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Aromatization of propane over MFI-gallosilicates

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Abstract

The results of propane aromatization over gallium containing HZSM-5 zeolites are described. Highly dispersed gallium in the zeolite (framework or extra-framework) was found to possess dehydrogenation activity, especially in the presence of strong Brønsted acid sites. The extra-framework gallium was introduced by mildly steaming a H-(Ga)ZSM-5 zeolite or by physically mixing Ga_2O_3 or a GAPSO-11 molecular sieve with H-(Al)ZSM-5. The higher dehydrogenation rates in the presence of gallium facilitated the formation of carbonaceous products, resulting in higher deactivation rates. A mechanism for hydrogen formation is discussed.

INTRODUCTION

The conversion of small alkanes and alkenes into more valuable products such as aromatics has received a great deal of attention during the past decade. Platinum loaded H-(Al)ZSM-5 zeolites are suitable catalysts for such transformations, as the formation of aromatics larger than C_{10} is prevented by the shape selective restrictions of the zeolite [1–4].

Side reactions such as catalytic cracking over strong acid sites and hydrogenolysis over platinum particles also occur over the Pt/H-(Al)ZSM-5 system, however. This results in the formation of large amounts of methane and ethane, which lower the aromatics selectivity [3,4]. The occurrence of these side reactions was found to be less over H-(Al)ZSM-5 zeolites loaded with zinc- [5,6] or gallium oxide [7–10], enabling the formation of molecular hydrogen and larger amounts of aromatics. Similar results are obtained using gallosilicates (H-(Ga)ZSM-5 zeolites) [11–17].

Several investigations have been carried out with respect to zinc containing catalysts regarding hydrogenation reactions and the interaction between alkenes and zinc oxide [6,18,19]. Some studies were also carried out in the field of gallium containing zeolites to investigate the role of the gallium species in the different steps of the aromatization reaction. The results of these

experiments, however, are still rather controversial. Several authors conclude from their experiments that gallium does not participate in the activation of the propane, but only serves for an efficient transformation of alkenes into aromatics [10–12]. In contrast to this, others have shown that the gallium is very active in the dehydrogenation of the starting alkane [9,12–16], which is assumed to be the rate-determining step of the reaction. In this approach, the role of gallium in the aromatization of the higher alkenes is assumed to be negligible. Recently, the dehydrogenation properties of gallium were also studied by Mariaudeau et al. [20], who found di- and tri-alkenes to be very important intermediates for benzene formation from cyclohexane or cyclohexene conversions over gallium oxide.

Kazansky et al. [21] investigated the chemical properties of the zinc or gallium modified zeolites and discovered, from IR and electron spin resonance (ESR) experiments, the occurrence of strong Brønsted/Lewis acid pairs in the zeolites containing gallium or zinc. A similar study was carried out by Inui et al. [22], who proposed the occurrence of strong hydride attraction to the gallium site (Lewis acidity), which should prevent the hydrogenation of intermediate alkenes, thus lowering the selectivity to small alkanes.

Basically, the main uncertainty of the aromatization reaction is still the question which gallium species (framework or extra-framework) is mainly active in what part of the reaction, and what mechanism serves the formation of molecular hydrogen. To elucidate these problems, isomorphously substituted H-(Al)ZSM-5 zeolites containing gallium were prepared and their behaviour in the aromatization of propane was compared with their aluminum analogues. The reaction was also carried out with zeolites in which an extra-framework gallium species was introduced by physically mixing the zeolite with Ga_2O_3 or a GAPSO-11 molecular sieve. To investigate the role of the gallium in the reaction, model reactions were carried out for the different reaction steps: the dehydrogenation of propane, the cyclization of hexene and heptene and the dehydrogenation of cyclohexane and cyclohexene. In order to investigate the influence of the zeolite acidity on the conversion, propane and propene transformations were also carried out over a HY and a gallium loaded HY zeolite. As in the presence of gallium, higher dehydrogenation rates were measured, and a difference in catalyst deactivation rate due to coke formation was expected. To investigate this aspect, deactivation runs were carried out in combination with thermogravimetric coke determinations.

EXPERIMENTAL

Catalyst preparation

H-(Al)ZSM-5 zeolites were prepared according to the patent of Chen et al. [23], using $Al_2(SO_4)_3 \cdot 18H_2O$ as the aluminum source. The isomorphously

substituted H-(Ga)ZSM-5 zeolites, containing gallium on framework posi-
tions, were prepared by the addition of Ga_2O_3 (Ingal, 4N5) as the gallium
source to the synthesis mixture. In the discussion of the results, these zeolites
will be referred to as Al(30), Ga(30), etc., meaning an alumino- or gallosili-
cate, respectively, with the Si/Al or Si/Ga ratio mentioned between brackets.
Crystallization was carried out at 443 K in a stirred autoclave for 6 days.
Activation of the zeolites was carried out by template destruction (3h, 823 K,
air), three times ion exchange with 2 M NH_4NO_3 (1h, 363 K) and ammonia
evaporization (3h, 823 K, air). Zeolite HY (Si/Al ratio 2.15) was obtained
from Ketjen Catalyst (Amsterdam). The gallium loaded HY zeolite was pre-
pared by pore volume impregnation of the zeolite with a gallium nitrate so-
lution and subsequent calcination.

A H-(Ga)ZSM-5 zeolite with Si/Ga ratio of 45 was mildly steamed at 823
K in a flow of steam saturated air (20 ml/min) for 3 h. More severe steam
treatments were carried out at 923 K for periods of 3, 6, 12 and 24 h. The
physical mixtures, containing 2 wt.-% gallium, were prepared by mixing Ga_2O_3
(Ingal, 4N5) and a H-(Al)ZSM-5 zeolite. These mixtures were used without
any calcination steps prior to the activity measurements. In the discussion of
the results, these catalysts will be referred to as Al(30)−2, etc, with the Si/
Al ratio between brackets and the wt.-% gallium mentioned after the dash.
The GAPSO-11 structure was prepared according to the patent of Lok et al.
[24]. The gallium content of the product was about 5.5 wt.-%. Calcination of
the GAPSO-11 was carried out at 823 K for 3 h in laboratory air. The physical
mixture applied for the aromatization reaction consisted of 50 wt.-% GAPSO-
11 mixed with an Al(30) zeolite.

Catalytic reactions and regenerations

Activity measurements were carried out in a micro-reactor, using 0.5 g cat-
alyst and a propane weight hourly space velocity (WHSV) of 2 h^{-1}, diluted
in helium (helium/propane ratio of 2). The temperature was varied between
623 and 873 K. Deactivation runs were carried out with the same WHSV at
873 K. Activity measurements of the physical mixture with GAPSO-11 were
carried out over the same temperature range using the fresh catalyst, but also
after various regenerations. Regeneration of the zeolites was carried out at
873 K in helium/air flow (50/50) for a period of 10 min.

In order to investigate the role of the gallium species in the separate reac-
tion steps, model reactions were carried out. For the first step in the reaction,
propane dehydrogenation was studied over pure Ga_2O_3 and over catalysts
consisting of gallium impregnated silicate-1 and alumina. Also, H-(Al)ZSM-
5 zeolites, H-(Ga)ZSM-5 zeolites and H-(Al)ZSM-5 zeolites, containing 2
wt.-% gallium (prepared by physically mixing with Ga_2O_3), were tested for
reaction. Reactions were carried out with a propane WHSV of 2 h^{-1}, diluted

in helium, at atmospheric pressure up to temperatures of 873 K. Propane and propene conversions were also carried out over a HY zeolite and a gallium loaded HY zeolite under the same conditions.

The cyclization step in the reaction was studied by reactions of hexene and heptene over the various gallium containing catalysts mentioned above. These reactions were carried out at a WHSV of 0.7 h^{-1} at temperatures up to 873 K. For the last step of the reaction, the dehydrogenation of the cyclo-compounds, the dehydrogenation of cyclohexane and cyclohexene was studied. The reaction conditions were the same as those specified for the cyclization step of the reaction.

Coke determination

Coke formation was also determined by thermogravimetric experiments. This was done by interrupting the deactivation experiment at various time intervals, taking about 25 mg of catalyst from the catalyst bed and burning off the coke at 873 K in a Cahn electrobalance in a stream of helium/oxygen (80/20). By taking into account the mean conversion during time on stream, the selectivity to carbonaceous products was calculated.

RESULTS

Conversion of propane

Upon the application of gallosilicates instead of aluminosilicates for propane aromatization, lower conversions were measured, as shown in Fig. 1. This is in accordance with results published earlier [15,17]. Upon measuring the conversions at different temperatures, some coke deposition on the catalyst could not be avoided. To check the effect of this coke on the activity at the highest temperatures, the measurement at 873 K was repeated after the regeneration of the catalyst and a 10 min feed of propane. The result of this measurement is also included in Fig. 1. The product selectivities as obtained over H-(Al)ZSM-5 and H-(Ga)ZSM-5 zeolites, are presented in Fig. 2a and b, respectively. The main differences between these catalysts are the much higher selectivity to aromatics and and the smaller tendency towards the formation of small alkanes, over the gallosilicate. Considerable amounts of hydrogen are also formed over the gallosilicates, in contrast with H-(Al)ZSM-5 zeolites, where hydrogen formation is negligible. Moreover, the total amount of small alkenes (ethene and propene) in the product stream is lower over the gallosilicates, indicating a more rapid transformation of the formed alkenes to aromatics.

The conversions and selectivities to methane and aromatics at 873 K over a series of catalysts are shown in Table 1. This table shows that gallium im-
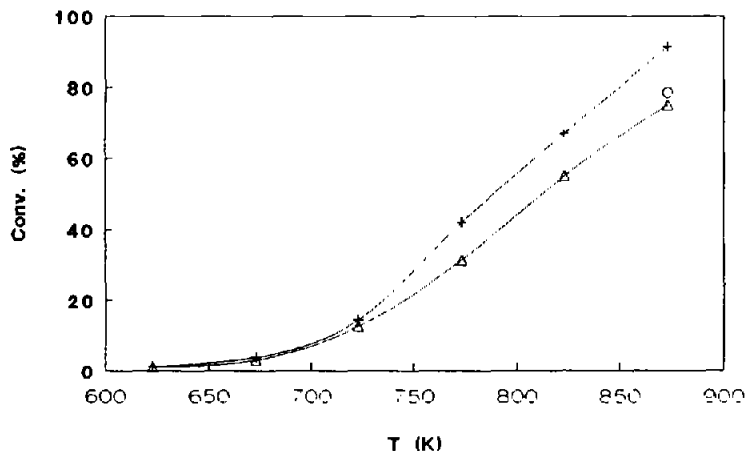
Fig. 1. Propane conversions versus temperature (propane WHSV = 2 h^{-1}): + = Al(45):
△ = Ga(45); ○ = conversion at 873 K over Ga(45) after regeneration.

proves the selectivity to aromatics, while a strongly reduced selectivity to methane is measured. This behaviour was measured for both the gallosilicates and the physical mixtures of H-(Al)ZSM-5 and Ga$_2$O$_3$ powder. This table also shows some results that were obtained over pure Ga$_2$O$_3$ powder and some supported Ga$_2$O$_3$ samples. Obviously, the latter systems have only low activities.

The results of the propane and propene aromatization reactions over a HY zeolite and a gallium impregnated HY zeolite are presented in Table 2. It can be seen that propane conversions are low over both catalysts. With propene as reactant, much higher conversions are measured, although in this case extremely high deactivation rates are observed.

The results of hexene and heptene conversion over various catalytic systems are summarized in Table 3. In all cases, high conversions (about 90%) are measured, but the application of supported gallium oxide catalysts gives mainly isomers of the starting alkene, and only small amounts of aromatics. In the presence of HZSM-5 zeolites, possessing strong Brønsted acid sites, the selectivity to aromatics at 873 K is 48 C%. This selectivity does not change upon loading the zeolite with gallium by physically mixing it with Ga$_2$O$_3$. Upon the application of gallosilicates instead of aluminosilicates, however, an increase in aromatic selectivity from about 48 to 70 C% is observed for both hexene and heptene conversion. This indicates that a short distance between the acid site and the gallium site is important for this reaction.

The results of the dehydrogenation reaction of cyclohexane and cyclohexene over various catalyst systems are presented in Table 4. Obviously, when considering the dehydrogenation of the cyclohexane, low conversions are also
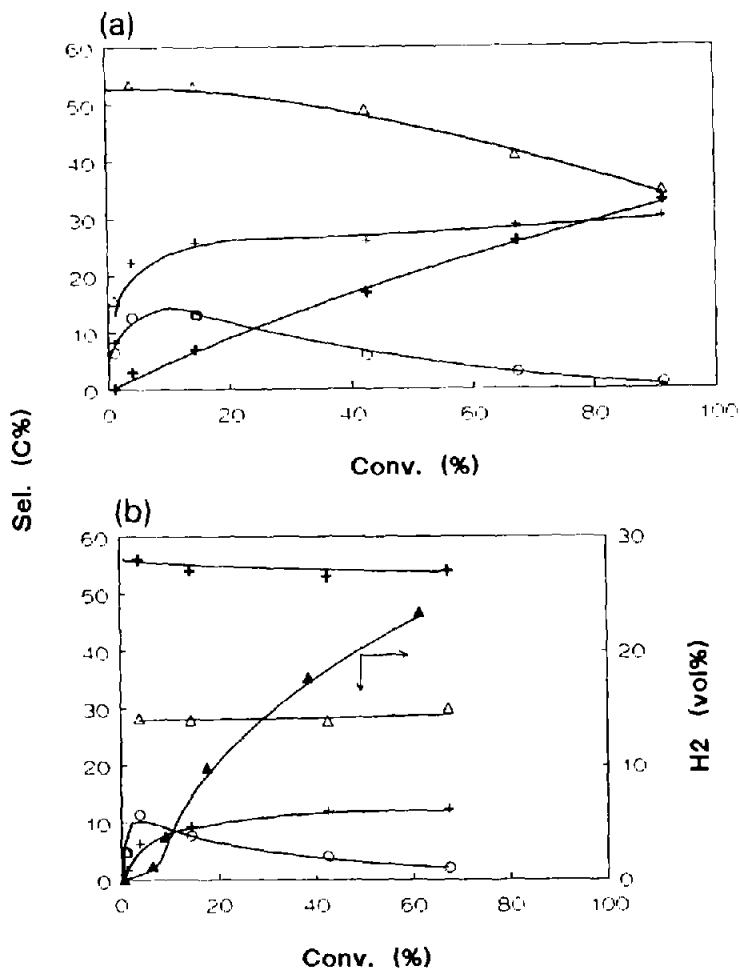
Fig. 2. (a) Product selectivities of propane aromatization over zeolite Al(45); + = methane + ethane; △ = ethylene + propylene; ○ = butanes + butenes; + = aromatics.
(b) Product selectivities of propane aromatization over zeolite Ga(45); + = methane + ethane; △ = ethylene + propylene; ○ = butanes + butenes; + = aromatics; ▲ = hydrogen (mol-%).

measured for the supported gallium oxide systems, which are similar to the observations for propane dehydrogenation. In the presence of strongly acidic zeolite structures, considerably higher conversions are measured, similar to the observations for propane dehydrogenation. Moreover, introduction of the gallium in the zeolites increases the benzene selectivity, independent of the method of gallium introduction in the zeolite.

Table 4 also shows that cyclohexene is far more reactive than cyclohexane. Even over the supported systems, high activities can be measured, and the

TABLE 1

Dehydrogenation of propane over different catalyst systems

$T = 873$ K, propane WHSV $= 2$ h^{-1}

Catalyst	Conversion (%)	Selectivity (C%)	
		CH$_4$	aromatics
Al(30)	96.4	31.0	40.0
Al(45)	97.3	30.0	33.0
Al(60)	60.0	24.0	32.5
Ga(30)	72.0	10.4	57.6
Ga(45)	62.6	10.0	54.0
Ga(60)	41.0	15.9	58.0
Al(30)−2[a]	93.6	13.2	59.0
Al(45)−2[a]	95.3	10.8	62.2
Al(60)−2[a]	68.9	11.4	53.1
Ga$_2$O$_3$	7.4	10.0	−
2 wt.% Ga$_2$O$_3$/Silicalite − 1[b]	5.0	14.0	−
2 wt.% Ga$_2$O$_3$/Al$_2$O$_3$[b]	30.2	6.0	3.0

[a] Physical mixture.
[b] Impregnated sample.

TABLE 2

Conversion of propane and propene over a HY and a Ga loaded HY zeolite

$T = 773$ K, propane WHSV $= 2$ h^{-1}

Reactant	Catalyst	Conversion (%)	Selectivity (C%)	
			CH$_4$	aromatics
Propane	HY	5.9	13.5	−
	4 wt.% Ga/HY[a]	6.5	8.5	−
Propene	HY	37.0	3.3	23.8
	5 wt.% Ga/HY[a]	24.6	3.5	21.9

[a] Impregnated sample.

application of zeolites always results in a complete conversion of the cyclohexene, while both the supported systems and the H-(Al)ZSM-5 zeolites give aromatics selectivities of 60–70 C%. After the introduction of gallium in the zeolites by physically mixing the zeolite with Ga$_2$O$_3$ or by isomorphous substitution of aluminum, benzene is almost exclusively formed.

TABLE 3

Cyclization of higher alkenes over gallium containing catalysts systems.

$T = 873$ K, WHSV $= 0.7$ h^{-1}

Reactant	Catalyst	Conversion (%)	Aromatic selectivity (C%)
Hexene	Al(45)	100.0	48.7
	Ga(45)	100.0	71.6
	Al(45)−2[a]	98.5	49.5
Heptene	Al(45)	100.0	49.0
	Ga(45)	99.0	69.0
	Al(45)−2[a]	100.0	49.2
Hexene	2 wt.% Ga$_2$O$_3$·Silicalite − 1[b]	90.7	5.4
	3.4 wt.% Ga$_2$O$_3$/SiO$_2$[b]	100.0	12.6
Heptene	2 wt.% Ga$_2$O$_3$·Silicalite − 1[b]	90.0	4.0

[a]Physical mixture.
[b]Impregnated sample.

TABLE 4

Dehydrogenation of cyclo-hexane and cyclo-hexene over different gallium containing catalyst systems

$T = 873$ K, WHSV $= 0.7$ h^{-1}

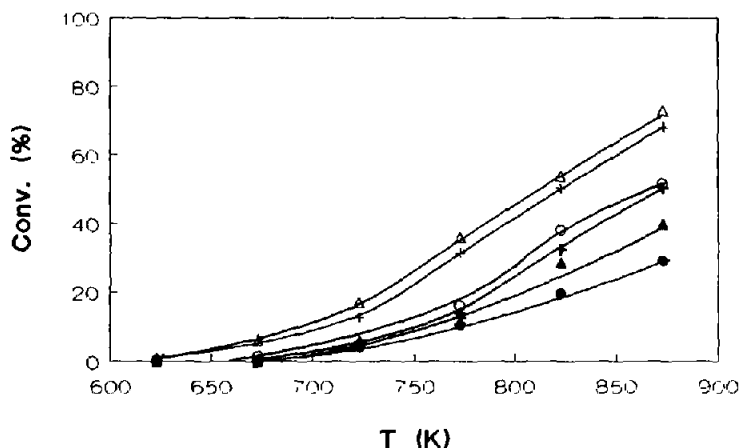| Reactant	Catalyst	Conversion (%)	Aromatic Selectivity (C%)
Cyclo-hexane	2 wt.% Ga$_2$O$_3$/Silicalite − 1[a]	2.8	15
	3.4 wt.% Ga$_2$O$_3$/SiO$_2$[a]	3.1	45
	3.4 wt.% Ga$_2$O$_3$/Al$_2$O$_3$[a]	2.3	23
Cyclo-hexene	5 wt.% Ga$_2$O$_3$/SiO$_2$[a]	88.5	69
	3.4 wt.% Ga$_2$O$_3$/Al$_2$O$_3$[a]	52.3	74
Cyclo-hexane	Al(45)	99.0	60
	Al(45)−2[b]	99.4	96
	Ga(45)	98.9	97
Cyclo-hexene	Al(45)	100	78
	Al(45)−2[b]	100	89
	Ga(45)	100	94

[a]Impregnated sample.
[b]Physical mixture.

Fig. 4. Effect of various steam treatments on the activity of zeolite Ga(45); + =before steaming:
△ =steaming 3 h, 823 K; O =steaming 3 h, 923 K; + =steaming 6 h, 923 K; ▲ =steaming 12 h,
923 K; ● =steaming 24 h, 923 K.
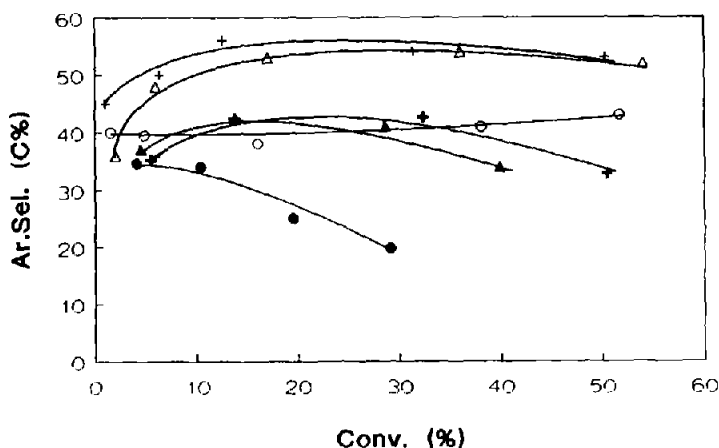
Fig. 5. Effect of steaming on the aromatics selectivity of the Ga(45) zeolite: + =before steaming:
△ =steaming 3 h, 823 K; O =steaming 3 h, 923 K; + =steaming 6 h, 923 K; ▲ =steaming 12 h,
923 K; ● =steaming 24 h, 923 K.

Deactivation of the catalysts

The results of the deactivation runs over gallo- and aluminosilicates are
presented in Fig. 6. This figure shows clearly that the gallosilicates deactivate
much faster than their aluminum analogues. As the colour of the catalyst bed,
after one reaction cycle over the temperature range from 523–873 K, was dark
grey in the case of an aluminosilicate and deep black in the case of a gallosili-

Introduction of extra-framework gallium

The conversion and product distribution over a catalyst consisting of 50 wt.-% GAPSO-11 molecular sieve (about 5.5 wt.-% gallium), physically mixed with H-(Al)ZSM-5 zeolite (Si/Al=30), are presented in Fig. 3. In this figure the conversions and aromatics selectivities are given for the fresh catalysts and for the catalysts after 1 and 3 regenerations. Comparison with Fig. 1 shows that for the fresh catalyst the effect of the GAPSO-11 addition on both the activity and the aromatics selectivity is almost negligible. After the first regeneration, however, an increase in activity and a much higher aromatics selectivity is observed, especially at the lower temperatures. Additional increases in activity and aromatics selectivity are observed after the second and third regeneration. More regenerations did not lead to a further improvement of the catalytic properties.

The catalytic activities and aromatics selectivities of a Ga(45) zeolite after steaming under different conditions are shown in Figs. 4 and 5, respectively. After a mild steam treatment (3 h, 823 K), an increased activity is measured (Fig. 4), which has been ascribed to the introduction of extra-framework gallium during the steam treatment. The selectivity to aromatics remained almost unaffected during this treatment (Fig. 5). More severe steaming at 923 K, however, causes a considerable loss of framework gallium, a decrease in the acid site density, and probably an agglomeration of the non-framework gallium oxide (lower gallium dispersion). This results in strongly reduced activities for these samples (Fig. 4), and also the apparent selectivities to aromatics were considerably lower.

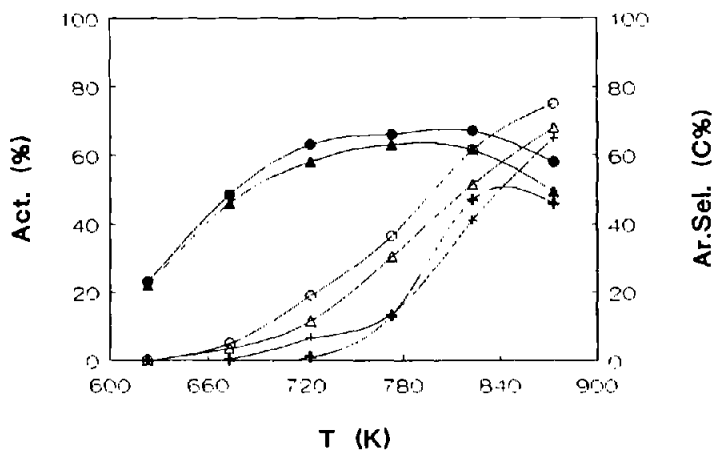Fig. 3. Conversions and aromatics selectivities obtained over a physical mixture of zeolite Al(30) and a GAPSO-11 molecular sieve; Al(30)/GAPSO-11 = 50/50 (wt./wt.); + = activity of the fresh catalyst; △ = activity after 1st regeneration; O = activity after 3rd regeneration; + = aromatic selectivity of the fresh catalyst; ▲ = aromatic selectivity after 1st regeneration; ● = aromatic selectivity after 3rd regeneration.
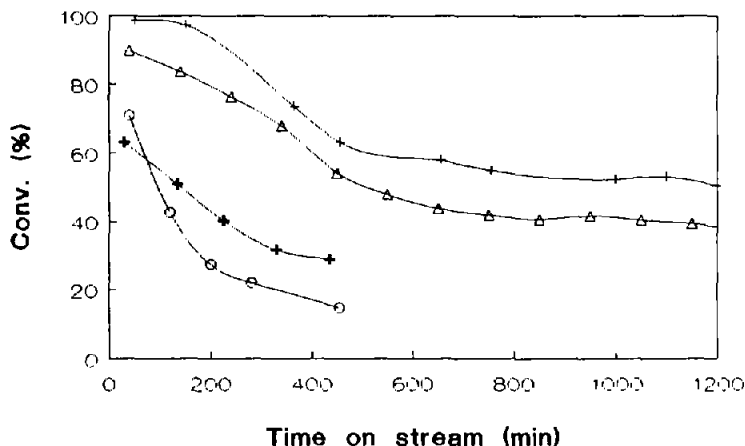
Fig. 6. Deactivation of the different zeolites (propane WHSV 2 h^{-1} T=873 K); + =Al(30; △ = Al(45); ○ =Ga(30; + =Ga(45).

TABLE 5

Coke formation on Al(30) and Ga(30).

Propane WHSV=2 h^{-1}; He/C$_3$H$_8$=2; 500 mg catalyst; temperature=873 K

Catalyst	Time on stream (min)	C$_3$ passed (g)	Average conversion (%)	C$_3$ consumed (g)	Coke (wt.%)	"Coke-sel." (%)
Ga(30)	170	4.64	65	3.01	2.26	0.38
Al(30)	150	4.09	88	3.59	0.42	0.06

cate, increased coke formation was supposed to be the most important reason for the more rapid catalyst decay. To investigate this supposition, the average coke selectivities during a particular reaction time were calculated from the thermogravimetric experiments for an Al(30) and a Ga(30) zeolite. The results are presented in Table 5. It is clear that more coke is formed over the gallosilicates, although not more than 0.38 C% of the converted propane is transformed to coke during the first 150 min of the reaction. In the case of the aluminosilicate this value is about 0.06 C%.

DISCUSSION

Conversion of propane

The lower activities for propane conversion as measured over the H-(Ga)ZSM-5 zeolites (Fig. 1) will be due to the lower acid strength of the

gallosilicates, as measured earlier by ammonia temperature-programmed desorption (TPD) experiments and infrared analysis [25]. In addition, the deposition of some coke on the gallosilicate during subsequent measurements at different temperatures can give rise to some activity loss. In a second experiment, carried out at 873 K after regeneration and ten minutes propane feed before sampling, however, a small increase in activity is measured (as shown in Fig. 1), but this activity is still much lower than the activity of the aluminosilicate. The activity enhancement can be ascribed to the introduction of extra-framework gallium in the zeolite during the regeneration treatment (see further in the discussion). This experiment also proves that the reduced activity over the gallosilicates is caused by its lower Brønsted acid strength and that the deposition of small amounts of coke is of less importance. Upon comparison of the product distributions obtained over H-(Al)ZSM-5 (Fig. 2a) and H-(Ga)ZSM-5 (Fig. 2b), it is clear that in the latter case much larger amounts of aromatics are formed, while the selectivity to small alkanes is lower. Moreover, it seems that the rate of conversion of alkenes to oligomers and aromatics is higher over H-(Ga)ZSM-5, as the total amount of small alkenes is also smaller in this case. Over H-(Al)ZSM-5 zeolites, a large part of the small alkanes is formed via hydrogen transfer reactions that serve to remove hydrogen atoms from the intermediates, but which also consume part of the small alkenes which are, thus, no longer available for aromatization. The formation of molecular hydrogen is possible in the presence of gallium, so more alkenes are left to be incorporated in the aromatics. It can thus be concluded that at higher temperatures the mechanism of aromatization is changed from a hydrogen transfer mechanism over the H-(Al)ZSM-5 zeolite to a dehydrogenation mechanism over the H-(Ga)ZSM-5 zeolite or the physical mixture of Ga_2O_3 and a H-(Al)ZSM-5 zeolite. This is also visible in the formation of considerable amounts of molecular hydrogen, as indicated in Fig. 2b. The type of gallium species active for dehydrogenation and a more detailed description of the dehydrogenation mechanism will be discussed later.

In Table 1, the results of propane conversion over some supported gallium systems are compared with the activities of the acidic zeolites. Pure Ga_2O_3 has low dehydrogenation activity, which may be due to a low specific surface area of the material (about 5 m^2/g). However, low activities are also measured over the supported gallium oxide catalysts. For this observation, two explanations are possible. Firstly, due to the method of gallium introduction (incipient wetness impregnation), low dispersions of the gallium oxide are obtained, resulting in low activities. Secondly, it can be assumed that highly dispersed gallium particles only possess dehydrogenation activity in the presence of strong Brønsted acid sites, like those present in HZSM-5 zeolites. In that case, the main role of the acid sites is the removal of propene from the propane/propene equilibrium by oligomerization, thus enhancing the pro-

pane conversion. In order to investigate the importance of strong Brønsted acid sites for propane dehydrogenation, the reaction was repeated, using a HY zeolite and a gallium loaded HY zeolite. Over both catalysts, however, low propane conversions are measured (Table 2), although propene conversions are relatively high with an aromatics selectivity of about 25 C%. This indicates that the presence of a strong acid site is essential for the activation of the starting alkane. It can thus be concluded that the active site for dehydrogenation consists of gallium in combination with a Brønsted acid site, with an acid strength comparable to that of a HZSM-5 zeolite. The fact that the introduction of gallium by physically mixing the H-(Al)ZSM-5 zeolite with Ga_2O_3 powder modifies the reaction mechanism in a way similar to the isomorphous substitution of aluminum by gallium in the framework indicates that the dehydrogenation reaction can also occur on the interface between the Ga_2O_3 particle and the zeolite. Sublimation of Ga_2O_3 into the zeolite pores at high temperatures ($T > 600°C$), however, can also not be excluded.

From Table 3, it can be concluded that the cyclization of higher alkenes (hexene and heptene), is also a bifunctional reaction. Over all the catalyst systems, a near complete conversion of the alkenes is measured, but in the case of the supported gallium oxide systems, the main products are isomers of the starting alkene at moderate temperatures, with an increasing contribution of cracking products at high temperatures, but a negligible formation of cyclo-compounds (aromatics). Over the H-(Al)ZSM-5 zeolites, the selectivity to cyclo-compounds, mainly aromatics, is about 50 C%. An increase of these products from about 50 to 70 C% is measured after isomorphous substitution in the H-(Al)ZSM-5 framework, replacing aluminum by gallium. In contrast with the dehydrogenation step, such an increase is not observed when physical mixtures of Ga_2O_3 and a H-(Al)ZSM-5 zeolite are applied. This indicates that for this step, a short distance between the gallium site and the acid site is preferred. Investigations on the interaction of alkenes with gallium oxide have been published by various authors [26–28]. It has been shown that chemical bonds can be formed between the alkene and the gallium oxide species. In these complexes, electrons are released to the oxide surface, leaving a net positive charge on the adsorbed alkene which may have an interaction with the π-electrons of another alkene. In this way, an extra number of oligomerization sites for alkenes are created in the zeolite pores. When interactions like these are also possible on the framework gallium in the zeolites, the extra oligomerization sites are located in the vicinity of the Brønsted acid sites which makes the rapid cyclization of higher alkenes possible, which will increase the aromatics selectivity. In physical mixtures of Ga_2O_3 and H-(Al)ZSM-5 zeolites, the surface area of the gallium oxide can be too small to have a positive effect on the selectivity to cyclo-compounds (aromatics), or the distance between the gallium and the acid site is too large.

The results of cyclo-hexane dehydrogenation, as shown in Table 4, are sim-

ilar to the results obtained for the dehydrogenation of the starting alkane: gallium possesses dehydrogenation activity only in combination with Brønsted acid sites, and large amounts of molecular hydrogen are formed. The addition of gallium to the zeolites enhances the selectivity to aromatics, independent of the method of gallium introduction. The conversion of cyclohexene is much higher over the different systems. This is not only caused by the higher cracking ability of the cyclohexene molecule, but is also due to the fact that the aromatization of cyclohexene is thermodynamically more favourable. For this conversion, the selectivity to aromatics also increases upon the introduction of gallium.

In conclusion, this study on separate reaction steps shows that highly dispersed gallium in combination with strong Brønsted acid sites has a dehydrogenation activity. For the dehydrogenation reactions, the gallium may be present as framework gallium, but also as extra-framework gallium. For an effective aromatization (cyclization) of the higher alkenes, gallium in the vicinity of the Brønsted acid site (framework gallium) is preferred.
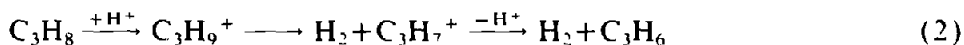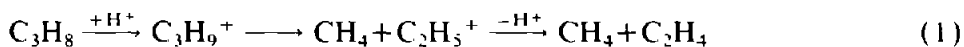
Influence of extra-framework gallium

The fact that extra-framework gallium can also be active for the dehydrogenation is confirmed by the experiment applying 50 wt.-% of a GAPSO-11 molecular sieve, physically mixed with a H-(Al)ZSM-5 zeolite (Si/Al = 30) (Fig. 3). Initially, a typical H-(Al)ZSM-5 conversion and aromatics selectivity pattern is measured, which indicates that the gallium, present in the GAPSO-11 structure as tetrahedral framework gallium, is inactive, which may be due to the large distance between the gallium in the GAPSO-11 structure and the acid site. The lower conversion as compared to the pure H-(Al)ZSM-5, is due to the dilution of the zeolite by the inactive GAPSO-11 material. After regeneration, an increase in propane conversion is measured and simultaneously an enhancement of the aromatics selectivity, especially at lower temperatures. This can be ascribed to the removal of gallium from the GAPSO-11 framework, which is transferred to extra-framework positions in- or outside the GAPSO-11 structure and probably (by sublimation) in the zeolite pores. In this way, the extra-framework gallium becomes increasingly located in the vicinity of the acid sites of the zeolites, which becomes visible in an increased aromatization activity. Evidence for the activity of the extra-framework gallium can also be obtained from the introduction of the extra-framework species in a H(Ga)ZSM-5 zeolite by a mild steam treatment. After such treatment, a small enhancement of the activity is measured, as indicated in Fig. 4, while the aromatics selectivity remains almost unchanged (Fig. 5). This suggests that the dehydrogenation activity of extra-framework gallium in combination with a Brønsted acid site is probably even higher than the activity of framework gallium in combination with a Brønsted acid site. The

decline in activity and aromatics selectivity after more severe steam treatments at 923 K may be caused by a further loss of framework gallium, decreasing the acid site density. The loss of framework gallium has also been confirmed by ^{71}Ga MAS-NMR measurements [29]. In addition, an agglomeration of the finely divided non-framework gallium species may occur, lowering the specific surface area of this species.

Mechanism of molecular hydrogen formation

The activation of the starting alkane over acidic H-(Al)ZSM-5 zeolites is assumed to be the protonation of the alkane, forming a pentacoordinated carbonium ion, as described by Haag and Dessau [30]. After the formation of this carbonium ion, bond cleavage may occur in two ways, as shown in eqns. 1 and 2.

$$C_3H_8 \xrightarrow{+H^+} C_3H_9^+ \longrightarrow CH_4 + C_2H_5^+ \xrightarrow{-H^+} CH_4 + C_2H_4 \qquad (1)$$

$$C_3H_8 \xrightarrow{+H^+} C_3H_9^+ \longrightarrow H_2 + C_3H_7^+ \xrightarrow{-H^+} H_2 + C_3H_6 \qquad (2)$$

The first possibility is the breakage of a C–C bond with the formation of methane and ethene, while the second possibility is a dehydrogenation to propene with the concomitant formation of molecular hydrogen.

H-(Ga)ZSM-5 zeolites have a lower acid strength in comparison to their aluminum analogues. Moreover, gallium can have Lewis acidic properties, as has been shown earlier by Kazansky et al. [21], giving it the possibility for hydride bonding, as proposed by Inui et al. [22]. Based on these characteristics, the mechanism of dehydrogenation can be completely changed after the introduction of gallium.

The observations described above strongly suggest that highly dispersed gallium (framework or extra-framework) in combination with Brønsted acid sites is active for the dehydrogenation of alkanes to alkenes and molecular hydrogen. A mechanism, in which Brønsted acid sites and gallium play an important role can be based on the presence of coordinatively unsaturated (framework or non-framework) gallium species, e.g. originating from broken Si–O–Ga bonds in the zeolite framework or from amorphous Ga_2O_3. These sites may act as Lewis acidic centres and will be able to abstract hydride ions from the starting alkane, resulting in the formation of a carbenium ion (eqn. 3). More support for a dissociative adsorption of hydrogen on Ga_2O_3 can be obtained from the IR experiments of Mariaudeau et al. [31], who measured IR vibrations attributed to hydride ions, bound to the gallium atoms of gallium oxide, and IR vibrations, attributed to protons, which are bound to the oxygen atoms of the gallium oxide.

A mechanism for dehydrogenation that can be derived from the observa-

tion that both acid sites and gallium are necessary for the dehydrogenation steps can be described as follows. Firstly, a hydride ion is abstracted from the alkane and bound to the Lewis acid sites, present as coordinatively unsaturated gallium species:

$$L + C_nH_{2n+2} \longrightarrow L\text{-}H^- + C_nH_{2n+1}^+ \tag{3}$$

Next, an interaction of the carbenium ion with the Brønsted acid site can occur. The acidic proton combines with the hydride ion to form molecular hydrogen, and the carbenium ion will take its place on the framework oxygen (eqn. 4).

$$C_nH_{2n+1}^+ + H^+ + L\text{-}H^- \longrightarrow C_nH_{2n+1}^+ + H_2 + L \tag{4}$$
$$\quad\quad\; Z\text{-}O^- \quad\quad\quad\quad\quad Z\text{-}O^-$$
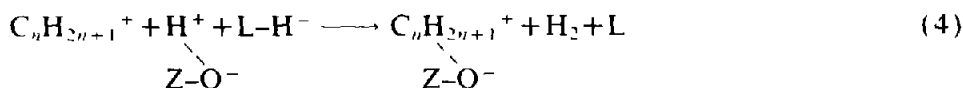
Finally, the carbenium ion will decompose to reform the Brønsted acid site and an alkene (eqn. 5).

$$C_nH_{2n+1}^+ \longrightarrow H^+ + C_nH_{2n} \tag{5}$$
$$\; Z\text{-}O^- \quad\quad Z\text{-}O^-$$
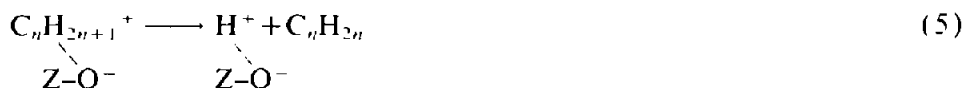
In this way, synergysm occurs between the Lewis and Brønsted acid sites, leading to the formation of the alkene and molecular hydrogen. The primary role of the gallium species in this model is hydride abstraction from the alkane, forming the reactive carbenium ion. The prevention of the hydrogenation of intermediates because of this hydride bonding, as proposed by Inui et al. [22], may also occur but is supposed to be less important.

Deactivation of the catalyst

The modified reaction mechanism for dehydrogenation over the gallium containing zeolites has also consequences for the rate of deactivation by coke formation. From Fig. 6, it is clear that a gallosilicate deactivates much faster than its aluminum analogue. This is also confirmed by the thermogravimetric determination of coke selectivity, as shown in Table 5. Several studies have been carried out dealing with the mechanism of coke formation of acid zeolites. In these studies, the Brønsted acid sites have been assumed to be the active sites for the reaction [32,33]. It has been suggested, however, that Lewis acid sites can also play an important role in coke formation [34,35]. The occurrence of synergysm between the Lewis and Brønsted acid sites can also occur over the gallosilicates. In this context, the increased coke formation is explained by the possibility that the Lewis acid sites are able to accommodate hydride ions and also alkyl radicals [35], which may grow in this adsorbed state, leaving large hydrogen deficient compounds in the zeolite pores, which can act as coke presursors and block the active sites. Investigations with re-

spect to the characteristics of carbenaceous products is in progress and will be published in a subsequent paper. The maximum amount of coke observed did not exceed 8 wt.-%, indicating that the coke is mainly formed in the pores [35], and less on the outer surface of the zeolite particles.

CONCLUSIONS

(i) The application of gallosilicates instead of aluminosilicates results in slightly lower conversions of propane but much higher aromatics selectivities.

(ii) The active sites for dehydrogenation are coordinatively unsaturated gallium species, able to accommodate hydride ions abstracted from alkanes, in combination with strong Brønsted acid sites.

(iii) The coordinatively unsaturated gallium species may be present as framework gallium, but also as highly dispersed non-framework gallium.

(iv) For the dehydrocyclization of higher alkenes to aromatics a gallium site at a short distance from the acid site is preferred.

(v) Deactivation by coke formation is much faster over gallosilicates when compared to the aluminosilicates.

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REFERENCES

1   A.A. Slinkin, A.V. Kucherov, D.A. Kondratyev, T.N. Bondarenko, A.M. Rubinstein and Kh. M. Minachev, J. Mol. Catal., 35 (1986) 97.
2   O.V. Bragin, E.S. Shpiro, A.V. Preobrazhensky, S.A. Isaev, T.V. Vasina, B.B. Dyusenbina, G.V. Antoshin and Kh. M. Minachev, Appl. Catal., 27 (1986) 219.
3   J.H.C. van Hooff, C.W.R. Engelen and H.W. Zandbergen, Chem. Express, 1 (1986) 725.
4   N.S. Gnep, J.Y. Doyemet, A.M. Seco, F. Ramao Ribeiro and M. Guisnet, Appl. Catal., 35 (1987) 93.
5   T. Mole and J.P. Anderson, Appl. Catal., 17 (1985) 141.
6   J. Kanai and N. Kawata, J. Catal., 114 (1988) 284.
7   J. Weitkamp, H.K. Beyer, G. Borbely, V. Cortes-Corberan and S. Ernst, Chem.-Ing.-Tech., 58 (1986) 969.
8   T. Inui, O. Yamase, K. Fukuda, A. Itoh, J. Tarumoto, M. Morinaga, T. Hagiwara and T. Takegami, Proc. 8th Int. Congr. Catal., Berlin, 2-6 July 1984, Verlag Chemie, Basel, 1984, Vol. III, p. 569.
9   J. Kanai and N. Kawata, Appl. Catal., 55 (1989) 115.
10 V. Kanazirev, G.L. Price and K.M. Dooley, J. Chem. Soc., Chem. Comm., (1990) 712.
11 H. Kitagawa, Y. Sendoda and Y. Ono, J. Catal., 101 (1986) 12.
12 N.S. Gnep, J.Y. Doyemet and M. Guisnet, J. Mol. Catal., 45 (1988) 281.

13 N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro and M. Guisnet, Appl. Catal. 43 (1988) 155.
14 D.K. Simmons, R. Szostak, P.K. Agrawal and T.L. Thomas, J. Catal., 106 (1987) 206.
15 J.M. Thomas and X-S. Liu, J. Phys. Chem., 90 (1986) 4843.
16 T. Inui, A. Miyamoto, H. Matsuda, H. Nagata, Y. Makino, K. Fukuda and F. Okazumi, in Y. Murakami, A. Iijima and J.W. Ward (Editors), Proc. 7th Zeolite Conf., Tokyo, Kodansha-Elsevier, Tokyo, 1986, p. 859.
17 T. Inui, Y. Makino, F. Okazumi, S. Nagano and A. Miyamoto, Ind. Eng. Chem. Res., 26 (1987) 647.
18 R.J. Kokes, Catal. Rev., 6 (1972) 1.
19 R.J. Kokes, Acc. Chem. Res., 6 (1973) 226.
20 P. Mariaudeau, J. Mol. Cat., 50 (1989) L7.
21 V.B. Kazansky, L.M. Kustov, and A. Yu Khodakov, in P.A. Jacobs and R.A. van Santen (Editors), Zeolites: Facts, Figures, Future (Stud. Surf. Sci. Catal., Vol. 49B), Elsevier, Amsterdam, 1989, p. 1173.
22 T. Inui, K. Kamachi and H. Matsuda, in P.A. Jacobs and R.A. van Santen (Editors), Zeolites: Facts, Figures, Future (Stud. Surf. Sci. Catal., Vol 49B), Elsevier, Amsterdam, 1989, p. 1173.
23 N.Y. Chen, J.N. Miale and N.Y. Reagan, U.S. Pat., 4 112 056 (1978).
24 B.M.T. Lok, L.D. Vall and E.M. Flanigen, EP Pat., 0 161 491 (1985).
25 C.T-W. Chu and C.D. Chang, J. Phys. Chem., 89 (1985) 1569.
26 F.B. Carleton, T.A. Gilmore and J.J. Rooney, in G.C. Bond, P.B. Wells and F.C. Tompkins (Editors) Proc. 6th Int. Congr. Catal., London, 12-16 July 1976, 1976 p. 291.
27 F.B. Carleton, H.A. Quinn and J.J. Rooney, J. Chem. Soc., Chem. Commun., (1973) 231.
28 S.A. Mitchell, P.A. Hackett, D.M. Rayner and M. Cantin, J. Phys. Chem., 90 (1986) 6148.
29 C.R. Bayense and J.H.C. van Hooff, J. Phys. Chem., submitted for publication.
30 W.G. Haag and N.M. Dessau, Proc. 8th Int. Congr. Cat., Berlin, 2-6 July 1984, Verlag Chemie, Basel, 1984, Vol. III, p 569.
31 P. Meriaudeau and M. Primet, J. Mol. Catal., 61 (1990) 227.
32 H.G. Karge and J. Ladebeck, in P. Fejes (Editor), Proc. Symp. Zeolites, Sept. 11-14 1978, Szeged, Hungary, p. 161.
33 J.R. Anderson, Y.F. Chang and R.J. Western, J. Catal., 118 (1989) 466.
34 B.E. Langner and S. Meyer, Stud. Surf. Sci. Catal., 21 (1980) 91.
35 P. Magnoux, M. Guisnet, S. Mignard and P. Cartraud, J. Catal., 117 (1989) 495.