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Methane to Liquid Fuels over Metal Loaded HZSM-5 Catalyst

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Abstract: ZSM-5 zeolite is an acidic catalyst that is highly potential for the conversion of natural gas to liquid fuels. One of the variables that controls the acidity of the ZSM-5 is its Si/Al ratio. Loading the ZSM-5 zeolite with transition metals produces a catalyst with dual function – acidic and oxidative. These two functions need to be balanced to promote certain reactions such as dehydrogenation and oligomerization and to suppress the combustion reaction. The purpose of this study is to modify the ZSM-5 zeolite by substitution of aluminium in the zeolitic framework with an oxidative element, and test its performance for the conversion of methane to liquid fuels. Metal loaded dealuminated ZSM-5 zeolite was prepared by the acidic ion exchange method. Cr, Cu and Ga were chosen based on their role as a metal-oxide catalyst in reforming and dehydrogenation processes. The oxidation of methane was carried out in a micro-packed bed reactor at atmospheric pressure, 800°C, F/W = 10440 ml/g.hr and 9 vol% O_2. The experimental results indicated that methane oxidation over the metal loaded dealuminated ZSM-5 produced gasoline with an encouraging Research Octane Number. The conversion of methane and the selectivity of gasoline obtained demonstrate that these catalysts have the potential to convert methane to C_5+ liquid hydrocarbons.

1. Introduction

HZSM-5 zeolite has Si/Al ratios from 10 to ∞ and heterogeneous hydrophobic surfaces within their intracrystalline structure. Their hydrophobic character increases with decreasing aluminium content. Diffusion limitations affect the apparent reaction rates of related hydrocarbons and explain to some extent the absence of major counter-diffusion limitations in the conversion of light molecules to aromatics by the occurrence of a molecular traffic control effect. This is because of differences in the channel shapes and sizes. The size and shape of the pore opening of zeolite is determined by five factors: configuration of the T (Si or Al) and O atoms relative to each other, silica/alumina ratio, size of the cation, location of the cation, and temperature [1].

The reactivity and the selectivity of molecular sieve zeolite as catalysts are determined by active sites provided by an imbalance in charge between the silicon and the aluminium ions in the framework. Each aluminium atom contained within the framework structure induces a potential active acid site. Three major factors influence the activation process for the final acid catalyst: the type of exchange treatment, the degree of ion exchange, and the conditions of calcination following the exchange treatment.

High acid strength as well as high thermal and chemical stability are desirable properties of these types of catalyst. In general, all these properties are improved when the framework Si/Al ratio is increased. However, a lot of zeolites can only be synthesized with relatively low Si/Al ratios. Thus, they have to be subjected to various post-synthesis dealumination treatments in order to remove Al from the framework and increase its Si/Al ratio.

The properties of the resulting catalysts depend on factors such as the framework Si/Al ratio, the concentration and state of non-framework Al species, and the creation of mesopores. The bulk Si/Al ratio as determined by elemental analysis often does not change because the aluminium that is removed from the framework during dealumination is deposited on the outer surface or in the micropores of the zeolite crystals.

Literature data on the acid dealumination of Al containing Mordenite Framework Inverted (MFI) show a great variety of results [2-4]. Aqueous Hydrogen fluoride (HF) was not used as the dealuminated agent, because it is well known that even diluted HF not only dissolves aluminium from a zeolite framework, but that silicon is also dissolved creating mesopores. Although hydrochloric acid treatment is often used to dealuminate ZSM-5, several researchers use hydrochloric acid ion exchange as a means to convert ZSM-5 to the H-form [5]. The direct incorporation of some transition metals into the ZSM-5 framework is not straightforward [6]; it can be beneficial to follow a secondary synthesis route, in which Al-containing ZSM-5 is first dealuminated via acid treatment to create silanol nests. Subsequently the desired transition metal is inserted into or attached to the silanol nests, creating a transition metal containing ZSM-5.

The direct catalytic conversion of methane, the principal component of natural gas, to liquid fuels and chemicals of commercial importance remains an intensely sought after goal. However, except for hydrogen and methanol production, no large-scale process is currently competitive with petroleum refining [7].

Metal-HZSM-5 catalysts encourage: (a) the oxidation of methane to methyl species, (b) the dehydrogenation of paraffin gas hydrocarbons to olefin forms, and the dehydrogenation of alicyclic liquid hydrocarbons to aromatic forms, and (c) the oligomerization of ethylene and propylene to oligomers (C_5^+) [8]. The purpose of this research is to develop, characterize and test the performance of an acidic ion exchange ZSM-5 zeolite with chromium, copper and gallium for the conversion of methane to liquid fuels.

2. Experimental

2.1 Preparation of the Catalysts

ZSM-5 zeolite with a SiO_2/Al_2O_3 mole ratio of 30 was supplied from Zeolyst International Co., Ltd., Netherlands. The surface area of the zeolite is 400 m^2/g. The zeolite was modified by loading it with chromium (Cr), copper (Cu) and gallium (Ga) using the ion exchange method.

2.2 Characterization and Testing of the Catalysts

Characterizations of these catalysts were performed using Fourier Transform Infrared (FTIR), Silicon Nuclear Magnetic Resonance (Si-NMR). The catalytic performance of the catalysts was tested for methane conversion to liquid hydrocarbons (LHC) via a single step reaction in a fixed-bed micro reactor (Figure 1). Methane with 99.9% purity was reacted with compressed air at atmospheric pressure and a temperature of

800°C at WHSV of 10440 ml.g^{-1}.hr^{-1} with 9 vol% O_2 (CH_4 : O_2 = 10 : 1) The reactor was first preheated to 800°C under a 100-ml/min-nitrogen stream for 2 hour to activate the catalyst. The reaction products were separated into liquid and gas fractions through an ice-trap. A Gas Chromatographer with FID and HP-1 capillary columns analyzed the gas and liquid products.

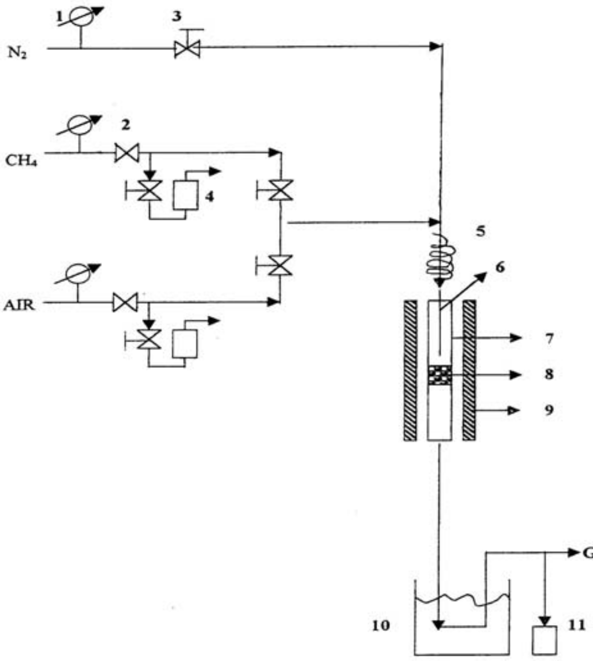

Figure 1. Reactor Set-Up for methane oxidation: 1. Regulator; 2. Safety Valve; 3. Valve; 4. Flow meter; 5. Preheat; 6. Thermocouple; 7. Reactor; 8. Catalyst; 9. Furnace; 10. Ice-Trap; 11. Bottle.

3. Results and Discussion

The Si/Al ratios of zeolite catalysts by Nuclear Magnetic Resonance (NMR) analysis are tabulated in Table 1. The results reveal that the Si/Al ratio of the metal loaded HZSM-5 zeolite catalyst sample is:

HZSM-5 ≈ Cu-ZSM-5 < Cr-ZSM-5 < Ga-ZSM-5

The Si/Al ratio of HZSM-5 is similar with Cu-ZSM-5. This reveals that probably very small amounts of copper atoms manged to replace the aluminium atoms on the zeolite framework. The Si/Al ratio of Ga-ZSM-5 was the highest indicating that more gallium atoms successfully replaced the aluminium atoms on the zeolite framework.

Table 1. Si/Al ratio of zeolite catalysts.

Zeolite	Si/Al (nmr)
HZSM-5	61.6
Cr-ZSM-5	157.9
Cu-ZSM-5	55.1
Ga-ZSM-5	175.3

From the NMR analysis, we predicted that the metal atom radius affected the replacement of aluminium on the zeolite framework. If the metal atom radius was nearly the same as the aluminium atom radius, the metal atoms are easier to replace aluminium atoms on the zeolite framework; Hence, its Si/Al ratio becomes higher. The relation between the atom radius of the metal and Si/Al ratio is shown in Figure 2.

This figure indicates that the radius of a gallium atom (1.41 Å) is close to the radius of a aluminium atom (1.43 Å) while the radius of a copper atom (1.28 Å) is smallest.

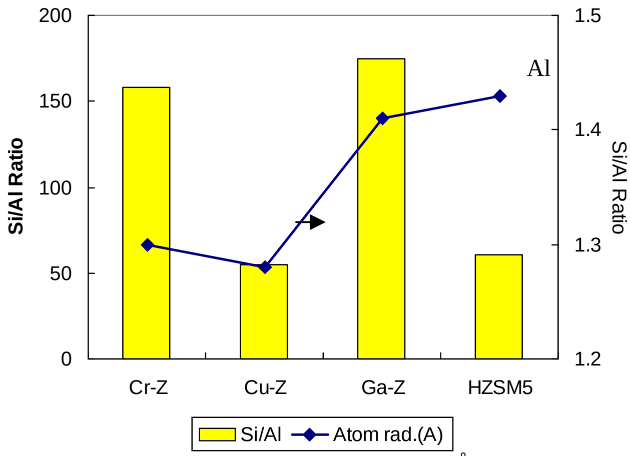

Figure 2. The Relation between Atomic radius (Å) with Si/Al ratio.

The results reveal the FT-IR frequency framework region of the zeolite catalysts, when compared to the parent zeolite (HZSM-5). The frequency showed that the 1099 cm^{-1} band, assigned to the asymmetric stretching of framework Si-O-Si or Si-O-Al bonds [9], did not experience any significant frequency shift or decrease in the intensity. This indicates that there was no significant change in the number of those forming framework bonds.

The ν(OH) region of the IR spectrum of HZSM-5 contains bands at around 3610 and 3740 cm^{-1} [10]. The former has been assigned to an acidic bridging OH while the latter is attributed to terminal SiOH or extraframework silica gel. The band near 3,500 cm^{-1} is attributed to hydrogen bonding between adjacent hydroxyl groups.

The composition of liquid hydrocarbon products over metal loaded HZSM-5 by acidic ion exchange is shown in Figure 3.

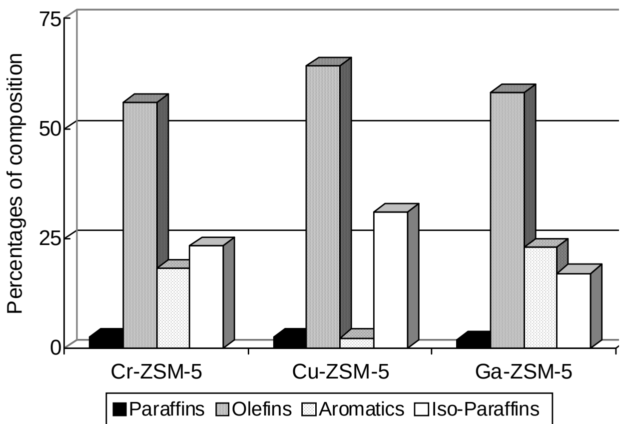

Figure 3. The composition of liquid hydrocarbon products over metal loaded HZSM-5 by acidic ion exchange.

The performance of the catalysts on methane conversion were highest for Cr-ZSM-5 at 46 % followed by 41 % for Ga-ZSM-5. The conversion over Cu-ZSM-5 was lowest at 30 %.

The composition of the liquid hydrocarbon reveal that with the exception of aromatics, paraffins, olefins and iso-paraffins are highest over Cu-ZSM-5. Gallium is well known as a good aromatization agent and this is indicated by the composition of aromatics over Ga-ZSM-5.

Methane Conversion:	CU-ZSM-5 < GA- ZSM-5 < CR- ZSM-5
Paraffins:	CU- ZSM-5 > CR- ZSM-5 > GA- ZSM-5
Olefins:	Cu- ZSM-5 > Cr- ZSM-5 > Ga- ZSM-5
Aromatics:	Ga- ZSM-5 > Cr- ZSM-5 > Cu- ZSM-5
Iso-paraffins:	Cu- ZSM-5 > Cr- ZSM-5 > Ga- ZSM-5

Copper loaded HZSM-5 is the {best? Or 'is a potential} potential catalyst because the highest Iso-paraffins composition is obtained. However, its methane conversion is the lowest. The Iso-paraffins composition over Ga-ZSM-5 by the acidic ion exchange method is the lowest, but the highest aromatic is obtained. According to the Losavic [11] equation for determination Research Octane Number (RON), the RON of all zeolite catalysts are similar; about 69.

The oligomerization and cracking processes are dependent on the zeolite acidity [12-13]. If the zeolite acidity is weak, then the oligomerization of olefins to oligomers is difficult. In contrast, if the zeolite acidity is high, the oligomerization of olefins to oligomers and the cracking of oligomers to gas hydrocarbons are easy.

Meriaudeau et al [14] reported that the optimal oligomers yield resulted from a good balance between the dehydrogenating function of the metal and the acid function of HZSM-5. Thus, the successful production of gasoline depends on oxidation of methane using zeolite catalysts with medium acidity.

The zeolite acidity depends on the amount of aluminium on the zeolite framework. If the amount of aluminium on the zeolite framework decreases, the zeolite acidity will decrease. Therefore, the liquid hydrocarbon composition from methane conversion also depends on the amount of aluminium on the zeolite framework or Si/Al ratio.

The relationship between liquid hydrocarbon and Si/Al ratio is shown in Figure 4.

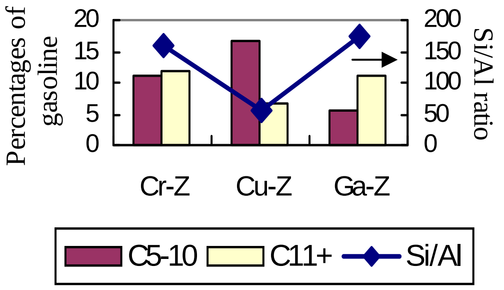

Figure 4. The relation between of Si/Al Ratio with Gasoline Composition.

The result indicated that gasoline composition (C_{5-10}) of Cu-ZSM-5 is highest and Si/Al ratio is lowest. This is because amount of aluminium on zeolite framework is more than other zeolite. Hence, its acidity zeolite is stronger than others.

4. Conclusions

Metal loaded HZSM-5 using the acidic ion exchange method increases liquid hydrocarbons product. Cu loaded HZSM-5 by acidic ion exchange method is a potential catalyst. Types of metal and aluminium acid sites have function on methane conversion to liquid hydrocarbons process.

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