CATAL. REV.—SCI. ENG., 36(2), 271–304 (1994)

Transformation of LPG into Aromatic Hydrocarbons and Hydrogen over Zeolite Catalysts

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Key Words: Bifunctional mechanism; Cyclar process; Ga/zeolites; Gallo- and galloaluminosilicates; LPG aromatization; Reaction mechanism; Reaction pathway.

I. INTRODUCTION

A way to increase the value of LPG cut from petroleum feedstocks is its direct transformation to H_2 and aromatic products; these aromatic products, BTX—essentially benzene (B), toluene (T), and C_8-aromatics (X)—can be used as raw material for the petrochemical industry or as a blending mixture to enhance the octane number of gasoline. However, these transformations require high temperatures. Thermodynamic data show that the conversion of paraffins into aromatics is favored by increasing the length of the chain, and that aromatics are favored in relation to olefins (Table 1) [1, 2]. Whereas aromatization of propane and higher paraffins can be carried out at temperatures lower than 500°C, transformation of ethane, and especially that of methane, requires much higher temperatures. This is experimentally supported by the transformation of various hydrocarbons, at constant temperature and space velocity. For instance, over H-[Al]-ZSM-5, butane and isobutane react four times faster than propane and 100 times faster than ethane [3].

Earlier studies on aromatization of paraffins were carried out by Csicsery in 1970 and were called dehydrocyclodimerization of alkanes [4–9]. The main reaction product was obtained from the dehydrogenation and subsequent cyclodimerization of paraffin. Thus, xylenes were the main products obtained from butanes. The other aromatic hydrocarbons were pro-

TABLE 1

Thermodynamics of Conversion of Paraffins into Aromatics and Alkenes: Temperature (°C) to Achieve $\Delta G_R = 0$

	To aromatic	To olefin	
Methane	1075	1350	Ethylene
Ethane	575	774	Ethylene
Propane	450	665	Propylene
Hexane	320	575	Isohexene

From Refs. 1 and 2.

duced in much lower quantities. These transformations were carried out in the absence of hydrogen and using bifunctional catalysts containing an acidic function (alumina) and a dehydrogenating function (Pt, Pd, Cr, Mo, Mn, V, and W oxides). However, the process required high temperatures (~550°C), produced great quantities of methane and ethane, and presented a high rate of coke formation which reduced the time of the reaction to 90 min only. All these facts, together with the low selectivity toward aromatics (~30%) significantly lowered the profitability of the process.

With the discovery of medium-pore zeolites by Mobil Oil Co., especially those MFI-type zeolites (ZSM-5), these solids began to be used in the study of processes involving reactions of paraffin aromatization. Their use in these reactions was due both to the size of the pores and to their low density in acid sites (ratio $Si/Al > 10$), factors which significantly reduce the deactivation rate of catalysts by coke formation [10].

Chen [11] and Cattanach [12], from Mobil Oil Co., reported for the first time the use of [Al]-ZSM-5 zeolites for aromatization of C_5-C_7 liquid paraffins. Moreover, in these works reference was made to the addition of promoters (in this case, Zn^{2+} ions) which led to more selective transformations. Later, these same Zn/H-[Al]-ZSM-5 catalysts were successfully used in the aromatization of C_3-C_4 light paraffins [13]. An example of this transformation is shown in Table 2 [14], in which the effect of the addition of zinc ions on the activity and selectivity of the reaction is pointed out. Then, Davis and Kolombos [15], from British Petroleum Co. (BP), found that both the conversion and the selectivity of the reaction could be significantly increased, if H-[Al]-ZSM-5 was exchanged and/or impregnated with Ga^{3+} ions. This can be observed in Table 3 [16], which shows that,

TABLE 2

Conversion of Propane over H-[Al]-ZSM-5 and Zn/H-[Al]-ZSM-5: $T = 500°C$; $p = 1$ bar; WHSV $= 0, 18\ s^{-1}$

	H-[Al]-ZSM-5	Zn/H-[Al]-ZSM-5
Conversion (%)	25	35
Methane	19	6
Ethylene	5.9	1
Ethane	20	14
Propylene	0.3	Traces
C_4 + aliphatics[a]	8	Traces
Benzene	4.8	17
Toluene	14	25
Xylenes	12	21
C_{9+}[b]	16	16

From Ref. 14.

[a] Mainly alkanes.

[b] Benzenic aromatics, naphthalene, methylnaphthalenes, and dimethylnaphthalenes.

TABLE 3

Aromatization of Propane over H-[Al]-ZSM-5 and Ga/H-[Al]-ZSM-5 at Three Temperatures: $p = 1$ bar; N_2/propane = 4; WWH = 2 h^{-1}

	H-[Al]-ZSM-5			Ga/H-[Al]-ZSM-5		
	450°C	500°C	600°C	450°C	500°C	600°C
Conversion[a] (%)	1.1	4.0	34.1	2.0	7.6	49.6
Methane	14.4	19.1	25.3	9.4	13.0	18.8
Ethane	9.4	11.6	19.7	6.1	7.1	13.4
Ethylene	29.4	28.6	12.9	11.9	12.1	6.5
Propylene	11.1	17.9	11.0	19.8	14.1	6.5
Isobutane	29.4	8.4	0.8	14.8	5.8	0.7
n-Butane	3.8	6.4	1.4	8.6	6.9	1.4
Isobutene	0.9	1.8	1.1	2.0	1.6	0.5
n-Butene	0.8	2.5	1.4	2.6	2.2	0.8
C_5 + aliphatics	0.8	2.3	0.9	3.2	2.5	0.4
Aromatics	0.0	1.4	25.5	21.6	34.7	51.0

From Ref. 16.

[a] Obtained by changing space velocity after the deactivation of the catalysts.

regardless of the reaction temperature, the catalyst promoted with gallium ions is always more active and selective toward BTX than the acidic zeolite.

This finding by BP, properly combined with the technology of continuous catalyst regeneration by Universal Oil Products, led to the Cyclar process for conversion of paraffins C_3-C_4 into aromatics and hydrogen [17–20]. A demonstration unit, with a transformation capacity of 1000 bbl/day, entered into service by the end of 1989 in the refinery of BP in Grangemouth, Scotland, and closed down by the end of 1991.

Gallium-promoted zeolites are preferred to the zinc-promoted ones. One of the greatest disadvantages of these latter catalysts is the fact that under conditions of paraffin conversion, zinc is eluted from the catalyst. The elution is produced by the reduction of the zinc oxide into metal, due to the strong reducing action of hydrogen and carbon, two products formed during the aromatization reaction [1]. Given the low melting point and boiling point of zinc, the promoter volatilizes from the catalyst.

Other processes have been proposed for the conversion of LPG into aromatics.

- The M-2 forming process by Mobil Oil Co., which uses a purely acidic H-[Al]-ZSM-5 catalyst [21, 22]. Even though it is very stable compared to other acid supports, H-[Al]-ZSM-5 is deactivated by the formation of coke, which means that aromatics production requires a cyclic process. Although this process has been invoked for LPG aromatization, it seems to be more interesting for the production of high octane number products from pyrolysis gasoline and paraffinic naphthas [22]. Since dehydrogenation reactions take place by hydride transfer reactions, aromatization of LPG over H-[Al]-ZSM-5 limits the production of aromatics and significantly reduces hydrogen production in the process, which (as will be noted in the Cyclar process) is one of the products whose production economically justifies the implementation of the process.

- The Aroforming process, recently developed by IFP and Salutec, has been reported to aromatize a wide range of aliphatic hydrocarbons, either LPG or light naphthas [23, 24]. The catalyst used is a shape-selective zeolite doped with metal oxides. It is reported that for LPG conversion, the product distribution is close to that obtained with the Cyclar process.

II. CYCLAR PROCESS

The Cyclar process is a very attractive technology for the production of aromatics, since it uses a low-value product as LPG and, without previous treatment, transforms it into aromatics and hydrogen which do not need subsequent purification. Although the transformation requires some exothermic steps, the predominance of dehydrogenation reactions causes the total reaction to be highly endothermic.

The process basically consists of three sections (Fig. 1): reactors, regeneration, and product recovery sections [17–20]. The reactor section was designed to continuously produce aromatics and hydrogen from LPG. The reaction is carried out in a series of adiabatic stacked reactors, to facilitate the continuous catalyst circulation to and from the regeneration section. The catalyst flows by gravity from one reactor to the next. From the last reactor, the catalyst is transferred, by lift gas, to the regeneration section, where it flows by gravity. Finally, the regenerated catalyst is transported by lift gas to the top of the first reactor. The regeneration section uses carefully controlled conditions to continuously restore fresh catalyst. Feed consists of LPG and recirculated unconverted reactants. In the product recovery section, effluents are compressed and separated into hydrogen (95% pure), light by-products (basically methane and ethane), unconverted feed (to be recycled), and aromatic products. The average catalyst life is expected to be about 2 years.

Yield in aromatics and hydrogen is virtually independent of reactor feed. For a charge with 100% of butane, yield in BTX and H_2 is 65.9 and 5.2 wt%, respectively, of fresh feed. For 100%-propane feedstock, yield in BTX is 63.1 wt%, whereas H_2 is 5.9 wt%. In both cases, fuel gas by-product contains about 75 mol% of methane and 25 mol% of ethane. Liquid products are almost exclusively aromatics. This fraction contains about 95% of BTX (Fig. 2), which gives it great value as a source of benzene, toluene, and *para*- and *ortho*-xylenes.

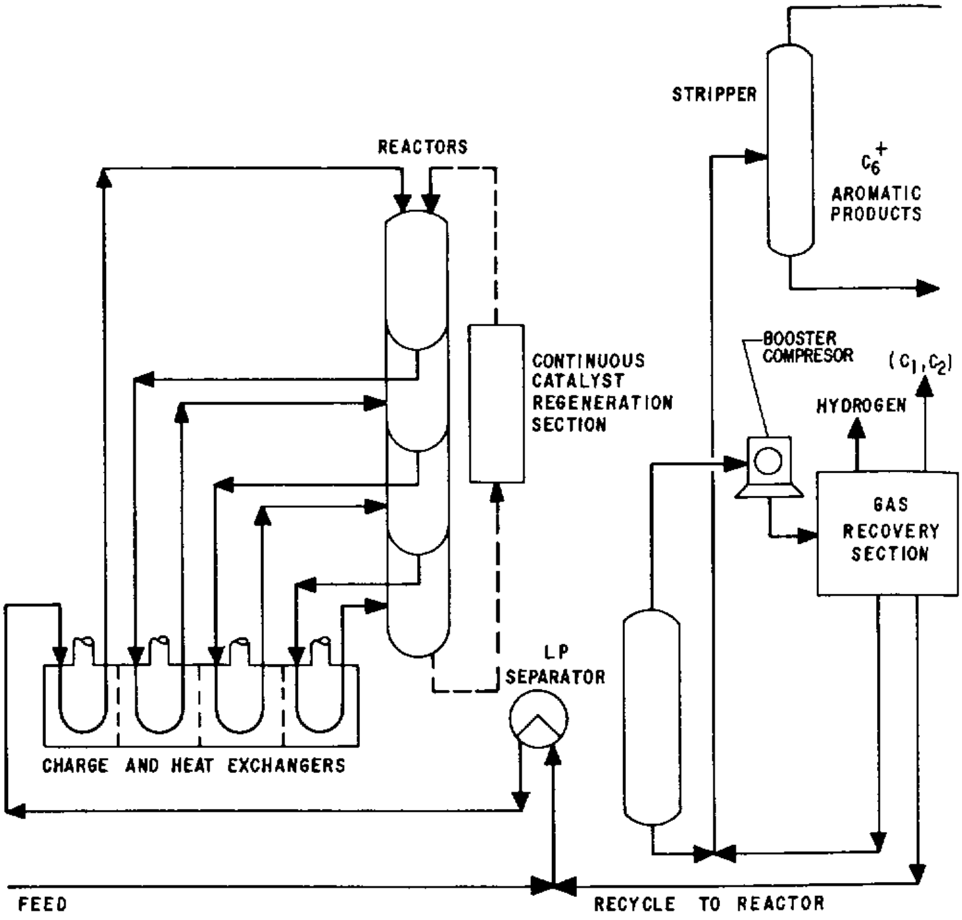


FIG. 1. Flow diagram of the Cyclar process for LPG aromatization (from Refs. 19 and 20).

Benzene product, recovered through conventional fractionation, has a freezing point of 5.4°C, and can be marketed or processed without further extraction. Alternatively, aromatic fraction may be used as an additive to increase the octane number of gasolines, since liquid products from Cyclar process have a research octane number (RON) between 111 and 113, a motor octane number (MON) between 100 and 103, a density about 0.89, and a relatively low vapor pressure of 0.7–1.6 psia [19, 20].

An idea of the process profitability can be obtained through the following data [20]. If a barrel of oil costs $15–20, LPG price will be ~$110/t (110 dollars per tonne or $2.75/million Btu), that of BTX $200–300/t, hydrogen, $300–700/t, and in the case of light by-products (methane and ethane) $110/t. Prices of BTX and hydrogen will be determined by the use these products will have. An economic analysis leads to the conclusion that a plant processing 15,000 barrels equivalent per day of LPG will recover its investment within a period of 2–5 years [20].

III. REACTION PATHWAY AND MECHANISM OF PROPANE AROMATIZATION OVER ACIDIC AND OVER BIFUNCTIONAL CATALYSTS

A. *Reaction Pathway*

The aromatic product distribution obtained from transformation of propane and butane over Ga/H-[Al]-ZSM-5 is basically the same, with toluene being the main product (Fig. 2). This means that aromatization reaction over these zeolitic catalysts does not take place due to a mere dehydrocyclodimerization such as that observed by Csicsery [4–9]. At this point, it is necessary to pose some questions:

How is paraffin aromatization really carried out? What is the reaction pathway?
Why do promoters such as gallium and/or zinc increase activity and selectivity of the reaction?
What is the nature of these active species? Are they framework or extraframework species?

To answer these questions we can start by analyzing the evolution of the various products of the propane aromatization reaction as a function of the conversion degree obtained by changing space velocity (Fig. 3). Note that over the acidic catalyst H-[Al]-ZSM-5 as well as over the acidic catalyst

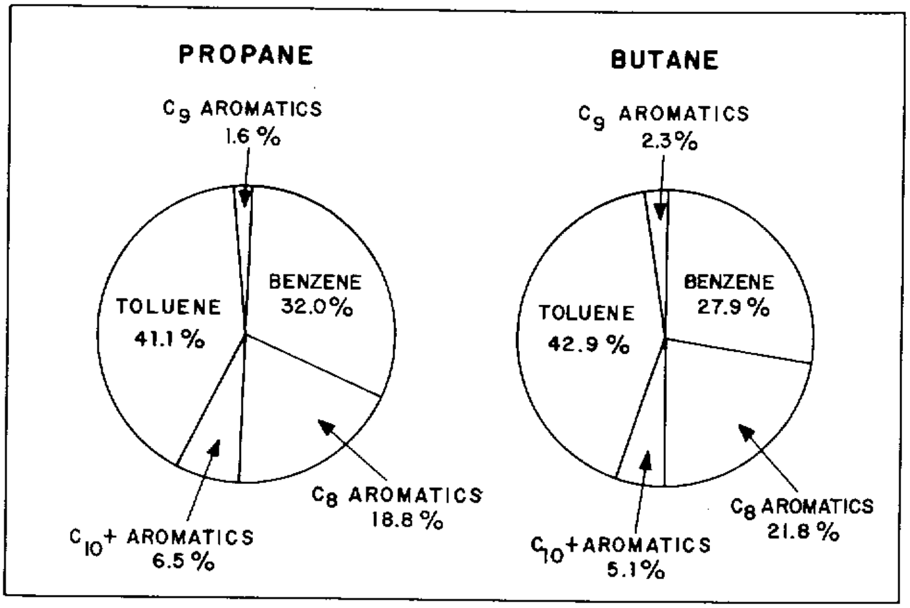


FIG. 2. Distribution of aromatics obtained from transformation of propane and butane (from Refs. 19 and 20).

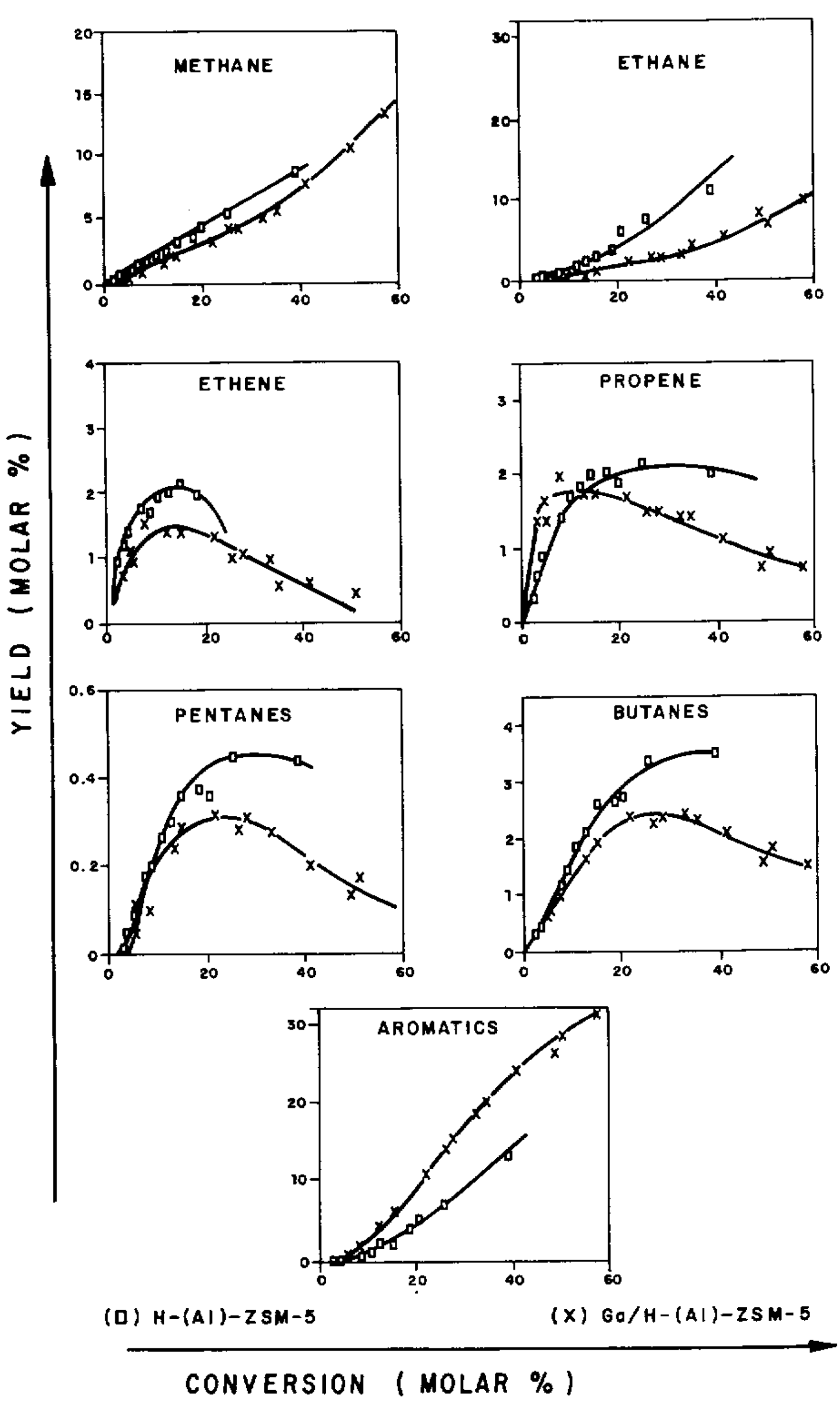


FIG. 3. Evolution of various products of the reaction of propane aromatization as a function of the conversion obtained by varying space velocity at 530°C (from Ref. 16).

Ga/H-[Al]-ZSM-5, which is impregnated and/or exchanged with gallium ions, this evolution shows that:

a. Methane, ethylene and propylene are primary products (at low conversions they are strongly prevailing).
b. Light olefins (ethylene and propylene) and C_4 and C_5 hydrocarbons are transition products (they are initially important but then decrease as conversion increases).
c. Aromatic hydrocarbons and ethane are secondary products (they are virtually nonexistent at low conversions and progressively increase as conversion level increases).

Moreover, an analysis of aromatic product distribution indicates that

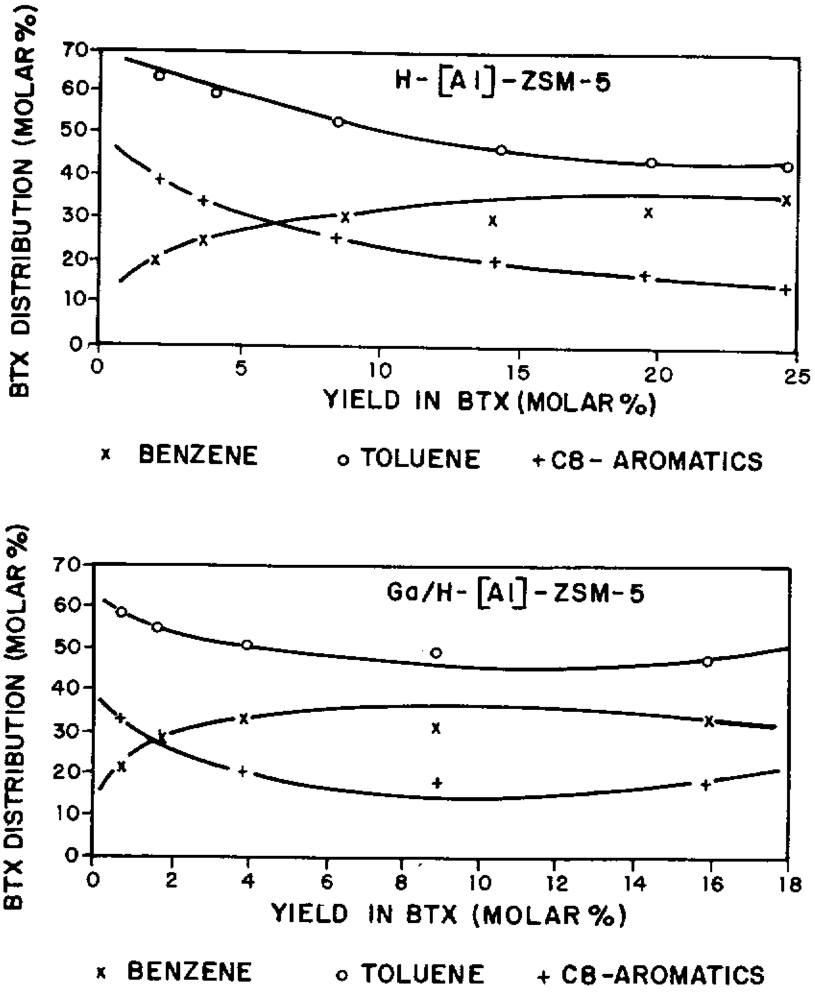
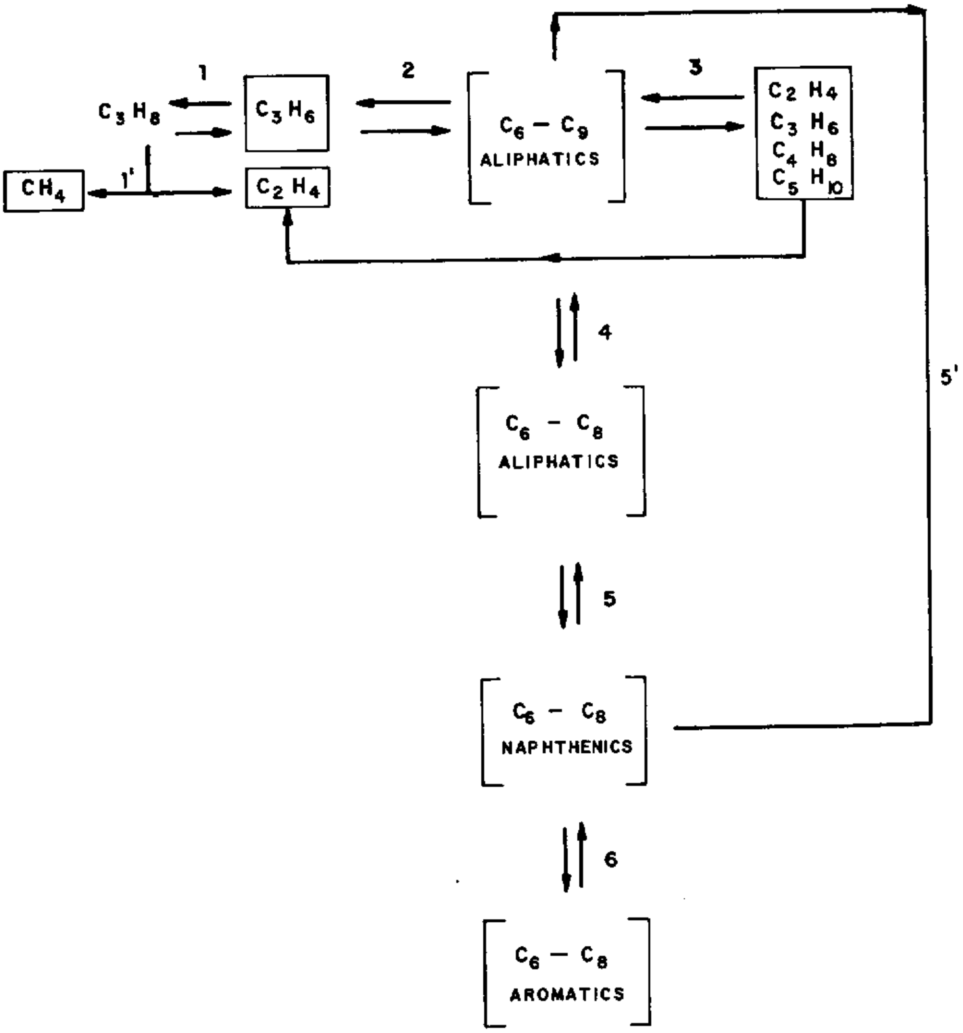


FIG. 4. Evolution of the aromatic product distribution as a function of the yield in BTX obtained at 530°C by varying space velocity (from Ref. 16).

the initial formation rates of toluene and C_8 aromatics are higher than the formation rate of benzene (Fig. 4), its formation being the priority if the aromatization reaction of propane takes place through a mere dehydrocyclodimerization reaction.

This evidence shows that the reaction pathway for propane aromatization is carried out through the following steps (Scheme 1):

a. Olefin formation, through dehydrogenation to propene and/or through cracking to methane and ethene (steps 1 and 1′ in Scheme 1).
b. Oligomerization of olefins and subsequent cracking (olefin interconversion) (steps 2 and 3).
c. Formation of new oligomers through olefin alkylation (step 4).



SCHEME 1. Reaction pathway of propane aromatization.

d. Cyclization (steps 5 and 5′).
e. Aromatization (step 6).

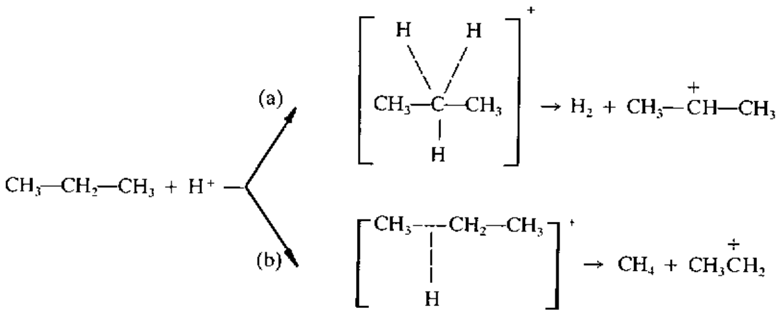
This kind of reaction pathway means that such transformation are better defined as a dehydrocycloligomerization reaction [25]. Cracking steps of oligomers (step 3) and subsequent reoligomerization (step 4) are absolutely necessary to explain distribution of aromatic products as well as their independence of the feedstock used [19, 20]. Although gallium addition to a H-[Al]-ZSM-5 zeolite has virtually no affect on aromatic product distribution (Fig. 4), Ga/H-[Al]-ZSM-5 is much more selective toward aromatics (Fig. 3). This increase in BTX is accompanied by a reduction in C_1 and C_2 fractions. Besides, Ga/H-[Al]-ZSM-5 is more active than acidic catalyst (Table 4).

B. *Differences in Activity between H-[Al]-ZSM-5 and Ga/H-[Al]-ZSM-5 Catalysts*

Differences in reaction rate observed between H-[Al]-ZSM-5 and Ga/H-[Al]-ZSM-5 can be attributed to differences in the mechanism of propane activation.

1. *Propane Activation over Acidic Catalyst*

Over acidic catalyst this activation is probably carried out through protonation of propane formula (1) [26]:



(1)

These carbonium ion intermediates, first proposed by Olah [27], in the

TABLE 4

Aromatization of Propane over H-[Al]-ZSM-5 and Over Ga/H-[Al]-ZSM-5 Catalyst: $T = 530°C$; $p = 1$ bar; N_2/propane = 4; WWH = 2 h^{-1}

	H-[Al]-ZSM-5	Ga/H-[Al]-ZSM-5
Conversion (%)[a]	12	85

From Ref. 45.
[a] Initial molar conversion, extrapolated at $t = 0$.

transformation of alkanes in superacid media, explain the formation of equimolar amounts of propene and hydrogen, on one hand, and of methane and ethylene, on the other. As happens in the superacid media [28], over H-[Al]-ZSM-5 [29, 30], cracking (b) is faster than dehydrogenation (a). Regardless of the zeolite framework composition, the cracking/dehydrogenation rate ratio is always close to 2.5 [3]. Moreover, this ratio is independent of the temperature, because the apparent activation energy is equal to 34 kcal mol^{-1} for both reactions [30]. According to Guisnet [3a], the facts that cracking is faster than dehydrogenation and that the cracking/dehydrogenation rate ratio is independent of the temperature show that the formation of the pentacoordinate carbonium ions is the limiting step of the aromatization reaction.

2. *Propane Activation over Ga/H-[Al]-ZSM-5 Catalyst*

For the gallium-based catalyst, three assumptions have been proposed:

- The assumption by Ono and co-workers [31] suggests that the steps of propane activation and formation of oligomeric intermediates take place, as in H-[Al]-ZSM-5, on protonic sites of zeolite. Gallium species would not play any role in the activation of propane (step 1, Scheme 1). They only participate by catalyzing dehydrogenation reactions of oligomeric olefinic intermediates, thus favoring their aromatization at the expense of their cracking. According to these authors, increase in reaction rate is barely apparent and it is due to an increase in the aromatization rate of olefinic intermediates, at the expense of their cracking. Since propane is one of the prevailing products in this cracking (it can be formed through the transference of a hydride from an olefinic intermediate to an adsorbed $C_3H_7^+$), modification of zeolite with these metal ions (Ga^{3+} or Zn^{2+}) diminishes its regeneration rate.
- The assumption by Inui [32], Le Van Mao, and co-workers [33–36] and Iglesia et al. [37] points out that gallium species would have no dehydrogenation activity and that their role would be to remove the hydrogen species released by the zeolite acid sites (hydrogen back-spillover [36]).
- The assumption by Guisnet and co-workers [29, 38] and Meriaudeau and Naccache [39] suggests that metal species participate in the reaction of propane activation, catalyzing its dehydrogenation to propene.

There is evidence that supports this last assumption. For instance, it explains the higher rate of propene formation over Ga/H-[Al]-ZSM-5 (Fig. 3). In fact, the initial rate of propene formation over gallium-promoted catalysts is about 3–4 times higher than over the acidic catalyst [3, 29]. The increase in the rate of the limiting step of the reaction (propane dehydrogenation) due to the presence of gallium, clearly indicates that these species participate in this dehydrogenation reaction. Other evidence is offered by catalytic tests carried out with mechanical mixtures of Ga_2O_3 and H-[Al]-ZSM-5 [38–46] and with catalysts in which gallium species are supported over a very dealuminated Y-zeolite, Ga/Y (unit cell parameter, a_0 = 24.185; dealuminated by $SiCl_4$ and various HNO_3 treatments [47]) or exchanged over H-Beta (Si/Al = 10) zeolite, Ga/H-[Al]-Beta [44, 45].

Figure 5 shows that initial rate in propane transformation increases with the percentage of Ga_2O_3 in the mechanical mixture. This evolution in the activity in line with the amount of gallium oxide in the catalysts indicates

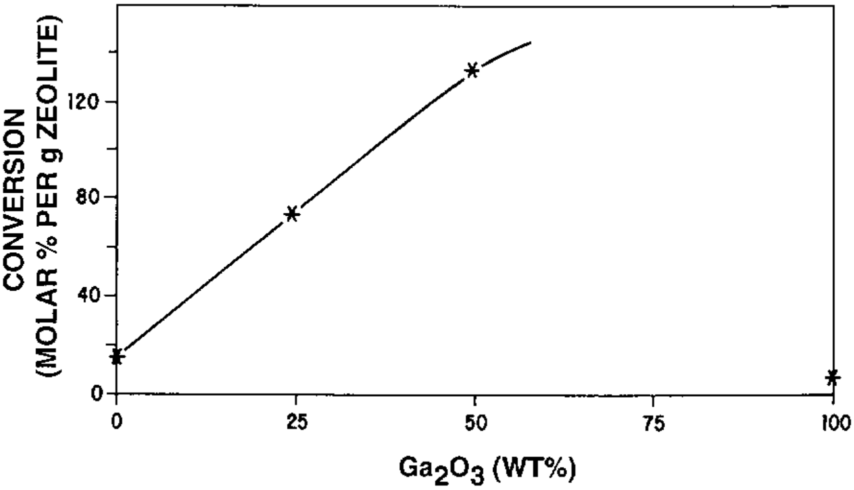


FIG. 5. Evolution of conversion (molar %/g zeolite) as a function of the percentage of Ga_2O_3 in the mechanical mixture. (T = 530°C; p = 1 atm; N_2/propane = 4; WWH = 2 h^{-1}.)

TABLE 5

Product Molar Distributions Obtained Through Variation of Space Velocity at 530°C, by % Conversion

	Si/Al > 50: Ga/Y			Si/Al = 10: Ga/H-[Al]-Beta			Si/Al = 44: Ga/H-[Al]-ZSM-5		
	7.3%	4.3%	3.0%	7.5%	5.0%	3.6%	7.6%	5.1%	3.4%
C_1	6.4	0	0	1.2	0.9	0.8	14.3	15.1	12.0
C_2	0	0	0	1.1	1.0	1.1	5.5	5.1	3.6
$C_2^=$	6.4	0	0	2.5	1.6	1.3	20.7	19.8	22.6
$C_3^=$	87.2	100.0	100.0	78.5	84.0	84.4	25.8	27.4	42.0
$C_4 + C_5$	0	0	0	7.2	8.0	10.0	13.5	17.1	13.4
BTX	0	0	0	9.5	4.5	2.4	20.2	15.5	6.4

From Refs. 44 and 45.

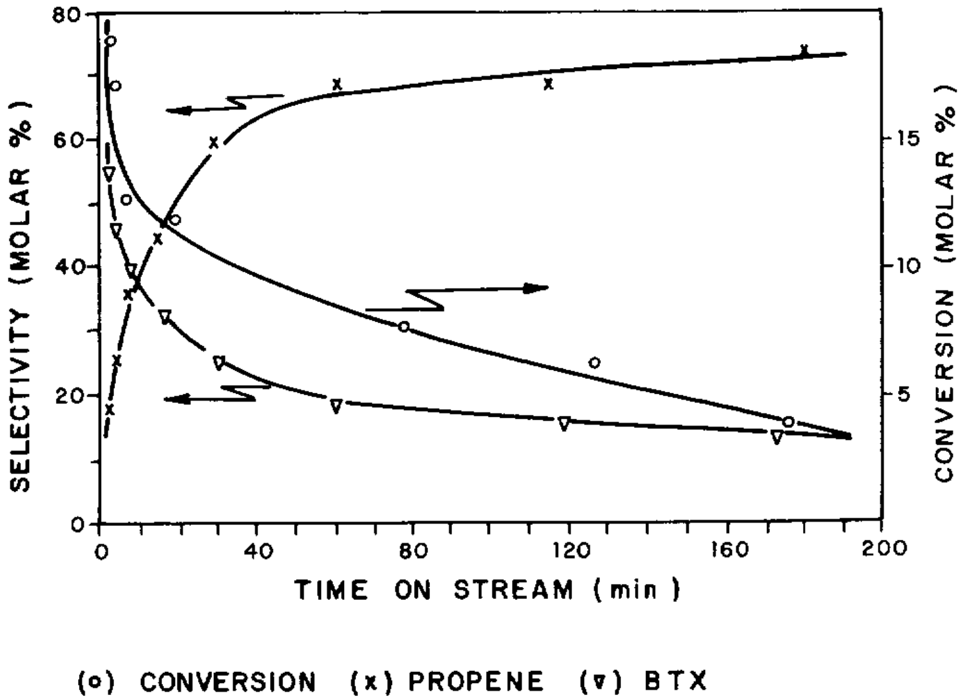


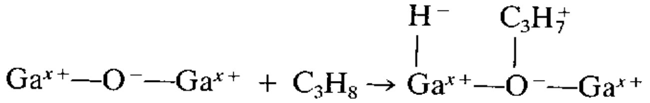
FIG. 6. Evolution of the conversion and of the molar percentages of propene and BTX as a function of time on stream for the transformation of propane over Ga/H-[Al]-Beta (T = 530°C; N_2/propane = 4; p = 1 bar; WWH = 2 h^{-1}; from Refs. 44 and 45.)

that the limiting step of the reaction, propane dehydrogenation, is being catalyzed by these species. Moreover, when propane reacts over Ga_2O_3, the main product is propene ($\geq$90 mol%) and fragments higher than C_3 are not observed at all [38, 39, 44, 45]. Again, this activation of propane by gallium species is clearly proved by observing the product molar distribution of the propane reaction over highly dealuminated Ga/Y catalyst (Table 5) [44, 45]. Note that the main product is propene, even at conversions near 7%. Besides, neither aliphatic products higher than C_3 nor aromatics are produced. All this indicates that the role of the gallium species consists of catalyzing the reaction of propane dehydrogenation; however, they are not capable of catalyzing oligomerization reactions of the formed olefinic species. Note that, at an equal conversion level, conventional Ga/H-[Al]-ZSM-5 catalyst produces relatively large fractions of aliphatics C_4-C_5 and of BTX (Table 5). The dehydrogenating activity of gallium species can also be determined by analyzing the evolution of the molar distribution in the products of the reaction of propane aromatization, over a Ga/H-[Al]-Beta catalyst, during its strong deactivation (Fig. 6). This deactivation is accompanied by important variations in the propene and aromatic fractions. Whereas BTX strongly diminishes, propene increases in a similar proportion. This shows that even though the dehydrogenating function continues to produce propene, acid sites of the support are not capable of aromatizing it, because their greatest part has been deactivated by coke formation. After an almost total deactivation of the acid sites of the catalyst, C_4-C_5 fractions and BTX are only observed as traces, and the conversion is virtually exclusive toward the production of propene. Similar results have been found for Ga/H-Y and Ga/H-Mordenite catalysts [48]. These results are very important because they indicate that dehydrogenating gallium species are much less sensitive to coke poisoning than acid sites in the zeolite. The same has been reported by Meriaudeau and Naccache [49]. The strong deactivation of these acid sites has the effect that, at isoconversion, Ga/H-[Al]-Beta (although it forms much more propene) produces much less aromatics than Ga/H-[Al]-ZSM-5 (Table 5). At the same time, these results allow us to conclude that medium-pore zeolites are preferred to large-pore zeolites, because of the higher resistance to deactivation by coke.

The incapability of gallium species of oligomerizing olefins clearly indicates that in Ga/H-[Al]-ZSM-5 there exists a synergetic effect between these species and acid sites of the zeolite. Now, since percentages by weight of gallium in these catalysts are generally equal to or higher than the amount necessary to exchange all acid sites of the zeolite and since acid sites are necessary for oligomerization, cracking, and cyclization reactions, all or a great part of these dehydrogenating species do not occupy exchange positions; after the activation process they are probably in the form of Ga_2O_3 and/or GaO(OH), deposited in the pores or on the outer surface of the zeolite crystallites. This last statement is supported by the increases in the activity observed by adding Ga_2O_3 to a H-[Al]-ZSM-5 zeolite (Fig. 5). Moreover, recent studies reported by Kazansky et al. [50] and Yakerson et al. [51] indicate that the concentration of —OH groups is not affected when gallium ions are added to the support. Catalytic tests with model reactions of acid catalysis (*n*-heptane cracking and *m*-xylene isomerization) show that the acidic and the gallium-promoted catalysts present almost the same activity [29, 52]. This supports the aforementioned statement on the nature of the gallium species.

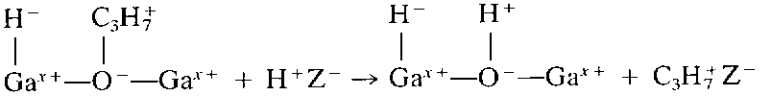
Although it could be thought that propane dehydrogenation is carried out individually over gallium species, experimental evidences show that the propane dehydrogenation rate is much higher over Ga/H-[Al]-ZSM-5 than over Ga/Na,H-[Al]-ZSM-5 [52]. The following bifunctional mechanism was proposed by Meriaudeau and Naccache in order to explain the positive effect of the protonic sites on the dehydrogenation activity of the gallium species [52]:

A dissociative adsorption of the paraffin with formation of gallium hydride and of gallium alkoxide species:



$$Ga^{x+}—O^-—Ga^{x+} + C_3H_8 \rightarrow \overset{\overset{H^-}{|}}{Ga^{x+}}—\overset{\overset{C_3H_7^+}{|}}{O^-}—Ga^{x+} \quad (2a)$$

A rapid exchange of the alkyl carbonium ions with zeolite protons:



$$\overset{\overset{H^-}{|}}{Ga^{x+}}—\overset{\overset{C_3H_7^+}{|}}{O^-}—Ga^{x+} + H^+Z^- \rightarrow \overset{\overset{H^-}{|}}{Ga^{x+}}—\overset{\overset{H^+}{|}}{O^-}—Ga^{x+} + C_3H_7^+Z^- \qquad (2b)$$

A rapid desorption of propene from the zeolite:

$$C_3H_7^+Z^- \rightarrow C_3H_6 + H^+Z^- \qquad (2c)$$

Buckles et al. [46] propose that the initial C–H bond scission is carried out by a concerted action of the gallium species and the acid sites in the zeolite:

$$C_3H_8 \xrightarrow{Ga_xO_y} \overset{\delta-}{H}---\overset{\delta+}{C}H(CH_3)_2 \xrightarrow{H^+Z} H_2 + C_3H_7^+Z^- \qquad (2d)$$

Finally, van Hooff and co-workers [53] indicate that the dehydrogenation reactions are produced by combination of hydride ions—abstracted from propane by gallium species—and zeolite protons, with the production of H_2 and carbenium atoms which take the place of the protons:

$$\begin{aligned} &CH_3CH_2CH_3 + Ga^{n+} \rightarrow CH_3\overset{+}{C}HCH_3 + (Ga—H)^{(n-1)\cdot} \\ &CH_3\overset{+}{C}HCH_3 + (Ga—H)^{(n-1)+} + H^+Z^- \rightarrow Ga^{n+} + H_2 + CH_3\overset{+}{C}HCH_3Z^- \end{aligned} \qquad (2e)$$

It should be pointed out that even though the presence of gallium favors the reaction of propane dehydrogenation toward propene (step 1, Scheme 1), acidic catalysis is always present. In fact, since propene production over the gallium-promoted catalysts is 3–4 times higher than over the acidic catalyst, this indicates that about 70% of propene is produced over the gallium species and about 30% over the acid sites [3, 29].

C. Differences in Selectivity between H-[Al]-ZSM-5 and Ga/H-[Al]-ZSM-5: Mechanisms of Propane Aromatization

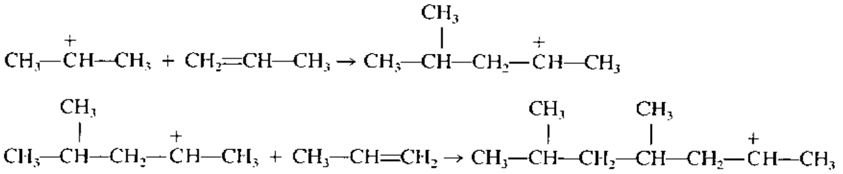
The introduction of gallium in an acidic zeolite produces an increase in the selectivity toward aromatics, which is accompanied by a reduction in the C_1 and C_2 fractions (Fig. 3). This is also observed in the case of mechanical mixtures [33–36, 38–46]. This indicates that gallium should participate in other reactions in addition to the dehydrogenation of the alkane to alkene.

For a given reaction, changes in selectivity observed over various catalysts depend upon relative rates of different steps which lead to final reaction products. That is why, to understand this difference, it is necessary to know the reaction pathway.

As mentioned before, the first step in the aromatization of light alkanes is the production of olefins (steps 1 and 1′, Scheme 1). The olefins will be protonated over Brønsted acid sites [54]:

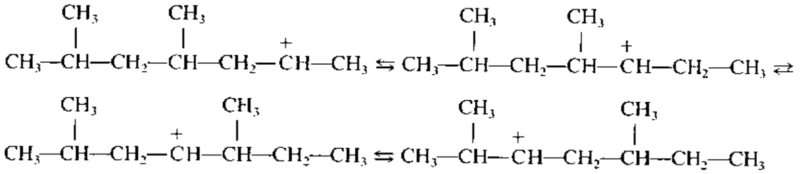
$$CH_2{=}CH-CH_3 + H^+ \rightarrow CH_3-\overset{+}{C}H-CH_3 \tag{3}$$

and subsequently, due to reactions of olefin alkylation, oligomers will be produced [54–56]. For example:



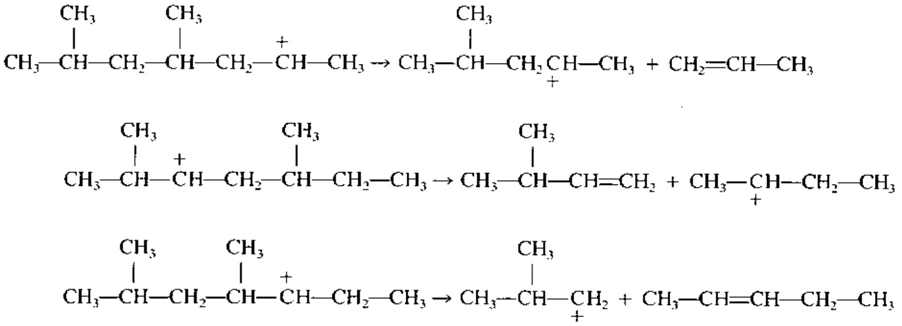
$$\begin{gathered}CH_3-\overset{+}{C}H-CH_3 + CH_2{=}CH-CH_3 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{+}{C}H-CH_3\\ CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{+}{C}H-CH_3 + CH_3-CH{=}CH_2 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{+}{C}H-CH_3\end{gathered} \tag{4}$$

which, once formed, may rapidly isomerize to each other through hydride and alkyl transfer reactions [55, 56]:



$$\begin{gathered}CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{+}{C}H-CH_3 \leftrightarrows CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{C}H-CH_2-CH_3 \rightleftarrows\\ CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{+}{C}H-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3 \leftrightarrows CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{C}H-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3\end{gathered} \tag{5}$$

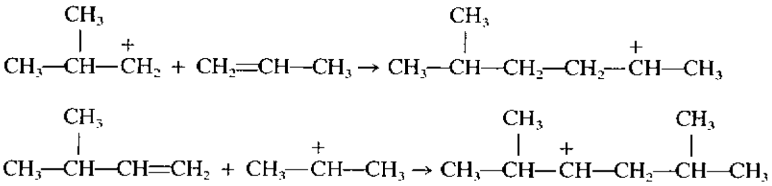
Since oligomerization is reversible, cracking of this oligomer will yield light products. For example:



$$\begin{gathered}CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{+}{C}H-CH_3 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2\underset{+}{C}H-CH_3 + CH_2{=}CH-CH_3\\ CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{C}H-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-CH{=}CH_2 + CH_3-\underset{+}{C}H-CH_2-CH_3\\ CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{C}H-CH_2-CH_3 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{+}{C}H_2 + CH_3-CH{=}CH-CH_2-CH_3\end{gathered} \tag{6}$$

This fast interconversion of olefins has been evidenced [55].

The new products, in turn, will give rise to new oligomers, due to reactions among themselves and with propylene and ethylene molecules (from steps 1 and 1′, Scheme 1). For example:



$$\begin{gathered}CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{C}H_2 + CH_2{=}CH-CH_3 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_2-\overset{+}{C}H-CH_3\\ CH_3-\overset{CH_3}{\overset{|}{C}H}-CH{=}CH_2 + CH_3-\overset{+}{C}H-CH_3 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{C}H-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_3\end{gathered} \tag{7}$$

Dehydrogenation and/or subsequent cyclization of oligomers from reaction (7), followed by dehydrogenation reactions, will lead to the aromatic mixture [54, 57].

On acidic catalysts, aromatization is carried out through hydride transfer reactions between aliphatic and/or cyclic oligomers and carbocations present in the reaction medium, which leads to the formation of an important quantity of paraffins, among them ethane and propane [16, 54, 57]. As an example, Fig. 7 shows the mechanism of toluene formation over these catalysts.

Unlike most light products with 2 to 5 carbon atoms, which are transition products, ethane evolves similarly to aromatics (they are secondary products which continuously increase as conversion increases—Fig. 3). Although Ono and co-workers [31] suggest that this similarity indicates that both products come from the same intermediate species, the possibility cannot be eliminated that a great part of ethane comes from hydride transfer reactions, from intermediate oligomeric species toward $C_2H_5^+$ cations. These species coming from propane cracking (reaction 1) are kinetically very reactive; therefore, they must take part, preferably, in hydride transfer reactions. Since, at low conversion, only the formation of methane, ethene, and propene is observed, these hydride transfer reactions will occur once the intermediate oligomeric species are formed; thus, ethane appears as a secondary reaction product like BTX. The fact that methane (the specie formed together with ethene during propane cracking) continuously in-

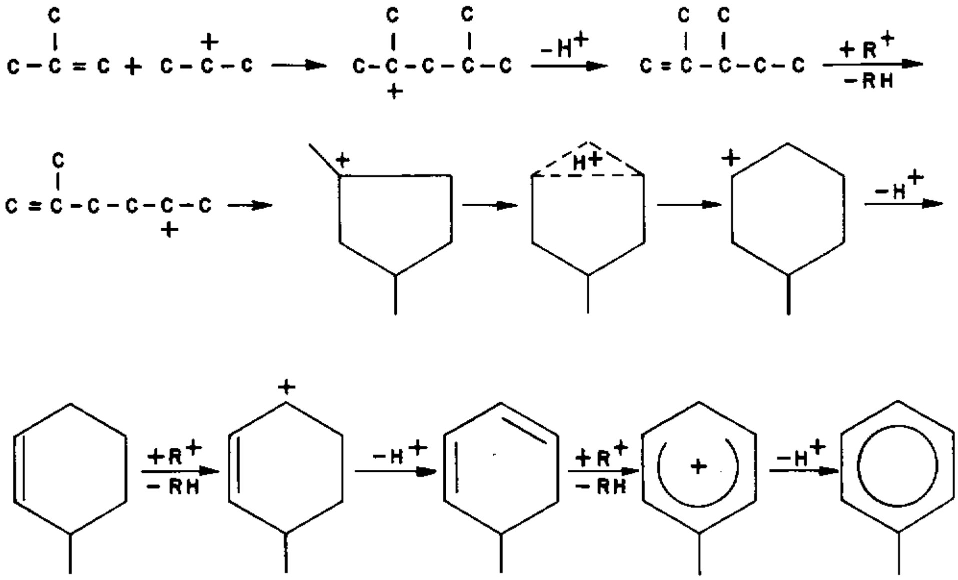


FIG. 7. Mechanism of toluene formation over acidic catalysts (from Ref. 16).

creases as the conversion does (Fig. 3) supports the aforementioned statement.

Although products are basically the same over both catalysts (Fig. 3), we have seen that the deposition of gallium on the zeolite considerably increases aromatics production. This cannot be attributed to an increase in the acidity of the catalyst, because this would lead to a greater formation of light products. The effect of gallium species on the selectivity of the reaction must be related to their dehydrogenating activity, which intervenes not only in propane dehydrogenation but also in dehydrogenation of oligomeric intermediates. This considerably increases the rate of aromatization, thus reducing oligomer cracking reactions.

Results reported by Meriaudeau and Naccache [39] when studying the transformation of various hydrocarbons (propane, 1-hexene, 1,5-hexadiene, and cyclohexane) over Ga_2O_3 show that gallium species, besides catalyzing propane dehydrogenation, take part:

- In dehydrogenation reactions to form di- and triolefins from intermediate olefinic oligomeric species, with trienes being rapidly cyclized through noncatalytic reactions in the gas phase.
- In dehydrogenation reactions of saturated and unsaturated naphthenic intermediates.

However, Gnep et al. [38] found that Ga_2O_3 can dehydrogenate propane and aromatize unsaturated naphthenes, but that it is virtually inactive in 1-hexene, 1-heptene, and methylcyclohexane aromatization. Based on these results, the authors state that over Ga/H-[Al]-ZSM-5, the cyclization reactions of aliphatic oligomeric intermediate are produced by hydride transfer reactions over acid sites in the zeolite [38]. Differences in the results obtained by the two research groups may be attributed to differences in operating conditions and in Ga_2O_3 samples [3a]. However, although the results of Meriaudeau and Naccache indicate that over Ga_2O_3, cyclization is produced by triene intermediates—by a noncatalytic gas-phase reaction—they accept that over Ga/H-[Al]-ZSM-5 the formation of naphthenes occurs mainly through cyclization over acid sites of dienes resulting from alkene dehydrogenation over gallium species [58]. Isotopic studies carried out by Iglesia and co-workers [37a] on Te/NaX catalyst, using competitive reactions of 1-heptene and n-[1-^{13}C]-heptane, show that subsequent olefin dehydrogenation steps produce heptatriene intermediates that undergo thermal cyclization.

Our results [59] tend to confirm the findings by Meriaudeau and Naccache [39]. Table 6 shows that aromatic product distributions of propane (C_3), n-hexane (n-C_6) and cyclohexane (CyC_6) over H-[Al]-ZSM-5 are very similar. The same happens in the case of n-heptane (n-C_7) and methylcyclohexane ($MCyC_6$) over H-[Al]-ZSM-5. However, whereas the BTX distribution of C_3 over Ga/H-[Al]-ZSM-5 is virtually equal to the one over H-[Al]-ZSM-5, it varies in the case of higher hydrocarbons. In fact, Table

TABLE 6

Aromatic Product Distribution Obtained from the Transformation of Various Hydrocarbons Over Acidic and Bifunctional Catalysts: $T = 530°C$; N_2/hydrocarbon = 4; p = 1 bar; WWH = 2 h^{-1}

	Yield in BTX (molar %)	Distribution in H-[Al]-ZSM-5[a]			Distribution in Ga/H-[Al]-ZSM-5[a]		
		B	T	X	B	T	X
Propane	10	32	43	25	35	40	25
	18	35	42	23	37	40	23
n-Hexane	10	20	45	35	30	40	30
	35	28	45	27	40	38	22
Cyclohexane	10	28	45	27	74	19	7
	35	25	45	30	73	20	7
n-Heptane	10	14	45	41	14	52	34
	35	16	44	40	18	50	34
Methylcyclohexane	10	17	45	38	28	62	12
	35	16	44	40	28	62	12

From Ref. 59.

[a] B, benzene; T, toluene; X, C_8 aromatics.

6 shows that the fraction of aromatic isomer of transformed hydrocarbon is always higher on the bifunctional catalyst. As a matter of fact, comparing, at isoconversion in BTX, the aromatic product distribution of *n*-hexane transformations over acidic and over bifunctional catalysts shows that over Ga/H-[Al]-ZSM-5 the benzene fraction is higher than over H-[Al]-ZSM-5. The same happens with the toluene fraction in the case of *n*-heptane. On the other hand, the aromatic product distribution obtained from naphthene transformations over the bifunctional catalysts shows the existence of a very important direct dehydrogenation reaction of naphthenes over active gallium species. Cyclohexane and cyclohexene strongly favor the production of benzene, whereas methylcyclohexane favors toluene formation. This fact, accompanied by a very low production of light products [59], shows that during the transformation of gaseous paraffins over Ga/H-[Al]-ZSM-5, once naphthenic intermediates are formed, they are rapidly transformed—by dehydrogenation over gallium species—in their respective aromatic isomers. This significantly increases the BTX fraction, with detriment to the light products obtained from cracking these naphthenic intermediates, a very important competitive reaction which is clearly evidenced when transformation is carried out over acidic catalyst.

The similarity between aromatic product distribution of C_3, n-C_6, and CyC_6; and that of n-C_7 and $MCyC_6$, obtained over H-[Al]-ZSM-5, clearly indicates that direct aromatization of C_6-C_7 hydrocarbons is not carried out over acidic catalysts, but that it occurs through a reaction pathway which implies a previous cracking step before giving way to the reactions of oli-

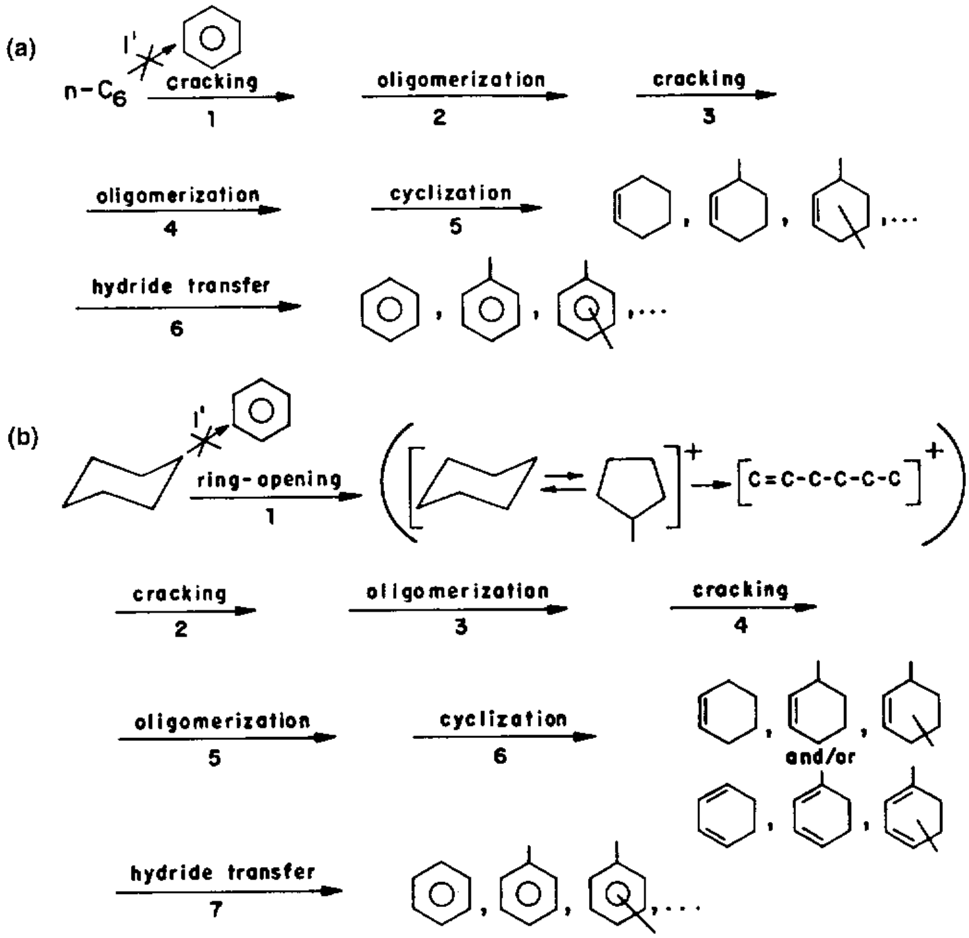


FIG. 8. Reaction pathway for *n*-hexane (a) and cyclohexane (b) aromatization over H-[Al]-ZSM-5 catalyst (from Ref. 59).

gomerization, cracking, reoligomerization, cyclization, and dehydrogenation (Fig. 8). On the other hand, over Ga/H-[Al]-ZSM-5, the reaction of aromatization of higher hydrocarbons is carried out (Fig. 9).

- Through a monofunctional mechanism by direct dehydrogenation over active gallium species, favoring the formation of the aromatic isomer of the reactant.
- Through a conventional acid and/or bifunctional mechanism.

The relative importance of the direct dehydrogenation reaction will depend on the dehydrogenating activity of gallium species toward the reactant used. Then, direct aromatization is higher for cyclohexane, cyclohexene, and methylcyclohexane than for *n*-hexane and *n*-heptane. The fact that *n*-C_6 and *n*-C_7 favor only slightly the formation of their aromatic isomers suggests, as previously expressed by other authors [38, 58], that over Ga/H-[Al]-

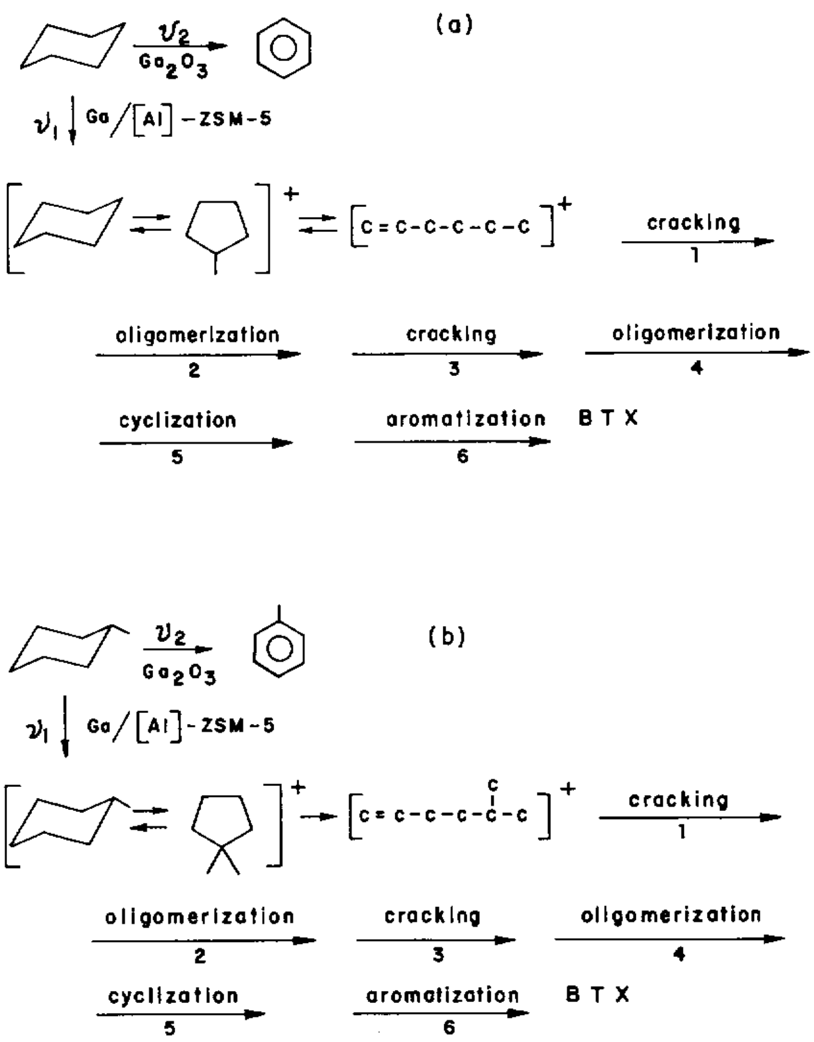
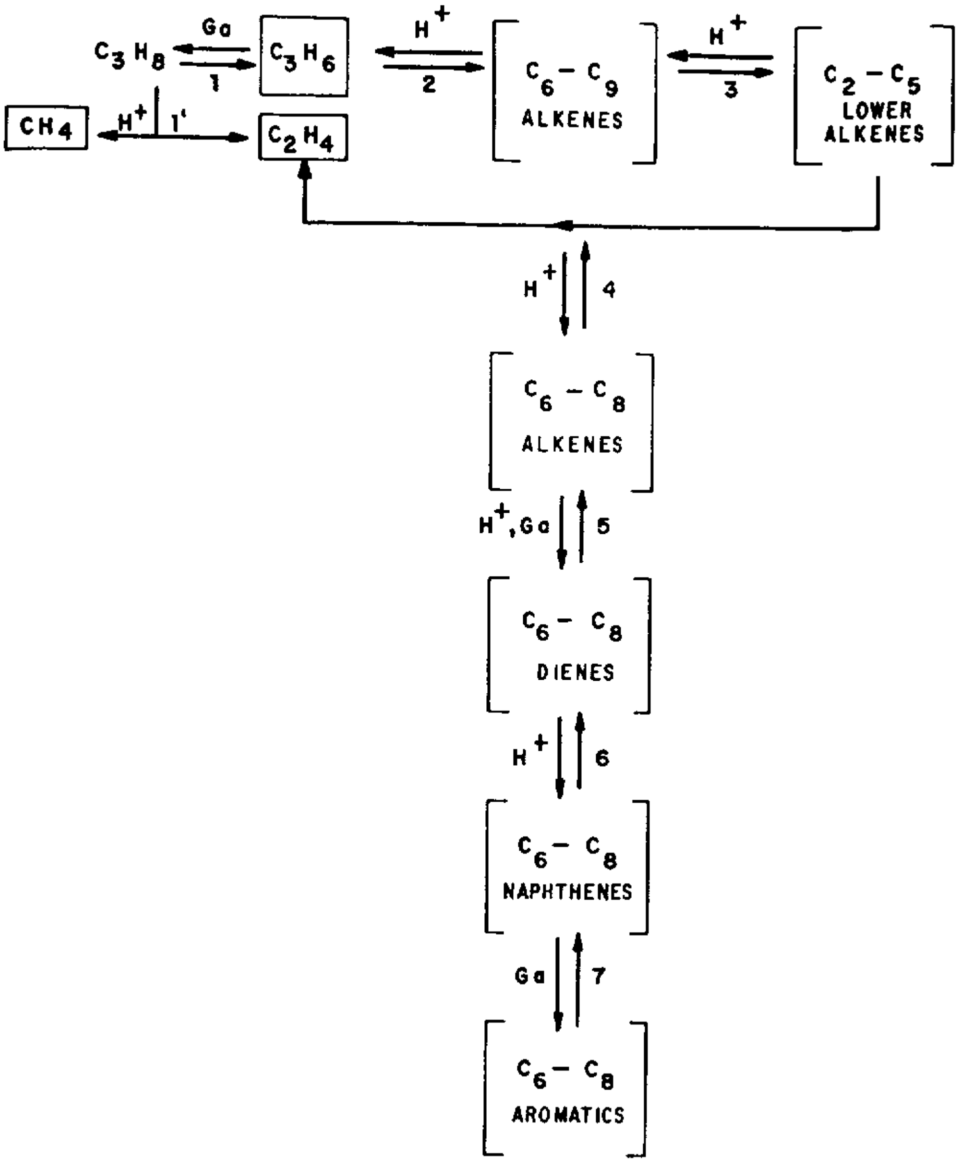


FIG. 9. Reaction pathway for cyclohexane (a) and methylcyclohexane (b) aromatization over bifunctional Ga/H-[Al]-ZSM-5 catalyst (from Ref. 59).

ZSM-5 catalysts, the formation of naphthene intermediates would occur mainly through cyclization of alkene and diene intermediates over acid sites of the zeolite.

Based on this statement, we can conclude that during propane aromatization over Ga/H-[Al]-ZSM-5 catalysts, gallium species take part in all dehydrogenation reactions involved within the aromatization process. This accounts for the considerable production of H_2 and for the increases in the activity and selectivity in BTX. Acid sites, for their part, catalyze the reactions of oligomerization, cracking, and cyclization of olefinic intermediates. A small fraction of this last reaction is able to occur by triene cyclization through a noncatalytic gas-phase reaction [3a, 37, 39]. The low production



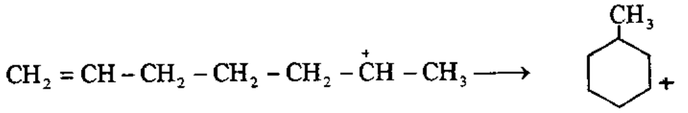
SCHEME 2. Main reaction pathway of the aromatization of propane over Ga/H-[Al]-ZSM-5.

of H_2 on acidic catalysts is due to the fact that dehydrogenation reactions of oligomeric intermediates are carried out by hydride transfer reactions. The difference in H_2 production may be estimated from the difference between the contents of hydrogen in the products and in the reactant. On the acidic catalyst, propane aromatization generates about 2 mol of H_2 per mol aromatic hydrocarbon, against more than 4 mol on the bifunctional catalyst [38].

Scheme 2 summarizes the most important reaction steps and the species participating catalytically in each one of them during propane aromatization over Ga/H-[Al]-ZSM-5.

In relation to aromatics C_6-C_8, it is observed, particularly at low conversions, that the rate of toluene and xylenes formation is much higher than that of benzene (Fig. 4). This fact suggests the existence of a rapid interconversion of olefins followed by the formation of new oligomers, which, subsequently, when cyclized and dehydrogenated, will give rise to the formation of the mixture of aromatics. Moreover, this higher rate of toluene and xylene formation clearly shows that steps 3, 4, and 5 in Scheme 1 are much faster than step 5′. This is supported by the aromatic product distribution obtained from cyclohexane, over acidic catalysts, which is very similar to that of C_3 and n-C_6 hydrocarbons (Table 6). Moreover, the formation of toluene and xylenes in considerable amounts shows that the concentrations of butenes and pentenes in the reacting medium are relatively important. This would coincide with the existence of C_9 oligomeric intermediates, products of the reaction of propane oligomerization, which through cracking would give rise to the formation of C_4 and C_5 alkene species [55]. As expected, reactions of C_4 and C_5 species with propene will lead to the formation of C_7 and C_8 hydrocarbons which finally produce toluene and xylenes. The fact that benzene is formed more slowly than toluene may be attributed to a secondary cracking of C_6 species formed by C_9 oligomer intermediate cracking [reaction (6)]. Other factors might explain the higher rate of toluene and xylene formation with respect to benzene [57]:

1. Direct formation of a 6-membered ring to produce toluene and xylenes:

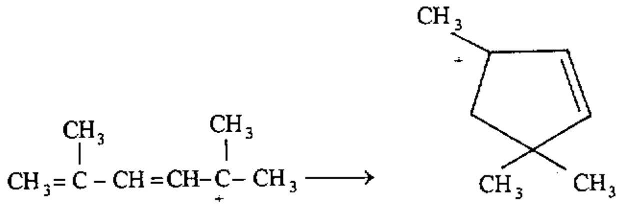


$$CH_2=CH-CH_2-CH_2-CH_2-\overset{+}{C}H-CH_3 \longrightarrow \qquad (8a)$$

This is slightly likely for benzene, since this requires the formation of primary carbonium ions:

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}\overset{+}{C}H_2 \quad \text{or} \quad CH_2{=}CH{-}CH{=}CH{-}CH_2{-}\overset{+}{C}H_2 \qquad (8b)$$

2. The higher number of possibilities that C_7 and C_8 oligomers have to cyclize, and the higher stability of the carbocations involved in these cyclizations; for instance, the formation of a 5-membered ring may occur from a tertiary diolefinic carbonium ion C_8:



$$CH_2{=}\underset{}{\overset{CH_3}{\overset{|}{C}}}{-}CH{=}CH{-}\underset{+}{\overset{CH_3}{\overset{|}{C}}}{-}CH_3 \longrightarrow \qquad (9)$$

whereas carbonium ion must be primary or secondary in the case of benzene.

IV. NATURE OF GALLIUM SPECIES CATALYTICALLY ACTIVE IN DEHYDROGENATION

All evidence presented to this point indicates that in Ga/H-[Al]-ZSM-5 catalysts (prepared through exchange and/or impregnation of a H-[Al]-ZSM-5 zeolite), gallium species, catalytically active in dehydrogenation, are extraframework, very likely of the type Ga_2O_3 and/or GaO(OH). That is, they are not found either as Ga^{3+} (neutralizing net negative charges of the zeolitic structure) or as tetrahedral framework gallium (product from a galliation of the aluminosiliceous zeolitic support). This has been demonstrated through ^{71}Ga MAS-NMR [60] and catalytic properties of H-[Ga]-ZSM-5 (where gallium occupies tetrahedral framework positions) and Ga/H-[Ga]-ZSM-5 catalysts (prepared through exchange and/or impregnation of H-[Ga]-ZSM-5 with Ga^{3+}) [44, 45, 61, 62]. Acidic gallosilicate, even though it presents an activity slightly lower than its homologous aluminosilicate (Table 7), shows a very similar selectivity (Fig. 10). However, addition of extraframework gallium to acidic gallosilicate produces a strong increase in initial activity of the catalyst which is very similar to the increase observed when gallium is added to H-[Al]-ZSM-5 zeolite (Table 7). This confirms that the extraframework gallium species are catalytically much more active in dehydrogenation than the framework gallium atoms, which activate propane by an acidic reaction such as in H-[Al]-ZSM-5 [reaction (1)].

The lower activities of acidic and bifunctional gallosilicates catalysts, with respect to their homologous aluminosilicates, are due to the lower acidity of the gallosilicates [62].

Although bifunctional Ga/H-[Ga]-ZSM-5 catalyst is initially more active and selective in BTX, after its deactivation it is less selective than the acidic catalyst H[Ga]-ZSM-5 [62]. This lower selectivity toward BTX of

TABLE 7

Initial Conversion (molar %) Obtained from Propane Transformation over Acidic and Bifunctional Catalysts: $T = 530°C$; N_2/propane = 4; $p = 1$ bar; WWH = 2 h^{-1}

Catalyst	Conversion (molar %)
H-[Ga]-ZSM-5(30)	7
H-[Al]-ZSM-5(23)	12
Ga/H-[Ga]-ZSM-5(30)	40
Ga/H-[Al]-ZSM-5(23)	85

From Refs. 44 and 45.

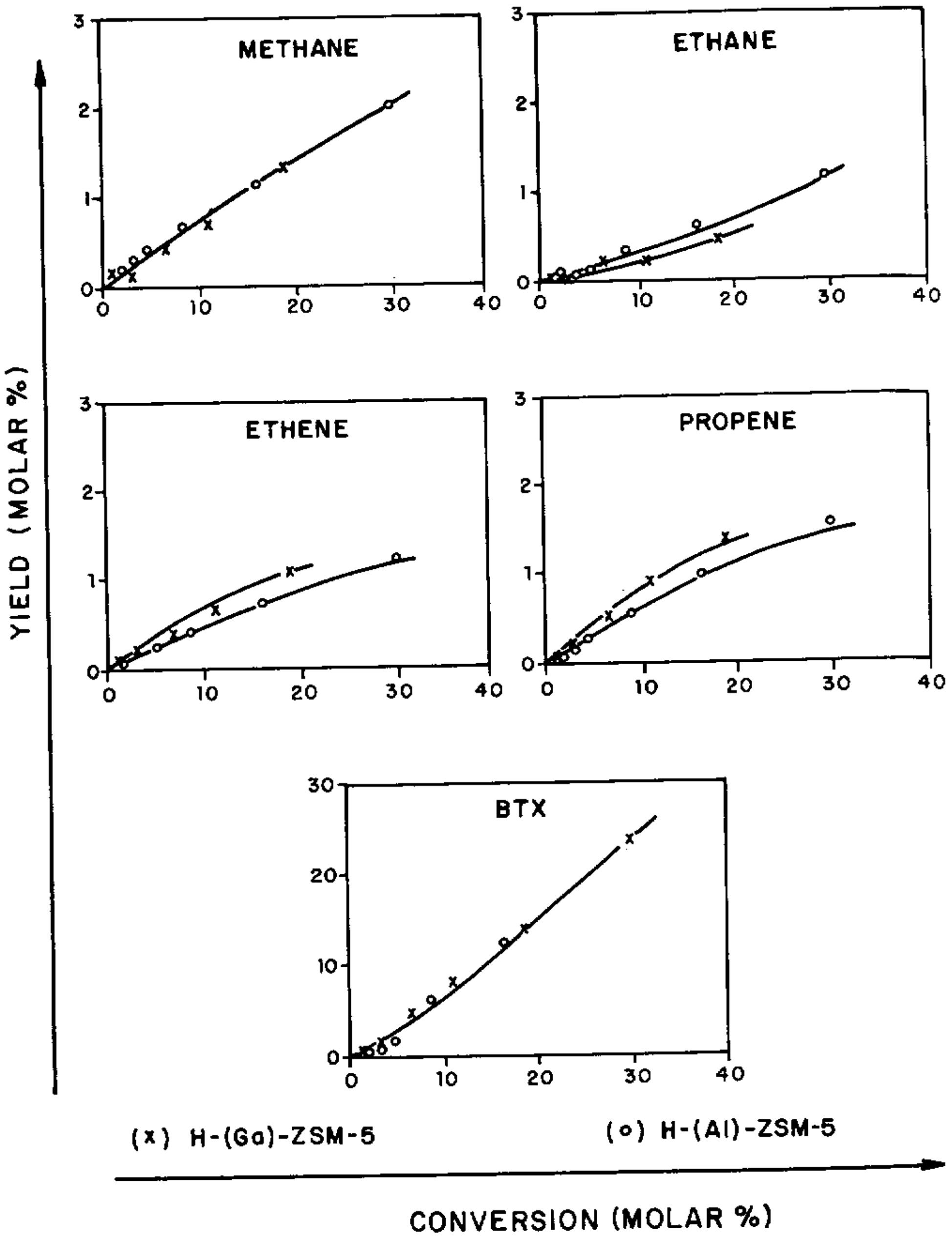


FIG. 10. Evolution of various products of propane transformation over H-[Ga]-ZSM-5 and H-[Al]-ZSM-5. (T = 530°C; p = 1 atm; from Refs. 44 and 45).

Ga/H[Ga]-ZSM-5 is attributed to its strong deactivation due to the formation of coke over acid sites of the catalyst, which considerably diminishes the number of active sites capable of catalyzing oligomerization reactions of an important number of olefinic intermediates formed by dehydrogenation over active gallium species. This is confirmed by the existence of a relatively important propylene fraction present in the reaction products, after the deactivation of Ga/H-[Ga]-ZSM-5 [62].

The use of gallo- and galloaluminosilicates treated at high temperatures allows us to confirm that extraframework gallium species are much more active in dehydrogenation than the framework species. These treatments, when producing a partial degalliation of the zeolitic structure and the subsequent formation of extraframework gallium species [53, 63–72], lead to catalysts which are more active and more selective in aromatization than the original solids. This degalliation is confirmed by solid-state ^{71}Ga MAS-NMR [69, 72] and by a steady decrease in the unit cell parameters with the increase of the calcination temperature of NH_4-[Ga]-ZSM-5 (Table 8) [68]. As a matter of fact, since the distance of the Ga–O bond (1.83Å) is greater than that of Si–O bond (1.63Å), the greater the degalliation degree, the greater the decrease in the unit cell parameters. The octahedral extraframework species, probably of Ga_2O_3 and/or GaO(OH) remaining in the outer surface or inside the zeolite pores, are responsible for the increase in the activity and in the selectivity of the catalysts (Fig. 11). The higher the calcination temperature (up to 800°C), the higher the amount of dehydrogenating extraframework gallium species, and the higher the activity and the selectivity toward aromatics.

Additional evidence that a change has taken place in the reaction mechanism can be presented through the H_2/aromatics ratio and/or the amount of hydrogen produced [38] (Table 9). At isoconversion, the amount of H_2, very small on the catalyst calcinated at 530°C (H_2 molar % = 0.10 at 10% of conversion rate), regularly increases as calcination temperature increases (H_2 molar % = 0.38 at 10% of conversion rate for T_c = 800°C). This difference becomes more significant at higher conversion. Likewise, the H_2/aromatics molar ratio, which on the catalyst calcinated at 530°C is approximately equal to 2 (at high conversion), goes to values over 4 when increasing gallosilicate calcination temperature (Table 9). In fact, a bifunctional mechanism in which the gallium oxidic species (increasingly more numerous when raising calcination temperature) catalyze dehydrogenation

TABLE 8

Unit Cell Parameters of Gallosilicates Obtained after Calcination of NH_4-[Ga]-ZSM-5 at Different Temperatures

Unit cell parameters (Å)	As synthesized [Ga]-ZSM-5	Calcinated [Ga]-ZSM-5 zeolite			
		530°C	600°C	700°C	800°C
$\bar{a}$	20.1582	20.1566	20.1139	20.0567	20.0502
$\bar{b}$	19.9393	19.9004	19.8955	19.8723	19.8518
$\bar{c}$	13.3622	13.3586	13.3636	13.3636	13.3235

From Ref. 68.

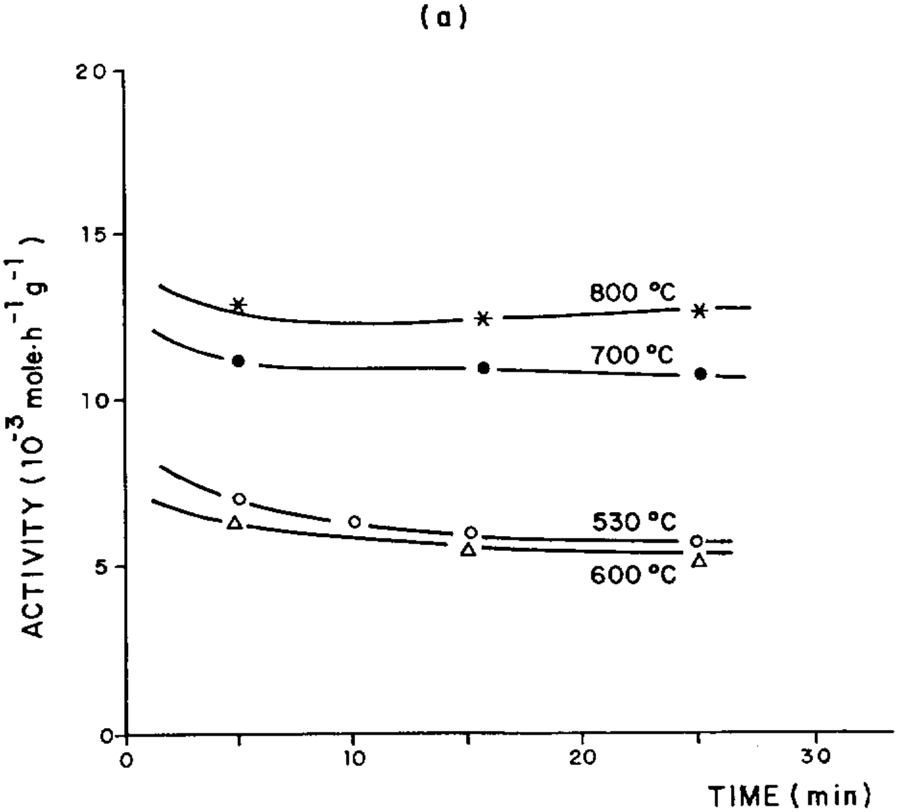


FIG. 11. Aromatization of propane (T = 530°C; p = 1 atm; N_2/hydrocarbon = 0) over [Ga]-ZSM-5 zeolites calcinated at different temperatures (T_c) (from Ref. 68). (a) Propane transformation (A, 10^{-3} mol g^{-1} h^{-1}) as a function of time on stream (t, min). (b) Yield of aromatic products (wt%) as a function of total propane conversion (wt%). (△, T_c = 530°C; ○, T_c = 600°C; ●, T_c = 700°C; *, T_c = 800°C.)

reactions of intermediate oligomers (alkenes and naphthenics) explains the increase observed both in the amount of produced hydrogen and in the H_2/aromatics molar ratio.

Gallosilicates and galloaluminosilicates treated under appropriate conditions appear to be the most selective and most stable catalysts toward coke formation for alkane aromatization.

Although different studies have been carried out to determine the nature of dehydrogenating extraframework gallium species [37, 40, 43, 50, 51, 64, 73, 75], their characterization requires supplementary studies. A positive effect of hydrogen treatment on the activity and on the selectivity has been observed by Changyu et al. [74] and by Price and co-workers [40, 43, 75]. This positive effect has been attributed to the dehydrogenating activity of the gallium species produced by their reduction and/or an increase

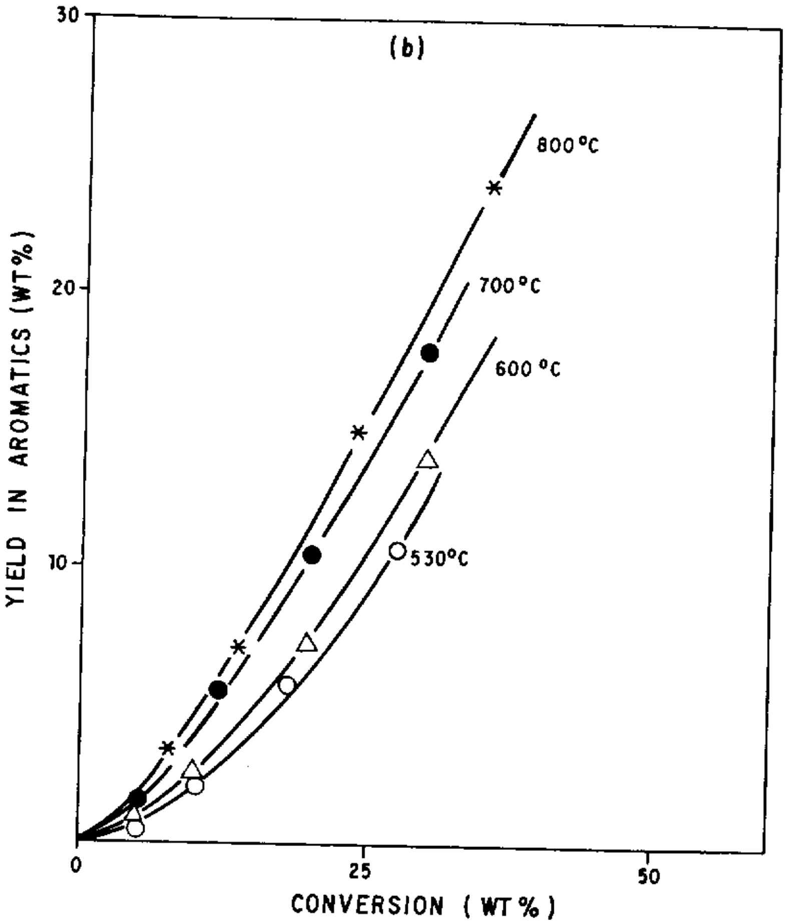


FIG. 11. (*Continued*)

TABLE 9

Evolution of H_2 (molar %) and H_2/Aromatics Molar Ratio as a Function of Calcination Temperature (°C) of [Ga]-ZSM-5 Zeolite

Calcination temperature (°C)	H_2 (molar %) (10 wt% conversion)	H_2/aromatics molar ratio (35–50 wt% conversion)
530	0.10	2.07
600	0.11	2.21
700	0.31	4.00
800	0.38	4.33

From Ref. 68.

in their dispersion. If the reason for this positive effect is a change in the oxidation state [37, 40, 43, 75], it requires assistance of acid sites because no reduction is observed with pure Ga_2O_3 or with mechanical mixtures of Ga_2O_3 and NaX zeolite. Nevertheless, it is difficult to rationalize that a reduced gallium oxidation state (Ga_2O) is more effective as an oxidizing agent than gallium species with a higher oxidation state [Ga_2O_3 or GaO(OH)]. In any case, reduced gallium species cannot be Ga^+ species which neutralize the other acid sites of the zeolite [43], because acid sites are absolutely necessary to catalyze the reactions of oligomerization, cracking, and cyclization; and without them, aromatization would not take place. Even though a partial neutralization of protonic sites was accepted, this should be evidenced through a reduction in the reaction rate, and this is not observed [43]. Recently, Meitzner and co-workers [37b] published a study on physical and chemical state of gallium (on Ga/H-[Al]-ZSM-5 catalysts) using *in situ* x-ray absorption at the Ga *K*-edge. They indicate that Ga^{3+} species, reduced during hydrogen pretreatment or propane reaction, are present in highly dispersed form, probably as monomeric GaH_x hydride species, coordinated to basic oxygens within zeolite channels. According to these authors, these GaH_x species catalyze dehydrogenation steps during alkane aromatization, promoting the recombinative desorption of H-adatoms as H_2. However, further research is necessary to elucidate the nature and the oxidation state of gallium active species.

V. COMPARATIVE STUDY OF THE AROMATIZATION OF C_2–C_4 ALKANES

As compared with propane aromatization, there are few studies of ethane and butane aromatization [3, 76, 77]. In all cases, and regardless of the catalyst—pure acidic or gallium-promoted acidic zeolite—the higher the hydrocarbon chain, the higher the reactivity of the hydrocarbon [3, 77]. Once again, the presence of a dehydrogenation function increases the activity and the selectivity during the transformation of ethane and butane toward aromatics. The reaction pathways for these hydrocarbons are similar to the one showed in the case of propane aromatization. Aromatics are always secondary products, with toluene being the main product. But, whereas molar distributions of benzenic C_6-C_8 products are similar for propane and butanes, the proportion of benzene is more significant for ethane than that of C_8 aromatic, these aromatic hydrocarbons being formed only at very high conversion.

VI. CONCLUSIONS

1. The transformation of LPG into aromatics and H_2 is more efficient on gallium-promoted acidic zeolite catalysts than on pure acidic zeolites. This is due to a change in the mechanism of the aromatization reaction:

- Extraframework gallium species catalyze the dehydrogenation reaction of alkane reactants and of aliphatic and naphthenic oligomeric intermediates. The first dehydrogenation reaction is responsible for the reaction rate increase and the second for the selectivity increases toward aromatics and for the high H_2 production.

- The other reactions necessary for the formation of aromatics (oligomerization, cracking, and cyclization) are catalyzed by the acid sites of the zeolite.

2. Because of their structure and their high Si/X (X = Al and/or Ga) ratios, which drastically decrease the deactivation of the acid sites of the support by coke deposition, medium-pore MFI-type zeolites are preferred rather than conventional large-pore material (Beta, Mordenite, Y).

3. Bifunctional catalysts may be prepared through the mechanical mixture of Ga_2O_3 and an acidic zeolite, through the exchange and/or impregnation of acidic zeolites, or through the degalliation—under appropriate conditions—of gallo- or galloaluminosilicate zeolites. The latter are probably the most selective and stable catalysts for alkane aromatization.

4. Extraframework gallium species are much more active in dehydrogenation reactions than framework species. The determination of the nature and the oxidation state of these gallium extraframework species needs more research.

5. The longer the hydrocarbon chain, the higher the alkane reactivity. Moreover, whereas propane and butane aromatization gives almost the same aromatics molar product distribution, ethane favors the formation of benzene at the expense of C_8 aromatic.

REFERENCES

1. D. Seddon, *Catal. Today, 6*(3) 351 (1990).
2. M. S. Scurrell, *Appl. Catal., 32*, 1 (1987).
3. (*a*) M. Guisnet, N. S. Gnep, and F. Alario, *Appl. Catal. A: General, 89*, 1 (1992); (*b*) M. Guisnet, J. Y. Doyemet, D. Aittaleb, and N. S. Gnep, Symposium alkylation, aromatization, oligomerization and isomerization of short chain hydrocarbons over heterogeneous catalysts, *ACS Prepr., 36*(4), 668 (1991); (*c*) M. Guisnet, N. S. Gnep, D. Aittaleb, and J. Y. Doyemet, *Appl. Catal., 87*, 255 (1992).
4. S. M. Csicsery, *J. Catal., 17*, 209 (1970).
5. S. M. Csicsery, *J. Catal., 17*, 216 (1970).
6. S. M. Csicsery, *J. Catal., 17*, 315 (1970).
7. S. M. Csicsery, *J. Catal., 17*, 323 (1970).
8. S. M. Csicsery, *J. Catal., 18*, 30 (1970).
9. S. M. Csicsery, *Ind. Eng. Chem. Proc. Des. Dev., 18*(2), 191 (1970).
10. G. Giannetto, *Zeolitas: Características, Propiedades y Aplicaciones Industriales*, Ed. Innovación Tecnológica, Fac. Ingeniería, UCV, Caracas, Venezuela, 1990.
11. N. Y. Chen, US Pat. 27563 (1970); SE Pat. 361897 (1973).
12. J. Cattanach, US Pat. 253942 (1972); BE Pat. 799627 (1973).
13. J. Cattanach, US Pat. 3756942 (1973).

14. T. Mole, J. R. Anderson, and G. Creer, *Appl. Catal., 17*, 141 (1985).
15. E. E. Davis and A. J. Kolombos, GB Pat. 53012 (1976); AU Pat. 509285 (1980).
16. G. Giannetto, R. Sciamanna, J. Papa, and R. Monque, *Technical Report*, INTEVEP, INT-02006,88, 1988.
17. J. A. Johnson, J. A. Weiszmann, G. K. Hilder, and H. P. Hall, presented at NPRA Annual Meeting, San Antonio, TX, March 25–27, 1984, Paper AM-84-85.
18. J. R. Mowry, D. C. Martindale, and H. P. Hall, *Arab J. Sci. Eng., 10*, 367 (1985).
19. D. C. Martindale, P. J. Kuchar, and R. Kolson, presented at AICE Summer National Meeting, Denver, CO, March, 21–24, 1988.
20. P. C. Doolan and P. R. Pujado, presented at Dewitt's Petrochemical Review Meeting, Houston, TX, March, 29–30, 1989.
21. N. Y. Chen, W. E. Garwood, and F. G. Dwyer, *Shape Selective Catalysis in Industrial Applications*, Chem. Ind. Ser., 36, Dekker, New York, 1989.
22. N. Y. Chen and T. Y. Yan, *Ind. Eng. Chem. Proc. Des. Dev., 35*, 151 (1986).
23. N. G. Roosen, A. Orieux, and J. Andrews, presented at Dewitt's Petrochemical Review Meeting, Houston, TX, March 1989.
24. L. Mank, A. Minkkinen, and J. Shaddick, *Hydrocarbon Tech. Int., 69* (1992).
25. O. V. Braggin, A. V. Preobrazhenskii, and A. L. Liberman, *Izv. Akad. Nauk., SSSR*, Ser. Khim., 1670 (1984).
26. W. O. Haag and R. M. Dessau, in *Proceedings of the 8th International Congress of Catalysis*, Berlin, Dechema, 1984, Vol. 2, p. 305.
27. G. A. Olah, *J. Am. Chem. Soc., 94*, 808 (1972).
28. G. A. Olah, Y. Halpern, J. Chen, and Y. K. Mo, *J. Am. Chem. Soc., 95*, 4960 (1973).
29. N. S. Gnep, J. Y. Doyemet, A. M. Seco, F. R. Ribeiro, and M. Guisnet, *Appl. Catal., 43*, 155 (1988).
30. J. Bandeira and Y. Ben Taarit, *Appl. Catal., 62*, 309 (1990).
31. H. Kitagawa, Y. Sendoda, and Y. Ono, *J. Catal., 101*, 12 (1986).
32. T. Inui, *Successful Design of Catalysts* (T. Inui, ed.), Studies in Surface Science and Catalysis Vol. 44, Elsevier, Amsterdam, 1989, p. 189.
33. R. Le Van Mao and J. Yao, *Appl. Catal. A, 79*, 77 (1991).
34. J. Yao, R. Le Van Mao, and L. Dufresne, *Appl. Catal., 65*, 175 (1990).
35. R. Le Van Mao, L. Dufresne, J. Yao, and D. Ly, Symposium Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts, ACS Prepr., *336*(4), 716 (1991).
36. R. Le Van Mao and L. Dufresne, *Appl. Catal., 52*, 1 (1989).
37. (*a*) E. Iglesia, J. E. Baumgartner, and G. L. Price, *J. Catal., 134*, 549 (1992); (*b*) G. D. Meitzner, E. Iglesia, J. E. Baumgartner, and E. S. Huang, *J. Catal., 140*, 209 (1993).
38. N. S. Gnep, J. Y. Doyemet, and M. Guisnet, *Zeolites as Catalysts, Sorbents and Detergent Builders* (H. G. Karge and J. Weitkamp, eds.), Studies in Surface Science and Catalysis Vol. 46, Elsevier, Amsterdam, 1989, p. 153.
39. P. Meriaudeau and C. Naccache, *J. Mol. Cat., 50*, L–7 (1987).
40. V. Kanazirev, G. L. Price, and K. M. Dooley, *J. Chem. Soc. Chem. Commun.*, 1990, p. 712.

41. V. Kanazirev, R. Dimitrova, G. L. Price, A. Yu. Khodakov, L. M. Kustov, and V. B. Kazansky, *J. Mol. Catal.*, *70*, 11 (1991).
42. G. L. Price and V. Kanazirev, *J. Mol. Catal.*, *66*, 115 (1991).
43. G. L. Price and V. Kanazirev, *J. Catal.*, *126*, 267 (1990).
44. G. Giannetto, *Rev. Soc. Venezolana de Catálisis*, *5*, 1 (1991).
45. G. Giannetto, *Proc. 6. Seminario Brasileiro de Catalise*, IBP Editions, Brazil, 1991, p. 595.
46. G. Buckles, G. H. Hutching, and C. D. Williams, *Catal. Lett.*, *11*, 89 (1991).
47. (*a*) G. Giannetto, S. Sansare, and M. Guisnet, *J. Chem. Soc. Chem. Commun.*, 1986 p. 1302; (*b*) G. Giannetto, S. Sansare, and M. Guisnet, *Rev. Sec. Venezolana de Catálisis*, *2*(1), 75 (1988).
48. G. Giannetto, R. Monque, and R. Galiasso, to be published.
49. P. Meriaudeau and C. Naccache, in *Catalyst Deactivation* (C. H. Bartholomew and J. B. Butt, eds.), Studies on Surface Science and Catalysis, Vol. 68, Elsevier, Amsterdam, 1991, p. 767.
50. V. B. Kazansky, L. M. Kustov, and A. Yu. Khodakov in *Zeolites: Facts, Figures, Future* (P. A. Jacobs and R. A. Van Santen, eds.), Studies in Surface Science and Catalysis, Vol. 49, Part B, Elsevier, Amsterdam, 1989, p. 1173.
51. V. I. Yakerson, T. V. Vasina, L. I. Lafer, V. P. Sytnyk, G. L. Dykh, A. V. Markhov, O. V. Bragin, and Kh. M. Minachev, *Catal. Lett.*, *3*, 339 (1989).
52. P. Meriaudeau and C. Naccache, *J. Mol. Catal.*, *59*, L31 (1990).
53. C. R. Bayense, A. J. H. P. Van der Pol, and J. H. C. Van Hooff, *Appl. Catal.*, *72*, 81 (1991).
54. (*a*) M. L. Poutsma, in *Zeolite Chemistry and Catalysis* (J. A. Rabo, ed.), ACS Monograph 171, Am. Chem. Soc., Washington, DC, 1976, p. 437; (*b*) H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions*, New York, Academic Press, 1981.
55. W. E. Garwood, in *Intrazeolite Chemistry* (G. D. Stucky and F. G. Dwyer, eds.), ACS Symp. Series 218, Am. Chem. Soc., Washington, DC, 1983, p. 383.
56. S. Bessel and D. Seddon, *J. Catal.*, *195*, 270 (1987).
57. N. S. Gnep, J. Y. Doyemet, A. M. Seco, F. R. Ribeiro, and M. Guisnet, *Appl. Catal.*, *35*, 93 (1987).
58. P. Meriaudeau and C. Naccache, in *Zeolite Chemistry and Catalysis* (P. A. Jacobs, N. I. Jaeger, L. Kubelkova, and B. Wichterlova, eds.), Studies in Surface Science and Catalysis, Vol. 69, Elsevier, Amsterdam, 1991, p. 405.
59. G. Giannetto, J. A. Pérez, R. Sciamanna, L. García, R. Galiasso, and R. Monque, Symposium on Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts, New York City, *ACS Prepr.*, *36*(4), 659 (1991).
60. Z. Gabelica, R. Monque, R. Galiasso, and G. Giannetto, to be published.
61. G. Giannetto, L. García, J. Papa, J. Pérez, R. Sciamanna, and R. Monque, *Proceedings of the XII Iberoamerican Symposium on Catalysis, Rio de Janeiro*, 1990, Vol. 1, p. 8.
62. H. Pinto, N. Mora, M. Villamizar, R. Sciamanna, L. García, G. Giannetto, and R. Monque, *Technical Report*, INTEVEP, 1990.
63. D. K. Simmons, R. Szostak, P. K. Agrawal, and T. L. Thomas, *J. Catal.*, *106*, 287 (1987).

64. L. Petit, J. P. Bournonville, and F. Raatz, in *Zeolites: Facts, Figures, Future* (P. A. Jacobs and P. A. Van Santen, eds.), Studies in Surface Science and Catalysis, Vol. 49B, Elsevier, Amsterdam, 1989, p. 1163.
65. J. Kanai and N. Kawata, *Appl. Catal.*, *55*, 115 (1989).
66. J. Kanai and N. Kawata, *Appl. Catal.*, *62*, 141 (1990).
67. A. Yu. Khodakov, L. M. Lustov, T. N. Bondarenko, G. Borbely, and H. K. Bayer, *Zeolites*, *10*, 603 (1990).
68. G. Giannetto, A. Montes, N. S. Gnep, A. Florentino, P. Cartreau, and M. Guisnet, *J. Catal.* (in press).
69. Z. Gabelica, C. Mayanez, R. Monque, R. Galiasso, and G. Giannetto, in *Synthesis in Microporous Materials*, Vol. 1: *Molecular Sieves* (M. L. Ocelli and H. E. Robson, eds.), Van Nostrand Reinhold, New York, 1992, pp. 190–222.
70. Z. Gabelica, G. Giannetto, F. Dos Santos, R. Monque, and R. Galiasso, in *Proc. 9th International Zeolite Conference*, Montreal, July 1992 (R. von Ballmoos et al., eds.), Butterworth–Heinemann, Stoneham, 1993, p. 231.
71. Z. Gabelica, R. Monque, and G. Giannetto, US Pat. application (1993).
72. C. R. Bayense, J. H. C. Van Hooff, Ketgens, J. W. De Haag, and L. J. M. Van der Ven, *J. Chem. Soc., Chem. Commun.*, 1989, p. 1292.
73. J. F. Joly, H. Ajot, E. Merlen, F. Raatz, and F. Alario, *Appl. Catal A*, *79*, 249 (1991).
74. T. Changyu, C. Changrüi, Z. Lixin, and P. Shaoryi, in *Proc. 9th Int. Congr. Catal., Calgary, 1988* (M. J. Phillips and M. Ternan, eds.), Chem. Inst. of Canada, Ottawa, 1988, p. 445.
75. V. Kanazirev, G. L. Price, and G. Tyuliev, *Zeolites*, *12*, 846 (1992).
76. Y. Ono, H. Nakataini, H. Kitagawa, and E. Suzuki, in *Successful Design of Catalysts* (T. Inui, ed.), Studies on Surface Science and Catalysis, Vol. 44, Elsevier, Amsterdam, 1989.
77. T. Inui, Y. Makino, F. Okazumi, S. Nagano, and A. Miyamoto, *Ind. Eng. Chem. Res.*, *26*, 647 (1987).