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Kinetic Model of Methanol to Gasoline (MTG) Reactions over H-Beta,H-ZSM5 and CuO/H-BetaCatalysts

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Abstract: The catalytic conversion of methanol to hydrocarbons of gasoline range has been studied over H-Beta, CuO/H-Beta, and HZSM-5. The catalysts were characterized by X-ray diffraction and TGA technique. The performances of the catalysts were evaluated by conducting experiments in a Microcatetest unit (MCB 890) fixed bed reactor made of stainless steel. Experiments were carried out at 10 bar and different reaction temperatures (300, 350, and 400 ◦C) at constant flow rate of methanol (0.2 ml/min) and constant pressure (10bar). GC technique was used to quantify the reaction products. The major products were methyl benzene, octane, 1,2,3- trimethyl benzene, 1,2,4,5- tetramethyl benzene, pentamethyl benzene, and hexamethyl benzene. The results obtained after catalytic cracking of methanol were also validated by using several kinetic models proposed worldwide.The kinetic parameters for various models were calculated by solving the equation of mass conservation inthe reactor for the lumps of the kinetic models.The Kinetic Model of Methanol to Gasoline (MTG) Reactions over H-Beta,H-ZSM5 and CuO/H-Beta Catalysts is second order (since reaction is carried out different temperature and constant partial pressure) using Arrhenius equation by using Polymath and Excel software.
Key words: *Kinetic Model ,Catalytic Conversion, Methanol, Gasoline, Zeolite Catalyst (H-Beta, and HZSM-5), CuO.*

1. Introduction

The conversion of methanol over zeolite catalyst was first investigated by Chang andSilvestry at Mobil Corporation. They were developed that the (MTG) process in the early 1970's. In the 1970's, Mobil synthesised a new zeolite catalyst, which became a key element in the MTG process. Zeolites are porous, crystalline materials with three dimensional framework composed of Al_2O_3 and SiO2 tetrahedra. This catalyst known as ZSM-5 that can convert methanol to hydrocarbon products which are similar to the gasoline fraction of conventional petroleum. The conversions of methanol to gasoline - range compounds over ZSM-5 are a widely studied class of reactions. The conversion of higher alcohols over ZSM-5 to produce hydrocarbons has not been studied as extensively. In 1979, the New Zealand government decided to employ the Mobil MTG process as an alternative in reducing the dependence on imported crude oil. A plant was built at Motunui with a production of about 14,000 barrels per day of unleaded gasoline, having an octane rating of 92 to 94.

The transformation of methanol to various products may be explained by the following mechanisms. In a primary reaction, methanol is first dehydrated to dimethyl ether (DME). In a secondary reaction, the equilibrium mixture formed of methanol, dimethyl ether and water, is then converted to light olefins. The final reaction step leads to the formation of paraffins, aromatics and higher olefins. Light olefins can oligomerize to form products in the

gasoline boiling range. These products can react with oxygenates or with light olefins to produce additional gasoline products.As can been seen from the reaction scheme, methanol is first dehydrated to dimethylether (DME). The equilibrium mixture of methanol, DME and water is then converted to light olefins (C_2–C_4). A final reaction step leads to a mixture of higher olefins, n/iso-paraffins, aromatics and naphthenes. An interruption of the reaction leads to a production of light olefins instead of gasoline.

Kinetic investigations related to the methanol to hydrocarbons conversion normally consider the methanol-dimethyl ether mixture as a single species. This seems to be justified, since the dimethyl ether formation is much faster than the subsequent reactions, so that oxygenates are at equilibrium. Fitting experimental data obtained on H-ZSM-5 with varying concentrations of acid sites showed a linear correlation between the rate constant of the reaction of oxygenates with olefins and the intrinsic acid activity of the catalyst.

2. Methodology

2.1 Catalyst Preparation

ZSM-5 and H-Beta catalysts were used in the current research. Both catalysts were pretreated before use to convert them from the sodium form to H-form using ion-exchange technique. TGA technique was used to select the most proper calcination temperature for the catalyst as well as to quantify the carbon deposited on the surface of the catalyst. Different catalysts namely (HZSM-5, H-Beta, and CuO) were prepared by impregnation technique. Atomic absorption technique (AA) was used to determine the concentration of CuO on the support.The sodium form of the zeolite was converted to the acid form using the following procedure: the NaZSM-5 zeolite is placed in a 100 ml beaker and stirred with a 1.0M (NH_4NO_3) (aq.) solution (10 ml/g zeolite) for 10 to 15 minutes at ambient temperature. H-ZSM-5 prepared by ionic change from 0.25 M aqueous solution of ammonium nitrate (NH_4NO_3) with ZSM-5, at constant temperature (60^0C), and maintained with constant stirring for 24 hour. Then zeolite was separated by centrifuge equipment following dring at 120^oC for 12hrfollowed by calcination at 550^oC for 5hr. CuO/H-Beta was prepared by two methods ion-exchange and Impregnation technique. CuO/ H-Beta prepared byImpregnation technique. 7 g of CuO was mixed with 93g of distillate water and put in burette. 20 ml was taken from the solution and added to 1 g of support (H-Beta).

2.2 Catalyst Characterization

XRDtechnique has been used in this research on order monitor the catalyst crystallinity. The powder XRD patterns of the ZSM-5**,** calcined and H-Betawere recorded in the range 2° e 2e 70° with a Philips PW 1800/10 diffractometer. CuO content was determined by Atomic Absorption Spectrophotometry using (UNICAM, GF90 AA Spectrometer). The samples were solubilized in a mixture of HF, HCl and HNO_3. The concentration of CuO was found 7% by wt.

2.3 Experimental Setup

The methanol to gasoline reaction was carried out in a stainless steel fixed bed reactor of 0.0095m i.d. and a length of 0.04 m. The reactor was placed in a cylindrical electrical oven, and the temperature of the catalyst was measured by thermocouple to an accuracy of 1^oC. For each run 1.2 g of the catalyst was used. The reactions was carried out under the following conditions: temperatures(300, 350,400^{o}C), N_2 pressure 10bar, methanol was introduced into the reactor via a simplex pump at WHSV (weight hourly space velocity) =7.75 h^{-1} and time of reaction is 2 hr.

2.4 Desecration of the Setup (MCB 890 Microcatetest unit)

The MCB Microcatetest (supplied by VINCI TECHNOLOGIES) unit is ideal for continuous catalytic reactions of very small amounts of product, within a wide range of temperature and pressure.

The MCB 980 unit consists of 4 parts:

- The liquid input.
- The gas input.
- The reactor.
- The output for the product with separator.

Figure (1) shows the photograph of the Microcatetest unit (MCB 890) used in the current research whilst, the figure (2) shows the Schematic diagram of experimental setup used.

Figure 1: Microcatetest unit (MCB 890)

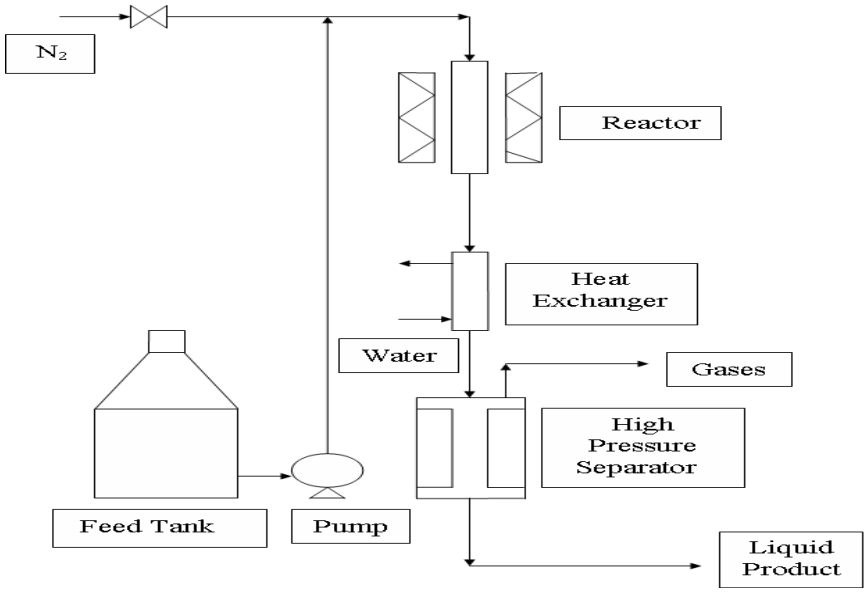

Figure 2: Schematic diagram of experimental setup used.

3. Results and Discussion

3.1 Kinetic Model.

The reaction of methanol to gasoline is given below:

Methanol →Gasoline

The reaction is second order (since reaction is carried out different temperature and constant partial pressure). And the rate law can be written:

$$r_M = -\frac{dC_M}{dt} = kC_M^2 \quad \text{---------- (1)}$$

By integration

$$-\int_{C_{M0}}^{C_M} \frac{dC_M}{C_M^2} = k\int dt \quad \text{---------- (2)}$$

$$\left[\frac{1}{C_M}\right]_{C_{Mo}}^{C_M} = kt \quad \text{---------- (3)}$$

$$\frac{1}{C_M} - \frac{1}{C_{M0}} = kt \quad \text{---------- (4)}$$

$$\frac{1}{C_{M0}(1-x)} - \frac{1}{C_{M0}} = kt \text{----------(5)}$$

$$\frac{1}{C_{M0}}\left[\frac{1}{(1-x)} - 1\right] = kt \quad \text{---------- (6)}$$

$$\frac{1}{C_{M0}}\left[\frac{x}{(1-x)}\right] = kt \quad \text{---------- (7)}$$

$$C_{M0} = \frac{P_{M0}}{RT} \text{----------(8)}$$

Where R = 8. 314 J /mol

Arrhenius equation: An equation that represents the dependence of the rate constant k of a reaction on the absolute temperature T:

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \text{---------- (9)}$$

We plot between ln k vs. (1/T), therefore determined the activation energy (E) from the slope of the line, and also determined (A) from intercept of the line.Where Y = ln k, X = (1/T), intercept = ln A, and the slope = - (E/R)

3.2 Kinetic Parameter Estimation

The pre-exponential factor (A) and the activation energy (E) for used catalyst from figures 3,4 and 5by using Polymath software are listed in table 2. In case of CuO/H-Beta catalyst, it has been found that the activation energy required for the reaction is the highest among the catalysts tested. And the table 3 shows the effect of reaction temperature on the conversion and rate constant. And figures 6, 7, and 8 showed the relation between ln kvs. 1/T by using Excel software.

Table 2: The pre-exponential factor (A) and the activation energy (E) for used catalyst

Catalyst	E (J/Mol)	A (1/sec)
H-Beta	59208	87541
CuO/H-Beta	61392	156652
HZSM-5	41570	1575.4

Table 3: Effect of reaction temperature on the conversion and rate constant

T(K)	1/T	H-Beta			CuO/H-Beta			HZSM-5		
		X	K	Lnk	X	K	Lnk	X	K	Lnk
573	0.00175	0.24	1156.73	7.053	0.26	1287	7.160	0.20	915.75	6.819
623	0.0016	0.50	4048.57	8.306	0.55	4948.26	8.506	0.31	1818.92	7.506
673	0.0015	0.61	6684.13	8.807	0.65	7936.42	8.972	0.43	3223.83	8.078

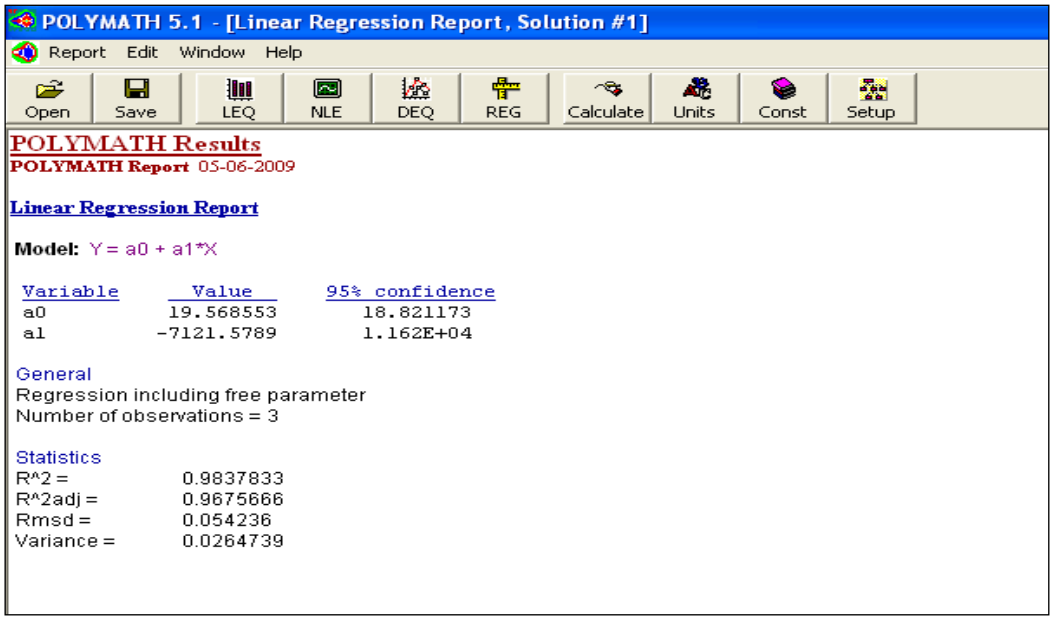

Figure 3: The parameters (a0, and a1) for H-Beta catalyst by using Polymath software.

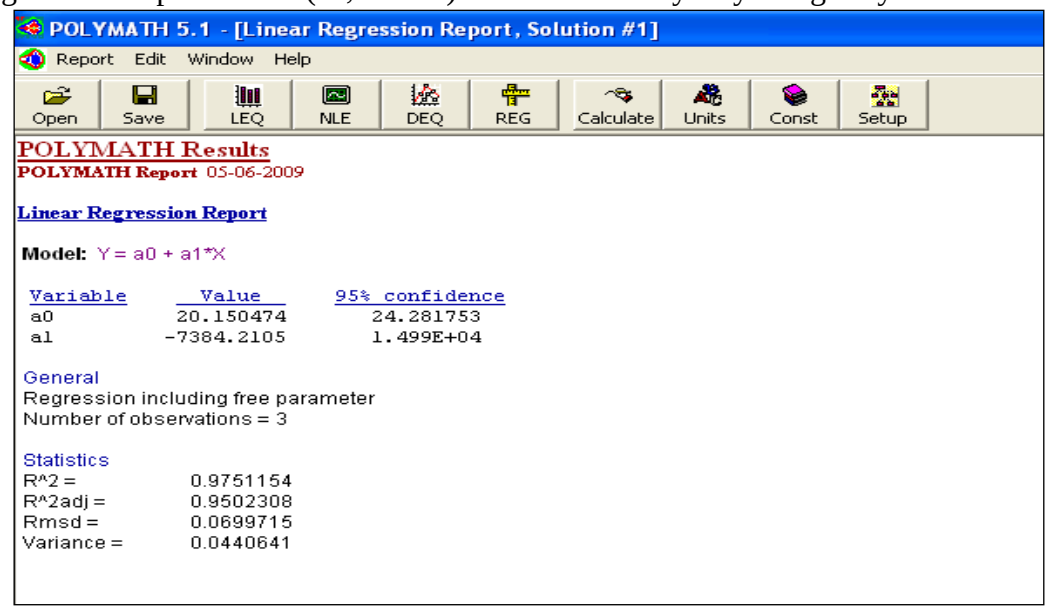

Figure 4: The parameters (a0, and a1) for CuO/H-Beta catalyst by using Polymath software.

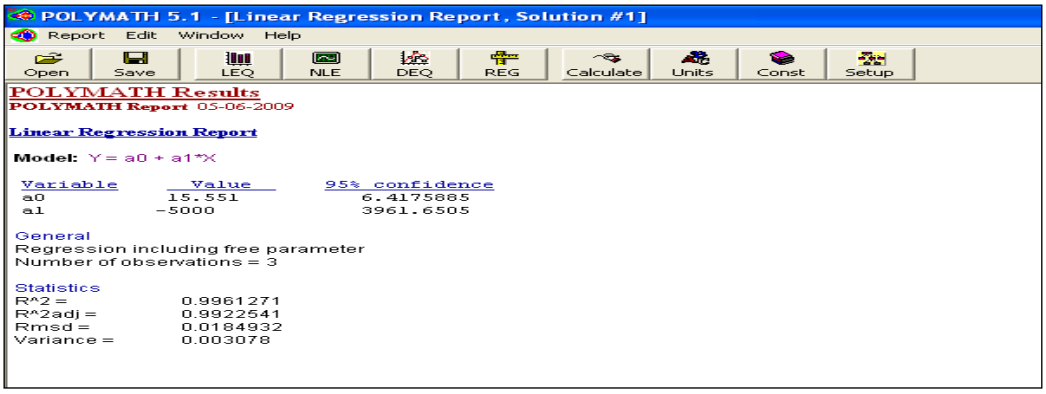

Figure 5: The parameters (a0, and a1) for HZSM-5 catalyst by using Polymath software**.**

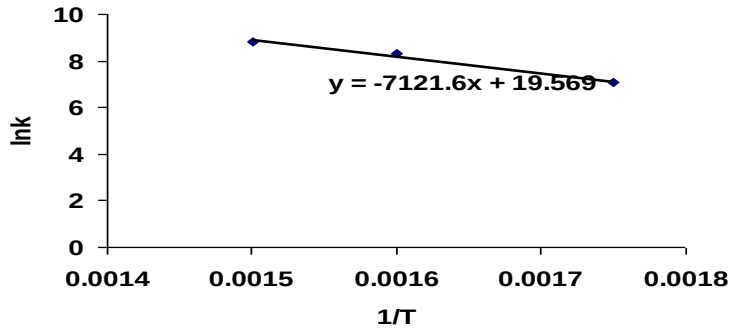

Figure 6: The relation between ln k vs. (1/T) for H-beta catalyst by using Excel software**.**

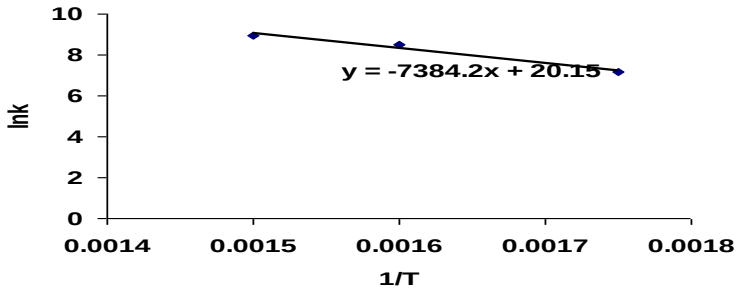

Figure 7: The relation between ln k vs. (1/T) for CuO/H-Beta catalyst by using Excel software.

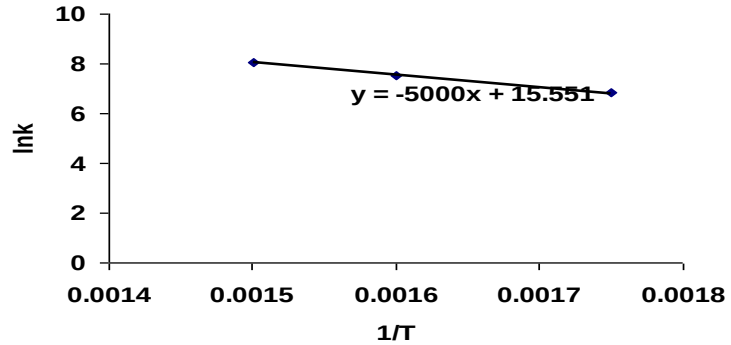

Figure 8: The relation between ln k vs. (1/T) for HZSM-5 catalyst by using Excel software.

4. Conclusions

In the present study, Kinetic Model ofcatalytic conversion of methanol to gasoline over H-Beta, CuO/H-Beta, and HZSM-5 were investigated. From the results, the following conclusions are obtained:

1. A higher amount of methanol was converted to hydrocarbons of the gasoline range before the catalyst completely deactivated.The present investigation suggests that incorporating CuO into H-Beta significantly enhances the hydrocarbon yield. It was concluded that new active sites were created on the surface of the catalyst, which were highly selective to hydrocarbons of the gasoline range.
2. The activation energies have been found of the order of 59208 J/mol with H-Beta catalyst, whilst, in case of H-ZSM5 the activation energy was found nearly 41570 J/mol, also the energy of CuO/H-Beta catalyst was 61392 J/mol.In case of CuO/H-Beta catalyst, it has been found that the activation energy required for the reaction is the highest among the catalysts tested.

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