

Catalytic Conversion of Methanol to Hydrocarbons over MgO and CaO Modified HZSM-5 Catalyst

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Abstract : The fixed bed reactor was heated to temperatures varying from 643 to 673 K during the experiment, with contact times ranging from 0.047 to 0.14 (g catalyst*h /g methanol supplied). The impact of process variable on the activity of a 0.2 wt% MgO/1wt% CaO/HZM5 catalyst for converting methanol to gasoline-like hydrocarbons was studied. Different contact times (W/F_{A0}) and temperatures were investigated, and conversion and hydrocarbon yield increased as temperature and weight hour space velocity (WHSV) increased.

Keywords- Catalyst, weight hour space velocity, conversion, hydrocarbons yield, Kinetics.

I. INTRODUCTION

Biomass, natural gas, and coal can all be used to make methanol. Gasification can be used to convert them to syngas, which can then be turned into methanol[1]–[3]. This methanol can next be utilized to produce gasoline or olefins depending on the catalyst and process conditions. Because of the recent rise in oil prices, some researchers were interested in converting methanol to gasoline-like hydrocarbons [3]–[6]. Methanol is now being pursued to produce olefins and other hydrocarbons [1], [7]–[11]. Methanol can be made from coal and biomass as a raw source[2], [12], [13]. Zeolites have a large surface area, which allows for a high degree of active metal dispersion over the HZSM-5 catalyst, allowing for the most metal to be deposited [14].

0.2wt% MgO/1wt% CaO/HZSM-5 catalyst was developed for the synthesis of gasoline-range hydrocarbons from methanol in this study. Because of its lower acidic sites, the HZSM-5 catalyst has a faster rate of deactivation due to coke, according to kinetic models [1][6].

The results demonstrate that the 0.2wt% MgO/1wt% CaO/HZSM-5 catalyst had better conversion and hydrocarbon yields than other catalysts. The effect of process factors such as temperature and contact duration on methanol conversion and hydrocarbon formation has been investigated using experiment runs.

II. EXPERIMENTAL

2.1 Preparation of Catalyst

The pH of the Calcium nitrate slurry was raised to 5 with the addition of NH_4OH solution and catalyst. The finished solution was agitated for 12 hours at 303 K. The addition of ammonia to the solution delays the reaction, allowing Ca complexes to better disperse into the HZSM-5 pores, and the final catalyst slurry was dried in a 393 K oven for 12 hours. The dried pellets were calcined for 5 hours at 823 K to break down the Ca complex to CaO. The surface of the HZSM-5 catalyst was doped with a specified amount of magnesium nitrate salt Merck. Over a 1wt% /CaO/HZSM-5 catalyst, MgO was doped. A 0.2wt% MgO/1wt% CaO/HZSM-5 catalyst, abbreviated as HZ(Mg-Ca) catalyst, was prepared using the wet impregnation process.

2.2 Catalytic Testing

The catalyst pellets were crushed and sieved into particles ranging in size from 2.5 to 1 mm for the experiments. The first research looked at the details of the experimental setup and procedure. The tubular reactor was built entirely of stainless steel tubing. The reactor was heated in three zones between 643 and 683 K during the operation using an electric furnace. To minimize heat losses between the preheater and reactor was suitably insulated with magnesia wool. The experimental runs were conducted at various contact times ranged from 0.047 to 0.14(g catalyst*h /g methanol supplied).

III RESULTS AND DISCUSSION

3.1 Kinetic Study

Methanol conversion at 1 atm pressure and 0.14(g cat*h/g methanol supplied) on the HZ(Mg-Ca) catalyst, with a significant increase in hydrocarbon output when the temperature was increased from 643 K to 673 K.

MgO and CaO impregnated HZSM-5 catalysts positively affect the reaction, reducing additional acidic sites responsible for rapid coke deposition over the catalyst's surface.

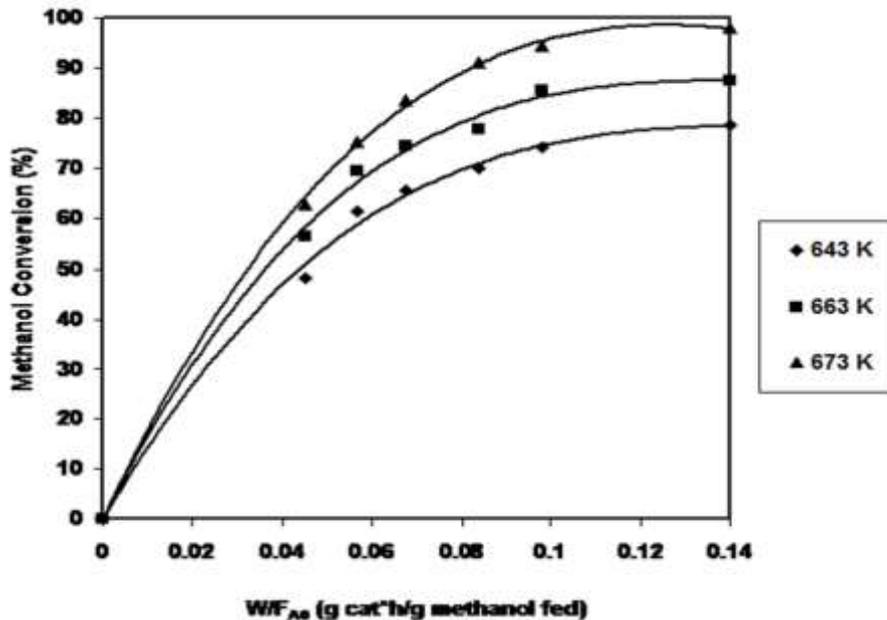


Fig. 1 Methanol Conversion variation as a Function of Contact Time with an HZ (Mg-Ca) Catalyst (T=643K-673K, P=1atm)

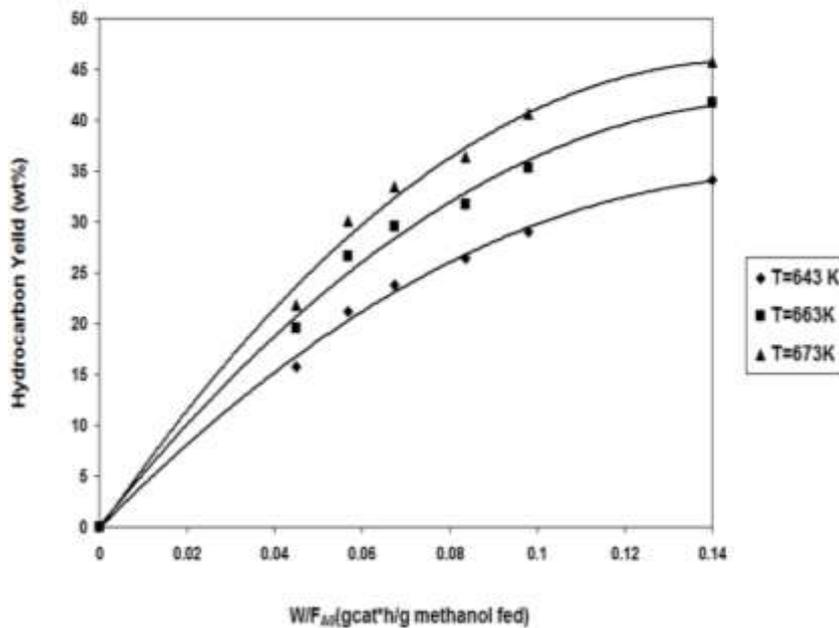


Fig. 2 Hydrocarbons Yield variation as a Function of Contact Time with an HZ (Mg-Ca) Catalyst (T=643K-673K, P=1atm)

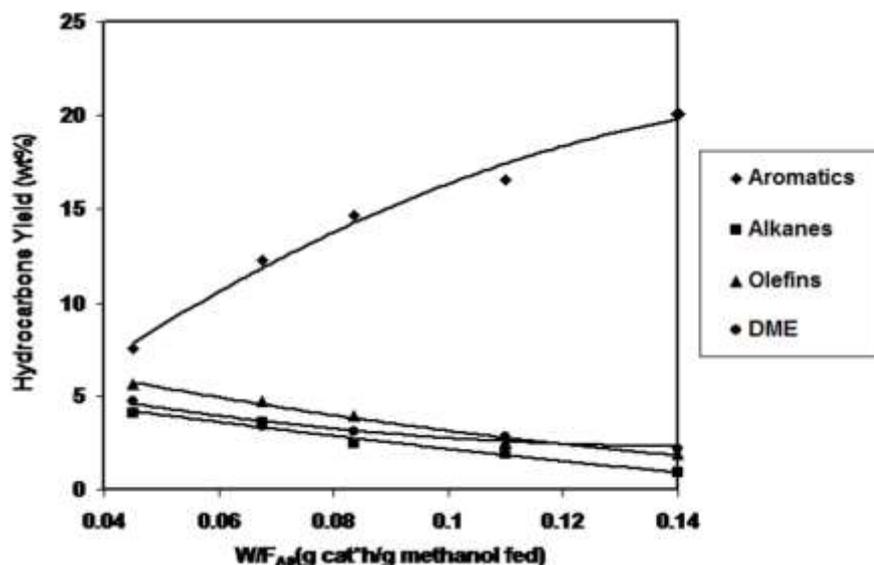


Fig. 3. The yield of Hydrocarbons vs. Contact Time over an HZ (Mg-Ca) Catalyst [T=643K, P=1 atm]

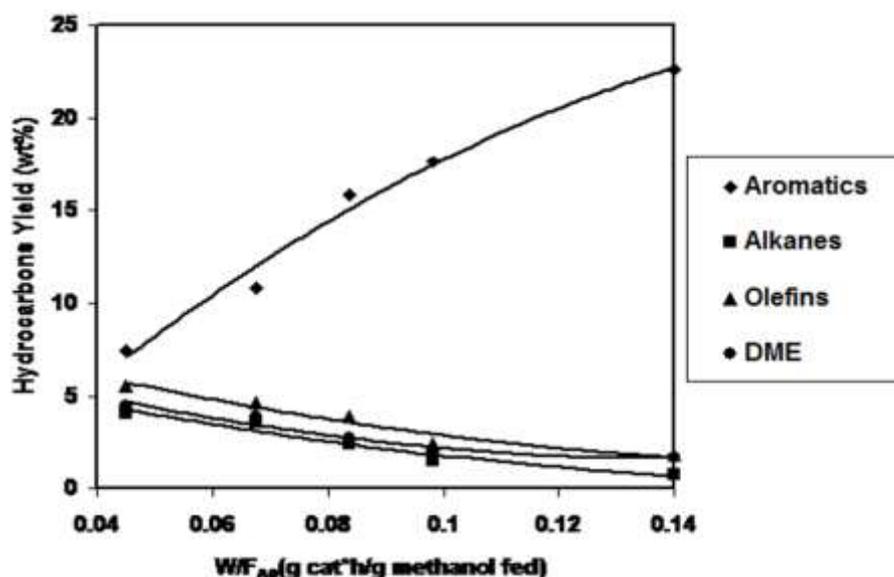


Fig. 4 The yield of Hydrocarbons vs. Contact Time over an HZ (Mg-Ca) Catalyst [T=663 K, P=1 atm]

3.1.1 The Influence of Contact Time on Methanol Conversion and Hydrocarbon Yield

In the experiments, different contact times (W/F_{A0}) and temperatures were utilized. Figures 1 and 2 indicate the effect of contact time and temperature on methanol conversion and hydrocarbon yield. Methanol conversion and total hydrocarbon output increase due to the rise in W/F_{A0} ranging from 0 to 0.14 (g cat*h/g methanol supplied). Figure 1 demonstrates that as the temperature rises, so does the contact time, increasing conversion, whereas Figure 2 shows a rise in hydrocarbons yield with an increase in temperature. Figures 3–4 show how product distribution changes with contact time at three different temperatures: 643 K, 673 K, and 673 K. As contact time increases simultaneously, the conversion increased, due to which the aromatic hydrocarbon yields rose. Lighter olefin yields, on the other hand, have decreased. Large quantities of olefins and DME were obtained at low conversion, but aromatic yields declined.

Aromatic yields increased as contact time increased, whereas olefin and DME yields decreased, indicating that alkenes (olefins) and DME are intermediates to aromatics [13][15]. As conversion increased, alkane yields decreased. At higher temperatures, up to 673 K, methanol conversion and liquid products increased.

The primary gaseous products were ethane, methane, propylene, ethylene, dimethyl ether, propane, butane, and pentane. The major liquid products were benzene, toluene, xylene, ethyl benzene, trimethyl benzene, tetramethyl benzene and C_{5+} .

3.1.2 Methanol Conversion and Hydrocarbon Yield as a Function of Temperature

Experimental runs were conducted To investigate the effect of temperature on methanol conversion and hydrocarbon generation at various temperatures over a 0.2wt% MgO/1wt% CaO impregnated HZSM-5 catalyst. The product yield is depicted in Figure 3 to Figure 5 at different temperatures and contact times. The transformation of methanol and the generation of hydrocarbons improved as the temperature rose.

Figure 5 depicts the distribution of main hydrocarbon products such as olefins, alkanes, aromatics, and C₅₊ on a water-free basis at different contact times at 673K and 1 atm.

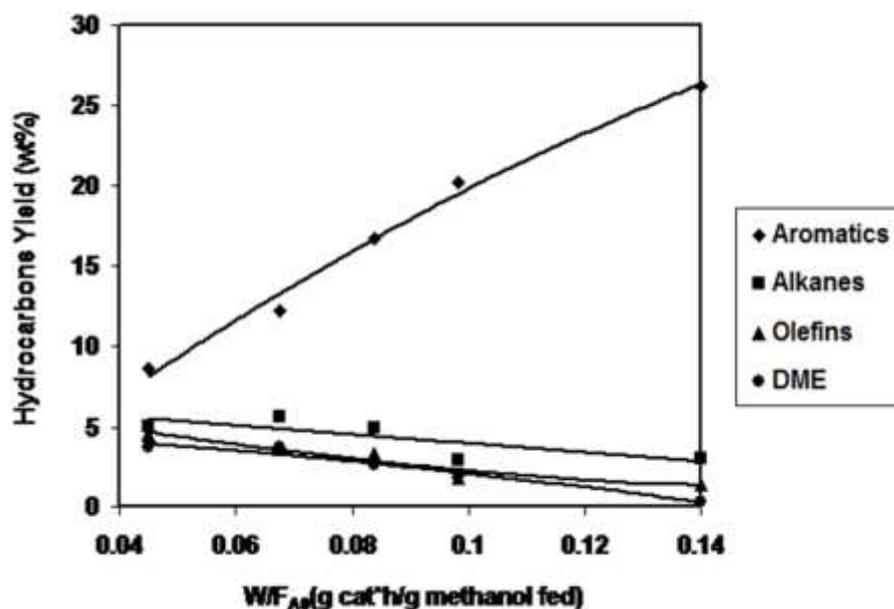


Fig. 5 Yield of Hydrocarbons vs. Contact Time over an HZ (Mg-Ca) Catalyst [T=673K, P=1 atm]

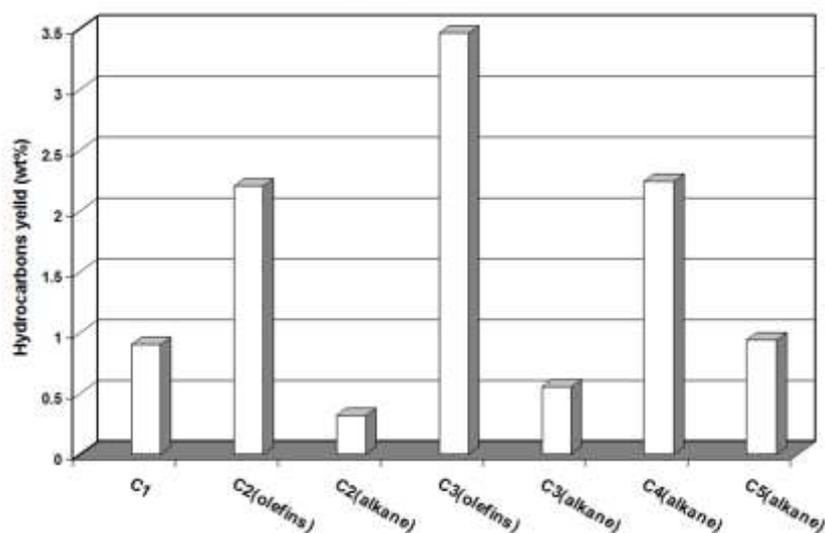


Fig. 6 Product Distribution for Methanol Conversion to Hydrocarbons over HZ (Mg-Ca) [T=673 K, W/F_{A0} (g cat*/h/g of methanol fed)=0.14

Although conversion and liquid hydrocarbon yield increased, there was no significant improvement in hydrocarbon yield above 673K[16]. The catalyst deactivated quickly at 683 K due to the rapid formation of coke on the surface. When oligomers are broken down into smaller molecules and coke, the catalyst is deactivated.

The oligomerization and cracking are better balanced at 673 K, and the cracking isn't severe enough to produce extra coke; thus, the catalyst activity lasts longer. Experiments indicated several qualitative MTG reactions that were fascinating. According to the results of the experiments, the temperature range of 643 K to 673 K was the best favorable for the selective transformation of methanol to aromatic hydrocarbons. The first olefin hydrocarbons generated during methanol conversion are expected to be ethylene and propylene. The temperature range of 643 K to 673 K can be easily oligomerized to yield desired hydrocarbons.

These results show that MgO and CaO doped catalysts are very active dehydrogenation catalysts with excellent aromatic selectivity in methanol conversion. The product distribution of gaseous and liquid products over the HZ (Mg-Ca) catalyst is depicted in Figures 6 and 7. Methane, ethylene, propylene, dimethyl ether, toluene, xylene, isopropyl benzene, ethyl toluene, trimethyl benzene, and tetramethyl benzene and C₅₊ were the most important products of the reaction.

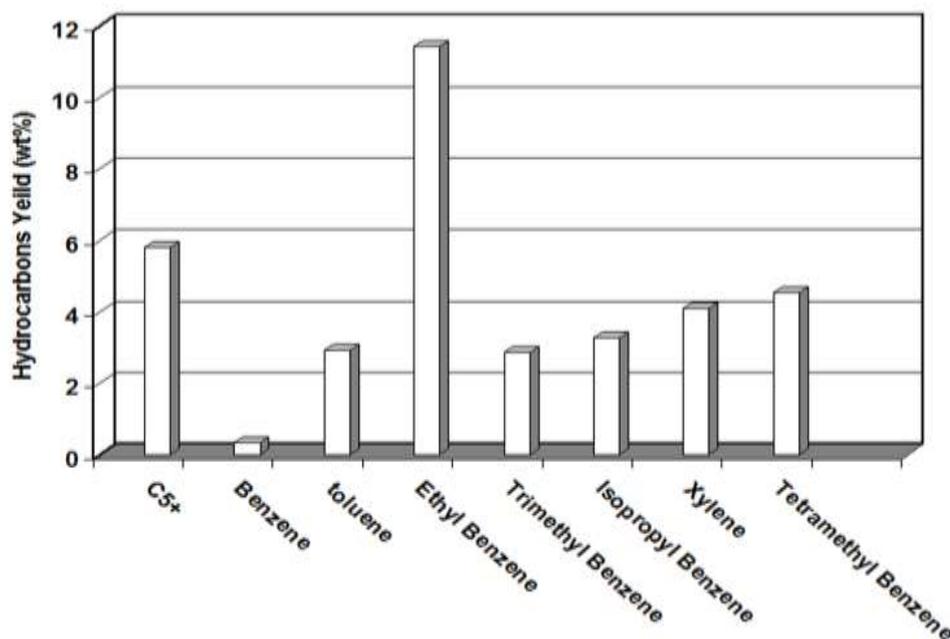


Fig. 7 Product Distribution for Methanol Conversion to Hydrocarbons over HZ (Mg-Ca) [T=673 K, W/F_{A0} (g cat*h/g of methanol fed)=0.14]

IV. CONCLUSION

With increasing contact time, the yield of gasoline range liquid hydrocarbons increased, whereas the yield of lighter olefins declined. High yields of olefins and DME were achieved at low conversion, whereas aromatic yields were minimal.

Lighter olefins and DME are partially converted to heavy hydrocarbons, demonstrating that methanol-to-hydrocarbon conversion processes produce intermediate products. The output of methanol conversion and hydrocarbon was found to increase significantly when the temperature was raised. The conversion and liquid hydrocarbon yields increased up to 673 K, but beyond that, the major liquid product yields decreased as the temperature rose to utilize the HZ(Mg-Ca) catalyst.

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