

CONVERSION OF METHANE TO GASOLINE RANGE HYDROCARBONS OVER W/HZSM-5 CATALYST: EFFECT OF CO-FEEDING

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Abstract

The conversion of methane in the presence of co-feedings into hydrocarbons in gasoline range over W/HZSM-5 catalyst has been studied in a fixed bed reactor at atmospheric pressure. The effect of CH₄/C₂H₄ ratio in the methane and ethylene feed shows that the fraction of gasoline hydrocarbon (C₅⁺ aliphatics and aromatics) in the product distributions increased with high ethylene concentration. The effect of loading W into HZSM-5 catalyst for the conversion of methane and ethylene (ratio CH₄/C₂H₄=86/14) shows that W/HZSM-5 has higher conversion and higher resistance towards deactivation than that on HZSM-5. The influence of temperatures (250-450 °C) on the conversion of methane and ethylene feed shows that increasing temperature, the selectivity to aromatic products increased. In addition, the conversion of methane with co-feeding of methanol and mixtures of ethylene and methanol were also studied. The result shows that the production of C₅⁺ aliphatics increase with the introduction of ethylene and methanol into the methane feed.

Keywords: methane, gasoline, W/HZSM-5 catalysts, co-feeding

1. Introduction

The catalytic activation of methane, the main component of natural gas is important since it can be converted into higher hydrocarbons. The formation of synfuels from natural gas appears to be interesting. Current process available is by indirect process in a large commercial scale (Aguiar *et al.*, 2005). The first is the trans-formation of natural gas into synthesis gas (CO + H₂), by a steam reforming process, autothermal reforming or partial oxidation. The synthesis gas undergoes a Fischer-Tropsch reaction, forming hydrocarbons in the diesel and petrochemical naphtha range, in a route known as traditional gas-to-liquid (GTL), as it transforms gas into liquid derivatives. The second is the transformation of natural gas into synthesis gas, as in the previous example, but this, however, reacts to form other gases, i.e. methanol. Then methanol is transformed to gasoline by using a methanol-to-gasoline (MTG). The MTG process yields high octane gasoline that is rich in aromatics (Lunsford, 2000).

A few studies have been reported on the direct conversion of methane into higher hydrocarbons or motor fuels. The direct conversion transformation of methane to aromatics has attracted increasing attention. However, the process has limitation due to serious coke formation leading to deactivation of the catalyst at a temperature as high as 973 K and under non oxidative condition (Szoke and Solymosi, 1996). Conversion of methane in the presence of small amounts of light hydrocarbons into higher hydrocarbons rich in aromatics under non-oxidizing conditions over Mo-zeolite at low pressures (1–2 atm) has been reported by Pierella *et al.* (1997). In the previous study, Alkhawaldeh *et al.* (2003) converted methane into higher molecular weight hydrocarbons. Methane is first converted into acetylene. Acetylene is then either mixed with methane and converted directly into higher molecular weight hydrocarbons over metal-loaded zeolites or hydrogenated into ethylene over HZSM-5 where ethylene in a feed mixture comprising methane is then reacted over a catalyst to produce higher molecular weight hydrocarbons.

In the present study, the conversion of methane in the presence of ethylene and methanol respectively was investigated for the production of higher hydrocarbon products in the gasoline range. The introduction of co-feeding methanol and ethylene into the feed methane is also reported.

2. Experimental Procedure

2.1. Catalyst preparation

The 2 wt. % W/HZSM-5 catalyst was prepared by impregnation method. The HZSM-5 zeolite (SiO₂/Al₂O₃=30) (commercially available from Zeolyst international Co. Ltd) was impregnated with a calculated amount of the aqueous solution of ammonium tungstate (NH₄)₆H₅[H₂(WO₄)₆].H₂O (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. Catalytic activity

The catalytic reaction was carried out in a fixed bed continuous-flow system. The schematic diagram of the experimental setup is shown in Figure 1. The reactor was 15 cm long, 9 mm internal diameter made up of stainless steel. The reactor was heated up by means of an electric furnace at the temperature range between 250 and 450 °C at $p=101$ kPa. The catalyst was placed in the middle of the reactor and supported by quartz wool. Prior to the catalytic reaction, the catalyst was preheated in situ in a flow of nitrogen for one hour at reaction temperature to activate the catalyst. A feed consisting of methane and ethylene mixtures was flowed into the reactor at a GHSV of 1200 ml/g h with a $\text{CH}_4/\text{C}_2\text{H}_4$ molar ratio of 80/20 and 14/86, respectively. In the case of methanol as co-feed, the methanol was added at a flow rate of 5 ml/h into methane-ethylene feed by using a syringe pump (model A-99 EZ Razel Scientific Instrument, Inc.). In another case, the reaction was carried out using methane and methanol as a feed. The GHSV of methane was 1200 ml/g.h and flow rate of methanol was 5 ml/h. The gases leaving the reactor were cooled in a water bath. The uncondensed gaseous products were analyzed by means of a on-line gas chromatograph (GC) type HP 5890 series II using a TCD. The GC equipped with two columns Porapak Q and molecular sieve 5A for separation of N_2 , CH_4 , 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 which accumulated over a reaction time comprising of C_5^+ aliphatics and aromatics hydrocarbons were analyzed on a flame ionization detector (FID) chromatograph using HP-1 capillary column.

3. Results and discussion

Table 1 shows a comparison of products distribution obtained from reacting methane and ethylene in the feed at high ethylene concentration (molar ratio $\text{CH}_4/\text{C}_2\text{H}_4$:10/80) and low ethylene concentration (86/14), respectively over W/HZSM-5 catalysts at 400 °C and atmospheric pressure. As can be seen, the products reaction consisted of C_2 - C_4 alkanes (ethane, propane, butane,); C_2 - C_4 alkenes (ethylene, propylene); C_5^+ aliphatics and aromatics including benzene, toluene, ethyl benzene, trimethyl benzene, isopropyl benzene, and xylene.

The effect of $\text{CH}_4/\text{C}_2\text{H}_4$ ratio on the distribution of products shows that a decrease of ethylene concentration in the feed decreases the fraction of higher hydrocarbons (C_5^+ and aromatics) content in the product. When high ethylene concentration ($\text{CH}_4/\text{C}_2\text{H}_4$ ratio of 10/80) was fed, the percentage of higher hydrocarbons (C_5^+ and aromatics) and lighter hydrocarbons (C_2 - C_4 alkenes and alkanes) products were 70.20 % and 29.8 %, respectively. At low ethylene concentration in the feed ($\text{CH}_4/\text{C}_2\text{H}_4$ molar ratio=86/14), the percentage of higher hydrocarbons was lower to 47.61 % while the lighter products increased to 52.9 %. The result is in agreement with the results reported by Anunziata *et al.* (1999). They reported the C_1 + LPG conversion to higher hydrocarbon and aromatic products over Zn-ZSM-11 at GHSV (LPG) = 810 ml/g h and 450 and 550 °C, respectively. The results of the reaction of methane and methanol over W/HZSM-5 catalyst are summarized in Table 2. As can be seen from Table 2, the gasoline range hydrocarbon, aromatics were the major products from the conversion of methane and methanol. In the presence of ethylene, the heavy hydrocarbons of 47.61 % were obtained while the introduction of methanol to the feed increased the fraction of heavy hydrocarbons (67.9 %). The fraction of C_5^+ aliphatics (12.3 %) was observed from the reaction of methane and methanol, with the presence of ethylene in the methane feed, the fraction of C_5^+ aliphatics was lower (7.31 %).

The proposed mechanism of the transformation of methane and methanol to gasoline boiling range might be explained by the following mechanisms. Methanol is first dehydrated to dimethyl ether (DME) which is then converted to light olefins (Zaidi and Pant, 2004). Then, methane and light olefins react to form C_2^+ carbenium ions which undergo the formation of higher hydrocarbons as has been proposed by Pierella *et al* (1997). The reaction of ethylene with methane yielded propylene which is an intermediate molecule for the production of higher hydrocarbons as suggested by Baba and Abe (2003).

The percentage of C_5^+ aliphatics of 20.7% was observed with the adding of methanol to methane and ethylene feed. When methane and ethylene was used as feed, C_5^+ aliphatics was 12.3 %. This results suggest that the introduction of methanol to the mixture of methane and ethylene is intend to generate the carbenium ions which help to initiate the reaction and produce heavier components that is in accordance with the result reported by Alkhawaldeh *et al.* (2003).

The influence of temperature on the products distribution at GHSV ($\text{CH}_4 + \text{C}_2\text{H}_4$) = 1200 ml/g h and a molar ratio of CH_4 : C_2H_4 in the feed = 86:14 (v/v), over W/HZSM-5 is shown in Figure 2. The C_2H_6 , C_4H_{10} and C_5^+ aliphatics selectivity remained very low with the temperature increase whereas the C_3H_8 and aromatics selectivity increased. The C_2H_4 and C_4H_8 decreased with increasing temperature. Higher hydrocarbons product in the gasoline range mainly contains aromatic hydrocarbons in the whole range of the temperature studied. The activation of methane with LPG using zinc-loaded ZSM-11 zeolite has been studied over Zn-ZSM-11 (Anunziata, 1999). The influence of temperature on the products distribution at GHSV (LPG) = 810 ml/g h and LPG molar fraction in the feed $\text{LPG}/(\text{LPG} + \text{C}_1) = 0.15$ showed that the C_2 and $\text{C}_5\text{--C}_6$ yield remained very low with the temperature increase whereas the $\text{C}=2$ and aromatic hydrocarbons yield increased. Aromatic hydrocarbons were the main products in the whole range of temperatures studied, reaching a total of 12 % at 550 °C.

Figure 3 shows the comparison of the conversion of dilute ethylene over time on stream for the HZSM-5 and W/HZSM-5 catalysts at $T = 400\text{ °C}$, $P = 1\text{ atm}$. The W/HZSM-5 shows relatively prolonged time of high conversion. For the first 2 hour the ethylene conversion was almost 100 % over W/HZSM-5 catalyst, whereas this number decreased to 75.91 % for W-loaded ZSM-5. On the other hand non-loaded HZSM-5 shows a high conversion (100 %) at the second hour of operation then it decreases gradually to reach 45.4 % at the end of the reaction. The W/HZSM-5 catalyst shows increased resistance towards deactivation as compared to the HZSM-5 catalyst. Among the catalysts used, Pd/ZSM-5 showed an improved performance in terms of the product distribution and conversion over all the other loaded and non-loaded HZSM-5 catalysts (Alkhaldeh, 2003).

The aromatic content over the HZSM-5 catalyst was 14.93 mol % and W/HZSM-5 catalyst results in an increase in aromatic content up to 36.5 mol % as can be seen in Figure 4. As can be seen in Figure 4, C_5^+ production is observed over W/HZSM-5 and HZSM-5 catalysts. The production of C_5^+ liquid from CH_4 over metal-containing ZSM-5 catalyst has been reported by Han *et al.* (1994). They suggested that the C_5^+ could be produced from methane and O_2 via an MTG mechanism. They proposed mechanisms for the C_5^+ production from CH_4 are as follows: the methane is first converted to CH_3OH which is further transformed to olefins, the initiation for the C_5^+ production.

4. Conclusions

Methane containing ethylene or methanol, respectively, can be converted to higher hydrocarbons in the gasoline boiling range at low temperatures of 250 - 450 °C. Ethylene or methanol, respectively, was used as co-feeding to activate methane to form higher hydrocarbons. The aromatic hydrocarbons are the main reaction products obtained from the reaction of methane-ethylene and methane-methanol, respectively. The effect of $\text{CH}_4/\text{C}_2\text{H}_4$ ratio on the distribution of products shows that a decrease in ethylene concentration in the feed decreases the fraction of higher hydrocarbons (C_5^+ and aromatics) content in the product. The effect of adding co-feeding methanol to the methane and ethylene feed on the distribution of hydrocarbons was also studied. The production of C_5^+ aliphatics increase significantly with the introduction co-feeding methanol to methane and ethylene feed. The influence of temperature on the products distribution shows that with increasing temperature, the selectivity to aromatic products increased. The reaction of methane and ethylene was also studied over the parent HZSM-5 and W/HZSM-5 catalysts. As compared to HZSM-5, W/HZSM-5 has an improved performance in terms of the product distribution and conversion.

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Table 1 Conversion and hydrocarbon distribution at two different $\text{CH}_4/\text{C}_2\text{H}_4$ molar ratios: 10/80 and 86/14, respectively

Compound	$\text{CH}_4 : \text{C}_2\text{H}_4 = 10:80$ (v/v)	$\text{CH}_4 : \text{C}_2\text{H}_4 = 86:14$ (v/v)
Conversion, ethylene %	96.6	97.5
$\text{C}_2\text{-C}_4$ alkanes	24.1	33.01
$\text{C}_2\text{-C}_4$ alkenes	5.7	19.2
C_5^+ aliphatics	49.67	7.31
Aromatics	20.53	40.3

Reaction condition: $T=400^\circ\text{C}$, 1 atm, GHSV= 1200 ml/g.h.

Table 2 Conversion and hydrocarbon distribution for methane+ethylene, methane+methanol, and methane+ethylene+methanol feed

Compound	$\text{CH}_4 : \text{C}_2\text{H}_4 = 86:14$ (v/v)	$\text{CH}_4 / \text{CH}_3\text{OH}^*$	$\text{CH}_4 / \text{C}_2\text{H}_4 / \text{CH}_3\text{OH}^{**}$
Conversion, ethylene %	97.5	-	98.5
$\text{C}_2\text{-C}_4$ alkanes	33.01	25.4	26.2
$\text{C}_2\text{-C}_4$ alkenes	19.2	6.7	15.9
C_5^+ aliphatics	7.31	12.3	20.7
Aromatics	40.3	55.6	37.2

Reaction condition: $T=400^\circ\text{C}$, 1 atm, GHSV ($\text{CH}_4+\text{C}_2\text{H}_4$)= 1200 ml/g.h, *GHSV $\text{CH}_4=1200$ ml/g.h + $\text{CH}_3\text{OH} = 5$ ml/h, ** GHSV ($\text{CH}_4+\text{C}_2\text{H}_4$)= 1200 ml/g.h + $\text{CH}_3\text{OH} = 5$ ml/h.

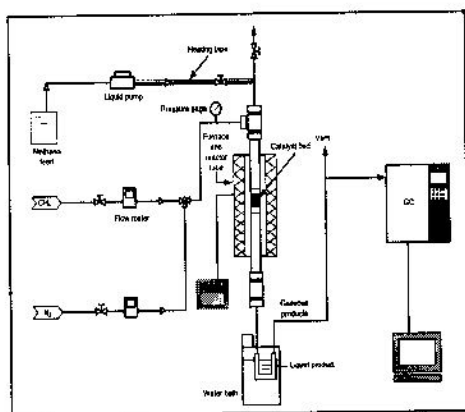


Figure 1 Experimental rig set up

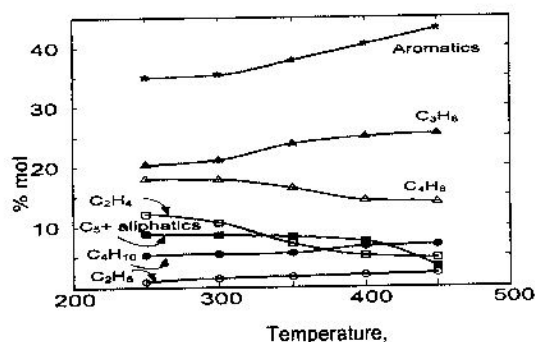


Figure 2 Hydrocarbons products distribution as a function of reaction temperature with methane and ethylene as a feed. GHSV($\text{CH}_4+\text{C}_2\text{H}_4$) =1200 ml/g h, $\text{CH}_4:\text{C}_2\text{H}_4$ molar ratio=86:14.

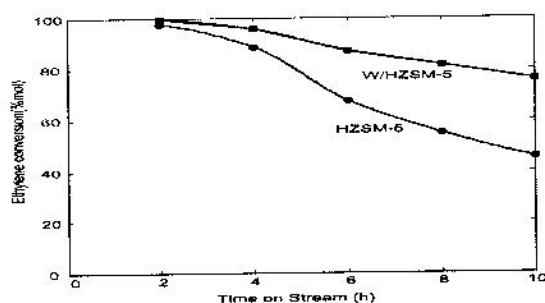


Figure 3 Ethylene conversion with time on stream for the reaction of methane and ethylene over W/HZSM-5 and HZSM-5 catalysts. Reaction condition : $T=400^\circ\text{C}$, GHSV($\text{CH}_4+\text{C}_2\text{H}_4$) =1200 ml/g h, $\text{CH}_4:\text{C}_2\text{H}_4$ molar ratio=86:14

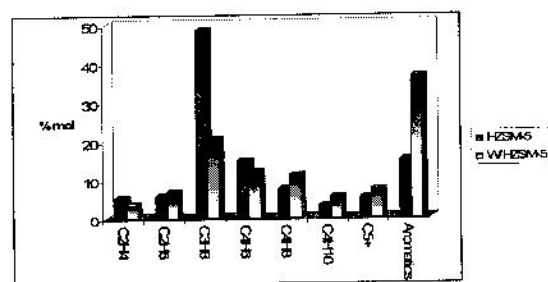


Figure 4 Product distribution for the reaction of methane and ethylene over HZSM-5 and W/HZSM-5 catalysts, $T = 400^\circ\text{C}$, and GHSV($\text{CH}_4+\text{C}_2\text{H}_4$) =1200 ml/g h, $\text{CH}_4:\text{C}_2\text{H}_4$ molar ratio=86:14.