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On the role of gallium for the aromatization of lower paraffins with Ga-promoted ZSM-5 catalysts

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Abstract

Aromatization of butane or propane was conducted with a series of ZSM-5 catalysts. A small amount of oxygen in the feed promoted butane conversion to aromatic hydrocarbons on H-ZSM-5. It suggests that if hydrogen atoms on the zeolite surface are removed effectively, H-ZSM-5 exhibits a high selectivity for aromatic hydrocarbons. A hybrid catalyst composed of the physical mixture of Ga/SiO_2 and H-ZSM-5 showed comparable activity and aromatic selectivity to those of the Ga-supported ZSM-5 zeolite, whereas the Ga/SiO_2 itself exhibited little catalytic activity for the paraffin conversion and olefin aromatization. The excellent promotional effect of Ga/SiO_2 for aromatics formation was observed only when it was intimately contacted with H-ZSM-5. These results suggest that the supported Ga promotes the zeolite-catalyzed aromatization of lower paraffins by promoting hydrogen desorption via the 'reverse spillover' effects.

1. Introduction

Conversion of lower paraffins into aromatic hydrocarbons has been attracting great attention from both an industrial and academic point of view. It has been found that Ga or Zn supported ZSM-5 type zeolites are exceptionally effective catalysts for this type of reactions [1]. Ga and Zn are effective in promoting the reaction in the impregnated form [2,3], in the ion exchanged form [1,4], in the physically mixed form [5] or even when they are incorporated in the zeolite framework [6].

There are many interpretations postulated as to why Ga or Zn are so effective in promoting the formation of aromatic hydrocarbons. Mole and Anderson suggested that the dehydrogenation of propane was promoted by Zn on ZSM-5 [1]. Kitagawa et al. has concluded from the study of pentane conversion that the Ga-loading does not affect the cracking ability of the zeolite, but enhances the activity of the aromatization of the olefin [7]. They also observed that Ga-loading promoted propane conversion and suggested that the Ga-promoted aromatization suppressed the formation of propane from intermediate products [7]. Inui et al. showed that Pt-ion-exchanged Ga-silicate exhibited excellent performance for the conversion of C_2–C_5 paraffins and claimed that Pt promoted the paraffin dehydrogenation to olefins and Ga promoted the aromatization of olefins [6]. Yashima et al. claimed that Ga on ZSM-5 promoted the dehydrogenation of cycloparaffins or cycloolefins which were formed on zeolite [3]. Gnep et al. pointed out that Ga existing on ZSM-5 as Ga_2O_3 showed a catalytic activity for both propane

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dehydrogenation and naphthene dehydrogenation to promote propane aromatization on Ga-ZSM-5 [8].

On the other hand, the present authors have found that added oxygen gas in the propane or butane conversion on H-ZSM-5 selectively oxidized hydrogen on the zeolite to promote the conversion of the feed and especially the formation of aromatic hydrocarbons. The authors claimed that H-ZSM-5 exhibits an excellent ability for paraffin conversion and aromatics formation if the hydrogen atom on the zeolite surface is effectively removed [9]. Also, the authors have found that the hybrid catalyst composed of a compressed physical mixture of finely powdered H-ZSM-5 and alumina-supported Ga_2O_3 exhibited activity for butane conversion and the selectivity to aromatics which were comparable to those for Ga-ZSM-5 and they have postulated a concept that hydrogen atoms on the zeolite surface leave through the Ga-site (resulting in the promoted aromatics formation) [10,11]. Le Van Mao et al. found that an H-ZSM-5 to which a small quantity of zinc oxide/alumina co-precipitate was admixed mechanically, could convert selectively light olefins and/or paraffins to aromatic hydrocarbons and claimed that the high aromatic selectivity should be attributed to hydrogen 'back-spillover' from the zeolite to Zn/Al_2O_3 [12].

Concerning a physically mixed catalyst of Ga_2O_3 and H-ZSM-5, Price and Kanazirev found a strong enhancement in the propane aromatization activity of Ga_2O_3/H-ZSM-5 catalyst by activating the catalyst by either hydrogen pretreatment or long-term exposure to a propane reactant and they concluded that the active species should be the Ga^I cation, introduced by the solid–solid reaction of Ga_2O_3 and H-ZSM-5 [13–15].

The present work tries to clarify the role of gallium on ZSM-5 in the conversion of lower paraffins from the standpoint of hydrogen spillover and reverse spillover by using a hybrid catalyst composed of the physical mixture of Ga/SiO_2 and H-ZSM-5.

2. Experimental

The ZSM-5 zeolite was supplied by Tosoh Chemical Ind. Ltd. (Si/Al atom ratio: 50, 850 NAA). A protonic ZSM-5 (H-ZSM-5) was prepared by repeated ion exchange of the Na-ZSM-5 with aqueous ammonium nitrate solution (5 ×) followed by calcination in air at 500°C. Ga was supported on the H-ZSM-5 by ion exchanging with an aqueous solution of gallium nitrate. Ga and other metal supported silica catalysts were prepared by impregnating a commercially available SiO_2 (Aerosil 380, specific surface area 380 m^2/g) with aqueous solution of gallium nitrate or other metal salts. Ga contents were 1.5 and 5 wt% for Ga-ZSM-5 and Ga/SiO_2, respectively. Hybrid catalysts were prepared by co-grinding the two types of catalyst into fine powder and then pressure-molding the mixture to granules (20–40 mesh).

Conversion of butane or propane was conducted with a flow type fixed bed reaction apparatus operated under atmospheric pressure. Catalysts were packed in a stainless steel tube with an inner diameter of 4 mm. Products were analyzed by gas chromatography. Adsorption of hydrogen and its desorption were measured using a flow through cell connected to a conventional glass vacuum system. The adsorption measurement was carried out at 400°C and the temperature programmed desorption (TPD) was carried out from room temperature to 800°C with a heating rate of 400°C/h. The desorbed hydrogen was determined by mass spectrometry.

3. Results and discussion

3.1. Conversion of propane on ZSM-5 catalysts

In Fig. 1, the propane conversion and the aromatics yield on variety of Ga-containing catalysts are plotted versus time on stream in variety of reaction conditions.

In the nitrogen atmosphere, the Ga-ZSM-5 showed excellent catalytic activity for the

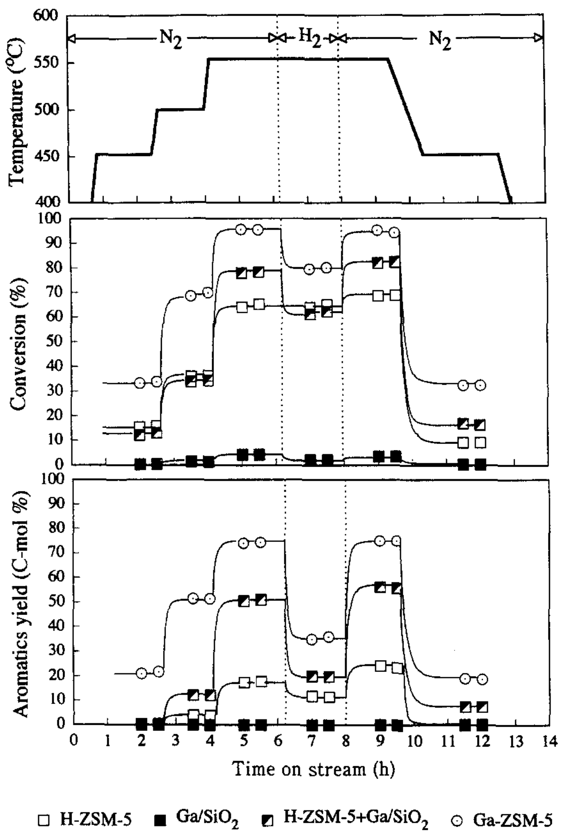

Fig. 1. Aromatization of propane on ZSM-5. Reaction temperature 550°C, $C_3H_8 = 20$ kPa, $N_2 = 80$ kPa, $W/F = 10$ g h mol^{-1}.

propane aromatization. The protonic ZSM-5 (H-ZSM-5) showed activity for propane conversion to some extent whereas the amount of aromatic hydrocarbons was 1/4 of that of Ga-ZSM-5. The hybrid catalyst containing Ga/SiO_2, which was finely powdered and pressed into granules with H-ZSM-5, exhibited high catalytic activity for the propane aromatization, whereas the Ga/SiO_2 itself exhibited little catalytic activity for propane conversion.

However, in the case of the Ga-ZSM-5 and the hybrid catalyst of Ga/SiO_2 and H-ZSM-5, the propane conversion and the yield of aromatic hydrocarbons decreased drastically, changing the atmosphere from nitrogen to hydrogen. In the case of H-ZSM-5, hydrogen in the gas phase affected neither the propane conversion nor the aromatic yields. The effect of hydrogen will be discussed later.

Kanazirev and co-workers found a strong enhancement in the propane aromatization activity of Ga_2O_3/H-ZSM-5 catalyst by either hydrogen pretreatment or long-term exposure to a propane reactant [13–15]. They concluded that the active species is probably the Ga^I cation introduced by solid phase ion exchange, which proceed over 480°C [14]. However, activity of the hybrid catalyst composed of H-ZSM-5 and Ga/SiO_2 in nitrogen atmosphere show a small increase even after the reaction in hydrogen atmosphere at 550°C. Price and Kanazirev claimed that reduction of Ga_2O_3 to Ga_2O does not proceed without the following ion exchange process of Ga^I cation and the ion exchange process needs anion sites in the zeolite. In the hybrid catalyst, Ga was loaded on silica support and most of the Ga on silica should migrate on silica surface at first to reach H-ZSM-5. Silica support have no anion sites. Therefore, only a small amount of the gallium was introduced to H-ZSM-5 in the hybrid catalyst system.

Few decay of the ZSM-5 containing catalysts was shown, because propane was diluted with nitrogen or hydrogen.

Table 1 shows some of the results of the propane conversion with varying Ga-containing catalysts at 550°C (time on stream = 5.5 h). The H-ZSM-5 produced methane, ethane and ethylene as the main products, with only a small amount of aromatic hydrocarbons. The former studies indicated that the higher aromatic selectivity of the Ga-ZSM-5 catalyst compared to H-ZSM-5 should be attributed to the dehydroaromatization of olefins over Ga particles [8]. However, the Ga/SiO_2 alone exhibited little catalytic activity for propane conversion and its propene selectivity was very high (96.1%). The result means that Ga/SiO_2 has little catalytic activity for both olefin aromatization and paraffin dehydrogenation, whereas it exhibited an excellent promotional effect for aromatics formation when it was intimately contacted with H-ZSM-5.

It should be also noted that the content of the ZSM-5 zeolite in the hybrid catalyst was only

Table 1
Aromatization of propane on ZSM-5 catalysts [a]

Catalyst	H-ZSM-5	Ga/SiO_2	Ga-ZSM-5	H-ZSM-5 + Ga/SiO_2 [b]
Conversion/%	65.5	4.3	95.4	78.4
H_2/converted propane (molar ratio)	0.4	1.1	1.4	1.2
Product distribution (C%)				
CH_4	29.7	0.6	13.0	15.2
C_2H_6	10.9	0.1	5.3	6.2
C_2H_4	17.6	1.1	2.4	8.0
C_3H_6	11.3	96.1	1.3	4.5
C_4H_{10}	1.0	1.8	0.1	0.4
C_4H_8	1.7	0.0	0.0	0.4
C_5^+ aliphatics	0.5	0.0	0.0	0.1
Aromatics	27.3	0.3	77.9	68.7
Aromatics distribution (%)				
Benzene	12.3	100	48.3	45.6
Toluene	41.9	0.0	37.2	37.7
A8	42.5	0.0	6.5	8.7
A9$^+$	3.3	0.0	8.0	8.0

[a] Time on stream 5.5 h, reaction temperature 550°C, $P_{C_3H_8} = 20$ kPa, $P_{N_2} = 80$ kPa, $W/F = 10$ g h mol^{-1}.
[b] Powdery mixture, content of Ga/SiO_2 was 20 wt%.

80 wt% and thus the catalytic activity of the H-ZSM-5 hybrid catalyst is estimated to be 1.4 times higher than for H-ZSM-5 alone.

3.2. Aromatization of naphthenic hydrocarbon on ZSM-5 catalysts

The former studies indicated that the higher aromatic selectivity of the Ga-ZSM-5 catalyst compared to H-ZSM-5 should be attributed to the dehydroaromatization of naphthene over Ga particles [3,12]. Temperature programmed dehydrogenation (TPRe) of methylcyclohexane (MCH) was performed to obtain information on the activity of Ga on ZSM-5 for aromatization of naphthenic hydrocarbons. The TPRe measurement showed significant differences between Pt-ZSM-5 compared to Ga-ZSM-5 and H-ZSM-5, as shown in Fig. 2. In case of Pt-ZSM-5, formation of aromatics and corresponding hydrogen formation began at 220°C, and large peaks both of aromatization and hydrogen formation were found at 380°C. In case of Ga-ZSM-5, the formation of aromatics and hydrogen began at 300°C and the peaks shown for the Pt-ZSM-5 system were not well-defined. It should be noted that the TPRe profile of Ga-ZSM-5 was similar to that of H-ZSM-5, whereas the rates of hydrogen formation and aromatization were about 1.5 times that of the H-ZSM-5 through the TPRe measurement. These results suggest that Ga itself has little activity for naph-

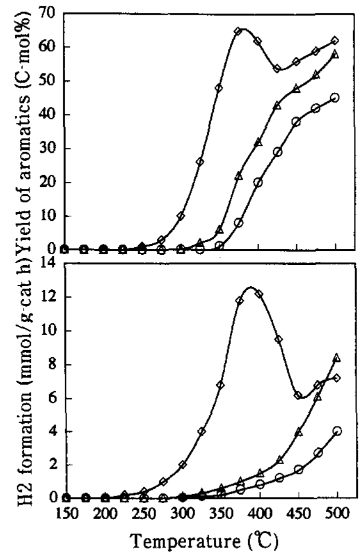

Fig. 2. Temperature programmed reaction of methylcyclohexane (MCH). MCH 5.3% in Ar, 5°C min^{-1}, $W/F = 9.3$ g h mol^{-1}. ◆ Pt-DM-5, △ Ga-ZSM-5, ○ H-ZSM-5.

thene aromatization, only promotes dehydroaromatization of naphthenic hydrocarbons over H-ZSM-5 by reverse spillover effects, which will be discussed later.

3.3. *Conversion of butane on ZSM-5 catalysts*

Price and Kanazirev found a strong enhancement in the propane aromatization activity of Ga_2O_3/H-ZSM-5 catalyst by introduction of Ga^I cation to H-ZSM-5, which proceed over 480°C [14]. To eliminate the influence of the solid state ion exchange of Ga to H-ZSM-5, all of the following aromatization reactions were carried out using butane as a feed to lower the reaction temperature under 480°C, whereas effect of Ga introduction to ZSM-5 was small in the hybrid catalyst system even at 550°C.

3.3.1. *Catalytic performances of Ga-containing hybrid catalysts*

Table 2 shows some of the results for the butane conversion on a variety of Ga-containing catalysts at 450°C. As has been pointed out already, the protonic ZSM-5 (H-ZSM-5) produced propane and C_2–C_4 olefins as the main products, with only a small amount of aromatic hydrocarbons. The hybrid catalyst containing Ga/SiO_2, which was finely powdered and pressed into granules with H-ZSM-5, exhibited high aromatic selectivity which was comparable to those of the Ga-ZSM-5 catalyst, whereas the Ga/SiO_2 itself exhibited little catalytic activity for the butane conversion and propene aromatization. These results suggest that promotional effect of Ga in paraffin aromatization over ZSM-5 catalyst was observed without the solid phase ion exchange of Ga to H-ZSM-5, which needs high reducing temperature to form Ga^+.

The other important point is that the physical mixture of granular Ga/SiO_2 and granular H-ZSM-5 showed catalytic performances much lower to the powdery mixed hybrid catalyst with the same composition. If the promotional effect of gallium is attributed to its dehydrogenation activity as mentioned in previous stud-

Table 2
Conversion of butane on ZSM-5 catalysts [a]

Catalyst	H-ZSM-5	Ga/SiO_2	Ga-ZSM-5	H-ZSM-5 + Ga/SiO_2 [b]	H-ZSM-5 + Ga/SiO_2 [c]	Ga/SiO_2 [d]
Conversion/%	41.6	0.4	47.9	47.7	45.8	1.6
H_2/converted butane (molar ratio)	0.3	–	1.4	1.3	0.8	–
Product distribution (C%)						
CH_4	2.7	0.5	2.6	3.2	3.1	3.7
C_2H_6	6.9	2.5	6.9	7.8	7.7	1.1
C_2H_4	5.2	0.6	3.4	5.1	7.0	8.6
C_3H_8	58.6	3.5	52.5	51.7	67.5	20.2
C_3H_6	7.5	0.8	4.5	5.7	6.8	/
i-C_4H_{10}	3.7	0.0	3.5	3.2	3.0	30.7 (C_4H_{10})
C_4H_8	3.6	86.7	2.1	2.2	2.4	8.5
C_5^+ aliphatics	3.0	0.5	2.5	1.7	2.3	6.3
Aromatics	8.8	4.9	22.0	19.4	11.2	20.9
Aromatics distribution (%)						
Benzene	12.3	–	13.6	13.9	13.6	22.5
Toluene	41.9	49.0	43.4	41.8	41.1	27.8
A8	42.5	51.0	38.9	37.6	39.2	48.3
$A9^+$	3.3	–	4.1	6.7	6.1	1.4

[a] Reaction temperature 450°C, $P_{C_4H_{10}} = 20$ kPa, $P_{N_2} = 80$ kPa, $W/F = 10$ g h mol^{-1}, time on stream 2.5 h.
[b] Powdery mixture, content of Ga/SoP_2 was 20 wt%.
[c] Granular mixture, content of Ga/SiO_2 was 20 wt%.
[d] Propene was reacted instead of butane.

ies [1,7], the granular mixture of Ga/SiO_2 and H-ZSM-5 should exhibit comparable performances to that of the hybrid catalyst. On the other hand, it was reported that supported metal or metal sulfide promoted dehydrogenation of paraffins or naphthenes on active carbon by a 'reverse spillover' effect through enhanced desorption of hydrogen formed in the dehydrogenation [16]. The reverse spillover between two particles is also a well known phenomenon [17], which needs intimate contact between particles. The role of Ga in the aromatization may be understood by this reverse spillover effect.

3.3.2. Catalytic performances of supported transition metal containing H-ZSM-5 catalysts

In order to make the ' reverse spillover' concept clearer, the catalytic performance of a hybrid catalysts composing H-ZSM-5 and the Ni/SiO_2 or other supported metal catalyst was studied (Table 3). The Ni/SiO_2 was sulfided before use by treating it with a H_2–H_2S mixed gas at 400°C to suppress its catalytic activity for dehydrogenation or decomposition. Although a Ni-ion exchanged ZSM-5 (Ni-ZSM-5) was much less effective than Ga-ZSM-5 in making aromatic hydrocarbons, the Ni/SiO_2–H-ZSM-5 hybrid catalyst exhibited comparable catalytic performances in, i.e., n-butane conversion or selectivity for aromatics to that of Ga-ZSM-5 while the Ni/SiO_2 has little catalytic activity for either n-butane conversion or butene aromatization as was the case of Ga/SiO_2. Hybridization of Mo(S)/SiO_2 to H-ZSM-5 showed a similar effect to that of Ni/SiO_2 on the butane aromatization. The high performances of the hybrid catalysts should be attributed to the inter-particle transfer of hydrogen atoms from H-ZSM-5 to Ni/SiO_2 or Mo(S)/SiO_2 and the desorption of the hydrogen atoms as hydrogen molecules through the reverse spillover on the supported metal catalyst.

3.3.3. Effects of oxygen

In Table 4, some of the results of butane conversion over H-ZSM-5 and Ga-ZSM-5 in the presence and absence of oxygen are shown. When the feed gas contained 5 vol% oxygen, butane conversion on the H-ZSM-5 catalyst increased considerably and the selectivity of the

Table 3
Conversion of butane on ZSM-5 catalysts [a]

Catalyst	H-ZSM-5	Ni/SiO_2	Ni-ZSM-5	H-ZSM-5 + Ni/SiO_2 [b]	H-ZSM-5 + Mo/SiO_2 [b]	Ga-ZSM-5
Conversion/%	41.6	0.3	40.6	47.0	46.6	47.9
H_2 converted butane (molar ratio)	0.3	–	0.4	1.4	1.4	1.4
Product distribution (C-%)						
CH_4	2.7	0.0	3.0	2.2	1.6	2.6
C_2H_6	6.9	0.0	7.1	6.1	6.3	6.9
CDHD	5.2	0.0	5.3	2.7	4.4	3.4
C_3H_8	58.6	1.5	59.5	52.3	49.7	52.5
C_3H_6	7.5	2.3	7.1	3.5	5.5	4.5
i-C_4H_{10}	3.7	0.0	3.5	5.4	4.5	3.5
C_4H_8	3.6	88.5	5.5	1.4	3.1	2.1
C_5^+ aliphatics	3.0	0.0	3.0	3.6	2.4	2.5
Aromatics	8.8	7.7	6.0	22.8	22.5	22.0
Aromatics distribution (%)						
Benzene	12.3	–	9.6	11.7	12.6	13.6
Toluene	41.9	100	39.0	42.3	42.5	43.4
A8	42.5	–	45.8	42.2	40.9	38.9
$A9^+$	3.3	–	5.6	3.8	4.0	4.1

[a] Time on stream 2.5 h, reaction temperature 450°C, $P_{C_4H_{10}} = 20$ kPa, $P_{N_2} = 80$ kPa, $W/F = 10$ g h mol^{-1}.

[b] Powdery mixture, content of Metal/SiO_2 was 20 wt%.

Table 4
Conversion of butane on ZSM-5 catalysts [a]

Catalyst	H-ZSM-5			Ga-ZSM-5	
O_2 (mol% in feed)	0.0	0.0 [b]	5.0	0.0	5.0
n-C_4 conversion (%)	39.5	41.0	50.9	49.0	54.2
H_2/converted n-C_4	0.40	–	0.16	1.4	0.94
Product distribution (C-%)					
C_1+C_2 paraffins	9.8	9.7	8.5	10.7	10.4
C_3H_8	59.7	60.8	55.6	58.0	50.5
C_2–C_4 olefins	22.7	22.0	15.4	15.8	12.1
C_5^+ aliphatics	3.7	3.6	2.3	2.4	1.9
Aromatics	4.1	3.9	16.1	13.1	22.8
$CO+CO_2$	0.0	0.0	2.1	0.0	1.9

[a] Reaction temperature 450°C, $W/F = 10$ g h mol^{-1}, $P_{C_4H_{10}} = 20$ kPa, time on stream 2.5 h.

[b] Hydrogen was introduced instead of oxygen.

aromatic hydrocarbons increased drastically from 4.1 to 16.4%. Since the yield of dehydrogenated products or oxygenated products was less than 1% in the non-catalyzed reaction, the higher conversion for the reaction in the presence of oxygen should never be attributed to the oxygenation of butane. Also, since the non-catalyzed oxidation of hydrogen under the same reaction condition was less than 10% [9], the low hydrogen production should be attributed to the direct oxidation of hydrogen on the zeolite surface. Results shown in Table 4 suggest that if hydrogen atoms on the zeolite surface are removed effectively, H-ZSM-5 exhibits a high selectivity for aromatic hydrocarbons, even when little Ga was introduced into H-ZSM-5.

3.3.4. Effects of hydrogen

In Fig. 3, the results of the temperature programmed reaction (TPRe) of ethylene in hydrogen atmosphere on H-ZSM-5, Ga-ZSM-5 and Pt-ZSM-5 are shown. On Pt-ZSM-5, ethylene was converted completely at any temperature producing mostly ethane. On H-ZSM-5, on the other hand, the conversion of ethylene started at 150°C and reached 100% at around 300°C. Neither ethane formation nor hydrogen consumption occurred below 450°C, which means that H-ZSM-5 exhibits little catalytic activity for the olefin hydrogenation under the reaction conditions previously mentioned. Ga-ZSM-5 showed a similar catalytic character to H-ZSM-5, except that a slight hydrogenation of ethylene proceeded above 350°C, pointing out that the hydrogenation activity of Ga-ZSM-5 was quite low, while its activity for olefin conversion is similar to that of H-ZSM-5. Thus, ethylene was mostly polymerized to higher hydrocarbons. The low hydrogenation activity of Ga-ZSM-5 should contribute to the high aromatic selectivity during the paraffin conversion.

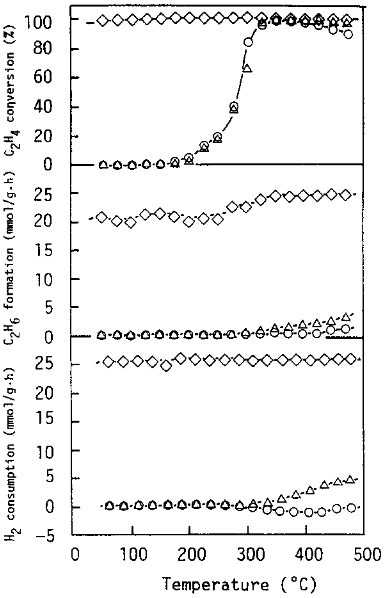

Fig. 3. Temperature programmed reaction of C_2H_4 with hydrogen. C_2H_4 25% in H_2, 5°C min^{-1}, $W/F =$ 9.3 g h mol^{-1}. ◆ Pt-ZSM-5, △ Ga-ZSM-5, ○ H-ZSM-5.

Table 5 shows the effects of hydrogen on the

Table 5
Effects of hydrogen on the butane conversion [a]

Catalyst	H-ZSM-5		Ga-ZSM-5		Pt-ZSM-5	
Atmosphere	N_2	H_2	N_2	H_2	N_2	H_2
Conversion of butane/%	59.0	60.0	57.7	56.3	91.2	96.3
Product distribution (C-%)						
C_1+C_2 paraffins	7.8	8.0	9.4	11.7	37.9	21.6
C_3H_8	57.6	59.3	47.2	53.4	29.5	69.3
C_4H_{10} isomer	6.5	6.6	7.2	10.6	4.3	3.8
C_2–C_4 olefins	10.3	10.8	8.9	7.0	7.2	0.8
C_5^+ aliphatics	2.3	2.3	3.1	3.1	0.9	0.3
Aromatics	15.6	13.5	26.5	14.2	20.2	4.2

[a] Reaction temperature 455°C, $P_{C_4H_{10}} = 20$ kPa, $P_{N_2(H_2)} = 80$ kPa, $W/F = 10$ g h mol^{-1}, time on stream 2.5 h.

conversion of butane over H-ZSM-5, Pt-ZSM-5 and H-ZSM-5. In case of H-ZSM-5, hydrogen in the gas phase affected neither butane conversion nor product selectivity. This phenomenon is consistent with the fact that the H-ZSM-5 has no hydrogenation activity. The catalytic activity of the Pt-ZSM-5 was promoted slightly by hydrogen while the selectivities of aromatic hydrocarbon and C_2–C_4 olefins were markedly suppressed. The phenomena should be attributed to its excellent hydrogenation activity. In case of Ga-ZSM-5, the selectivity of aromatic hydrocarbons was much lower in the presence of hydrogen as compared to nitrogen. On the other hand, the effect of hydrogen on the selectivity of C_2–C_4 olefins was low, because Ga-ZSM-5 exhibits a little hydrogenation activity, as shown in Fig. 2. The lower selectivity of aromatics should not be attributed to the hydrogenation activity but should be explained in terms of the spillover of hydrogen. This inconsistency will be discussed later in this paper.

3.4. Adsorption and desorption of hydrogen

Fig. 4 shows the adsorption of hydrogen at 400°C on H-ZSM-5, Ga-ZSM-5 and hybrid samples composed of H-ZSM-5 and Ga/SiO_2. Apparently from the figure, a fairly large amount of hydrogen was adsorbed on Ga-ZSM-5, while little hydrogen was adsorbed on H-ZSM-5. The difference between H-ZSM-5 and Ga-ZSM-5 is explained as follows. In case of Ga-ZSM-5, Ga has the function to adsorb hydrogen molecule and to dissociate the hydrogen molecule to hydrogen atoms, then the hydrogen atom on the Ga particle moves to ZSM-5 zeolite by spillover effect. On the other hand, H-ZSM-5 has no porthole for hydrogen in a spillover phenomenon as Ga-ZSM-5 does, the hydrogen adsorption rate of H-ZSM-5 is very low. The most important results seen from Fig. 3 is that with the physical mixture of H-ZSM-5 and Ga/SiO_2 more hydrogen was adsorbed than on Ga/SiO_2 only. This results suggests that hydrogen spills over H-ZSM-5 via Ga/SiO_2.

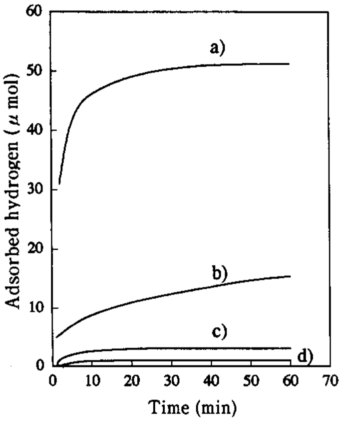

Fig. 4. Hydrogen spillover on ZSM-5 catalysts. Pretreatment; 600°C 1 h evacuated, adsorption temperature; 400°C. (a) Ga-ZSM-5 1.0 g, (b) (Ga/SiO_2 0.25 g + H-ZSM-5 1.0 g) hybrid catalyst, (c) Ga/SiO_2 0.25 g, (d) H-ZSM-5 1.0 g.

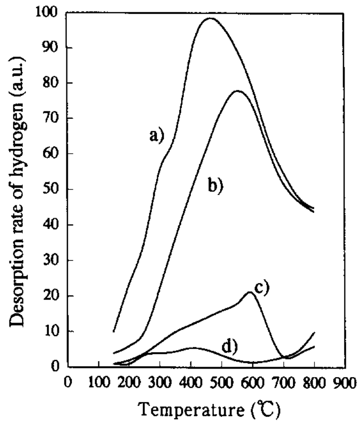

Fig. 5. Temperature programmed desorption spectra of hydrogen on ZSM-5 hybrid catalysts, heating rate; 400°C h^{-1}, mass number 2: (a) Ga-ZSM-5 1.0 g, (b) (Ga/SiO_2 0.2 g + H-ZSM-5 0.8 g) hybrid catalyst, (c) Ga/SiO_2 0.2 g, (d) H-ZSM-5 1.0 g.

Fig. 5 shows the TPD spectra of molecular hydrogen. From H-ZSM-5 the hydrogen molecule desorbed mostly at temperatures higher than 700°C. The TPD spectra of H_2 desorption from Ga-ZSM-5 is characterized by its large peak at 400°C, however with Ga/SiO_2 a considerably smaller peak at 600°C is seen as compared to the former. The TPD spectrum of the Ga/SiO_2 and H-ZSM-5 hybrid is similar to that of Ga-ZSM-5 as compared to Ga/SiO_2 or H-ZSM-5 but the peak top was shifted to a higher temperature (by about 100°C). The amount of desorbed hydrogen from the Ga/SiO_2 and H-ZSM-5 hybrid was almost 80% of Ga-ZSM-5 and so it corresponds to the amount of zeolite in the catalyst. These phenomena clearly suggest that even the hydrogen on H-ZSM-5 is desorbed at much lower temperature when the zeolite is hybridized with Ga/SiO_2. The desorption of H_2 below 600°C from the hybrid catalyst should be attributed to the reverse spillover of hydrogen including inter-particle hydrogen transfer.

3.5. Reaction model

The most probable explanation of the promotional effect of gallium should be attributed to the 'reverse spillover' effects [18] whose model is shown in Fig. 6. In the model, gallium acts as a porthole for hydrogen on the zeolite surface. It has been reported in many studies that the conversion of lower paraffins on H-ZSM-5 gives a small amount of aromatic hydrocarbons or hydrogen but a large amount of lower paraffins such as propane and ethane [2,7]. This means that hydrogen atoms generated upon aromatization reaction do not dissolve from the zeolite surface into the gas phase as with hydrogenate ethylene or propene which are intermediates in paraffin-to aromatic conversion.

On the gallium-supported ZSM-5 zeolite, on the other hand, hydrogen atoms on the zeolite surface migrate to a Ga site where they recombine to form hydrogen molecules and then desorb into the gas phase.

When hydrogen atoms on a zeolite surface are effectively removed, their concentration in the zeolite surface should be reduced. As is the case for the reaction in the presence of oxygen, H-ZSM-5 itself exhibits a high conversion activity and aromatic selectivity, if the surface hydrogen is effectively removed. The desorbed hydrogen is rather inactive for a hydrogenation reaction in the Ga-ZSM-5 catalyzed system as shown in Fig. 2. In case of hybrid catalysts, their high catalytic performances should be attributed to inter-particle hydrogen transfer and reverse spillover as demonstrated in Fig. 6. The hydrogen atom on H-ZSM-5 moves to the SiO_2 surface and then goes into the gas phase through the Ga site (reverse spillover). It is reasonable that the granular mixture of Ga/SiO_2 and H-ZSM-5 exhibited a significantly inferior ability for butane conversion as compared to the hybrid catalyst. In the granular system, the poor contact between the two components impede hydrogen transfer from the H-ZSM-5 to the Ga/SiO_2.

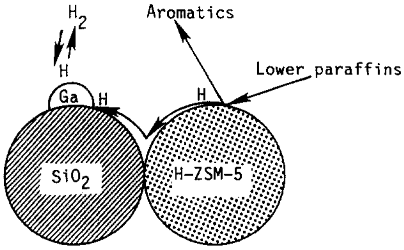

Fig. 6. Model of inter-particle hydrogen reverse spillover.

The concept of spillover also reasonably explains the fact that the selectivity of aromatic hydrocarbons on the Ga-ZSM-5 was suppressed by hydrogen in the gas phase in spite of its low hydrogenation activity. When hydrogen exists in the gas phase, the desorption of hydrogen atoms from the zeolite is suppressed by the spillover effect. If the hydrogen desorption is slow, it will react with olefins or carbenium ions to form paraffins, suppressing the formation of aromatic hydrocarbons.

References

[1] T. Mole and J.R. Anderson, Appl. Catal. 17 (1985) 141.

[2] C. Tan, C. Cheng, L. Zhou and S. Peng, Proc. 9th Int. Congr. Catal. 1 (1988) 445.

[3] T. Yashima, T. Sasaki, Takahashi, S. Watanabe and S. Namba, J. Jpn. Petrol. Inst. 31 (1988) 154.

[4] G. Sirokman, Y. Sendoda and Y. Ono, Zeolites 6 (1986) 299.

[5] N.S. Gnep., J.Y. Doyemet and M. Guisnet, J. Mol. Catal. 45 (1988) 281.

[6] T. Inui, Y. Makino, F. Okazumi, S. Nagano and A. Miyamoto, Ind. Eng. Chem. Res. 26 (1987) 647.

[7] H. Kitagawa, Y. Sendoda and Y. Ono, J. Catal. 101 (1986) 12.

[8] N.S. Gnep., J.Y. Doyenet, A.M. Seco, F.R. Ribeiro and M. Guisnet, Appl. Catal. 43 (1988) 155.

[9] K. Fujimoto, I. Nakamura and K. Yokota, Zeolite 9 (1989) 120.

[10] K. Fujimoto and I. Nakamuara, Proc. 3rd China-Jpn.-USA Symp. Catal. (1988).
[11] K. Fujimoto, I. Nakamura, K. Yokota and K. Aimoto, Bull. Chem. Soc. Jpn. 64 (1991) 2275.
[12] R. Le Van Mao and L. Dufresne, Appl. Catal. 52 (1989) 1.
[13] V. Kanazirev, G.L. Price and K.M. Dooley, J. Chem. Soc., Chem. Commun. (1990) 712.
[14] G.L. Price and V. Kanazirev, J. Catal. 126 (1990) 267.
[15] G.L. Price and V. Kanazirev, J. Mol. Catal. 66 (1991) 115.
[16] K. Fujimoto and S. Toyoshi, Proc. 7th Int. Congr. Catal. (1980) 235.
[17] P.A. Sermon amd G.C. Bond, Catal. Rev. 8 (1973) 211.
[18] S. Asaoka, S. Masamizu, K. Fujimoto and T. Kunugi, Nihon Kagakukai-shi (1976) 388.