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Effect of Kinetic Parameters on Activity of Kaolin and Silver Modified HZSM–5 Zeolite in the Methanol-to-Olefins (MTO) Process

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Abstract

In this paper the effect of kinetic parameters, such as temperature, space-time and catalysts size on the conversion of methanol to C_2 to C_4 olefins over kaolin and silver modified HZSM–5 zeolite was studied. The catalyst and reaction condition leading to a maximum yield of C_2 to C_4 olefins were also determined, for a broad range of methanol conversions. Kaolin caused an appreciable decrease in the acidity of HZSM–5 zeolite, due to a solid-ion exchange between protons of zeolite and cations of the clay during the calcinations. The neutralization of some zeolite acid-sites caused a decrease in the methanol conversion for HZSM–5 zeolite. However, the conversion of methanol to olefins was found maximum. Incorporation of silver imparts dehydrogenation activity to the catalyst and thus paraffins which are the end products of the methanol conversion on zeolite, have been transformed to olefins resulting in enhanced selectivity towards C_2 to C_4 olefins. Reaction condition (T, W/FAo and catalyst size), are more determining. The effect of temperature, space-time and catalyst size on selectivity towards C_2 to C_4 olefins were also studied. With these modifications of HZSM–5 with kaolin and silver, the highest selectivity towards lower olefins was obtained by choosing the correct reaction conditions.

1. Introduction

Lower olefins (C_2-C_4) have been used as raw materials for polypropylenes and as the starting materials for various chemicals in the petrochemical industry. For the past many decades, most of the olefins are being produced by the thermal cracking of naphtha [1]; the thermal cracking of ethane [2] and the fluidized catalytic cracking of middle distillate [3] have become important as the supplementary production process of the lower olefins. However, the depleting source and rising cast of crude oil lower the feasibility of the thermal cracking of naphtha, because of the later high price. The high-temperature operation of the thermal cracking process inevitably requires a large amount of energy and causes a large amount of carbon dioxide to be emitted. As a result, alternative processes for the production of lower olefins from non-petroleum sources without using a large amount of energy have been steadily studied [4–6].

In recent years, the conversion of methanol to olefin (MTO) on acidic zeolite catalysts and the process of obtaining light olefin through it have received considerable attention. For this main reason is syngas via methanol can be easily produced from carbonized sources such as coal, natural gas and biomass [7–10]. In addition, literature has also shown that HZSM–5 zeolite is one of the most effective catalysts for MTO due to its excellent catalytic performance [11].

Various researches have been done to study the effect of doped metals on ZSM for product selectivity.

Schulz and Bandermann et al. demonstrated modification of zeolite with alkaline metals (sodium (Na), potassium (K), caesium (Cs), and rubidium (Rb)). These modifications effectively controlled the acidity of zeolite to tune its catalyst performance for the MTO process [12]. Stelzer et al. modified ZSM–5 with strontium (Sr). It showed promising results to get light olefins from the conversion of methanol. This modification diluted strong acid sides results enhanced selectivity [13]. Xiaoning and his co-workers performed series of experiments to modify HZSM–5 with rare earth metals (La, Ce, Pr, Nd, Sm, Eu or Gd). Nd modified HZSM–5 showed the highest yield for propane along with Ce modified HZSM-5 prepared showed the highest yield for total olefins [14]. Mao et al. also the investigated performance of modified ZSM–5 with Mn. They found 94% conversion for methanol by using 2.8% Mn/ZSM–5 prepared by wet impregnation. Mohammadrezaei et al. used Fe as a promoter and found the best result. They reported impregnation of iron and iridium (0.3 wt%) increased the propylene methanol conversion and selectivity. However, methanol conversion drastically decreased after six days when iridium was used as a promoter [15]. A summary was also reported in 1999 mainly covered the chemistry and mechanism of reactions including the catalysts involved and their behavior due to crystal size, pore architecture, acidity and reaction conditions, covering the time since around 1990 [16].

Therefore, acidity adjustment of acidity plays a major role in the catalyst development for the MTO process. The desired product distribution can also be obtained by suitably controlling the kinetic parameters viz, temperature, space-time, particle size, etc.

In the present paper, we report our work on the methanol-to-olefins process over HZSM–5 zeolite containing 25% kaolin and 1% silver by weight. The effects of kinetic parameters, such as temperature, space-time and catalysts size on product distribution have been discussed.

2. Methodology

2.1 Catalyst Preparation

HZSM–5 was obtained from m/s Zeochem, Switzerland having Si/Al ratio of 100. Modification of HZSM–5 was carried out by mixing aqueous slurries of HZSM–5 with the 25 wt% of kaolin (AR Grade make Thomas Baker Pvt. Ltd, Mumbai, India). This resulting mixture was dried over a water bath with continuous stirring. The mixture was then dried in an air oven at 393 K for 6 h. Finally, the resulting mass was heated in a muffle furnace at 673 K. Further modification of HZSM–5 containing 25 wt% of kaolin was carried out by impregnating with the requisite amount of 0.01 M ammoniacal solution of $AgNO_3$. The slurry was dried over a water bath and subsequently in an air oven. Finally, the catalysts were reduced by hydrogen at 673 K for 4 h. The final composition of the catalyst was 1% Ag by weight in the Catalyst.

2.2 Experiments

Activities (Yield, Selectivity and Conversion) of the catalysts were measured in a fixed bed tubular glass reactor (10.0 mm id and 380 mm long) kept inside a tubular furnace as shown in **Fig. 1**. The upper section of the reactor was filled with inert silica particle which served the purpose of preheating reactant. The temperature of the furnace was controlled with the help of a PID controller. The temperature variation across the reactor was ±3 K. Methanol was introduced into the reactor by vaporization at a controlled temperature of 323 K. Nitrogen gas was used as a carrier. Nitrogen gas (primary nitrogen) was allowed to enter the methanol vaporizer through a sparger of porous sintered glass. The temperature of the vaporizer was controlled with the help of a contact thermometer and a relay. Additional nitrogen gas (secondary nitrogen) could also be mixed, when desired, to change the inlet concentration of methanol. The flow rates of primary and secondary nitrogen were controlled using an electronic mass flow meter and controllers (Nucon, India). The schematic diagram of the experimental setup is shown in Fig 1. The product coming out from the reactor was analyzed by a gas chromatograph (Make Varian, USA, and "Model 3600") equipped with a flame ionization detector using DHA (Detailed Hydrocarbon Analyzer) software. Helium gas was used as a carrier and a 100 m PONA capillary column was used for analysis. The software had the capability of analyzing the products in terms of carbon number, types of hydrocarbons (Olefins, Aromatics, and Paraffins etc.). For quantitative analysis calibration standard "POINA Mix (Make: Varian, USA) was used. Yield, selectivity and conversion were calculated using the formula given below:

$$\% \, coversion = (C_{A_i} - C_{A_o}/C_{A_i}) \times 100$$ **Eqn. 1**

$$\% Yield = \frac{Mass\ of\ desired\ product\ formed}{Mass\ of\ methanol\ cosnumed} \times 100$$ **Eqn. 2**

$$\% \, Selectivity = \frac{Mass\ of\ desired\ prodcut\ fomred}{Mass\ of\ undesried\ product\ formed} \times 100$$ **Eqn. 3**

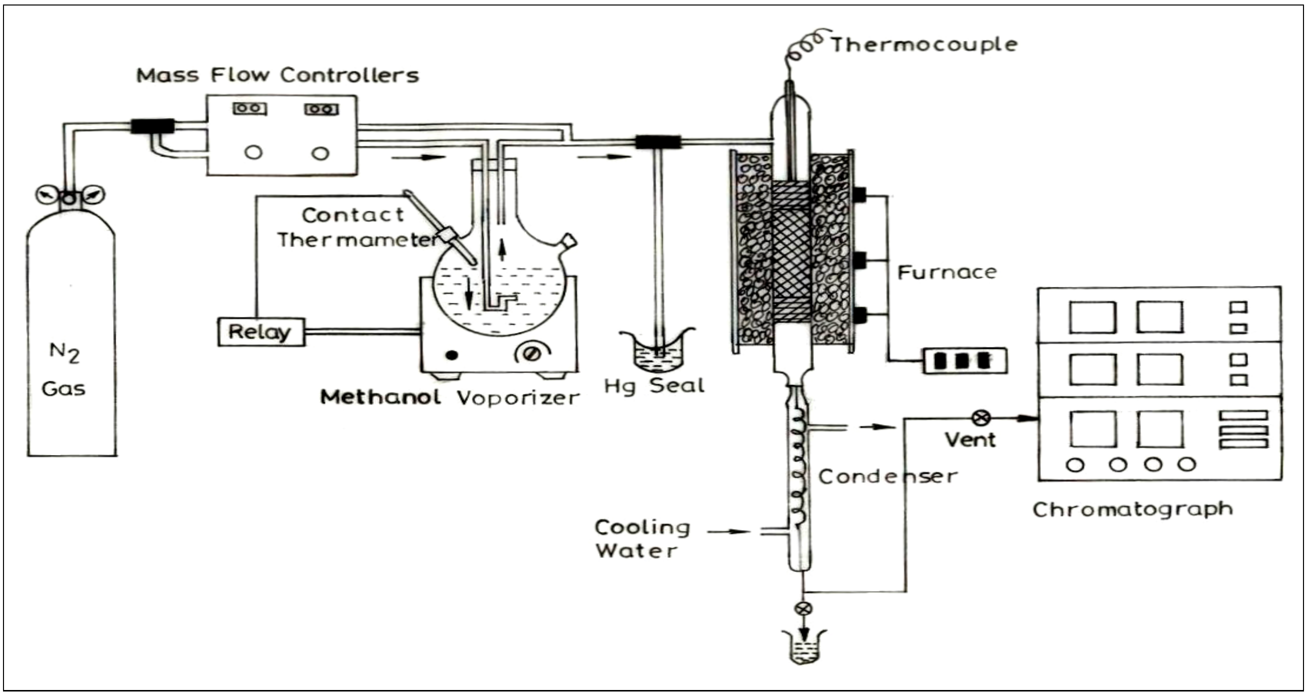

Fig. 1. Schematic Diagram of the Experimental Setup

3. Results and Discussion

3.1 Effect of Kinetic Parameters

The production of lower olefins from methanol follows a complex reaction pathway. The lower olefins can be the primary intermediate products. These can also form by the cracking of higher olefins. Further, when metal is incorporated in the zeolite, dehydrogenation of paraffins may be catalyzed giving higher olefins which on cracking will produce lower olefins. Thus, it is possible to increase the yield and selectivity of lower olefins by a proper combination of the kinetic parameters viz. reaction temperature, W/F_{Ao} and catalyst size, such that the rates of the desired reactions which produce lower olefins are exchanged.

3.2 Product yield

The effect of reaction temperature was investigated at constant W/F$_{Ao}$ of 11 g.cat.h.mole^{-1}, small catalyst size of –1.7+1.4 mm was taken to minimize the effect of pore diffusion resistance. The concentration of methanol in the feed was 1.05×10^{-5} mol.mL^{-1}. The temperature was varied from 598 to 648 K. The results obtained are given in Table 1. It is observed that when the temperature is raised from 598 to 648 K, total conversion of methanol increased from 89.7 to 92.9% and its conversion to C_2 to C_4 olefins also increased from 38.2 to 63.2%. The total yield of C_2 to C_4 olefins increased from 23.9% at 598 K to a maximum of 29.6 % at 648 K. The selectivity to C_2 to C_4 olefins followed the same trend as the total yield of C_2 to C_4 olefins and increased from 54.0% at 598 K to 70.4 % at 648 K. Further, at low temperature, ethene was the most abundant lower olefins. However, at the higher reaction temperature, ethane was a minor component while butene and especially propene became the most abundant. However, the yield and selectivity of aromatics and paraffins decreased concurrently. Literatures [17–19] also reported such type of results that high temperature favors olefins formation at the expense of the aromatization reactions. The yield of ethene decreased with increasing temperature, in contrast to the yields of propene and butene.

Table 1 Effect of Temperature on the Conversion, Selectivity and Yield

Product	**% Conversion at Temperature (K)**			**% Selectivity at Temperature (K)**			**% Yield at Temperature (K)**		
	598	**623**	**648**	**598**	**623**	**648**	**598**	**623**	**648**
Ethene	15.6	15.6	15.6	18.5	16.3	13.1	8.6	7.2	6.3
Propene	16.1	16.1	16.1	22.3	28.2	39.0	10.1	12.3	15.1
Butene	6.5	6.5	6.5	13.2	19.5	18.3	5.2	6.1	8.2
Ethene-Butene	38.2	38.2	38.2	54.0	64.1	70.4	23.9	25.6	29.6
Methane	2.6	2.6	2.6	5.3	4.8	5.5	1.0	1.2	1.4
Ethane	4.4	4.4	4.4	3.0	2.3	2.7	2.2	1.7	1.0
Propane	6.4	6.4	6.4	3.4	2.6	2.9	2.7	2.4	1.5
Butane	10.1	10.1	10.1	4.2	2.8	1.4	3.3	3.2	1.2
Methane-butane	23.5	23.5	23.5	15.9	12.5	13.3	9.2	8.5	5.1
AN	9.9	9.9	9.9	2.5	2.0	1.6	4.0	3.4	2.7
Aromatics	8.2	8.2	8.2	12.2	9.2	4.7	3.1	2.3	1.2
DME	9.9	9.9	9.9	15.2	12.3	10.1	17.0	14.0	12.0
Total	89.7	89.7	89.7						

Inlet concentration = 1.05×10^{-5} mol.mL^{-1}
W/FAo = 11 g.cat.h.mol^{-1}
Catalyst size = 1.44 mm
AN = C_5+ Aliphatic and Naphthenes
DME = Dimethyl ether

3.3 Effect of Space-Time (W/FAo)

The effect of space-time (W/FAo) on the conversion of methanol to hydrocarbons and their yield and selectivity was studied at constant temperature of 648 K. Small catalyst size (–1.7+1.4 mm) was taken to minimize the effect of pore diffusion resistance. The concentration of methanol in the feed was 1.05×10–5 mol.mL^{-1}. The space-time (W/FAo) was varied from 11–21 g.cat.h.mol^{-1} by varying molar feed rate of methanol. The results are given in Table 2. It is observed that with the increase in the space-time from 11–21 g.cat.h.mol^{-1}, total conversion of methanol increased from 92.9 to 97.7%, however, its conversion to C_2 to C_4 olefins decreased from 63.2 to 46.1%. The total yield of C_2 to C_4 and decreased from 70.0 to 55.8%. On the other hand, conversion to aromatics and paraffins and their yield and selectivity increased steadily. Since the reaction sequence is quite complex, therefore, it is difficult to predict the influence of contact time on the yield and selectivity of lower olefins. But as seen from the results, lowering the contact time results in a greater yield and selectivity of lower olefins indicates that the reaction sequence was curtailed at some intermediate steps, thus forming a large proportion of lower olefins [20–22].

Table 2 Effect of Space-Time on the Conversion, Selectivity and Yield

Product	% Conversion at W/FAo ($g.cat.h.mol^{-1}$)			% Selectivity at W/FAo ($g.cat.h.mol^{-1}$)			% Yield at W/FAo ($g.cat.h.mol^{-1}$)		
	11	16	21	11	16	21	11	16	21
Ethene	9.8	7.8	4.6	13.1	11.2	8.1	6.3	5.0	4.5
Propene	38.2	34.4	32.3	39.0	37.1	33.2	15.1	12.5	10.4
Butene	15.2	11.6	9.2	18.3	16.7	14.5	8.2	6.2	5.7
Ethene-Butene	63.2	53.8	46.1	70.4	65.0	55.8	29.6	23.7	20.6
Methane	3.2	2.3	2.3	5.5	5.2	5.2	1.4	1.5	1.5
Ethane	2.7	3.5	4.6	2.7	2.7	3.1	1.0	1.5	2.2
Propane	3.5	4.6	7.0	2.9	3.7	4.2	1.5	2.2	3.0
Butane	3.0	6.3	9.1	1.4	4.4	5.9	1.2	3.2	3.4
Methane-butane	12.4	16.7	23.0	13.3	16.0	18.4	5.1	8.4	10.1
AN	7.3	10.7	12.1	1.6	2.6	6.7	2.7	4.7	5.2
Aromatics	3.6	7.3	11.1	4.7	7.2	10.4	1.2	2.2	3.5
DME	6.4	5.8	5.4	10.1	9.2	8.7	12.0	11.0	10.0
Total	92.9	94.3	97.7						

Inlet concentration = 1.05×10^{-5} $mol.mL^{-1}$
Temperature = 648 K
Catalyst size = 1.44 mm
AN = C_5+ Aliphatic and Naphthenes
DME = Dimethyl ether

3.4 *Effect of Catalyst Size*

The effect of pore diffusion resistance on the conversion of methanol to hydrocarbons and their yield and selectivity was studied by varying size of the catalyst. Three catalysts, of size ranges–3.38+2.8, –2.8+1.7 and –1.7+1.4 mm corresponding to average diameters of 3.08, 2.25, and 1.45 mm, respectively were taken. The reaction was carried out at constant temperature of 648 K and space-time (W/FAo) of 11 $g.cat.h.mol^{-1}$. Methanol concentration in the feed was 1.05×10^{-5} $mol.mL^{-1}$. Results are given in Table 3.

Table 3 Effect of Catalyst size on the Conversion, Selectivity and Yield

Product	% Conversion at Catalyst size (mm)			% Selectivity at Catalyst size (mm)			% Yield at Catalyst size (mm)		
	1.44	2.25	3.08	1.44	2.25	3.08	1.44	2.25	3.08
Ethene	9.8	7.8	6.2	13.1	10.9	6.9	6.3	5.7	5.2
Propene	38.2	32.7	27.5	39.0	32.1	26.0	15.1	14.0	12.7
Butene	15.2	12.8	10.1	18.3	22.0	19.9	8.2	6.8	5.5
Ethene-Butene	63.2	53.3	40.8	70.4	65.0	52.7	29.6	26.5	23.4
Methane	3.2	2.3	2.3	5.5	5.4	5.5	1.4	1.5	1.7
Ethane	2.7	3.2	3.8	2.7	2.8	3.0	1.0	1.3	1.5
Propane	3.5	4.5	6.3	2.9	4.0	4.4	1.5	2.7	3.2
Butane	3.0	6.5	8.6	1.4	4.7	5.4	1.2	3.0	3.0
Methane-butane	12.4	16.5	21.0	13.3	16.9	18.3	5.1	8.5	9.4
AN	7.3	8.5	10.9	1.6	2.7	8.5	2.7	4.0	5.3
Aromatics	3.6	10.0	14.8	4.7	6.3	11.5	1.2	2.4	3.2
DME	6.4	5.6	5.3	10.1	9.1	8.9	12.0	10.0	9.0
Total	92.9	93.9	95.8						

The results show the total conversion of methanol is only marginally affected, whereas the conversion to C_2 to C_4 olefins decreased from 63.2 to 40.8% with the increase in the size of the catalyst. The total yield of C_2 to C_4 olefins decreased from 29.6 to 23.4%. The selectivity to C_2 to C_4 olefins also followed the same trends as the total yield of C_2 to C_4 olefins and decreased from 70.4 to 52.7%. Owing to the complex nature of the reaction, i.e., involving a number of series and parallel reactions, the qualitative prediction of the effect of pore diffusion is rather difficult. The formation of 'primary' olefins which are the intermediate in the series reaction may get enhanced for smaller size catalyst providing low pore diffusion resistance whereas production of lower olefins from cracking of paraffins and higher olefins (end-products) will be favored when pore diffusion resistance is high, i.e., when the catalyst is large. Since the yield and selectivity of lower olefins were observed to increase when catalyst size decreased, it may be concluded that the first effect dominated over the second.

Conclusion

HZSM–5 is an active catalyst for the conversion of methanol to hydrocarbons by a complex reactions mechanism. All such reaction involves carbon-cations intermediates and takes place at rates governed by nature, number and strength of acidic sites. With the modification of HZSM–5 with kaolin and silver, the highest selectivity towards lower olefins is obtained by choosing the correct reaction conditions. The highest yields of C_2 to C_4 olefins are obtained at high temperature and low space-time and small catalyst size. Optimum conditions for a particular olefin depend upon the type of olefin. The ethene yield is optimum at low temperatures, low space-time and small catalyst size, while the propene and the butene yield are highest at high temperature.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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