethylene conversion decreases. The difference could be interpreted in terms of copper deposited over the BZSM-5 zeolite. At 1 wt% of copper loading, copper oxide may not be totally deposited over the surface of the BZSM-5 zeolite. Many active sites of BZSM-5 zeolite remain vacant and are responsible for ethylene activation. At high copper loading, the ethylene conversion decreases because of the deposition of the metal species over the acid sites together with the blocking of the channels.

BZSM-5 is seen to have reasonable activity but slightly lower selectivity towards higher hydrocarbons since mainly carbon oxides are formed. The selectivity towards $\text{C}_2\text{--C}_4$ for all the catalyst was between 45% up to 66%, where BZSM-5 shows the highest $\text{C}_2\text{--C}_4$ selectivity. On the other hand, Cu1%BZSM-5 shows the lowest $\text{C}_2\text{--C}_4$ selectivity. Furthermore, Cu1%BZSM-5 shows the lowest selectivity towards carbon oxides when compared to higher loading of copper on BZSM-5. These results were consistent with the result obtained by Min and Mizuno [25] in their study on the effects of copper additives on the selective oxidation of light alkanes. Min and Mizuno [25] demonstrated that the addition of copper enhanced the catalytic performance for oxidation light alkanes under oxygen-poor condition to CO_x .

Based on the above results, the only way to relate the activity with the acidity of zeolite is by consid-

ering 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, was observed to provide a higher conversion of ethylene and higher hydrocarbon selectivity than the other catalysts. Following this observation, the amount of acid can be used to explain the activity of the catalyst. This finding is in-line with the result reported by Guisnet *et al.* [26], where the oligomerization process was dependent on the zeolite acidity. Nor Aishah and Anggoro [4] reported that the oligomerization of ethylene was 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 is not the only cause of the catalyst being active, rather the presence of copper ions may also affect its activity as in case of Cu4%BZSM-5. It is seen from Figure 4 that the acidity of Cu4%BZSM-5 is lower than that of BZSM-5; however, its selectivity towards C_{5+} is higher. Only weak acid site is required to activate ethylene or olefin to gasoline range hydrocarbon [27]. Kitigawa *et al.* [28] studied the requirement of acid site in the C-H bond activation on weakly acidic borosilicates with ZSM-5 structures. He reported that Zn exchanged borosilicates did not catalyze propane dehydrocyclodimerization but these catalysts could convert propene to aromatics at a significant rate.

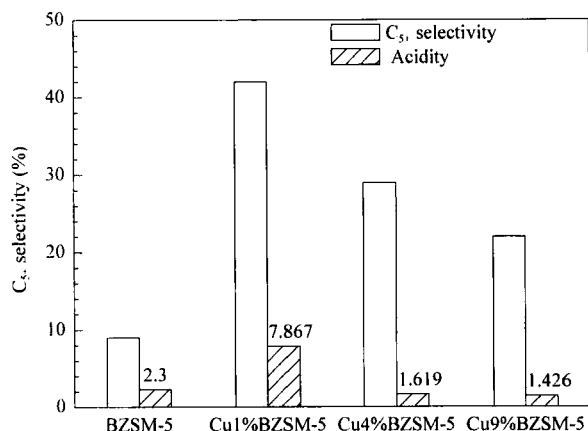


Figure 4. Effect of the amount of acid (mmol/g) on the C_{5+} selectivity for ethylene conversion

Introducing metal into the zeolite resulted in an increase of the conversion and selectivity. This finding was in agreement with the finding by Nishi *et al.* [29], Liu *et al.* [30], and Biscardi and Iglesia [31]. They claimed that introducing the metal component to the zeolite catalyst will improve the product selectivity.

Biscardi and Iglesia [31] reported that the introduction of Ga, Zn, or Pt species into zeolites increased the rate and selectivity for 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* a sequence of acid-catalyzed shape-selective oligomerization reaction over zeolites. Furthermore, aromatization of the product formed required a concerted reaction between the acid and metal cation sites.

4. Conclusions

The conversion of ethylene toward higher hydrocarbon is dependent on the acidity of the catalyst. Only weaker acid site is required to convert ethylene to higher hydrocarbons. Loading of Cu on BZSM-5 improves the selectivity for higher hydrocarbons, especially at lower percentage. The reactivity of ethylene is dependent on the amount of acidity as well as the presence of metal on the catalyst surface. Cu1%BZSM-5 is capable of converting ethylene to higher hydrocarbons. The 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 .

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