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CHARACTERIZATION OF MODIFIED HZSM-5 WITH GALLIUM AND ITS REACTIVITIY IN DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS

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Abstract. The HZSM-5 zeolite catalyst was modified by an acidic ion exchange method to produce the Ga-HZSM-5 zeolite catalyst. The catalytic activity of HZSM-5 and Ga-HZSM-5 were studied at reaction temperature of 800°C and gas hourly space velocities (GHSV) of 7500 hr^{-1}. HZSM-5 and Ga-HZSM-5 catalysts were characterized by XRD, NMR, Nitrogen Adsorption and TPD. The characterization results revealed that aluminium was removed from the parent framework. Gallium loaded HZSM-5 is a better catalyst than HZSM-5 zeolite catalyst to produce liquid hydrocarbons.

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

Abstrak. Mangkin zeolit HZSM-5 diubahsuai secara kaedah pertukaran ion berasid bagi menghasilkan mangkin zeolit Ga-HZSM-5. Aktiviti bermangkin bagi HZSM-5 dan Ga-HZSM-5 dikaji pada suhu tindak balas 800°C dan halaju ruang jaman masa (GHSV) 7500 jam^{-1}. Mangkin HZSM-5 dan Ga-HZSM-5 dicirikan secara XRD, NMR, Penjerapan Nitrogen dan TPD. Hasil pencirian menunjukkan aluminium keluar dari kerangka asal. HZSM-5 yang mengandungi galium adalah mangkin yang lebih baik daripada mangkin zeolit HZSM-5 bagi menghasilkan cecair hidrokarbon.

Kata kunci: Ga-HZSM-5, metana, pertukaran ion berasid, cecair hidrokarbon

1.0 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

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chemical industries [1]. 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 principle component, methane, to useful products especially into gasoline range has been the subject of intense study over the past decade [2]. In general, there are two routes for converting methane to gasoline: indirectly or/and 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 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 [3].

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 [4]. The main concern is to modify the ZSM-5 zeolite catalyst framework with suitable oxidative elements to develop a highly active bifuntional oxidative-acid catalysts could be developed. Recent studies have shown that modification of ZSM-5 zeolite by ion exchange, direct synthesis or wet impregnation method with metal oxides of different size and chemical properties are very important to control its acidity and shape selectivity. These modification methods led to an improvement in the catalytic activity and gasoline selectivity [3–7].

Ernst and Weitkamp [5] reported in a paper on the conversion of methane over zeolite-based catalysts that the presence of strong acid sites in the zeolite catalyst is detrimental for the selective oxidation of methane to higher hydrocarbons; otherwise oxidized products, CO_x (CO, CO_2) 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.* [6] demonstrated the successful production of higher hydrocarbons from methane oxidation using a ZSM-5 zeolite catalyst containing metal oxides. The metal oxides with sufficiently high dehydrogention and low olefin oxidation activities reduces acidiy of ZSM-5. Aa a result, the metal containing ZSM-5 can produce higher hydrocarbons in methane oxidation.

Gallium is one of the potential elements that could modify the properties of zeolites. Over this catalyst, higher quality gasoline yield was obtained in the oxidative methane conversion [3]. Ga loaded on HZSM-5 is claimed to be very efficient for the aromatisation of light alkenes and alkanes [8], and has the potential to convert methane to liquid hydrocarbons with high selectivity [3,6,7]. In this study, HZSM-5 was modified with gallium by ion exchange to create a bifunctional catalyst with sites active in both acid catalysed and oxidation reactions for the conversion of methane to liquid hydrocarbons in a single catalytic step. The prepared catalyst, Ga-HZSM-5, could act as a better bifunctional catalyst than its parent catalyst, HZSM-5 zeolite, and it will be characterized and tested in a micro packed bed reactor.

2.0 MATERIAL AND METHOD

2.1 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.* [9]. A gel was prepared by mixing sodium silicate (BDH), aluminium 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: Al_2O_3: 20 Na_2O: 70 SiO_2: 7 TPABr: 2200 H_2O. The gel was heated in an oven at 170°C for 7 days. After crystallization of the gel, the template containing ZSM-5 precursor was separated by filtration, washed with distilled water, dried at about 100°C over night and finally, calcined at about 550°C for five hours to obtain the sodium form of ZSM-5.

The thus prepared Na-form was converted into the NH_4-form by ion exchange using 1M solution of ammonium nitrate. This procedure was repeated three times to ensure complete exchange of the ions. Finally, after being dried at 100°C overnight, the product was calcined at 550°C for five hours in a flow of air, herein the final product is designated as HZSM-5. An ion exchange method described by Sharifah Bee *et al.* [10] was applied to prepare Ga-HZSM-5 zeolite. A suspension of HZSM-5 in a gallium nitrate solution (1g in 5mL 0.05M solution) was refluxed at 100°C under stirring for 4 hours. Then the product was filtered, dried and calcined at 500°C for five hours, herein the final product is designed as Ga-HZSM-5.

2.2 Catalyst Characterization

2.2.1 X-Ray Diffraction Measurement

The XRD analysis was carried out at the Material Science Laboratory, Faculty of Mechanical Engineering. XRD measurements were performed in the range of $2\theta = 5°$ to 50° using a Siemens 5000 diffractometer with vertical goniometer and CuKα radiataion ($\lambda = 1.542$ Å) at 35 kV and 35 mA (scanning speed: 4°/minute).

2.2.2 Nuclear Magnetic Resonance (NMR)

The ^{29}Si MAS NMR experiments were performed at NMR, Laboratory Chemistry Department, Faculty of Science using the Varian $^{\text{Unity}}$ INOVA 400 MHz 9.4T spectrometer. The ^{29}Si MAS NMR chemical shifts were related to TMS use as external reference. The spectra were recorded at a radio frequency pulses, a recycle delay of 12s, a number of trancients of 4500, and a spinning rate of 5.5 kHz. The ^{29}Si MAS NMR analysis was performed.

2.2.3 Nitrogen Adsorption

The adsorption isotherm measurement was carried out by Quanta Chrome Autosorb-1, using the nitrogen as the adsorbate at 77 K. This analysis was conducted at Petronas Research & Scientific Services Sdn. Bhd.(PRSS), Bangi, Selangor.

2.2.4 Temperature Programmed Desorption

Temperature programmed desorption (TPD) of ammonia was carried out with a Du Pont 9900 thermogravimetric system with a heat conductivity detector, TCD. Before adsorption, the catalyst (0.4 gram) was dried in a flow of 23 mL/min of pre-dried He for two hours at 500°C. Then it was contacted with a flow of 20% NH_3 in He at 70°C for 0.5 hour. Finally, the catalyst was flused with He at 70°C for 1 hour. Desorption was done by heating the catalyst from 70°C to 600°C with a linear heating schedule. The amount of desorbed NH_3 was measured with a heat conductivity detector. The TPD measurements were conducted at PRSS, Bangi.

2.3 Catalytic Testing

The performance of the catalyst in the conversion of methane was tested using a packed-bed continuous flow micro reactor. The stainless steel tube reactor (9 mm in diameter and 300 mm in length) was mounted vertically and heated by an electric furnace. The reaction was carried out at 800°C and atmospheric pressure, cofeeding the reactant gases (methane and air) with a gas hourly space velocity (GHSV) of 7500 HR^{-1}.

The reactor was loaded with one gram of catalyst supported by glass wool. Activation of catalyst was performed by preheating in a flow of nitrogen (100 mL/min) at 800°C for 1 hour. Then, methane and air were fed into the reactor (9 vol. % of oxygen in the feed) for every GHSV. The products were separated into liquid and gas fractions in 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 off-line analyzed by a gas chromatography (Perkin Elmer) using HP-1 capillary column.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Catalyst

3.1.1 X-Ray Diffraction

X-ray diffraction provides information on the structure and unit cell parameter of zeolites, XRD analyses of gallium loaded zeolites was typical of crystalline HZSM-5 and did not reveal clear XRD lines attributable neither to oxide phases nor to metal oxide clusters (Figure 1). This indicated the presence of small metal oxide clusters of several nm-size that do not show X-ray diffraction. Meanwhile, the peak intensity of Ga-HZSM-5 is slightly more intense than HZSM-5. Jia *et al.* [11] reported that the band intensities could be influenced by various factors such as the size of particles, the

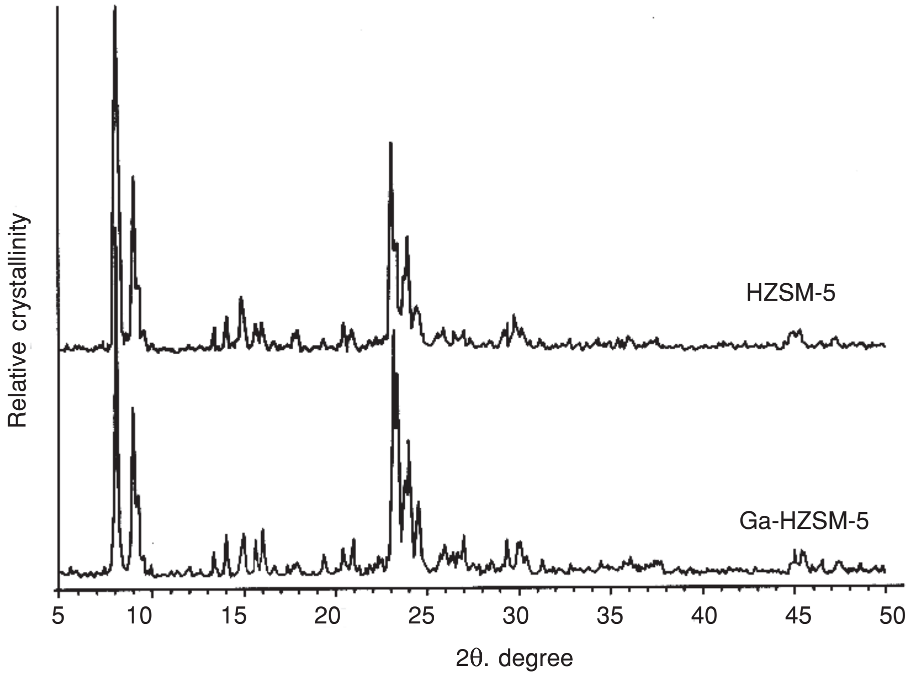

Figure 1 XRD diffractograms of HZSM-5 and Ga-HZSM-5 zeolite catalysts

surface effect, and the dispersity of the metal, which resulted in a little change of the band intensity. However, this finding indicates that there occurred no significant change in the crystal structure upon introduction of gallium.

The unit cell parameters and unit cell volume of the zeolite catalysts are present in Table 1. The unit cell parameters of the modified HZSM-5 are different form those of the parent material. The unit cell volume of Ga-HZSM-5 are different from those of the parent material. The unit cell volume of Ga-HZSM-5 is smaller than that of HZSM-5, due to the removal of some of the aluminium from the zeolite framework. It because of the ionic radii of tetrahedral structure of Si^{4+} is lower than $A1^{3+}$, 0.40Å and 0.53Å,

Table 1 The Si/A1 ratio and unit cell parameters of zeolites

Sample	**The Si/A1 ratio (*)**	**Unit cell parameters (**)**			
		***a*(Å)**	**b(Å)**	***c*(Å)**	**V(Å^3)**
HZSM-5	76	19.674	20.725	14.665	5979.56
Ga-HZSM-5	133	19.505	20.627	13.825	5562.21

(*) : Calculated based on deconvolution of ^{29}Si MAS NMR spectra
(**): Calculated based on XRD data with orthorhombic phase.

respectively [12]. So, as the aluminium framework decrease, the unit cell parameters decrease, and the unit cell volume also decrease.

3.1.2 ^{29}Si MAS NMR

The structure of tetrahedral framework TO_4 (T = Si, Al) may be determined using ^{29}Si MAS NMR technique. This technique may be used to determine the tetrahedral SiO_4 environment in its next nearest neighbor in the zeolite framework. Usually, the environment of tetrahedral SiO_4 is aluminium [Si;(4-n)A1] (n = 0-4), but there may be structural defects such as SiOX (X = M or H) [13].

The ^{29}Si MAS NMR spectra of both zeolite catalysts are shown in Figure 2. A strong signal at the chemical shift around $\delta = -115$ ppm, typical of Si(0A1) indicates that this silicon type is predominant in both zeolites. The weak signal at around $\delta = -105$ ppm is the sum of Si(1A1) and SiOX contributions [19]. However, the frequency of Ga-HZSM-5 typical of Si(0A1) is higher than HZSM-5 (–115.9 and –115.1 ppm, respectively) and the signal at around $\delta = -105$ ppm of Ga-HZSM-5 is slightly less intense than HZSM-5. This indicates that aluminium have been removed from the parent framework. This finding can be supported by calculation of Si/A1 ratio using deconvolution of ^{29}Si MAS NMR spectra by assuming that a signal at around $\delta = -105$ ppm is only ppm is only typical of Si (1A1). Table 1 shows the Si/A1 ratio of zeolite catalysts calculated by equation 1. From Table 1, the ratio of Si/A1 for the parent zeolite, HZSM-5, is lower than the metal-loaded zeolite. This indicates that dealumination occured in the Ga-HZSM-5 catalyst, consistent with XRD data analysis.

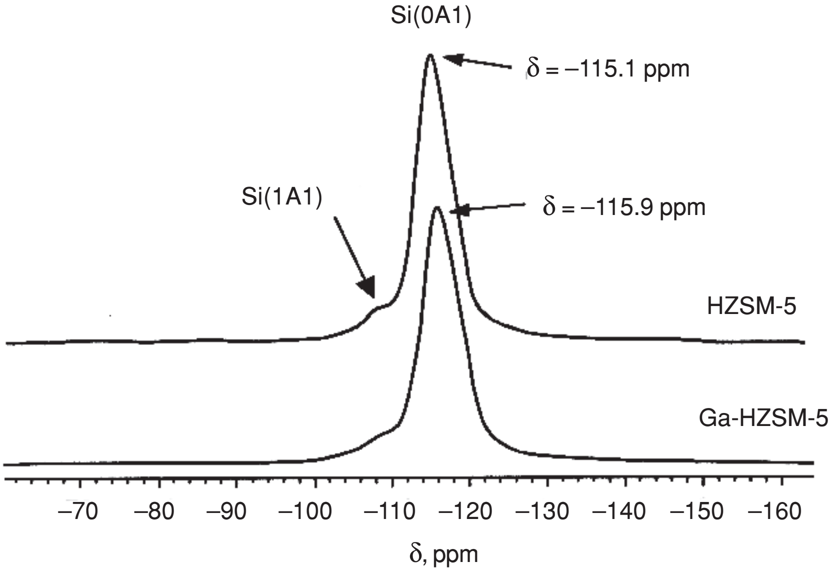

Figure 2 ^{29}Si MAS NMR spectra of HZSM-5 and Ga-HZSM-5 zeolite catalyst

$$\mathrm{Si/A1}_{({}^{29}\mathrm{Si\ MAS\ NMR})} = \frac{I_{\mathrm{Si(0A1)}} + I_{\mathrm{Si(1A1)}}}{0.25\, I_{\mathrm{Si(1A1)}}} \quad (1)$$

3.1.3 Nitrogen Adsorption

The microstructure characteristic of the zeolite catalysts were further studied by analysis of nitrogen adsorption. Table 2 reveals that the loading of Ga onto HZSM-5 did not affect the surface area, but decreased the micropore areas and volumes. It is shown that Ga-HZSM-5 had larger external surfaces. The micropore volume of the loaded zeolite is lower than that of the parent HZSM-5 due to the presence of metal oxide particles into the channels of the zeolite. Nor Aishah and Didi Dwi Anggoro [14] and Gervasini [15] also reported the same result.

Table 2 Nitrogen adsorption data

Sample	BET surface are (m^2/g)	Micropore area (m^2/g)	Micropore volume (m^3/g)
HZSM-5	434.8	251.9	0.105
Ga-HZSM-5	433.6	233.7	0.098

3.1.4 Temperature Programmed Desorption

The acidity of the catalysts was examined by using temperature programmed desorption of ammonia. The amount of acid or acidity on a solid is expressed as moles of acid sites per unit weight of the solid. The result of the TPD is show in Table 3. The amount of chemisorbed NH_3 on the HZSM-5 zeolite catalyst is much higher than that bound by the modified zeolite catalyst. It indicates that the parent zeolite has more acid sites than the gallium zeolite. However, both low temperature (LT) and high temperature (HT) of Ga-HZSM-5 are lower than that of HZSM-5. Koval *et al.* [14] reported that the desorption of NH_3 at the LT and HT is related to the acid strength of the zeolites. Both the zeolite catalyst contain LT and HT that suggest there is no significant changes in the acid strength, but Ga-HZSM-5 zeolite contains less number of acid sites than HZSM-5 zeolite.

Table 3 Acidity data of zeolites

Sample	Amount of chemisorbed (moles/kg)	Low temperature (°C)	High temparature (°C)
HZSM-5	0.5424	214	415
Ga-HZSM-5	0.1418	209	414

Topsoe *et al.* [16] have postulated that the number of acid sites decreases as aluminium is removed from the crystal lattice and increases as aluminium is inserted into the framework of HZSM-5. The acidity also decreased with a decreasing micropore volume of HZSM-5, which caused a reduction in ammonia adsorption [17]. Based on the XRD, ^{29}Si MAS NMR, and nitrogen adsorption data, the decrease in acidity is due to the effects of the removal of aluminium from the framework and metal oxide trapped inside the channels of modified zeolite.

3.2 The Catalytic Activity of HZSM-5 and Ga-HZSM-5

The catalytic performance of HZSM-5 and Ga-HZSM-5 in the conversion of methane with 9% volume of oxygen under atmospheric pressure at 800°C and GHSV of 7500 hr^{-1} is specified in Table 4.

Table 4 Catalytic conversion of methane with 9% vol. of O_2 over HZSM-5 and Ga-HZSM-5 catalysts at 800°C, atmospheric pressure and a GHSV of 7500 hr^{-1}

Sample	HZSM-5	Ga-HZSM-5
Methane conversation (%)	55.8	35.6
Liquid yield (wt.%)	2.2	24.3
C_5–C_{10} composition of liquid hydrocarbons (wt.%)	96.9	97.4
C_{11+} composition of liquid hydrocarbons (wt.%)	3.1	2.6

As shown in Table 4, the conversion of methane is 55.8% and 35.6% for HZSM-5 and Ga-HZSM-5 catalysts, respectively. This result indicates that the oxidation of methane is more dominant over HZSM-5 than over the gallium-loaded HZSM-5 catalyst. The findings can be attributed to the higher acid sites of the HZSM-5 compared to Ga-HZSM-5. The results are consistent with Weckhusyen *et al.* [18] results where methane conversion is also observed to increase with acidity.

Over HZSM-5 and Ga-HZSM-5 the liquid yield amounted to 2.2% and 24.3%, respectively (Table 4). The higher conversion to liquid over Ga-HZSM-5 can be attributed to the dehydrogenation and oligomerization functions of the Ga metal and the acidity of the zeolite. Over both catalysts the fraction of gaseous C_2–C_4 hydrocarbons consisted exclusively of the respective olefinic compounds, i.e., no gaseous paraffines were formed (Table 5). Eventhough the gas hydrocarbons over both catalysts contain 100% olefins, the liquid yield of Ga-HZSM-5 is higher than HZSM-5 zeolite catalyst.

Table 5 Gas hydrocarbons products over HZSM-5 and Ga-HZSM-5 catalysts

Sample	HZSM-5	Ga-HZSM-5
C_2–C_4 hydrocarbon products (wt. %)		
C_2–C_4 Paraffins	0	0
C_2–C_4 Olefins	100	100

As reported by Nor Aishah and Sharif Hussin [7], Vermeiren *et al.* [8], and Meriaudeu [19], Ga-HZSM-5 is an active catalyst in the dehydrogenation and oligomerization activity of C_2–C_4 hydrocarbons. The existence of gallium as metal oxide on the internal surface of the catalyst has reduced the acid sites that were available on the parent HZSM-5 zeolite. Consequently, gallium encouraged the production of the methyl species, and enhanced the dehydrogenation of C_2–C_4 paraffin to C_2–C_4 olefins, which leads to the oligomerization of the olefins to C_{5+} hydrocarbons. As a result, the liquid yield over Ga-HZSM-5 is higher compared to HZSM-5 zeolite catalyst.

As mentioned earlier, the strength of acid sites and their amount in HZSM-5 zeolite were higher than in Ga-HZSM-5. It is believed that HZSM-5 favours cracking reactions to a higher degree than the oligomerizaton reactions over HZSM-5 zeolite catalyst. As a result, the liquid yield over HZSM-5 is lower compared to that obtained over Ga-HZSM-5 zeolite catalyst. Didi Dwi Anggoro [3] reported that the successful production of C_{5+} hydrocarbons depends on the oxidation of methane over metal-load ZSM-5 with medium acidity. Halasz *et al.* [20] reported that stronger acidic catalyst would encourage the cracking of C_{5+} hydrocarbons to C_2–C_4 hydrocarbons.

4.0 CONCLUSIONS

The preparation of Ga-HZSM-5 zeolite catalyst by an ion exchange method revealed that aluminium are removed from the zeolite framework. Metal oxides also covered the internal surface of the pores or channels of the zeolite catalyst. The total amount of acid sites in Ga-HZSM-5 zeolite catalyst decreased. The methane conversion over Ga-HZSM-5 is lower than the parent catalyst due to its lower acidity, but the liquid yield is higher due to the existence of gallium in the zeolite.

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