CONVERSION OF METHANOL TO HYDROCARBONS OVER NI-ZSM-5 CATALYST

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ABSTRACT

As stock of crude oil is limited, new resources for fuel and petrochemicals are required to be developed. Natural gas or biogas can be easily converted into methanol which can be converted into gasoline and olefins. This study uses zeolite catalyst (ZSM-5) and its modification by Ni to convert methanol to hydrocarbons (MTH). Catalysts are studied at different temperatures and at different loadings of Ni for their performance in the MTH reaction. Modified ZSM-5 catalysts are characterized by XRD and BET. It was found that 8%Ni-ZSM-5 catalyst gives better results at 723K.

Keywords: Methanol To Hydrocarbons, Methanol To Olefins, Methanol To Gasoline, Zeolite, ZSM-5

I. INTRODUCTION

Conversion of methanol to light olefins (MTO) and other hydrocarbons including aromatics (MTH) is an important new viable chemical technology. Zeolites are often used to convert methanol into olefins [1], gasoline [2] and aromatics [3]. Solid acids can effectively catalyze this reaction to form hydrocarbons However, the selective production of light olefins, especially ethylene and propylene is a challenge to catalysis. Olefins can be converted to an entire spectrum of products, through another ZSM-5 based process. ZSM-5 is characterized by several methods like XRD, SEM, BET etc. [4, 5]. Modification of ZSM-5 by impregnation can be of two types: frame-work or non-framework [6, 7]. Incorporation inside zeolite pores can improve selectivity towards aromatics [8-10] but extra framework studies on the subject are limited [11]. Several workers have studied the effect of different metals on product selectivities and catalyst deactivation [12-14]. They have reported different metals for increasing the selectivity of different products. The detailed reaction mechanism varies among zeolites with different pore architectures and acidic strengths/densities [15-17].

II. EXPERIMENTAL

2.1 Catalyst Preparation

The HZSM-5 zeolite with a Si/Al ratio of 80 was purchased from Sud Chemie. The HZSM-5 zeolites were impregnated with Nickel Nitrate solution. Subsequently, the samples were dried at 110°C for 5 h and then calcined at 550°C for 5 h. The samples thus obtained were denoted as HZ (xNiO). ZSM-5 with x weight percent

representing the Ni element. The ZSM-5 with zeo weight percent of Ni is shown as HZ (0). Prepared catalysts are characterized by XRD and BET.

2.2 Experimental Setup

Flow rate of Nitrogen is adjusted and kept constant during the experiment. Methanol flow rate is controlled by using peristaltic pump. Experimental setup is shown in Fig.1. Mixture of methanol and Nitrogen is passed through preheater so that methanol is converted into vapour and mixes uniformly with carrier gas Nitrogen. Feed is then sent to reactor at pre-set temperature. Liquid and gaseous products collected from the bottom of reactor are analysed using GC.

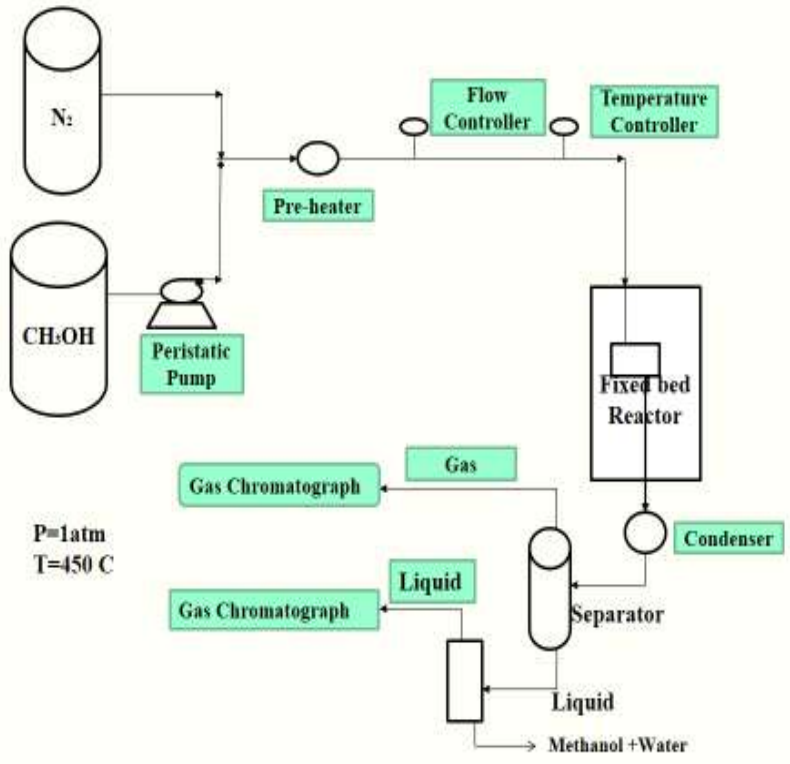

Fig.1 Schematic Diagram of Experimental Setup

III. RESULTS AND DISCUSSION

3.1 Physical Properties Of The Catalysts

Table 1- Physical properties of the catalysts

Catalyst	Metal content (Wt. %)	S_{BET} (m^2/g)		Pore volume (cm^3/g)	
	NiO	Fresh	Coked *	Fresh	Coked*
HZ (9NiO)	9.0	207.5	192.6	0.271	0.262
HZ (8NiO)	8.0	210.5	198.5	0.272	0.265

HZ (7NiO)	7.0	212.4	200.5	0.273	0.268
HZ (0)	0	227	215	0.28	0.27

*Run time 15 h

With increase in weight % of Ni, BET surface area and pore volume are reduced as shown in Table 1. This is because of Ni occupying sites in ZSM-5. Coking reduces surface area but pore volume is not changed significantly. This means coking is mainly on the surface of catalyst and not inside the pores.

3.2 XRD Analysis

All curves are similar in Fig.2 and give Peaks at same 2θ angle. This shows that there is no change in the structure of catalyst due to modifications by metal doping. Intensity of peaks have been modified which indicates successful incorporation of metals in the catalyst. The higher intensity was observed for the starting zeolite (HZSM-5). The decrease in the intensities may be due to higher absorption coefficient of modified catalyst.

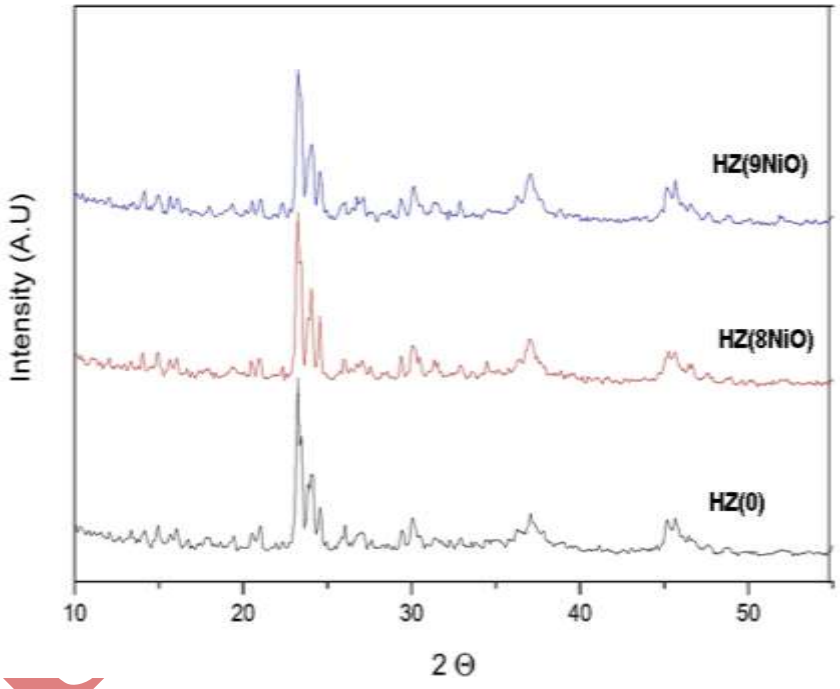

Fig. 2 XRD Patterns of HZ (0), HZ (8NiO) and HZ (9NiO) Catalysts

3.3 Effect Of W/F_{A0} On Methanol Conversion

Fig.3 shows effect of W/F_{A0} on conversion with respect of different temperatures. As we increase W/F_{A0}, conversion increases and finally becomes 100%. Similarly increase in temperature from 350 ^{o}C to 450 ^{o}C also has positive effect on conversion.

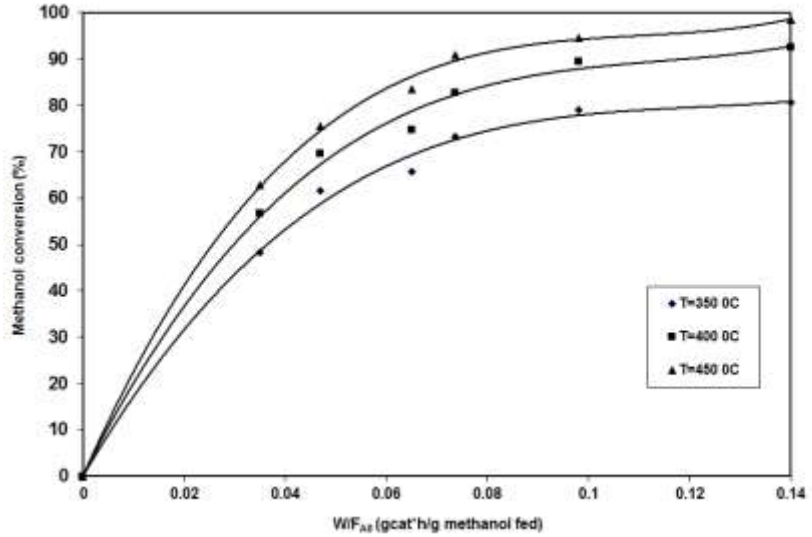

Fig. 3 Variation of methanol convversion with contact time over HZ(8NiO) catalyst [T=350^{0}C-450^{0}C, P=1atm, W/F$_{A0}$=0-0.14(gcat*h/g methanol fed)]

3.4 Effect Of W/F$_{A0}$ On Hydrocarbons Yield

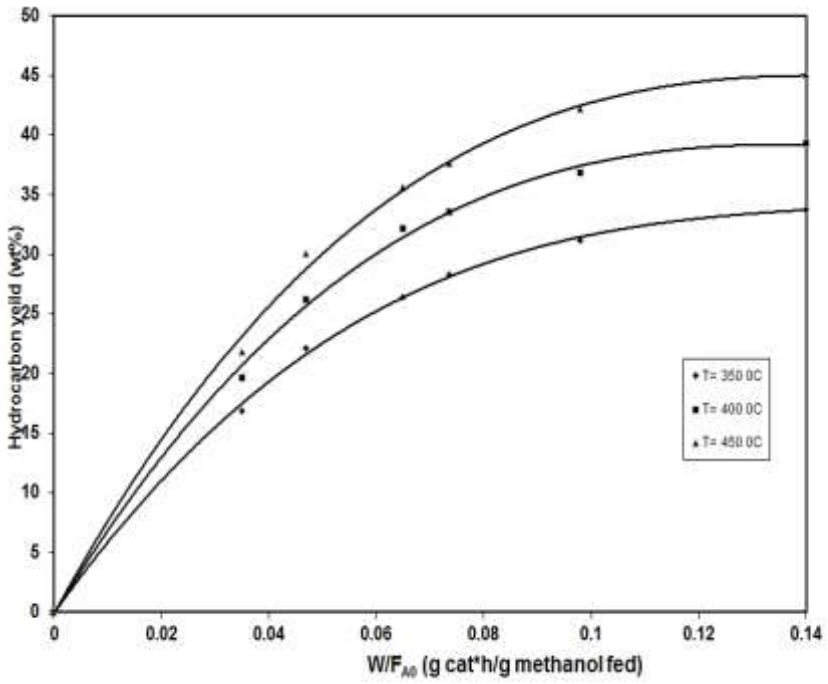

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Fig.4 shows that hydrocarbon yield significantly rises with increase in W/F$_{A0.}$ Low flow rate of methanol helps in better yield due to more residence time in the reactor. Increase in surface area of catalyst by reducing its size can therefore increase the yield of hydrocarbons. Optimum temperature for yield is found 450 ^{o}C. When temperature is increased beyond this, cracking may occure and products may be of lower quality.

3.5 Effect Of Runtime On The Conversion Of Methanol

Conversion is significantly improved when Ni content is 8%. The catalyst can retain its activity after 15 hours without much loss in conversion. ZSM-5 without modification losses its activity much faster in the same time sine conversion of methanol is reduced as shown in graph.

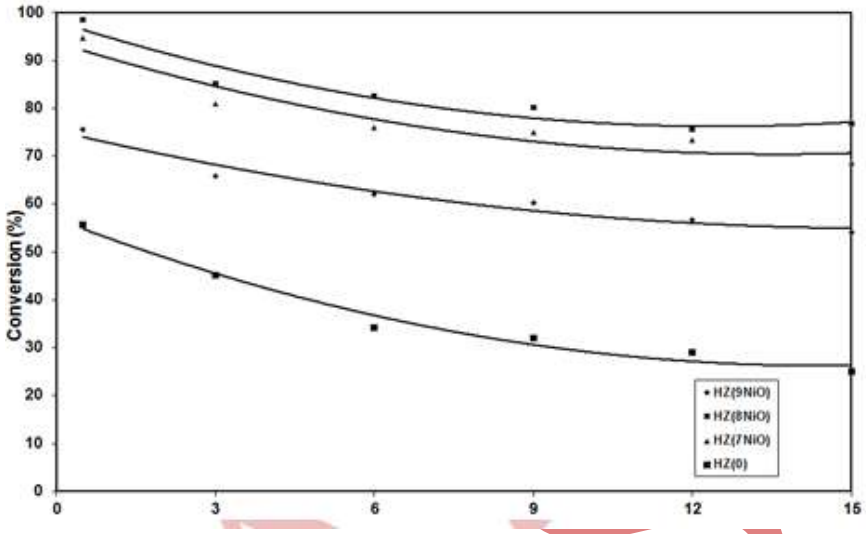

Fig.5 Effect of runtime on the conversion of methanol [T=450^{0}C, P=1atm, W/F_{A0}=0-0.14 (gcat*h/g methanol fed)]

3.6 Effect Of Runtime On The Yield Of Total Hydrocarbons

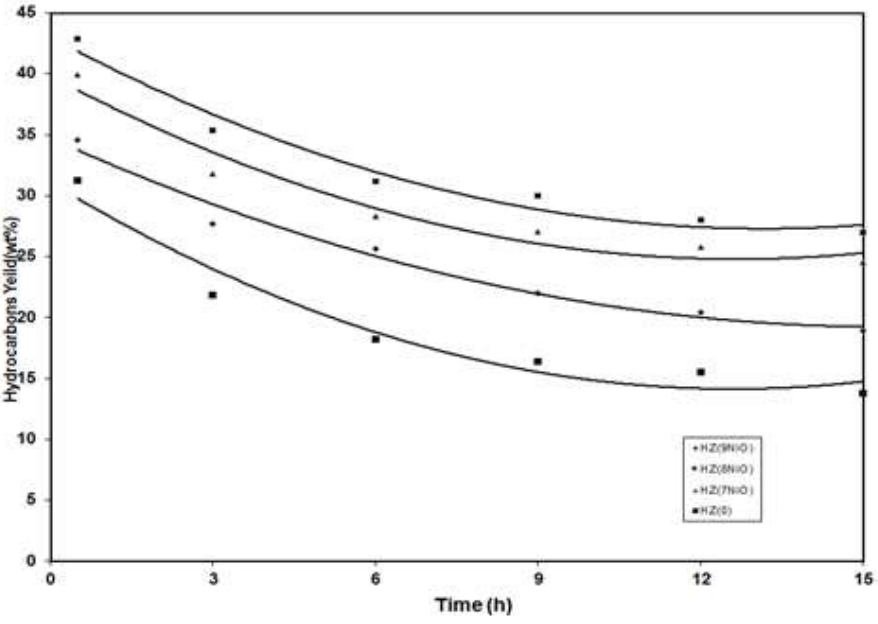

Fig.6 Effect of runtime on the yield of total hydrocarbons [T=450^{0}C, P=1atm, W/F_{A0}=0-0.14 (gcat*h/g methanol fed)]

The increase in time of reaction results in a decrease in the yield of hydrocarbons as shown in Fig.6. After 15 hours of operation, hydrocarbon yield of 8% and 9% Ni modified catalyst is nearly double as compared to unmodified catalyst. This means catalyst can be used for more time before regeneration and hence lower cost of operation.

IV. CONCLUSIONS

The catalytic performance of catalysts consisting of Ni-loaded ZSM-5 have been studied in conversion of hydrocarbons from methanol. Methanol conversion and hydrocarbons yield increased progressively on increasing W/F_{A0} with HZ (NiO). These findings suggest that Ni species would interact with the acid sites of ZSM-5 to reduce the strength of strong acidic sites. A significant effect of temperature on the methanol conversion and hydrocarbons yield was observed. There was an increase in conversion and hydrocarbon yield. HZ (8NiO) is the recommended catalyst and 450 ^{o}C is the recommended temperature. Therefore Ni-loaded ZSM-5 catalyst is effective in the selective synthesis of the gasoline-ranged hydrocarbons from Methanol.

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