Aromatization of Light Paraffins over Ga-containing MFI-type Catalyst

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Abstract−Aromatization of light paraffins such as propane and butane was investigated on MFI-type catalysts containing Ga as an active component. Even with less amount of Ga loading, Ga ion-exchanged MFI exhibited higher selectivity for aromatics, mainly benzene, toluene and xylene (BTX), than that of H-Ga-Silicate. This may be attributed to the presence of Al in Ga ion-exchanged MFI which increases the catalyst acidity. Further development was done by preparing H-Ga, Al-bimetallosilicate with the purpose of minimizing the catalyst preparation procedure. It has been found that H-Ga, Al-bimetallosilicate having Si/Ga ratio of 155 and Si/Al ratio of 40 exerted considerably high selectivity for aromatics, ca. 64% for BTX. This selectivity was comparable to that of H-Ga ion-exchanged MFI with the same amount of Ga loading. However, the bimetallosilicate catalyst can be prepared in only one step crystallization, which minimizes the catalyst preparation procedure.

Key words: Light Paraffins, Liquefied Petroleum Gas (LPG), Aromatization, Ga-containing MFI Catalyst, Ga-containing ZSM-5

INTRODUCTION

Effective utilization of light paraffins such as propane and butane is one of the most important subjects in the petrochemical industry. Much attention has steadily been given to a catalytic process for the direct conversion of light paraffins to aromatic hydrocarbons, particularly benzene, toluene and xylene [Chu, 1978; Chester and Chu, 1982; Dave et al., 1982; Inui and Okazumi, 1984a; Mole et al., 1985; Inui et al., 1986a]. These aromatics can be used as a booster for the high octane number gasoline and are important as the major feedstock in petrochemical-related industries. A number of publications have revealed the effective utilization of MFI-type catalysts (previously known as ZSM-5) containing gallium or zinc as the active catalysts for the aromatization of light paraffins [Chu, 1978; Chester and Chu, 1982; Dave et al., 1982; Inomata et al., 1985; Inui et al., 1987; Seddon, 1990]. Gallium may be either incorporated to replace aluminium in the zeolite framework or ion-exchanged with the existing cations in MFI-type catalyst. Although Ga ion-exchanged MFI-type catalyst has been proposed as the suitable catalyst for the reaction [Seddon, 1990], there is only little information on the comparative study of MFI-type catalysts into which Ga was introduced by different means. Therefore, this research aims to investigate the catalytic performance of various Ga-containing MFI-type catalysts on light paraffin aromatization, and the optimum method of Ga introduction has been proposed.

EXPERIMENTAL

1. Catalyst Preparation

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The MFI-type catalysts were prepared by adopting the rapid crystallization method [Inui, 1989]. The detailed preparation procedure is shown in Fig. 1. A gel mixture was prepared by adding solutions G-1 and G-2 into solution G-3 while maintaining a pH within 9-11 at room temperature and vigorously stirring with a homogenizer. After centrifugal separation of the gel mixture from mother liquor, the gel was mechanically ground for 15 min by a motor-driven mortar. This procedure was repeated twice and the
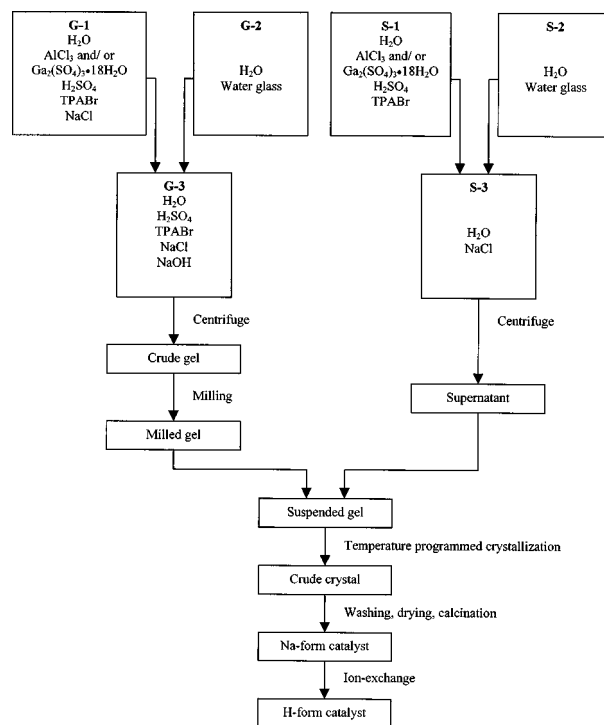

Fig. 1. Procedure for preparation of H-MFI and Ga-containing MFI catalysts.

final grinding time was extended for another 15 min. The ground gel mixture was returned to the supernatant of the decant solution prepared from S-1, S-2 and S-3. The gel mixture was then charged in a one-litre stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas. The mixture was heated from room temperature to 160 °C and from 160 °C to 210 °C with constant heating rates of 1.5 °C/min and 12 °C/h, respectively. The crude crystals produced were washed with distilled water by repeated cycles of centrifugation and decantation. The washed crude crystals were dried overnight at 100 °C and then calcined in air at 540 °C for 3.5 h. The resulting Na-form MFI-type catalysts were converted to protonated form by ion-exchange twice with 1 M (mole/litre) NH_4NO_3 solution at 80 °C for 1 h. The catalysts then were washed with distilled water, dried overnight at 100 °C, and subsequently heated in air at 540 °C for 3.5 h.

With the above-mentioned procedures, four kinds of catalyst were prepared: H-MFI (Si/Al=40), H-Ga-silicate (Si/Ga=40), H-Ga, Al-bimetallosilicate (Si/Ga=40-520, Si/Al=20-2000) and Ga ion-exchanged MFI designated herein as Ga/MFI. The Ga/MFI catalyst was obtained by treating the H-MFI with $Ga_2(SO_4)_3$ solution at 100 °C for 3 h. It was heated in air with a constant heating rate of 10 °C/min up to 350 °C and maintained at that temperature for 2 h. The loading amount of Ga was in the range of 0.3-2.0% by weight. All the catalysts were tableted, crushed and sieved to 8-16 mesh to provide the reaction.

CATALYST CHARACTERIZATION

The X-ray diffraction patterns of the catalyst were observed by X-ray diffractometer. The BET surface areas were calculated on the basis of N_2 adsorption at liquid nitrogen temperature by using ASAP-2000 surface area analyzer of Micromeritics. The results of which, shown in Fig. 2, confirm that the prepared catalysts have substantially the same structure identical to MFI-type zeolite [Inui, 1989].

APPARATUS AND REACTION METHOD

The conversion of light paraffins was carried out by using a conventional tubular flow reactor under atmospheric pressure. A 0.5 g portion of the catalyst was packed in a quartz reactor of 6-mm inner diameter. The reaction gas composed of 20% light paraffins and 80% nitrogen was made to flow through the catalyst bed at 450-600 °C with space velocities of 2,000-8,000 h^{-1}. After 1 h on stream, the products were taken and analyzed by two
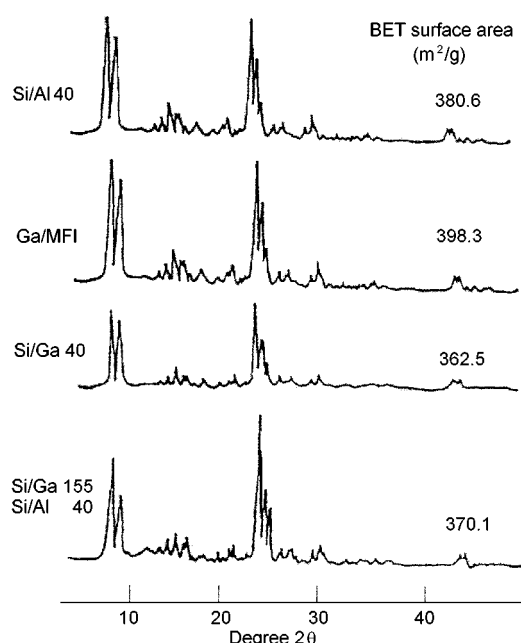

Fig. 2. XRD patterns and BET surface area of H-MFI and Ga-containing MFI catalysts.

SHIMADZU GC-14A gas chromatographs using the flame ionization detector. The gaseous hydrocarbons and gasoline-range hydrocarbons were analyzed on VZ-10 and Silicon OV-1 columns, respectively.

RESULTS AND DISCUSSION

1. Effect of Ga Introduction by Incorporation and Ion-Exchange

Table 1 shows the catalytic performance on propane aromatization of Ga/MFI with Ga loading content of 0.5 wt% and H-Ga-silicate with Si/Ga ratio of 40, which was equivalent to approximately 3 wt% of Ga. The result of H-MFI is also shown for comparison. The catalyst containing Ga exhibited much higher activity and selectivity than those of H-MFI. Even with less Ga loading content, Ga/MFI gave better catalytic performance than H-Ga-silicate. The reason for which should be ascribed to the effect of the presence of Al in zeolite framework on increasing the catalyst acidity. Another reason for the better activity of Ga/MFI compared to H-Ga-silicate may be found in Ga location in addition to the presence of Al in Ga/MFI zeolite. Framework Ga in H-

Table 1. Propane aromatization of H-MFI and Ga-containing MFI catalysts

CAT	Conv. (%)	Product distribution (C-wt%)										
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Arom	B	T	EB	X	A_9^+
H-MFI	75.54	25.04	6.31	31.83	16.42	5.07	15.31	7.22	5.89	0.20	1.36	0.64
H-Ga-silicate (Si/Ga=40)	70.96	9.91	2.93	16.64	16.40	2.34	51.48	25.26	19.51	0.31	5.02	1.38
Ga/MFI (0.5 wt%)	86.70	11.53	3.30	13.95	10.00	1.35	59.75	31.88	20.84	0.29	4.65	2.21

Feed: 20% propane balanced with N_2, Reaction conditions: 6,000 °C, GHSV 2,000 h^{-1}, 1 h on stream [C_1: methane; C_2: ethane; $C_2^=$: ethylene; $C_3^=$: propylene; C_4^+: C_4 fraction or higher; Arom: Aromatics; B: Benzene; T: Toluene; EB: Ethylbenzene; X: Xylenes; A_9^+: C_9 aromatics or higher].

Table 2. Propane aromatization on Ga/MFI catalysts with various Ga loading content

Ga/MFI (wt%)	Conv. (%)	Product distribution (C-wt%)										
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Arom	B	T	EB	X	A_9^+
0.3	86.23	12.88	2.98	21.66	31.02	2.32	28.99	16.18	8.77	0.16	2.30	1.59
0.5	86.70	11.53	3.30	13.95	10.00	1.35	59.75	31.88	20.84	0.29	4.65	2.21
0.7	94.80	8.55	2.53	13.43	17.62	2.14	55.73	21.07	17.19	0.46	7.57	3.90
1.0	95.12	11.98	3.93	7.69	4.30	0.11	72.19	35.40	22.99	0.21	4.06	9.52
2.0	90.15	12.09	4.78	9.23	5.86	0.62	67.42	34.85	22.51	0.21	4.18	5.78

Feed: 20% propane balanced with N_2, Reaction conditions: 6,000 °C, GHSV 2,000 h^{-1}, 1 h on stream.

Ga-silicate may not be directly involved in catalytic aromatization due to rigid bond to framework oxygen. Some Ga during synthesis and thermal treatments are reportedly extracted from framework sites to ion-exchanged sites, and the extracted Ga may be directly involved in the catalysis. Thus lower activity may be expected in H-Ga-silicate.

2. Effect of Ga Loading Amount in Ga/MFI Catalysts

Table 2 shows the catalytic performance in propane aromatization of Ga/MFI catalysts having different amounts of Ga loading. The catalyst activity and selectivity for aromatics increased with the increasing amount of Ga loading. Ga/MFI with 1 wt% Ga loading exhibited approximately 62.5% selectivity for BTX. When the Ga loading was increased to 2%, the activity and selectivity for aromatics declined slightly probably due to crowdedness of aromatization processes in an interconnected channel area due to high Ga loading, which could cause steric hindrance towards formation of aromatics.

3. Catalyst Performance of H-Ga, Al-bimetallocilicate Catalysts

The catalytic performance of H-Ga, Al-metallosilicate in propane aromatization is shown in Table 3. First, Si/Al ratio was fixed at 40 and Ga incorporation was varied from the Si/Ga ratio of 520 to that of 40. The activity and selectivity for aromatics increased with the increasing amount of Ga (or decreasing Si/Ga ratio), and H-Ga, Al-bimetallosilicate with the Si/Ga ratio of 155 exerted as high as 64% selectivity for BTX. It should be noted

that the Si/Ga ratio of 155 is equivalent to 1 wt% Ga loading in Ga/MFI; and the catalytic performance of both catalysts was roughly comparable. Further increase of Ga incorporation (Si/Ga=40) did not enhance the catalyst activity and selectivity, and thus the Si/Ga ratio of 155 was considered to be optimum. Then the catalysts having the Si/Al ratios other than 40, i.e., the Si/Al ratios of 2000 and 20, with the optimum Si/Ga ratio of 155 were prepared and their catalytic performances were observed. It has been clearly shown that a certain amount of Al was necessary to provide enough acidity required for the propane aromatization. Finally, H-Ga, Al-bimetallosilicate with the Si/Ga ratio of 155 and the Si/Al ratio of 40 was selected with economic concern.

4. Effect of Reaction Temperatures on Propane Aromatization

The temperature dependence of propane aromatization is shown in Table 4. The propane conversion decreased with the decreasing temperature and so did the aromatics selectivity. It was understood that the reaction temperature range about 550-600 °C was required to achieve a considerably high propane conversion.

5. Effect of GHSV on Propane Aromatization

Table 5 shows the product distribution of propane aromatization at 600 °C with space velocities ranging from 2,000 to 8,000 h^{-1}. The light olefins fraction such as ethylene and propylene gradually increased with the increasing GHSV, and thus the aromatics selectivity decreased. This should be ascribed to the short contact time at high GHSV.

Table 3. Propane aromatization on H-Ga, Al-bimetallosilicate catalysts

CAT	Conv. (%)	Product Distribution (C-wt%)										
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Arom	B	T	EB	X	A_9^+
Si/Ga=520 Si/Al=40	85.48	17.61	4.06	17.16	8.98	1.68	50.51	27.15	17.18	0.39	3.37	1.94
Si/Ga=310 Si/Al=40	92.04	15.75	4.04	13.01	6.48	0.85	59.83	33.27	20.30	0.36	3.65	2.25
Si/Ga=155 Si/Al=40	96.15	13.90	4.27	10.17	4.77	0.28	66.62	37.75	22.43	0.23	3.80	2.41
Si/Ga=40 Si/Al=40	95.12	12.29	6.35	9.09	5.08	0.56	66.60	34.49	21.60	0.21	4.39	5.91
Si/Ga=155 Si/Al=2000	38.49	12.24	1.72	24.96	35.81	4.48	20.78	10.55	7.81	0.16	1.88	0.38
Si/Ga=155 Si/Al=20	96.50	15.00	5.61	9.16	3.78	0.16	66.29	37.29	21.85	0.23	3.48	2.81

Feed: 20% propane balanced with N_2, Reaction conditions: 6,000 °C, GHSV 2,000 h^{-1}, 1 h on stream.

Table 4. Propane aromatization on H-Ga, Al-bimetallosilicate catalyst (Si/Ga=155, Si/Al=40) at various reaction temperatures

Temp (°C)	Conv. (%)	Product distribution (C-wt%)										
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Arom	B	T	EB	X	A_9^+
450	22.34	12.25	3.44	15.12	15.66	7.50	46.07	23.32	16.84	0.57	4.55	0.78
500	59.95	11.91	3.34	13.41	11.73	3.15	56.43	28.93	20.83	0.50	4.56	1.61
550	76.36	13.25	3.90	9.35	7.00	1.64	64.88	33.38	23.74	0.48	5.12	2.15
600	96.15	13.90	4.27	10.17	4.77	0.28	66.62	37.75	22.43	0.23	3.80	2.41

Feed: 20% propane balanced with N_2 Reaction conditions: GHSV 2,000 h^{-1}, 1 h on stream.

Table 5. Propane aromatization on H-Ga, Al-bimetallosilicate catalyst (Si/Ga=155, Si/Al=40) at various space velocities

GHSV (h^{-1})	Conv. (%)	Product distribution (C-wt%)										
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Arom	B	T	EB	X	A_9^+
2000	96.15	13.90	4.27	10.17	4.77	0.28	66.62	37.75	22.43	0.23	3.80	2.41
4000	91.32	9.95	2.36	13.54	8.80	0.97	64.40	33.78	22.83	0.28	4.88	2.63
6000	84.38	8.98	1.94	15.72	13.18	1.46	58.75	30.34	21.02	0.30	4.71	2.38
8000	77.51	8.23	1.62	16.75	16.18	1.79	55.39	26.64	19.83	0.30	4.48	2.14

Feed: 20% propane balanced with N_2, Reaction conditions: 600 °C, 1 h on stream.

Table 6. Aromatization of propane, butane, and their mixtures on H-Ga, Al-bimetallosilicate catalyst (Si/Ga=155, Si/Al=40)

Feed	Conv. (%)	Product distribution (C-wt%)										
		C_1	C_2	$C_2^=$	$C_3^=$	C_4^+	Arom	B	T	EB	X	A_9^+
20% C_3	96.15	13.90	4.27	10.17	4.77	0.28	66.62	37.75	22.43	0.23	3.80	2.41
14% C_3 6% C_4	97.45	12.47	4.63	7.75	3.19	0.16	71.79	35.27	24.28	0.24	4.26	7.64
10% C_3 10% C_4	96.62	13.14	5.26	8.72	4.00	0.38	68.51	36.02	24.96	0.25	4.28	3.00
6% C_3 14% C_4	97.36	13.50	5.74	8.37	3.59	0.18	68.56	35.55	25.74	0.25	4.44	2.58
20% C_4	99.96	13.65	6.71	8.44	3.29	0.26	67.63	33.57	25.16	0.25	4.36	4.29

Feed: 20% light paraffin(s) balanced with N_2, Reaction conditions: 600 °C, GHSV 2,000 $^{-1}$, 1 h on stream.

6. Effect of Feed Composition on the Aromatization Reaction

The catalytic performance of H-Ga, Al-bimetallosilicate having Si/Ga ratio of 155 and Si/Al ratio of 40 was extensively investigated by using feed composed of propane only, butane only, and their mixtures. As shown in Table 6, the catalyst exhibited steadily high activity and selectivity for aromatics irrespective of the feed composition. Therefore, it should be noted that H-Ga, Al-bimetallosilicate can be exploited with the LPG aromatization as well.

CONCLUSION

The Ga-containing MFI-type catalysts were found to exhibit good performance for light paraffin aromatization. Gallium ion-exchanged MFI, Ga/MFI, even with less Ga loading content, exerted surpassing activity and selectivity for aromatics over those of H-Ga-silicate whose structure was deprived of Al. The strong acid sites derived from the existence of Ga and Al should be responsible for the olefin oligomerization, cyclization and aromatization. H-Ga, Al-bimetallosilicate with the Si/Ga ratio of 155 and the Si/Al ratio of 40 combined the favorable effects of both Ga and Al, and can be prepared in only one-step crystallization. Thus,

it was proposed to be one of the promising catalysts for light paraffin aromatization. Furthermore, H-Ga, Al-bimetallosilicate proved to be an active catalyst for the aromatization of propane and butane mixtures irrespective of their compositions.

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