REACTIVITY OF INCOPORATED COPPER IN BORON-ZSM-5 ZEOLITE FOR METHANE CONVERSION TO HIGHER HYDROCARBONS

Ramli Mat, Nor Aishah Saidina Amin, Zainab Ramli* and
W. Azelee W. Abu Bakar*
Dept. of Chemical Engineering, *Dept. of Chemistry
Universiti Teknologi Malaysia
Skudai, 81310 Johor Bahru

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ABSTRACT

The modification of Boron ZSM-5 zeolite with copper for methane conversion to higher hydrocarbons is reported. Catalyst characterization was carried out using XRD and TPD. Direct substitution of boron for aluminium in the ZSM-5 structure result in slightly lower activity for methane conversion due to its lower acidity, however it improved the C_5^+ and C_2-C_4 yield. Introduction of copper species has improved the catalyst activity.

INTRODUCTION

Methane represents over 90% of the natural gas content and hence is considered as promising source for higher hydrocarbon in the new millennium. Not all the available and produced methane is utilized. At present, most of the methane is used as fuel and only in a few instances it is applied as a chemical feed stock. Modern industry supports a change of feedstock towards better and cheaper raw material. Therefore, the direct conversion of methane to desirable commodity chemicals, such as liquid hydrocarbons, is a challenging approach to the utilization of methane resources. Numerous recent research projects have been demonstrated the feasibility of direct transformation of methane into products of higher added values such as olefins, aromatics and oxygenous derivatives (Yoon et al., 1997; Choudary et al., 1998; Herman et al., 1997; Raja et al., 1997; Pierella et al., 1997; Weckhuysen et al., 1998). These processes are possible if the reaction is carried out by controlled oxidation over a suitable catalyst. In

practice, three routes for direct methane conversion to higher hydrocarbons are identified: oxidative coupling (Yoon et al., 1997; Choudary et al., 1998), partial oxidation (Herman et al., 1997; Raja et al., 1997) and methane aromatization (Pierella et al., 1997; Weckhuysen et al., 1998). Numerous catalysts have been discovered which possess different activities and selectivities for methane conversion to higher hydrocarbon. Most of them are based on metal or transition metal oxides, which are often supported on silica and alumina. The main shortcoming of these reactions is, however, the low methane conversion required for high desired product selectivities in an one-pass operation thorough a catalytic reactor leading to significant recycle expenses as well as to expensive separation of products from methane.

Zeolite based catalysts are successfully employed in a variety of commercial process in the petroleum and petrochemical industries. Despite this fact, there are only a few investigations on the potentials and usefulness of modified zeolite as catalyst for the formation of higher hydrocarbons from methane. Vermeiren et al. (1989) and Ernst et al. (1989) used zeolite based catalyst for the conversion of methane to higher hydrocarbon. They reported that acid zeolites were shown to have reasonable activity but very low selectivity towards hydrocarbons as mainly carbon oxides were formed. Ernst et al. (1989) reported that the presence of acid sites was detrimental to obtain reasonable selectivity for the formation of C_2^+ hydrocarbons. When the acidity was reduced by exchanging the zeolite with alkali metal cations, the selectivity to C_2^+ hydrocarbons was slightly enhanced. Nor Aishah and Anggoro (1998a&b) and Han et al (1994) reported that modification of ZSM-5 with transition metal has resulted in lower acidity and thus improved methane conversion. They reported that the activity of the catalyst was strongly dependent on the type of transition metal and acidity.

Modification by incorporation of elements of different size and different chemical features on zeolite is important to control the acidity and/or the shape selectivity of a specific zeolite structure. One possibility for modifying zeolites is the replacement of some of the silicon (Si) and aluminum (Al) with boron (B). Boron can be loaded onto the zeolites following the procedure of direct synthesis or post (secondary) synthesis. Direct synthesis procedure is carried out by introducing the element during the synthesis or crystallization, and secondary synthesis is carried out after crystallization.

The previous study has shown that direct synthesis of boron loading on zeolite has higher performance than post synthesis modification (Ramli et al, 1999).Then, taking into account these reactions results, the present study will examine the addition of copper in the catalyst in order to improve the catalyst.

EXPERIMENTAL

Catalyst Preparation

Synthesis of HZSM-5 and BZSM-5

The ZSM-5 zeolites were synthesized by hydrothermal crystallization at 160°C for five days from mixtures containing sodium silicate, aluminium sulfate, and tetrapropylammonium bromide, based on method described by Plank et al. (1974). The reaction mixture was prepared according to the following molar compositions: Al_2O_3: 20 Na_2O: 70 SiO_2: 7TPABr:2200H_2O. The crystalline white solid product was filtered, washed thoroughly with deionized water, dried at 120°C for 12 hours. The resultant material was calcined at 550°C for five hours to remove the organic material and to obtain the sodium form of the ZSM-5. The Na-form so obtained was converted into the NH_4-form by ion exchange using 1M solution of ammonium nitrate. The procedure was repeated three times. Finally, the catalyst is dried and calcined at 550°C and marked as HZSM-5. BZSM-5 was prepared according to the above method except that boric acid was used to replace aluminium sulfate. BZSM-5 obtained were impregnated with copper nitrate solution to give 1wt% of metal. The solid catalyst was labeled as CuBZSM5. Since copper-based catalysts are active in oxidation processes, it is possible that the presence of copper species at the surface of the BZSM-5 catalyst can enhance the oxidation reaction.

Catalyst Characterization

X-Ray Diffraction (XRD) Studies

The structures of the zeolite were determined by X-Ray Diffraction techniques. This method was based on the fact that every crystalline material has its own characteristic diffractogram. 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. All the samples were fully dried before XRD diffactograms were measured.

Temperature Programmed Desorption (TPD)

Temperature Programmed of ammonia Desorption technique is used to investigate the acidity of the catalyst. The catalyst was dried in a flow of He for 2 hours. Adsorption took place with 20% NH_3 in the He flow at 70°C for 0.5 hour. Desorption was done by heating the catalyst from 70 to 600°C with linear heating schedule. The amount of desorbing NH_3 was measured with a thermal conductivity detector.

Reactivity Test

The performance of the catalyst for methane conversion was tested using the micro reactor as previously reported (Ramli et al., 1999). The reaction was carried out at 800°C, under atmospheric pressure by cofeeding the reactant gases (methane and air) into a stainless steel tube reactor (9 mm in diameter and 300 mm in length) mounted vertically, and heated by an electric furnace. The effects of temperature and feed flowrate on methane activity were studied using CuBZSM5.

RESULTS AND DISCUSSION

Characterization of Catalyst

The XRD patterns of BZSM-5, and CuBZSM-5 were similar to the HZSM-5 as shown in Figure 1. These indicate that the structure of the zeolites remained unchanged even though aluminium was replace by boron in BZSM5. Impregnation of the BZSM-5 sample with copper also does not alter the zeolites structure. There is no evidence of copper species in the pattern.

Temperature Programmed of Ammonia Desorption is used to estimate acidic property of the catalysts quantitatively and qualitatively: From the total amount of NH_3 desorption, the number of acidic sites is calculated and from the desorption temperature the strength of acidic sites is suggested. The results of NH_3-TPD of the catalysts are tabulated in Table 1. The amount of acid or acidity is expressed as moles of NH_3 desorbed per unit weight of the solid. From these results, it can be concluded that HZSM-5 is more acidic than BZSM-5.

Both low temperature and high temperature peaks of HZSM-5 are higher than that of BZSM-5. This indicates that HZSM-5 has higher acid strength than BZSM5. The result was in agreement with Topsoe et al.(1981) and Taramaso et al. (1980) explanation that the acidity decreases as Al ion is removed from the framework of HZSM-5.

Catalyst Activity

The results of the various catalytic performances for the reaction of methane and oxygen at 800°C and atmospheric pressure are given in Table 2. It summarizes the methane conversion and the carbon yields of C_2-C_4 and C_5^+ for the catalyst tested. In this work, methane conversion is defined as

Conversion of methane = Moles of CH_4 reacted / moles of CH_4 in feed

and the % carbon yield (Y_c) was computed as

%Y_c= (mol of carbon of desired product / mol of carbon of CH_4 reacted.) x 100%

BZSM-5 was slightly less effective for methane conversion as compared to HZSM-5. The acidity of BZSM-5 was lower than HZSM-5 and thus BZSM-5 was less effective for methane conversion.
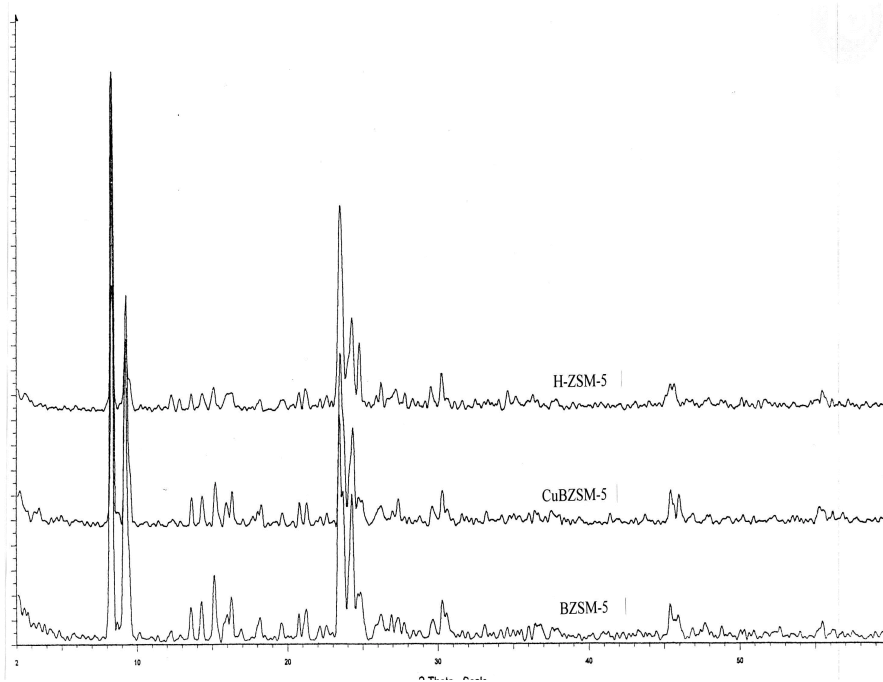

FIGURE 1: Comparisons on XRD pattern

TABLE 1: Comparison of acid property of zeolites estimated by NH_3-TPD.

Sample	Amount of Chemisorbed (moles/kg)	Low Temperature (^{o}C)	High Temperature (^{o}C)
HZSM-5	0.6585	204	401
BZSM-5	0.0574	165	-

TABLE 2: Result of the catalyst testing on methane reaction with 9% oxygen at 800°C.

Catalyst	Methane conversion (%)	C$_2$-C$_4$ yield (wt%)	C$_5^+$ yield (wt%)
H-ZSM-5	35	1.0	0
BZSM-5	23	4	0.5
CuBZSM-5	50	0.5	2

The C$_5^+$ and C$_2$-C$_4$ yields were enhanced with BZSM5 catalyst. This might be due to weaker acidity of BZSM5 as compared to the other catalyst. The results were consistent with the result obtained by Colorio et al. (1996) in their study on partial oxidation of ethane over alumina-boria catalysts. Colorio et al (1996) reported that at high loading of boron, weak acid sites were generated by the formation of oxide agglomerates. These weakly acidic sites were active for ethane oxidative dehydrogenation into ethylene.

The introduction of copper ions enhanced the activity of BZSM5 catalyst where higher methane conversion and C$_5^+$ yield was achieved by CuBZSM5 catalyst. This improved result might be due to the interaction of Cu species in the zeolite with boron as reported by Sofranco et al. (1988) in their study for methane conversion. Sofranco et al. (1988) reported that methane conversion to C$_2^+$ was improved when reducible metal oxide in the presence of boron was used as compared to reducible metal oxide only.

Influence of Feed flowrate

Results showing the influence of feed flowrate on the conversion methane and on the products distribution over CuBZSM5 at 800°C are presented in Figure 2. The methane conversion decreased when feed flowrate increased due to a shorter contact time. The C$_5^+$ yield increased with increased feed flowrate up to 200 ml/min, but decreased beyond that as shown in Figure 2. It is expected that the longer contact time will encourage C$_5^+$ hydrocarbon to oxidize to form CO$_x$ and H$_2$, As a result, the C$_5^+$yield was reduced at low flowrate. The yield of C$_5^+$ decreased at higher flowrates (>200ml/min). This is probably due to low methane conversion and shorter contact time for the oligomerization of C$_2$- C$_4$ to form C$_5^+$
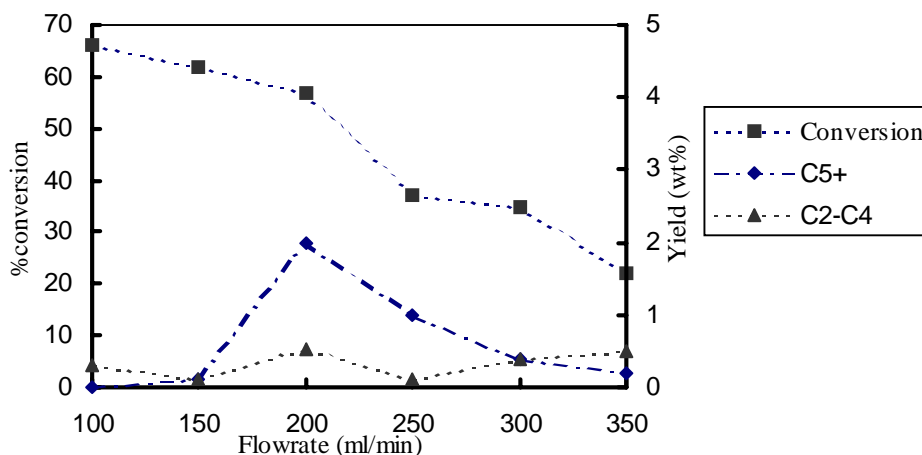
FIGURE 2: Effect of the feed flowrate on the methane conversion and hydrocarbons yields over CuBZSM5. Feed contains 9 volume % oxygen at reaction temperature of 800°C.

Influence of temperature

Figure 3 shows the influence of temperature on the conversion of methane and on the products distribution over CuBZSM5. The results clearly indicated that the catalytic activity is strongly dependent on the reaction temperature. As the temperature increased, the methane conversion increased appreciably reaching about 78% at 900°C. The results were supported by Lunsford (1990), Yagita et al. (1996) and Weckhuysen et al (1998). They reported that methane activation was a slow process except at high temperature. This lack of activity is essentially due to the stability of the bonds linking the carbons to hydrogen.

It can be seen in Figure 3 that the highest C_5^+ yield occurs at 800°C. At the reaction temperature beyond 800°C, the yields for C_5^+ and C_2-C_4 were decreased. Theses probably arise from the oxidation of C_5^+ and C_2-C_4 hydrocarbons to form COx and H_2 at higher temperature.
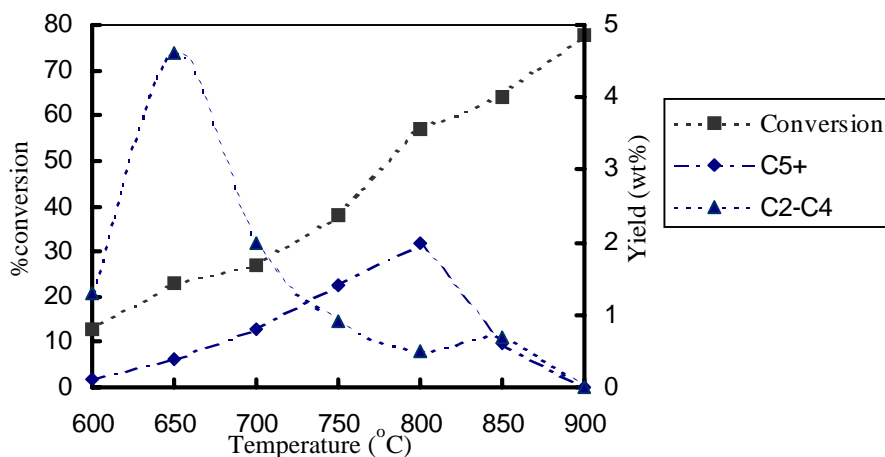
450

FIGURE 3: Effect of the reaction temperature on the methane conversion and hydrocarbons yield over CuBZSM5. Feed contains 9 volume % oxygen at feed flowrate of 200ml/min.

CONCLUSIONS

From the above results, one may conclude that:

1. Direct substitution of boron for aluminium in the ZSM-5 structure result in slightly lower activity for methane conversion due to its lower acidity, but improved C_5^+ and C_2-C_4 yields.
2. Impregnation of copper species on BZSM5 has improved the catalyst activity.
3. The methane conversion and hydrocarbons yield was dependent on feed flowrate and reaction temperature.

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