Reaktor, Vol.7 No. 1, Juni 2003, Hal.: 7 - 13

DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS USING HZSM-5 ZEOLITE CATALYST LOADED WITH METAL

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Abstract

Methane is the main component of natural gas and this research provides the platform on the potential of utilizing natural gas, found abundant in Indonesia, to form gasoline. The objectives of the research are to modify HZSM-5 zeolite with a series of transition metals (Cr, Mn, Co, Ni, Cu and Pt) and Ga, and to evaluate the performances of these catalysts for the single step conversion of methane to gasoline. The oxidation of methane were carried out in a micro-packed bed reactor at atmospheric pressure, temperature 800°C, F/W= 10440ml/g.hr and 9 vol% O_2. Metals were loaded into the HZSM-5 zeolite by the wetness incipient impregnation method. The characterization results indicated that the ionic metals (M^{n+}) occupy the H^+ positions of HZSM-5 and metal loaded HZSM-5. Ni-HZSM-5, Cu-HZSM-5 and Ga-HZSM-5 gave a high methane conversion and a high gasoline selectivity. Among the catalysts samples tested, Cr-HZSM-5 showed the highest Research Octane Number (RON=86). These catalysts have the potential to convert natural gas to C_5^+ liquid hydrocarbons provided the oxidation, dehydrogenation and oligomerization functions of the metals are in balance.

Keywords: *direct conversion; methane; liquid hydrocarbons; metal; HZSM-5*

Introduction

Transportation fuels are one of the products of crude oil. The economic importance of gasoline can be further attested to by the considerable growth in demand over the years, which is expected to continue. The technology for the conversion of natural gas to gasoline has recently become commercially viable. Natural gas is an environmentally friendly feedstock because its product is free of sulfur and nitrogen (Maxwel *et al.* 1994).

In general, there are two routes for converting methane to gasoline: direct and indirect. 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. The indirect route is a two-step process whereby natural gas is first converted into synthesis gas (a mixture of H_2 and CO), and then converted into gasoline.

The technology for achieving conversions of methane to transportable liquid hydrocarbon fuel has been demonstrated in New Zealand (methanol to gasoline route) and South Africa (Fischer Tropsch route), but with the current price of oil the process is not economical. This is because the steam reforming of methane to syngas is a high temperature, endothermic, and the most expensive part of the process (Fox *et al.* 1990).

The alternative production of gasoline from methane is oxidative dehydrogenation whereby methane could be converted to ethylene or methane could be partially oxidized and then converted to methanol, which in turn could be reacted over HZSM-5 zeolite catalysts to gasoline range. The main aim of this research is to obtain gasoline by single step conversion of methane over modified HZSM-5 zeolite catalysts.

Zeolite catalysts are predominantly used in their acidic form. An important industrial process fluidized catalytic cracking (FCC) used ZSM-5, based on rare earth exchanged zeolites of faujasite structure with small admixtures of ZSM-5. The majority of the industrially applied transition metal/zeolite catalysts are bifunctional, i.e. strong acid sites and metal sites are present in the same zeolite (Sachtler, 1992).

ZSM-5 has been the preferred zeolite owing to the following reasons (Rao and Gormley, 1990):

a) the medium pore opening (5.5 Å) provides a shape-selective effect, restricting the formation of product molecules to sizes below C_{10}.
b) the highly acidic nature of ZSM-5 helps catalyze oligomerization, cracking, isomerization and aromatization reaction.
c) ZSM-5 is highly resistant to coking owing to the medium pore size, which prevents the formation of coke product.

The function of metal sites is to produce methyl species (Szoke and Solymosi, 1996) and dehydrogenate ethane to ethylene and alicyclic to aromatics (Gnep *et al.* 1988 and Guisnet *et al.* 1991).

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The work reported in the paper focuses on the modification and characterization of zeolite HZSM-5 loaded with transition metals, and the conversion and yield of the catalytic oxidation of methane to gasoline.

Experimental

Modifications of zeolite HZSM-5 was carried out by incorporating chromium, manganese, cobalt, nickel, copper, gallium and platinum into the zeolite HZSM-5 by incipient wetness impregnation. Ni, Cu, Cr, Mn, and Co were representatives of the first row transition metals. Ga and Pt were used as a comparison. Ga is a non-transition metal, while Pt is a third row transition metal (a non-fist row transition metal). Commercial HZSM-5 used was supplied by The P.Q. Company, Seoul, Korea (Si/Al ratio= 30).

Since the crystal structure of zeolite ZSM-5 is complicated, no satisfactory results can be presented by one technique of characterization. Therefore, a number of instruments and complementary analysis techniques are required for complete characterization of these materials. Characterization of each sample was done using X-ray Diffraction (XRD), Temperature Programmer Desorption (TPD), Scanning Electron Microscopy (SEM) combined with Energy Dispersive Analysis of X-rays (EDAX), and Isotherm Adsorption by Accelerated Surface Area and Porosimetry (ASAP).

The final part of the experiment was catalytic testing. Nitrogen is used only to preheat the catalyst at 800°C for 2 hours. The liquid and gas products were analyzed by gas chromatography using a capillary HP-1 column and quantified using a FID detector. A continuous flow micro packed reactor was utilized for the catalytic oxidation of methane as shown in Figure 1.

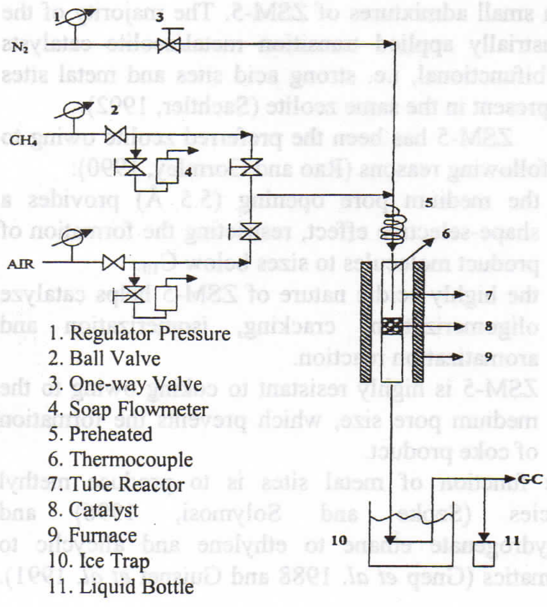

Figure 1. Schematic diagram of the continuous flow micro packed reactor .

The reactor was made of stainless steel tube having internal diameter and length of 9 mm and 300 mm, respectively. One gram of catalyst, placed on a glass wool was loaded in the reactor.

Results and Discussion

Characterization of zeolites

Scanning Electro Microscopy (SEM) provides information about the morphology and the size of the zeolite crystal. The combination of SEM with Energy Dispersive Analysis of X-rays (EDAX) relays information on the zeolite compositions given in Table 1.

Among the first row transition metals, Cr and Cu gave the lowest metal percentage, of 0.22% and 0.3%, respectively. Co-HZSM-5 indicates the highest percentage of metal content (0.8%) among the first row transition metals. The percentage of metal for Ga, which is a metal, is 3.7%, close to Pt (3.7%). This indicated that gallium and platinum have more presence on the zeolite surface.

X-ray diffraction provides information on unit cell parameters and crystallinity of zeolites, as shown in Table 1. Unit cell parameters and crystallinity of zeolites were calculated from XRD Diffractograms. From XRD diffractograms, all metal-HZSM-5 are crystalline and similar to the parent HZSM-5. These phenomena indicated that no drastic change in the crystal structure of metal-HZSM-5 and that metal did not exist in the zeolitic framework.

Table 1 shows that the crystallinity reduced for metal-HZSM-5. Since there is no change in the quantity of silicon and aluminium, the decrease in cryatallinity must be due to the influence of the treatment rather than the thermal and chemical effect. Cr-HZSM-5 has the highest crystallinity overall (94%). Among the first row transition metals, Mn and Cu gave the lowest crystallinity, of 90% and 86% respectively.

The results in Table 1 indicate that the metal loading of HZSM-5 affect the unit cell parameter and volume unit cells. The data show that the unit cell parameters as well as the unit cell volumes do not vary in a consistent pattern with the metal loading. These results are indication that metal ions are dispersed on the surface of the HZSM-5, which probably causes the exchange of H^+ to M^{n+} (metal) to occur. The metal replaces the proton and causes a decrease in Brönsted acidity followed by the enhancement of Lewis acidity due to its character as an electron acceptor, shown as below (Didi, 1998).

Nitrogen adsorption BET method gives information on the surface area, micropore area, micropore volume, and average pore size of zeolite, as shown in Table 1.

Table 1. Characterize of Zeolite Catalysts by SEM, XRD, N_2 Adsorption, and TPD

Sample	SEM	XRD			N_2 ADSORPTION				TPD
	% Mt.	*a* (Å)	Vuc (Å^3)	Crystal linity	S.A. (m^2/g)	M.A. (m^2/g)	M.V. (m^3/g)	A. P.S. (Å)	Acidity (moles/Kg)
HZSM-5	-	21.9	5738.4	100%	439.0	272.4	0.1118	32.5	0.6329
Cr-HZSM-5	0.2	20.0	5279.8	94 %	436.1	243.5	0.1016	30.1	0.5022
Mn-HZSM-5	0.4	19.9	5310.3	90 %	433.8	249.8	0.1036	34.4	0.4987
Co-HZSM-5	0.8	21.0	5564.2	93 %	429.1	241.4	0.1007	34.9	0.4474
Ni-HZSM-5	0.4	21.7	5655.4	93 %	430.0	244.8	0.1018	30.0	0.5411
Cu-HZSM-5	0.3	19.9	5322.5	86 %	429.1	245.5	0.1020	29.9	0.5794
Ga-HZSM-5	3.7	21.0	5556.8	94 %	429.7	247.3	0.1026	35.6	0.4959
Pt-HZSM-5	3.7	19.9	5262.1	90 %	437.2	246.6	0.1026	30.1	0.4576

S.A.= Surface Area (BET); M.A.= Micropore Area; M.V.= Micropore Volume; A.P.S. = Avarage Pore Size

As seen from Table 1, the loading of metals into HZSM-5 decreases the surface area, micropore area, and micropore volume. This means that some of the metal oxide were trapped in the pores or channels of the catalyst. This reduced the pore volume which caused a reduction in nitrogen adsorbed. The existence of metal oxides had reduced the surface area of the catalyst compared to HZSM-5. Among the transition metals, Cu-HZSM and Mn-HZSM5 have the smallest surface area while Cr-HZSM has the largest. The surface area for Ga-HZSM-5 is among the lowest of the samples while the surface area for Pt-HZSM-5 is the largest overall.

Among the first-row transition metals, the pore sizes for Mn-HZSM-5 and Co-HZSM-5 are larger than the pore sizes of HZSM-5 while the pore sizes for Cu-HZSM-5 are smallest. Similarly, Ga-HZSM-5 possesses larger pore sizes than HZSM-5. However, the Pt-HZSM-5 pore sizes are smaller than HZSM-5.

Temperature Programmed Ammonia Desorption gives information on the amount of chemisorbed (acidity), weak acid sites (low temperature) and strong acid sites (high temperature) of the various zeolites, as shown in Table 1. The amount of acid / acidity on a solid is usually expressed as the number or mmol of acid sites per unit weight or per unit surface area of the solid. The acidity of the catalysts was examined by carrying out temperature-programmed desorption of ammonia. From Table 1, the amount of chemisorbed decrease in the following order:

HZSM-5 > Cu-HZSM-5 > Ni-HZSM-5 >Cr-HZSM-5 > Mn-HZSM-5 Ga-HZSM-5 > Pt-HZSM-5 > Co-HZSM-5.

Some researchers (Topsoe *et al.* 1981; Chu and Chang, 1985; Segawa *et al.* 1988) have postulated that the acidity decrease as aluminium is removed from the crystal and increase as aluminium is inserted into the framework of HZSM-5. Koval *et al.* (1996) reported that the acidity decrease with decreasing micropore volume of HZSM-5. However, this trend is not observed in this study.

Table 1 shows that the acidity of metal-HZSM-5 is generally decreased. Since there is no change in the quantity of aluminium in the zeolitic framework, the decreases in acidity must be due to the micropore volume of the zeolite which caused a reduction in ammonia adsorption (Koval *et al.* 1996). Co-HZSM-5 is the least acidic among the samples because the micropore volume of this sample is smallest compared to the other samples.

The metals affected the unit cell parameter and volume unit cells, because metal is dispersed on the surface of the HZSM-5 which probably caused the exchange of H^+ to M^{n+} to occur. HZSM-5 loaded with metals also affected the surface area, micropore area, and micropore volume. All three parameters decrease, because some of the metal oxides covered the outer framework of the catalyst, while other metal oxides blocked the pores of the catalyst. The acidity of metal-HZSM-5 decreased with decreasing micropore volume of zeolite. Except for Co, the samples loaded with the first-row transition metals are more acidic than Ga-HZSM-5 and Pt-HZSM-5.

Effect of temperature and oxygen

The temperature range of HZSM-5 zeolite catalyst pretest performance is between 700 and 900°C. We have neglected the effect of pressure in this study. The reaction is carried out at atmospheric pressure in view of a more simplied process technology when P=1 atm is considered. The conversion of methane under 900°C is the lowest (4.0%). This is because HZSM-5 zeolite catalyst is deactivated at around 900°C (Volter *et al.* 1988). The conversion of methane under 700°C and 800°C is similar, 4.7% and 4.6%, respectively. Larkin and Nordin, 1988 reported that the methane conversion remained constant and gas hydrocarbons (C_2^+) increased if the reaction temperature increased.

The selectivity of gasoline (C_{5-10}) under reaction temperature 800°C and 900°C is similar, 21.6% and 21.7%, respectively. The reaction temperature at 800°C is the optimum condition for methane conversion to gasoline for the range studied.

It is observed that both the methane conversion and the gasoline selectivity gave the highest value.

The results of the catalytic performance of HZSM-5 zeolites catalyst for the reaction of methane with 5%, 7%, 9% and 11%vol. oxygen at 800°C under atmospheric pressure clearly indicated that the catalytic activity is strongly dependent on the oxygen concentration. Increasing the oxygen concentration was the major variable that could be used to increase the methane conversion.

Edwards and Tyler (1988) and Ekstrom (1991) reported that the methane conversion increased and C_2^+ selectivity decreased with increasing oxygen concentration. The result seemed to agree with the result of the present work. The conversion of methane under 11%vol. oxygen was the highest (5.6%), but the selectivity of gas hydrocarbons (C_{2-4}) was lower (2.0%) than 9%vol. oxygen (3.5%). This is because the oxidation of methane to CO_x under 11%vol. oxygen is relatively easier than lower O_2 vol%. The selectivity of CO_x at 11%vol. oxygen is the highest (53.4%). From the results, the conversion of methane as well as the selectivity of CO_x increased if the oxygen is more concentrated. The range of temperature for the pretest performance of HZSM-5 zeolite is between 700°C and 900°C for the conversion of methane to liquid fuels. The range is chosen because no liquid is observed when the temperature is below 700°C (Didi, 1998).

The selectivity of gasoline (C_{5-10}) at 9%vol. oxygen is the highest (22.7%). However, the methane conversion under 9 %vol. oxygen is less than under the 11 %vol. oxygen. The reaction temperature at 800°C and 9%vol. O_2 in the feed is the optimum condition for the range studied.

Catalytic activity of zeolites

The proposed reaction path for methane reaction over HZSM-5 and metal-HZSM-5 catalysts is explained in previous study (Didi, 1998). The reaction of methane with oxygen is almost complete oxidation and CO_2 formation. The initial step should be the methyl radical formation. It is considered that methyl radicals can be oxidized to CO_x if the metal loaded HZSM-5 has a strong oxidation strength and a high presence of metal oxides on the catalyst surface. Another alternative is for the methyl radicals to combine and form C_2H_6. If the amount of oxygen in the feed is in excess, ethane is oxidized to CO_x.

The presence of metal oxides on the zeolite surface increased the amount of metal and oxygen on the zeolite surface. The existence of the metal oxides blocked the pores and reduced the micropore volumes as well as the surface areas. The selectivity of CO_x is dependent on the metal oxides on the zeolite surface and also oxygen concentration. If the amount of oxygen on the zeolite surface increased, the oxidation of methane to CO_x increased. Larkins and Nordin (1988) reported that the presence of transition metal oxide on the surface increased the concentration of surface oxygen and hence the oxidative reaction is facilitated (selectivity of CO_x is increased). However, the existence of the metal oxides also helps the oxidation of methane to methyl species and triggers other reactions such as oligomerization and dehydrogenation.

The presence of transition metal oxide on the surface also increased the concentration of surface metal. The supported metals can produce methyl species via: (Szoke and Solymosi, 1996)

$$CH_4 \ + \ M^{n+} \longrightarrow CH_3^* \ + \ H + M^{(n-2)+}$$

The oligomerization and cracking processes are dependent on the zeolite acidity (Gnep *et al.* 1988 and Guisnet *et al.* 1991). If the zeolite acidity is weak, than 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 C_{2-4} are less difficult.

Meriaudeau *et al.* 1990 studied propane reaction over Ga_2O_3 and ZnO loaded into HZSM-5. They 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. Ga_2O_3 and ZnO are potential catalysts to support dehydrogenation of oligomers to aromatics. Thus, the successful production of gasoline depends on the oxidation of methane over zeolite catalysts with medium acidity.

The result of the catalytic performances of various HZSM-5 zeolites loaded with metals for the reaction of methane with oxygen at 800°C and atmospheric pressure, is given in Figure 2. This figure summarizes the methane conversion and the carbon selectivity toward CO_x (Carbon monoxide CO, Carbon dioxides CO_2), gas hydrocarbons (C_{2-4}), gasoline (C_{5-10}), and kerosene (C_{11-15}) as a function of the various metals loaded HZSM-5.

The conversion of methane and the selectivity of CO_x using HZSM-5 are lowest among the eight samples, of 5% and 42.5%, respectively. This can be attributed to no metal oxide present in the catalyst and it has the largest micropore volume and surface area.

From the effect of acidity, The results depicts that the acidity of HZSM-5 is the highest among the samples (0.6329 moles/Kg). As stated earlier strong acidic sample will encourage oligomerization and cracking process. As a result, the selectivity of C_{2-4} is highest (3.5%) while the selectivity of C_{5-10} as well as the selectivity of CO_x are the lowest for the HZSM-5 sample Figure 2.

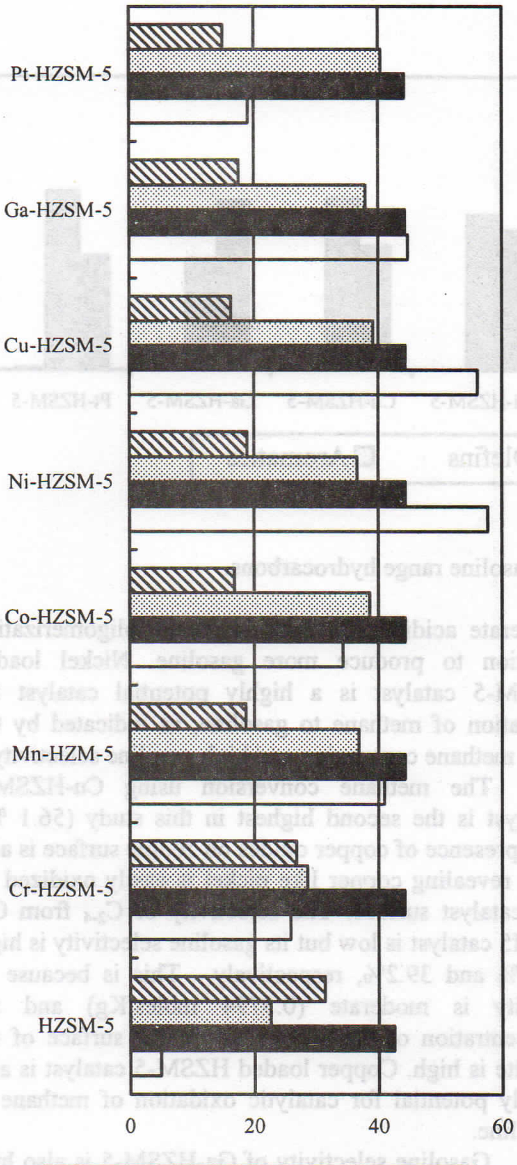

Figure 2. The catalytic performance of various HZSM-5 zeolites loaded with metals for the reaction of methane with 9 vol.% O_2 at 800°C and 1 atm.

The results from Figure 3 indicated that C_{2-4} product gases using HZSM-5 catalyst contain more paraffins, but C_{2-4} product gases using metal-HZSM-5 catalysts contain more olefins. The result supported the study by Gnep *et al.* (1988) and Guisnet *et al.* (1991). Both studies revealed that the dehydrogenation of paraffins to olefins increases when there are more metal species and less aluminium in the zeolite sample.

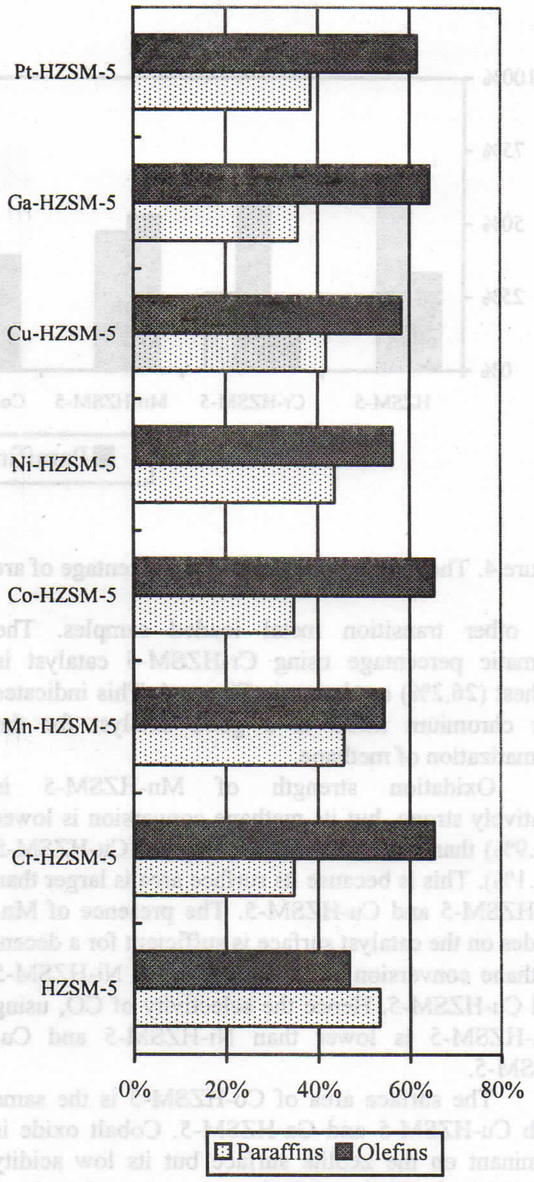

Figure 3. Product gases C_{2-4} from HZSM-5 and various metal-HZSM-5 catalysts.

Effect of metals loaded HZSM-5 on the catalyst activity

The results in Figure 2 clearly indicated that the catalytic performances are strongly dependent on the type of the various metals. Although, the acidity and oxidation strength of Cr-HZSM-5 is relatively strong, its methane conversion is the lowest (25.9%) among the transition metals, due to its small micropore and micropore volume among the other transition metals. This indicates a low presence of Cr oxides on the catalyst surface, hence selectivity of CO_x using Cr-HZSM-5 is lowest than other transition metals. The relatively strong acidity of Cr-HZSM-5 (0.5022 moles/Kg) produces a large amount of C_{2-4} (highest selectivity of C_{2-4}, lowest selectivity of C_{5-10}) among

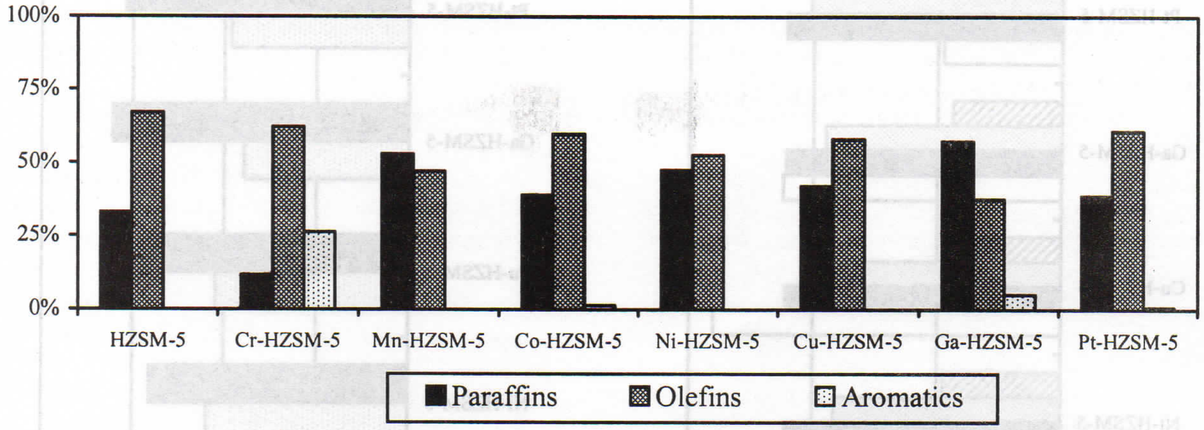

Figure 4. The effect of metals on the percentage of aromatics in gasoline range hydrocarbons.

the other transition metal loaded samples. The aromatic percentage using Cr-HZSM-5 catalyst is highest (26.2%) as shown in Figure 4. This indicates that chromium metal is a good catalyst for the aromatization of methane.

Oxidation strength of Mn-HZSM-5 is relatively strong, but its methane conversion is lower (40.9%) than Ni-HZSM-5 (57.7%) and Cu-HZSM-5 (56.1%). This is because its surface area is larger than Ni-HZSM-5 and Cu-HZSM-5. The presence of Mn-oxides on the catalyst surface is sufficient for a decent methane conversion but still lower than Ni-HZSM-5 and Cu-HZSM-5. Hence the selectivity of CO_x using Mn-HZSM-5 is lower than Ni-HZSM-5 and Cu-HZSM-5.

The surface area of Co-HZSM-5 is the same with Cu-HZSM-5 and Ga-HZSM-5. Cobalt oxide is dominant on the zeolite surface but its low acidity (0.4474 moles/Kg) retards the conversion of methane (34.3%). Selectivity of $C_{2\text{-}4}$ using Co-HZSM-5 is low (0.2%). The acidity of Co-HZSM-5 is the lowest among the samples as indicated in Table 1. Co-HZSM-5 produced aromatics in gasoline range about 1.4 % (see Figure 4), indicating cobalt metal encourages the dehydrogenation of oligomers to aromatics.

The conversion of methane using Ni-HZSM-5 catalyst is the highest (57.7%), due to a large presence of nickel oxides on the catalyst surface. The acidity of Ni-HZSM-5 is moderate (0.5411 moles/Kg) and there is a high nickel oxide concentration on the surface of the zeolite. If the metal oxide increases, the amount of oxygen increases. According to Ekstrom *et al.* (1991) ethene selectivity decreases and methane conversion increases with oxygen concentration. The result indicates a similar trend where selectivity of $C_{2\text{-}4}$ is the lowest (0.1%) among other catalysts. The moderate acidity also encourages the oligomerization reaction to produce more gasoline. Nickel loaded HZSM-5 catalyst is a highly potential catalyst for oxidation of methane to gasoline, as indicated by the high methane conversion and high gasoline selectivity.

The methane conversion using Cu-HZSM-5 catalyst is the second highest in this study (56.1 %). The presence of copper oxides on zeolite surface is also high revealing copper like nickel is easily oxidized on the catalyst surface. The selectivity of $C_{2\text{-}4}$ from Cu-ZSM5 catalyst is low but its gasoline selectivity is high, 0.12% and 39.2%, respectively. This is because its acidity is moderate (0.5794 moles/Kg) and the concentration of copper oxides on the surface of the zeolite is high. Copper loaded HZSM-5 catalyst is also highly potential for catalytic oxidation of methane to gasoline.

Gasoline selectivity of Ga-HZSM-5 is also high (37.9%) but its methane conversion is lower (44.8%) than Ni-HZSM-5 (57.7%). This is because the acidity of Ga-HZSM-5 is lower than Ni-HZSM-5 (see Figure 4) and Ga metal has a weak oxidation strength. On the other hand, oxidation of methane using Ga-HZSM-5 produced aromatics in the gasoline range of about 5.11 % (see Figure 6), indicating that gallium metal encourages the dehydrogenation of oligomers to aromatics.

The selectivity of gasoline using Pt-HZSM-5 is the highest (40.4 %). This is because Pt-HZSM-5 has a moderate acidity (0.4576 moles/Kg). However its methane conversion is lowest (19.1 %) among the other metal-HZSM-5. This revealed that the concentration of Pt-oxide on the catalyst surface is low, curtailing the conversion of methane. Platinum-HZSM-5 also produced aromatics in the gasoline range about 0.69 % (see Figure 6).

Conclusions

The characterization of the metal impregnated HZSM-5 zeolite catalysts revealed the presence of metal oxide on the surface of HZSM-5. The metals are dispersed on the surface of the HZSM-5 which probably caused the exchange of H^+ to M^{n+} to occur and affected the unit cell parameter and volume unit cells. The surface area, micropore area, and micropore volume decreased after metal oxides covered the surface of the catalyst. The micropore volume of HZSM-5 decreased leading to a reduction in the catalyst acidity. The samples loaded with the first-row transition metals are more acidic than the acidity of Ga-HZSM-5 and Pt-HZSM-5.

Metal-HZSM-5 catalysts encouraged: (a) the oxidation of methane to methyl species, (b) the dehydrogenation of paraffins gas hydrocarbons to olefin forms, and (c) the dehydrogenation of alicyclic liquid hydrocarbons to aromatic form, and the oligomerization of ethylene and propylene to oligomers (C_5^+). Ni-HZSM-5, Cu-HZSM-5 and Ga-HZSM-5 catalysts are the most potential catalyst for the oxidation of methane to gasoline for the range studied. Over these catalysts, higher gasoline yields were obtained.

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