

CATALYTIC STUDIES OF BORON-HZSM-5 ZEOLITE FOR METHANE CONVERSION TO HIGHER HYDROCARBONS

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ABSTRACT

The direct conversion of methane to liquid hydrocarbons either over metal catalyst or zeolite is so far not successful in achieving the methane conversion and liquid hydrocarbons selectivity within the economic range due to oxidation of the product. The present research concern the modification of HZSM-5 catalyst with boron in order to reduce the acidity of the catalyst and thus reduce its oxidation activity. A series of boron was loaded into HZSM-5 zeolite via impregnation. Catalyst characterization was carried out using XRD and TPD. The catalytic activity for methane conversion depends on the boron loading. A higher loading of boron on HZSM-5 results in lower activity for methane conversion.

Key Words : Boron, ZSM-5, Methane, Higher hydrocarbons, Conversion

1.0 INTRODUCTION

The direct conversion of natural gas to liquid hydrocarbon has not yet been successfully economized in an inexpensive process. 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 [1-6]. These processes are possible if the reaction is carried out by controlled oxidation in the presence of appropriate catalyst. In practice, three routes for direct methane conversion to higher hydrocarbon are identified : Oxidative coupling [1, 4,], partial oxidation [2,5] and methane aromatization [3,6].

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.* [7] and Ernst *et al.* [8] 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.* [8] reported that the presence of acid sites was detrimental to obtain reasonable selectivity for the formation of C₂⁺ hydrocarbons. When the acidity was reduced by exchanging the zeolite with alkali metal cations, the selectivity to C₂⁺ hydrocarbons was slightly enhanced.

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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 is carried out by introduction of the element during the synthesis or crystallization. On the other hand secondary synthesis is carried out after crystallization. In the secondary synthesis method, boron is introduced by impregnation. The different methods of elements loading on the zeolites modify a different aspect of the material.

The present study will examine the properties and activities of H-ZSM-5 containing various amounts of boron for methane conversion. The zeolites obtained were characterized by means of X-Ray Diffraction (XRD) and Temperature Program Desorption (TPD). The conversion of methane in the presence of oxygen using packed bed micro reactor has been investigated over different concentration of boron loading on H-ZSM-5 zeolite.

2.0 EXPERIMENTAL

2.1 Catalyst Preparation

Synthesis of HZSM-5

The ZSM-5 zeolites were synthesized by hydrothermal crystallization at 160°C for five days from mixtures containing sodium silicate, aluminium sulfate, tetrapropylammonium bromide, based on method described by Plank *et al.* [9]. The crystalline white solid product was filtered, washed thoroughly with deionized water, dried at 12 °C for 12 hours. The resultant material was calcined at 550 °C for five hours to remove the organic material and to obtain sodium form of the ZSM-5. The Na-form so obtained was converted into the NH₄-form by ion exchanging it with 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 were prepared according to the above method except that boric acid was used to replace aluminium sulfate.

Zeolite Modification

The HZSM-5 catalyst was modified by introducing boron by impregnation method to give 5, 10, and 15 weight %. It was prepared by mixing 10g of HZSM-5 with 50ml solution of boric acid of different concentration (5,10, 15 wt%). The suspension was stirred using magnetic stirrer. The solid was dried at 110°C before it was calcined at 550°C for five hours. The solid was label as B5ZSM-5, B10ZSM-5 and B15ZSM-5 for 5, 10 and 15 weight % of boron in the zeolite respectively.

2.2 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 Philips 1840 vertical goniometer CuK α

radiation in the range of 2θ from 2° to 60° at a scanning speed of 4° per minute. All the samples were fully dried before XRD diffractograms were measured.

2.3 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.

2.4 Reactivity Test

Performance of the catalyst for methane conversion was tested using the micro reactor as shown in Figure 1. The reaction was carried out at 800°C , under atmospheric pressure by cofeeding of the reactant gases (methane, and air) into a stainless steel tube reactor (9mm in diameter and 300mm in length) mounted vertically and heated by an electric furnace. Methane and air were then fed into the reactor with a 9% oxygen in feed. The total gas flow was $110\text{ cm}^3/\text{min}$ with 0.6 g catalyst loading, giving rise to a space velocity of $11000\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$. The products were separated into liquid and gas fractions through a series of two condensers cool with ice. Samples of the gaseous product stream were filled and sealed in pre evacuated glass ampoules. The liquid and gaseous products were analyzed by gas chromatography (Perkin Elmer) using HP-1 capillary column. The selectivity and methane conversion were calculated for all the catalyst.

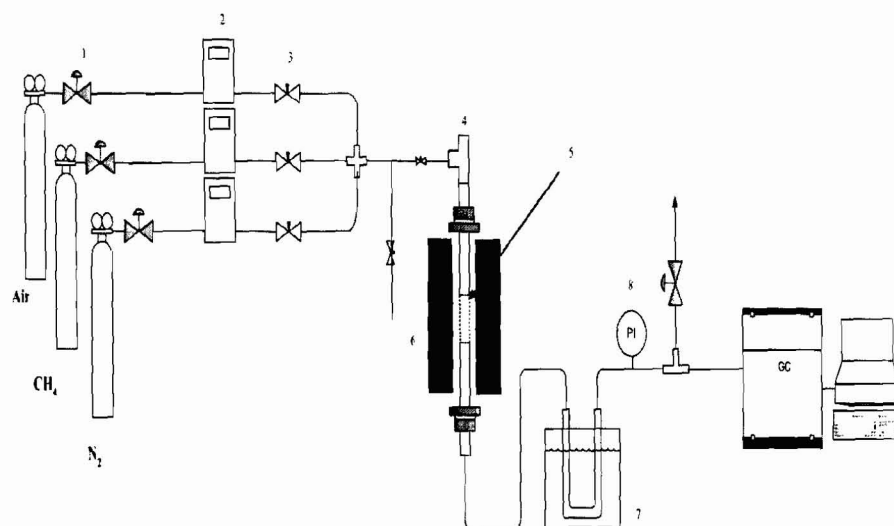


Figure 1 Schematic layout of the rig of the methane conversion. 1. Regulator 2. Flowmeter 3. Valve 4. Micro reactor 5. Catalyst bed 6. Furnace 7. Condenser 8. Valve

3.0 RESULTS AND DISCUSSION

XRD pattern was obtained for all the zeolite samples. XRD patterns of BZSM-5, B5ZSM-5, B10ZSM-5 and B15ZSM-5 were similar to the HZSM-5 as shown in Figure 2. However, the peaks in the modified zeolite shifted slightly toward the higher angle side (about 1°) and the intensities were reduced in the following order:

$$\text{HZSM-5} \approx \text{BZSM-5} > \text{B5ZSM-5} > \text{B10ZSM-5} > \text{B15ZSM-5}$$

The decrease in intensities with modification may be due to :

- Slight contractions in the interplanar spacing
- Creation of lattice disorder

The crystalline phase of B₂O₃ first observed when the loading of boron about 5wt%. Its relatively sharp diffraction peaks at $2\theta = 15.75^\circ$ and 28.75° become more prominent when the loading of B₂O₃ further increases. When the loading of boron is low, B₂O₃ may form monolayers surrounding the ZSM-5 particle and become multiple layer with the further loading of boron[10,11].

Temperature Programmed of Ammonia Desorption is used to estimate acidic property of the catalysts quantitatively and qualitatively. From the total amount of NH₃ desorption, the number of acidics sites is suggested and from the desorption temperature the strength of acidic sites. The results in Table 1 show that with the introduction of boron into the HZSM-5 zeolite, the number of acidic sites decreased, and the extent of the elimination of strong acid sites increased with an increase in boron loading.

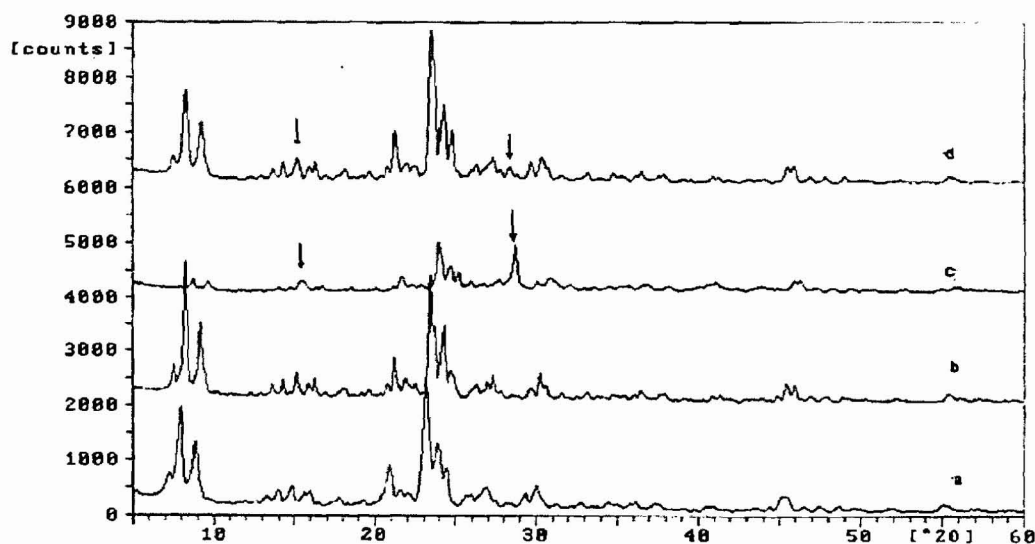


Figure 2 Comparisons on XRD pattern on unmodified and modified HZSM-5 catalyst. a) H-ZSM-5 b) BZSM-5 c) B15ZSM-5 and d) B5ZSM-5

The results of the catalytic performance of the catalyst for reaction of methane with oxygen at 800°C and atmospheric pressure, are given in Table 2. This Table

summarizes the methane conversion and the carbon selectivities toward CO_x, C₂-C₄, C₅⁺ for the catalyst tested. In this work, methane conversion was defined as;

$$\text{Conversion of methane} = \text{Moles of CH}_4 \text{ reacted} / \text{moles of CH}_4 \text{ in feed}$$

and the carbon selectivity (Sc) was computed as;

$$\text{Sc} = \text{Wt of carbon of desired product} / \text{wt of carbon of CH}_4 \text{ reacted.}$$

Table 1 The results of the NH₃-TPD experiments

Sample	Temperature (°C)	Amount of chemisorbed (mmol/g)	Total amount of chemisorbed (mmol/g)
HZSM-5	180	6.005	8.58
	480	2.575	
B5ZSM	150	6.724	7.73
	340	1.006	
B10ZSM	180	2.652	2.673
	340	0.021	
BZSM-5	150	2.289	2.302
	450	0.013	

The results show that boron loading at low concentration promotes the methane conversion. However at higher concentration of boron loading, the methane conversion was decreased. The difference could be interpreted in terms of coverage of ZSM-5 zeolite with boron. At 5wt% of boron loading, the amount of boron oxide may not high enough to cover the total surface of ZSM-5. Many active sites of ZSM-5 zeolite remained uncovered and were responsible for methane activation. It was reported that boric acid and its derived products were utilized as inhibitors for the oxidation of alkanes or other organic products[11].

The selectivity towards C₂-C₄ was slightly enhanced with boron loading. These results were consistent with the result obtained by Colorio *et al.* [11] in their study on partial oxidation of ethane over alumina-boria catalysts. At high loading of boron oxide, weak acid sites were generated by formation of oxide agglomerates. These weakly acidic sites were active for ethane oxidative dehydrogenation into ethylene. Sofranco *et al.* [12] reported that methane conversion to C₂⁺ was improved when reducible metal oxide in the presence of a boron was used as compared to reducible metal oxide only.

BZSM-5 was slightly less effective for methane conversion as compared to HZSM-5. The slightly lower activity of BZSM-5 might be due to lower acidity as explained by Taramasso *et al.* [13] and Howden [14].

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Table 2 Result of the catalyst testing on methane reaction with oxygen

Catalyst	Methane conversion (%)	Carbon selectivity (wt%)		
			C ₂ -C ₄	C ₅ ⁺
ZSM-5	35	93	1	6
BZSM-5	23	89	5	6
B5ZSM-5	39	92	2	6
B10ZSM-5	15	92	2	6
B15ZSM-5	15	90	7	4

4.0 CONCLUSIONS

Catalytic studies of boron-HZSM-5 zeolite for methane conversion to higher hydrocarbons were investigated. From this investigation, it can be concluded that at high percentage of boron loading on HZSM-5, crystallites were present on the surface as determined by the XRD characterization. Boron oxide covered the active site of HZSM-5 which were responsible for activation of methane thus resulted in lower methane conversion at higher boron loading. The acidity of the catalyst HZSM-5 was reduced upon modification with boron. The selectivity to C₂-C₄ were slightly improved with boron loading on HZSM-5 catalysts.

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