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Aromatization of propane over GaHMFI catalysts. Reaction scheme, nature of the dehydrogenating species and mode of coke formation

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Abstract

The kinetic modelling of propane aromatization over a Ga/HMFI catalyst and the comparison of Ga_2O_3-HMFI mixtures with different compositions has allowed us to specify the respective roles of dehydrogenating species and of protonic sites. Propane aromatization over Ga/HMFI catalyst occurs mainly through a conventional bifunctional reaction scheme (with desorbed intermediates) in which the dehydrogenating gallium species are responsible for dehydrogenation of propane, of oligomers and of cyclic olefins and diolefins while protonic sites are responsible for oligomerization, cyclization and cracking. This bifunctional transformation is kinetically limited by propane dehydrogenation. Unfortunately, gallium species also catalyze alkane cracking and hydrogenolysis as well as alkene hydrogenation with formation of the undesired products methane and ethane. From the comparison of the catalytic properties of MFI gallosilicates calcined under air flow at various temperatures, it can be concluded that tetrahedral gallium is inactive in dehydrogenation reactions. Dehydrogenation occurs through a bifunctional mechanism involving the joint participation of gallium oxide (extra framework species) and of protonic sites. Coke formed during propane aromatization causes a blockage of the access to the protonic sites of the zeolite which is responsible for deactivation. Ga decreases the coking/aromatization rate ratio of HMFI and facilitates the coke removal through oxidative treatment, both effects being more pronounced after Ga/HMFI pretreatment at high temperature under hydrogen because of the better dispersion of the Ga species.

Keywords: Aromatization of propane; GaHMFI catalysts; Reaction scheme; Dehydrogenating species; Coke formation

1. Introduction

During the last decade, the transformation of liquefied petroleum gas (LPG) into BTX hydrocarbons (benzene, toluene, xylenes) has been investigated by numerous industrial and university teams. BTX which are very important base chemicals also constitute a significant part of the gasoline pool because of their high octane number. Furthermore for economic reasons it could be interesting to substitute LPG for naphtha now used in the synthesis of BTX. Various processes: M2 forming from Mobil [1], Cyclar from UOP and BP [2–8], Aroforming from IFP and Salutec [9,10], Z-forming from Mitsubishi and Chiyoda [11] have been developed for LPG aromatization. All these processes used as catalyst an average pore size zeolite (generally of the MFI type) often doped with dehydrogenating species (generally gallium).

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The reaction pathway of short chain alkane aromatization is complex, the formation of aromatics requiring various steps and being accompanied by various secondary reactions. Moreover, the catalyst system is very complex: gallium species can be introduced in many different ways; the protonic sites and the gallium species can interact during the catalyst activation and/or the reaction with modification of their respective activity. They can play an independent or a joint role in the various steps of the aromatization pathway.

Both the industrial interest in LPG aromatization and this complexity of the reaction scheme and of the catalyst system incited various teams to investigate the aromatization of short chain alkanes, in particular that of propane, on MFI zeolite catalysts doped with gallium. The number of papers published on this subject is now very great and review papers have already appeared [12–15].

A preliminary remark must be made. To investigate a reaction as complex as propane aromatization, the product distribution must be established from very low to high conversions (or at least the catalyst selectivities compared at identical conversions). The large range of conversions can be obtained either by varying the reaction temperature at constant contact time or the contact time at constant temperature. We have chosen the second way because the temperature can modify the thermodynamic equilibrium and can affect differently the rates of the various steps [13].

Our first investigation of propane aromatization was carried out over Pt/HMFI catalysts [16]. The reaction scheme as well as the effect of platinum content on the rate and selectivity of aromatization were established. A bifunctional mechanism, in which platinum participated in propane and naphthene dehydrogenation and acid sites in propene oligomerizaton, oligomer cyclization, etc. was proposed. The transformation of propane and of the possible intermediates of propane aromatization was later investigated on physical mixtures of Ga_2O_3 and of HMFI as well as on the pure components [17,18]. This allowed us to specify the respective roles of the protonic sites and of the gallium species. The rates and selectivities of the C_2–C_4 alkanes (ethane, propane, *n*-butane and isobutane) transformation were also compared

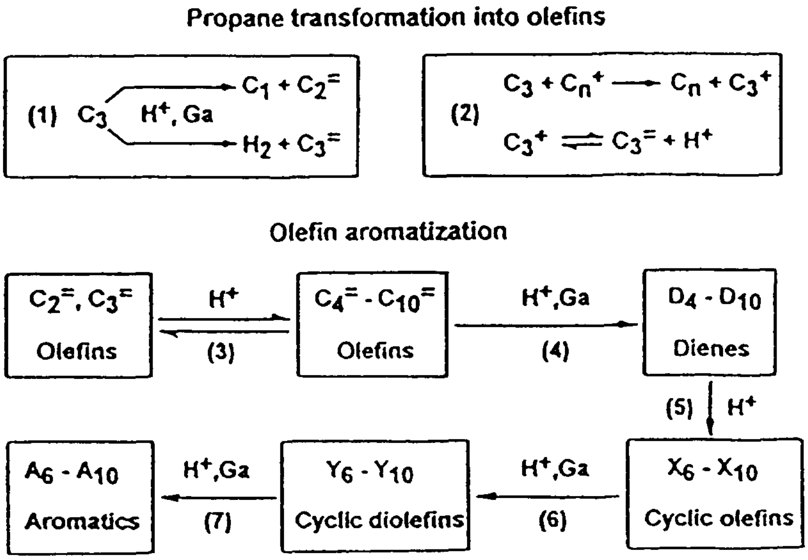


Fig. 1. Pathway of propane aromatization reaction over HMFI and GaHMFI. From [28].

on HMFI and on gallium impregnated HMFI catalysts [19–21]. These results being discussed in detail in [13] will be simply quoted here.

The objective of this paper is to discuss on the basis of recent data three aspects of propane aromatization over Ga/HMFI catalysts which remain the object of controversy:

(i) The reaction scheme of propane aromatization in particular the role of redox species and of acid sites in the various steps of this aromatization.

(ii) The nature of the dehydrogenating species. Is tetrahedral framework Ga active in dehydrogenation and do the dehydrogenating species result from an interaction between Ga species and protonic sites?

(iii) The deactivation of GaMFI catalysts by coking. What is the mode of coke formation and what is the effect of coking on the activity of the protonic sites and of the dehydrogenating species?

2. Reaction scheme of propane aromatization over Ga/HMFI catalysts. Role of gallium species and of acid sites

HMFI zeolites without gallium additives are able to catalyze propane aromatization [16,22–26]. The reaction scheme is now well established (Fig. 1). The first step is the dehydrogenation and the cracking of the reactant through carbonium ion intermediates (reaction 1). However propane can also dehydrogenate through another path: hydride transfer from propane to carbenium ions resulting from the adsorption of product alkene followed by propene desorption (reaction 2). Propene and ethylene resulting from reactions 1 and 2 undergo rapid successive reactions via carbenium ion intermediates: oligomerization, cyclization, hydrogen transfer leading finally to C_6–C_9 aromatics. Unfortunately, hydrogen transfer reactions (reactions 4, 6 and 7 in Fig. 1) lead not only to the desired products but also to short chain alkanes (from olefins) whose transformation requires, as a first step, the slow reactions 1 or 2.

The addition of Ga species to HMFI zeolites in different manners (mechanical mixtures with Ga_2O_3, impregnation with Ga salts then calcination, chemical vapor deposition, etc.) increases the rate and the selectivity of propane aromatization as well as the rate of hydrogen production. This shows that gallium species play a role in propane aromatization and most likely in dehydrogenation steps. We have furthermore shown that pure Ga_2O_3 was active for dehydrogenation of propane into propene and of methylcyclohexene into toluene [17,18], i.e. for reactions 1 and 6 + 7 in Fig. 1. While most of the authors agree that both Ga species and protonic sites participate in propane aromatization over Ga/HMFI catalysts (hence that aromatization occurs through bifunctional catalysis), their respective role in each step of the aromatization scheme remains the object of controversy. This is why we have attempted to clarify this point:

(i) By developing a kinetic model for short-chain alkane aromatization over HMFI and Ga/HMFI catalysts [27–29]. This model will allow to specify the relative significance of the steps involved in aromatization.

(ii) By determining the effect of the composition of mechanical mixtures of Ga_2O_3 and of HMFI zeolite on their activity and selectivity for propane aromatization as well as on their activity for model acid and redox reactions [30,31].

2.1. Kinetic modelling of aromatization. Reactions steps involved in propane aromatization on HMFI and on Ga/HMFI

A large amount of data was collected on propene and propane aromatization over HMFI (Si/Al = 40) and a 4 wt% Ga/HMFI catalyst (prepared by impregnation of the HMFI zeolite with a gallium nitrate solution) pretreated under nitrogen flow at 530°C for 10 h. These data were reported previously by Gnep et al. [26], Doyemet [32] and Aittaleb [33] and were obtained under non-deactivating conditions (time-on-stream was 2–3 min) in a flow reactor at 530°C and hydrocarbon pressure of 1 bar. Contact time was varied from about 1×10^{-3} h to 40×10^{-3} h for propene transformation and from 10×10^{-3} h to 500×10^{-3} h for propane transformation so as to obtain conversions in the 5–90% range. Moreover additional data existed on the transformation of C_2–C_8 hydrocarbons on the same catalysts and on Ga_2O_3 [34]. All these make kinetic modelling of the complex reaction of propane aromatization possible.

Propane aromatization over HMFI and Ga/HMFI catalysts can be represented as a two-stage process: (i) propane transformation into propene and ethylene (+methane) and (ii) aromatization of these olefins (Fig. 1). Both stages are complex reactions. Thus with HMFI, the first stage includes two routes: protolytic cracking which is the only route at low conversion (reaction 1) and hydride transfer from propane to carbenium ions R^+ generated from product olefins produced (reaction 2). The second stage proceeds through a number of oligomerization, cracking, cyclization and hydrogen transfer steps. Gallium species provide dehydrogenation routes both in the first and the second stages.

Kinetic modelling of propane aromatization was divided into various steps. First a kinetic model for propene aromatization (second stage in Fig. 1) was developed and the rate constants of the various steps were estimated for HMFI then for the Ga/HMFI catalyst. After, the kinetic model for propane aromatization was obtained by adding the reactions of propane to the model established for propene aromatization. Again the rate constants were estimated by comparison between experimental and simulated data, first for HMFI then for the Ga/HMFI catalyst.

The kinetic models, derived from the reaction scheme in Fig. 1 take into account the transformation of all the hydrocarbon species present in the reactor effluents (either on the acid sites or on the gallium species or on both). Various simplifying assumptions were introduced: in particular, adsorption equilibrium was considered to be established while adsorption constants were considered independent of hydrocarbon molecular weight. The equations for the rates of the reaction steps were derived on the basis of the mass action law. More information on the kinetic modelling can be obtained from [27–29].

2.1.1. *Kinetic modelling of propene aromatization over HMFI and Ga / HMFI*

A good agreement was finally obtained between experimental and simulated data. This is

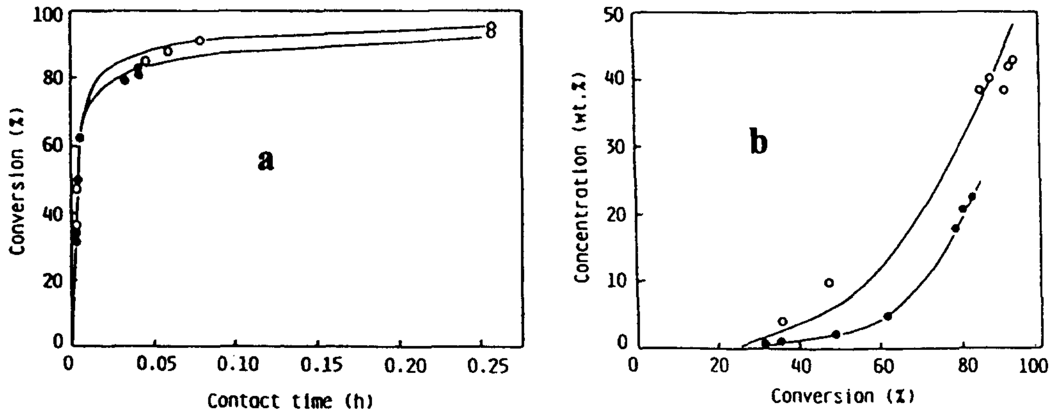


Fig. 2. Final description of propene aromatization over HMFI (●) and GaHMFI (○) zeolites. Experimental data (points) and calculated curves. (a) Propene conversion as a function of contact time, (b) aromatic concentration as a function of propene conversion. Adapted from [27].

shown in Fig. 2 which gives propene conversion versus contact time (a) and aromatic concentration versus propene conversion (b) over HMFI and Ga/HMFI.

From this kinetic modelling it can be concluded that:

(i) On HMFI the hydrogen transfer responsible for diene formation (reactions 4 in Fig. 1) is the limiting step of propene aromatization. The rate constants of diene formation are indeed 10–100 times lower than the rates constants of olefin oligomerization (reactions 3), of diene cyclization (reactions 5) or of cyclic diolefin formation through hydrogen transfer (reactions 6). The formation of aromatics (reactions 7) is slightly faster than olefin oligomerization.

(ii) As previously proposed by Meriaudeau et al. [35,36], gallium species participate in the dehydrogenation of oligomers into dienes (reactions 4 in Fig. 1) and of cyclic olefins into aromatics (reactions 6 + 7). They do not catalyse the oligomerization–cracking steps (reactions 3) nor the diene cyclization (reactions 5). However like over HMFI the diene formation (reactions 4) is the limiting step of propene aromatization over Ga/HMFI.

(iii) On the Ga/HMFI used in this work gallium species participate for about 70% in diene formation and for about 25% in cyclic olefin aromatization (reactions 6 + 7), protonic sites being responsible for the remaining part. This confirms that the bifunctional aromatization of propene superposes itself on (and does not substitute for) the acid scheme.

(iv) On HMFI and on Ga/HMFI the formation of aromatics has two contrary effects on propene conversion. On one hand the aromatic formation causes an increase in the olefin conversion due to the olefin consumption, on the other, aromatics inhibit the olefin conversion because of their preferential adsorption on the acid sites [37–40].

2.1.2. *Kinetic modelling of propane aromatization over HMFI and over Ga/HMFI*

The kinetic model for propane aromatization was obtained by adding to the kinetic model developed for propene aromatization the protolytic cracking of propane and hydrogen transfer on the protonic sites (reactions 1 and 2, Fig. 1) and the alkane dehydrogenation on the gallium species. Moreover, so as to attain a good agreement between experimental and simulated data, it was necessary to introduce into the kinetic model two supplementary reactions catalyzed by gallium species:

1. cracking of propane into methane and ethylene
2. hydrogenation of olefins.

The first type of reaction was found to occur competitively with the dehydrogenation of propane on Ga_2O_3 [17]. This reaction was also

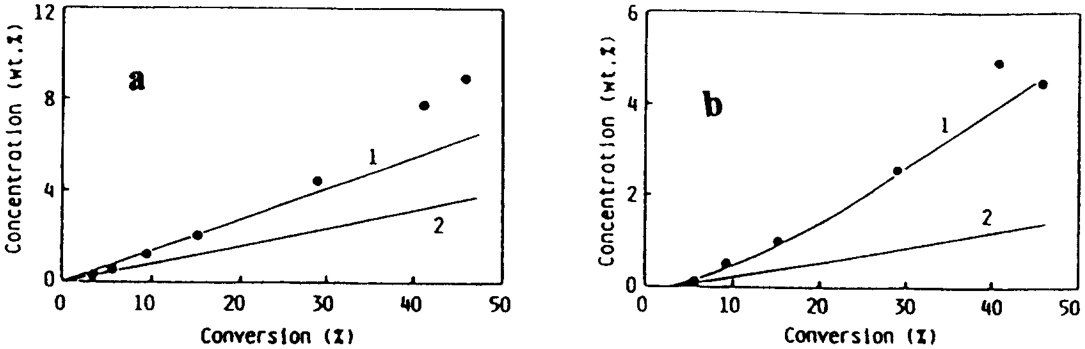
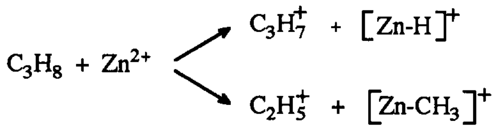


Fig. 3. Propane aromatization over GaHMFI. Experimental data (points) and calculated curves for the concentrations of methane (a) and ethane (b) as functions of propane conversion. Curves 1: final description, curves 2: methane and ethane formation considered to occur only on zeolite acid sites. From [28].

demonstrated in the case of Zn/HMFI catalysts and the following mechanism was proposed [23,12]:



The second type of reaction was also catalyzed by gallium species [34]. Indeed it has been shown that on a Ga_2O_3 sample pretreated under nitrogen at 600°C, hydrogenation of ethylene and propene at 530°C, $p_{H_2} = 0.9$ bar, $p_{\text{olefin}} = 0.1$ bar, occurred rapidly. However the lower the $p_{H_2}/p_{\text{olefin}}$ ratio the slower the hydrogenation. A positive value (0.6) was found for the reaction order with respect to hydrogen and a negative value (-0.7) for the order with respect to ethylene.

Fig. 3 shows the agreement between experimental data for methane and ethane formation during propane transformation over Ga/HMFI and simulated data when cracking of propane and ethylene hydrogenation over gallium species were, or not, considered. From this figure it is clear that both reactions participate in propane transformation. However, a discrepancy between simulated and experimental data was observed in methane formation at high propane conversion. This discrepancy, as well as another discrepancy observed in hydrogen formation, can be attributed to the hydrogenolysis of methyl substituted aromatics. This assumption is furthermore supported by recent results showing a significant hydrogenolysis activity of Ga/HMFI catalysts pretreated by hydrogen [31].

Besides the confirmation of the existence of cracking, hydrogenation and hydrogenolysis reactions on Ga species during propane aromatization on Ga/HMFI catalysts, kinetic modelling leads to the following important conclusions:

(i) Over HMFI there are two routes of propane activation: protolytic cracking of C–C and C–H bonds and hydrogen transfer between propane and carbenium ions resulting from the adsorption of product olefins on the zeolite protonic sites. On the HMFI used in this work the contribution of this second route to the overall propane transformation, zero at low conversion, is about 20% at conversions of 20–40%.

Propane transformation into olefins is the limiting step of aromatization. Indeed the rate constants of this transformation are at least 1000 times lower than the rate constants of diene formation (reactions 4, Fig. 1) which is the limiting step of propene aromatization.

(ii) Over Ga/HMFI, dehydrogenation of propane on the Ga species becomes the main route of propane activation: on the 4 wt% Ga catalyst used in this work more than 75% of propane activation occurs on the Ga species. Ga species contribute also to 90% of diene formation (reactions 4) and to more than 50% of aromatic formation (reactions 6, 7). This means that over this catalyst propane aromatization occurs through the following bifunctional scheme in which Ga species are mainly responsible for dehydrogenation steps and protonic sites for olefin oligomerization, cyclization and cracking

$$C_3 \overset{\text{Ga}}{\rightleftharpoons} C_{3=} \overset{H^+}{\rightleftharpoons} \text{Oligomers} \overset{\text{Ga}}{\rightleftharpoons} \text{Dienes}$$

$$\overset{H^+}{\rightarrow} \text{Cyclic olefins} \overset{\text{Ga}}{\rightleftharpoons} \text{Aromatics}$$

Like in the acid scheme, propane transformation into olefins (mainly into propene) is the limiting step of propane aromatization through bifunctional catalysis. Indeed this reaction remains much slower than all the steps involved in propene aromatization: oligomerization on the acid sites, dehydrogenation of oligomers into dienes on the Ga species, cyclization of dienes on the protonic sites and dehydrogenation of cyclic olefins on the Ga species.

2.2. *Is propane aromatization a conventional bifunctional process? What is the limiting step?*

Bifunctional redox–acid catalysts are employed in numerous processes in petroleum re-

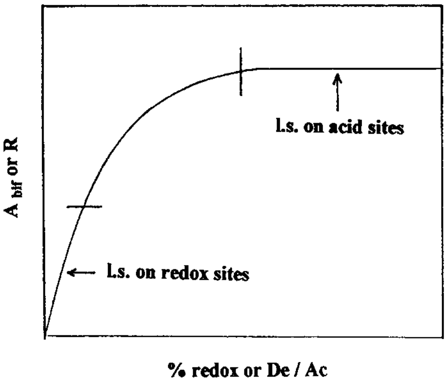


Fig. 4. Transformation through conventional bifunctional redox–acid catalysis. Influence of the percentage of the redox component on the bifunctional activity A_{bif} of physical mixtures or of *De/Ac* (the dehydrogenating/acid activity ratio) of physical mixtures on *R* the ratio between the bifunctional/acid activity: l.s., limiting step.

fining: hydrocracking, reforming, hydroisomerization of C_5–C_6 alkanes [41], etc., in petrochemicals: hydroisomerization of the C_8 aromatic cut [42,43] etc., in specialty or fine chemicals: e.g. synthesis of methylisobutylketone from acetone [44,45]. These bifunctional transformations involve successive chemical steps on redox sites: dehydrogenation, hydrogenation, etc., on acid sites: rearrangement, cracking, aldolization, dehydration, etc., and diffusion steps of intermediates from the redox to the acid sites and vice versa. Bifunctional catalysis of this type (with desorbed intermediates) can be demonstrated by using intimate physical mixtures of the monofunctional components with different concentrations [46,47]. A synergy effect is observed: i.e. the activities of the physical mixtures are definitely greater than the sum of the component activities. Moreover the activity of the mixtures per unit mass of the acid component A_{bif} changes with the percentage of the redox component as shown in Fig. 4: first, increase of A_{bif} proportionally to this percentage (limiting step on the redox sites) then a plateau for high percentage values (limiting step on the acid sites). This has been shown for various reactions: hydroisomerization and hydrocracking of C_{7+} alkanes [48], hydroisomerization of ethylbenzene [49], etc. and also for propane aromatization on Ga_2O_3-HMFI mixtures [18].

However this observation does not constitute a definite proof in favour of bifunctional catalysis. Indeed the catalytic properties of a monofunctional component can be modified by the other, either during the catalyst activation or during the reaction, which can lead to an apparently greater activity of the mixture. This type of complication exists in the case of GaHMFI catalysts: thus the pretreatment under hydrogen at high temperatures of Ga_2O_3/HMFI mixtures causes a decrease in the zeolite acidity and an increase in the dehydrogenation activity [50–61]. In this complicated case, the verification of the existence of a bifunctional process requires the determination, after pretreatment, of the acid and dehydrogenating activities of the physical mixtures. If propane aromatization occurs through a bifunctional scheme involving successive reactions on gallium species and on acid sites, a curve similar to that represented in Fig. 4 will be obtained if A_{bif} in ordinate is replaced by *R* (the ratio between the activity for propane aromatization and the acid activity) and the percentage of Ga_2O_3 in abcissa by *De/Ac*, the dehydrogenation/acid activity ratio. For low values of *De/Ac*, *R* must increase proportionally to *De/Ac* (dehydrogenation is the limiting step) while for very high values *R* must be constant (limiting step on the acid sites).

To verify this point, propane aromatization was carried out on HMFI (Si/Al = 44) and Ga_2O_3 (β Ga_2O_3 from Aldrich) and on five physical intimate mixtures of HMFI and Ga_2O_3 pretreated under nitrogen flow for 10 h at 600°C. With all the mixtures, aromatics appear as primary products (positive value of the initial slope of the curves giving the conversion into aromatics vs. contact time). With pure HMFI or gallium oxide the conversion into aromatics is very low. Moreover aromatics are not directly formed from propane (they are secondary products). The activities for propane transformation and for propane aromatization were determined from

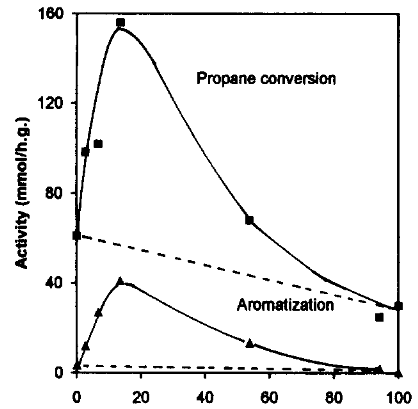


Fig. 5. Aromatization of propane on physical mixtures of Ga_2O_3 and HMFI pretreated under nitrogen at 600°C. Activity (mmol h^{-1} g^{-1}) for propane conversion and for propane aromatization as a function of the percentage of Ga_2O_3.

the initial slopes of the curves conversion vs. contact time. Fig. 5 shows that the activity of the mixtures is always greater than the sum of the component activities (dotted lines). The most active catalyst, i.e. the 13 wt% Ga_2O_3-87 wt% HMFI mixture is also the most selective towards aromatics: the highest value of the ratio of aromatics to undesired products (methane + ethane) is obtained.

The acid activity of the mixtures can be estimated from the initial rate of propane conversion into methane. Actually, methane results mainly from protolytic cracking of propane on the zeolite protonic sites which are also responsible for the catalysis of the acid steps of the bifunctional process. Moreover methane, contrary to ethylene which is simultaneously formed from propane cracking, does not undergo any secondary transformation. However the rate of methane formation gives only an approximate value of the acid activity for gallium oxide catalyzes also propane cracking [28,29]. Furthermore the dehydrogenating activity of the mixtures can be determined from the initial rate of propene formation. However the determination is rendered inaccurate because of the rapid secondary transformation of propene on the acid sites (reactions 3, Fig. 1).

That is why three model reactions were also used for characterizing the acid and dehydrogenating functions: *n*-heptane cracking and *m*-xylene isomerization at 350°C which are known to be catalyzed by protonic acid sites and methylcyclohexane transformation at 500°C. Methylcyclohexane undergoes two main reactions: cracking which is catalyzed by acid sites and aromatization which can occur either through hydrogen transfer on the acid sites or through dehydrogenation on the gallium species. Only an approximate value of the dehydrogenation

Table 1
Acid activity of HMFI and dehydrogenating activity of Ga_2O_3 in physical mixtures of Ga_2O_3 and HMFI pretreated at 600°C under nitrogen or under hydrogen flow

Ga_2O_3 (wt%)		0	2.7	6.7	13.4	53.8	94.1	100
		Acid activity (10^{-3} mol h^{-1} g^{-1} zeolite)						
$C_3 \rightarrow C_1$	N_2	10.9	10.3	8.6	11.5	8.9	18	
	H_2	7.8	5.7	6.3	6.9	1.7		
nC_7 cracking	N_2	25	25.7	26.8	28			
	H_2	25	13.3	7.5	5.8			
Mch cracking	N_2	50	43	42	44			
	H_2	60	58	37	28			
mX isomerization	N_2	30		32	35			
	H_2	36	24	16				
		Dehydrogenating activity (10^{-3} mol h^{-1} g^{-1} Ga_2O_3)						
$C_3 \rightarrow C_{3=}$	N_2		7800	5400	4800	130	25	11
	H_2		12500	9300	3900	290	15	5
Mch aromatization	N_2		670	130	160			3
	H_2		1900	850	350			3

nC_7, *n*-heptane; Mch, methylcyclohexane; mX, *meta*-xylene.

activity of the catalysts can therefore be obtained.

Table 1 shows that for all the catalyst mixtures the acid activity of the zeolite is practically unaffected by the presence of gallium oxide while the dehydrogenating activity of the gallium species is significantly increased by the presence of the zeolite. The smaller the percentage of gallium oxide in the mixture the greater the activity increase, this increase being more pronounced for propane than for cyclohexane dehydrogenation. The activity of gallium oxide in the catalyst with the lowest percentage of gallium oxide (2.7 wt%) is about 700 times higher than that of pure gallium oxide for propane dehydrogenation and 200 times for methylcyclohexane dehydrogenation.

Whatever the model reactions considered for estimating the acid and the dehydrogenating activities the ratio *R* between the aromatization and the acid activities is proportional to the dehydrogenation/acid activity ratio. Examples of this linear relationship are given in Fig. 6. Within the framework of a bifunctional mechanism, this means (Fig. 4) that propane aromatization is kinetically limited by a dehydrogenation step. This limiting step is most likely propane dehydrogenation (reaction 1, Fig. 1) as concluded from the kinetic modelling (part 2.1.1). The apparent direct formation of aromatics from propane is also in agreement with this conclusion.

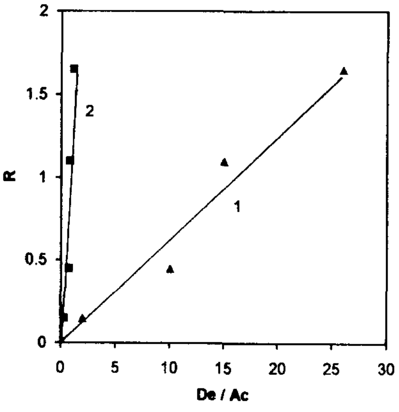


Fig. 6. Aromatization of propane on physical mixtures of Ga_2O_3 and HMFI pretreated under nitrogen at 600°C. *R* (aromatization/acid activity) versus *De/Ac* (dehydrogenation/acid activity). The acid activity is taken as the activity for *n*-heptane cracking, the dehydrogenating activity as the activity for propane dehydrogenation (curve 1) or for methylcyclohexane aromatization (curve 2).

Table 2
Dehydrogenating/acid activity ratio (*De/Ac*) of physical mixtures of Ga_2O_3 and HMFI pretreated under nitrogen or under hydrogen flow at 600°C. *De* is measured either for propane dehydrogenation (a) or for methylcyclohexane aromatization (b) and *Ac* for *n*-heptane cracking

Ga_2O_3 (wt%)		0	2.7	6.7	13.4	100
(a) *De/Ac*	N_2	1.6	10	16	27	∞
	H_2	1.3	29	93	110	∞
(b) *De/Ac*	N_2	0.35	0.7	0.7	1.2	∞
	H_2	0.4	4	8	13	∞

For the limiting step to be on the acid sites, hence the maximum activity (plateau in Fig. 4) obtained, it is necessary either to increase the dehydrogenating activity or to lower the acid activity. Both can be obtained by hydrogen pretreatment at high temperature. However although *De/Ac* is significantly increased (Table 2) *R* does not attain a plateau. This confirms the great difference between the rates of the facile acid reactions involved in the bifunctional propane aromatization (reactions 3, 5) and the rate of propane dehydrogenation (4 to 5 orders of magnitude) shown by kinetic modelling. It must be noted that the linear relation between *R* and *De/Ac* does not depend on the catalyst pretreatment (under nitrogen or under hydrogen) when *De* is determined from methylcyclohexane aromatization. Two different linear relations are found with *De* determined for propane dehydrogenation, the values measured after hydrogen pretreatment being most likely underestimated because of the very rapid secondary transformation of propene.

2.3. Conclusion

Kinetic modelling of propane aromatization on a 4 wt% Ga/HMFI catalyst allowed us to specify the respective roles of dehydrogenating species and of protonic acid sites in the various steps of this complex reaction system. Propane aromatization occurs mainly through a conventional bifunctional reaction scheme (with desorbed intermediates) in which the dehydrogenating gallium species are responsible for dehydrogenation of propane, of oligomers and of cyclic olefins and diolefins while protonic sites are responsible for oligomerization, cyclization and cracking. This bifunctional transformation is kinetically limited by propane dehydrogenation, another difficult step being oligomer dehydrogenation into diene. Unfortunately, gallium species catalyze also alkane cracking and hydrogenolysis as well as alkene (in particular ethene) hydrogenation with formation of the undesired products methane and ethane. The limitation of propane aromatization by the formation of propene is confirmed by the use of mixtures of Ga_2O_3 and HMFI with different concentrations, pretreated either under nitrogen or under hydrogen at high temperatures. Even for the highest values of the dehydrogenation/acid activities, the aromatization activity is proportional to the dehydrogenation/acid activity. Therefore an increase in the dehydrogenating activity should lead to more active and selective aromatization catalysts. Unfortunately, as shown with PtHMFI catalysts, this increase is generally accompanied by an increase in the rate of the undesired reactions of hydrogenation and hydrogenolysis.

3. Dehydrogenating Ga species

Gallium can be introduced into GaHMFI catalysts through different ways: impregnation with various salts, ionic exchange (as no exchange occurs this corresponds to ''wet'' impregnation), chemical vapor deposition [62–64], mechanical mixtures of Ga_2O_3 and HMFI, synthesis of MFI gallosilicates, etc. It is only in this latter case that Ga occupies tetrahedral framework positions. The dehydrogenating activity of extra framework Ga species and their positive effect on short-chain alkane aromatization are demonstrated by the use of mechanical mixtures of Ga_2O_3 and HMFI: Ga_2O_3 catalyzes the dehydrogenation of various hydrocarbons (propane, hexene, methylcyclohexene, etc. [18,35]) and increases the rate and selectivity of propane aromatization. As for extra framework gallium species can be created either during the synthesis of MFI gallosilicate or during their calcination and/or hydrothermal treatment (framework degalliation)[65–67], it is more difficult to conclude about the dehydrogenating activity of framework gallium. We have attempted to clarify this point by comparing the activities and the selectivities for propane aromatization of MFI gallosilicate samples pretreated at various temperatures [66,67].

Furthermore a synergy effect for dehydrogenation between Ga species and the protonic sites of HMFI is demonstrated (see for instance Table 1). This effect could be attributed to an increase in the dispersion of the gallium species and/or to a change in their nature (reduction) during hydrogen pretreatment or during the reaction (because of hydrogen production) with consequently an increase in their dehydrogenating activity. These changes would be facilitated by the zeolite acidity.

Two other proposals invoke the joint participation of gallium species and of the protonic sites in the dehydrogenation reaction [64]. In the first proposal, the activation of propane occurs on the gallium species. The protonic sites would facilitate either the desorption of propene [68] or the recombinative desorption of hydrogen [12] or both [69]. In the second one, propane activation occurs on the protonic sites of HMFI [70–74]. On this catalyst, the rate of propane dehydrogenation would be kinetically limited by the desorption of H adatoms whose removal implies cracking reactions. Ga species would act as ''porthole'' for the desorption of H adatoms in the form of H_2 thus allowing acid sites to dehydrogenate without cracking.

These hypothesis will be discussed in the light of the effect of hydrogen pretreatment of

Ga/MFI catalysts on their physicochemical and catalytic properties (3.2).

3.1. Is tetrahedral framework Ga active in dehydrogenation?

The activity and the selectivity for propane aromatization at 530°C of a MFI gallosilicate with a Si/Ga ratio of 30 (30 GaMFI) and of a MFI aluminosilicate (Si/Al = 30; 30 AlMFI) are very different: lower activity of GaMFI (7 times) but better selectivity to aromatics [66]. Both zeolites were pretreated at 530°C under air flow. On 30 GaMFI, since no extra framework Ga species are detected by ^{71}Ga MAS NMR, propane aromatization should occur like on 30 AlMFI through an acid mechanism provided however that framework Ga species are inactive for dehydrogenation steps. If this were the case, the differences in activity and selectivity between 30 GaMFI and 30 AlMFI would be due to differences in acidity (mainly in acid strength since the densities of acid sites are identical). However while the lower activity of 30 GaMFI could be related to the weaker strength of its acid sites this is not valid to explain the better aromatization selectivity which is most likely related to a dehydrogenation activity of Ga species.

Furthermore the ratio between the rates of

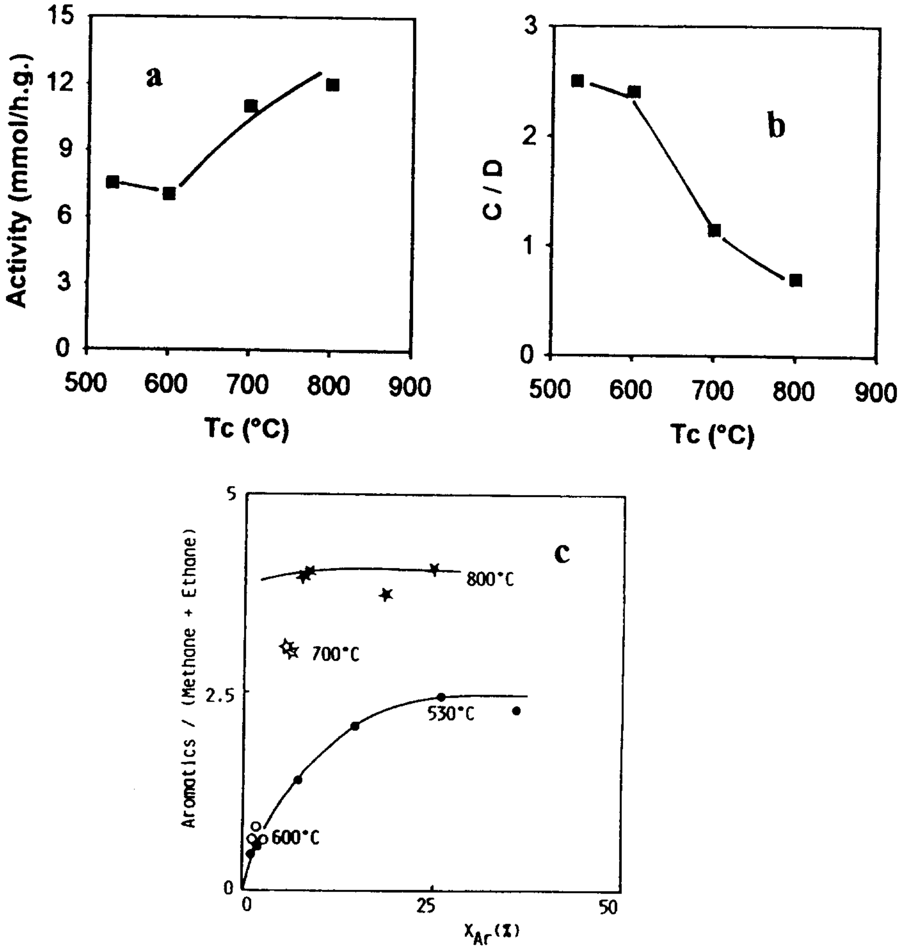


Fig. 7. Aromatization of propane on a MFI gallosilicate (Si/Ga = 30) calcined under air flow at various temperatures *Tc*. Influence of *Tc* on the activity for propane transformation (a), on *C/D* (the cracking/dehydrogenation rate ratio) at 10% conversion (b), on the mass aromatics/(methane + ethane) ratio at various propane conversions into aromatics X_{Ar} (c). Adapted from [66].

propane dehydrogenation and cracking C/D is initially lower with 30 GaMFI than with 30 AlMFI (1.7 instead of 2.5). This cannot be due to the weaker strength of the acid sites of 30 GaMFI for the limiting step of alkane dehydrogenation and cracking on the acid sites is most likely the formation of the carbonium ion through propane protonation [21,75,76]. From the C/D value it can be estimated that about 25% of propene is formed on the gallium species of 30 GaMFI and 75% on the acid sites [66].

However it is not possible to conclude definitely on the nature of the active gallium species. These active species could be the framework gallium or trace impurities of extra framework gallium created during the gallosilicate synthesis and too few to be detected by ^{71}Ga MAS NMR. Indeed the addition of extra framework gallium to 30 GaMFI (mechanical mixture or impregnation) increases significantly its activity for propane aromatization and dehydrogenation [14,34], which shows that extra framework gallium species are much more active than framework species.

Fig. 7a shows that the rate of propane transformation is identical at pretreatment temperatures Tc of 530 and 600°C and increases significantly at higher pretreatment temperatures. Likewise there are practically no differences in the selectivities of the samples pretreated at 530 and 600°C but there is a significant change at higher temperatures: decrease in the C/D ratio (Fig. 7b) and increase in the aromatics/(methane and ethane) ratio (Fig. 7c). These changes in activity and selectivity can be related to a degalliation of the framework. This degalliation causes a slight decrease in acidity shown in particular by the decrease in the rate of propane cracking. A decrease in this rate of less than 10% is found when Tc is increased from 530 to 800°C. This shows that the extraction of the gallium species from the framework is very limited, hence the amount of gallium extra framework species is very low ($<$ 10% of the Ga species).

These extra framework Ga species are highly active for dehydrogenation. Indeed after pretreatment at 800°C, the rate of propene formation is at least 5 times that found for $Tc = 530$ or 600°C and more than 85% of propene is formed on gallium instead of 25% for $Tc = 530$ or 600. This means that for $Tc = 800$°C the propene formation on gallium species is about 15 times faster than after pretreatment at 530 or 600°C. If we suppose that the dehydrogenating activity of gallium found for $Tc = 530$°C is due to the framework gallium it can be concluded that extra framework species are at least 150 times more active than the framework species. This means also that less than 1% of Ga extra framework impurities created during the synthesis could explain the differences in selectivity between the 30 GaMFI and 30 AlMFI samples and that framework gallium species are most likely inactive in dehydrogenation. The Ga extra framework impurities cannot be formed during the pretreatment since the dehydrogenating activity is the same for $Tc = 530$ and 600°C. Therefore these impurities result from gallosilicate synthesis.

3.2. *Influence of the pretreatment of Ga_2O_3/HMFI mixtures on the dehydrogenating properties. Nature of the dehydrogenating species*

The nature of the pretreatment gas (N_2 or H_2) has a significant effect on the activity and selectivity of the physical mixtures of Ga_2O_3 and HMFI. Large differences are also found in the acid and hydrogenating activities: (i) the synergy effect in dehydrogenation is more pronounced after H_2 pretreatment, (ii) after nitrogen pretreatment the acid activity of HMFI is not affected by the presence of gallium oxide while after hydrogen pretreatment this activity decreases significantly [30].

This decrease in activity was shown to be due to a neutralization of the zeolite protonic sites

$$Ga_2O + 2H^+Z^- \rightarrow 2Ga^+Z^- + H_2O$$

Ga_2O resulting from the reduction of Ga_2O_3

by hydrogen [50]. Ga_2O cannot be formed during nitrogen pretreatment, which explains that no decrease in acidity is observed.

As a synergy effect (although less pronounced than after hydrogen pretreatment) is found for the dehydrogenating activity of the Ga_2O_3/HMFI mixtures pretreated under nitrogen, Ga_2O and Ga^+ do not play a significant role in dehydrogenation.

A better dispersion of gallium oxide in the mixtures can no longer explain the synergy effect. Indeed after nitrogen pretreatment the activity of Ga_2O_3 in the mixture with 2.7 wt% Ga_2O_3 would be 700 times greater than that of pure Ga_2O_3 for propane dehydrogenation and 200 times for methylcyclohexane dehydrogenation. Such a difference in the accessible area between pure Ga_2O_3 and Ga_2O_3 in the mixture is impossible, all the more than the BET area of pure Ga_2O_3 is already equal to 40 m^2 g^{-1}. However the positive effect of hydrogen pretreatment (compared to nitrogen pretreatment) which is more limited (Table 1) could be due to an increase in the dispersion of gallium oxide [14].

Therefore the synergy effect in dehydrogenating activity is most likely due to a joint participation of the acid and gallium species in the dehydrogenation reactions. However, it is very difficult to discriminate between the two types of mechanisms proposed in the literature which differ mainly by the species responsible for propane activation: gallium species or protons. Indeed pure Ga_2O_3 as well as HMFI are active in propane dehydrogenation.

Within the framework of the first mechanism the protonic sites would increase the dehydrogenating activity of the gallium species by 2 to 3 orders of magnitude (Table 1). The lower the percentage of Ga_2O_3 in the mixture the greater the increase, which can be explained by a close proximity of the gallium species to the acid sites. Within the framework of the second mechanism the gallium species would increase the dehydrogenating activity of the protonic sites by one order of magnitude. This increase is maximum for a content of Ga_2O_3 between 6.7 and 13.4 wt% [30]. This maximum is unexpected for the acid sites must be the closest to the gallium species for catalyst mixtures rich in Ga_2O_3.

3.3. Conclusion

From the comparison of the catalytic properties of MFI gallosilicates calcined in dry air at various temperatures, it can be concluded that tetrahedral framework Ga does not participate in dehydrogenation reactions. Over the physical mixtures of Ga_2O_3 and HMFI (and probably over all the Ga/HMFI catalysts), dehydrogenation occurs through a mechanism involving the joint participation of gallium oxide and of protonic sites. The active gallium species would be rather Ga_2O_3 than Ga_2O. The mechanisms involving as first step the activation of propane on gallium oxide seem more likely than those involving propane activation on the protonic acid sites.

4. Deactivation of Ga / HMFI catalysts

The deposit of carbonaceous compounds (coke) inside the pores and/or on the outer surface of the crystallites is generally the main cause of deactivation of zeolite catalysts [77–79]. This is the case for alkane aromatization catalysts. The formation of coke was investigated during propane aromatization on a gallium impregnated HMFI catalyst. The composition of coke was determined, which allowed to establish the mode of coke formation. The deactivating effect of coke on the aromatization activity and selectivity as well as on the dehydrogenating and acid activities was measured.

The removal of coke through an oxidative treatment is the main step of the regeneration of zeolite catalysts [79]. The effect of gallium species on the rate of coke oxidation will be discussed.

4.1. Mode of coke formation

Due to the high temperature of propane aromatization (> 500°C) the coke formed is very polyaromatic and the distribution of its components cannot be obtained. That is why the composition of coke was determined for a large range of temperatures (250–530°C) during the aromatization of propene which is much more reactive than propane. This reaction was carried out on a HMFI zeolite (Si/Al = 40) and on a Ga/HMFI catalyst (2 wt% of Ga) prepared by impregnation of the HMFI zeolite with a $Ga(NO_3)_3$ solution and pretreated under nitrogen at 530°C. The operating conditions were: $P_{\mathrm{propene}} = 1$ bar, WHSV (weight of reactant injected per weight of catalyst and per hour) equal to 1.7 h^{-1}.

The higher the temperature the greater the initial conversion of propene into aromatics, this conversion being always greater on Ga/HMFI than on HMFI. With both catalysts, the total conversion of propene and specially the conversion into aromatics decrease with increasing time-on-stream. This deactivation can be related to a blockage by coke deposit of the access of the reactant to the zeolite pores. Indeed coke has the same effect on the capacity for nitrogen adsorption as on the rate of aromatization [30].

The initial rate of coking does not depend on the catalyst. But whatever the temperature the ratio between the rates of coking and of aromatization is greater with HMFI than with Ga/HMFI. The lower ratio found with Ga/HMFI could be related to the formation of hydrogen by dehydrogenation of oligomers or of naphthenes. This hydrogen activated by gallium species could limit the concentration of carbocations involved in the condensation reactions of coke formation. Furthermore this effect of activated hydrogen has been demonstrated in toluene transformation on zeolite catalysts [80]. For both catalysts a minimum in the initial rate of coking is observed at a reaction temperature of 400–450°C. This minimum is due to the fact that coking is determined by two parameters: the rate of the reactions involved which increases with temperature and the facility of retention in the pores of coke molecules which decreases with the temperature [79].

Gallium has practically no effect on the coke composition. As generally observed this composition depends very much on the coke content and on the reaction temperature [81]. Thus at 250°C, whatever the coke content, coke (after dissolution of the catalyst in a hydrofluoric acid solution) is totally soluble in methylene chloride. At 350°C the insoluble coke results from the secondary transformation of the molecules of coke soluble in methylene chloride (initial slope of formation equal to zero). At 400 and 450°C a large part of the insoluble coke appears as a primary product, the remainder resulting from the secondary transformation of the soluble coke (plateau in the percentage of soluble coke, increase in the selectivity to insoluble coke over 6% coke. At 530°C the coke is totally insoluble in methylene chloride.

For a coke content of about 10%, coke formed at 250°C is constituted of C_{13}–C_{24} hydrocarbons presenting two unsaturations + one cycle (general formula: C_nH_{2n-4}), of C_9–C_{15} alkylbenzenics (C_nH_{2n-6}) and of traces of C_{11}–C_{15} naphthalenes (C_nH_{2n-12}). At 350°C the soluble coke comprises C_{11}–C_{15} alkynaphthalenes, C_{14}–C_{19} alkyfluorenes (C_nH_{2n-16}) and C_{15}–C_{19} alkylanthracenes and/or phenanthrenes (C_nH_{2n-18}). At 400 and 450°C alkylfluorenes are accompanied by C_{17}–C_{24} alkylpyrenes (C_nH_{2n-22}) and by more unsaturated compounds (C_nH_{2n-34} and C_nH_{2n-38}) which present most likely the following "linear" structures.

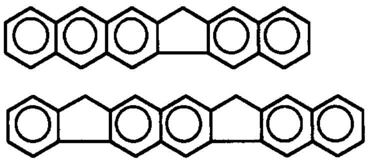


Fig. 8 shows as an example the change with the coke content of the amounts of the various soluble coke components found at 450°C with HMFI or GaHMFI. Alkylfluorenes (C_nH_{2n-16}) and alkylpyrenes (C_nH_{2n-22}) appear as primary products, the bulkier and the more polyaromatic compounds (C_nH_{2n-34} and C_nH_{2n-38}) as secondary products [82].

The change with coke content in the distribution of all the coke components shows that at high reaction temperatures ($\geq$ 400°C) there are two modes of growth of the coke molecules. The first mode is the classical one which involves a succession of alkylation, cyclization and hydrogen transfer on the acid sites (and dehydrogenation with Ga/HMFI) steps. This mode is responsible for the formation of the soluble aromatic molecules such as alkylnaphthalenes, fluorenes, anthracenes, phenanthrenes, pyrenes and for the formation of a large part of the insoluble coke. The second one whose existence was recently demonstrated in the case of dealuminated HY zeolites [83] is the dehydrogenative coupling of polyaromatic molecules. This second mode is most likely responsible for the formation of the very polyaromatic "linear" molecules (C_nH_{2n-34} and C_nH_{2n-38}) from alkylnaphthalene and alkylfluorene molecules and for the formation of part of the insoluble coke.

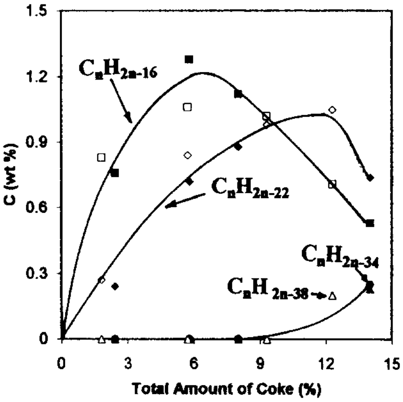


Fig. 8. Formation of coke on HMFI (open symbols) and Ga/HMFI (filled symbols) during propene transformation at 450°C. Percentages of soluble coke components versus the total amount of coke.

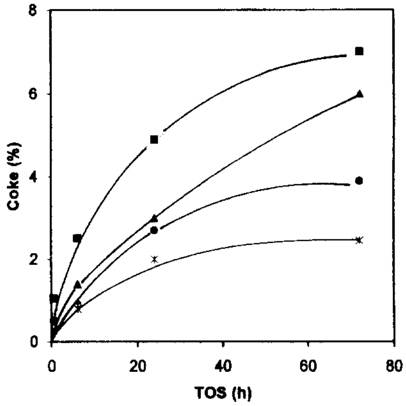


Fig. 9. Formation of coke as a function of time-on-stream (TOS) during propane aromatization at 530°C on HMFI and Ga/HMFI pretreated at various temperatures under nitrogen or under hydrogen. HMFI, 530°C, N_2 (Δ); Ga/HMFI, 530°C, N_2 (□); Ga/HMFI, 530°C, H_2 (○); Ga/HMFI, 600°C, H_2 (∗).

The soluble coke molecules and the very polyaromatic molecules of the insoluble coke formed through the second mode are most likely located inside the linear channels of the HMFI zeolite. On the other hand most of the insoluble coke molecules formed through the alkylation–cyclization–hydrogen transfer (or dehydrogenation) mode result from the growth of coke molecules trapped at channel intersections close to the outer surface of the zeolite crystallites with overflow onto this surface [78].

The formation of coke was also investigated during propane aromatization at 530°C. Contrary to what was observed during propene aromatization for pretreatment under nitrogen flow at 530°C the rate of coking is greater with GaHMFI than with HMFI. However the pretreatment under hydrogen which increases the aromatization rate and selectivity causes a significant decrease in coking. The higher the pretreatment temperature the lower the coking rate (Fig. 9) and the coking/aromatization rate ratio. This effect of hydrogen pretreatment can be explained by a better dispersion of the gallium species hence by a decrease in the concentration of coke precursors by hydrogenation on these species. At this high reaction temperature coke is very polyaromatic and can be characterized only by its H/C ratio. This H/C ratio is practically identical on HMFI and GaHMFI catalysts, decreasing from 0.5 to 0.4 when the coke content increases.

4.2. *Influence of coke deposit on the catalytic properties of GaHMFI*

Methylcyclohexane transformation at 450°C was used to determine the effect of deactivation of the Ga/HMFI catalyst during propene transformation at 450°C on its acid and on its dehydrogenating activities. Both functions are deactivated (decrease in the cracking and aromatization rates) and practically to the same extent: indeed the cracking/aromatization rate ratio is close to 5 whatever the methylcyclohexane conversion and whatever the degree of catalyst deactivation.

It was concluded above that the deactivating effect of coke on propene aromatization was due to the blockage of the access to the interior sites. The fact that coke affects to the same extent the dehydrogenating and the acid activities could therefore be interpreted by supposing that the active gallium species are located inside the zeolite pores. However as it has been shown that the dehydrogenating activity of gallium species was considerably increased by the proximity of acid sites another interpretation could be that coke deposits limit the interaction between acid sites and gallium species.

Identical conclusions can be drawn from methylcyclohexane transformation on the same Ga/HMFI catalyst deactivated during propane transformation at 530°C. In agreement with this identical effect of coke on the acid and dehydrogenating functions the cracking/dehydrogenation rate ratio of propane measured at identical propane conversion does not change with time-on-stream (hence with catalyst deactivation). Meriaudeau and Naccache [84], from the results obtained during propane aromatization on a Ga impregnated MFI with a Si/Al ratio of 14 concluded differently. With their sample they observed a decrease in the selectivity to C_1 (and to aromatics) when increasing time-on-stream. From the decrease in C_1 selectivity they concluded that coke deactivated more the acid function than it did the dehydrogenating function. However in their experiment the selectivity was not determined at isoconversion and its decrease could be attributed to the decrease in conversion due to coking rather than to a preferential deactivation of the acid function [82].

4.3. *Removal of coke through oxidative treatment*

The removal of coke from HMFI and GaHMFI samples coked during propane aromatization at 530°C was carried out with pure oxygen in a fixed bed reactor with stepwise programmed temperature in the range of 25 to 550°C [30]. Whatever the catalysts the rate of coke removal is practically independent of the coke content and of the hydrocarbon used for aromatization but is higher with GaHMFI than with HMFI as already shown by Kwak and Sachtler [63]. Furthermore the removal of coke is easier when GaHMFI is pretreated under hydrogen at 600°C instead at 530°C under nitrogen (Fig. 10), which can be related to a better dispersion of gallium species or to the closer

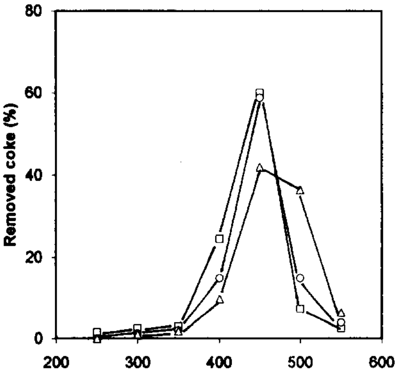


Fig. 10. Oxidation of HMFI pretreated under nitrogen (△) and of Ga/HMFI samples pretreated under nitrogen (○) or under hydrogen (□), coked at about 7 wt% during propene aromatization. Normalized amounts of carbon evolved as $CO + CO_2$ versus the oxidation temperature.

proximity of these species and of the coke deposits. It can therefore be concluded that gallium species participate in coke oxidation.

4.4. Conclusion

Aromatization of propane is accompanied by the formation of coke in the pores of the zeolite and/or on the outer surface of the crystallites. This coke causes a blockage of the access to the protonic sites of the zeolite which is responsible for the catalyst deactivation. Deactivation affects to the same extent the acid and dehydrogenating functions for, as shown in part 3, dehydrogenating active sites of GaHMFI are constituted of gallium oxide and of protonic sites. The mode of coke formation was established from the composition of coke formed during propene aromatization between 250 and 530°C. The presence of gallium does not affect the coke composition. Coke formation occurs through a succession of alkylation, cyclization and hydrogen transfer steps on the acid sites, these latter being partially replaced by dehydrogenation steps with GaHMFI catalysts. Dehydrogenative coupling of aromatics is also involved.

Whatever the conditions of pretreatment of GaHMFI catalysts Ga decreases the coking/aromatization rate ratio and increases the rate of coke oxidation. Both effects are more pronounced for GaHMFI pretreated at 600°C under hydrogen because of the better dispersion of the Ga species.

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