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Effect of Ga/Proton Balance in Ga/HZSM-5 Catalysts on C_3 Conversion to Aromatics

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Ga/HZSM-5 catalysts prepared by chemical vapor deposition (CVD) of $GaCl_3$ into the pores of HZSM-5 have been characterized by temperature programmed techniques, such as reduction (TPR), oxidation (TPO), and desorption of NH_3 (NH_3-TPD), X-ray powder diffraction (XRD), and catalytic tests including propane and propene conversions and toluene disproportionation (TD). TPR shows formation of $(GaO)^+$ ions and Ga_2O_3 particles. With increasing Ga loading, the formation of $(GaO)^+$ ions is favored. Unlike methods which introduce Ga into HZSM-5 from Ga salts in aqueous solution, the CVD technique acts as a true ion exchange, replacing protons by $(GaO)^+$ ions. As more protons are replaced by $(GaO)^+$ ions, the conversion of propene decreases, but that of propane passes through a maximum and so does the selectivity to aromatics, both for propane and for propene. This is consistent with a bifunctional mechanism in which Brønsted acid sites catalyze oligomerization and ring closure, but Ga, in concert with protons, acts as a dehydrogenating site. Optimum yields are obtained with catalysts having Ga/(Ga + H^+) ratios between 0.4 and 0.5.

I. INTRODUCTION

Aromatization of light paraffins over metal-free and Ga or Zn loaded HZSM-5 catalysts has been intensely studied in recent years. Some important questions have been answered, but there is still an apparent contradiction between mechanistic concepts and numerous observations. Most authors appear to agree that aromatization over Ga or Zn containing HZSM-5 catalysts occurs via a *bifunctional* mechanism; i.e., some steps are catalyzed by acid sites and others by Ga or Zn sites (1–10). The selectivity to aromatics is significantly higher for catalysts containing Ga (2–9) or Zn (7, 10) than on metal-free HZSM-5. Confining ourselves further to Ga/HZSM-5, the Ga sites are thought to catalyze the dehydrogenation steps, including release of H_2 (11).

A logical consequence of the bifunctional concept is that aromatization activity and selectivity should depend on the balance between Brønsted acid and Ga or Zn sites; there should be an optimum ratio of metal ions and protons leading to a maximum yield of aromatics. One should thus expect that a plot of the yield of aromatics against the Ga/(Ga + H^+) ratio should show a maximum.

Casual inspection of published data appears to contradict this concept; results by Gnep *et al.* (12, 13) and Kitagawa *et al.* (14) show a monotonic increase of aromatic yield with Ga content and data of Bayense and van Hooff (15) suggest that the performance is independent of the Ga content even beyond 100% exchange. Closer inspection reveals, however, that the apparent contradiction might be due to the implicit assumption that Ga is brought into the zeolite by ion exchange; i.e.,

$$Ga^{3+}_{aq} + 3\,H^+_{zeol} = Ga^{3+}_{zeol} + 3H^+_{aq}, \qquad [1]$$

which implies that for a given zeolite the sum ($3Ga^{3+}$ + H^+) = N should stay constant for a given catalyst, N being equal to the number of Al-centered tetrahedra in the zeolite matrix. If this assumption is correct, high Ga load implies low proton concentration and low activity for a bifunctional reaction. The absence of a maximum of the yield as a function of the Ga load, as reported by several researchers, thus suggests that one of the above assumptions is not valid: either the mechanism is not bifunctional or the loading of HZSM-5 with Ga, as carried out by most authors, is not a true ion exchange. Indeed, Gnep *et al.* (12) and Kitagawa *et al.* (14) observed that, with their preparation method, gallium loading of HZSM-5 did not lead to a noticeable decrease in acidity, in contradiction to the chemistry of Eq. [1]. There is evidence that at elevated temperature and under reducing conditions Ga^+ ions are able to enter the zeolite channels. This process is probably initiated by reduction of Ga_2O_3 with H_2, followed by ion migration (16, 17):

$$Ga_2O_3 + 2H_2 + 2H^+ = 2Ga^+ + 3H_2O. \qquad [2]$$

In the present work gallium is introduced into ZSM-5 by chemical vapor deposition (CVD) of $GaCl_3$; the resulting change in proton concentration is followed by NH_3 TPD

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and an acid catalyzed probe reaction. In a previous paper (18) it was shown that $GaCl_3$ enters the zeolite more easily than $Ga^{3+}(H_2O)_6$ ions do (19, 20); reaction of $GaCl_3$ with H_2O and protons results in the formation of the gallyl ion, $(GaO)^+$, as a primary species (16, 18):

$$GaCl_3 + H_2O + H^+ = (GaO)^+ + HCl\uparrow. \quad [3]$$

Under severe reduction conditions the gallyl ion is reduced to Ga^+. With this idealized chemistry, the sum of the charge compensating ions,

$$(GaO)^+ + Ga^+ + H^+ = N, \quad [4]$$

should be constant. In the present study, the proton concentration for samples with different Ga loadings is measured independently by two methods: temperature programmed desorption of NH_3 and toluene disproportionation, TD, a catalytic probe which is generally assumed to be specific for Brønsted sites (21, 22). To identify the first dehydrogenation step, the aromatization of propane is compared to that of propene, both measured in the kinetic regime, as a function of the gallium loading up to high values of the molar fraction $Ga/(Ga + H^+)$.

While ion exchange by CVD is assumed to be more efficient than ion exchange from an aqueous solution of a Ga^{3+} salt, it would be unrealistic to assume 100% efficiency; some gallium will be present as Ga_2O_3 in the calcined catalyst also after loading by the CVD method. The ratio of the gallyl ions to gallium trioxide in the catalysts is, therefore, estimated from temperature programmed reduction (TPR) data.

In this paper aromatization activities and selectivities will be plotted each as a function of the atomic ratio $\gamma_{Ga} = Ga/(Ga + H^+)$ without explicit assumptions on the distribution of the Ga atoms over the species Ga^+, Ga^{3+}, $(GaO)^+$, and Ga_2O_3. The value of γ_{Ga} is calculated from the chemical analysis of the Ga content and the proton concentration derived from TPD of NH_3. In order to eliminate contributions from NH_3 adsorbed on extraframework sites, samples were purged with H_2O at 120°C prior to NH_3 TPD.

As decreases in catalytic activity can be caused by deposition of carbonaceous overlayers, an analysis of the amount of coke by temperature programmed oxidation (TPO) has also been included in this study. X-ray powder diffraction (XRD) was used to detect Ga_2O_3 in the samples.

II. EXPERIMENTAL

Catalyst Preparation

HZSM-5 zeolite was provided by UOP (Lot #13923-57C). The Si/Al ratio was 20.5; the Na content was analyzed by ICP and found to be below 0.01%. The dried zeolite was first calcined at 500°C and mixed with $GaCl_3$ in a glove box; the mixture was transferred to a quartz tube reactor. The reactor was heated from room temperature to 200°C at a rate of 0.25°C/min. After it was held for 2 h at 200°C, heating was resumed up to 500°C (0.5°C/min). The reactor was then kept at 500°C for an additional 2 h. The samples contained 0.77, 1.36, 2.95, 2.97, 3.70, and 3.76% Ga, respectively.

Catalytic Reactions

Propane conversion was carried out at atmospheric pressure and 530°C in a quartz microflow reactor. The space velocity (WHSV, 50%/50% mixture of propane and Ar) was 456 h^{-1}. Propene conversion was carried out at 500°C and 2156 h^{-1} using a 50%/50% mixture of propene and Ar. Before the catalytic tests, all Ga-containing samples were calcined for 1 h (O_2) and reduced for 2 h (H_2) at 580°C. HZSM-5 was also calcined at 580°C for 2 h before test. Hydrocarbon products were analyzed at 10 min on stream using a Hewlett–Packard (HP) 5890 series II gas chromatograph (GC) equipped with an FID detector and a 50-m PLOT KCl/Al_2O_3 column.

Toluene disproportionation (TD) was performed at 400°C over unreduced catalysts. Toluene was fed to the reactor in an Ar carrier gas through a saturator at room temperature. The Ar flow rate was varied between 20 and 190 ml/min using 60 mg of catalyst. For product analysis, the same GC with a 50-m HP PONA column was used.

Temperature Programmed Studies

To study the extent of coking, catalysts that had been on stream for 3 h at 530°C and a WHSV of 42 h^{-1} were purged with Ar for 15 min at 530°C and analyzed by TPO. The CO_2 product was monitored with a mass spectrometer (MS); these tests will therefore be referred to as TPOMS. The MS was calibrated using known volumes of CO_2. A flow of 5% O_2 in He was used (23).

Temperature programmed reduction with H_2 was done in a flow system similar to the one described elsewhere (24). The TCD cell was calibrated by injecting H_2 pulses of known volume. In all cases, 150 mg samples were used; the data were found reproducible within $\leq 10\%$.

NH_3-TPD was carried out using the same system as for TPR. First, anhydrous NH_3 (99.99% minimum purity, Matheson) was passed for 30 min over 400 mg of catalyst at 120°C. After adsorption, the sample was purged with He for 1 h at 120°C. TPD data were collected from 120°C to 700°C at a ramp rate of 8°C/min. Pulses of ammonia were used to calibrate the cell.

X-Ray Powder Diffraction

XRD patterns were recorded using a Scintag PAD-V X-ray diffractometer with a CuK_α radiation source oper-

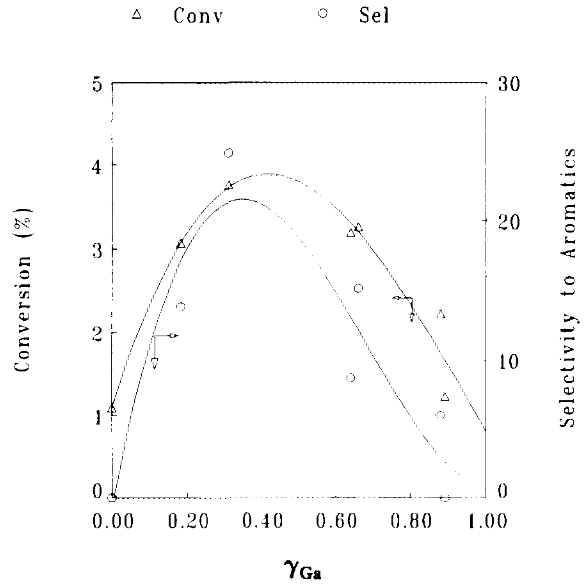

FIG. 1. Propane aromatization at 530°C and WHSV of 456 h^{-1}.

ated at 40 KV and 40 mA. The detailed procedure was similar to the one described elsewhere (25).

III. RESULTS

Propane and Propene Conversion

The results of catalytic propane conversion tests over catalysts with widely different values of the ratio

$$\gamma_{Ga} \equiv \frac{[Ga]}{[Ga + H^+]}$$

are presented in Fig. 1 and Table 1. Clearly, the catalytic activity increases steeply with γ_{Ga} up to a value of 0.45, passes through a maximum, and decreases for high values of γ_{Ga}. This activity profile is in agreement with the bifunctional model, applied to catalysts for which Ga loading is carried out via a true ion exchange. The result distinctly differs from those observed for catalysts that were loaded via exposure to aqueous solutions of Ga salts (12, 14, 15). For the present samples, a similar profile is observed for selectivity to aromatics. Major coproducts with all samples at low conversion are methane, ethene, and propene. On HZSM-5, almost equimolar amounts of methane and ethene are formed by cracking. Propene is clearly formed as a primary product, presumably via acid catalyzed cracking of a pentacoordinated carbonium ion (26–28). Upon addition of Ga to HZSM-5, propene formation by dehydrogenation dominates over acid-catalyzed cracking in accordance with previous findings (8, 28). This is evident from the H/C ratio. Ga is thus instrumental in catalyzing propane dehydrogenation, as suggested previously by Iglesia *et al.* (11); i.e., part of the hydrogen is released as H_2 instead of being redistributed.

TABLE 1

Selectivity Pattern of Ga/HZSM-5 Catalysts for the Conversion of Propane at 530°C and WHSV of 456 h^{-1}

wt% Ga	C_1	C_2	C_2^{2-}	C_3^{2-}	C_4^{a}	C_4^{2-}	Arom	γ_{Ga}	H/C
0	22.6	0	39.4	34.9	3.1	0	0	0	2.74
0.77	8.1	3.1	15.5	55.5	0.9	3.1	13.9	0.18	2.42
1.36	6.7	3.4	13.3	45.2	3.1	3.4	24.9	0.31	2.43
2.95	4.5	3.9	10.6	62.1	−0.1	3.8	15.2	0.64	2.28
2.97	4.3	2.8	11.1	68.9	−0.5	4.7	8.7	0.66	2.26
3.70	3.7	4.6	10.0	73.1	−1.2	3.9	6.0	0.88	2.20
3.76	1.0	3.3	7.4	89.1	−5.0	4.2	0	0.89	1.96

[a] Isobutane is present in the feed.

TABLE 2

Reaction Rate of Propane Conversion at 530°C

Sample	Reaction rate (mole/g · h)
HZSM-5	5.9
1.70% Ga/SiO$_2$	2.2
1.36% Ga/HZSM-5	20.5
1.36% Ga/HZSM-5(Im)[a]	2.9

[a] Imaginary mixture of HZSM-5 and 1.70% Ga/SiO$_2$ having 1.36% Ga.

Reaction rate data for propane conversion at 530°C are compiled in Table 2. Clearly, the activity is lower for 1.70% Ga/SiO$_2$ than for 1.36% Ga/HZSM-5, in accordance with the concept that acid protons are required even in the conversion of propane to propene. The real activity of the 1.36% sample is ca. seven times higher than that of an imaginary mixture of HZSM-5 (20%) and Ga/SiO$_2$ (80%). Apparently, acid and metal sites do not operate independently one from another.

The conversion of propene is 10–30 times higher than that of propane, as shown in Fig. 2. This result is in accordance with the findings by Gnep *et al.* (12). A small addition of Ga to HZSM-5 has a slight positive effect on the activity but a large effect on the selectivity. However, the activity decreases for $\gamma_{Ga} > 0.2$. The product pattern for propene is quite different from that for propane; ethene, butenes, and C_5^+ nonaromatic hydrocarbons are major products (Table 3). Ethene is formed by acid-catalyzed cracking of C_6^{2-} intermediates that can also be formed by olefin redistribution, which keeps all the olefins virtually in thermodynamic equilibrium (29). Among the C_5^+ nonaromatic hydrocarbons, C_5–C_6 olefins and smaller amounts of paraffins are dominant. Production of CH_4 is

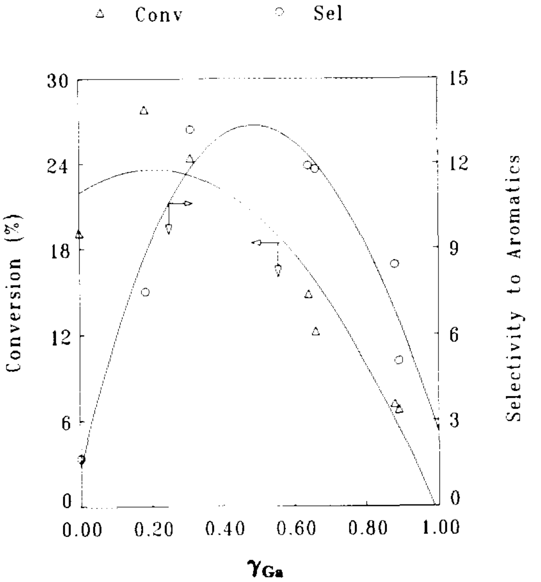

FIG. 2. Propene conversion at 500°C and WHSV of 2156 h^{-1}.

far below that observed with propane and becomes zero for high Ga loading. Gallium addition to HZSM-5 clearly promotes the formation of aromatic hydrocarbons up to the γ_{Ga} ratio of ca. 0.5. Further addition of Ga leads to a decrease of the selectivity to aromatics, which remains, however, higher for all Ga-containing samples than for HZSM-5 without gallium. In contrast to the case of propane conversion, the H/C ratio does not change with Ga loading.

In Fig. 3, the TPOMS spectra of HZSM-5 and 1.36% Ga/HZSM-5 catalysts are shown. More coke is formed on Ga/HZSM-5 than on HZSM-5, but combustion occurs at a lower temperature on Ga/HZSM-5. The TPOMS results show that higher steady state activities on Ga/HZSM-5 are not caused by lower coking levels.

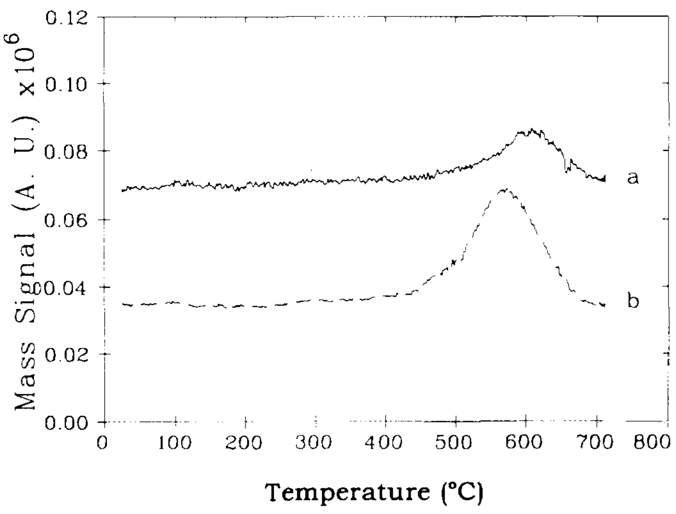

FIG. 3. TPOMS spectra of (a) HZSM-5; (b) 1.36% Ga/HZSM-5.

TABLE 3

Selectivity Pattern of Ga/HZSM-5 Catalysts for the Conversion of Propene at 530°C and WHSV of 2156 h^{-1}

wt% Ga	C_1	C_2	C_2^{2-}	C_3	C_4^a	C_4^{2-}	C_5^+	Arom	H/C
0	0.3	0.2	16.0	3.3	1.3	42.8	34.4	1.7	2.00
0.77	0.3	0.2	15.8	4.0	1.8	42.6	27.7	7.5	1.96
1.36	0.4	0.3	14.9	4.8	2.1	37.9	26.6	13.2	1.98
2.95	0.4	0.2	14.5	4.8	1.2	34.3	32.7	11.9	1.99
2.97	0.4	0.2	14.8	5.3	1.3	33.0	33.2	11.8	1.98
3.70	0	0.2	15.6	4.4	0.6	31.7	39.1	8.4	1.98
3.76	0	0.1	16.4	4.4	0.4	32.3	41.2	5.1	1.98

[a] Isobutane is present in the feed.

TPR and XRD Results

TPR profiles are shown in Fig. 4; the results are summarized in Table 4. There are two major peaks; the α-peak (near 450°C) was previously assigned to the reduction of finely dispersed Ga_2O_3 and the β-peak (near 630°C) to that of the $(GaO)^+$ ion (16). With increasing Ga content, the

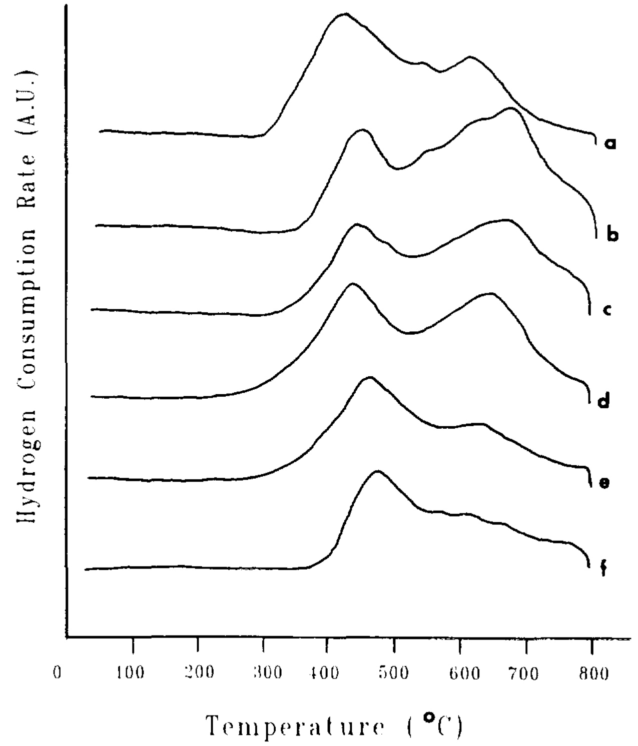

FIG. 4. TPR profiles of Ga/HZSM-5 catalysts. (a) 3.76%; (b) 3.70%; (c) 2.97%; (d) 2.95%; (e) 1.36%; (f) 0.77%.

TABLE 4

Summary of the TPR Results

wt% Ga	T_α	T_β	H_2/Ga	A_β/A_{tot}[a]
0.77	470	620	1.70	0.40
1.36	465	620	1.27	0.44
2.95	440	640	0.85	0.63
2.97	440	650	0.77	0.67
3.70	440	665	0.70	0.70
3.76	420	610	0.63	0.55

[a] $A_{tot} = A_\alpha + A_\beta$.

position of the α peak shifts to lower temperatures and that of the β peak to higher temperatures, except for the 3.76% sample. The extent of reduction below 800°C is highest for the 0.77% Ga sample and decreases with increasing Ga loading. The ratio of A_β/A_{tot} increases with Ga loading, suggesting that $(GaO)^+$ ions are favored at high loading.

The XRD patterns of Ga/HZSM-5 catalysts show no significant signals for any of the five known modifications of Ga_2O_3. This indicates that the Ga_2O_3 particles are very finely dispersed, in agreement with the low TPR temperature and also with the electron microscopy results (30).

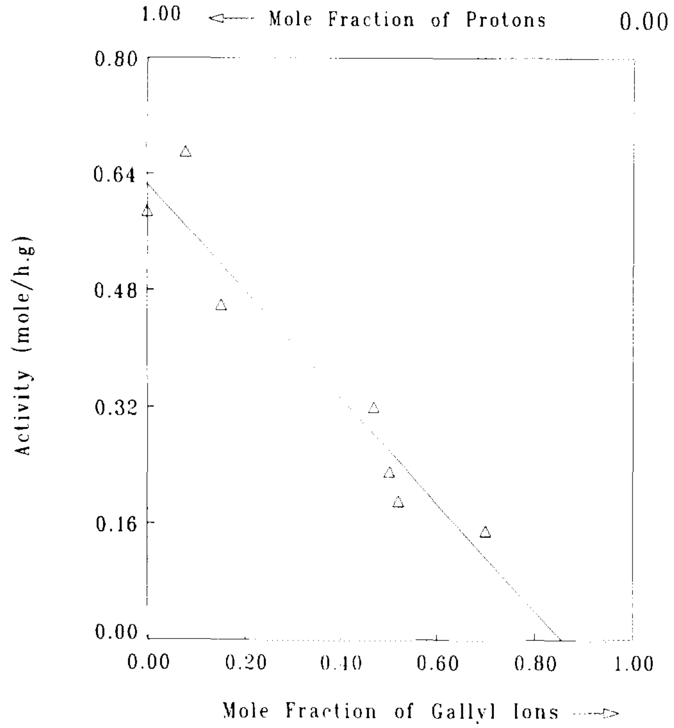

FIG. 5. Effect of gallyl ion concentration on toluene disproportionation at 400°C.

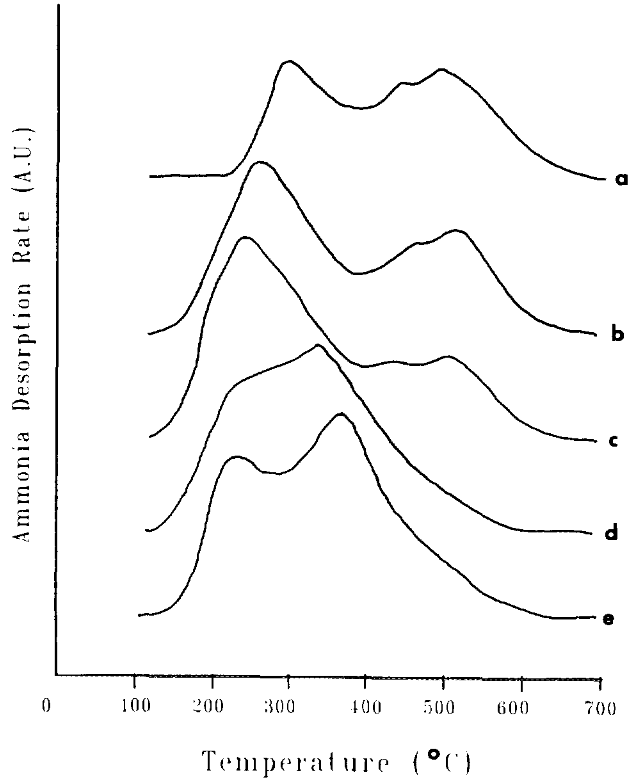

FIG. 6. NH_3-TPD spectra of (a) water treated HZSM-5; (b) untreated HZSM-5; (c) 0.77% Ga/HZSM-5; (d) 2.97% Ga/HZSM-5; (e) 3.70% Ga/HZSM-5.

No dealumination or damage of the zeolite structure is detected from the XRD patterns.

Acidity of the Catalysts

In Fig. 5 the activity for toluene disproportionation (TD) is graphed vs mole fraction of gallyl ions. The TD activity decreases linearly with the gallyl ion content. As this activity is controlled by the Brønsted acidity of the catalyst (21, 22), this result is in agreement with the chemistry of Eq. [3]. Main products are benzene and xylene isomers. Small amounts of C_9^+ aromatics were also detected. On all catalysts, the xylenes/benzene ratio is close to 0.9, which is higher than the thermodynamic equilibrium value of 0.72 (31).

NH_3-TPD spectra are shown in Fig. 6. Two major peaks are detected for HZSM-5. Peak l at 270°C results from the desorption of NH_3 from weak acid sites and peak h at 500°C from strong Brønsted acid sites (32, 33). The total uptake equals 1.68 (NH_3/H^+). However, when catalysts are exposed to water vapor at 120°C after ammonia saturation, the amount of NH_3 drops to 1.36 (Table 5) and the area of peak l decreases 35%, while the area of peak h remains unchanged. The results show that weakly adsorbed NH_3, which survives purging with He for 1 h at

TABLE 5

NH_3-TPD Results

Sample	Uptake (NH_3/H^+)[a]			
	Site 1	Site 2	Site 3	Total
HZSM-5				
Water treated HZSM-5[b]	0.86	0.0	0.82	1.68
0.77% Ga/HZSM-5	0.55	0.0	0.78	1.33
2.97% Ga/HZSM-5	0.85	0.16	0.63	1.64
2.97% Ga/HZSM-5	0.85	0.44	0.39	1.68
3.70% Ga/HZSM-5	0.88	0.57	0.27	1.72

[a] Site 1: Desorption of physisorbed NH_3 + NH_3 adsorbed on nonframework sites. Site 2: Desorption from Lewis acid sites. Site 3: Desorption from Brønsted acid sites.

[b] Water treatment at 120°C after NH_3 saturation.

120°C, is displaced by H_2O. Addition of Ga decreases the size of peak h, without affecting that of peak l. Previously (34), we detected an appreciable amount of extra-framework alumina from this zeolite by FTIR spectroscopy. Therefore, this indicates that peak l represents the desorption of physisorbed NH_3 and NH_3 adsorbed on nonexchangeable cation sites; peak h results from the desorption of NH_3 from true exchangeable protonic sites. Remarkably, a new peak with a T_{max} of about 340–360°C appears; its area increases with Ga loading. This suggests that the addition of Ga creates Lewis acid sites. The sum of the areas of all peaks changes little with the Ga loading.

IV. DISCUSSION

Bifunctional Catalysis, Stoichiometry of Ion Exchange

This study addresses two crucial, interrelated questions:

(1) Is aromatization of propane over Ga/HZSM-5 a bifunctional catalysis?

(2) Does the present CVD method lead to a true ion exchange; i.e., is gallium replacing one zeolite proton per Ga, as stated in Eq. [3]?

The present data on toluene disproportionation in Fig. 5 and the NH_3 TPD data in Fig. 6 show that with the present CVD method the number of zeolite protons decreases with increasing amounts of Ga loading. This decrease is almost linear, as predicted by Eq. [4]; however, the extrapolated line intercepts the abscissa at a value near 0.85, instead of 1. The estimate of the proton concentration based on the appropriate peak intensity of the NH_3-TPD profile agrees, within experimental error, with that based on the relative activities for toluene disproportionation. In the unreduced catalyst, gallyl ions coexist with gallium oxide; only the gallyl ions act as charge compensating ions, replacing protons in the original HZSM-5.

In accordance with the basic postulate for bifunctional catalysis, the activity for propane conversion, when plotted vs. γ_{Ga} displays a clear maximum, as shown by Fig. 1. The activity is low at either limit (γ_{Ga} = 0 or 1) as has to be expected. The absence of such a maximum for some catalysts prepared by wet chemistry suggests that in those cases Ga addition does not lower the number of protons.

The concept of bifunctional catalysis is further confirmed by results in Table 2. The activity of Ga/SiO_2 for this probe reaction is low; the activity of Ga/HZSM-5 is about seven times higher than the sum of the activities of the monofunctional catalysts Ga/SiO_2 and HZSM-5 with the same total number of Ga atoms.

Reaction Mechanism and Causes of Maxima

In a formal way Ga ions can be described as Lewis acid sites; in accordance with previous authors (35, 36) the dehydrogenation of a paraffin at high temperature over a catalyst exposing both Brønsted (H^+) and Lewis (L) sites can be described as follows:

(i) H^- abstraction on a Lewis site:

$$C_3H_8 + L = C_3H_7^+ + L\text{-}H^- \qquad [5a]$$

(ii) Lewis site regeneration by interaction with a Brønsted proton:

$$L\text{-}H^- + H^+ = L + H_2 \qquad [5b]$$

(iii) Proton release from the carbenium ion:

$$C_3H_7^+ = C_3H_6 + H^+ \qquad [5c]$$

In the present work, the formation of strong Lewis acid sites (33, 37) is clearly shown by NH_3-TPD (Fig. 6); they are not detectable in gallium-free HZSM-5, their concentration increases with Ga loading, i.e., γ_{Ga}. These sites are composed of two Ga species, i.e., Ga_2O_3 (α peak) and $(GaO)^+$ (β peak) (Fig. 4 and Table 4). As more Ga is added, the fraction of the β peak, expressed as A_β/A_{tot}, increases with the loading at the expense of the Brønsted acid sites. It was shown by Kazansky *et al.* (20) from ESR studies that Ga forms strong Lewis acid sites which dehydrogenate saturated hydrocarbons by polarizing C–H bonds. Thus, incorporation of Ga provides the Lewis acid sites which effectively abstract hydride ions (Eq. (5a)). Under the strongly reducing conditions of propane or propene conversion $(GaO)^+$ ions will be reduced to Ga^+ ions which might also act as Lewis acid sites (38).

The selectivity for acid catalyzed cracking in propane conversion decreases in concert with toluene disproportionation.

The results also show that NH_3 adsorption and desorption can lead to misleading conclusions if only the total amount of NH_3 is considered. For the present catalysts the quantity of adsorbed NH_3 changes little with Ga content. Only the resolved TPD spectrum reveals that the acid site pattern changes: the concentration of Brønsted sites decreases, but that of Lewis sites increases with increasing Ga loading.

As both Lewis and Brønsted sites are required for bifunctional dehydrogenation, the optimum catalyst must contain both types of sites. Our data suggest that this optimum is realized in the range of γ_{Ga} of 0.3–0.6.

The comparison of the conversion rates of propene and propane shows that the dehydrogenation of the paraffin has a lower overall rate constant than that of the following reactions leading to aromatics. These subsequent steps include oligomerization, ring-closure, and dehydrogenation steps; the question can be asked, what role Ga plays in this catalysis.

If dehydrogenation of the paraffin were the only part of the reaction network in which Ga acts as an active site and if all subsequent steps made use only of Brønsted acid sites, the activity for aromatization of propene should be highest for the Ga-free catalyst. Moreover, catalytic activity would be expected to decrease monotonically with decreasing concentration of acid sites because such sites are needed for the oligomerization steps which are part of the aromatization network. The present results show a more complex pattern: although the rate of propene conversion is much higher than that of propane conversion the selectivity to aromatics initially increases with increasing γ_{Ga} for propene also. At higher γ_{Ga} this selectivity passes a maximum near $\gamma_{Ga} = 0.45$. The shape of this curve is very similar to that of the corresponding figure for propane, which suggests that Ga plays a significant role also in the formation of aromatics, as has been assumed by previous authors. Presumably Ga acts as a dehydrogenating site.

The present results show that the overall H/C ratio of the product remains near H/C = 2. This indicates that hydrogen redistribution, comparable to Mobil's MTG process (39), is more important than hydrogen release. However, the experimental error in the H/C ratio does not justify excluding the occurrence of some true dehydrogenation (2, 40). Gnep *et al.* (13) report that at a selectivity level comparable to the present data, about 1.8 mole of H_2 is formed per mole of hydrocarbon.

An advantage of the chemical vapor deposition method is that the maximum theoretical loading with Ga will be three times higher if protons are replaced by monopositive $(GaO)^+$ ions than by tripositive Ga^{3+} ions. For the ZSM-5 catalyst used here the theoretical maximum, assuming that each proton is replaced by one gallyl ion, would be 3.96% Ga. The maximum loading actually achieved is about 3.8%, i.e., 95% of the theoretical number. However, some of this Ga will be present as Ga_2O_3, though the majority of the Ga does replace protons, as follows from the TD and the NH_3-TPD data. The inconsistency of these numbers with the stoichiometry of proton replacement by Ga^{3+} lends further support to the concept that the prevailing ionic species of gallium, prior to reduction, is the gallyl ion (Fig. 5).

V. CONCLUSIONS

The Brønsted acidity of HZSM-5 is markedly lowered by introducing Ga via $GaCl_3$ vapor, followed by release of HCl. At high Ga loadings, the formation of gallyl ions prevails; each $(GaO)^+$ ion replaces one zeolite proton, which results in a linear decrease of acidity with Ga load. At low Ga load, significant amounts of highly dispersed Ga_2O_3 are also formed. At high temperature, $(GaO)^+$ is reduced to Ga^+. NH_3-TPD shows that introduction of Ga lowers the Brønsted acidity, but introduces new Lewis acid sites into the catalyst.

As protons are replaced by Ga, the catalyst activity for toluene disproportionation, the conversion of propene, and the selectivity for propane cracking decrease. The conversion of propane passes through a maximum, which contrasts with results obtained with Ga/HZSM-5 catalysts prepared by conventional methods. The selectivity to aromatics passes through a maximum both for propane and propene as the feed. Optimum performance is achieved for $Ga/(Ga + H^+)$ ratios between 0.4 and 0.5. Ga/HZSM-5 acts as a bifunctional catalyst, with Brønsted sites catalyzing olefin oligomerization, but Ga sites are involved in dehydrogenation steps, possibly via H^- abstraction from alkanes and oligomerized intermediates. The rate constant for propane dehydrogenation is lower than those for subsequent steps.

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