

# Aromatization of propane over gallium-containing H-ZSM-5 zeolites: influence of the preparation method on the product selectivity and the catalytic stability

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## Aromatization of propane over gallium-containing H-ZSM-5 zeolites

### Influence of the preparation method on the product selectivity and the catalytic stability

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#### Abstract

Three types of gallium-containing H-ZSM-5 zeolites were prepared in order to compare the catalytic stabilities during propane aromatization. The gallium was introduced into the zeolite in three different ways: isomorphous substitution of aluminum by gallium, impregnation of H-(Al)ZSM-5 with a GaCl<sub>3</sub> or a Ga(NO<sub>3</sub>)<sub>3</sub> solution, and physically mixing Ga<sub>2</sub>O<sub>3</sub> powder with a H-(Al)ZSM-5 zeolite. In all cases, addition of 0.6 Ga/unit cell or more enlarged the aromatics selectivity from about 35 C-% to 60 C-%, while the activity remained almost unaffected. A negative side effect was an enhanced rate of deactivation by coke formation, which was most severe for the Ga/H(Al)ZSM-5 catalyst prepared via impregnation or physical mixing, as the gallium is located on the outer surface of the zeolite particles in these samples.

*Keywords:* H-(Ga)ZSM-5, gallosilicates, isomorphous substitution, aromatization, zeolites, deactivation

#### INTRODUCTION

During the last few decades many investigations have been carried out on the conversion of small alkanes into more valuable products, such as aromatics [1-5]. Suitable catalysts for this reaction are platinum-loaded H-(Al)ZSM-5 zeolites, which yield aromatics selectivities of about 40 C-%. In addition to the aromatics, however, considerable amounts of small alkanes are formed via side-reactions, like catalytic cracking over the Brønsted acid sites and hydrogenolysis over the platinum particles [6,7].

These side reactions occur to a much lower extent over H-(Al)ZSM-5 zeolites into which highly dispersed gallium [8-10] or zinc oxide [11,12] particles are introduced. Moreover, formation of molecular hydrogen is possible over these catalysts, resulting in much higher aromatics selectivities during alkane conversion. Regarding the use of zinc containing zeolites, it is known that sub-

limination of the zinc species from the zeolite occurs, especially under severe reaction and regeneration conditions [13]. The zinc species are removed from the zeolite pores to the outer surface of the crystallites and also from the catalyst bed, and deposited on cooler parts of the reactor unit. This behaviour results in a strongly reduced activity and an irreversible loss of aromatics selectivity at an early stage of the reaction.

Until now, few or no investigations have been carried out that deal with the deactivation of gallium-containing zeolites prepared in different ways. The present work shows that the aromatics selectivities do not depend on the method used for the introduction of gallium. By contrast, large differences in catalytic stability under reaction conditions are measured for catalysts prepared in different ways. The influence of catalyst composition and pretreatment on the catalytic stability was studied for isomorphously substituted H-(Al)ZSM-5 zeolites, for gallium-impregnated H-(Al)ZSM-5 zeolites and for physical mixtures consisting of Ga<sub>2</sub>O<sub>3</sub> and H-(Al)ZSM-5. Based on deactivation/regeneration cycles, the most suitable method for introduction of gallium in a H-ZSM-5 zeolite has been determined, from viewpoint of activity, aromatics selectivity and catalytic stability.

## EXPERIMENTAL

For the present investigations three series of gallium-containing zeolites were prepared: a (partly) isomorphously substituted series, H-(Al + Ga)ZSM-5 with a Si/(Al + Ga) ratio of about 45 (series 1), a series consisting of a H-(Al)ZSM-5 zeolite with a Si/Al ratio of about 45, impregnated with a GaCl<sub>3</sub> or a Ga(NO<sub>3</sub>)<sub>3</sub> solution (series 2a and 2b, respectively), and a series consisting of Ga<sub>2</sub>O<sub>3</sub> powder (Ingal 4N5), physically mixed with a H-(Al)ZSM-5 zeolite (Si/Al ratio 45, series 3). The zeolites of series 1 were prepared by a method based on a patent of Chen et al. [14], using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O (Merck) and Ga<sub>2</sub>O<sub>3</sub> (Ingal 4N5) as the aluminium and gallium source, respectively. After crystallization the zeolites were calcined for 3 h at 823 K, ion exchanged three times with a 2 M NH<sub>4</sub>NO<sub>3</sub> solution at 363 K for one hour, and calcined for a second time (3 h, 823 K). The chemical compositions of these zeolites (AAS determination), are shown in Table 1, where the samples are named AlGa-*x*, where *x* represents the number of Ga atoms/unit cell. The catalysts of series 2 were prepared by pore volume impregnation of a H-(Al)ZSM-5 catalyst with a GaCl<sub>3</sub> solution (series 2a). The samples of series 2b were prepared using a Ga(NO<sub>3</sub>)<sub>3</sub> solution for the impregnation, followed by a calcination in a helium-oxygen mixture (80/20) at 723 K. The compositions of these zeolites, which will be referred to as GaIm-*x*/Cl and GaIm-*x*/NO<sub>3</sub>, respectively, are also shown in Table 1. Table 1 also contains the compositions of the catalysts of series 3, which were prepared by physically mixing of Ga<sub>2</sub>O<sub>3</sub> powder with an H-(Al)ZSM5 zeolite (Si/Al=45). These samples, which were used without any calcination steps prior to the measurements, will be referred to as GaPm-*x*.

TABLE 1

## Compositions of the zeolites

Series	Name	Al/u.c.	Ga/u.c.	Si/(Al+Ga) ratio
1	AlGa-0	1.99	0	45
	AlGa-0.22	1.90	0.22	42
	AlGa-0.74	3.19	0.74	25
	AlGa-1.23	1.97	1.23	28
	AlGa-2.08	0	2.08	44
2a	GaIm-0/Cl	1.99	0	45
	GaIm-0.23/Cl	1.99	0.23	42
	GaIm-0.47/Cl	1.99	0.47	38
	GaIm-1.07/Cl	1.99	1.07	30
	GaIm-2.15/Cl	1.99	2.15	22
	GaIm-4.37/Cl	1.99	4.37	15
2b	GaIm-0/NO <sub>3</sub>	3.30	0	28
	GaIm-1.06/NO <sub>3</sub>	3.30	1.06	21
	GaIm-3.01/NO <sub>3</sub>	3.30	3.01	14
	GaIm-4.23/NO <sub>3</sub>	3.30	4.23	12
3	GaPm-0	1.99	0	45
	GaPm-0.42	1.99	0.42	39
	GaPm-0.84	1.99	0.84	33
	GaPm-1.68	1.99	1.68	25
	GaPm-2.53	1.99	2.53	20
	GaPm-4.27	1.99	4.27	14
<i>Other catalysts used in this work:</i>				
	Al-4.51	4.51	0	21
	Al-1.71	1.71	0	55
	Ga-3.28	0	3.28	28
	Ga-1.42	0	1.42	67
	GaPm-1.68 (4.51) <sup>a</sup>	4.51	1.68	15

<sup>a</sup>Zeolite Al-4.51, physically mixed with Ga<sub>2</sub>O<sub>3</sub>, 1.68 Ga/unit cell.

In addition to the catalysts of the three series mentioned above, some zeolites with deviating gallium or aluminium contents, coded Ga-*x* and Al-*y*, have also been used in the aromatization reaction (*x* and *y* represent the number of Ga atoms/unit cell and Al atoms/unit cell, respectively). The compositions of these catalysts are also shown in Table 1.

Propane aromatization reactions were carried out at atmospheric pressure in a microflow reactor using 0.5 g catalyst and a propane W H S V of 2 h<sup>-1</sup> (He/C<sub>3</sub>H<sub>8</sub> = 2). Temperatures were varied between 623 and 873 K.

Deactivation runs were carried out at the same W H S V at a temperature of 873 K. Regeneration of the catalysts was performed in flowing helium-oxygen at 873 K for ten minutes.

EDX analysis was done on a Scanning Electron Microscope JEOL JSM-840A.

Thermogravimetric experiments were carried out on a Cahn electrobalance at 823 K using 30 mg sample and a total gas flow of 50 ml/min ( $\text{He}/\text{C}_3\text{H}_8=10$ ).

## RESULTS

The propane conversions at 873 K for the differently prepared catalysts as function of the gallium content are shown in Fig. 1. It is clear that, independent of the method of gallium introduction, gallium loadings up to about 2 Ga/unit

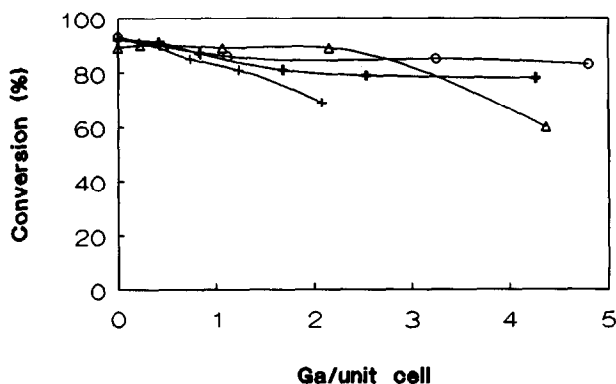


Fig. 1. Propane conversions at 873K over different catalyst systems; + isomorphously substituted zeolites (series 1),  $\Delta$  gallium chloride impregnated zeolites (series 2a),  $\circ$  gallium nitrate impregnated zeolites (series 2b), + physical mixtures of zeolite and gallium oxide (series 3).

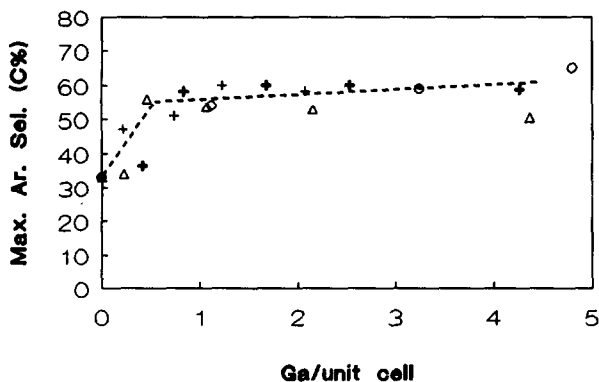


Fig. 2. Maximum aromatics selectivities obtained over different catalyst systems; + isomorphously substituted zeolites (series 1),  $\Delta$  gallium chloride impregnated zeolites (series 2a),  $\circ$  gallium nitrate impregnated zeolites (series 2b), + physical mixtures of zeolite and gallium oxide (series 3).

cell (u.c.) do not change the activity of the zeolite significantly, except in the case of isomorphous substitution of aluminium (series 1), where a gradually decreasing activity with increasing gallium content is measured. A considerable loss of activity is also observed when more than 3 Ga/u.c. are introduced by  $\text{GaCl}_3$  impregnation (series 2a).

The presence of gallium, introduced by either of the methods, increases the aromatics selectivity from about 35 C-% to 60 C-% as shown in Fig. 2. This high selectivity was measured over a broad conversion range (10–80%). For the catalysts of series 1, 2b and 3, the aromatics selectivity decreased slightly (4–6 C-%) upon reaction at the highest temperature (873 K). However, for the  $\text{GaCl}_3$ -impregnated zeolites (series 2a), a decline in aromatics selectivity was observed at a much lower temperature, as shown in Fig. 3, where the aro-

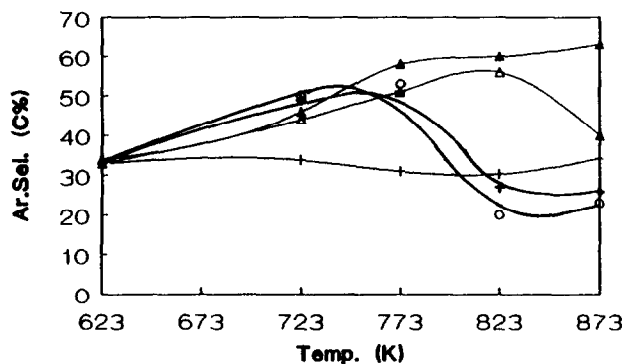


Fig. 3. Aromatics selectivities versus temperature over the gallium impregnated zeolites (series 2); + GaIm-0.23/Cl,  $\Delta$  GaIm-0.47/Cl,  $\circ$  GaIm-2.15/Cl, + GaIm-4.37/Cl,  $\blacktriangle$  GaIm-4.23/ $\text{NO}_3$ .

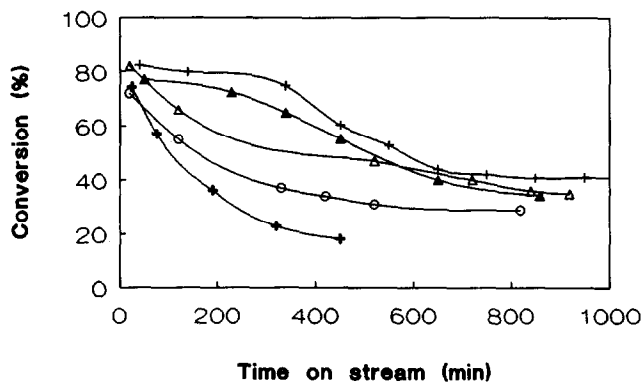


Fig. 4. Influence of isomorphous substitution of aluminium by gallium on the deactivation rate at 873 K; + AlGa-0,  $\Delta$  AlGa-0.74,  $\circ$  AlGa-2.08,  $\blacktriangle$  Al-1.71, + Ga-3.28.

matics selectivities of these samples are shown as function of reaction temperature. Increasing the temperature above 773 K causes a rapid decrease in aromatics selectivity and simultaneously a yellow-brown deposit is formed on the reactor outlet. EDX analysis showed the presence of gallium and gallium chloride in this substance. Fig. 3 also indicates that a gallium loading of 0.4 Ga/u.c., introduced by  $\text{GaCl}_3$  impregnation, is not sufficient for an improvement in the aromatics selectivity. For the sample prepared by impregnation with a  $\text{Ga}(\text{NO}_3)_3$  solution and subsequent calcination, the aromatics selectivity remains high, even at the highest temperature (873 K).

Fig. 4 shows the decreasing activity with time on stream of the pure aluminosilicates (AlGa-0 and AlGa-2.08, respectively). The deactivation curve of a gallo-aluminosilicate with a comparable  $\text{Si}/(\text{Al} + \text{Ga})$  ratio is also included

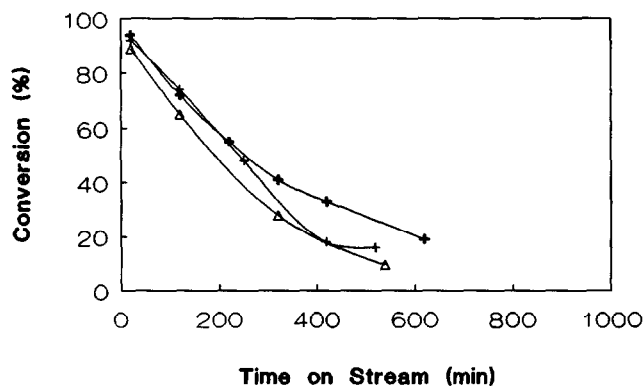


Fig. 5. Deactivation of physical mixtures at 873K, containing 2 wt.-% gallium, and a zeolite impregnated with gallium nitrate, containing 5.65 wt.-% Ga,  $T=873\text{K}$ ; + GaPm-1.68(30),  $\Delta$  GaPm-1.68,  $\blacktriangle$  GaIm-4.23/ $\text{NO}_3$ .

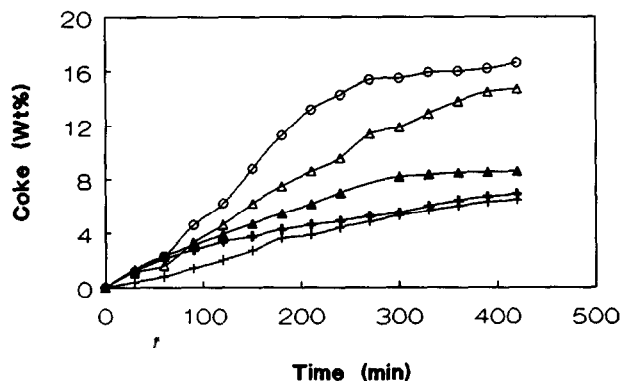


Fig. 6. Influence of introduction of gallium into the zeolite on the coke formation; + AlGa-0,  $\bullet$  AlGa-0.74,  $\blacktriangle$  AlGa-2.08,  $\Delta$  GaPm-0.84,  $\circ$  GaPm-2.53.

in this figure (AlGa-0.74). In addition, the curves of some zeolites with another acid site density (Al-1.71 and Ga-3.28) are shown. Obviously, both isomorphous substitution of aluminium by gallium and a higher acid site density lead to a higher deactivation rate.

The deactivation curves measured for a gallium impregnated sample (GaIm-4.23/NO<sub>3</sub>) and the physical mixtures GaPm-1.68 and GaPm-1.68 (Al-4.51) are presented in Fig. 5. It can be seen that the rates of deactivation of these systems are even higher than these of the isomorphously substituted zeolites (series 1). Another remarkable point is that the catalyst prepared by impregnation with a gallium nitrate solution and subsequent calcination, deactivates at a rate comparable to the physical mixture of Ga<sub>2</sub>O<sub>3</sub> and H-(Al)ZSM5.

The results of the thermogravimetric determinations for investigation of the

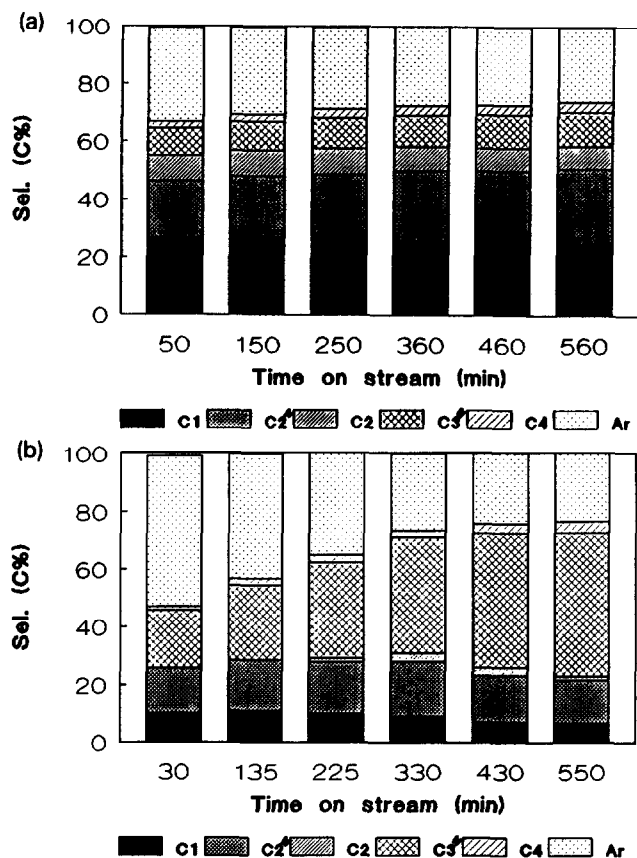


Fig. 7 (a). Changes in product selectivity during time on stream over the aluminosilicate AlGa-0 at 873K. (b) Changes in product selectivity during time on stream over the gallosilicate AlGa-2.08 at 873K.



coking rates of differently prepared catalysts are shown in Fig. 6. Obviously, the rates of coke formation increase with the degree of isomorphous substitution of gallium in the framework (series 1), while much higher rates of coke formation are observed for the physical mixtures (series 3).

The changes in selectivities to different hydrocarbons during time on stream for propane conversion at 873 K, observed over the alumino- and gallosilicates (series 1) are shown in Figs. 7a and 7b, respectively. Over the aluminosilicate, the changes in product selectivity with time on stream are very small. By contrast, over the gallosilicates, simultaneously with the decline in activity, a strong decrease in aromatics selectivity occurs, with the concomitant formation of much larger amounts of propene.

The changes observed in the product selectivity with time on stream for the physical mixtures are shown in Fig. 8. These systems also show a loss of aromatics selectivity during deactivation, but in this case the major product that arises with time on stream is ethene. Moreover, the loss of activity and aromatics selectivity seem to be reversible since the initial activity and aromatics selectivity are restored after subsequent deactivation/regeneration cycles (Fig. 9).

The deactivation rates of the different catalyst systems have been quantified assuming a model of a first-order deactivation approximation for a fixed bed reactor with a plug flow, as described by Levenspiel [15]:

$$\ln(\ln(1/(1-x))) = \ln(k''/k_d) - k_d t \quad (1)$$

From this equation it follows that a plot of  $\ln(\ln(1/1-\text{conv}))$  versus time on stream should give a straight line from which a deactivation rate constant,  $k_d$ , can be calculated. The  $k_d$  values determined in this way for different catalyst systems are presented in Table 2.

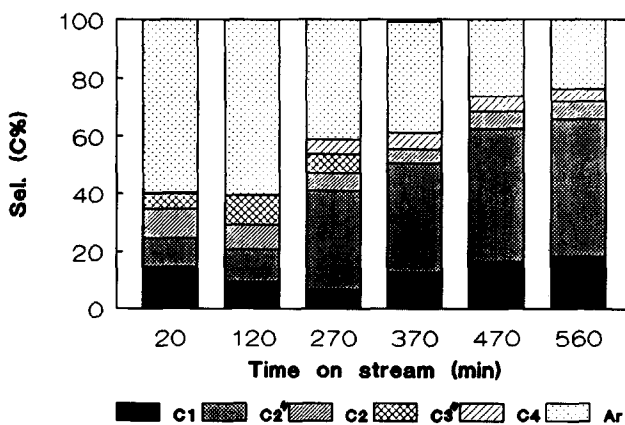


Fig. 8. Changes in product selectivity during time on stream over the physical mixture GaPm-1.68 at 873K.

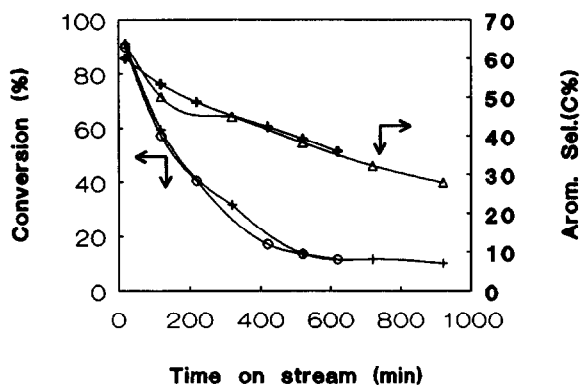


Fig. 9. Effect of regenerations on the deactivation behaviour of the physical mixture GaPm-1.68 (Al-4.51); fresh catalyst:  $\bullet$  activity,  $\Delta$  aromatics selectivity; catalyst after three regenerations:  $\circ$  activity,  $+$  aromatics selectivity.

TABLE 2

First order deactivation rate constants for different catalyst systems

Catalyst	$K_d (\times 10^{-3})$
Al-4.51	0.69
Al-1.71	0.23
AlGa-0.22	0.89
AlGa-0.74	1.55
AlGa-1.23	2.59
Ga-3.28	4.91
Ga-1.42	1.12
GaPm-1.68 (Al-4.51)	8.00
GaPm-1.68	5.47

## DISCUSSION

Fig. 1 shows that introduction of gallium into the zeolite by either of the methods has only a small effect on the conversion of propane at low gallium contents. Only at high degrees of isomorphous substitution (series 1) does conversion become significantly lower. This is due to the fact that the framework  $-\text{Ga}(\text{OH})\text{Si}-$  site has a weaker Brønsted acidity than the  $-\text{Al}(\text{OH})\text{Si}-$  site [16]. As these sites, in combination with the gallium, were found to be the active centres for the dehydrogenation of the starting alkane (the rate determining step of the reaction) [17], an increasing number of the weaker Brønsted acid sites ( $-\text{Ga}(\text{OH})\text{Si}-$ ) will reduce the overall conversion.

The small enhancements in propane conversion that were measured at low gallium contents for the gallium-impregnated zeolites of series 2a are due to

the high dehydrogenation activity of non-framework gallium in the presence of Brønsted acid sites [17,18]. At the higher gallium contents of the  $\text{GaCl}_3$  impregnated samples, a strongly reduced activity is observed. This is probably due to a substantial removal of aluminium from the framework, caused by the treatment with the acidic  $\text{GaCl}_3$  solution, resulting in a lower acid site density. Moreover, sublimation of the gallium species may readily occur. An exchange reaction of three  $\text{H}^+$  sites by a  $\text{Ga}^{3+}$  ion is less plausible because of (i) the relative large distance between the  $\text{H}^+$  sites in the unit cell and (ii) the acidity of the solution (all gallium present as a large  $\text{Ga}(\text{H}_2\text{O})_6^{3+}$  complex and not as, e.g.,  $\text{Ga}(\text{OH})_2^+$ ). The effect of gallium addition by physical mixing of the zeolite with  $\text{Ga}_2\text{O}_3$  powder (series 3) on the activity is also small, even at high gallium loadings.

Fig. 2 shows that the method by which gallium is introduced is not important for obtaining high aromatics selectivities. It seems, however, that gallium introduced by isomorphous substitution is most effective for the aromatization reaction as, for the zeolites of series 1, a gallium loading of 0.47 Ga/u.c. is sufficient to obtain an aromatics selectivity of more than 45 C-%, in contrast to the results obtained over the zeolites of series 2 and series 3. This indicates that the gallium site in the vicinity of the Brønsted acid site is preferred for a certain step in the reaction. This was also confirmed by model reactions on the separate reaction steps, where it turned out that, for the transformation of higher alkenes into cycloalkanes, framework gallium in the zeolite is more effective than extra-framework gallium, introduced by impregnation [17], for example.

The high selectivities to aromatics are obtained over a broad conversion range (10–80%), but it is important to notice that the aromatics selectivities mentioned in this figure are the maximum selectivities, which are generally measured at 823 K. At higher temperatures, the aromatics selectivities are lower due to a larger contribution of cracking products. For the samples of series 2a (impregnated with  $\text{GaCl}_3$ ), the maximum is reached at a lower temperature, as indicated in Fig. 3. For these samples, the aromatics selectivities increase up to a temperature of 773 K, but decrease rapidly at higher temperatures. The fact that, in the yellow-brown layer which is deposited on the cooler parts of the reactor outlet, small (metallic) gallium spheres and traces of gallium chloride are detected, indicates that at high temperatures, sublimation of the gallium species from the zeolite surface occurs, resulting in an irreversible loss of aromatics selectivity. This can be explained by the high vapour pressure of the gallium chloride, even at relatively low temperatures [19].

Impregnation with a  $\text{GaCl}_3$  solution is therefore not a suitable method for preparation of the catalysts. For the samples of series 2b, impregnated with the  $\text{Ga}(\text{NO}_3)_3$  solution and subsequent calcination, sublimation of the gallium species is much less pronounced since in the impregnated zeolite, gallium oxide is formed during calcination of the  $\text{Ga}(\text{NO}_3)_3$ , which has a much lower vapour

pressure than gallium chloride [19]. In this way, catalysts with a higher thermal stability are obtained.

In addition to the increased aromatics selectivity after gallium introduction in the zeolites, a more rapid deactivation occurs, as shown in Fig. 4 for the (partially) isomorphously substituted series. The deactivation problem, however, is much more severe upon application of an impregnated H(Al)ZSM5 zeolite (GaIm-4.23/NO<sub>3</sub>) or a physical mixture of Ga<sub>2</sub>O<sub>3</sub> and H-(Al)ZSM5 zeolite (series 3), as shown in Fig. 5.

An explanation for the increased deactivation rate after gallium introduction may be a (partial) reduction of gallium (III) oxide to gallium (I) oxide at high temperatures, due to the strongly reducing atmosphere in the catalyst bed under reaction conditions [20]. Our temperature-programmed reduction experiments did not confirm this: no reduction peak of any gallium oxide species was measured up to the maximum reaction temperature (873 K).

Another reason for the higher deactivation rate may be a higher rate of coke formation, which is confirmed by our thermogravimetric coke determinations (Fig. 6). With these experiments similar trends are observed in the deactivation behaviour of the samples of series 1 and series 3: the rate of coke formation increases with an increasing degree of isomorphous substitution (series 1), while extremely high coking rates are measured over the physical mixtures (series 3).

These results show the great importance of the shape selective properties of the zeolite for inhibition of the coking reaction [21,22]. In the pores of the isomorphously substituted zeolites, alkylated aromatics and polyaromatics cannot be formed for steric reasons, so systems with a relatively high catalytic stability are obtained. In contrast, over the physical mixtures and the impregnated samples, the reaction mainly occurs on the interface between the zeolite crystallite and the Ga<sub>2</sub>O<sub>3</sub> particle, where the product selectivity and thus the coke formation are less well controlled by the shape selective restrictions of the zeolite. This will result in excessive coke formation. The fact that the activity decline, as observed for the calcined sample GaIm-4.23/NO<sub>3</sub> in this figure, has a great resemblance to the curves of the physical mixtures (series 3) strongly indicates that the gallium oxide, introduced by impregnation and subsequent calcination, is exclusively located on the outer surface of the zeolite particles.

Another important factor that may facilitate the rate of coke formation can be the Lewis acidic properties of that fraction of the gallium that is present as a coordinatively unsaturated (extra)-framework gallium species. This property enables the accommodation of hydrogen radicals and stabilization of other radicals, which may act as precursors for coke [23,24]. In combination with Brønsted catalysed hydride abstractions, large hydrogen deficient products may be formed on the catalyst, blocking the active sites [25].

The changes in product selectivity during the deactivation runs are negligi-

ble over the aluminosilicates as shown in Fig. 7a. This means that there is one type of active site in the zeolite, which is gradually blocked during time on stream, or becomes inaccessible. The activity decline may therefore be ascribed to a loss of acid sites, which are active for the activation of the starting alkane (the rate determining step) and the oligomerization of the primary alkenes. From the fact that the selectivity to aromatics does not change upon deactivation, it seems that the amount of acid sites that is left, even after 9 h of reaction, is still sufficient for the oligomerisation of the small alkenes and the aromatisation of the higher alkenes via hydrogen transfer reactions.

The behaviour of the gallosilicate (Fig. 7b) can be explained by assuming that the acid sites are much more rapidly deactivated by coke formation than the gallium sites. This makes the oligomerization activity of the zeolite a relative slow step in the reaction, while the dehydrogenation activity remains intact. These effects result in large amounts of propene in the product stream after longer times on stream. For the physical mixtures of series 3, too, a rapid decline in aromatics selectivity is observed with time on stream (Fig. 8), and similar changes in product distribution were observed for the impregnated sample (GaIm-4.23/NO<sub>3</sub>). In contrast with the isomorphously substituted zeolites (Fig. 7a), the main product that arises with time on stream is ethene. After a long time on stream the effect of the gallium is no longer visible and the aromatics reaches the level of the pure aluminosilicate. These observations can be explained by the model of Mariaudeau et al. [26], who supposed that the introduction of gallium oxide changes the major reaction for propane activation from a cracking mechanism (formation of methane and ethene) to a dehydrogenation mechanism (formation of propene and hydrogen).

The deactivation behaviour of these samples indicates that the gallium oxide deactivates very rapidly, probably due to the coking reaction. This can be explained by two factors. Firstly, the specific surface area of the Ga<sub>2</sub>O<sub>3</sub> powder is low (<5 m<sup>2</sup>/g) and, secondly, the fact that the aromatization reaction over the physical mixtures occurs to a greater extent on the interface between the zeolite particles and the gallium oxide, as described above. Both factors cause a relatively rapid coverage of the gallium oxide with coke, making it inactive for dehydrogenation so, after longer times on stream, activation of the starting alkane occurs by cracking once again, thus increasing the selectivity to ethene.

The fact that both the activity and the aromatics selectivity of the physical mixtures are restored after subsequent deactivation/regeneration cycles (Fig. 8) indicates that the loss of gallium by sublimation or migration of the gallium species from the catalyst bed is negligible.

The values for  $k_d$ , as calculated from the model assuming a first order deactivation behaviour (Table 2) are in full agreement with the order measured in the deactivation experiments: physical mixtures >> isom. subst. Al-Ga silicates > aluminosilicates. It also seems that this approximation gives a reason-

ably good description of the deactivation behaviour of the H(Al)ZSM5 zeolites, both before and after the introduction of gallium by a variety of methods.

## CONCLUSIONS

- (i) H-(Al)ZSM5 zeolites loaded with gallium have to be preferred for the propane aromatization reaction, rather than pure gallosilicates, in order to obtain high activities in combination with high aromatics selectivities.
- (ii) Introduction of gallium into H-(Al)ZSM5 by either of the methods described has only a small effect on the activity of the aluminosilicates in propane conversion but results in all cases in a strongly enhanced aromatics selectivity.
- (iii) The main cause of the higher deactivation rate after the introduction of gallium is an increasing rate of coke formation with gallium content. The order in deactivation rate for the different systems is: physical mixtures > gallosilicates > aluminosilicates.

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## REFERENCES

- 1 J.P. van den Berg, J.P. Wolthuizen and J.H.C. van Hooff, in L.V.C. Rees (Editor), Proc. 5th Int. Congress on Zeolites, 1980, Heyden, London, 1980, p. 649.
- 2 H. Rastelik, B.M. Cok, J.A. Duisman, D.E. Earls and J.T. Mullhaupt, Can. J. Chem. Eng., 60 (1982) 44.
- 3 P.B. Venuto, and E.T. Haber, Cat. Rev.-Sci. Eng., 18 (1978) 1.
- 4 A.A. Shipkin, A.V. Kucherov, D.A. Kondratyev, T.N. Bondarenko, A.M. Rubinstein and Kh.M. Minachev, J. Mol. Catal., 35 (1986) 97.
- 5 O.V. Dass and A.L. Odell, J. Catal., 113 (1988) 259.
- 6 O.V. Bragin, T.V. Vasina, Y.I. Isakov and Kh.M. Palinshkina, in P.A. Jacobs, N.I. Jaeger, P. Jiru, V.B. Kazansky and G. Schulz-Ekloff (Editors), Stud. Surf. Sci. Catal., Vol. 18, Elsevier Amsterdam, 1984, p. 273.
- 7 N.S. Gnep, J.Y. Doyemet, A.M. Seco, F. Ramao Ribeiro and M. Guisnet, Appl. Catal., 35 (1987) 273.
- 8 M. Shibata, H. Kitagawa, Y. Sendoda and Y. Ono, Proc. 7th Int. Congress on Zeolites, 1986, Kodansha Elsevier, Tokyo, 1986, p. 717.
- 9 T. Inui, Y. Makino, F. Okazumi, S. Nagano and A. Miyamoto, Ind. Eng. Chem. Res., 26 (1987) 647.
- 10 H. Kitagawa, Y. Sendoda and Y. Ono, J. Catal., 101 (1986) 12.
- 11 T. Mole, J.R. Anderson and G. Creer, Appl. Catal., 17 (1985) 141.
- 12 J. Kanai and N. Kiwata, J. Catal., 114 (1988) 284.
- 13 C.J. Planck, E.J. Rosinski, and E.N. Givens, U.S. Patent 4,157,293, 1979.

- 14 N.Y. Chen, J.N. Miale and N.Y. Reagan, U.S. Patent 4,112,056, 1978.
- 15 O. Levenspiel, *Chemical Reactor Engineering*, John Wiley & Sons, New York, 1972, p. 544.
- 16 C.T.-W Chu and C.D. Chang, *J. Phys. Chem.*, 89 (1985) 1569.
- 17 C.R. Bayense and J.H.C. van Hooff, *Appl. Catal.*, 72 (1991) 81.
- 18 D.K. Simmons, R. Szostak, P.K. Agrawal and T.L. Thomas, *J. Catal.*, 106 (1987) 287.
- 19 I.A. Sheka, I.S. Chaus and T.T. Mityureva, *The Chemistry of Gallium*, Elsevier Publishing Company, Amsterdam, 1966.
- 20 L. Petit, J.P. Bournonville and F. Raatz, in R.A. van Santen and P.A. Jacobs (Editors), *Stud. Surf. Sci. Catal.*, Vol. 49b, Elsevier Amsterdam, 1989 pp. 1163.
- 21 M. Guisnet and P. Magnoux, *Appl. Catal.*, 54 (1989) 1.
- 22 M. Guisnet, P. Magnoux and C. Canaff, *Proc. 7th Int. Conf. on Zeolites*, Kodansha-Elsevier, Tokyo, 1986, p. 701.
- 23 J. Karger, H. Pfeiffer, J. Caro, M. Bulow, H. Schlodder, R. Mostowicz and J. Vltter, *Appl. Catal.*, 29 (1987) 21.
- 24 T. Inui, I. Ishihara, K. Kamachi and H. Matsuda, in R.A. van Santen and P.A. Jacobs (Editors), *Stud. Surf. Sci. Catal.*, Vol. 49, Elsevier Amsterdam, 1989, p 1183.
- 25 B.E. Langner and S. Meyer, *Stud. Surf. Sci. Catal.*, 21 (1980) 91.
- 26 P. Mariaudeau, *J. Mol. Catal.*, 50 (1989) L-7.