AROMATIZATION OF PENTANE CATALYZED OVER VARIOUS METALLOSILICATES

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Abstract – Various metallosilicates were synthesized using a hydrothermal method and characterized by SEM, XRD, ^{29}Si MAS NMR, chemical analysis and surface area measurements. These results showed that they had a MFI structure. The pentane aromatization reaction was carried out over these metallosilicates in a continuous flow reactor at 550 °C, He/pentane=3, WHSV=1.5 h^{-1} and 1 atm. Among the various metallosilicates, [Ga]ZSM-5(20) (52.3 %) and [Zn]ZSM-5(40) (37.6 %) showed higher aromatic selectivities for pentane aromatization. When [Al] ZSM-5(40) was ion-exchanged with gallium nitrate and zinc chloride, the selectivities for aromatics increased from 23.0 % to 35.5 % and to 32.7 %, respectively. The Si/metal mole ratios of [Ga]ZSM-5 and [Al]ZSM-5 were changed from 20 to 250 and NH$_3$ temperature programmed desorption (TPD) was carried out. As the Si/metal ratio was changed from 250 to 20, the selectivities for aromatics were increased from 5.3 % to 52.3 % over [Ga]ZSM-5 and from 10.1 % to 25.7 % over [Al]ZSM-5. NH$_3$ TPD of [Ga]ZSM-5 indicated that the sites of medium acidity play an important role in the formation of aromatics. When H$_2$ and CO were added to the reactant of pentane, the production of methane and ethane increased and that of aromatics decreased.

Key words: Aromatization, Metallosilicate, Acidity, Ion-Exchange, NH$_3$ TPD

INTRODUCTION

Over the past years significant progress has been made in the catalytic conversion of light hydrocarbons to chemicals and liquid fuels by direct routes. Several quite different approaches have been proposed, including selective oxidation of alkanes to aldehydes, alcohols or other higher hydrocarbons by the use of nitrous oxide [Anderson and Tsai, 1985], the coupling of light alkanes and light alkenes in the presence of superacid or transition metals [Loffler et al., 1984] and aromatization reactions catalyzed by acid zeolites [British Petroleum co., Int. Patent, 1984; Engelen et al., 1985; Kwak and Sachtler, 1996; Rhee et al., 1996; Sirokman et al., 1986]. Specifically, there are many studies about the conversion of light hydrocarbons (C$_1$-C$_4$) to aromatics and higher hydrocarbons [Anderson, 1979; Chang, 1983; Chen and Garwood, 1986a; Chen and Yan, 1986b; Mole, 1985; Scurrell, 1988]. It is known that catalysts having ZSM-5 structure show good activity and selectivity for the conversion of light alkanes to aromatics. However, further efforts have been undertaken to increase aromatic selectivity by chemically modifying the ZSM-5 catalyst. One of these modifications involves the isomorphous substitution of zeolite framework SiO$_4^{4-}$ ions using such metal ions as Ga, Fe, Ti and Zr [Ione et al., 1984; Ione et al., 1985; Inui et al., 1984b] to prepare metallosilicates.

Since most of the previous aromatization reactions were done using propane and butane as a reactant, we have investigated the catalytic properties of various metallosilicates for the pentane aromatization. To know the effect of various metal ions for pentane aromatization, metallosilicates were ion-exchanged with metal salts and reaction was carried out. In order to check the possibility of an one-step process to prepare aromatics from the products of Fischer-Tropsch reaction (CO, H$_2$, alkane and alkene), CO and H$_2$ (Syngas) were also added to the reactant of pentane .

EXPERIMENTAL

1. Synthesis of [M]ZSM-5s

Metallosilicates having MFI structure were synthesized by a hydrothermal crystallization method, where NaOH [Howden, 1985] or NH$_4$F [Guth et al., 1986; Mobil patent, 1972] were used as a charge balancing cation. Ludox HS-40 (Si source), tetra propyl ammonium bromide (TPABr, templating agent), NaOH and a metal source were added to the water and the solution was crystallized hydrothermally in a Teflon-coated steel reactor at 170 °C for 5 days. The crystallized metallosilicates were washed with water, dried at 120 °C for 24 hrs and then calcined at 550 °C for 5 hrs. Detailed information on the preparation of metallosilicates is shown in Table 1.

When NaOH was used as a charge balancing cation, metallosilicates were ion-exchanged 5 times with 0.1 M NH$_4$OH, washed with excess water and then calcined at 550 °C for 5 hrs to make H-form. However, using NH$_4$F as a charge balancing cation, the H-form was obtained directly by calcining

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Table 1. Detailed information on the preparation of metallosilicates

Samples	Metal sources	Mole ratio of reactants					pH of reactant mixture
		Si	M	Na	TPA$^+$	H$_2$O	
[Ga]ZSM-5(20)	Ga(NO$_3$)$_3 \cdot$ xH$_2$O	40	2	4	6	1600	11.3
[Ga]ZSM-5(40)	Ga(NO$_3$)$_3 \cdot$ xH$_2$O	40	1	4	6	1600	11.2
[Ga]ZSM-5(80)	Ga(NO$_3$)$_3 \cdot$ xH$_2$O	40	0.5	4	6	1600	12.0
[Ga]ZSM-5(250)	Ga(NO$_3$)$_3 \cdot$ xH$_2$O	40	0.16	4	6	1600	10.9
[Al]ZSM-5(20)	NaAlO$_2$	40	2	4	6	1600	11.5
[Al]ZSM-5(40)	NaAlO$_2$	40	1	4	6	1600	12.3
[Al]ZSM-5(80)	NaAlO$_2$	40	0.5	4	6	1600	11.1
[Al]ZSM-5(250)	NaAlO$_2$	40	0.16	4	6	1600	11.0
[Zn]ZSM-5(40)*	Zn(NO$_3$)$_2$ 6H$_2$O	40	1	4	6	1600	10.9
[Ni]ZSM-5(40)*	Ni(NO$_3$)$_2$ 6H$_2$O	40	1	4	6	1600	7.7
[Cr]ZSM-5(40)*	Cr(NO$_3$)$_3$ 9H$_2$O	40	1	4	6	1600	7.6
[Co]ZSM-5(40)*	Co(NO$_3$)$_2$ 6H$_2$O	40	1	4	6	1600	7.6
[Fe]ZSM-5(40)*	Fe(NO$_3$)$_3$ 9H$_2$O	40	1	4	6	1600	7.8
Silicalite		40	–	4	6	1600	11.2

*: Synthesized from the reaction mixture containing NH$_4$F instead of NaOH.

the metallosilicates at 550 °C for 5 hrs.

[Al]ZSM-5(40) was ion-exchanged with Ga(NO$_3$)$_3 \cdot$ xH$_2$O, Pt(NH$_3$)$_4$Cl$_2$, ZnCl$_2$, NiCl$_2 \cdot$ 6H$_2$O, IrCl$_3$ and ReCl$_3$. 1.5 g of [Al] ZSM-5(40) was ion-exchanged with 150 ml water solutions having 1 wt% metal salt for 2 days, washed with excess water, dried at 120 °C for 24 hrs and calcined with O$_2$. The calcination was carried out by raising the temperature from 25 °C to 300 °C over a period of 5 hrs and then maintaining it at 300 °C for 2 hrs. Prior to the aromatization reaction, ion-exchanged catalysts were reduced with H$_2$ at the reaction temperature for 3 hrs.

The notation, I/[M]ZSM-5(R) is used, where M indicates the kinds of metal in the metallosilicate having MFI structure, R indicates the atomic ratio of Si/M and I indicates the kinds of metal ion-exchanged (For example, Pt/[Ga]ZSM-5(40) is [Ga]ZSM-5 ion-exchanged with platinum and having Si/Ga ratio= 40).

2. Characterization of Metallosilicates

The metallosilicates were characterized by surface area, elemental analysis, SEM, XRD and ^{29}Si MAS NMR. BET surface area of prepared metallosilicates were measured by Micrometritics Digisorb 2600. Elemental analysis was done by atomic absorption spectroscopy. X-ray diffraction patterns were taken on a Rigaku D/Max II-A diffractometer using Ni-filtered Cu Kα radiation. The ^{29}Si MAS NMR spectra were obtained on a Bruker AM-200 high resolution solid state NMR spectrometer.

2-1. NH$_3$ TPD

For NH$_3$ TPD, 0.2 g of the sample was put in a quartz reactor and the system was purged with He at 600 °C for 2 hrs. NH$_3$ was adsorbed at room temperature for 10 min and then purged with 60 ml/min He for 2 hrs to remove physisorbed NH$_3$. TPD spectra were obtained by raising the temperature at a rate of 10 °C/min in 60 ml/min He.

3. Pentane Aromatization Reaction

The aromatization of pentane was carried out in a differential tubular reactor (3/8" stainless steel tube) at various temperatures. The pentane was fed by the liquid syringe pump (Sage instruments, 341B) and mixed with He carrier gas at a He/pentane mole ratio of 3. The products were analyzed by the on-line HP 5890 G.C. equipped with a 50 m crosslinked methylsilicon capillary column and a FID detector. The capillary column was temperature programmed from 40 °C to 200 °C at a rate of 10 °C/min.

RESULTS AND DISCUSSION

1. Characterization of Metallosilicates

1-1. Elemental Analysis and Surface Area

Metallosilicates were synthesized from the reaction mixtures described in Table 1 according to the method of Howden [1985] and Guth [1986] as well as that of Mobil patent [1972]. The final compositions and the surface areas of the prepared metallosilicates can be found elsewhere [Park et al.,

Table 2. Chemical compositions and surface areas of [Al]ZSM-5 and [Ga]ZSM-5 with different Si/metal ratios

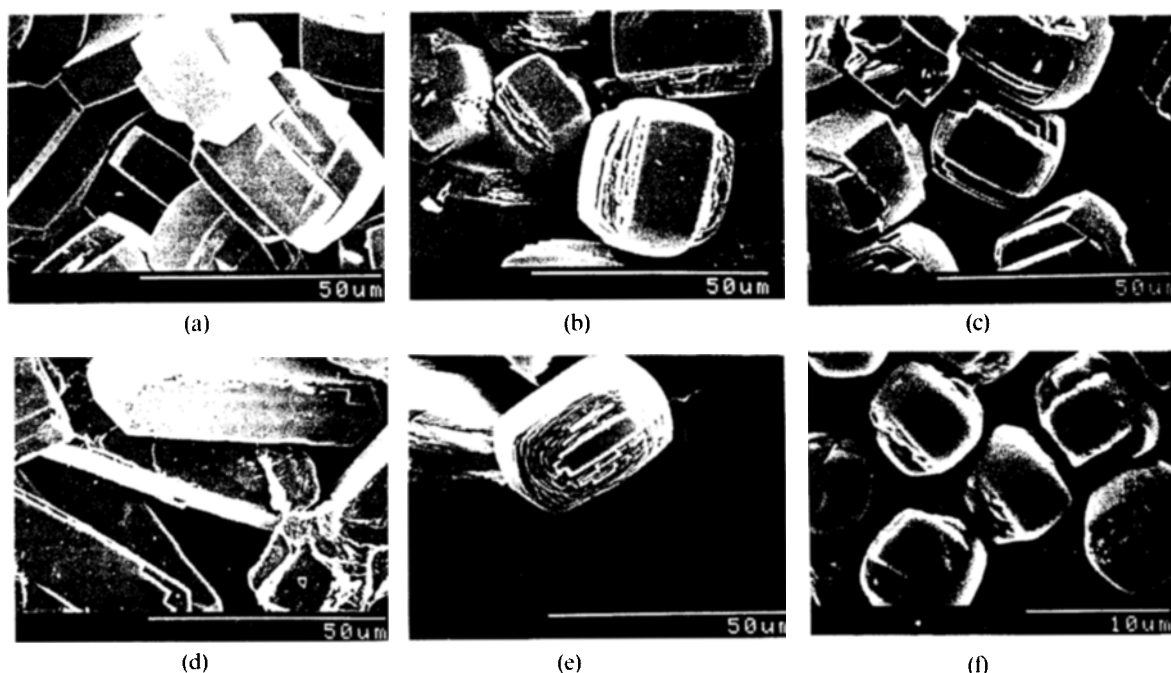| Catalyst	wt %				Atomic ratio		Surface area (m^2/g)
	Si	Ga	Al	Na	Si/Ga	Si/Al	
[Ga]ZSM-5(20)	44.0	1.19	0.082	0.056	37	–	269
[Ga]ZSM-5(40)	45.1	0.67	0.091		67	–	277
[Ga]ZSM-5(250)	44.7	0.10	0.084		440	–	295
[Al]ZSM-5(20)	45.3	–	1.41	0.029	–	32	260
[Al]ZSM-5(40)	45.5	–	0.71		–	64	271
[Al]ZSM-5(250)	44.9	–	0.13		–	345	282

Fig. 1. SEM pictures of various metallosilicates; (a) Silicalite, (b) [Al]ZSM-5(40), (c) [Ga]ZSM-5(40), (d) [Ni]ZSM-5(40), (e) [Zn] ZSM-5 and (f) [Fe]ZSM-5.

1994] and those of [Al]ZSM-5 and [Ga]ZSM-5 are summarized in Table 2. All the metallosilicates are highly porous and have the surface area of 260-295 m²/g. As shown in Table 2, the surface area of [Al]ZSM-5 and [Ga]ZSM-5 was reduced as the Si/metal ratio decreased, which is consistent with the result of Inui et al. [1989]. Elemental analysis indicates that most of the metal sources in the reactant mixtures are incorporated in the metallosilicate framework (Table 2). The incorporation of metal sources in metallosilicate framework was further evidenced by ^{29}Si MAS NMR spectra reported elsewhere [Park et al., 1994].

1-2. XRD and SEM

XRD patterns of metallosilicates exhibited that of ZSM-5 having characteristic diffraction peaks at $2\theta=6\text{-}11°$, $22.5\text{-}23.5°$,

and $45\text{-}46°$ except for some variations in peak intensities which may be due to the change of either framework metal ions or charge-balancing cations [Inui et al., 1989]. The XRD patterns can be found in the previous report [Park et al., 1994].

SEM pictures of prepared metallosilicates show that they have the shape of twined spherical crystals interconnected with two elongated hexagonal plates or hexagonal prism with the square plate at the center of hexagon (Fig. 1). This result is similar to that obtained by Inui et al. [1986], except for the crystal size. The metallosilicates prepared in this experiment are bigger than those prepared by the rapid crystallization method [Inui et al., 1986].

2. Pentane Aromatization

Various metallosilicates such as [Al]ZSM-5 [Chen and Yan,

Table 3. Product distribution in pentane aromatization over [Al]ZSM-5 and [Ga]ZSM-5 with different Si/metal ratios

Catalyst	[Al]ZSM-5				[Ga]ZSM-5			
Si/metal	20	40	80	250	20	40	80	250
XC_5H_{12} (%)	97.6	89.5	72.6	32.1	92.1	43.1	34.9	19.1
Selectivity (C wt %)								
C_1	34.0	29.7	32.5	35.9	23.4	32.7	33.2	35.0
C_2	33.8	35.1	40.5	38.7	19.5	36.6	37.8	41.4
C_3	4.4	8.0	9.9	7.5	3.4	7.9	7.1	8.2
C_4	0.9	1.7	2.1	6.0	0.8	5.4	5.8	7.4
C_{5+} aliphatics	1.2	2.5	2.6	2.0	0.6	2.1	2.2	2.7
Aromatics	25.7	23.0	12.4	10.1	52.3	15.3	13.9	5.3
Benzene	24.3	14.9	16.0	6.8	32.2	18.6	21.3	20.8
Toluene	45.0	35.0	42.3	16.3	43.1	46.8	39.8	37.7
Xylene	25.4	25.6	31.4	9.5	18.6	33.1	31.1	29.8
other*	5.3	24.5	10.3	67.4	6.1	1.5	7.8	12.7

Reaction condition: Temp.=550 °C, He/pentane=3, WHSV=1.5 h^{-1}, Time on stream=1 hr.
*: other aromatics.

Table 4. Product distribution in pentane aromatization over various metallosilicates

Catalyst	Silicalite	[Cr]ZSM-5	[Fe]ZSM-5	[Co]ZSM-5	[Ni]ZSM-5	[Zn]ZSM-5
Si/metal	∞	40	40	40	40	40
$X_{C_5H_{12}}$ (%)	4.9	6.9	26.3	6.6	44.1	41.2
			Selectivity (C wt %)			
C_1	41.1	41.0	28.6	36.8	45.5	23.4
C_2	34.4	33.7	25.8	32.8	25.1	24.8
C_3	5.5	6.1	5.6	8.7	4.1	3.9
C_4	14.8	12.2	5.3	10.7	1.4	4.7
C_{5+} aliphatics	3.6	4.1	4.6	9.3	2.0	5.6
Aromatics	0.6	2.9	30.1	1.7	21.9	37.6
Benzene	–	–	23.0	–	33.1	19.7
Toluene	–	–	38.8	–	17.1	35.3
Xylene	–	–	29.1	–	1.6	38.2
other	–	–	9.1	–	48.2	6.8

Reaction condition: Temp.=550 °C, He/pentane=3, WHSV=1.5 h^{-1}, Time on stream=1 hr.
*: other aromatics.

1986b], [Ga]ZSM-5 and [Zn]ZSM-5 [Inui et al., 1988] have been tested for light hydrocarbon aromatization. For selective aromatization of light hydrocarbon, the catalysts must have multi-functional capabilities such as dehydrogenation, oligomerization and aromatization. In this study, pentane aromatization was carried out over the various metallosilicates. The results are shown in Table 3 and 4.

In pentane aromatization, [Ga]ZSM-5(20) (52.3%) and [Zn] ZSM-5(40) (37.6%) showed higher aromatic selectivities than other metallosilicates. Most of the aromatics produced by these metallosilicates were benzene, toluene and xylene. This is consistent with the previous reports [Inui et al., 1986, 1988, 1989], in which [Zn]ZSM-5 and [Ga]ZSM-5 are known to be good candidates for selective aromatization in light alkane aromatization (ethane, propane and butane). [Zn]ZSM-5 and [Ga] ZSM-5 also showed good aromatic selectivity in pentane aromatization. Inui et al. [1988] who used propane as a reactant explained this high aromatic selectivity by suggesting that Zn and Ga ion species existing in the zeolite framework enhance aromatization of olefins by hydrogen abstraction. However, these are not enough to explain the function of metal ions existing in zeolite framework for good aromatic selectivity. The [Ni]ZSM-5(40) showed higher production of methane (45.5%) although it was accompanied by similar aromatic selectivity (21.9%) to that of [Al]ZSM-5(20) (25.7%). This enhanced yield of methane may be the result of a hydrogenation reaction by the Ni species existing in the zeolite framework. Silicalite, [Cr]ZSM-5(40) and [Co]ZSM-5(40) showed lower aromatic selectivities and higher methane and ethane yields than [Al]ZSM-5(40).

Fig. 2 and 3 show NH₃ TPD spectra of [Ga]ZSM-5 and [Al] ZSM-5 for different Si/metal ratios. Three desorption peaks shown in Fig. 2 and 3 correspond to the sites of weak (373 -473 K), medium (523-723 K) and strong (> 773 K) acidities. Fig. 2 and 3 also show that the peak areas depend on the Si/metal ratio. Comparing Fig. 2 with Fig. 3, the [Ga] ZSM-5 has more medium acid sites than [Al]ZSM-5 and the peak area of medium acidity increases as the Si/Ga ratio is decreased. As the Si/metal ratio changed from 250 to 20,

the selectivity towards aromatization increased from 10.1% to 25.7% over [Al]ZSM-5 and from 5.3% to 52.3% over [Ga]ZSM-5 (see Table 3). Thus the aromatic selectivity is more dependent on the Si/metal ratio in [Ga]ZSM-5 compared to [Al]ZSM-5. The more medium acid sites in the catalyst, the higher the aromatic selectivity in pentane aromatization. The results from both NH₃ TPD and pentane aromatization imply that in pentane aromatization the aromatic selectivity is correlated with the concentration of so called "medium" acid sites.

2-1. Deactivation

Usually, deactivation of the catalyst is caused by coking, poisoning and sintering. Specifically, in zeolite catalysts the main cause of deactivation is coking [Bhatia et al., 1989]. Fig.
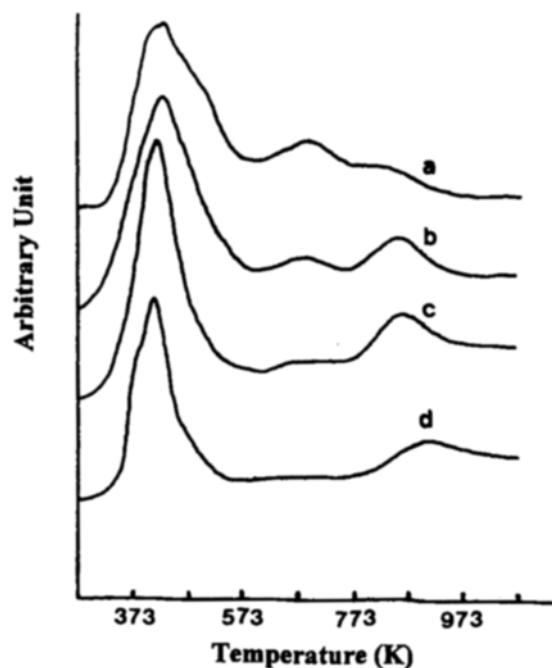
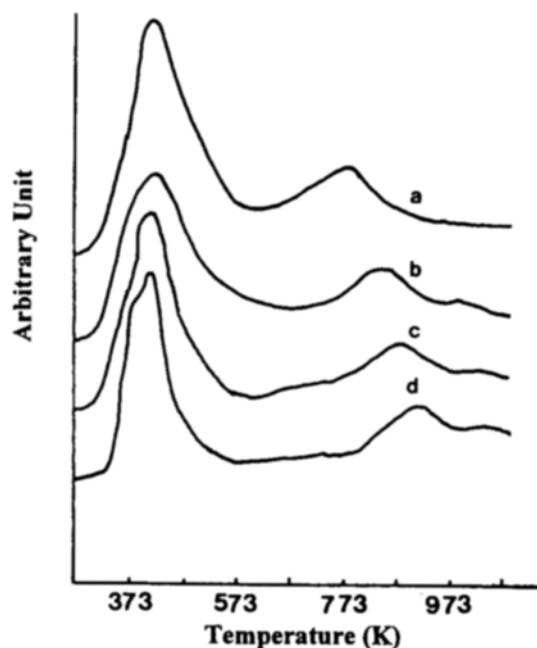**Fig. 2. NH₃ TPD of [Ga]ZSM-5s with different Si/Ga ratios. Si/Ga ratio; (a) 20, (b) 40, (c) 80 and (d) 250.**

Fig. 3. NH$_3$ TPD of [Al]ZSM-5s with different Si/Al ratios. Si/Al ratio; (a) 20, (b) 40, (c) 80 and (d) 250.

Fig. 5. Changes in total conversion with time on stream in pentane aromatization catalyzed over [Al]ZSM-5s at 550 °C, He/pentane=3, WHSV=1.5 h^{-1}. Si/Al atomic ratio=20 (●), 40 (■), 80 (▲) and 250 (▼).

4 and 5 show that the deactivation of [Ga]ZSM-5 was more severe than that of [Al]ZSM-5 at low Si/metal ratio. Thus although [Ga]ZSM-5(20) exhibited a high selectivity towards aromatization, it deactivated more rapidly than other metallosilicates. This deactivation sound to be the coke formation caused by high molecular weight aromatics. This is consistent with the fact that [Al]ZSM-5 deactivated more slowly than [Ga] ZSM-5 because of the lower aromatic selectivity (see Fig. 5).

2-2. Effect of Reaction Temperature
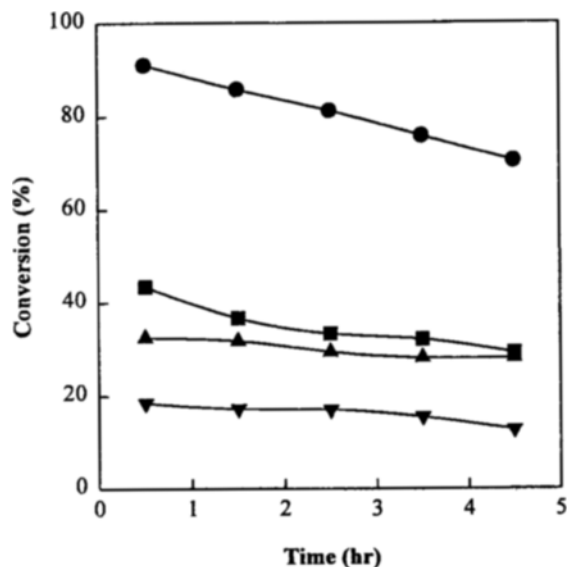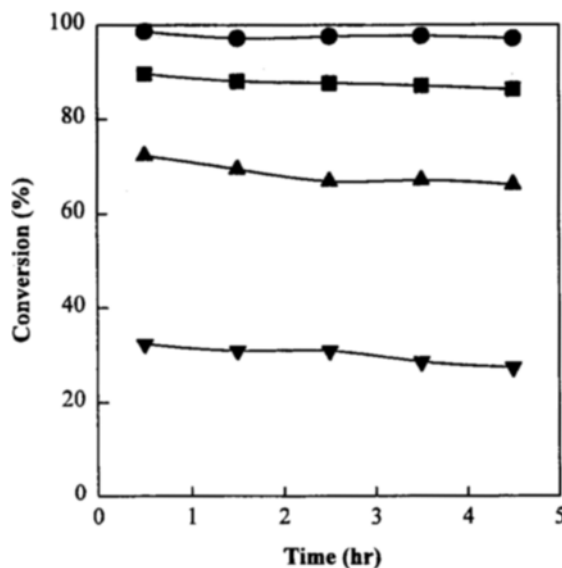
Fig. 6 shows the effect of reaction temperature on con-

version and aromatics selectivity. The conversion of pentane increased gradually with reaction temperature but the product distributions showed maximum point at a certain reaction temperature. As the temperature increased, the selectivity of aromatics increased and showed a peak maximum (50%) at 600 °C but decreased to only 30% above 600 °C. In contrast to the aromatics, the methane yield increased gradually and above 600 °C the rate of increase was more rapid. These results indicate that above 600 °C aromatics and higher hydrocarbons formed in zeolite pores were converted to light hydrocarbons through thermal cracking enhanced by the pres-

Fig. 4. Changes in total conversion with time on stream in pentane aromatization catalyzed over [Ga]ZSM-5s at 550 °C, He/pentane=3, WHSV=1.5 h^{-1}. Si/Ga atomic ratio=20 (●), 40 (■), 80(▲) and 250(▼).
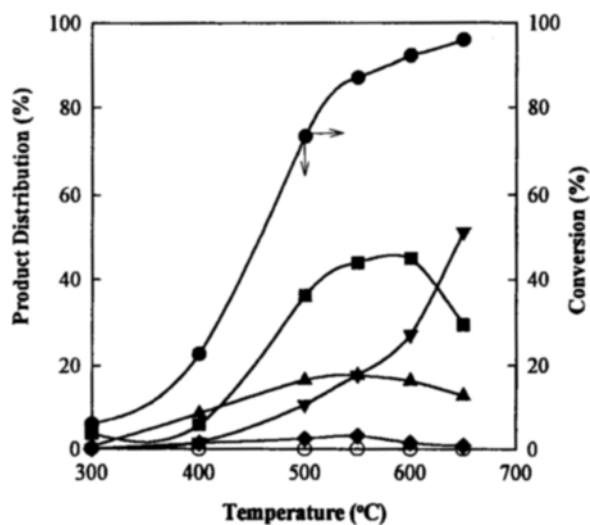

Fig. 6. Changes in the total conversion (●) and product distribution with reaction temperature in the pentane aromatization catalyzed over [Ga]ZSM-5(20) at 550 °C, He/pentane=3; WHSV=1.5 h^{-1}. Methane (▼), C$_2$ fragments (▲), C$_3$ (◆), C$_{4+}$ (○) and aromatics (■).

Table 5. Product distribution in pentane aromatization over ion-exchanged [Al]ZSM-5(40)

Catalysts	$X_{C_5H_{12}}(\%)$	Product distribution (wt%)					
		C_1	C_2	C_3	C_4	C_{5+}	Aromatics
H/[Al]ZSM-5(40)	89.5	29.7	35.1	8.0	1.7	2.5	23.0
Pt/[Al]ZSM-5(40)	99.8	55.1	5.1	0.3	0.1	1.1	39.4
Ir/[Al]ZSM-5(40)	82.5	29.1	35.5	9.5	2.1	2.7	21.1
Zn/[Al]ZSM-5(40)	89.4	25.7	33.3	6.0	1.2	1.1	32.7
Ni/[Al]ZSM-5(40)	87.6	32.6	30.3	5.4	1.1	1.5	29.0
Ga/[Al]ZSM-5(40)	98.3	33.7	25.4	4.1	0.7	0.9	35.5
Re/[Al]ZSM-5(40)	94.2	32.9	36.3	3.6	1.2	1.5	24.6

Reaction condition: Temp.=550 °C, He/pentane=3, WHSV=1.5 h^{-1}, Time on stream=1 hr.
The amount of ion-exchange=1 wt% metal/g catalyst.

ence of Ga metal, resulting in a concomitant increase in methane formation. Similar results have been reported for propane aromatization over [Al]ZSM-5 by Kitagawa et al. [1986].

2-3. Effect of Ion-exchange on Pentane Aromatization

In order to investigate the dependence of aromatic selectivity on ion-exchange, [Al]ZSM-5(40) was ion-exchanged with various metal ions and the pentane aromatization reaction was carried out at 550 °C. The results are summarized in Table 5. Among the various ion-exchanged [Al]ZSM-5s, Pt/[Al]ZSM-5, Zn/[Al]ZSM-5 and Ga/[Al]ZSM-5 showed higher aromatic selectivity than H/[Al]ZSM-5. In the case of Pt/[Al]ZSM-5, it is thought that Pt ions present in zeolite pores enhance the alkane dehydrogenation and the hydrogenation of fused aromatics (precursor of coke) through hydrogen spillover, which results in increased aromatic selectivity and lower deactivation. This enhancement of aromatic selectivity has been reported in propane aromatization over Pt/[Al]ZSM-5[Sirokman et al., 1986]. Mole et al. [1985] compared Zn/[Al]ZSM-5 with H/[Al]ZSM-5 for propane aromatization and observed that Zn plays an important role in the dehydrogenation of propane which results

in the increase in aromatic selectivity. Kitagawa et al. [1986] and Gnep et al. [1988] have reported that Ga ions strongly inhibit hydrogenation of olefins through hydrogen abstraction and enhance dehydrogenation of alkanes. These results are consistent with the idea that in pentane aromatization the dehydrogenation of pentane is the rate determining step. Consequently, the [Al]ZSM-5s ion-exchanged with such metal ions as Pt, Zn and Ga which have dehydrogenation ability show a higher aromatic selectivity.

2-3. The Effect of H$_2$ and CO on Product Distribution

Because light hydrocarbons such as ethane, propane, butane and pentane are products in Fischer-Tropsch (FT) reaction, it is desirable to convert these light hydrocarbons to aromatics and higher hydrocarbons by one step reaction from the CO and H$_2$. In this FT reaction, unreacted CO and H$_2$ would coexist with light hydrocarbons and they would affect the conversion of light hydrocarbons. In order to understand the effects of H$_2$ and CO on pentane aromatization, H$_2$ and CO were added to the reactant and the H$_2$/pentane and CO/pentane mole ratios were changed from 0 to 2. The results are shown in
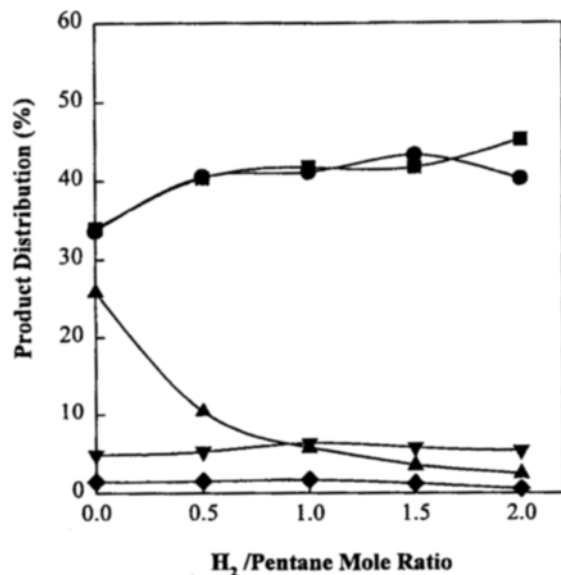
Fig. 7. Effect of CO addition on the product distribution in pentane aromatization over [Al]ZSM-5(20) at 550 °C. He/pentane=3, WHSV=1.5 h^{-1}. Methane (●), C$_2$ fragments (■), C$_3$ (▼), C$_{4+}$ (◆) and aromatics (▲).
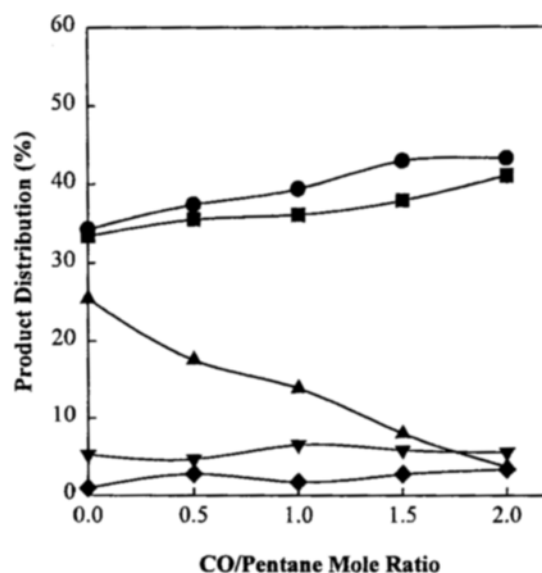
Fig. 8. Effect of H$_2$ addition on the product distribution in pentane aromatization over [Al]ZSM-5(20) at 550 °C. He/pentane=3, WHSV=1.5 h^{-1}. Methane (●), C$_2$ fragments (■), C$_3$ (▼), C$_{4+}$ (◆) and aromatics (▲).

Fig. 7 and 8, respectively. As CO and H_2 mole ratios increased, the aromatics selectivity decreased rapidly, while that of methane and ethane increased. Chen and Yan [1986b] explained this effect on the basis of the fact that the decrease in aromatic selectivity with increasing H_2 content is due to the enhancement of hydrogenation and the concomitant inhibition of H atom abstraction from intermediate species. In the case of adding CO, the aromatic selectivity decreased, which might be due to the weakening of Lewis acid site of Al and Ga ions arising from the coordination of CO on these atoms. The presence of H_2 and CO in the reactant prohibited the aromatic formations and increased methane and ethane formations.

CONCLUSIONS

Various metallosilicates were synthesized by a hydrothermal method and characterized by SEM, XRD, chemical analysis and surface area measurement, which showed that they were highly porous and had the structure of MFI.

In pentane aromatization, [Ga]ZSM-5(20) (52.3%) and [Zn]ZSM-5(40) (37.6%) showed higher selectivities toward aromatics than any other metallosilicate. Most of the aromatics produced by [Ga]ZSM-5(20) and [Zn]ZSM-5(40) were benzene, toluene and xylene, while the contents of other aromatics were less than 10%.

[Al]ZSM-5(40) was ion-exchanged with various metal salts. When [Al]ZSM-5(40) was ion-exchanged with gallium nitrate and zinc chloride, the selectivity for aromatics increased from 23.0% to 35.5% and 32.7%, respectively. We suggest that Ga and Zn ion species enhance pentane aromatization.

As the Si/metal ratio was changed from 250 to 20, the selectivity for aromatics changed from 5.3% to 52.3% over [Ga] ZSM-5 and from 10.1% to 25.7% over [Al]ZSM-5, respectively. Through NH_3 TPD and pentane reaction, the catalyst having medium acidity showed high aromatic selectivity and the medium acidity played an important role in the formation of aromatics.

The addition of H_2 and CO to the reactant decreased the production of aromatics and increased that of methane and ethane.

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