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METHANE CONVERSION TO LIQUID HYDROCARBONS OVER Ga-HZSM-5 ZEOLITE CATALYST

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ABSTRACTS

The HZSM-5 zeolite catalyst was modified by an acidic ion exchange method to produce the Ga-HZSM-5 zeolite catalyst. The effects of different reaction temperatures on the catalytic activity of Ga-HZSM-5 catalyst were studied. Catalytic testing was carried out in a micro packed bed reactor where the catalyst was placed in a stainless steel tube reactor supported by glass wool. The direct oxidation of methane was carried out at reaction temperature, under atmospheric pressure, and 9 vol. % of O₂ in the feed. The catalytic activity was tested with six different reaction temperatures. The liquid and gas products were analyzed by gas chromatography. In the range studied, the optimum reaction temperature to produce the highest yield of liquid hydrocarbons was observed at 800 °C.

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

INTRODUCTION

There are a lot of natural gas reserves around the world, and there is a great interest among many researchers to find the way to produce liquid hydrocarbons from natural gas especially in the gasoline fuel range in an economical process. Natural gas, which contains 60-90% methane, depending on its source, is formed by anaerobic decay (decay in the absence of air) of plants. The other components of natural gas include ethane and propane, along with nitrogen and carbon monoxide. The deposits of natural gas are usually found with petroleum deposits.

Traditionally, there are two competing demands for natural gas. It is used as a clean fuel as in power generation, industrial kilns and furnaces, vehicles fuel, and domestic heating. Natural gas is also demanded as a feedstock for petrochemical and chemical industries (9). In either case, there is a need for an efficient utilization of natural gas for both energy industry as well as feedstock for petrochemical industry. The conversion of natural gas, and in particular, the principal component, methane, to useful products especially into gasoline range has been the subject of intense study over the past decade (7). In general, there are two routes for converting methane to gasoline: indirect and direct. The indirect route is a two-step process whereby natural gas is first converted into synthesis gas (a mixture of H₂ and CO), and then converted into gasoline range. The direct route is the one step process in which the natural gas is reacted with oxygen (or another oxidizing species) to give the desired product directly (1).

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 (10). 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 (1, 2, 4, 6 and 10).

Ernst and Weitkamp (1989) on the study of the conversion of methane using zeolite-based catalysts have reported that the presence of strong acid sites on zeolite is detrimental for the selective oxidation of methane to higher hydrocarbons; instead, deeply oxidized products, CO_x (CO, CO₂) predominate. When the acidity is reduced by exchanging the zeolite with alkali metal cations, the selectivity to higher hydrocarbons is slightly enhanced. Han, et. al, (1994) demonstrated the successful production of higher hydrocarbons from methane oxidation using ZSM-5 zeolite catalyst containing metal oxides. The metal oxides with

sufficiently high dehydrogenation and low olefin oxidation activities reduced the acidity of ZSM-5. As a result, the metal containing ZSM-5 can produce higher hydrocarbons from methane oxidation.

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 O₂ was obtained (1). Ga loaded on HZSM-5 is claimed to be very efficient for the aromatisation of light alkenes and alkanes (13), and has the potential to convert methane to liquid hydrocarbons at a high selectivity (1, 4 and 6). In this study, modification of HZSM-5 zeolite catalyst with gallium metal by 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 will be tested at different reaction temperatures in a micro packed bed reactor.

MATERIALS AND METHODS

Catalyst Preparation - Synthesis of HZSM-5 and Ga-HZSM-5

ZSM-5 zeolite was prepared by direct synthesis based on the method described by Plank, et. al (1974). A gel was prepared by mixing sodium silicate (BDH), aluminum sulfate (Fluka), tetrapropyl ammonium bromide, TPABr (Fluka), metal salts, and water in a stainless steel autoclave. The reaction mixture was prepared according to the following molar composition: Al₂O₃: 20 Na₂O: 70 SiO₂: 7 TPABr: 2200 H₂O. The gel will be heated in an oven at 170 °C for 7 days. After the gel had crystallized, the ZSM-5 solid obtained was then filtered, washed with distilled water, and dried at about 100 °C over night. Finally, ZSM-5 zeolite catalyst was calcined at about 550 °C for five hours to obtain the sodium form of the ZSM-5.

The Na-form so obtained was converted into the NH₄-form by ion exchange using 1M solution of ammonium nitrate. This method was repeated three times to ensure complete exchange of the ions. Finally, after being dried at 100 °C overnight, the catalyst was calcined at 550 °C for five hours under hot airflow and the solid marked as HZSM-5. An acidic ion exchange method as described by Sharifah Bee, et. al (1994) was applied to produce Ga-HZSM-5 zeolite catalyst. For every 5 ml (0.05 M) of gallium nitrate solution, it was stirred with 1 g of HZSM-5. The mixture was refluxed for 4 hours at 100 °C. Then, it was filtered, dried and calcined at 500 °C for five hours and the solid catalyst labeled as Ga-HZSM-5.

Catalytic Testing

The performance of the catalyst for methane conversion was tested using a continuous flow micro packed bed reactor. The reaction was carried out at reaction temperature, under atmospheric pressure by cofeeding the reactant gases (methane and air) into a stainless steel tube reactor (9 mm in diameter and 300 mm in length) mounted vertically, and heated by an electric furnace. 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 of 600, 650, 700, 750, 800, and 850 °C at gas hourly space velocity (GHSV) of 6000 hr⁻¹. The objectives are to analyze the effect of reaction temperature and to determine the optimum reaction temperature of Ga-HZSM-5 catalyst activity. 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 Figure 1 and given in Table 1. The reaction temperature is in the range of 600 to 850 °C. The results shown in Figure 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. Lunsford, (1990), Yagita, et. al (1996) and Weckhusyen, et. al (1998) 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

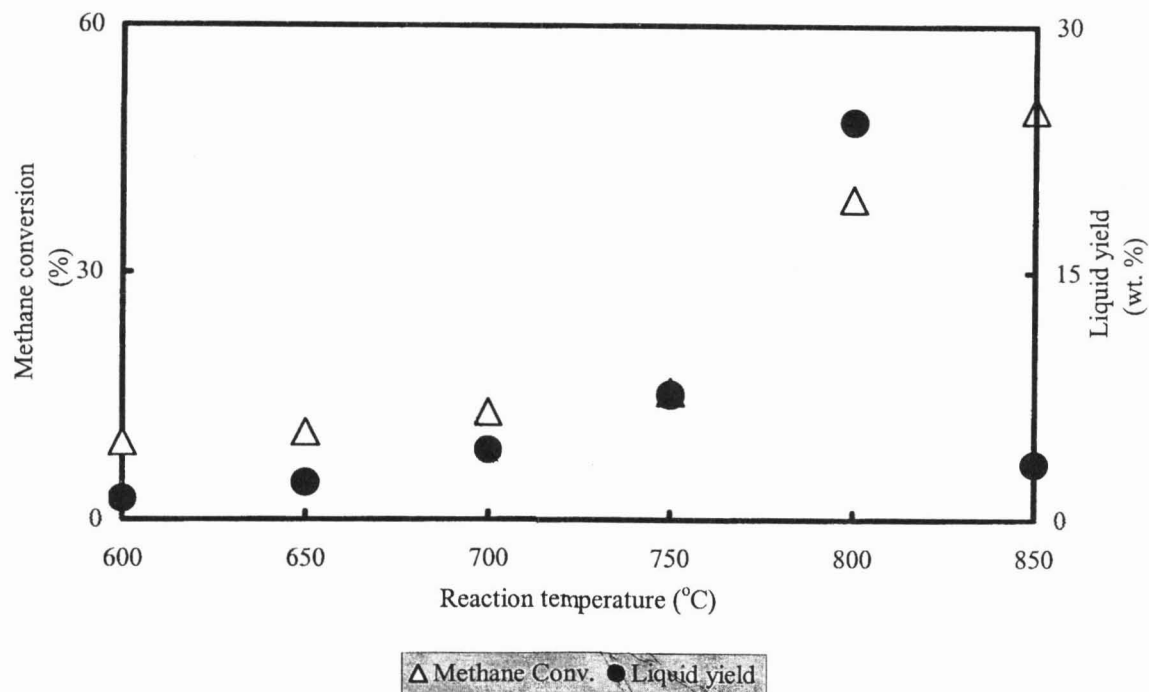


Table 1. The composition of liquid hydrocarbons

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

As shown in Figure 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 C₂-C₄ hydrocarbons and triggers the oligomerization of olefins to C₅₊ 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 C₅₊ 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 C₅-C₁₀ composition of liquid hydrocarbons for the range tested was around 87% to 95%, and it revealed that oligomerization of C₂-C₄ olefins gas would dominantly produce gasoline range hydrocarbons products.

The highest liquid yield occurs at 800 °C, and as shown in Table 2, the highest C₂-C₄ olefins in the C₂-C₄ hydrocarbons is also encountered at 800 °C. Based on these temperature, it shows that 800 °C is the optimum reaction temperature for producing C₂-C₄ hydrocarbons and enhanced the dehydrogenation process of C₂-C₄ paraffin gas to C₂-C₄ olefins gas and propelled the oligomerization of olefins to C₅₊ 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 C₂-C₄ olefins is more than C₂-C₄ 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 C₂-C₄ hydrocarbons are probably oxidized to form CO_x instead of oligomerized to C₅₊ hydrocarbons.

Table 2. Gas hydrocarbons products over Ga-HZSM-5 at different reaction temperature at GHSV = 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%

From the catalytic activity of methane over Ga-HZSM-5 zeolite catalyst, it can be concluded that the liquid yield and the products distribution were dependent on the reaction temperature. The production of C₅₊ 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 condition for the studied range. Under these conditions, the highest liquid yield was obtained.

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