

Synthesis and characterization of galloaluminosilicate/gallosilicalite (MFI) and their evaluation in methane dehydro-aromatization

Ding Ma, Yuying Shu, Chunlei Zhang, Weiping Zhang,
Xiuwen Han, Yide Xu*, Xinhe Bao*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
457 Zhongshan Road, Dalian 116023, PR China

Received 10 July 2000; received in revised form 11 September 2000; accepted 27 September 2000

Abstract

MFI-type gallosilicalite and galloaluminosilicate were synthesized by hydro-thermal method. For all the as-synthesized Ga-containing samples, ^{71}Ga MAS NMR spectra confirmed that the Ga^{3+} cations are located in the zeolite framework. As for the case in galloaluminosilicate, Ga^{3+} and Al^{3+} cations can enter the zeolitic site at the same time, but there is a competition between the two cations to incorporate into the zeolite framework. Quantitative MAS NMR results suggest that the incorporation of the Ga^{3+} cations is seriously inhibited by that of the Al^{3+} cations if they existed together, while the reversed process is not observed. The catalytic performances of non-oxidative aromatization of methane on these zeolite catalysts, with or without loading of MoO_3 , have been investigated. The results show that zeolites containing framework Ga species, which are excellent catalysts for propane aromatization, are poor catalyst supports for methane dehydro-aromatization. The catalytic performance of the molybdenum-loaded H-gallosilicate (MFI) catalysts present an activity for methane activation and subsequent aromatization, however, it is not as good as that of the Mo-loaded H-galloaluminosilicate (MFI) catalysts. Bearing this in mind, it was suggested that zeolitic acidity that originated from the heteroatom substitution is essential for catalyzing methane aromatization. The weaker acidity of framework GaO_4^- tetrahedral species as compared to framework AlO_4^- tetrahedral species is suggested to be responsible for the inferior activity for methane aromatization reaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gallosilicalite (MFI); Galloaluminosilicate (MFI); MAS NMR; Methane; Aromatization

1. Introduction

Heteroatom-substituted zeolites, especially those with MFI structure have been received increasing interest recently. It has been shown that different catalytic properties are presented with the introduction

of different heteroatoms, e.g. titanium-silicate is efficient for hydroxylation of aromatics [1], whereas Fe-zeolites is a good catalyst for redox reaction [2]. Gallosilicate has been used for the aromatization of light paraffin, with the benefit of being more stable in reaction as compared with a Ga-ion-exchanged HZSM-5 catalyst [3]. The incorporation of gallium into the framework of HZSM-5 to produce galloaluminosilicate has been investigated by various authors through the application of XRD, IR, and ^{27}Si MAS

* Corresponding author. Fax: +86-411-469-1570.
E-mail addresses: xuyd@ms.dicp.ac.cn (Y. Xu),
xhbao@ms.dicp.ac.cn (X. Bao).

NMR, etc. [4–6]. ^{71}Ga MAS NMR, however, is the direct method to examine whether the gallium has entered the zeolitic framework, though it is difficult to record a good spectrum due to the lower sensitivity and quadrupolar nature of ^{71}Ga nuclei [7]. In this work, various gallosilicalite and galloaluminosilicate zeolites were synthesized and the framework structure of these zeolites are carefully analyzed by ^{27}Al and ^{71}Ga MAS NMR, particularly, the feature of the co-incorporation of gallium and aluminum into the zeolitic framework has been emphasized. At the same time, the dehydro-aromatization of methane, the homologous compounds of light paraffin, has been tested on those gallosilicalite and galloaluminosilicate zeolites with or without loading molybdenum. Along this line, the requirements for methane activation and its succeeding aromatization are discussed.

2. Experimental

2.1. Synthesis of Ga-containing zeolites

The gallosilicalite and galloaluminosilicate (MFI) with different Si/Al and Si/Ga ratios were synthesized by the hydrothermal crystallization from gels (pH about 11), consisting of SiO_2 , Ga_2O_3 , $\text{Al}_2(\text{SO}_4)_3$ and TPA-Br. For example, galloaluminosilicates (MFI) with Si/Al = 25 and Si/Ga = 25 were synthesized as follows. Ga_2O_3 was dissolved in 4 ml of 98% H_2SO_4 diluted in 15 ml H_2O , 2.8 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 1 g TPA-Br were then added. SiO_2 was dissolved in 30 ml 10 wt.% NaOH, then 2 g TPA-Br was added into the mixture of 34 ml saturated NaCl solution and 15 ml 10 wt.% NaOH. The former two solutions were added into the third one under vigorous stirring for 30 min. Then, the pH value of the solution was adjusted to about 10 by 10 wt.% NaOH. The resulting gel was introduced into a Teflon-lined autoclave and statically heated at 433 K for about 80 h. The solid product was recovered after filtering, washing, and succeeding drying at 393 K. After calcination at 823 K for 8 h to remove the organic templates, the zeolites was ion-exchanged with 1 M NH_4NO_3 solution (358 K, 4 h) for five times. The ammonium exchanged zeolite was calcined at 773 K for 3 h to get the H-formed zeolite. Similar to this process, HZSM-5 (Si/Al = 25), H-gallosilicalite (MFI, Si/Ga = 25), and

Table 1
Zeolites synthesized and used in this work

Type	Zeolite	Gel		Framework ^a	
		Si/Al	Si/Ga	Si/Al	Si/Ga
HZSM-5	HZSM-5	25	–	27.7	–
MFI-2	H-gallosilicalite	–	25	–	26.5
MFI-3	H-galloaluminosilicates	25	50	26.7	–
MFI-4	H-galloaluminosilicates	25	25	26.9	79.5
MFI-5	H-galloaluminosilicates	50	25	53.4	44.7

^a Determined by MAS NMR experiments.

H-galloaluminosilicates (MFI, Si/Al = 25, Si/Ga = 50; Si/Al = 25, Si/Ga = 25; Si/Al = 50, Si/Ga = 25) were synthesized, and they are denoted in Table 1, respectively. The framework Si/Al and Si/Ga ratios are determined by NMR experiments which will be illustrated in the following sections. If not specially pointing out, the Si/Al and Si/Ga ratios used in the manuscript refer to those in the original synthesis gel.

2.2. Preparation of MoO_3 modified HZSM-5 and Ga-containing zeolites

MoO_3 modified HZSM-5 and Ga-containing zeolites were prepared by physical-mixing method, and the nominal content of MoO_3 was 3% in all catalysts. The H-formed zeolite was mixed with a desired amount of MoO_3 and ground at room temperature for no less than 30 min, then it was calcined at 773 K for 4 h. The samples were pressed into tablets, crushed and sieved into appropriate grains.

2.3. Characterization

XRD patterns were measured by a Shimadzu XD-3A diffractometer using $\text{Cu K}\alpha$ radiation, operating at 30 kV, 20 mA, and with a scan speed of $4^\circ/\text{min}$.

FT-IR was recorded at room temperature on a Nicolet Compact 410 spectrometer using the conventional KBr disk technique. Self-supporting wafers were prepared with a zeolite:KBr = 1:200 under a pressure of 90 kgf/cm².

All the NMR spectra were obtained at 9.4 T on a Bruker DRX-400 spectrometer using 4 mm ZrO_2 rotors. ^{27}Al MAS NMR spectra were recorded at 104.3 MHz using a 0.75 μs ($\pi/12$) pulse with a 2 s recycle delay and 400 scans. The sample was spun

at 8 kHz. In the case of the ^{71}Ga MAS NMR, a $2\ \mu\text{s}$ ($\pi/12$) pulse, 3 s repetition time and MAS rate of 10 kHz were used; 7000 scans were accumulated, 1% aqueous $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Ga}(\text{NO}_3)_3$ solution [7] were used as references of chemical shifts, respectively. ^{29}Si MAS NMR spectra were recorded at 79.5 MHz using a $1.6\ \mu\text{s}$ ($\pi/4$) pulse with a 4 s recycle delay and 2000 scans. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium (DSS).

2.4. Catalytic evaluation

The reactions were performed in a quartz tubular fixed-bed reactor. Usually, 1 g catalyst and FW of 1500 ml/g h were used. Before the introduction of methane, the catalyst was activated in air at 973 K for 30 min and purged with helium at the same temperature for 10 min. The products were analyzed by on-line gas chromatography (Shimadzu GC-8A) equipped with a thermal conductive detector using a Porapak-Q column. The conversion of methane and selectivity of the products were calculated based on carbon number balance, and coke formation was ignored.

3. Results and discussion

3.1. Characterization of the as-synthesized zeolites by XRD and FT-IR

The XRD patterns of the as-synthesized zeolites show that all of them have the MFI structure, which is similar to the pattern of HZSM-5, as shown in Fig. 1. No peaks belonging to Ga_2O_3 could be resolved in the XRD spectra, indicating that Ga_2O_3 was not isolated from the crystallites, but was incorporated into the crystallites or at least into the precursors of the crystallites [8]. IR spectra recorded from the Ga containing zeolites show the same bands as those recorded on HZSM-5, as shown in Fig. 2. It is, therefore, evident that all the Ga-containing zeolites were of the MFI type. The absorption bands at 1220 and $1100\ \text{cm}^{-1}$ correspond to TO_4 asymmetric stretching vibration, while those at 880, 550, and $450\ \text{cm}^{-1}$ correspond to TO_4 symmetric stretching, double-ring and bending vibrations, respectively. With the increase of the Ga/Si ratio the absorption bands at 1200 and $1100\ \text{cm}^{-1}$ shift towards higher wave numbers,

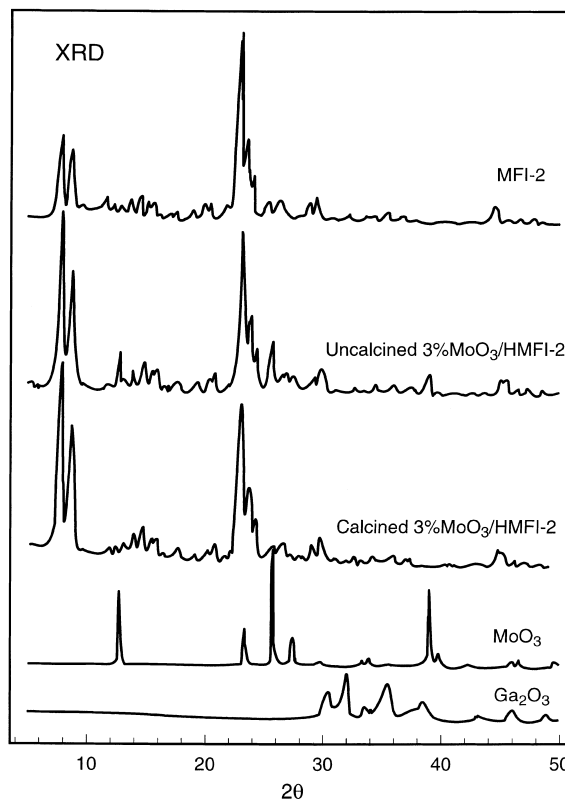


Fig. 1. XRD patterns of catalyst, catalyst precursor and references (gallosilicalite, MFI-2, Si/Ga = 25).

which seems to indicate the incorporation of gallium into the framework of the zeolite.

3.2. Characterization of the as-synthesized zeolites by ^{71}Ga and ^{27}Al MAS NMR

^{71}Ga MAS NMR is the powerful tool in the identification of whether gallium has entered zeolite framework [7]. ^{71}Ga MAS NMR spectra of the as-synthesized zeolites are shown in Fig. 3. For all the Ga-containing samples, only a peak centered at about 150 ppm could be resolved. Resonance at this region has been reported for gallosilicalite structures, especially for MFI-type gallosilicalite [7,9]. This peak was attributed to tetrahedral coordinated framework gallium. Since the samples were fully hydrated in air for more than three months before the NMR measurements, it is possible to make a quantitative

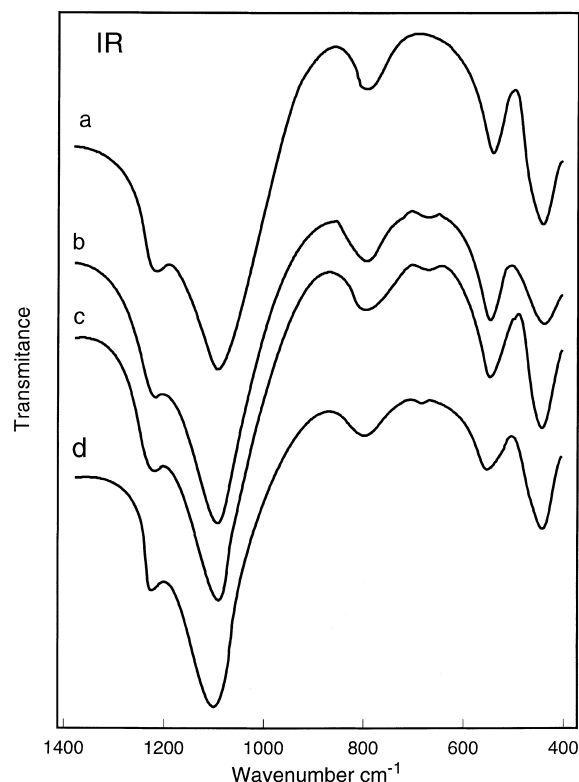


Fig. 2. IR spectra of various zeolites: (a) galloaluminosilicate (MFI-3, Si/Ga = 50, Si/Al = 25); (b) galloaluminosilicate (MFI-4, Si/Ga = 25, Si/Al = 25); (c) galloaluminosilicate (MFI-5, Si/Ga = 25, Si/Al = 50); (d) gallosilicalite (MFI-2, Si/Ga = 25).

analysis of the amount of gallium entering the framework of the zeolite by ^{71}Ga MAS NMR spectra [7]. By comparing the ^{71}Ga MAS NMR spectra of MFI-2 with that of MFI-4, it is interesting to notice that the amount of gallium entering the zeolite framework was different, despite the fact that the same Si/Ga ratios were used in the synthesis process. The intensity of the tetrahedral framework gallium resonance in the ^{71}Ga MAS NMR spectra of the MFI-4 sample was only about 40% of that of the MFI-2 sample. This strongly suggests that there is a competition between the aluminum and the gallium in incorporating into the framework during the synthesis of the zeolites. On the other hand, all the ^{27}Al MAS NMR spectra of the samples with the same Si/Al ratio exhibited almost the same intensity for the framework aluminum resonance (51 ppm) in the spectra, indicating that similar

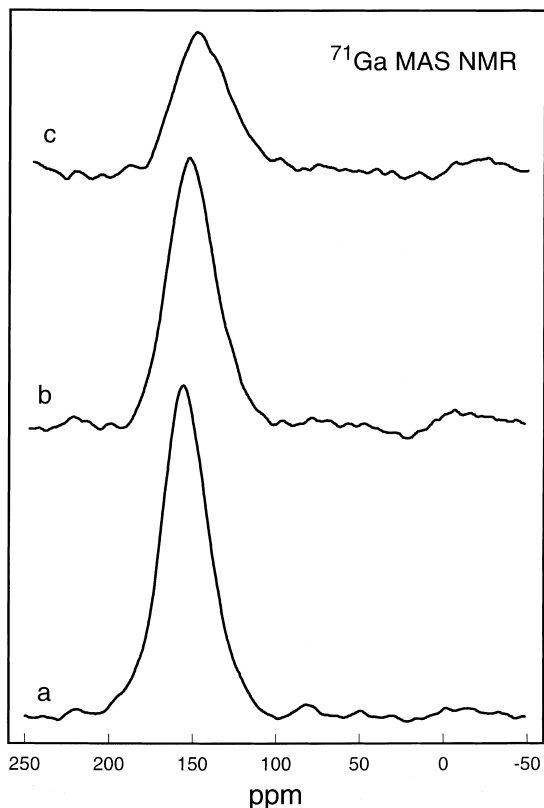


Fig. 3. ^{71}Ga MAS NMR spectra of different zeolites: (a) gallosilicalite (MFI-2, Si/Ga = 25), (b) galloaluminosilicate (MFI-5, Si/Ga = 25, Si/Al = 50), (c) galloaluminosilicate (MFI-4, Si/Ga = 25, Si/Al = 25).

amount of aluminum had entered into the zeolite lattice (see Fig. 4). The framework Si/Al and Si/Ga ratio of these samples are listed in Table 1. The framework Si/Al ratio of HZSM-5 is resulted from deconvolution of its ^{29}Si MAS NMR spectra, and framework Si/Ga ratio of H-gallosilicalite is from deconvolution of its ^{29}Si MAS NMR spectra. However, due to the overlap of chemical shifts of Si(1Al) and Si(1Ga) in ^{29}Si MAS NMR, one cannot get the exact framework Si/Al and Si/Ga ratios from the ^{29}Si MAS NMR spectra [10,11]. On the other hand, the framework Si/Al ratios of H-galloaluminosilicate is obtained by comparison of corresponding peak intensity of tetrahedral aluminum (51 ppm) species in ^{27}Al MAS NMR with that of HZSM-5, and normalized according to ^{27}Al spectra. A similar case holds for the calculation of framework Si/Ga ratios. As shown in Table 1, for MFI-2, MFI-5,

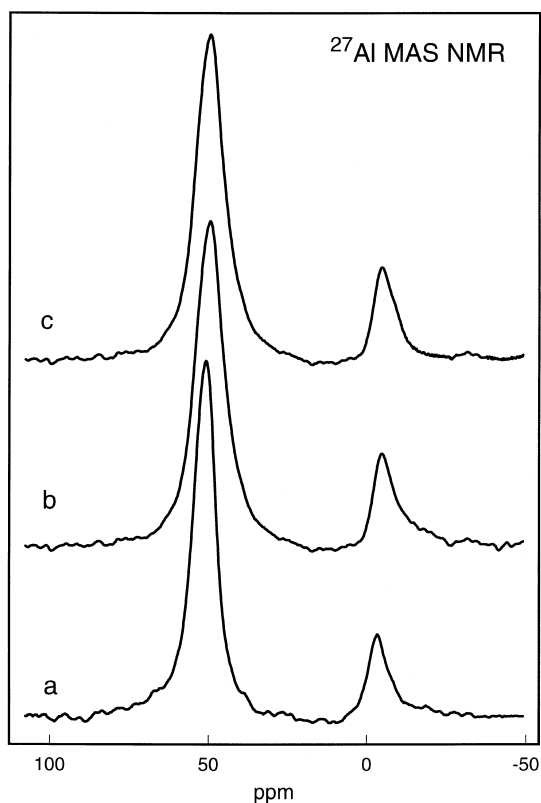


Fig. 4. ^{27}Al MAS NMR spectra of different zeolites: (a) aluminosilicate (HZSM-5, Si/Al = 25); (b) galloaluminosilicate (MFI-3, Si/Ga = 50, Si/Al = 25); (c) galloaluminosilicate (MFI-4, Si/Ga = 25, Si/Al = 25).

and MFI-4, although with identical Si/Ga ratio in the original gel, they have different framework Si/Ga ratios after crystallization. The higher the aluminum contents in the gel, the higher the framework Si/Ga ratio. At the same time, a reverse effect of the presence of Ga in gel on the incorporation of Al is not observed. Therefore, it is suggested that in the case of galloaluminosilicate, both Al and Ga can enter the zeolitic site. However, the addition of aluminum in the zeolite synthesis hinders the incorporation of gallium into the zeolite framework, whereas a controversial effect was not concluded, i.e. the presence of gallium in the zeolite synthesis does not hinder the incorporation of aluminum into the zeolite framework. One may expect that probably the larger size of gallium as compared with that of aluminum may be responsible for this. It is reported that in the case of

[Fe, Al]-zeolite [12], there is a competition between Fe and Al species for the occupation of tetrahedral framework position. Interestingly, it is Fe rather than Al species that are favored in the competition despite the fact that the size of the Fe cations is larger than that of the Al cations. Therefore, it is necessary to conduct further investigation in order to understand what is the crucial factor for in this kind of competition during the preparation of two components heteroatom-containing zeolite system.

Non-framework Ga, if there is any, will show a band at about 0 ppm in the ^{71}Ga MAS NMR spectra, which is analogous to the extra-framework aluminum resonated at 0 ppm in ^{27}Al MAS NMR. However, no such kind of band could be detected in the present ^{71}Ga MAS NMR spectra. This cannot be due to the absence of extra-framework gallium, but rather to the presence of large quadrupolar constant that gallium possesses, which will make them invisible to NMR. When the content of tetrahedral framework Ga increases, the corresponding chemical shift in the ^{71}Ga MAS NMR spectra will shift to a higher value (from 147 ppm for MFI-4 sample to 157 ppm for MFI-2 sample). Similar to ^{27}Al MAS NMR spectra, the relation of the chemical shifts of Ga with the mean zeolite T–O–T* bond angle [9,13] can be expressed in the following equation:

$$\delta(^{71}\text{Ga}) = -1.42\theta + 369.06$$

Therefore, with the increase of the amount of gallium incorporated into the zeolite framework, the chemical shift will move to higher values, implying that the mean (Si–O–Ga) bond angle θ decreases.

When the zeolite was mixed and ground with 3% MoO_3 for at least 0.5 h, sharp peaks attributed to MoO_3 was clearly resolved in their XRD patterns. Meanwhile, those peaks ascribed to characteristic MFI structured zeolites are also observed. If the samples were calcined at 773 K for 4 h, the patterns corresponding to MoO_3 disappeared. It appears that the Mo species migrated easily and dispersed on the MFI-type zeolites [14–16]. When MoO_3 was ground with the zeolite, most of the MoO_3 particles resided at the external surface of the zeolite in a three-dimensional mode. If the sample was calcined at 773 K, part of the MoO_3 would migrate into the zeolite channels and highly dispersed there and, therefore, no MoO_3 phase could be detected in the XRD patterns [17].

Table 2
Catalytic performance on various zeolite catalysts^a

	Reaction time (min)	Methane conversion (%)	Selectivity (%)			
			C ₂ ⁺	C ₂ ²⁻	CO	CO ₂
MFI-2	5	0.71			63.20	36.80
	60	0.33		5.18	93.30	1.51
	180	0.15	5.80	36.90	57.30	
MFI-3	5	2.17			86.07	13.93
	65	0.36		9.60	90.40	
	180	0.20	1.70	48.0	50.30	
MFI-4	5	2.02			63.40	26.40
	55	0.44		6.72	92.40	0.88
	180	0.23	6.02	42.50	50.48	
MFI-5	5	1.88			73.30	26.70
	55	0.47			100	
	180	0.21		35.70	64.30	

^a Reaction conditions: $T = 973$ K; $SV = 1500$ ml/g h.

3.3. Catalyst evaluation

The aromatization of the homologous compounds of methane, such as butane, propane [18–22], and ethane [23], etc. has been extensively investigated and commercialized [24] on gallium or zinc modified HZSM-5 and/or MFI-structured zeolites. Since there are some similarities between the dehydro-aromatization of light paraffins (C₂–C₄) and the dehydro-aromatization of methane, it is reasonable to consider the latter as an extension of the former.

Methane dehydro-aromatization was performed over the Ga-containing zeolites and the results are shown in Table 2. All of the zeolites exhibit similar behaviors. The highest methane conversion was <2% at the beginning of the reaction. The main products were CO and CO₂. This is probably resulted from the reaction of adsorbed oxygen species with methane [15,16]. With the increase of reaction time, the selectivity of C₂H₄ increased gradually at the expense of the CO₂, whereas the selectivity of CO passed a maximum. After running the reaction for more than 50 min, methane conversion was greatly suppressed (<0.5%). At the same time, no detectable benzene formation was observed during all the reaction processes.

It has been generally accepted that in the process of propane aromatization, Ga oxide alone or that incorporated into the zeolite framework plays an important role both in the cleavage of the propane C–H bond

and the succeeding hydrogen desorption [18–22]. Some authors pointed out that it is the cooperation of Ga and Bronsted acid sites that leads to the activation of propane [21]. In the present case, we could not observe any apparent consumption of methane in the reaction. This implies that neither Ga nor the combination of Ga and the Bronsted acid sites can efficiently activate methane. This is conceivable since compared with other paraffins, methane possesses the highest bonding strength of the C–H bond, and is the most stable molecule in the paraffin groups. Therefore, the catalysts that have the ability to activate propane may not be a suitable one for methane activation.

After the introduction of the second component, i.e. molybdenum oxide, the catalytic performance was greatly enhanced. Fig. 5 shows the conversion of methane and the selectivity towards benzene on the Ga-containing zeolites modified with molybdenum oxide. The 3% MoO₃/HMFI-4 catalyst shows good activity (about 5%) and benzene selectivity (80%). After running for about 3 h, the conversion of methane remained at 3.7%, whereas the benzene selectivity was 76% and ethene selectivity was 15.2%. With the increase of the Ga content in the framework, the conversion of methane and the selectivity of benzene decreased sharply. When the Si/Ga ratio was kept at 25 and the aluminum content was gradually increased, a reverse catalytic behavior was observed (not shown). On the 3% MoO₃/MFI-2 catalyst

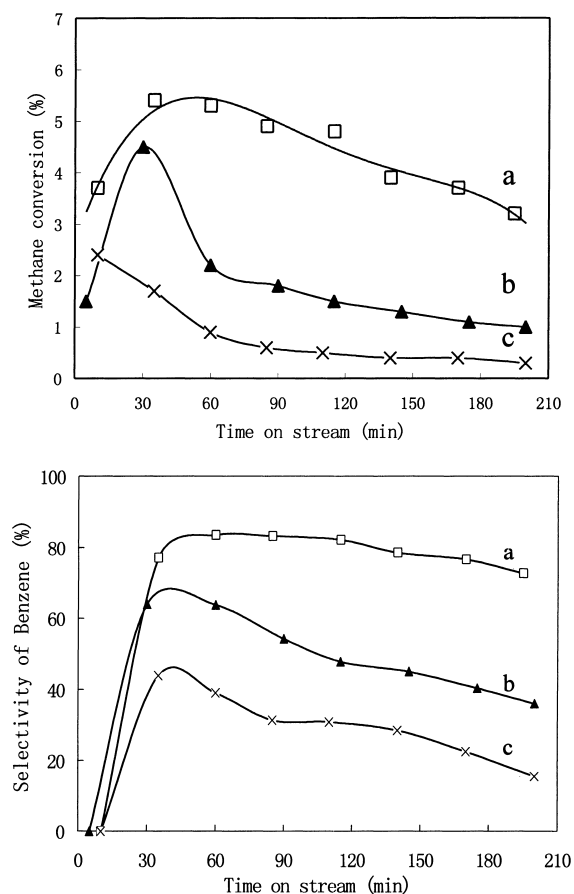


Fig. 5. Catalytic performance of different molybdenum loaded catalysts: (a) 3% MoO₃/HMFI-3; (b) 3% MoO₃/HMFI-4; (c) 3% MoO₃/HMFI-2.

(Si/Ga = 25, without aluminum), a poor performance was resulted (Fig. 5d). However, we still could observe the formation of benzene, though it was very small in quantity, as compared with those obtained on the catalysts containing aluminum.

The present results show that both gallosilicalite and galloaluminosilicate (MFI) zeolites, which are good catalysts for propane aromatization [25], have little activity in methane dehydro-aromatization. On the other hand, the introduction of the Mo species plays a key role in the initial activation of methane. Molybdenum supported either on gallosilicalite or galloaluminosilicate exhibited rather good catalytic performances. It is generally accepted that the acid strength sequence undergoes the following order for heteroatom-substituted

silicates [26]:

[Al]-ZSM-5 > [Ga]-ZSM-5

> [Fe]-ZSM-5 ≫ silicalite

The weak strength of acid sites of the gallosilicalite, in comparison with that of aluminosilicate (MFI) or galloaluminosilicate (MFI), may be responsible for the observed poor activity of its methane dehydro-aromatization. This implies that the acid sites of gallosilicalite (MFI) is too weak to accomplish successfully the transformation of the primary products of this reaction to the final product, namely benzene, when in combination with the Mo species [27–29]. Ga³⁺ cations, although compatible with Al³⁺ cations in the framework, do not play the same role as the Al³⁺ cations in the framework for methane dehydro-aromatization. Therefore, it appears that the activation and aromatization of methane need stronger acid sites as compared with those of its homologous compounds.

4. Conclusions

The H-gallosilicalites and H-galloaluminosilicates with various Si/Al and Si/Ga ratios, respectively, have been synthesized by the hydrothermal method. By using ⁷¹Ga and ²⁷Al MAS NMR, it is confirmed that Ga³⁺ cations are incorporated into the zeolite framework and that the presence of Al³⁺ cations in the parent gel will inhibit the incorporation of the Ga³⁺ cations into the zeolite framework. On the other hand, the presence of Ga³⁺ cations does not have obvious effect on the incorporation of the Al cations into the zeolite framework. Both of the H-galloaluminosilicate and H-gallosilicalite zeolites show little activity for methane dehydro-aromatization. The introduction of the second component MoO₃ is a crucial factor for methane dehydro-aromatization. Due to the different strength of acid sites of the H-gallosilicalite, H-galloaluminosilicate and H-aluminosilicate (MFI), the corresponding supported Mo catalysts show their catalytic performances according to the following sequence: Mo/HZSM-5 > Mo/H-galloaluminosilicate > Mo/H-gallosilicalite. It appears that the aromatization of methane and its other homologous compounds have the different routes.

Acknowledgements

We are grateful to the supports of the National Natural Science Foundation of China and the Ministry of Science and Technology of China.

References

- [1] B. Notari, *Catal. Today* 18 (1993) 163.
- [2] R. Szostak, T.L. Thomas, *J. Catal.* 100 (1985) 555.
- [3] T. Inui, Y. Makino, F. Okazumi, S. Nagase, A. Miyamoto, *Ind. Eng. Chem. Res.* 26 (1987) 647.
- [4] X. Liu, J. Klinowski, *J. Phys. Chem.* 96 (1992) 3403.
- [5] J. Kanai, N. Kawata, *Appl. Catal.* 55 (1989) 115.
- [6] G. Fiannetto, A. Montes, N.S. Gnep, A. Florentino, P. Cartraud, M. Guisnet, *J. Catal.* 145 (1993) 86.
- [7] C.R. Bayense, A.P.M. Kentgens, J.W. de Haan, L.J.M. van de Ven, J.H.C. van Hooff, *J. Phys. Chem.* 96 (1992) 775.
- [8] T. Inui, Y. Ishihara, K. Kamachi, H. Matsuda, *Zeolites: Facts, Figures, Future*, Elsevier, Amsterdam, 1989, p. 1183.
- [9] T. Takeguchi, K. Kagawa, J. Kim, T. Inui, D. Wei, G.L. Haller, *Catal. Lett.* 46 (1997) 5.
- [10] M.L. Occelli, H. Eckert, A. Wolker, A. Auroux, *Microporous Mesoporous Mater.* 30 (1999) 219.
- [11] M. Fitzgerald, D. Sutton, J. Thomson, *J. Chem. Soc., Faraday Trans.* 94 (1998) 3511.
- [12] F. Testa, F. Crea, G.D. Diodati, L. Pasqua, R. Aiello, G. Terwagne, P. Lentz, J.B. Nagy, *Microporous Mesoporous Mater.* 30 (1999) 187.
- [13] S.M. Bradley, R.F. How, R.A. Kydd, *Magn. Reson. Chem.* 31 (1993) 883.
- [14] R.W. Borry III, Y.H. Kim, A. Huffsmith, J.A. Reimer, E. Iglesia, *J. Phys. Chem. B* 103 (1999) 5787.
- [15] D. Ma, Y. Shu, X. Bao, Y. Xu, *J. Catal.* 189 (2000) 314.
- [16] D. Ma, Y. Shu, M. Cheng, Y. Xu, X. Bao, *J. Catal.* 194 (2000) 105.
- [17] Y. Xie, Y. Tang, *Adv. Catal.* 37 (1990) 1.
- [18] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro, *Appl. Catal.* 43 (1988) 155.
- [19] P. Meriaudeau, C. Naccache, *J. Mol. Catal.* 50 (1987) L7.
- [20] P. Meriaudeau, C. Naccache, *J. Mol. Catal.* 59 (1987) L31.
- [21] G. Buckles, G.J. Hutchings, C.D. Williams, *Catal. Lett.* 11 (1991) 89.
- [22] C.R. Bayense, A.J.H.P. Van der Pol, J.H.C. van Hooff, *Appl. Catal.* 72 (1991) 81.
- [23] T. Mole, J.R. Anderson, G. Creer, *Appl. Catal.* 17 (1985) 141.
- [24] P.C. Dollan, P.R. Pujado, *Hydroc. Process* (1989) 72.
- [25] V.R. Choudhary, A.K. Kinage, C. Sivadinarayana, P. Devadas, S.D. Sansare, M. Guisnet, *J. Catal.* 158 (1996) 34.
- [26] *New Solid Acids and Based and their Catalytic Properties*, Kodansha, Tokyo, Japan, 1989.
- [27] Y. Xu, S. Liu, L. Wang, M. Xie, X. Guo, *Catal. Lett.* 30 (1995) 135.
- [28] D. Wang, J.H. Lunsford, M.P. Rosynek, *J. Catal.* 169 (1997) 347.
- [29] F. Solymosi, J. Cserenyi, A. Szoke, T. Bansagi, A. Oszko, *J. Catal.* 165 (1997) 150.