

Characterization of zeolite-based catalysts for methane conversion

A. Asmadi^a, M. Ramli^b, M. S. Azhar^c and H. B. Senin^c

^a*Department of Engineering Science, Faculty of Science and Technology, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia*

^b*Department of Chemical Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia*

^c*Department of Physical Sciences, Faculty of Science and Technology, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia*

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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. This process is possible if the reaction is carried out by controlled oxidation over a suitable catalyst. The main concern is to modify the ZSM-5 zeolite catalyst framework with suitable oxidative elements so that highly active bifunctional oxidative-acid catalysts could be developed. The objective of this study is to modify HZSM-5 zeolite catalyst with gallium metal by acidic ion exchange method to form a bifunctional oxidative and acid catalyst. The obtained catalyst, Ga-HZSM-5, might act as a better bifunctional oxidative-acid catalyst than its parent catalyst, HZSM-5 zeolite. ZSM-5 zeolite catalyst was prepared by direct synthesis to produce HZSM-5 catalyst. The HZSM-5 zeolite catalyst was modified by an acidic ion exchange method to produce Ga-HZSM-5 zeolite catalyst. HZSM-5 and Ga-HZSM-5 catalysts were characterized by X-Ray Diffraction Measurement (XRD), Nuclear Magnetic Resonance (NMR), Nitrogen Adsorption and Temperature Programmed Desorption (TPD). The characterization results revealed that Al ions were removed from the framework and/or replaced by Ga ions into the parent framework. Some of the metal oxides also covered the internal surface of the pores or channels of the modified zeolite. The total concentration of acidic centers or the acidity of Ga-HZSM-5 zeolite catalyst decreased with increasing silica to alumina ratio and decreasing micro pore volume.

I. INTRODUCTION

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 [1]. 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 [2].

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 [3]. The main concern is to modify the ZSM-5 zeolite catalyst framework with suitable oxidative elements so that highly active bifunctional 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 are very important to control its acidity and shape selectivity.

These modification methods showed an improvement in the catalytic activity and gasoline selectivity [3-6]. Han *et al.* [6] 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 [2].

Ga loaded on HZSM-5 is claimed to be very efficient for the aromatisation of light alkenes and alkanes [7], and has the potential to convert methane to liquid hydrocarbons at a high selectivity [2,5,6]. The objective of this study is to modify HZSM-5 zeolite catalyst with gallium metal by acidic ion exchange method to form a bifunctional oxidative and acid catalyst. 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

characterized by XRD, NMR, Nitrogen Adsorption and TPD.

II. MATERIAL AND METHODS

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

ZSM-5 zeolite was prepared by direct synthesis based on the method described by [8]. 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: Al_2O_3 : 20 Na_2O : 70 SiO_2 : 7 TPABr: 2200 H_2O . The gel will be heated in an oven at 170°C for 7 days. The crystalline white solid product filtered, washed thoroughly with deionized water, dried at 120°C for 12 hours. The resultant material was calcined at 550°C for five hours to obtain the sodium form of the ZSM-5. The Na-form so obtained was converted into the NH_4 -form by ion exchange using 1 M solution of ammonium nitrate. The procedure was repeated three times. Finally the catalyst is dried and calcined at 550°C and marked as HZSM-5. An acidic ion exchange method [9] 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 four 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.

Iib. X-Ray Diffraction Measurement

The XRD analysis was carried out at the Department of Physics, Faculty of Science, UTM. XRD measurements were performed using a Philips 1840 with $\text{CuK}\alpha$ radiation with $\lambda = 1.5456 \text{ \AA}$ at 40 kV and 30 mA in the range of $2\theta = 2^\circ$ to 60° at a scanning speed of 4° per minute, with vertical goniometer at room temperature.

Iic. Nuclear Magnetic Resonance (NMR)

The MAS NMR experiments were performed using Varian ^{Unity} INOVA 400 MHz 9.4T spectrometer. The ^{29}Si MAS NMR chemical shifts were quoted in ppm

from external TMS used as a reference. The ^{29}Si MAS NMR analysis was performed at Makmal NMR, Jabatan Kimia, Fakulti Sains, UTM Skudai.

IId. Nitrogen Adsorption

The adsorption isotherm measurement was carried out by Quanta Chrome Autosorb-1, using the nitrogen as the adsorbate at 77 K and the Micromeritics ASAP 2000 equipment. This technique was conducted at Petronas Research & Scientific Sdn. Bhd., Kajang, Selangor.

Ile. Temperature Programmed Desorption

Temperature programmed desorption (TPD) of ammonia was carried out with a Du Pont 9900 thermo-gravimetric system with a detector type, TCD and the method remarks as Micromeritics 29000 TPD/TPR. The TPD measurements were conducted at Petronas Research & Scientific Sdn. Bhd., Kajang, Selangor.

III. RESULTS AND DISCUSSION

NMR was used to find the ratio of Si/Al. Table I shows the ratio of Si to Al of HZSM-5 and Ga-HZSM-5 zeolite catalysts. The ratios can be calculated from the intensities of the peaks of the ^{29}Si NMR spectra. From Table I, the ratio of Si/Al for the parent zeolite, HZSM-5, is lower than the metal loaded zeolite. This indicates that Al ions could have been removed from the parent framework or replaced by the incorporation of Ga ions into the zeolite framework.

X-ray diffraction provides information on the structures and unit cell parameters of zeolites, as demonstrated in Fig. 1 and Table I. The XRD patterns of Ga-HZSM-5 was similar to the HZSM-5 as shown in Fig. 1. This phenomenon indicates that there is no drastic change in the crystal structure of the zeolites. The peak intensity of Ga-HZSM-5 is slightly intense than that of HZSM-5. It reveals that the possibility of isomorphous substitution of the Ga metal ions had occurred after modification. Jia *et al.* [10] reported that the band intensities could be influenced by various factors such as the size of particles, the surface effect, and the dispersity of the metal, which resulted in a little change of the band intensity.

TABLE I. The Si/Al ratio and unit cell parameters of zeolites.

Sample	The Si/Al ratio	Unit cell parameters			
		a(Å)	b(Å)	c(Å)	v(Å)
HZSM-5	76	19.674	21.097	14.665	6086.89
Ga-HZSM-5	133	19.505	21.159	13.825	5705.66

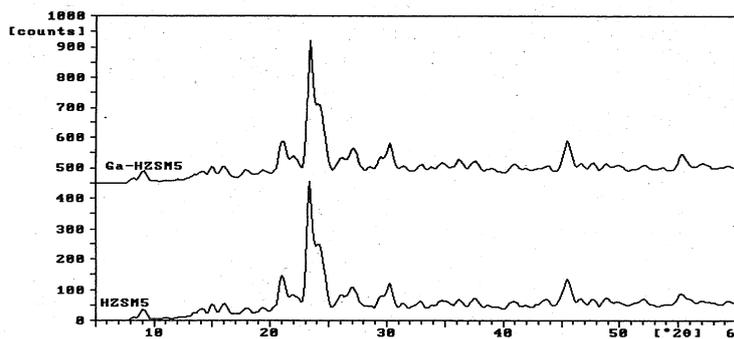


FIG. 1. XRD diffractograms of HZSM-5 and Ga-HZSM-5 zeolite catalysts.

The degree of unit cell parameters and unit cell volume of Ga loaded HZSM-5 and HZSM-5 zeolite is shown in Table I. The unit cell parameters of the modified HZSM-5 are different from its parent. The unit cell volume of Ga-HZSM-5 is smaller than HZSM-5. The effect is due to the removal of some of the Al ions from the zeolite framework. The framework contains more Si ions, which are smaller ionic crystals with a radius of 0.40 Å in tetrahedral coordination compared to Al ions, which has a radius of 0.53 Å [11].

Table II reveals that the loading of Ga onto HZSM-5 did not affect the surface area, but decreased the micropore areas and volumes. Amin and Anggoro [12] have reported that the decrease of the area and volume of the micropores are the results of the metal oxide being trapped inside the pores or channels. The acidities of the catalysts were examined by carrying out 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 shown in Table III.

TABLE II. Nitrogen adsorption data.

Sample	BET surface area (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

TABLE III. Acidity data of zeolites.

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

The amount of chemisorbed on the HZSM-5 zeolite catalyst is much higher than the modified zeolite catalyst. It shows that the parent zeolite has many acidic bases rather than the metal zeolite. Both low temperature (LT) and high temperature (HT) of Ga-HZSM-5 are slightly lower than that of HZSM-5. Koval *et al.* [13] reported that the decrement of low temperature (LT) and high temperature (HT) were due to the decrement of acid strength of the zeolites. This shows that Ga-HZSM-5 zeolite has a lower acid strength than HZSM-5 zeolite. Topsoe *et al.* [14] have postulated that the acidity decreases as Al ion is removed from the crystal and increases as Al ion 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 [13]. The decrease in acidity is due to the factors of the removal of Al ions from the framework, the replacement of Al ions by Ga ions in the zeolite parent framework, and metal oxide trapped inside the pores or channels of modified zeolite.

IV. CONCLUSION

The preparation of Ga-HZSM-5 zeolite catalyst by an acidic ion exchange method revealed that Al ions are removed from zeolite framework and or substituted by Ga ions into the zeolite framework. Metal oxides also covered the internal surface of the pores or channels of the zeolite catalyst. The total concentration of acidic centers or the acidity of Ga-HZSM-5 zeolite catalyst decreased with increasing silica to alumina ratio and decreasing micropore volume.

REFERENCES

[1] N. D. Parkyns, C. I. Warburton and J. D. Wilson, *Catalysis Today*, **18** 385-442 (1996).
 [2] D. D. Anggoro, "Single step conversion of methane to gasoline: Effect of metal loaded HZSM-5 zeolite catalysts", Msc. Thesis, Universiti Teknologi Malaysia (1998).

- [3] R. Mat, N. A. S. Amin, Z. Ramli and B. W. A. W. Abu, WEC Proceeding, K. Lumpur 249-254 (1999).
- [4] S. Ernst and J. Weitkamp, Oxidative coupling of methane using zeolite-based catalyst, (1998).
- [5] S. Han, D. J. Maternak, R. E. Palermo, J. A. Pearson and D. E. Walsh, Journal of Catalysis, **148**, 134-137 (1994).
- [6] N. A. S. Amin and S. H. S. Zein, WEC Proceeding, K. Lumpur, 223-227 (1999).
- [7] W. J. Vermeiren, I. D. Lenotte, J. A. Martens and P. A. Jacobs, "Zeolite based catalysts in the oxidative coupling of methane into higher hydrocarbons", in *Hydrocarbons Source of Energy*, G. Imarisio, M. Frias and J. M. Bemtgen (eds.), Graham & Trotman Ltd., London (1989) pp. 451- 460.
- [8] C. J. Plank, E. J. Rosiniski and A. B. Schwartz, UK Patent 1402981 (1974).
- [9] S. A. H. Bee, E. G. Deroune, G. Demortier, J. Riga and M. A. Yarmo, Applied Catalysis A. General, **108**, 85-96 (1994).
- [10] S. Jia, S. Wu and Z. Meng, Applied Catalysis A. General, **103**, 259-268 (1993).
- [11] R. Szostak, *Molecular Sieves Principle of Synthesis and Identification*, Van Nostrand Reinhold, Catalysis Series, New York (1999).
- [12] N. A. S. Amin and D. D. Anggoro, Jurnal Teknologi, **30(c)**, 21-32 (1999).
- [13] L. M.Koval, Y. I. Gaivoronskaya and Y. V. Patrushev, Russian Journal of Applied Chemistry, **69(2)**, 235-238 (1996).
- [14] N. Y. Topsoe, K. Pendersen and E. G. Derouane, Journal of Catalysis, **70**, 41-52 (1981).