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Propylene Aromatization on Ga-MFI Zeolites

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Abstract–Propylene aromatization reaction was performed on various MFI type zeolites containing Ga species. The Ga was introduced into the zeolites by substitution (Ga-MFI), ion exchange (GIZ) and physical mixing (GPZ). A commercialized zeolite (PQZSM-5) was also used for comparison. The catalysts prepared were characterized by using XRF, XPS, surface area measurement, NH_3-TPD, and H_2-TPR. Through the Ga substitution, the acidity of the modified catalysts was decreased, and dehydrogenation and aromatization reactions occurred more easily. The lattice Ga did not react well with hydrogen contrary to the Ga located at the outside of the lattice. It was also found that Ga-MFI catalysts facilitate alkylation reactions.

Key words: Propylene Aromatization, Ga-MFI Zeolite, Zeolite Preparation, Ga Substitution

INTRODUCTION

The bi-functionality of Ga-MFI zeolite makes it an effective catalyst for the aromatization of light hydrocarbons. It has been repeatedly shown that Ga facilitates the dehydrogenation of the light hydrocarbons, while acid sites facilitate the aromatization of the dehydrogenated olefin species [Gnep et al., 1988]. However, there is still a controversy about which Ga is responsible for the dehydrogenation of the light hydrocarbons-the Ga substituted in the zeolite frame work [Kanai and Kawata, 1990; Oda and Sayo, 1986] or the Ga located outside the zeolite frame [Choudhary and Devadas, 1998; Bayense et al., 1991; Khodakov et al., 1990]. In general, the aromatization of light alkanes takes place via corresponding alkene intermediates. It has been also generally known in the aromatization of propylene that metalosilicates show higher selectivity to aromatics than HZSM-5. Inui et al. [1985] explained this result by considering that the HZSM-5 possessing high hydrogen-transferring ability hydrogenates propylene to propane using the hydrogen produced in the process of the amortization.

Ga-substituted HZSM-5 shows better selectivity to aromatics in propylene aromatization than HZSM-5. Jia et al. [1993] explained this phenomenon by a reversible adsorption and desorption of hydrogen on Ga, together with a change in hydrogen transferring ability owing to the Ga substitution. There is also another explanation for that phenomenon. With an acid catalyst (such as HZSM-5), a corresponding paraffin is produced in the course of an olefin aromatization because of hydrogen-transferring reactions between the olefin and carbonium ions, as shown in Eq. (1), while with an acid catalyst containing Ga the aromatization takes place via a different reaction path without producing corresponding paraffin, as shown in Eq. (2) [Ono et al., 1987; Kitagawa et al., 1986].

$$5C_3H_6 \rightarrow C_6H_6+3C_3H_6 \tag{1}$$

$$2C_3H_6 \rightarrow C_6H_6+3H_2 \tag{2}$$

In this study, various MFI zeolites containing Ga were prepared and characterized by a number of analytical methods. Then, the catalysts prepared were applied to the propylene aromatization to examine their catalytic activity.

EXPERIMENTAL

1. Preparation of Zeolite Catalysts

The zeolites used in this work were prepared under atmospheric pressure [Park et al., 2001]. A commercialized zeolite (NH_4-ZSM-5, PQ Co.) was also used for comparison.

The materials for the synthesis of Ga-MFI were Ludox-AS40 (Du Pont Chem. Co.) as a silica source, sodium aluminate (Sunjeong Chem. Co.) as an alumina source, $Ga(NO_3)_3$ (Aldrich Chem. Co.) as a Ga source, NaOH as an alkali and inorganic cation source (Junsei Chem. Co.) and *tetra*-propyl ammonium bromide (TPABr) as an organic template (Dongkyung Hwasung Co.).

The zeolites were synthesized under atmospheric pressure in a 1.5 L Teflon reactor equipped with a condenser and stirrer, and the reactor was heated with an oil bath.

The gel composition of reaction mixtures used for the synthesis of Ga-MFI and ZSM-5 was determined based on the amount of SiO_2 of the aSiO_2-b(Ga_2O_3 or Al_2O_3)-cNa_2O-dTPA_2O-eH_2O. Ludox-AS40, 50 wt% NaOH solution, and distilled water were mixed in beaker I, while distilled water, 50 wt% NaOH solution, and $Ga(NO_3)_3$ were mixed in beaker II. After the solution of beaker II was poured into beaker I under agitating, then TPABr was added. The mixed solution was moved into the 1.5 L Teflon reactor and reacted at 100 °C. After a given period of crystallization, the product was filtered and washed with distilled water until the filtrate became neutral. The solid residue of the filtration was then dried at 110 °C and stored in a desiccator.

2. Catalyst Characterization

The weight percentage of Ga was determined by XRF (Rigaku 3270). For XRF analysis, samples and standard samples were pre-

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‡This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

pared by using Na_2CO_3, SiO_2, Ga_2O_3 and Al_2O_3 (all from Johnson Matthey Co., >99.99%), and LiB_4O_7 (Claisse Inc.) was used as a melting agent.

XPS analysis was performed by using ESCALAB 220i. For XPS analysis, samples were prepared by pressing the catalysts into a thin disk of 1 mm thickness. Correction for charging effects was made with the C(1s) peak at 285.0 eV from adventitious carbon.

N_2 BET surface areas and micropore areas of the catalysts were measured with a Micromeritics ASAP2000 analyzer.

NH_3-TPD and H_2-TPR analyses were conducted by using a Micromeritics 2900. For NH_3-TPD analysis, 0.3 g of a catalyst was loaded in a quartz reactor and heated under air (40 ml/min) up to 600 °C, and at this temperature the air was switched to Ar, then the catalyst was cooled to 100 °C. At 100 °C pure NH_3 gas was introduced into the reactor and adsorbed on the catalyst for 1 h. Then, to remove physically adsorbed NH_3 the catalyst was purged with Ar (100 ml/min) at 100 °C for 1 h. Finally, the catalyst was heated to 600 °C under flowing Ar (50 ml/min) at a rate of 10 °C/min, to measure the amount of the desorbed NH_3 with TCD.

H_2-TPR analysis was performed with 0.3 g of a catalyst in a quartz reactor. The catalyst was heated to 650 °C with a flow of 40 ml air/min, and the air was switched to Ar at the same temperature, and then the catalyst was cooled to room temperature. Then, the catalyst was reduced with a flow of 40 ml/min of a 10% H_2/Ar mixed gas with temperature raised to 650 °C at a ramping rate of 10 °C/min, to measure the consumed hydrogen with TCD.

3. Propylene Aromatization

3-1. Catalysts Pretreatment

In order to use the prepared catalysts, Ga-MFI and ZSM-5, in the propylene aromatization, the prepared catalysts were pretreated as follows. For Ga-MFI catalyst, the prepared catalysts were calcined in air at 550 °C to remove the organic template, and the catalysts became Na-type, and the Na-type catalysts were ion-exchanged two times with 0.6 N HCl solution at 60 °C for 2 h to obtain H-type Ga-MFI. Then, the Ga-MFI was used as a catalyst for propylene aromatization. ZSM-5 catalyst was also pretreated by the same procedure mentioned above to obtain HZSM-5. The HZSM-5 was used as a catalyst or used to prepare GPZ or GIZ catalysts. GPZ catalysts were prepared by physical mixing of HZSM-5 and GaO(OH) followed by calcination in air at 550 °C to obtain Ga_2O_3/HZSM-5 (GPZ). And, GIZ catalysts were also prepared by ion exchange of HZSM-5 with $Ga(NO_3)_3$ solution twice at 60 °C and calcined at 550 °C in air to obtain Ga-HZSM-5 (GIZ). For comparison, commercial NH_4-ZSM-5 (PQ Co.) was purchased and calcined in air at 550 °C to obtain HZSM-5 (PQZSM-5) and used as catalysts.

3-2. Propylene Aromatization

Propylene aromatization reaction was performed by using 1 g of a catalyst in a quartz reactor (OD, 10 mm). The catalyst was activated under air (40 ml/min) by increasing the temperature at a rate of 10 °C/min from room temperature to 550 °C and holding at this temperature for 2 h. Then, the reactor was purged with He, and propylene was flowing at a space velocity of 2,400 $cm^3g^{-1}h^{-1}$. Finally, the reaction was carried out at 500 °C. The products were analyzed with a GC (Chrompak 9001) equipped with two capillary columns.

RESULTS AND DISCUSSION

1. Physicochemical Properties of Catalysts

The prepared catalysts were denoted as follows, depending on the Si/Ga_2 or Si/Al_2 ratios and pretreatment. The catalysts prepared in this work were calcined and then ion-exchanged with 0.6 N HCl solutions to convert them into H-type zeolites. The Ga-MFI catalysts whose Si/Ga_2 ratios were 100 and 60 were called Ga-MFI(A) and Ga-MFI(B), respectively; the HZSM-5 catalyst whose Si/Al_2 ratios were 110 and 70 were called HZSM-5(A) and HZSM-5(B), respectively. The NH_4-ZSM-5 purchased from PQ Co. was calcined to convert it into HZSM-5, and they were called PQZSM-5(A) and PQZSM-5(B) according to their Si/Al_2 ratios, 112 and 75, respective-

Table 1. Characteristics of various catalysts

Catalyst**	Ga wt% by XRF	Desorption temperature by NH_3-TPD		BET surface area (m^2/g)		Binding energy (eV)* by XPS		
		Low (°C)	High (°C)	Total area	Micropore area	Ga(2*p*3)	O(1*s*)	Si(2*p*)
Ga-MFI(A)	2.18	188	379	426.7	267.1	1119.2	532.7	104.0
HZSM-5(A)		189	422	494.8	254.0		533.1	103.6
PQZSM-5(A)		200	422	359.1	128.8			
GIZ(A)	1.57	201	440	430.1	217.6			
1.5GPZ(A)	1.51	203	426	442.7	216.8			
Ga-MFI(B)	3.82	190	391	473.1	263.5	1119.2	532.3	103.6
HZSM-5(B)		212	447	425.9	247.2		533.1	103.7
PQZSM-5(B)		216	445	395.7	202.4		533.1	103.7
GIZ(B)	2.16	213	440	409.8	204.8	1118.9 1119.6	532.5	103.5
1.2GPZ(B)	1.23	208	444	400.8	210.6	1119.6	532.5	103.6
2.0GPZ(B)	2.03	208	444	395.4	205.2			

*Referenced to the binding energy of C(1s), 285 eV.

**Ga-MFI(A, B): gallosilicates, Si/Ga_2=110(A), 60(B); HZSM-5(A, B): Si/Al_2=110(A), 70(B), synthesized at atmospheric pressure; PQZSM-5(A, B): Si/Al_2=112(A), 75(B), purchased from PQ Co.; GIZ(A, B): Ga^{3+} ion-exchanged with HZSM-5(A) and (B); GPZ(A, B): GaO(OH) was physically mixed with HZSM-5(A) and (B).

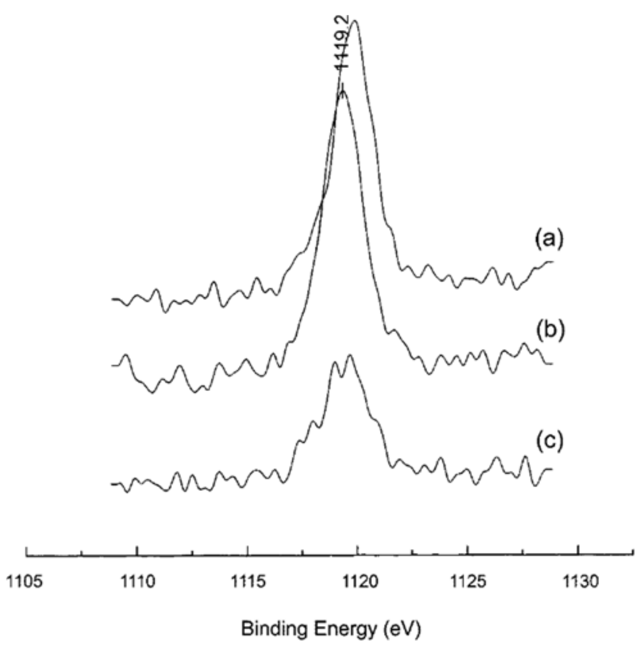

Fig. 1. XPS spectra of Ga(2P3); (a) 1.2GPZ(B), (b) Ga-MFI(B) and (c) GIZ(B) catalysts (referenced to C(1s)).

ly. The HZSM-5(A) was ion-exchanged with Ga$(NO_3)_3$ and it was called GIZ(A), and HZSM-5(B) was ion-exchanged with Ga$(NO_3)_3$ and it was also called GIZ(B). The catalyst prepared by physical mixing of HZSM-5(A) and GaO(OH) and calcined in air was called 1.5GPZ(A), in which Ga content was controlled to be 1.5 wt%. And, the catalysts prepared by physical mixing of HZSM-5(B) and GaO (OH) and calcined in air were called 1.2GPZ(B) and 2.0GPZ(B), depending on the Ga contents, 1.2 and 2.0 wt%, respectively.

The physicochemical properties of the catalysts prepared here are summarized in Table 1. When HZSM-5 (Si/Al_2=60) is ion-exchanged by Ga^{3+}, the maximum amount of exchangeable Ga is reported to be 1.2 wt% [Jacobs et al., 1981]. However, the amounts of exchanged Ga were 1.57 and 2.16 wt% as shown in Table 1. This can be attributed to the existence of un-exchanged Ga existing in the pore of the catalysts. In the XPS spectrum of GIZ(B), as shown in Fig. 1, two XPS peaks, corresponding to Ga($2P_3$), were observed. Among these two peaks, one peak, appearing at 1119.6 eV, has the same binding energy with 1.2GPZ(B), prepared via physical mixing. This stands for the existence of un-exchanged Ga species in the catalyst. From these results, it appears that in the process of the Ga ion-exchange the excess Ga may be left in the pore of the catalyst.

As shown in Table 1, the binding energies of Ga ($2P_3$) were different, depending upon the Ga state existing-the binding energies of Ga-MFI(A) and Ga-MFI(B) were both 1119.2 eV; the binding energies of the Ga ion-exchanged one, GIZ(B), were 1118.9 and 1119.6 eV; and the binding energy of the physically mixed one, 1.2GPZ(B), was 1119.6 eV. However, these differences in the binding energies are insignificant.

NH_3-TPD experiment was conducted to examine the acidity of the catalysts, and the results are represented in Figs. 2 and 3. As seen in Fig. 2, the Ga-MFI(A) catalyst shows a distinct difference in the desorption temperature, that is, about 40 °C lower when compared with the others. This phenomenon was also found with Ga-MFI(B) catalyst, as shown in Fig. 3. From these results, it appears that the acidity of the HZSM-5 catalyst is lowered by the Ga substitution.

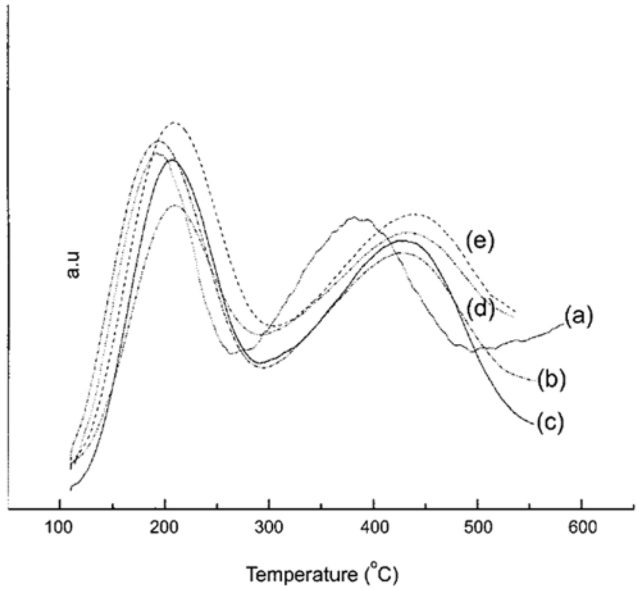

Fig. 2. NH_3-TPD curves for (a) Ga-MFI(A), (b) HZSM-5(A), (c) PQZSM-5(A), (d) 1.5GPZ(A) and (e) GIZ(A).

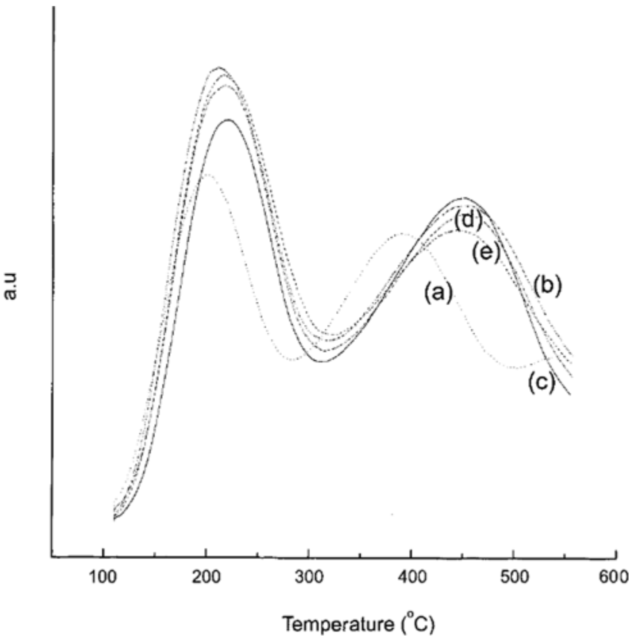

Fig. 3. NH_3-TPD curves for (a) Ga-MFI(B), (b) HZSM-5(B), (c) PQZSM-5(B), (d) 1.2GPZ(B) and (e) GIZ(B).

When comparing Fig. 2 and Fig. 3, it can be seen that the desorption peaks of Fig. 3 shift to a higher temperature. It implies that the acidity of the catalysts increases with decreasing Si/Ga_2 or Si/Al_2 ratios.

The surface areas of the catalysts are listed in Table 1. The surface areas of the HZSM-5 catalysts prepared in this study under atmospheric pressure were 30-100 m^2/g larger than those of the com-

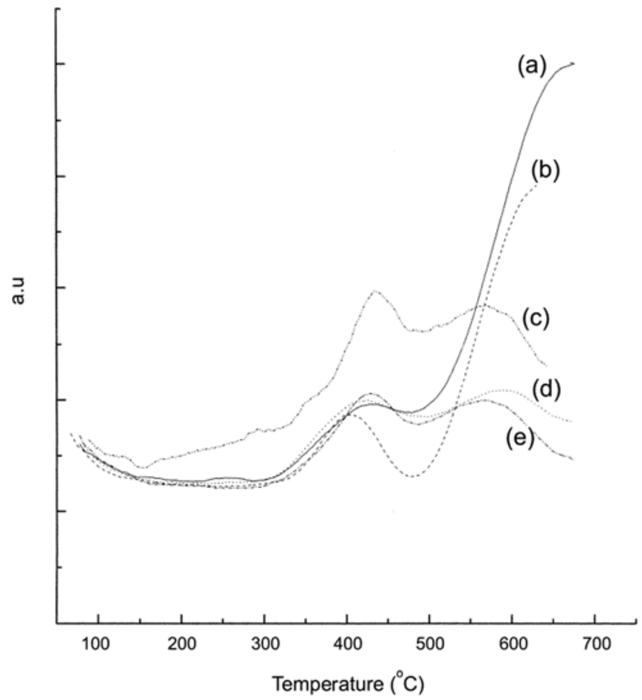

Fig. 4. H_2-TPR curves for (a) Ga_2O_3, (b) 1.2GPZ(B), (c) GIZ(B), (d) Ga-MFI(B) and (e) HZSM-5(B).

mercialized ones (PQ Co.). And, micropore areas of the HZSM-5 prepared under atmospheric pressure were also 40-120 m^2/g larger than those of the commercialized ones. The total surface area of Ga-MFI(A) was smaller than that of ZSM-5(A), whereas the micropore surface area of Ga-MFI(A) was larger than that of ZSM-5(A), indicating a well developed pore structure of the Ga-MFI catalyst. When Ga was introduced into ZSM-5, the surface areas of the Ga introduced ZSM-5 catalysts were generally reduced.

H_2-TPR experiment was conducted with Ga-MFI(B), HZSM-5(B), Ga_2O_3, 1.2GPZ(B) and GIZ(B) catalysts, and the results are in Fig. 4. It has been generally known that Ga_2O_3 does not reduce well even in a hydrogen environment. Jacobs et al. [1989] reported that Ga_2O_3 supported on ZSM-5 was partially reduced at 883 K. Through the H_2-TPD experiment, it was observed that hydrogen consumption was large with Ga_2O_3 and GPZ(B) catalysts above 600 °C, but small with Ga-MFI(B) and HZSM-5(B). This indicates that lattice Ga does not reduce well contrary to the Ga located at the outside of the lattice.

2. Propylene Aromatization

To examine the catalytic activities of the catalysts, a propylene aromatization reaction was performed with various catalysts at 500 °C with a space velocity of 2,400 $cm^3g^{-1}h^{-1}$. Product distributions with Ga-MFI(A), HZSM-5(A), PQZSM-5(A), 2.0GPZ(A) and GIZ(A) catalysts are listed in Table 2. With the Ga-MFI(A) catalyst, conver-

Table 2. Product distribution of propylene aromatization reactions with various catalysts

Catalyst Products distribution (wt%)	Ga-MFI(A)	HZSM-5(A)	PQZSM-5(A)	2.0GPZ(A)	GIZ(A)
Conversion (%)	89.0	84.9	84.3	92.7	91.6
Methane	1.1	1.1	1.1	1.4	1.4
Ethane	1.7	2.5	2.2	3.3	2.5
Ethylene	5.1	5.4	6	2.7	5.3
Propane	10.5	19.8	17.7	18.3	15.8
Propylene	9.6	9.5	11.3	4.9	7.6
i-Butane	8.8	8.5	7.9	8.3	8.8
n-Butane	3.7	5.7	5.3	5.3	4.7
Butene	4.4	4.1	5.0	2.1	3.1
C^{5+}-Aliphatic	7.9	8.7	11.0	6.0	7.4
Benzene	3.9	3.8	3.4	4.7	5.0
Toluene	18.3	12.8	12.2	16.2	17.1
Ethylbenzene	1.7	1.3	1.2	1.6	1.4
p,m-Xylene	11.5	9.6	9.3	12.6	12.3
o-Xylene	3.6	3.0	2.7	4.0	3.7
m-Ethyltoluene	2.3	1.3	1.2	1.9	1.5
p-Ethyltoluene	1.1	0.6	0.7	0.9	0.7
1,3,5-*tri*-MeBe				0.2	
o-Ethyltoluene				0.4	
1,2,4-*tri*-TMeBe	2.5	1.2	0.9	2.0	1.9
C^{9+}-Aromatics				0.5	
Indane				0.5	
Naphtha				2.8	
Total	100	100	100	100	100
Total aromatics	44.8	33.5	31.6	44.7	43.6
Selectivity to BTX in total aromatics	82.9	87.2	87.2	83.8	87.5

Table 3. Product distribution of propylene aromatization reactions with various catalysts

Catalyst Product distribution (wt%)	Ga-MFI(B)	HZSM-5(B)	PQZSM-5(B)	1.2GPZ(B)	2.0GPZ(B)	GIZ(B)
Conversion (%)	92.5	96.0	91.0	96.6	96.1	99.3
Methane	1.5	2.6	1.7	3.0	2.7	6.4
Ethane	2.3	4.4	3.1	4.2	3.9	4.7
Ethylene	4.5	2.2	4	2.7	3.0	1.0
Propane	11.4	25.9	24.2	21.1	19.9	17.4
Propylene	7.1	3.8	8.2	2.9	3.3	1.0
i-Butane	8.5	5.7	6.7	5.0	5.9	1.1
n-Butane	3.6	4.1	4.8	4.0	4.5	1.5
Butene	3.0	1.1	2.4	1.1	1.2	-
C^{5+}-Aliphatic	6.7	2.3	4.5	2.4	3.4	-
Benzene	4.9	7	5.0	8.3	7.4	12.1
Toluene	20.4	17.5	15.2	20.2	20.2	28.3
Ethylbenzene	1.8	1.1	1.2	1.2	1.2	0.8
p,*m*-Xylene	12.7	10.3	10.7	12.6	13.0	14.1
o-Xylene	4.0	3.3	3.4	4.0	4.1	4.6
m-Ethyltoluene	2.4	0.9	1.2	1.0	1.1	0.7
p-Ethyltoluene	1.1	0.5	0.6	0.5	0.5	0.3
1,3,5-*tri*-MeBe	0.6	0.5	0.4	0.6	0.6	0.7
o-Ethyltoluene	0.5	0.3	0.3	0.3	0.3	-
1,2,4-*tri*-MeBe	3.0	1.6	1.6	1.9	2	2.6
C^{9+}-Aromatics	-	1.5	-	1.5	0.7	0.5
Indane	-	0.5	-	0.4	0.4	1.2
Naphtha	-	3.2	0.4	1.5	0.8	1.1
Total	100	100	100	100	100	100
Total aromatics	51.5	44.4	39.6	52.0	51.2	64.7
Selectivity to BTX in total aromatics	81.6	85.8	86.6	86.8	87.5	91.4

sion and total selectivity to aromatics were 89 and 45%, respectively. These values are higher than those observed for HZSM-5(A) and PQZSM-5(A). However, selectivity to BTX with Ga-MFI(A) was 83%, which was lower than those with HZSM-5(A) and PQZSM-5(A). With the Ga-MFI(A) catalyst, the percentage of propane produced was about the half of the ones of HZSM-5(A) and PQZSM-5(A). And, the iso/normal ratios of butane produced were 2.4 with Ga-MFI(A) and 1.5 with HZSM-5(A) and PQZSM-5(A). It is well known that the stronger the acidity becomes, the easier the hydrogenation and dealkylation become [Ono et al., 1987; Wang et al., 1990; Kitagawa et al., 1986; Meriaudeau and Naccache, 1995]. These catalysts, HZSM-5(A) and PQZSM-5(A), showed a relatively stronger acidity than Ga-MFI(A) as shown in Fig. 2. From these results it is clear that the Ga-MFI(A) facilitates dehydrogenation and propylene aromatization, whereas the HZSM-5(A) and PQZSM-5(A) catalysts do the hydrogenation of propylene and the dealkylation of aromatics. It is also found that the Ga substitution increases the propylene aromatization, and increases the iso/normal ratios of the butane produced.

For the 2.0GPZ(A) and GIZ(A) catalysts, which were prepared by mixing HZSM-5(A) and Ga$_2$O$_3$ and by Ga ion-exchange, respectively, conversions and selectivities to aromatics were increased in comparison with HZSM-5(A) catalyst. However, selectivity to BTX was decreased to 84% with 2.0GPZ(A) catalyst and unchanged with GIZ(A) catalyst. With these catalysts the percentage of propane produced was reduced in comparison with HZSM-5(A) catalyst, and the iso/normal ratios of butane produced were increased to 1.6 with 2.0GPZ(A) and 1.9 with GIP(A). With the 2.0GPZ(A) catalyst, more aromatic compounds were produced. From these results, it is found that the physical mixing of Ga$_2$O$_3$ with HZSM-5(A) increases the propylene aromatization, dehydrogenation, and aromatics alkylation reactions.

Product distributions with Ga-MFI(B), HZSM-5(B), PQZSM-5(B), 1.2GPZ(B), 2.0GPZ(B) and GIZ(B) catalysts are listed in Table 3. Through comparing Tables 2 and 3, it is noticed that the hydrogenation of olefins increases with increasing acidity. With 1.2GPZ(B) and 2.0GPZ(B) catalysts, which were prepared by physical mixing of Ga$_2$O$_3$ and HZSM-5(B), propane and ethane were decreased and ethylene and aromatics were increased, indicating that the addition of Ga retarded hydrogenation reaction and increased the selectivity to aromatics. Ga-MFI(B) showed higher total aromatics selectivity and lower light alkanes selectivity than HZSM-5(B). This indicates that with the Ga substitution both the dehydrogenation and the aromatization are facilitated according to the Eq. (2) given above.

From Tables 2 and 3, the following is concluded. In the propylene aromatization reaction, product distributions are not affected largely by the Si/Ga$_2$ ratios in the Ga-MFI catalyst, but are affected by the Si/Al$_2$ ratio with HZSM-5 catalyst. Dehydrogenation and aromatization reactions occur more easily with Ga-MFI catalysts than with HZSM-5 catalysts. The hydrogenation of olefins and the dealkylation of aromatics occur more easily with HZSM-5 catalysts than with Ga-MFI catalysts, and these reactions are affected by the acidity of the catalysts. With the addition of Ga_2O_3 to HZSM-5, some improvements in conversion, aromatics selectivity and alkylation are observed.

CONCLUSIONS

From the NH_3-TPD experiment it is found that Ga-MFI catalyst reveals lower acidity than HZSM-5 catalysts. From the H_2-TPR experiment it is found that the lattice Ga does not react well with hydrogen contrary to the Ga existing outside of the lattice. When propylene aromatization was performed with Ga-MFI and HZSM-5 catalysts having similar Si/M_2 (M=Ga or Al) ratios, the aromatics selectivity with Ga-MFI catalyst was about 10% higher than that with HZSM-5 catalyst. The percentage of BTX produced with Ga-MFI catalyst was about 5% lower than that with HZSM-5 catalyst; moreover, the percentage of the produced light alkanes (less than C_3) with Ga-MFI was about 50% less than that with HZSM-5 catalyst. This would stem from the characteristics of Ga-MFI-Ga facilitates dehydrogenation reaction and the reduced acidity of the Ga-MFI catalyst makes the alkylation reaction easier. This shows that it would be worthwhile to study alkylation reactions with Ga-modified zeolite catalysts.

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