Kinetic Modeling of the transformation of Methanol into Hydrocarbons on HZSM-5 catalyst

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Abstract: HZSM-5 catalyst was modified with barium oxide and treated 1M oxalic acid(Ba-HZOX) used for the production of hydrocarbons in a fixed bed reactor and was investigated. 1wt% BaO was doped over HZSM-5(Ba-HZ) and was prepared by the wet impregnation method. The main liquid products formed were ethylene, propylene, dimethyl ether, cyclopentene, n-hexane, 1-octene, cycloheptane, 2,5-dimethyl hexane, nonane, cyclohexane, ethylbenzene, xylene, toluene, isopropylbenzene, trimethylbenzene, and tetramethyl benzene. It was investigated that the Ba/HZOX catalyst showed better stability than the HZSM-5, 1wt% Ba-HZSM-5 catalyst, and this study was made based on the effect of run time. Higher conversion and more hydrocarbon yield were obtained using Ba-HZOX and Ba-HZ catalyst compared to the use of parent HZSM-5 catalyst. The calculation of the kinetics parameter was done by solving mass conservation equations to determined the kinetic models. The experimental data fit with the simulated data, which is obtained from the kinetic model.

Index Terms: - HZSM-5, MTH, catalysis, impregnation, gasoline, deactivation.

I. INTRODUCTION

Various methods have been used to reduce the ZSM-5 zeolite catalyst's rapid deactivation due to carbon deposition. One of the important methods is acid treatment, such as oxalic acid, which reduces the acidic site responsible for coke formation. It also improves the reactant diffusivity to the available active sites[1–3]. Treatment with oxalic acid affects the catalyst's morphology, deactivation of the ZSM-5 catalyst's deactivation due to pore-blocking gets reduced, and the catalyst's stability is thereby increased. Catalyst deactivation can be reduced by reducing the number of acidic sites (especially Brønsted or Lewis acid sites) or increasing the Si/Al ratio during the reaction[4–7].

Researchers have modified the ZSM-5 catalyst using metal impregnations to transform MTG [8–13]. Ag modified ZSM-5 catalyst was studied and compared with Zn-modified ZSM-5 catalyst to transform methanol-to-aromatics (MTA). It was found that aromatics yield was significantly improved using Ag/ZSM-5[14]. The methanol transformation to olefins (MTO) reaction was studied using zinc incorporated ZSM-5 catalyst. Zn/ZSM-5 was observed to increase the Brønsted acidic site's concentration, which gradually increased the lighter olefins yield [15]. Using bimetallic catalyst Zn-Al/ZSM-5, the catalytic stability was improved to 160 h. The catalyst's overall activity was increased with a good BTX yield of 48% [13]. The use of the bimetallic Zn-Sn/ZSM-5 catalyst was studied in the production of the aromatic from methanol. The yield of BTX was 64.1%, but the catalyst stability was on the lower side [16]. Zn/HZSM-5 catalyst was modified with promoters such as Zr, Ce, Mo, and Cr to transform MTA. The maximum yield of aromatics with high methanol transformation was obtained using Cr-Zn/HZSM-5 catalyst [17]. A complete methanol conversion was achieved using CuO/ZSM-5 catalyst. It was observed that the yield of aromatics was improved significantly [18]. ZSM-5 catalyst was modified by impregnating with Gd metal in the MTG process. It was observed that metal impregnation using the ion-exchange technique showed better methanol conversion and high selectivity towards aromatics. The stability of the Gd/ZSM-5 catalyst was enhanced significantly [19]. The calculation of the kinetics parameter was done by solving the mass conservation equation to determined the kinetic models. The experimental data fit with the simulated data, which is obtained from the kinetic model.

II. EXPERIMENTAL

Ba-HZ was prepared by the wet impregnation technique. NH4-ZSM-5 (Si/Al = 50) was calcined in a muffle furnace under the airflow rate at 823 K for five h to prepare the HZSM-5 catalyst. Ba and Cd precursor Ba(NO3)2 6H2O was procured from Merck, Germany. Satisfying 1wt%, BaO was dissolved in deionized water, were mixed, and stirred well. The 1wt% BaO was obtained after drying at 383 K overnight and calcined at 823 K for 5 h to remove the residual precursor salt materials and oxide the active metal. Dealumination of Ba/HZOX was done using 1 M oxalic acid for 2 min at 323 K. It was then washed with deionized water and denoted as Ba/HZOX.

MTH reaction was conducted at 673 K and one atmospheric pressure in a fixed bed reactor using a 0.5 g catalyst [19–21]. All the samples were checked based on the performance in the transformation of hydrocarbons from methanol. Before the reaction, the sample of 0.5 g was placed in the reactor. The weight hourly space velocity was varied from 9.5—19 h⁻¹, and the temperature inside the reactor was 673 K. The reactor's product outlet was subjected to the condenser in which most of the heavier hydrocarbons were condensed. In contrast, some lighter hydrocarbons remaining in the gaseous state were also produced.

The analysis of liquids and gaseous hydrocarbons was performed in a gas chromatograph embedded with a flame ionization detector (FID). Gases such as carbon dioxide, carbon monoxide, etc., were detected using a thermal conductivity detector (TCD).
III. RESULTS AND DISCUSSION:

As per the experimental point of view, a conclusion was made based on the oxalic acid treatment on the HZSM-5 catalyst, which proved to have higher activity and stability, among others, to convert methanol to hydrocarbons[22-23]. Therefore kinetic study can be done on this, and the results obtained are mentioned.

Experimental runs have been performed at various residence times (WHSV) and 673 K temperature with Ba/HZOX catalyst. The impact of residence time and temperature for the transformation of methanol and yield of gasoline range hydrocarbons has been shown in Figures 1 and 2, respectively. When the WHSV was increased from 9.504 to 19.008 h⁻¹, the methanol transformation and hydrocarbons yield was increased progressively.

![Figure 1](image)

**Figure 1.** Change of methanol conversion with the increase in contact time over the Ba/HZOX catalyst (at T = 673 K, P = 1 atm, catalyst = 0.5 g)

The hydrocarbons such as alkanes, olefins, aromatics, and C₅⁺ showed the highest yields at different residence times. Figure 3 shows the gaseous and liquid hydrocarbons, respectively, along with varying times of contact. As the WHSV is increased, the aromatics yield was increased, while dimethyl ether and olefins yield was decreased. Olefins and DME are the intermediate products that are responsible for hydrocarbons production.

![Figure 2](image)

**Figure 2.** Change of hydrocarbons yield with the increase in contact time over the Ba/HZOX catalyst (at T = 673 K, P = 1 atm, catalyst = 0.5 g)

These models are of two types.

(a) Detailed parameter models include the individual reaction steps, and kinetics of reactions are time-consuming

(b) Lumped parameter models are simple to understand and easier to use, and it can be used for most of the problems.

In the present work, the kinetic model constant calculation has been done by employing the fitting of the experimental values of different lumps mass fractions to resemble mass conservation equations. The values of kinetic constants represent the similar reactions of complex systems in which there are many varieties of lumps having different concentrations.
Figure 3. Effect of temperature on the yield of total hydrocarbons [T = 673 K, P = 1 atm, WHSV (g of methanol fed/g of catalyst*h) = 9.504−19.008] using Ba/HZOX catalyst.

The procedure that has been applied is used in many kinetic modeling of various reactions involving catalysts. The conditions set for the reactor were isothermal and disregarding the radial concentrations gradient, now neglecting the water in the product stream and the catalyst inside the reactor. The mass conservation equation at the initial time is:

\[ \frac{-d c_i v}{dx} = (1 - \varepsilon) \sum_{j=1}^{m} \alpha_{ij} r_j^0; i = 1, m \] (1)

Where \( c_i \) is the concentration of species, \( v \) is the linear velocity, \( \varepsilon \) is the bed void fraction, \( \alpha_{ij} \) is the stoichiometric coefficient of the \( i^{th} \) chemical species in the \( j^{th} \) reaction, the reaction rate of the formation of the lump (i) at zero time on stream \( r_j^0 \).

These differential equations were solved using program code, which was written to calculate each reactant and product species' mass fraction. A fourth-order Range Kutta method was used for solving the differential equations for calculating the kinetic parameters for each kinetic model. The non-linear regression was carried out by minimizing the objective functions. The objective function \( F(x) \) is the arithmetic mean of reducing the difference between the experimental and model-predicted values of each lump (composition).

\[ F(x) = \sum_{i=1}^{N} \sum_{j=1}^{N_{exp}} \left( Y_{(exp)ij} - Y_{(cal)ij} \right)^2 / N \times N_{exp} \] (2)

where

- \( N \) = number of lumps
- \( N_{exp} \) = number of experimental points
- \( Y_{(exp)} \) = weight fraction for experimental lump \( i \) on a water-free basis
- \( Y_{(cal)} \) = weight fraction for calculated lump \( i \) on a water-free basis.

The reaction involved in methanol transformation to hydrocarbons:

\[ \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 \rightleftharpoons \text{H}_2\text{O} \rightarrow \text{X} \]

\[ \text{Paraffins} \rightarrow \text{Aromatics} \]

Model

Chen and Reagan [24] studied the model based on DME's dissipation over the ZSM-5 catalyst. The model has been depicted, as shown in equations 3 to 5.

\[ A \rightarrow B \] (3)

\[ A + B \rightarrow B \] (4)

\[ B \rightarrow C \] (5)

Where A is indicated by Oxygenates (Methanol + DME), B by Olefins, and C by Aromatics + Paraffins for the transformation reaction of hydrocarbons from methanol. In this model, the DME + Methanol has been taken as a lump in the form of oxygenates. The reaction for the disappearance of methanol has been indicated as oxygenates to olefins [22-23]. The equations of kinetics for the model mentioned above have been expressed in equations 6 and 7. Here Y refers to the mass fraction of the products formed and contact time, and \( t \) is the contact time:

\[ -dY_A/dt = k_1 Y_A + k_2 Y_A Y_B \] (6)
\[-\frac{dY_B}{d\tau} = k_1 Y_A + k_2 Y_A Y_B - k_3 Y_B \tag{7}\]

The equations mentioned above have been resolved using the method of 4th order Runge-Kutta as already debated before. The kinetic constants obtained after fitting the equations along with the experimental data are given in equations (8), (9), and (10), respectively.

\[
k_1 = 5.622 \times 10^{13} \exp(-102385/RT) \tag{8}\]
\[
k_2 = 8.77 \times 10^9 \exp(-70894/RT) \tag{9}\]
\[
k_3 = 4.436 \times 10^6 \exp(-96548/RT) \tag{10}\]

BaO doped HZSM-5 was used for the conversion of hydrocarbons at various WHSV ranging from 9.504 to 19.008 h\(^{-1}\) and at a constant temperature of 673 K. A graph has been plotted between the experimental values obtained after finishing experimental work such as oxygenates olefins, aromatics, and others. The data obtained from the model with different space-time varied from 9.504 to 19.008 h\(^{-1}\), as shown in Figure 4.

**Figure 4.** Differentiation between experimental and simulated results of the mass fraction obtained water-free basis using Ba/HZOX catalyst (T = 673 K, P = 1 atm)

**Figure 5.** The simulated vs. experimental mass fractions of hydrocarbons, olefins, and oxygenates on a water-free basis using parity plot over Ba/HZOX catalyst [WHSV (g of methanol fed/g of catalyst*h) = 9.504—19.008 h\(^{-1}\), T = 673 K, P = 1 atm]

The model proposed by equations (6) and (7) nicely fits the experimental data. A parity plot has been plotted between the mass fractions of experimental and modeling one at various residence times, and having isothermal conditions is shown in Figure 5. The difference between experimentation and simulation values was obtained using least-square analysis, and the error was obtained with the regression coefficient (R\(^2\)) equal to 0.983.

**IV. CONCLUSIONS**

Before the Ba/HZOX catalyst gets completely deactivated, a considerable amount of methanol is converted to hydrocarbons. The validation of the suggested kinetic model was evaluated by reducing the error among experimental and theoretical hydrocarbon yields.

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