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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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H–ZSM-5 showed a high selectivity of propane and low selectivity of aromatic hydrocarbons in butane conversion at 450 °C, whereas Ga-supportd ZSM-5 (Ga–ZSM-5) showed higher selectivities of aromatic hydrocarbons and hydrogen. A small amount of oxygen in the feed promoted butane conversion to aromatic hydrocarbons on H–ZSM-5. Hybrid catalysts composed of the physical mixture of Ga/Al_2O_3 and H–ZSM-5 showed comparable activities and aromatic selectivities to those of the Ga-supported ZSM-5 zeolite (Ga–ZSM-5). Hydrogen was adsorbed quickly on the Ga–ZSM-5 and on the hybrid catalyst at 400 °C and the adsorbed hydrogen was desorbed at around 450 °C during the temperature programmed desorption experiment from both catalysts. However, little hydrogen was adsorbed on H–ZSM-5 and was desorbed from it. It was pointed out that the supported Ga promoted the zeolite-catalyzed aromatization of lower paraffins by promoting hydrogen desorption via the "reverse spillover" effecct.

Conversion of lower paraffins into aromatic hydrocarbons is of great interest because of its potential application for producing transportation fuel or chemicals from natural gas. Cattanach has claimed that H–ZSM-5 type or Zn-supported ZSM-5 zeolites are effective catalysts for this reaction.[1] Recently, it has been found that a Ga-supported ZSM-5 type zeolite is an exceptionally effective catalyst for this type of reaction.[2] Ga and Zn are effective in promoting the reaction in the impregnated form,[3,4] in the ion exchanged form,[5,6] in the physically mixed form[7] or even when they are incorporated in the zeolite framework.[8]

There are many interpretations postulated as to why Ga or Zn are so effecctive in promoting the formation of aromatic hydrocarbons. Anderson and Mole suggested that the dehydrogenation of propane was promoted by Zn on H–ZSM-5.[9] Ono 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 aromatization of olefins.[10] They also observed that Ga-loading promotes propane conversion and suggested that the Ga-promoted aromatization suppresses the formation of propane from intermediate products.[10] 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 promotes the paraffin dehydrogenation to olefins and Ga promotes aromatization of olefins.[8] On the other hand, Yashima et al. claimed that Ga on ZSM-5 promotes the dehydrogenation of cycloparaffins or cycloolefins which are formed on zeolite.[3] Recently, Gnep et al. pointed out that Ga_2O_3 showed a catalytic activity for propane dehydrogenation and claimed that Ga on ZSM-5 exists as Ga_2O_3 and promotes the naphthene dehydrogenation.[11] The present authors have found that added oxygen gas in the propane or butane conversion on H–ZSM-5 selectively oxidizes hydrogen on the zeolite to promote the conversion of the feed and especially the formation of aromatic hydrocarbons. We 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. Also, the authors have found that the hybrid catalyst composed of the compressed physical mixture of finely powdered H–ZSM-5 and alumina-supported Ga_2O_3 exhibits the activity of butane conversion and the selectivity of aromatics which are comparable to those of Ga-supported H–ZSM-5 and have postulated a concept that hydrogen atoms on the zeolite surface come out through the Ga-site (to result in the promoted aromatics formation[12–14]. Recently, Mao et al. found that an H–ZSM-5 to which a small quantity of zinc oxide/aluminum oxide 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 ZnO/Al_2O_3.[16]

The present work tries to clarify the role of gallium on ZSM-5 in the conversion of lower paraffins from the stand point of hydrogen spillover and reverse spillover.

Experimental

The ZSM-5 zeolite was supplied by Tosoh Chem. Ind. Ltd. (Si/Al atom ratio: 50, 850 NAA). X-ray diffraction confirmed that the material was Na–ZSM-5. A protonic ZSM-5 (H–ZSM-5) was prepared by repeated ion exchange of the Na–ZSM-5 with aqueous ammonium nitrate solution (5 times) followed by calcination in air at 500 °C. Ga was supported on the H–ZSM-5 (Ga–ZSM-5) or a commercially available γ-alumina (Ga/Al_2O_3) by impregnating them with gallium nitrate from its aqueous solution and then calcining the precursors in air at 500 °C for 3 h. Ga contents were 1.5 wt%, and 5 wt% for Ga–ZSM-5 and Ga/Al_2O_3, respectively. Hybrid catalysts were prepared by co-grinding the two type of catalysts into a

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fine powder and then pressure-molding the mixture to granules (20—40 mesh).

Conversion of butane 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 crried 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^{-1}. The desorbed hydrogen was determined by mass spectrometry.

Results and Discussion

Effect of Oxygen. In Table 1 are shown some of the results of butane conversion over H-ZSM-5 and Ga-ZSM-5 in the presence and absence of oxygen. The product was propane with a small amount of isomerized butane, C_2—C_4 olefins and aromatic hydrocarbons. The composition of the aromatics was scarcely affected by the oxygen and was quite similar to those reported in other papers.[4,8,9] As it has been already pointed out, the protonic ZSM-5 (H-ZSM-5) producted propane and C_2—C_4 olefins as the main products, with only a small amount of aromatic hydrocarbons.[13] However, when the feed gas contained 5% oxygen, the butane conversion on the H-ZSM-5 catalyst increased considerably and the selectivity of the 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 oxidation of butane. Also, since the non-catalyzed oxidation of hydrogen under the same reaction condition was less than 10%, the low hydrogen production should be attributed to the direct oxidation of hydrogen on the zeolite surface.[13] Results shown in Table 1 suggest that if hydrogen atoms on the zeolite surface are removed effectively, H-ZSM-5 exhibits a high selectivity for aromatic hydrocarbons.

Effect of Additives. Figure 1 shows the results of butane conversion on H-ZSM-5, Ga-ZSM-5 and Pt-ZSM-5 as a function of reaction temperature. The catalytic activity of Pt-ZSM-5 was much higher than those of the other two catalysts. Also, the selectivity of aromatics over Pt-ZSM-5 was higher than those of the other catalysts. However, the aromatic selectivity on Ga-ZSM-5 increased markedly with increasing reaction temperature and reached a level comparable to that of Pt-ZSM-5 at around 500 °C, whereas the selectivity of the aromatics on H-ZSM-5 stayed at a much lower level than the other two catalysts. Also, the mole ratio of hydrogen to reacted butane on Ga-ZSM-5 catalyzed reaction increased with increasing temperature finally reaching that on Pt-ZSM-5.

Table 1. 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 (carbon %)					
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. b) Hydrogen was introduced instead of oxygen.

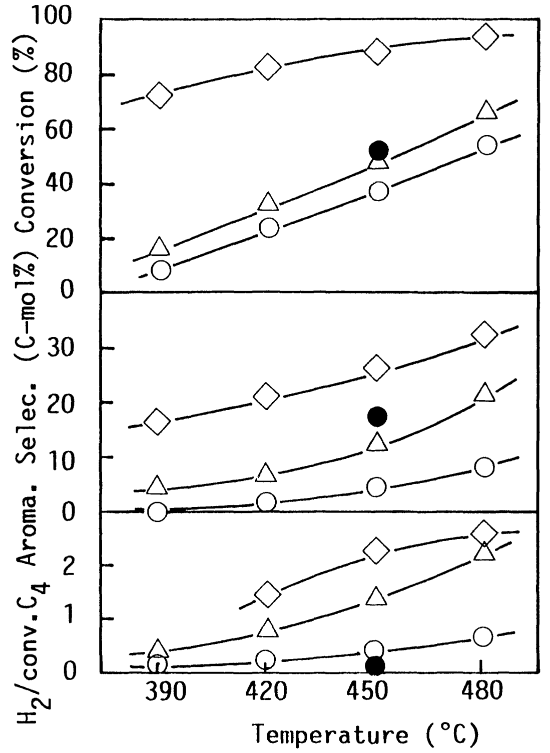

Fig. 1. Comparison of ZSM-5 catalysts for conversion of n-C_4. n-C_4 20%, N_2 80%, W/F; 10 g h mol^{-1}. ◇ Pt-ZSM-5, △ Ga-ZSM-5, ○ H-ZSM-5, ● H-ZSM-5 (5% O_2).

It has been well known that supported platinum on H-ZSM-5 promotes the dehydrogenation of lower paraffins to olefins,[8] which are much more reactive in dehydroaromatization.[14] The slight increase in the conversion activity and the drasic increace in the aromatics selectivity caused by adding Ga on H-ZSM-5 has been also reported in other papers,[2-8] which will be discussed in a later chapter.

Catalytic Performances of Ga-containing Hybrid Catalysts. Table 2 shows some of the results of the butane conversion on a variety of Ga-containing catalysts. The first point which should be noted is that the hybrid catalyst containing Ga/Al_2O_3, which was finely powdered and pressed in to granules with H-ZSM-5,

Table 2. Conversion of Butane on a ZSM-5 Catalysts (**1**)[a)]

Catalyst	H-ZSM-5	Ga-ZSM-5	Ga/Al_2O_3	H-ZSM-5+ Ga/Al_2O_3[b)]	H-ZSM-5+ Ga/Al_2O_3[c)]	Ga/Al_2O_3[d)]
Conversion of butane/%	41.6	47.9	0.7	47.7	46.8	1.6
H_2/converted butane (mol ratio)	0.3	1.4	—	1.3	0.8	—
Product distribution (carbon %)						
C_1+C_2 paraffins	9.6	9.5	3.0	11.0	10.8	3.9
C_3H_8	58.6	52.5	3.5	51.7	56.5	20.1
C_4H_{10} isomer	3.7	3.5	0.0	3.2	3.0	0.0
C_2–C_4 olefins	16.3	10.0	88.1	13.0	16.2	17.2
C_5^+ aliphatics	3.0	2.5	0.5	1.7	2.3	1.3
Aromatics	8.8	22.0	4.9	19.4	11.2	21.0

a) 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 Ga/γ-Al_2O_3 was 20 wt%. c) Granular mixture, Content of Ga/γ-Al_2O_3 was 20 wt%. d) Propene was reacted instead of butane.

exhibited high aromatic selectivity which was comparable to those of the Ga–ZSM-5 catalyst, whereas the Ga/Al_2O_3 itself exhibited little catalytic activity for the butane conversion and olefin aromatization. It should be also noted that the content of the ZSM-5 zeolite in the hybrid was only 80% and thus the catalytic activity of the H-ZSM-5 hybrid catalyst is estimated to be 1.4 times higher than that of only H-ZSM-5. The second important point is that the physical mixture of granular Ga/Al_2O_3 and granular H-ZSM-5 showed catalytic performances much inferior to the powdery mixed hybrid catalyst with the same composition.

The former studies indicated that the higher aromatic selectivity of the Ga-ZSM-5 catalyst than that of H-ZSM-5 should be attributed to the dehydrogenation or dehydroaromatization of olefins[4,7,15)] or the dehydrogenation of naphthenic hydrocarbons.[3,11)] However, the data in Table 2 show that Ga/Al_2O_3 showed little catalytic activity for both olefin aromatization and paraffin dehydrogenation, whereas it exhibited an excellent promotional effect for the aromatics formation when it was intimately contacted with H-ZSM-5. Thus, the promotional effect of gallium should be attributed to functions other than its dehydrogenation activity. If the promotional effect of the gallium is attributed to its dehydrogenation activity, Ga/Al_2O_3 should exhibit catalytic activity for the dehydrogenation of butane or the dehydroaromatization of propene and also the granular mixture of Ga/Al_2O_3 and H-ZSM-5 should exhibit comparable performances to that of the hybrid catalyst.

Hydrogen Effect. In Fig. 2 are shown the results of the Temperature Programmed Reaction (TPRE) of C_2H_4 in a hydrogen atmosphere on H-ZSM-5, Ga-ZSM-5, and Pt-ZSM-5. On Pt-ZSM-5, C_2H_4 was converted completely at any temperature producing mostly ethane. On H-ZSM-5, on the other hand, the conversion of C_2H_4 started at 150 °C and reached 100% at around 300 °C. Neither the ethane formation nor the 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 similar catalytic character to those of 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

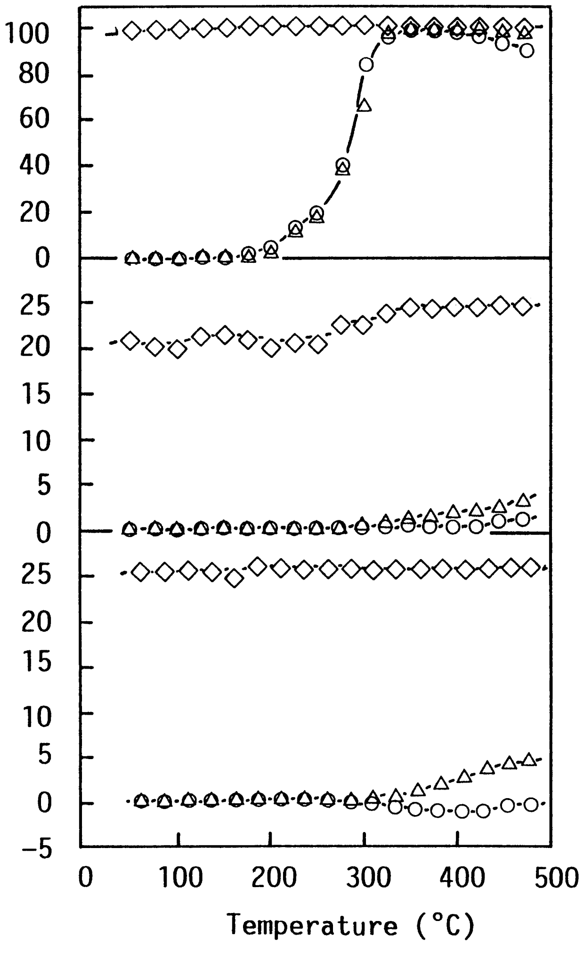

Fig. 2. TRPE of C_2H_4 with hydrogen. C_2H_4 25%, H_2 75%, 5 °C min^{-1}, W/F; 10 g h mol^{-1}. ◇ Pt-ZSM-5, △ Ga-ZSM-5, ○ H-ZSM-5.

Table 3. Effects of Hydrogen on the Conversion of Butane[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 (carbon %)						
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}.

to the high aromatic selectivity during the paraffin conversion.

Table 3 shows the effects of hydrogen on the conversion of butane over the 3 types of catalysts previously mentioned. In the case of the H-ZSM-5, hydrogen in the gas phase affected neither the butane conversion nor product selectivity. This phenomenon is consistent with the fact 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 the case of the Ga-ZSM-5, the selectivity of aromatic hydrocarbons and C_2—C_4 olefins were much lower in the presence of hydrogen than that in the presence of nitrogen. This should not be attributed to the hydrogenation of olefins, because the Ga-ZSM-5 exhibits little hydrogenation activity but should be explained in terms of the spillover of hydrogen. This inconsistency will be discussed later in this report.

Adsorption and Desorption of Hydrogen. Figure 3 shows the adsorptions of H_2 at 400 °C on H-ZSM-5, Ga-ZSM-5, and hybrid samples composed of H-ZSM-5 and Ga/Al_2O_3. Apparently from the figure, a fairly large amount of hydrogen was adsorbed quickly 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 the case of Ga-ZSM-5, Ga has the function to adsorb hydrogen molecule and to dissociate hydrogen molecule to hydrogen atom and then the hydrogen atom on Ga particle moves to ZSM-5 zeolite by spillover effect. On the other hand, H-ZSM-5 has no entrance of hydrogen such as Ga, so only little hydrogen was adsorbed to H-ZSM-5. The data in Fig. 3 shows that on the physical mixture of H-ZSM-5 and Ga/Al_2O_3 more hydrogen was adsorbed than on Ga/Al_2O_3 only.

Figure 4 shows the spectra of temperature programmed desorption (TPD) of adsorbed hydrogen from Ga-ZSM-5 and H-ZSM-5. The desorption of hydrogen was prominent at two temperature ranges around 400 °C and at higher than 700 °C, while H-ZSM-5 showed only one prominent desorption temperature at higher than 700 °C.

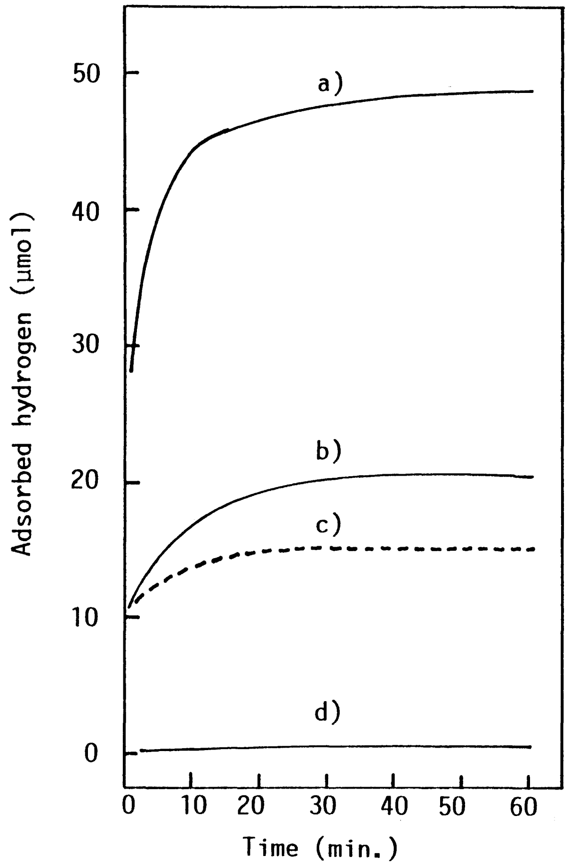

Fig. 3 Hydrogen spillover on ZSM-5 catalysts. Pretreatment; 600 °C 1 h evacuated, adsorption temperature; 400 °C. a) Ga-ZSM-5 1.0 g, b) (Ga/Al_2O_3 0.2 g+H-ZSM-5 0.8 g) hybrid catalyst, c) (Ga/Al_2O_3 0.2 g)+(H-ZSM-5 0.8 g) calculated value, d) H-ZSM-5 1.0 g.

The desorption of hydrogen at lower temperature range was in the molecular state whereas that at higher temperature range was in the atomic state. This suggests that desorption in the lower temperature range is of the "reverse spillover" type. The process is composed of (1) the transfer of hydrogen atoms on the solid surface to the gallium site, (2) the combination of two hydrogen atoms to form one hydrogen molecule, and (3) the desorption of the hydrogen molecule into gas phase. This is just the reverse process of hydrogen spillover. On the other hand, the desorption of hydrogen in the atomic state at higher temperature range may be attributed to the direct dissociation of zeolite-hydrogen bonds by thermal energy. Although the hydrogen atoms in the gas phase usually recombine quickly to molecules, the ultra high vacuum ($<10^{-8}$ Torr, 1 Torr=133.322 Pa) may prevent the collision between hydrogen atoms of the removal of excess energy from hot hydrogen molecules produced by the collision of two hydrogen atoms. Also this desorption of atomic hydrogen at high temperature was observed in the case of

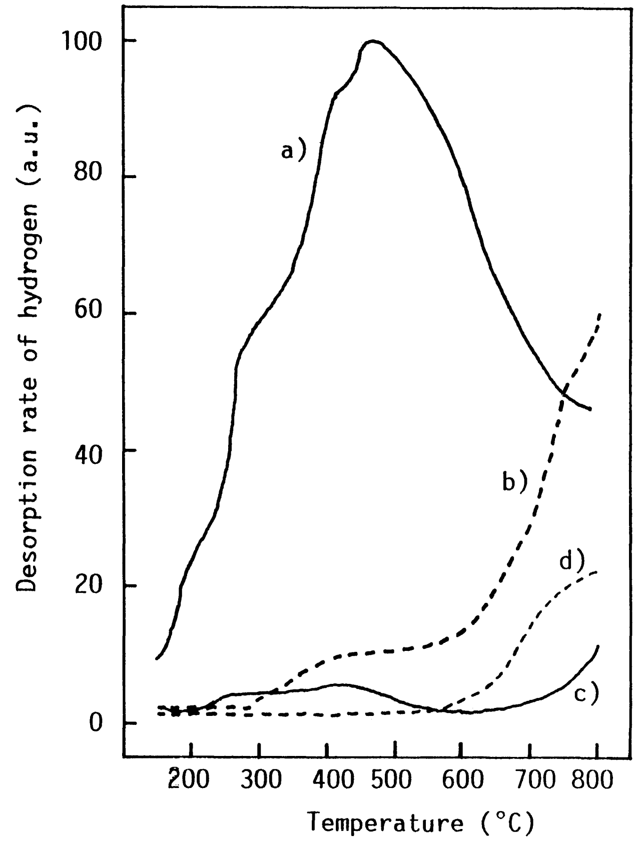

Fig. 4. Temperature programmed desorption spectra of hydrogen on ZSM-5 catalysts. Heating rate; 400 °C h^{-1}, a) Ga–ZSM-5 1.0 g mass number 2, b) Ga–ZSM-5 1.0 g mass number 1, c) H–ZSM-5 1.0 g mass number 2, d) H–ZSM-5 1.0 g mass number 1.

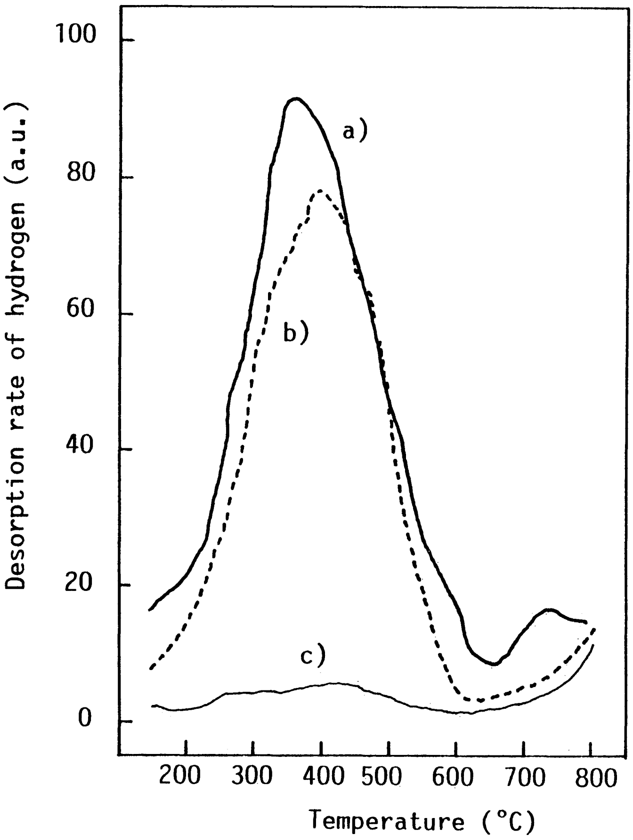

Fig. 5. Temperature programmed desorption spectra of hydrogen on ZSM-5 hybrid catalyst. Heating rate; 400 °C h^{-1}, mass number 2, a) (Ga/Al_2O_3 0.2 g+H–ZSM-5 0.8 g) hybrid catalyst, b) (Ga/Al_2O_3 0.2 g)+(H–ZSM-5 0.8 g) calculated value, c) H–ZSM-5 1.0 g.

hybrid catalyst. The more important process of hydrogen desorption for catalytic dehydrogenation is convinced to be the reverse spillover process.

Figure 5 shows the TPD spectra of molecular hydrogen. From H–ZSM-5 hydrogen molecule desorbed mostly at higher than 700 °C. The TPD spectra of H_2 desorption from Ga–ZSM-5 is characterized by its much larger peak between 300 and 600 °C and the peak at 700 °C. The TPD spectrum from Ga/Al_2O_3 is rather close to that from Ga–ZSM-5 but the peak top is shifted to lower temperature (by about 100 °C). The character of H_2 desorption from the Ga/Al_2O_3/H–ZSM-5 hybrid is quite close to that from Ga/Al_2O_3 but its amount is considerably larger than the former. These phenomena clearly suggest that hydrogen molecules are desorbed much more easily from Ga on Al_2O_3 than on zeolite, and that even the hydrogen on H–ZSM-5 is desorbed at much lower temperature when the zeolite is hybridized with Ga/Al_2O_3. 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 (Fig. 7).

Reaction Model. The most probable explanation of the promotional effect of gallium should be attributed to the "reverse spillover" effect whose model is shown in Fig. 6.[21)] In the model, gallium acts as the exit of 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.[4,9)] It means that hydrogen atoms generated upon aromatization reaction do not come out of the zeolite surface into the gas phase but 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 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 of 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

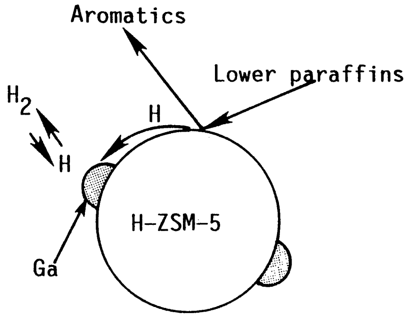

Fig. 6. Model of hydrogen reverse spillover.

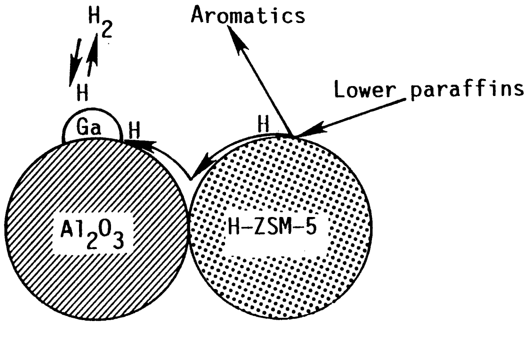

Fig. 7. Model of interparticle hydrogen reverse spillover.

Ga–ZSM-5 catalyzed system as shown in Fig. 2. In the case of hybrid catalysts, their high catalytic performances should be attributed to inter-particle hydrogen transfer and reverse spillover as demonstrated in Fig. 7. The hydrogen atom on H–ZSM-5 moves to the alumina surface and then goes into the gas phase through the Ga sites (reverse spillover). It is reasonable that the granular mixture of Ga/Al_2O_3 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/Al_2O_3.

The concept of spillover also reasonably explain 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 carbonium ions to form paraffins, suppressing the formation of aromatic hydrocabons.

Conclusion

1) Gallium on ZSM-5 promotes the formation of aromatic hydrocarbons in the conversion of lower paraffins through the reverse spillover of hydrogen atoms on the zeolite surface.

2) H–ZSM-5 is sufficiently active and selective for the conversion of butane to aromatic hydrocarbons if the hydrogen atoms on its surface are effectively removed during the reaction.

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