REACTIVITY OF METHANE OVER Ga-HZSM-5 ZEOLITE CATALYST

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Abstract The Direct conversion of methane to liquid hydrocarbons either over metal catalyst or zeolite catalyst is so far not successful in achieving the methane conversion and liquid hydrocarbons selectivity within the economic range. The present research concern is directed towards modifying HZSM-5 zeolite catalyst with the oxidative element to produce an active bi-functional oxidative-acid catalyst. This modification method has shown an improvement in the catalytic activity and product selectivity. The HZSM-5 zeolite catalyst was modified by an acidic ion exchange method to produce the Ga-HZSM-5 zeolite catalyst. The effect of different reaction temperatures on the catalytic activity of Ga-HZSM-5 catalyst was studied. Direct oxidation of mixture of methane and oxygen over the catalyst was carried out in a micro packed bed reactor. The liquid and gas products were analyzed by gas chromatography. The optimum reaction temperature at GHSV of 6000 hr^{-1} was observed at 800°C in order to obtain the optimum output.

KEYWORDS: Ga-HZSM-5, methane, acidic ion exchange, liquid hydrocarbons and liquid yield

Introduction

The direct conversion of natural gas to liquid hydrocarbons has not yet been successfully economized in an inexpensive process. The conversions of methane to gasoline by direct routes are still at low activity and selectivity. These processes are possible if the reaction is carried out by controlled oxidation over a suitable catalyst (Ramli Mat *et al.*, 1999).

The main concern is to modify the ZSM-5 zeolite catalyst framework with suitable oxidative elements so that highly active bi-functional oxidative-acid catalysts could be developed. Recent studies have shown that modification of ZSM-5 zeolite by ion exchange, direct synthesis and wetness impregnation method with metal oxides with different size and chemistry properties were very important to control its acidity and shape selectivity. These modification methods showed an improvement in the catalytic activity and gasoline selectivity (Ernst and Weitkamp, 1989; DiDi, 1998; Han *et al.*, 1994; Ramli Mat *et al.*, 1999; Nor Aishah and Sharif Hussein, 1999).

Gallium is one of the potential metals that could modify the properties of zeolite. Over this catalyst, higher quality gasoline yield from the reaction of methane with O_2 was obtained (DiDi, 1998). Ga loaded on HZSM-5 is claimed to be very efficient for the aromatization of light alkenes and alkanes (Weckhusyen *et al.*, 1998), and has the potential to convert methane to liquid hydrocarbons at

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a high selectivity (Han *et al.*, 1994; DiDi, 1998; Nor Aishah and Sharif Hussein, 1999). In this study, modification of HZSM-5 zeolite catalyst with gallium metal by an acidic ion exchange method to form a bifunctional oxidative and acid catalyst for the conversion of methane to liquid hydrocarbons in a single step catalytic process was carried out. The obtained catalyst, Ga-HZSM-5, might act as a better bifunctional oxidative-acid catalyst than its parent catalyst, HZSM-5 zeolite, and it had tested at different reaction temperatures in a micro packed bed reactor.

Experimental Details

The modified Ga-HZSM-5 catalyst was prepared based on method described by Plank *et al.*, (1974) and Sharifah Bee *et al.*, (1994). The performance of modified Ga-HZSM-5 catalyst for methane conversion was tested using a continuous flow micro packed bed reactor. The reactor was loaded with one gram of catalyst in a stainless steel tube and supported by glass wool. The reactor was first preheated at reaction temperature under 100 ml/min of nitrogen for 1 hour to activate the catalyst. Methane and air were then fed into the reactor with 9 vol.% of oxygen in the feed for every gas hourly space velocity (GHSV). The reactions were studied at different reaction temperatures. The products were separated into liquid and gas fractions through a condenser cooled with ice. Samples of the gaseous product stream were filled and sealed in pre-evacuated glass ampoules. The gas and liquid product were analyzed by a gas chromatography (Perkin Elmer) using HP-1 capillary column.

Results and Discussion

The catalytic results of Ga-HZSM-5 zeolite catalyst for the reaction of methane with 9% vol. of oxygen at gas hourly space velocity (GHSV) of 6000 hr^{-1} under atmospheric pressure is shown in Fig. 1 and given in Table 1.0. The reaction temperature is in the range of 600 to 850°C. The results shown in Fig. 1 clearly indicated that the catalytic activity is strongly dependent on the reaction temperature. Methane conversion increased with increasing temperature, where for the range of temperature tested, the lowest methane conversion corresponds to the lowest temperature. Weckhusyen *et al.*, (1998), Lunsford (1990) and, Yagita *et al.*, (1996) reported that methane activation was a slow process except at high temperature. This lack of reactivity is essentially due to the stability of the bonds linking the carbons to hydrogen.

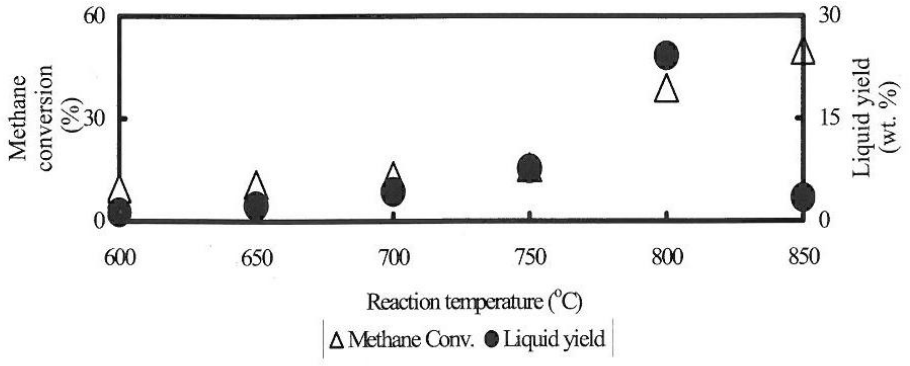

Figure 1. Effect of reaction temperature on methane conversion and liquid yield

As shown in Fig. 1, the liquid yield increased from 600°C up to 800°C, but decreased beyond that. The increase in temperature is believed to lead to an increase in the production of methyl species from methane to C_2-C_4 hydrocarbons and triggers the oligomerization of olefins to C_{5+} hydrocarbons.

Halasz *et al.*, (1996) reported that paraffin are first to dehydrogenate to olefins, which then dimerized or oligomerized to form liquid hydrocarbons over Ga-HZSM-5 catalyst. This result shows that oligomerization of olefins to C_{5+} hydrocarbons increased from 600°C up to 800°C, but decreased when the reaction temperature is higher than 800°C. As tabulated in Table 1, the C_5-C_{10} composition of liquid hydrocarbons for the range tested was around 87% to 95%, and it revealed that oligomerization of C_2-C_4 olefins gas would dominantly produce gasoline range hydrocarbons products.

Table 1. The composition of liquid hydrocarbons

Temperature (°C)	600	650	700	750	800	850
C_5-C_{10} composition of liquid hydrocarbons (wt.%)	94.0	93.6	88.8	87.5	95.7	90.1
C_{11+} composition of liquid hydrocarbons (wt.%)	6.0	6.4	11.2	12.5	4.3	9.9

The highest liquid yield occurs at 800°C, and as shown in Table 2, the highest C_2-C_4 olefins in the C_2-C_4 hydrocarbons is also encountered at 800°C. Based on these temperature, it shows that 800°C is the optimum reaction temperature for producing C_2-C_4 hydrocarbons and enhanced the dehydrogenation process of C_2-C_4 paraffin gas to C_2-C_4 olefins gas and propelled the oligomerization of olefins to C_{5+} hydrocarbons over Ga-HZSM-5 catalyst. At the reaction temperatures below than 800°C, the liquid yield is low because there is the possibly that cracking dominates over oligomerization.

Although the percentage of C_2-C_4 olefins is more than C_2-C_4 paraffins, the reactivity of oligomerization is suppressed. This indicates that acidity is not the sole characteristic in promoting the cracking function of the zeolite catalyst. Although the acidity in all the samples is constant, the results tabulated in Table 2 demonstrate that temperature is also critical in aggravating the oligomerization function of Ga metal. However at high temperature, the decrement in the liquid yield indicates that the C_2-C_4 hydrocarbons are probably oxidized to form CO_x instead of oligomerized to C_{5+} hydrocarbons.

Table 2. Gas hydrocarbons products over Ga-HZSM-5 at different reaction temperature and GHSV of 6000 hr^{-1}

Temperature (°C)	600	650	700	750	800	850
C_2-C_4 hydrocarbon products (wt. %)						
C_2-C_4 Paraffin	31%	12%	42%	21%	3%	6%
C_2-C_4 Olefins	69%	88%	58%	79%	97%	94%

Conclusion

The production of C_{5+} hydrocarbons over Ga-HZSM-5 catalyst is strongly related to the compositions of paraffin and olefins in the gas hydrocarbons products and the reaction temperature. The result

shows that reaction temperature of 800°C was found to be the optimum reaction temperature for the studied range. Under these conditions, the highest liquid yield was obtained.

References

DiDi, D. A. 1998. Single Step Conversion of Methane to Gasoline: Effect of Metal Loaded HZSM-5 Zeolite Catalysts. Universiti Teknologi Malaysia. Msc Thesis.

Ernst, S. and J. Weitkamp. 1989. Oxidative Coupling of Methane Using Zeolite-Based Catalyst. In Imarisio, G., M. Frias and J. M. Bemtgen. Hydrocarbons Source of Energy. London: Graham & Trotman Ltd. 461-469 pp.

Halasz, J., Z. Konya, A. Fudala, A. Beres and I. Kiricsi. 1996. Indium and Gallium Containing ZSM-5 Zeolites: Acidity and Catalytic Activity in Propane Transformation. Catalysis Today 31:293-304.

Han, S., D. J. Maternak, R. E. Palermo, J. A. Pearson and D. E. Walsh. 1994. Direct Partial Oxidation of Methane over ZSM-5 Catalyst: Metals Effects on Higher Hydrocarbon Formation. Journal of Catalysis 148:134-137.

Lunsford, J. H. 1990. The Catalytic Conversion of Methane to Higher Hydrocarbons. Catalysis Today 6(3):235-259.

Nor Aishah Saidina Amin and Sharif Hussein Sharif Zein. 1999. Screening of Metal Loaded HZSM-5 Zeolites Catalyst for Single Step Conversion of Methane to Liquid Hydrocarbon. WEC Proceeding, K. Lumpur. 223-227 pp.

Plank, C. J., E. J. Rosiniski and A. B. Schwartz. 1974. Method for Producing Zeolites. UK Patent 1402981.

Ramli Mat, Nor Aishah Saidina Amin, Zainab Ramli and W. Azelee W. Abu Bakar. 1999. Preparation, Characterization and Catalytic Studies of Boron-HZSM-5 Zeolite for Methane Conversion to Higher Hydrocarbons. WEC Proceeding, K. Lumpur. 249-254 pp.

Sharifah Bee Abdul Hamid, E. G. Deroune, G. Demortier, J. Riga and Mohd Ambar Yarmo. 1994. State, Activation and Migration of Gallium in Ga/H-MFI(Si/Al) Propane Aromatization Catalysts. Applied Catalysis A. General 108:85-96.

Weckhusyen, B. M., D. Wang, M. P. Rosynek and J. H. Lunsford. 1998. Conversion of Methane to Benzene over Transition Metal Ion ZSM-5 Zeolites. Journal of Catalysis 175:338-346.

Yagita, H., A. Ogata, A. Obuchi, K. Mizuno, T. Maeda and K. Fujimoto. 1996. Catalytic Dehydrogenative Coupling of Methane on Active Carbon. Effect of Metal Supported on Active Carbon. Catalysis Today 29:433-436.