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Conversion of Light Alkanes into Aromatic Hydrocarbons

VII. Aromatization of Propane on Gallosilicates: Effect of Calcination in Dry Air

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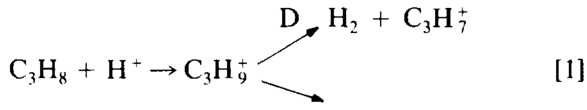
The aromatization of propane at 530°C on three MFI gallosilicates (Si/Ga = 30, 50 and 180) and on a MFI aluminosilicate (Si/Al = 30) was investigated. After pretreatment at 530°C under dry air flow, 30 Al MFI was seven times more active than 30 Ga MFI. This can be related to the greater strength of the acid sites of the aluminosilicate sample, which was shown by a calorimetric study of ammonia adsorption and by ammonia thermodesorption. On all the catalysts propene and methane + ethene in quasi-equimolar amounts appeared as primary products, whereas ethane, butenes, butanes, C_5^+ olefinic and naphthenic compounds, and C_6–C_8 aromatics were secondary products. However, large differences were found in the product distribution, namely a lower initial cracking/dehydrogenation ratio on 30 Ga MFI, greater selectivity to aromatics, and lower selectivity to alkanes (C_1, C_2, C_4) at high conversion, which can be explained by a dehydrogenating effect of gallium. The product distribution depended also on the Si/Ga ratio of the gallosilicate, a better selectivity to aromatics being found with 30 Ga MFI. The selectivity differences are mainly due to differences in the acid site density. The treatment of gallosilicates at 700–800°C under dry air flow caused a significant increase in their activity and in their selectivity for propane aromatization. This could be related to the formation of a small amount of extraframework gallium species, well dispersed in the crystallites and highly active for dehydrogenation of propane and of naphthene intermediates. On these catalysts propane aromatization occurred mainly through a bifunctional scheme and the formation of unwanted C_1–C_2 products, through acid cracking was very limited. The effect of the pretreatment temperature on the acid and dehydrogenating activity of the 30 Ga MFI sample showed that framework gallium species were much less active for dehydrogenation than extraframework species and indeed are probably inactive. © 1994 Academic Press, Inc.

INTRODUCTION

The transformation of short chain alkanes into BTX (benzene, toluene, xylenes) has been extensively investigated with various acid and bifunctional zeolite catalysts, in particular H-ZSM-5 and Ga-loaded H-ZSM-5 catalysts. With H-ZSM-5, the key step is the formation of carbenium ions by dehydrogenation and cracking of a carbonium ion intermediate (1–6); e.g.,



$$C_3H_8 + H^+ \rightarrow C_3H_9^+ \begin{cases} \xrightarrow{D} H_2 + C_3H_7^+ \\ \xrightarrow{C} CH_4 + C_2H_5^+ \end{cases} \qquad [1]$$

The protonation of the alkane reactant could be the limiting step of reaction [1] (6, 7). If this is the case, the dehydrogenation/cracking rate ratio (D/C) would be independent of the strength of the acid sites. Therefore MFI gallosilicates, whose acid sites are weaker than those of MFI aluminosilicates, would present the same D/C ratio. The first objective of this work is to investigate this by comparing the initial selectivity of propane transformation on various MFI aluminosilicates and gallosilicates.

With Ga-loaded H-ZSM-5 catalysts the aromatization occurs through a bifunctional scheme (2, 8–12), the gallium species catalyzing the dehydrogenation of the alkane reactant and that of the naphthene intermediates (Fig. 1). However, the acidic process continues to operate, the acid sites and the gallium species intervening simultaneously in steps 1 and 5, which has as a consequence the formation of unwanted products, namely methane and ethane. Thus the Cyclar catalyst (13) transforms only 70% of propane into valuable products, aromatics and hydrogen, the remaining 30% being converted into methane and ethane. The aromatization selectivity, aromatics/(methane + ethane), obviously depends on the relative significance of the acid and the bifunctional schemes: hence it depends on the balance between the dehydrogenation and acid functions and on the distribution of the corresponding sites within the zeolite. We show that a high selectivity can be obtained with gallosilicates which have been previously treated under dry air at high temperature. This

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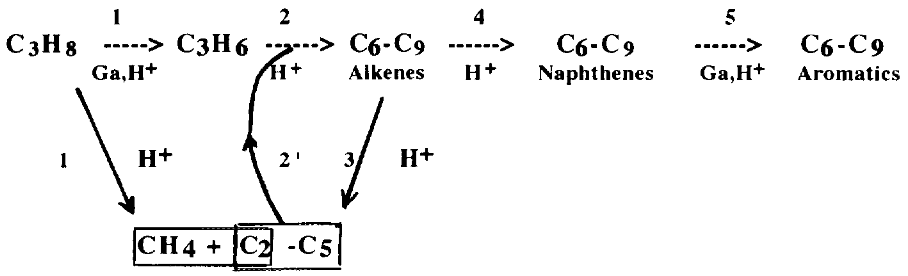

FIG. 1. Aromatization of propane on Ga/HZSM5 catalysts: reaction pathway.

treatment creates extraframework gallium species which are well dispersed in the gallosilicate crystallites and highly active for dehydrogenation.

EXPERIMENTAL

The gallosilicates (Si/Ga = 30, 50, 180) were synthesized according to Ref. (14) from gels prepared from sodium trisilicates (Merck), gallium nitrate (Aldrich), sodium chloride, sulfuric acid, demineralized water, and tetrapropylammonium bromide (Aldrich) as template agent. The aluminosilicate (Si/Al = 30) was synthesized according to Mobil patents (15). The samples were calcined for 6 h at 643 K, ion exchanged three times with a 5 *M* NH_4Cl solution at 353 K for 3 h, and calcined for a second time (12 h, 803 K). The composition of the samples was determined in the Centre d'Analyse du CNRS de Solaize and that of the framework by Ga-NMR according to the method developed by Gabelica *et al.* (16). Adsorption isotherms of nitrogen at 77 K and of 3-methylpentane at 298 K were determined with a Sartorius 4433 electrobalance. The acidity of the samples was characterized by a calorimetric study of ammonia adsorption and by ammonia thermodesorption. With the first method the amount of adsorbed ammonia and the differential heats of adsorption were measured simultaneously at 423 K on the samples pretreated under vacuum (about 10^{-4} Pa) at 723 K for 3 h. NH_3 was introduced in small amounts, the amount adsorbed being determined from pressure measurements and the amount of heat liberated with a flowmeter-type calorimeter. With the second method the zeolite sample was pretreated for 12 h under dry nitrogen flow at 773 K, then saturated by ammonia at 323 K. The temperature was then increased with plateaus every 50 K and the amount of ammonia desorbed under helium flow ($0.016\ cm^3 \cdot s^{-1}$) was determined with a catharometer.

The reactions were carried out in a flow reactor under the following conditions:

(i) Propane and propene transformation: 803 K; pressure of reactant, 1 bar; WWH (weight of reactant injected per unit weight of catalyst and per hour) between 0.2 and 80 h^{-1} for propane and 10 and 1000 h^{-1} for propene in order to obtain a wide range of conversion rates.

(ii) *m*-Xylene transformation: 623 K; *m*-xylene pressure = 0.2 bar; nitrogen pressure = 0.8 bar; WWH between 5 and 200 h^{-1}.

Reaction products were analyzed on line by gas chromatography; the conditions for analysis are reported elsewhere (3).

RESULTS

1. Comparative Study of Ga MFI and Al MFI Samples

1.1. Physicochemical properties of the samples calcined at 530°C. The total Si/Ga ratios of the Ga MFI samples, determined by elemental analysis, were 35, 59, and 200. After calcination under dry air flow at 530°C, the framework ratios estimated by ^{71}Ga-MAS NMR were 35, 50, and 180. The samples will be called 30, 50, and 180 Ga MFI, respectively. No extraframework Ga species were detected. The total and framework Si/Al ratios of the MFI aluminosilicate (30 Al MFI) were both close to 30. The unit cell formulas of these samples are given in Table 1. X-ray diffraction showed that all the samples were well crystallized.

The isotherms for adsorption of nitrogen and of 3-methylpentane were of type I in the Brunauer classification. The adsorption capacities estimated by extrapolation of the isotherms at $P/P_0 = 1$ were between 0.204 (30 Ga MFI) and 0.216 (30 Al MFI) cm^3g^{-1} for 3-methylpentane. The values obtained by extrapolation of the isotherms at $P/P_0 = 0$ were between 0.15 cm^3g^{-1} (Ga MFI samples) and 0.165 cm^3g^{-1} (30 Al MFI) for nitrogen and between 0.125 (Ga MFI samples) and 0.145 cm^3g^{-1} (30 Al MFI) for 3-methylpentane.

From the calorimetric study of ammonia adsorption it could be concluded that 30 Al MFI has stronger acid sites than 30 Ga MFI (maximal heat of adsorption, Q_{max}, equal to 135 and 110 kJ mol^{-1}, respectively) and that the greater the Si/Ga ratio of the Ga MFI samples, the lower the number of the acid sites. Furthermore, there was a slight difference in the strengths of the acid sites of Ga MFI

TABLE 1

Unit Cell Formula and Acidity of the MFI Samples

	Unit cell formula	*n*th	*n*80	*n*423	*n*673
30 Ga MFI	$H_{2.2}\ Na_{0.5}\ Ga_{2.7}\ Si_{93.3}\ O_{192}$	2.35	2.0	2.45	0.13
50 Ga MFI	$H_{1.75}\ Na_{0.15}\ Ga_{1.9}\ Si_{94.1}\ O_{192}$	1.8	1.45	2.1	0.15
180 Ga MFI	$H_{0.43}\ Na_{0.1}\ Ga_{0.53}\ Si_{95.5}\ O_{192}$	0.45	0.55	0.45	0.05
30 Al MFI	$H_{3.07}\ Na_{0.03}\ Al_{3.1}\ Si_{92.9}\ O_{192}$	3.2	3.0	3.0	0.39

Note. *n*th, *n*80, *n*473, *n*673: number of acid sites ($10^{20} g^{-1}$). *n*th derived from the unit cell formula, *n*80 for which the heat of ammonia adsorption was greater than 80 kJ mol^{-1}, *n*423 and *n*673 on which ammonia remained adsorbed above 423 K and 673 K.

samples (Table 1). Indeed, while all the acid sites of 180 Ga MFI were strong ($Q > 80$ kJ mol^{-1}), this was the case for only 80% of the acid sites of 30 and 50 Ga MFI. Ammonia thermodesorption confirmed that the sites of 30 Al MFI were stronger than those of 30 Ga MFI. Thus for 15% of the sites of 30 Al MFI ammonia remained adsorbed above 673 K, but only for 5–10% of the sites of the Ga MFI samples. Again 180 Ga MFI had slightly stronger sites than 30 and 50 Ga MFI samples (Table 1).

The rate of *m*-xylene transformation was greater on 30 Al MFI than on the Ga MFI samples, initially 3, 5, and 12 times greater than on 30, 50, and 180 Ga MFI samples. There was a slight deactivation during the first hour of reaction with 30 Al MFI and 30 Ga MFI samples. Isomerization into *para*- and *ortho*- xylenes was the only reaction. The isomerization selectivity was practically independent of the catalyst; for a conversion of about 10% the *para*/*ortho* ratio was equal to 1.9, 2.2, 1.7 with 30, 50, and 180 Ga MFI catalysts and to 2.1 with 30 Al MFI.

1.2. Propane transformation. The activity of 30 Al MFI was greater than that of the Ga MFI samples: 7, 9 and 18 times that of 30, 50, and 180 Ga MFI samples. With all the catalysts, propene and methane + ethene in quasi-equimolar amounts appeared as primary products while ethane, butenes, butanes, C_5^+ olefinic and naphthenic compounds, and aromatics were secondary products (Fig. 2). However, the product distribution depends on the catalyst, as follows.

(i) The rate ratio of cracking and dehydrogenation of propane (C/D) was lower at very low conversion on Ga MFI catalysts than on 30 Al MFI (Fig. 3). Methane, ethene, and also ethane were considered as cracking products and propene as a dehydrogenation product. With all the samples C/D increased with the conversion. The increase was more significant with 30 Ga MFI and 50 Ga MFI than with 30 Al MFI and above all with 180 Ga MFI.

(ii) All the olefinic products, ethene, propene, butenes, and C_5^+, underwent secondary transformations. These secondary transformations were faster with Ga MFI catalysts than with Al MFI. The lower the Ga/Si ratio the faster were these transformations; indeed, the lower the Ga/Si ratio the lower the maximum yield and the conversion for which this yield was obtained (Figs. 2b, c, e and g).

(iii) The aromatic yield was greater with Ga MFI catalysts than with 30 Al MFI. The lower the Ga/Si ratio, the greater was the yield (Fig. 2h).

(iv) The distribution of aromatics depended slightly on the catalyst: about 30 wt% benzene, 45% toluene, 25% C_8 aromatics with 30 and 50 Ga MFI, and 20% benzene, 50% toluene and 30% C_8 aromatics with 180 GaMFI and 30 Al MFI.

(v) For a given value of the aromatic yield the amount of unwanted products (methane and ethane) was lower with Ga MFI catalysts than with 30 Al MFI; hence the aromatic/(methane + ethane) ratio was lower on 30 Al MFI than on Ga MFI catalysts. The greatest value of this ratio (hence the highest selectivity to aromatics) was obtained for the 30 Ga MFI sample (Fig. 4). The production of hydrogen was estimated from the product distribution. The ratio of the rates of production of hydrogen and aromatics depended on the catalyst. For conversion into aromatics (X_{Ar}) above 5% the molar hydrogen/aromatic ratio was equal to 2.6–2.7 on 30 Al MFI, to 3.6–3.8 with 30 and 50 Ga MFI, and to 4.0 with 180 Ga MFI.

1.3. Propene transformation. The transformation of propene was carried out only on 30 Al MFI and 30 Ga MFI. The rate of propene transformation was about 50 times greater than that of propane transformation with 30 Al MFI and 350 times with 30 Ga MFI. For propene transformation 30 Al MFI was about 1.5 times more active than 30 Ga MFI. The product distributions were practically identical. With both catalysts the primary products were olefinic: ethene < butenes = C_5^+. Alkanes (methane < ethane ≪ propane = butanes) did not appear at low conversion. Aromatics were also secondary products with 30 Al MFI but seemed to result directly from propene with 30 Ga MFI (Fig. 5). With 30 Al MFI the C_2–C_4 alkane/aromatic molar ratio was close to 3, while it was between 1 and 1.5 with 30 Ga MFI.

2. *Influence of the Pretreatment Temperature T_c on 30 GaMFI*

The pretreated samples were characterized by X-ray diffraction and nitrogen adsorption and their activity and selectivity were determined for propane aromatization. X-ray diffraction showed that even after calcination at 800°C the crystallinity of the samples remained high. This was confirmed by nitrogen and 3-methylpentane adsorption. There was only a slight decrease in the

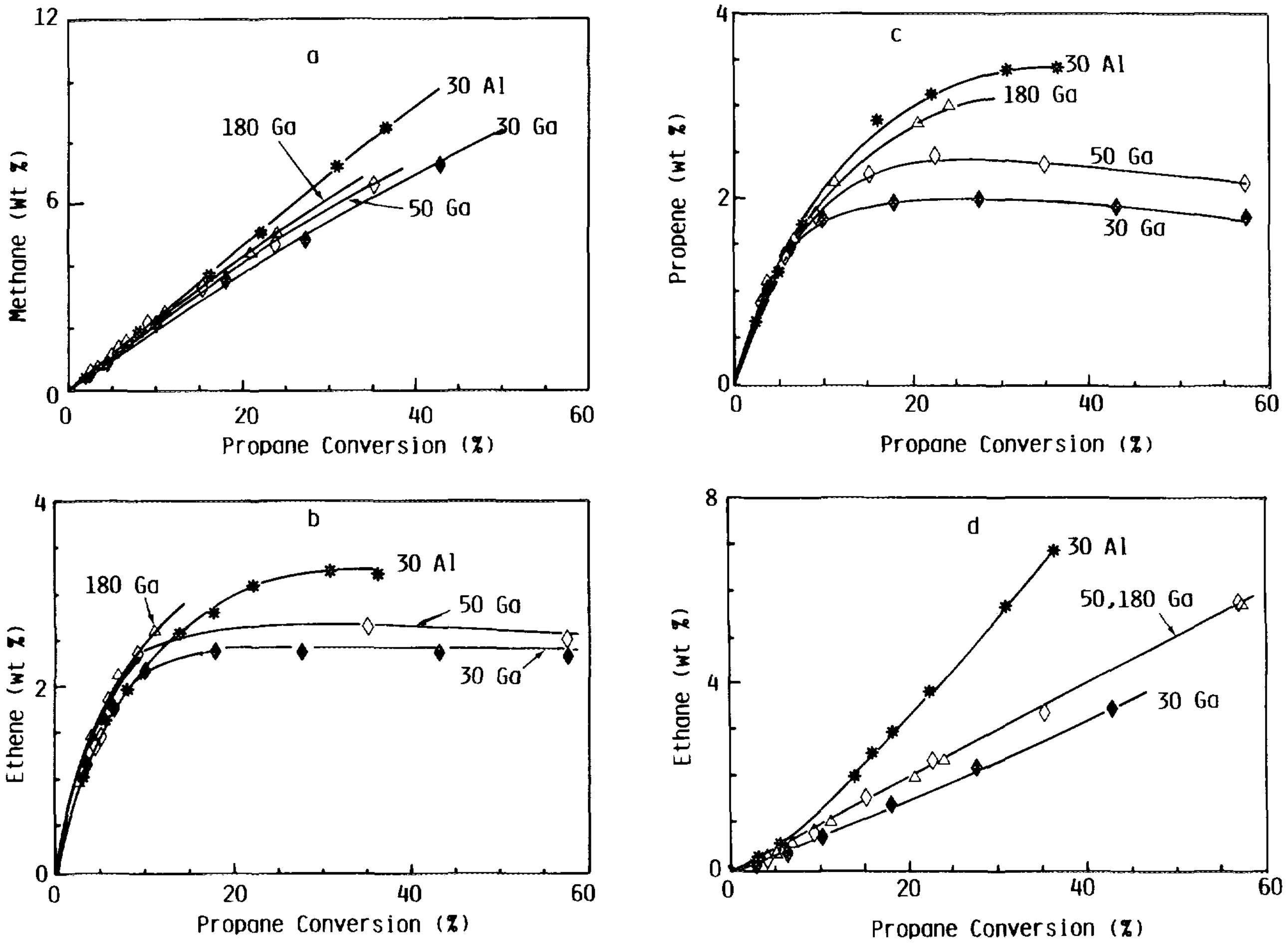

FIG. 2. Propane transformation on 30 Al MFI and on 30, 50, and 180 Ga MFI samples at 530°C. Yields of the products versus propane conversion.

adsorption capacity when T_c was increased (about 10% from 530 to 800°C).

Figure 6 shows that the activity did not change when T_c increased from 530 to 600°C but became twice as great for T_c equal to 700 or 800°C. Likewise the selectivity did not change until T_c = 600°C and differed completely for higher T_c values (Fig. 7). Thus, while propene and methane + ethene were directly formed on all the samples, the cracking/dehydrogenation rate ratio (C/D) was much lower for T_c = 700 and 800°C (close to zero at zero conversion) than for T_c = 530 or 600°C (Fig. 8). The secondary reactions of alkenes (ethene, propene, butenes, C_5^+) were more rapid for high T_c values (maximum yield obtained at lower conversion (Fig. 7b, c, e, g) and the yield in aromatics was higher (Fig. 7h). Consequently the selectivity to aromatics was much greater. Thus Fig. 9 shows for high aromatic yield that the mass ratio of aromatics to methane + ethane becomes equal to 4 for T_c = 800°C compared to 2.5 for T_c = 530°C.

DISCUSSION

1. Comparison of 30 Ga MFI and 30 Al MFI Samples

While the theoretical number of acid sites is practically the same with the two samples, the number of strong acid sites of 30 Al MFI is greater than that of 30 Ga MFI: n_{80} is 1.5 times greater and n_{673} 3 times. This smaller strength of the acid sites of Ga MFI samples has previously been underlined (17–23). The greater strength of the acid sites of 30 Al MFI is confirmed by its higher activity for *m*-xylene, propane, and propene transformations. The difference in activity depends on the reaction: 30 Al MFI is 7 times more active for propane transformation at 530°C, 3 times for *m*-xylene isomerization at 350°C, and 1.5 times for propene transformation at 530°C. The greater the difference the stronger the acid sites required for catalyzing the reaction (24). It must be underlined, however, that the differences in activity for propane and propene transformation could be influenced by a dehydrogenating effect of gallium.

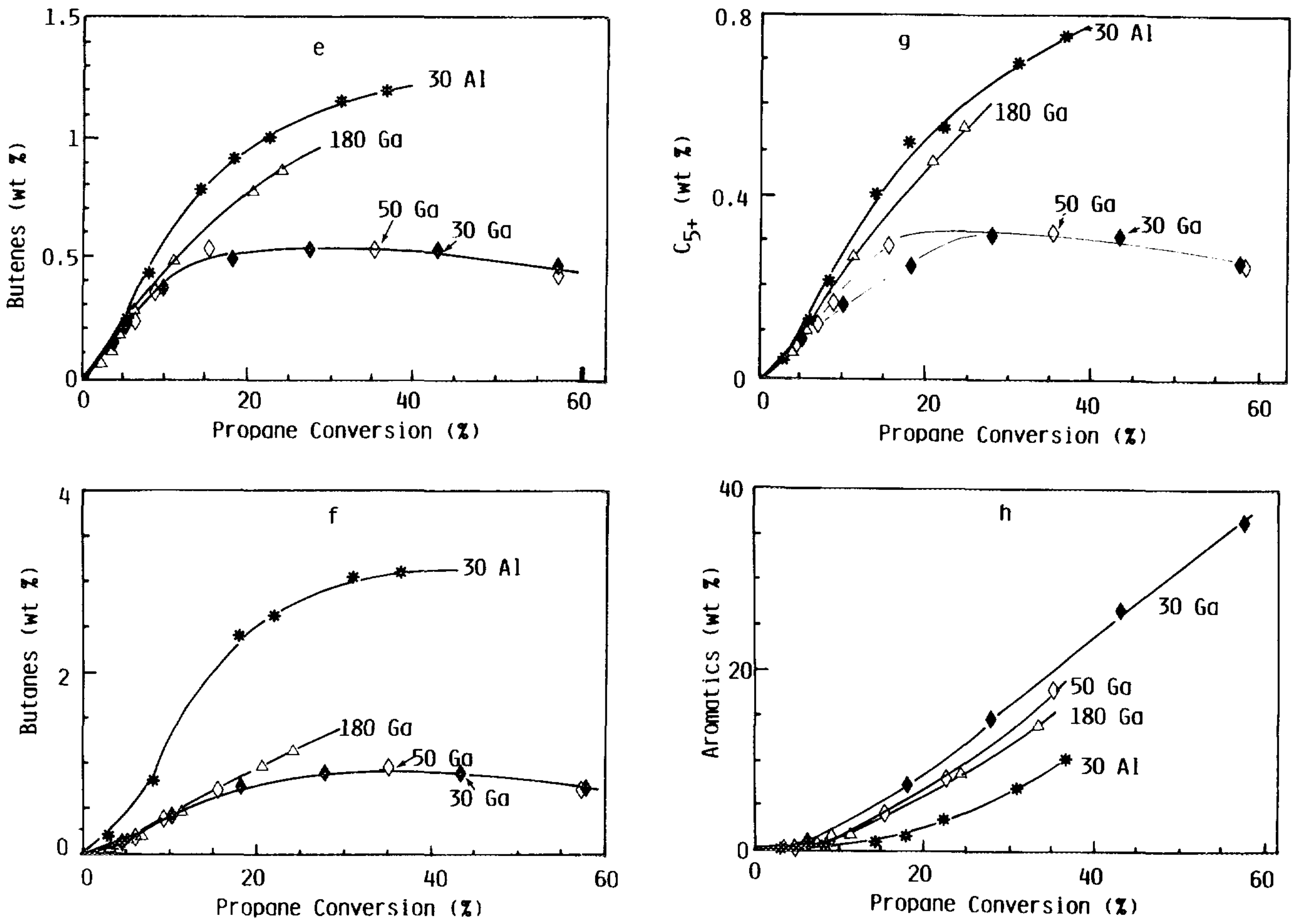

FIG. 2—*Continued*

This point can be discussed in the light of the product distribution on 30 Al and 30 Ga MFI samples. At low conversion, while propane leads directly to cracking (C) and dehydrogenation (D) products, the C/D ratio is slightly lower with 30 Ga MFI than with 30 Al MFI (1.8 at zero conversion compared to 2.5 (Fig. 3)). This slight difference could be attributed to differences in acidity or to a dehydrogenating effect of gallium. No effect of acid strength has been observed in various studies (5, 7), the reason being that the limiting step of alkane dehydrogenating and cracking on the acid sites would be the formation of the carbonium ion through propane protonation. A dehydrogenation of propane on gallium is more likely. If we admit this latter hypothesis it is possible to estimate from the C/D ratio that 25–30% of propene is formed on gallium and 70–75% on the acid sites.

Large differences exist between the product distributions on 30 Al MFI and 30 Ga MFI at high conversion. The maximum yield in C_2, C_3, C_4, and C_5^+ alkenes (Fig. 2b, c, e, and g) is lower with 30 Ga MFI and obtained at lower conversions showing a greater ratio between the rates of transformation and of production. This greater ratio is responsible for the greater selectivity to aromatics of the 30 Ga MFI sample (Fig. 2h). In contrast, the selectivity to C_2 and C_4 alkanes is lower on 30 Ga MFI than on 30 Al MFI. It has been well demonstrated that on aluminosilicates aromatics and alkanes result from hydrogen transfer from naphthenes to alkenes (e.g., alkane/aromatic ratio equal to 3 in propene transformation on 30 Al MFI). Since the selectivity to aromatics increases from 30 Al MFI to 30 Ga MFI while the selectivity to alkanes decreases, it can be concluded that another mechanism participates with hydrogen transfer in the formation of aromatics. This mechanism probably implies dehydrogenation steps of C_6–C_8 alkenes or naphthenic compounds on gallium species. This is suggested by the low values of the C_2–C_4 alkane/aromatic molar ratio found in propene transformation on 30 Ga MFI (1 to 1.5 compared to 3 with 30 Al MFI) and by the high value of the hydrogen/aromatic molar ratio: 3.6 to 3.8 moles of hydrogen are formed per

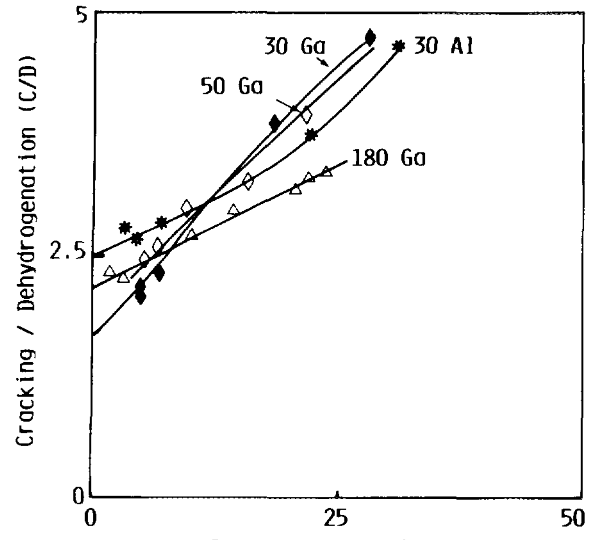

FIG. 3. Ratio of the cracking/dehydrogenation rates versus propane conversion on 30 Al MFI and on 30, 50, and 180 Ga MFI samples at 530°C.

mole of aromatic with 30 Ga MFI, compared to 2.6–2.7 with 30 Al MFI. With 30 Al MFI this corresponds to the dehydrogenation of propane into propene (2.5 mol of propene are necessary to obtain 1 mol of aromatic with the experimental distribution). With 30 Ga MFI one supplementary mole of hydrogen is formed per mole of aromatics. Since about 3 moles of hydrogen can be liberated per mole of aromatic produced from propene this means that ⅓ of the aromatics result from dehydrogenation on gallium species and ⅔ from hydrogen transfer on the acid sites.

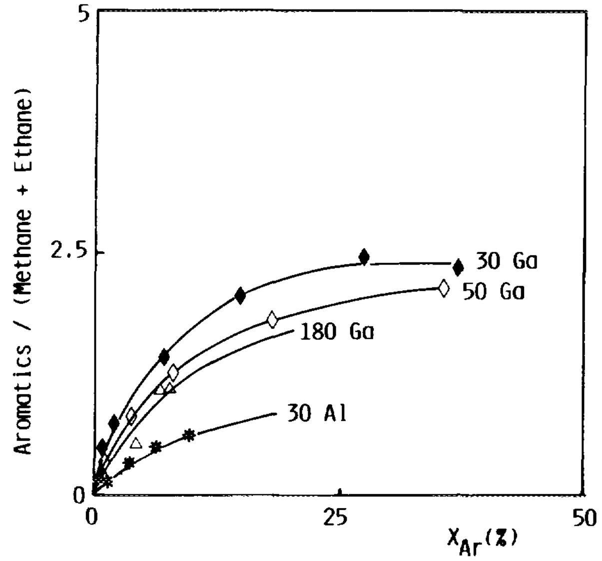

FIG. 4. Mass aromatics/(methane + ethane) ratio versus the conversion of propane into aromatics (X_{Ar}).

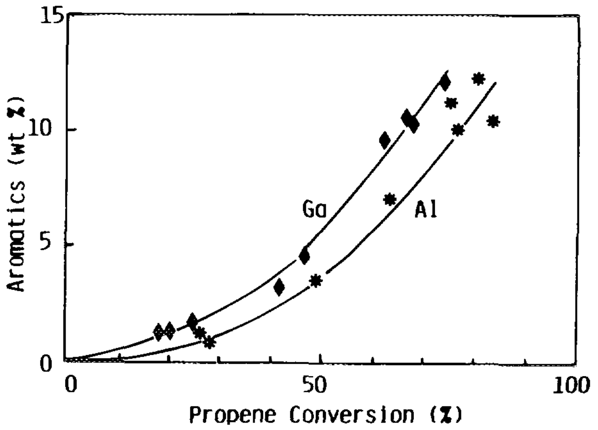

FIG. 5. Propene transformation on 30 Al and 30 Ga MFI samples at 530°C. Yield of aromatics versus propene conversion.

2. *Effect of the Si/Ga Ratio*

The acid strength of 180 Ga MFI seems to be slightly higher than that of 30 and 50 Ga MFI and the turnover number for propane transformation is 2 times greater and that for *m*-xylene transformation 1.5 times. However, there is practically no difference between the acid strength of 30 and 50 Ga MFI and between their activity per acid site. In *n*-butane cracking identical values of the turnover number have also been found with 35, 45, and 90 Ga MFI samples (18). Therefore the apparently higher acid

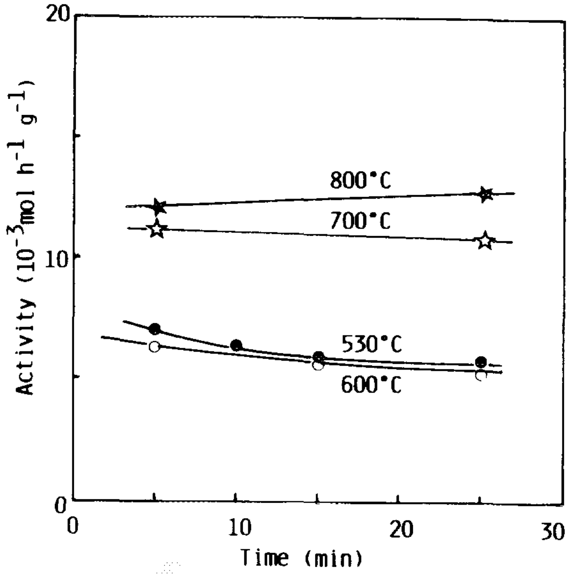

FIG. 6. Propane transformation at 530°C on the 30 Ga MFI samples pretreated at temperatures between 530 and 800°C. Activity versus time-on-stream.

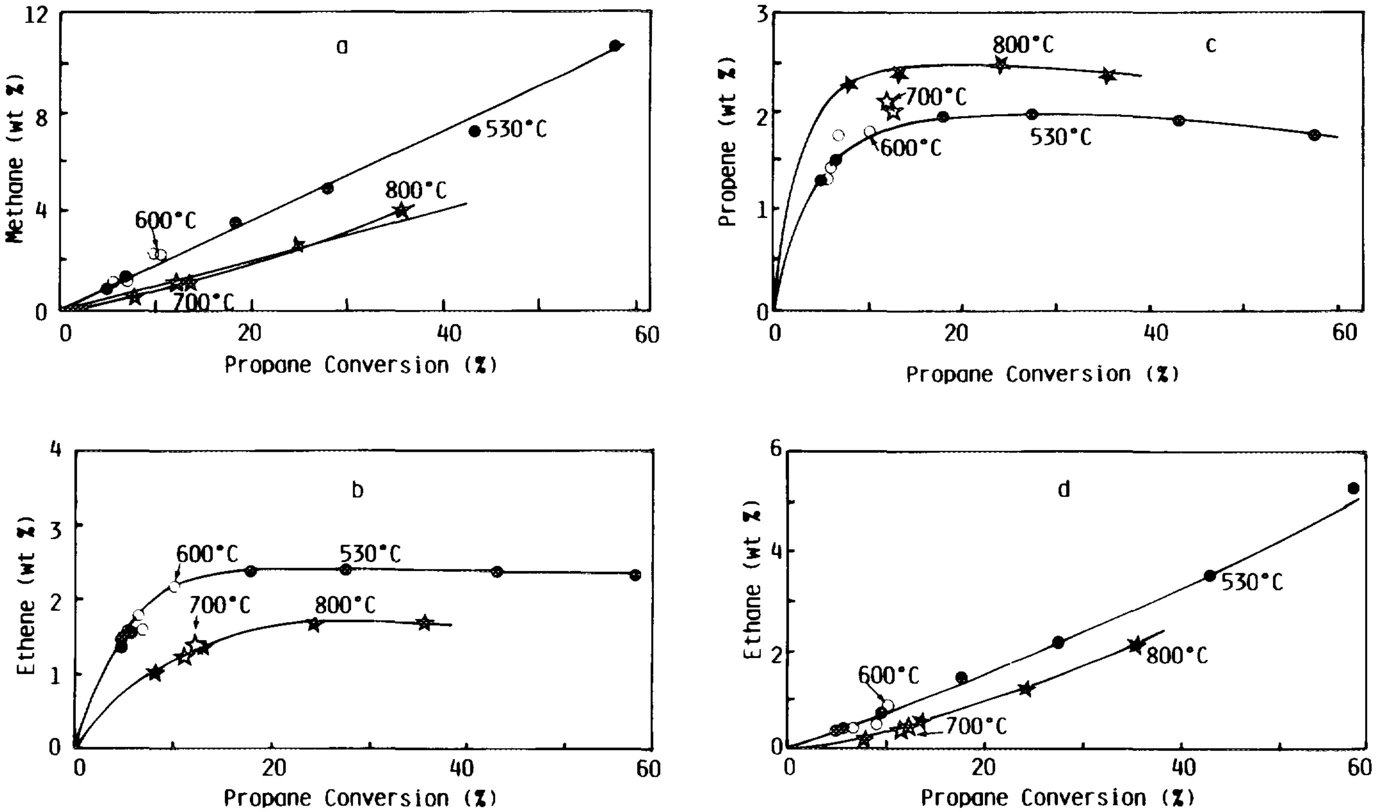

FIG. 7. Propane transformation at 530°C on the 30 Ga MFI samples pretreated at temperatures between 530 and 800°C. Yields of the products versus propane conversion.

strength and turnover number of 180 GaMFI could also be explained by an underestimation of its Si/Ga ratio. This is quite possible since the accuracy in the determination of high Si/Ga ratios is not very great.

The Si/Ga ratio has a pronounced effect on the product distribution (Fig. 2, 3, and 4). Figure 4 shows that from an applied point of view, the lower the Si/Ga ratio the better the zeolite. Indeed, the ratio between aromatics and methane + ethane (which can be used only as fuel) increases when decreasing the Si/Ga ratio.

On all the samples propene and methane + ethene are the primary products. However, the cracking/dehydrogenation ratio is initially greater on 180 Ga MFI than on 30 and 50 Ga MFI (2.2 at zero conversion compared to 1.8 (Fig. 3)). From this observation it can be estimated that with 180 Ga MFI only 12% of propene comes from dehydrogenation of gallium compared to 25–30% with 30 and 50 Ga MFI (see Section 1). This may be due to differences between acid sites (higher strength of the acid sites of 180 Ga MFI) or to the amount of gallium dehydrogenating species.

The number of moles of hydrogen produced per mole of aromatics is slightly greater with 180 Ga MFI (4 compared to 3.7 with 30 and 50 Ga MFI), which indicates that there is a greater participation of the Ga species in the aromatization of C_6–C_8 oligomers with 180 Ga MFI. This might seem to contradict the weaker effect of gallium in the dehydrogenation of propane. However, the formation of aromatics on the acid sites requires several successive hydrogen transfer steps and is unfavored for catalysts having a low density of acid sites such as 180 Ga MFI.

This decrease in the hydrogen transfer rate when the Si/Ga ratio increases is probably also responsible for the difference found in the yields in aromatics and in alkenes: there is a decrease in the yield in aromatics when the Si/Ga ratio increases and an increase in the maximum yield in C_2, C_3, C_4, and C_5^+ alkenes, this maximum yield being obtained at higher conversion. This shows that the ratio of the rates of transformation and of production of alkenes decreases when the Si/Ga ratio increases, and hence that the rate of hydrogen transfer decreases.

3. *Dehydrogenating Activity of Framework and Extraframework Ga Species*

Above 600°C the pretreatment temperature T_c has a positive significant effect on the activity and selectivity

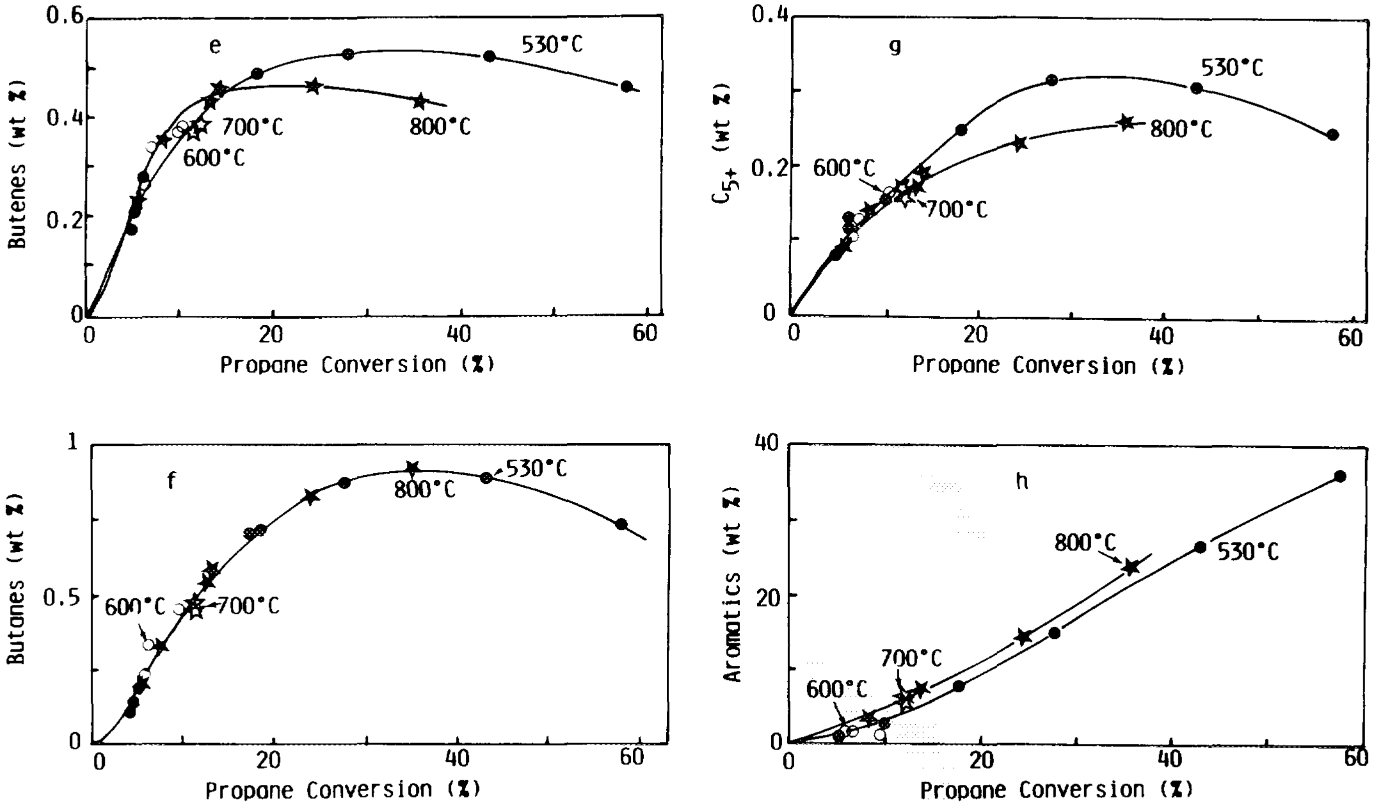

FIG. 7—*Continued*

of 30 Ga MFI for propane aromatization. This effect can be attributed to the formation of extraframework gallium species. This extraction of gallium from the lattice occurs only for $T_c > 600°C$; the activity and selectivity of the samples are identical for T_c equal to 530 or to 600°C. This extraction has secondary effects: decrease in acidity corresponding to the elimination of gallium from the framework, partial collapse of the gallosilicate, and blockage of the access of adsorbates and reactants to the pore volume by extraframework species. These two latter phenomena are responsible for the slight decrease which was observed in the pore volume accessible to nitrogen and to 3-methylpentane. The effect of the pretreatment on the acidity can be estimated from the rates of propane cracking into methane + ethene. Indeed, this reaction is catalyzed by the acid sites only. As ethene undergoes secondary reactions the effect of T_c on the acidity can be estimated from the rate of methane formation. A very low decrease in this rate (<10%) is found when T_c is increased from 530 to 800°C. This shows that the extraction of the gallium species from the framework is very limited (<10%) and hence the amount of Ga extraframework species is very low.

As has already been found (18–20, 22), these extraframework gallium species are highly active for dehydrogenation. Indeed, the rate of propene formation after pretreatment at 800°C is at least 5 times that found for T_c = 530–600°C. For T_c = 530–600°C, 25 to 30% of propene was formed by dehydrogenation on gallium, while for T_c = 800°C, this is the case for more than 85%. After pretreatment at 800°C the propene formation on gallium species is about 15 times faster than after pretreatment at 530°C. If we suppose that the dehydrogenating activity of gallium found for T_c = 530°C is due to the framework gallium it means that for an amount at least 10 times lower the dehydrogenating activity of the extraframework gallium is about 15 times greater. The extraframework Ga species formed by pretreatment at high temperature are therefore at least 150 times more active than the framework Ga species. This very high dehydrogenating activity could result from a concerted action of gallium species and of protonic sites (20, 25, 26). These extraframework species, well dispersed in the gallosilicate, could be close to the protonic sites and interact with them.

Given the very high dehydrogenating activity of the Ga extraframework species, the activity of framework Ga species can be questioned. The presence of a very small amount of well-dispersed Ga extraframework species (impossible to prove by ^{71}Ga NMR) is enough to explain the low dehydrogenating activity of 30 Ga MFI pretreated

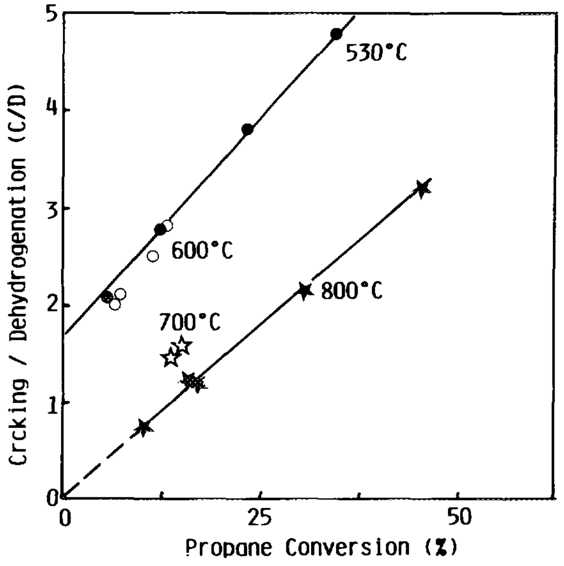

FIG. 8. Ratio of the cracking/dehydrogenation rates versus propane conversion at 530°C on the 30 Ga MFI samples pretreated at temperatures between 530 and 800°C.

at 530°C. However, these eventual extraframework Ga species cannot be formed during the pretreatment since the dehydrogenating activity of 30 Ga MFI is the same for T_c = 530 and 600°C. These species could, however, be created during the synthesis of the gallosilicate (22).

Whatever the pretreatment temperature, 30 Ga MFI is more selective for propane aromatization than Al MFI samples, even those impregnated with gallium nitrate. Thus the mass ratio aromatic/(methane + ethane) at high conversion is equal to 2.5 on 30 Ga MFI pretreated at 530°C compared to 1.2 on Ga impregnated 30 Al MFI samples (6 wt% Ga). This ratio increases with the pretreatment temperature T_c becoming equal to 4 for T_c = 800°C (Fig. 9). Unfortunately the activity of gallosilicates is much lower than that of the Ga impregnated Al MFI samples, i.e., too low for gallosilicates to be used as industrial catalysts.

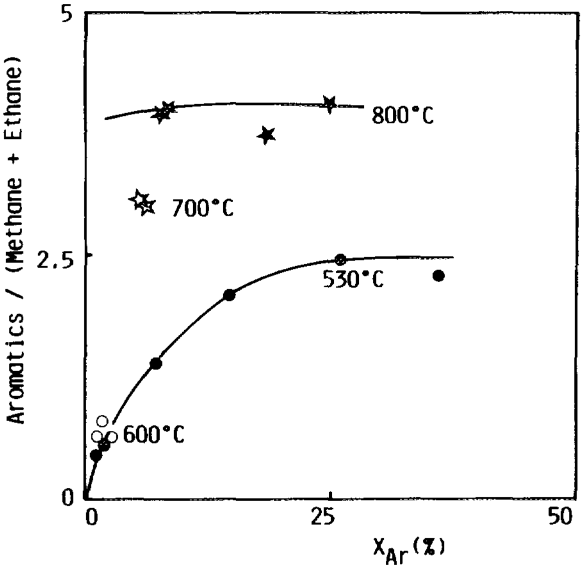

FIG. 9. Mass aromatics/(methane + ethane) ratio versus the conversion of propane into aromatics (X_{Ar}) on the 30 Ga MFI samples pretreated at temperatures between 530 and 800°C.

CONCLUSIONS

This study confirms that gallosilicates have a lower acidity than aluminosilicates and therefore are less active in acid-catalyzed reactions. Their treatment at high temperature (700–800°C) under dry air flow causes a partial extraction of gallium from the framework and a small decrease in the acidity and in the adsorption properties. The extraframework gallium species thus created are highly active for dehydrogenation, rendering the gallosilicates highly selective for propane aromatization. This high selectivity can be related to the fact that propane aromatization occurs mainly through a bifunctional mechanism, the significance of the acidic process responsible for the formation of unwanted products (methane, ethane) being very limited. Framework gallium species are much less active for dehydrogenation than extraframework species and probably not active at all.

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