Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 106 (2005) 271–274

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Production of gasoline range hydrocarbons from catalytic reaction of methane in the presence of ethylene over W/HZSM-5

Kusmiyati [1], Nor Aishah Saidina Amin *

Department of Chemical Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor, Malaysia

Available online 22 August 2005

Abstract

The catalytic conversion of a methane and ethylene mixture to gasoline range hydrocarbons has been studied over W/HZSM-5 catalyst. The effect of process variables, such as temperature, percentage of volume of ethylene in the methane stream and catalyst loading on the distribution of hydrocarbons was studied. The reaction was conducted in a fixed-bed quartz-micro reactor in the temperature range of 300–500 °C using percentage of volume of ethylene in methane stream between 25 and 75% and catalyst loading of 0.2–0.4 g. The catalyst showed good catalytic performance yielding hydrocarbons consisting of gaseous products along with gasoline range liquid products. The mixed feed stream can be converted to higher hydrocarbons containing a high-liquid gasoline product selectivity (>42%). Non-aromatics C_5–C_{10} hydrocarbons selectivity in the range of 12–53% was observed at the operating conditions studied. Design of experiment was employed to determine the optimum conditions for maximum liquid hydrocarbon products. The distribution of the gasoline range hydrocarbons (C_5–C_{10} non-aromatics and aromatics hydrocarbons) was also determined for the optimum conditions.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Gasoline range hydrocarbons; Catalytic conversion; Methane and ethylene mixture; Design of experiment; Optimum condition

1. Introduction

An excess consumption of petroleum resources has become significantly critical problems that may lead to acute energy crisis. Utilization of natural gas and coal has been considered as an effective way to reduce the dependence on liquid oil consumption. The transformation of methane (the main component of natural gas) to useful higher hydrocarbons and fuel can be performed by indirect and direct processes, which are carried out with and without passing through the syngas formation, respectively. Recently, the manufacture of synfuels from natural gas is available for large scale as demonstrated by the MTG plant and the Fischer–Tropsch (FT) by using indirect process technologies. Nevertheless, many attempts are being made to convert natural gas into liquid hydrocarbons by the direct method without passing through the intermediate syngas formation [1]. The direct conversion of methane to C_2 hydrocarbons via oxidative coupling of methane (OCM) has attracted academic and industrial interests due to its potential to be an effective method to utilize natural gas for industrial feedstocks. However, the usefulness of this process has been limited so far as it has low methane conversion and/or low hydrocarbons selectivity [2]. An approach to overcome the limitation of OCM process was reported and it consisted of a two-step process [3]. In the first step, methane or natural gas is converted into lower olefins, which is transformed

---

Abbreviations: ANOVA, analysis of variance; BET, Brunauer–Emmet–Teller; CCD, central composite design; DF, degree of freedom; FID, flame ionization detector; FT, Fischer–Tropsch; GC, gas chromatography; MS, mean square; MTG, methanol to gasoline; OCM, oxidative coupling of methane; RSM, response surface methodology; R^2, the coefficient of determination; Si/Al, silicon to aluminium ratio; SS, sum of squares; SSE, sum of squares due to residuals; SSR, sum of squares due to regression; SST, total of sum of squares; TCD, thermal conductivity detector; ZSM-5, zeolite secony mobil five

* Corresponding author. Tel.: +60 7 5535588; fax: +60 7 5581463.
E-mail address: noraishah@fkkksa.utm.my (N.A.S. Amin).

[1] Present address: Department of Chemical Engineering, Faculty of Engineering, Muhammadiyah University of Surakarta, UMS, Pabelan, Surakarta 57102, Indonesia.

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.145

directly into gasoline range hydrocarbons over a pentasil zeolite catalyst. More recently, Alkhawaldeh et al. [4] reported the conversion of methane into higher molecular weight hydrocarbons. In their study, methane is first converted into acetylene, which is followed by hydrogenation into ethylene. Then, the ethylene in a feed mixture comprising of methane was reacted over a catalyst to produce higher molecular weight hydrocarbons. It is therefore of great practical interest to convert dilute ethylene without being separated from the methane streams into a much less volatile product(s), such as gasoline hydrocarbons. In another development, the conversion of methane to higher hydrocarbons in the presence of ethylene proceeded over silver cations-loaded H-ZSM-5 (Ag/H-ZSM-5) [5]. Due to the increasing interest in the production of sulfur-free transportation fuels via lower olefins oligomerization, the optimization study on oligomerization of feed mixture containing methane and ethylene to produce higher hydrocarbons in the gasoline range over W/HZSM-5 is reported in this paper. The effect of process variables, such as temperature, percentage of volume of ethylene in the methane stream and catalyst loading on the distribution of hydrocarbons was studied according to statistic method with the application of design of experiment utilizing the STATISTICA software (Version 6.0; Statsoft Inc.).

2. Experimental procedure

2.1. Catalyst preparation

The 2 wt.% W/HZSM-5 catalyst was prepared by impregnation method. NH_4ZSM-5 ($SiO_2/Al_2O_3 = 30$; Zeolyst international Co. Ltd.) was converted to HZSM-5 by calcinations at 500 °C for 4 h. It was then impregnated with calculated amount of the aqueous solution of ammonium tungstate $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ (A. R.). The sample was dried at 110 °C overnight and calcined at 550 °C for 5 h. The catalyst was crushed and sieved into the size of 35–60 mesh for catalytic testing.

2.2. Activity testing

Catalytic testing was carried out at atmospheric pressure in a fixed-bed continuous flow system with a quartz reactor of 9 mm internal diameter and 300 mm length. Before reaction, the catalyst was pretreated in a flow of nitrogen at 100 ml min^{-1} for 1 h at 550 °C. A gas mixture comprised of CH_4, C_2H_4 and N_2 (N_2 was used as internal standard) was introduced into the reactor containing the catalyst. Catalytic reactions were performed with different reaction variables based on central composite design (CCD) method. The gaseous products was analyzed by an on-line HP 5890 series II GC-TCD equipped with Porapak Q and molecular sieve 5A columns for separation of N_2, CH_4 and C_2H_4, while UCW 982 12% and DC 200 26% columns were used to separate the lower hydrocarbons including C_3–C_5 hydrocarbons. The liquid products comprised of C_5^+ non-aromatics and aromatics hydrocarbons were analyzed on FID chromatograph equipped with HP-1 capillary column (Table 1).

Table 1
Properties of HZSM-5 zeolite and W/HZSM-5 catalysts

Properties	HZSM-5	W/HZSM-5
Si/Al ratio	30	30
BET surface area (m^2/g)	400	372
Pore size (nm)	0.53 × 0.56	Not available
Acidity (mmol NH_3/g)	1.251	1.164

3. Results and discussion

The study was performed based on design of experiment (DOE) method. The statistical method of factorial DOE eliminates the systematic errors with an estimate of the experimental error and minimizes the number of experiments [6,7]. A central composite design with three process variables was used. According to the CCD, the total number of experiments conducted is 16 with 2^3 two-level factorial design, two central points and six star points [8]. Each variable consists of three different levels from low (−1), to medium (0) and to high (1). The level value of star point is ±1.287 to make a central composite orthogonal design. The independent variables used in the statistical study were temperature, ethylene concentration in the feed mixture containing methane and ethylene, and catalyst loading. Table 2 presents the independent variables with the operating range of each variable. The levels of the independent variables were chosen based on a previous study reported in the literature [5].

The reaction of methane and ethylene mixture over W/HZSM-5 catalyst produced liquid hydrocarbons with high selectivity to gasoline range. The outlet reactor stream

Table 2
Independent variables with the operating range of each variable

Independent variables	Notations	Levels value				
		−1.287	−1	0	+1	+1.287
Temperature (°C)	X_1	271	300	400	500	529
Ethylene concentration in a methane-ethylene mixture	X_2	0.19	0.25	0.50	0.75	0.82
Catalyst loading	X_3	0.17	0.2	0.3	0.4	0.43

Table 3
An experimental plan based on CCD and the three responses

Run	Variables					
	X_1	X_2	X_3	Y, $S_{C_5^+}$	Y, $S_{C_5-C_{10}\text{ non-aromatics}}$	Y, $S_{\text{aromatics}}$
1	300	0.25	0.20	63.62	20.63	17.97
2	300	0.25	0.40	65.89	25.54	18.06
3	300	0.75	0.20	80.13	57.15	19.86
4	300	0.75	0.40	75.53	54.35	18.42
5	500	0.25	0.20	45.60	12.57	20.21
6	500	0.25	0.40	42.60	14.79	24.58
7	500	0.75	0.20	43.80	24.57	18.12
8	500	0.75	0.40	49.10	29.77	19.90
9	271	0.50	0.30	85.70	59.53	29.57
10	529	0.50	0.30	70.40	12.59	47.54
11	400	0.18	0.30	60.31	20.73	11.34
12	400	0.82	0.30	70.67	49.67	20.53
13	400	0.50	0.17	66.62	31.99	22.49
14	400	0.50	0.43	76.69	39.70	25.54
15	400	0.50	0.30	83.60	53.25	30.26
16	400	0.50	0.30	83.60	53.32	30.27

X_1, temperature (°C), X_2, ethylene concentration in a methane–ethylene mixture; X_3, catalyst loading; $S_{C_5^+}$, selectivities of C_5^+ hydrocarbons; $S_{C_5-C_{10}\text{ non-aromatics}}$, selectivities of non-aromatics (NA); $S_{\text{aromatics}}$, selectivities of aromatics.

comprised of gaseous products (C_3–C_5) and liquid products including C_5–C_{10} non-aromatics and aromatics in addition to heavy hydrocarbons (C_{11}^+). The composition of aromatics was benzene, toluene, ethylbenzene, xylene, tri-methyl benzene and tri-ethyl benzene. A series of statistically designed studies were performed to investigate the effect of independent variable, i.e. temperature, ethylene concentration in a methane–ethylene mixture and catalyst loading to optimize the liquid hydrocarbons, C_5–C_{10} non-aromatics hydrocarbons and aromatics products. In this study, a full central composite design with six star points and two replicates at the center point was used. Table 3 shows the experimental design and the results (observed and predicted values) of the three observed responses.

The relationship between the independent variables and response variable was estimated by using regression analysis program. A central composite is designed to estimate the coefficients of a quadratic model. Eq. (1) presents a quadratic model for predicting the optimal point for the selectivity of C_5^+ liquid hydrocarbons.

$$\begin{aligned} Y_1 = {} & -105.330 + 0.326\,X_1 + 257.391\,X_2 + 515.267\,X_3 \\ & - 201.014\,X_2^2 - 884.270\,X_3^2 - 0.107\,X_1X_2 \\ & + 0.058\,X_1X_3 + 7.150\,X_2X_3 \end{aligned} \tag{1}$$

The regression equation (Eq. (2)) for the selectivity of C_5–C_{10} non-aromatics hydrocarbons is expressed as follows:

$$\begin{aligned} Y_2 = {} & -163.783 + 0.498\,X_1 + 246.383\,X_2 + 417.049\,X_3 \\ & - 0.001\,X_1^2 - 116.781\,X_2^2 - 690.965\,X_3^2 - 0.912\,X_1X_2 \\ & + 0.066\,X_1X_3 - 23.650\,X_2X_3 \end{aligned} \tag{2}$$

Table 4
ANOVA for the second order model equations

	SS	DF	MS	F-value	$F_{(9,6,0.05)}^*$	R^2
C_5^+ hydrocarbon selectivity						
SS regression	3033.92	9	337.10	10.29	4.10	0.9392
SS residual	196.374	6	32.73			
SS total	3230.28	15				
C_5–C_{10} non-aromatics selectivity						
SS regression	4158.53	9	462.06	10.16	4.10	0.9384
SS residual	272.79	6	45.47			
SS total	4431.32	15				
Aromatics selectivity						
SS regression	887.83	9	98.65	4.44	4.10	0.8694
SS residual	133.35	6	22.22			
SS total	1021.18	15				

$F_{(9,6,0.05)}^*$, tabulated F-value at level significance $\alpha = 0.05$.

The regression equation (Eq. (3)) obtained for the selectivity of aromatics hydrocarbons is:

$$\begin{aligned} Y_3 = {} & -12.271 - 0.268X_1 + 187.086\,X_2 + 288.98\,X_3 \\ & - 160.282\,X_2^2 - 514.11\,X_3^2 - 160.282\,X_2^2 \\ & - 514.11\,X_3^2 - 0.045\,X_1X_2 + 0.094\,X_1X_3 \\ & - 20.600\,X_2X_3 \end{aligned} \tag{3}$$

where Y_1,Y_2 and Y_3 are the response variables corresponding to selectivity of C_5^+ liquid hydrocarbons, C_5–C_{10} non-aromatics and aromatics, respectively, and X_1, X_2 and X_3, represent the temperature, concentration of ethylene in a methane–ethylene mixture in the feed and catalyst loading, respectively, as independent variables.

The analysis of variance (ANOVA) for checking the significance of the second-order model equations is tabulated in Table 4. The statistical significance of the second-order model equation is determined by F-value. Generally, the calculated F-value should be greater than the tabulated F-value, if the model is good predictor of the experimental results [9]. The calculated F-value is defined as $MS_{\text{regression}}/MS_{\text{residual}}$, where $MS_{\text{regression}}$ and MS_{residual} are obtained by dividing SSR/DF and SSE/DF, respectively. $F_{(p-1,N-p,\alpha)}$ is the tabulated of the F distribution based on the value of $p-1$ and $N-p$ which are DF for regression and for residual, respectively, at a specified level of significance, α-value. The calculated F-values from the three equations greater than the tabulated F-value, $F_{(9,6,0.05)} = 4.10$ as shown in Table 4, provide evidence that the model fit the experimental data adequately.

Fig. 1 shows the comparison between the observed values with the predicted values. The value of R^2 was determined to evaluate the correlation between experimental and predicted value which yield 0.9392, 0.9384 and 0.8694 for the selectivity of C_5^+ liquid hydrocarbons, C_5–C_{10} non-aromatics (NA) and aromatics hydrocarbons, respectively. These results indicate that the predicted values show good agreement with those of experimental results.

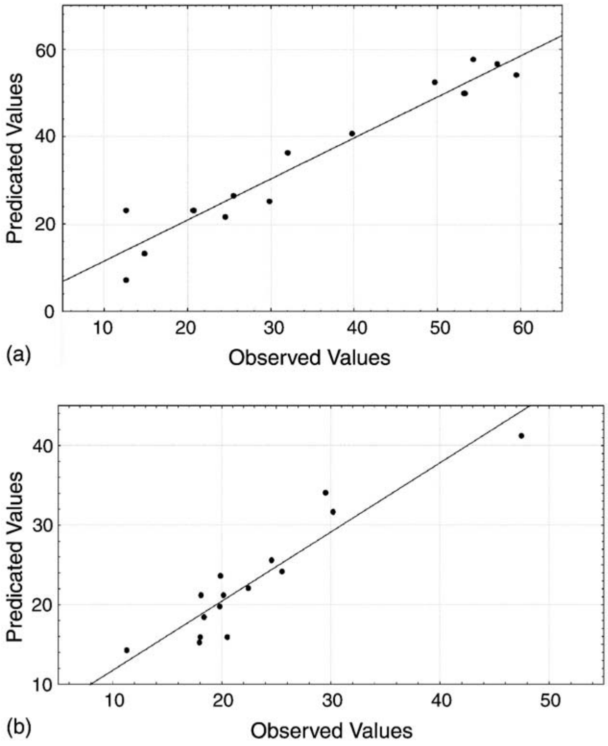

Fig. 1. Correlation of the observed and predicted value for (a) selectivity of C_5–C_{10} non-aromatics hydrocarbons and (b) selectivity of aromatics hydrocarbons.

Finally, a response surface methodology (RSM) was performed to optimize the operating conditions and maximize the selectivity to C_5–C_{10} hydrocarbons. The three-dimensional graph obtained from the calculated response surface is presented in Fig. 2. Three-dimensional response surface plots of reaction temperature and ethylene concentration against C_5–C_{10} hydrocarbons can further explain the results of the statistical and mathematical analyses [10]. It is evident from the plot that C_5–C_{10} non-aromatics hydrocarbons selectivity reached its maximum at reaction temperature being 268 °C with the concentration of ethylene in the methane–ethylene feed being 80.43% (v/v) and catalyst loading being 0.30 g. The maximum value for the C_5–C_{10} non-aromatics hydrocarbons selectivity predicted from the model is 64.78%.

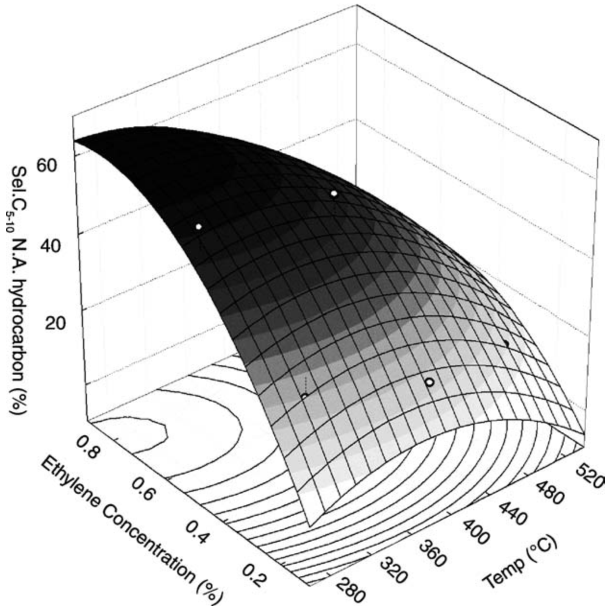

Fig. 2. Response surface methodology for the C_5–C_{10} non-aromatics hydrocarbons selectivity.

4. Conclusions

The reaction of methane–ethylene feed over W/HZSM-catalyst produces gasoline rich hydrocarbons in the C_5–C_{10} non-aromatics and also aromatics range. The central composite design coupled with response surface can predict the effect of reaction variables and their interaction on liquid hydrocarbons selectivity. The model equations obtained were statistically checked by ANOVA and the second order polynomial equations present the experimental results adequately. The optimum predicted value for the selectivity to C_5–C_{10} non-aromatics hydrocarbons was 64.78% obtained at reaction temperature being 268 °C with the concentration of ethylene in the methane–ethylene feed being 80.43% (v/v) and catalyst loading being 0.30 g.

Acknowledgements

The authors would like to express their sincere gratitude to the Ministry of Science, Technology and Innovation, Malaysia (MOSTI) for providing funds to support this research under the Strategic Research project (project no: 09-02-06-0057 or SR 0005/09-07).

References

[1] K.A. Petersen, J.H.B. Hansen, T.S. Christensen, I. Dybkjaer, P.S. Christensen, C.S. Nielsen, S.E.L.W. Madsen, J.R.R. Nielsen, Appl. Catal. A 221 (2001) 379.
[2] S.L.G. Cortes, J. Orozco, B. Fontal, Appl. Catal. A 213 (2001) 259.
[3] V.R. Choudhary, S. Banerjee, D. Panjala, Microporous Mesoporous Mater. 51 (2002) 203.
[4] A. Alkhawaldeh, X. Wu, R.G. Anthony, Catal. Today 84 (2003) 43.
[5] T. Baba, Y. Abe, Appl. Catal. A 250 (2003) 265.
[6] H. Gonzalez, A. Rodriguez, L. Cedeno, J. Ramirez, J. Aracil, Ind. Eng. Chem. Res. 35 (1996) 3964.
[7] Y.S. Ooi, R. Zakaria, A.R. Mohamed, S. Bathia, Biomass Bioenergy 27 (2004) 477.
[8] D.C. Montgomery, Design and Analysis of Experiments, fifth ed., John Wiley and Sons Inc., New York, 2001.
[9] M.K. Mahat, R.M. Illias, R.A. Rahman, N.A.A. Rashid, N.A.N. Mahmood, O. Hassan, S.A. Aziz, K. Kamaruddin, Enzyme Microbial. Technol. 35 (2004) 467.
[10] Q.H. Chen, G.Q. He, M.A.M. Ali, Enzyme Microbial. Technol. 30 (2002) 667.