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A new way to obtain acid or bifunctional catalysts. II. Straightforward calcination of as-synthesized [Ga,Al]-ZSM-5 zeolites obtained from alkali-free media

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Abstract

The acid or bifunctional behavior of catalysts obtained by the straightforward calcination (530–800°C) of as-synthesized [Ga,Al]-ZSM-5 zeolite, obtained from alkali-free media, was determined using propane, cyclohexane and cyclohexene transformations ($T = 530°C$, $p = 1$ atm) as reaction models. Solids were characterized by XRD, FTIR, N_2 adsorption, ^{27}Al and ^{71}Ga MAS NMR and chemical analysis. The catalyst acidities were evaluated using *n*-heptane cracking and *m*-xylene isomerization as reaction models. Results show that calcination temperatures (T_c) between 530 and 550°C, causes only the removal of organic molecules used for the synthesis of the zeolite, leading then to pure acidic catalysts. At $700 \leq T_c \leq 800°C$, simultaneously with the removal of those organic molecules, a significant chemical change of the zeolite framework composition take place (degalliation and dealumination). The presence of extraframework gallium species (EFGS), led to acid gallium promoted bifunctional catalysts with catalytic properties for propane and naphthenes aromatization almost identical to those for gallium promoted zeolites obtained by conventional methods (ion exchange and/or impregnation).

Keywords: Propane; Cyclohexane; Cyclohexene; Aromatization; [Ga,Al]-ZSM-5; Degalliation; Dealumination; Acidic and bifunctional catalysts

1. Introduction

Since Davis and Kolombos [1] from British Petroleum Co., published their patent in which they reported that light paraffin C_3–C_4 aromatization reactions were highly promoted when acid zeolites H-[Al]-ZSM-5 were ion exchanged and/or impregnated with gallium ions, an important number of papers has been published. These works are summarized in some recently published reviews [2–4]. The loading of extraframework gallium species (EFGS) by conventional methods (exchange and/or impregnation) [1–6], or their generation by degalliation of gallo- or galloaluminumsilicate MFI-type zeolites [7–13], produces an increase in the activity for light paraffins aromatization reactions, and in the selectivity toward aromatic products. This is due to the fact that EFGS catalyze the dehydrogenation reactions of reactants and intermediate products [14–16]. Nevertheless, the nature of these EFGS is still a matter of contro-

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versy [3,4,17–25]. Because conventional MFI-type zeolites (alumino-, gallo- or galloaluminumsilicates) are synthesized in the presence of an inorganic cation (i.e. Na^+) [7–11,26–31], the preparation of the final catalyst involves relatively long and costly intermediate steps (cationic exchanges and calcinations). Recently we reported the synthesis of MFI-type zeolites in the total absence of inorganic cations [32,33], and we demonstrated that, depending on the calcination temperature, gallosilicate MFI-type zeolites synthesized by this new method can lead to acid or bifunctional catalysts [33–35]. In this work we show that the same behavior is possible when [Ga,Al]-ZSM-5 zeolites obtained by the new method are used. Owing to differences in the degree of dealumination and degalliation, the activity of these catalysts is higher than the activity observed for catalysts obtained from pure gallosilicates. Nevertheless, the selectivity remains almost the same.

2. Experimental

The synthesis gel was prepared in the total absence of inorganic cations and using tetrapropylammonium bromide, TPABr, as a template agent, and methylamine, $MeNH_2$, as a complexing and mobilizing agent [32,33,36]. Silicon, gallium and aluminum sources were, respectively, Aerosil 200 (100% SiO_2; $S = 210$ m^2/g), gallium nitrate ($Ga(NO_3)_3 \cdot 9H_2O$) and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$). The following procedure was used to prepare the synthesis gel. Two aqueous solutions (A + B) were prepared as follows:

Solution A: 4.20 g of $Ga(NO_3)_3 \cdot 9H_2O$ and 7.10 g $Al(NO_3)_3 \cdot 9H_2O$ were simultaneously dissolved in 280 g of H_2O.

Solution B: 68.30 g TPABr were dissolved into 301 g of H_2O which was previously mixed with 155.98 g of methylamine (40% aqueous solution).

Solution A was added to solution B under continuous stirring at room temperature for 15 min. 55.91 g of SiO_2 were then slowly added under rapid stirring. The resulting galloaluminumsilicate hydrogel with the following chemical composition:

$$92.8SiO_2{:}0.61Ga_2O_3{:}1.0Al_2O_3{:}100.6$$
$$(MeNH_3)_2O{:}12.5(TPA)_2O{:}3780H_2O$$

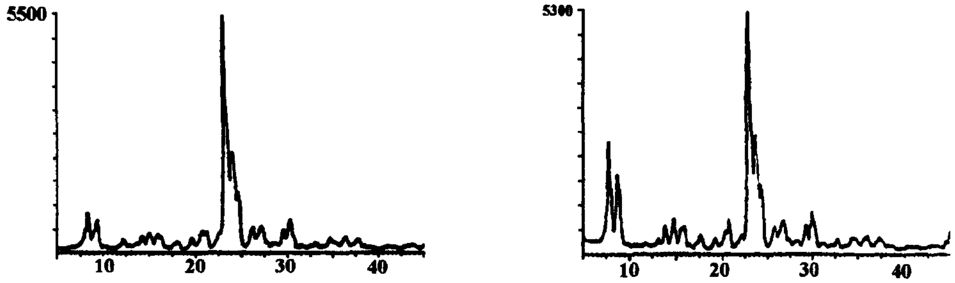
was allowed to react at 185°C, under autogenous pressure and rocking agitation during 8 days. The solid was washed with plenty of distilled water and dried at 120°C for 12 h [36]. Once characterized, the zeolite was calcined in dry air flow (shallow bed, 5 cm^3/g) and, according to the temperature (between 530 and 800°C), seven solids were obtained: GaAl-530, GaAl-550, GaAl-600, GaAl-650, GaAl-700, GaAl-750, GaAl-800, where the numbers indicate the calcination temperature. Samples were characterized by XRD [28], FTIR [37], nitrogen adsorption, ^{27}Al and ^{71}Ga MAS NMR [38] and chemical analysis [39].

The catalyst acidities were evaluated using *n*-heptane cracking and *m*-xylene isomerization as reaction models ($T = 350$°C; $p = 1$ atm; N_2/hydrocarbon = 4) [34,35]. Propane, cyclohexane and cyclohexene transformations ($T = 530$°C; $p = 1$ atm) were used to test the acidic, bifunctional or metallic behavior of the calcined zeolites. Conventional bifunctional 1.5 wt%Ga/H-[$Ga_{1.01}Al_{1.81}$]-ZSM-5 (1.5Ga/GaAl-530) catalyst, prepared through impregnation of GaAl-530 with 1.5 wt% of gallium, was used as a reference.

3. Results

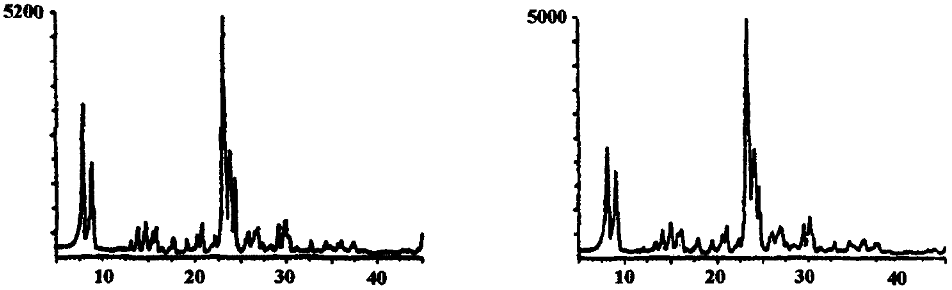
3.1. Physicochemical characterization of the solids

As for other zeolites prepared by this new method [32,33,36], the efficiency of the gallium and aluminum incorporation to the zeolite structure, from the gel of synthesis, is almost 100%. As a matter of fact, for solids obtained from a synthesis gel prepared with the theoretical



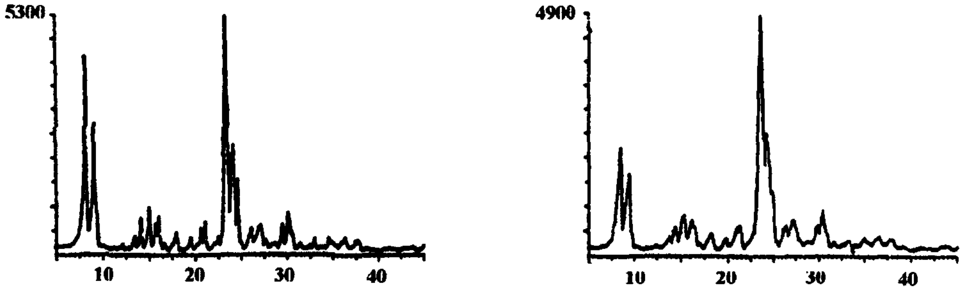
As-synthesized

Calcined at 530°C (Ga Al-530)



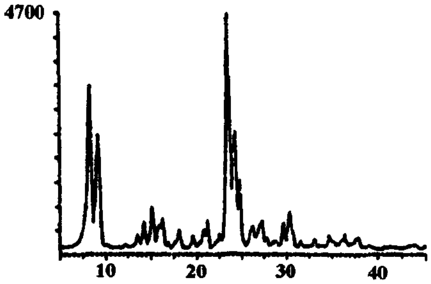
Calcined at 550°C (Ga Al-550)

Calcined at 600°C (Ga Al-600)



Calcined at 700°C (Ga Al-700)

Calcined at 750°C (Ga Al-750)



Calcined at 800°C (Ga Al-800)

Fig. 1. XRD patterns of as-synthesized and calcined zeolites.

amount of each metal, in order to obtain, when totally incorporated, 2.0 aluminum atoms per unit cell and 1.0 atom of gallium per unit cell (2.0 Al/u.c., 1.0 Ga/u.c.), the chemical analysis showed values of 1.92 Al/u.c. and of 1.02 Ga/u.c and the ^{27}Al and ^{71}Ga MAS NMR studies gave values of 1.90 Al/u.c. and 0.99 Ga/u.c. Moreover, XRD and IR studies show that the as-synthesized material is highly pure and crystalline (Fig. 1, Table 1). The physicochemical characterization of solids obtained after calcination under dry air shows that these zeolites are still highly pure and crystalline (Fig. 1, Table 1). However, a slight but progressive decrease of crystallinity upon heating under dry air at high temperature is observed. In fact, while solids calcined at temperatures between 530 and 600°C show very similar values of crystallinity (XRD), of ratios of optical densities of the bands located at 550 and 450 cm^{-1} (IR) and of BET surfaces, the sample calcined at 800°C shows an average decrease in crystallinity of 15%, when compared with solids calcined at lower temperatures (Table 1). This slight decrease is probably due to a partial structure collapse.

NMR studies show that whereas at 530–550°C the organic molecule removal from the zeolite occurs without any significant chemical framework modification (Table 1), at higher temperatures ($T \geq 600$°C) this removal is accompanied by degalliation and/or dealumination of the zeolite structure, being the degalliation process more sensitive to the calcination temperature than the dealumination process (Table 1, Fig. 2).

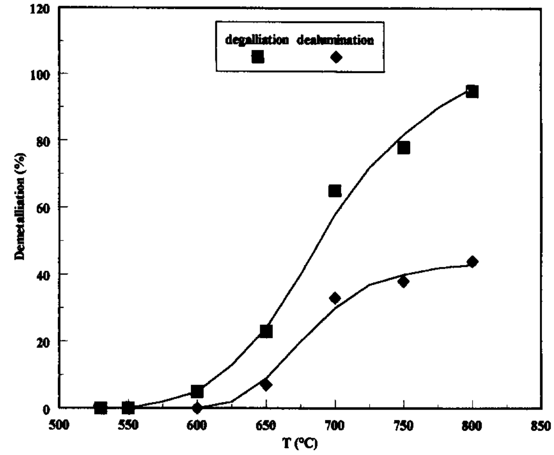


Fig. 2. Percentage evolution of dealumination (◆) and degalliation (■) of the zeolite framework structure as a function of the calcination temperature (*T*°C).

3.2. Catalytic characterization

3.2.1. n-Heptane cracking and m-xylene isomerization

The acidity of zeolites obtained at different calcination temperatures was characterized us-

Table 1
Physicochemical characterization of the solids

Sample	Calcination temperature (°C)	C_{XRD} [a]	I_{550}/I_{450} [b]	S (m^2/g) [c]	Ga/u.c. [d]	Al/u.c. [d]
TPA, Methylamine-[$Ga_{0.99}Al_{1.90}$]		100	0.80		0.99	1.90
GaAl-530	530	100	0.78	430	1.01	1.81
GaAl-550	550	94	0.80	400	0.92	1.86
GaAl-600	600	90	0.75	390	0.97	1.85
GaAl-650	650	88	0.72	380	0.75	1.72
GaAl-700	700	90	0.72	375	0.34	1.26
GaAl-750	750	85	0.73	370	0.22	1.17
GaAl-800	800	83	0.73	370	0.05	1.08
1% Ga/GaAl-530	530	98	0.79	390	1.00	1.87

[a] Relative crystallinity by XRD [28].
[b] Ratio of the optical densities of the bands located at 550 and 450 cm^{-1} [37].
[c] BET surface area.
[d] Aluminum and gallium by unit cell using ^{27}Al and ^{71}Ga MAS NMR [38].

ing *n*-heptane cracking and *m*-xylene isomerization as reaction models. While solids produced by calcination at temperatures between 530 and 550°C show basically the same activity for *n*-heptane cracking and *m*-xylene isomerization, those produced by calcination at higher temperatures show progressively lower activities for those reactions (Table 2). Thus, the initial activity for *n*-heptane cracking for the catalyst calcined at 530°C is 1.6 and 3.2 times higher than that observed for those prepared by calcination at 700 and 800°C, respectively. Moreover, GaAl-530 is 1.5 and 2.0 times more active for *m*-xylene isomerization than GaAl-700 and GaAl-800 respectively. In all cases, the ratio of *p*-xylene/*o*-xylene is nearby 4, which is high but a characteristic value for MFI-type zeolites [40]. This means that all solids keep their typical shape selectivity.

Finally, it is worthwhile to point out that 1.5Ga/GaAl-530, GaAl-530 and GaAl-550 present practically the same activity for both reactions, which means, as previously reported by other authors [3,4,6,15], that EFGS introduced by impregnation, and/or by ion exchange, do not modify the acidity of the zeolitic support.

3.2.2. Propane and naphthenes aromatization

Calcination temperatures between 530 and 600°C leads to solids with similar activities for propane aromatization (Table 2). However, higher calcination temperatures ($T_c > 600$°C) leads to catalysts whose activities for propane aromatization increase with the calcination temperature even when their acidities (as shown by *n*-heptane cracking and *m*-xylene isomerization) are lower (Table 2). In fact, GaAl-800 is 1.89 and 1.24 times more active than the GaAl-600 and GaAl-750, respectively.

As expected, due to the incorporation of gallium [3,4,6,15], the 1.5Ga/GaAl-530 catalyst is more active than the purely acidic ones: GaAl-530 and GaAl-550. However, in spite of its acidity (1.52 and 3.15 times higher than GaAl-700 and GaAl-800 respectively, as measured by the *n*-heptane cracking reaction), the activity of 1.5Ga/GaAl-530 is similar to the activity of GaAl-700 but 1.44 times lower than the activity of GaAl-800.

The decrease of solid acidities and the increase on the propane aromatization rate are followed by an increase of the selectivity toward aromatic products. Table 2 shows, for GaAl-530 and GaAl-550, values of BTX/light products molar ratio of 0.25 and of H_2/BTX molar ratio of about 2.50, which are characteristic of acid catalysts. [3,4,6,15]. Solids calcined at $T_c \geq 600$°C show higher values for both ratios, reaching practically a plateau for solids calcined at $T_c \geq 700$°C (BTX/light products $\cong$ 1.20; H_2/BTX $\cong$ 4.8). The BTX/light products and the H_2/BTX ratios, obtained with the con-

Table 2
Catalytic properties of the catalysts

Sample	Real catalysts [a]	A_o [b]			BTX/light products (molar conversion ≥ 40%)	H_2/BTX
		n-heptane cracking	*m*-xylene isomerization	C_3 aromatization		
GaAl-530	$H_{2.82}$-$[Ga_{1.01}Al_{1.81}]$-ZSM-5	42	38	21	0.25	2.50
GaAl-550	$H_{2.83}$-$[Ga_{0.97}Al_{1.86}]$-ZSM-5	40	39	22	0.25	2.60
GaAl-600	0.12 wt% Ga/$H_{2.76}$-$[Ga_{0.91}Al_{1.85}]$-ZSM-5	32	36	19	0.40	3.00
GaAl-650	0.31 wt% Ga/$H_{2.47}[Ga_{0.75}Al_{1.72}]$-ZSM-5					
GaAl-700	0.74 wt% Ga/$H_{1.60}[Ga_{0.34}Al_{1.26}]$-ZSM-5	27	26	26	1.25	4.7
GaAl-750	0.95 wt% Ga/$H_{1.37}[Ga_{0.22}Al_{1.17}]$-ZSM-5			29	1.15	5.0
GaAl-800	1.16 wt% Ga/$H_{1.13}[Ga_{0.05}Al_{1.08}]$-ZSM-5	13	19	36	1.15	4.8
1.5% Ga/GaAl-530	1.5 wt% Ga/$H_{2.82}[Ga_{1.01}Al_{1.81}]$-ZSM-5	41	38	25	1.20	5.0

[a] From ^{27}Al and ^{71}Ga MAS NMR.

[b] Initial activities in *n*-heptane cracking, *m*-xylene isomerization and propane aromatization, 10^{-3} mol g^{-1} h^{-1}.

Table 3
Aromatic product distribution of the cyclohexane transformation ($T = 530°C$, $P = 1$ atm, WWH = 2 h^{-1})

Catalysts	EFGS [b] (wt%)	Conversion toward BTX (%)	Distribution in BTX		
			Benzene	Toluene	C8-aromatics
H-[Al]-ZSM-5 [a]	0	35	25	45	30
H-[Ga]-ZSM-5	0	48	27	48	25
GaAl-530	0	70	29	45	26
GaAl-600	0.12	70	45	44	11
GaAl-700	0.74	71	71	21	8
GaAl-800	1.16	76	73	20	7
1.5 Ga/GaAl-530	1.50	71	69	22	9
1.0 Ga/H-[Al]-ZSM-5 [a]	1.50	45	73	20	7

[a] From [16].
[b] From ^{71}Ga MAS NMR.

ventional 1.5Ga/GaAl-530 catalyst, are very similar to those of GaAl-700, GaAl-750 and GaAl-800. Even when the activity of GaAl-600 is almost the same as for GaAl-530 and GaAl-550, the selectivity toward aromatic products is slightly higher (Table 2).

The study of the molar aromatic products distribution (APD) obtained from naphthene transformations, has been proposed to evaluate the presence of EFGS, independently of the way they have been introduced: by ion exchange and/or impregnation or by degalliation of gallo- or galloaluminumsilicate zeolites [35].

Table 3 shows that conventional acidic catalysts, H-[Al]-ZSM-5 and H-[Ga]-ZSM-5, present APD very similar to those obtained from GaAl-530, in which toluene is the main reaction product of the cyclohexane transformation. This APD is very similar to that obtained during the transformation of propane and *n*-hexane over acid catalysts [16]. As the calcination temperature increases ($T_c \geq 600°C$) the molar fraction of benzene increases until it became the main aromatic product for $T_c \geq 700°C$ (Table 3). In fact, GaAl-800 led to the same benzene molar fraction as GaAl-700 and GaAl-750, but 2.5 and 1.6 times grater than values obtained from GaAl-530 and GaAl-600, respectively. It is interesting to indicate that bifunctional catalysts in which gallium species have been introduced by ion exchange and/or impregnation, 1.5Ga/H-[Al]-ZSM-5 and 1.5Ga/GaAl-530, show almost the

Table 4
Aromatic product distribution of cyclohexene transformation ($T = 530°C$, $P = 1$ atm, WWH = 2 h^{-1})

Catalysts	EFGS [b] (wt%)	Conversion toward BTX (mol%)	Distribution in BTX		
			Benzene	Toluene	C8-aromatics
GaAl-530	0	69.0	30	45	25
GaAl-600	0.12	65.0	38	45	17
GaAl-700	0.74	77.0	70	20	10
GaAl-800	1.16	78.0	74	17	9
1.5% Ga/GaAl-530	1.50	76.0	69	22	9
1.0 Ga/H-[Al]-ZSM-5 [a]	1.00	40.0	73	20	7

[a] From [16].
[b] From ^{71}Ga MAS NMR.

same APD as GaAl-700, GaAl-750 and GaAl-800. Cyclohexene transformation gave very similar results (Table 4).

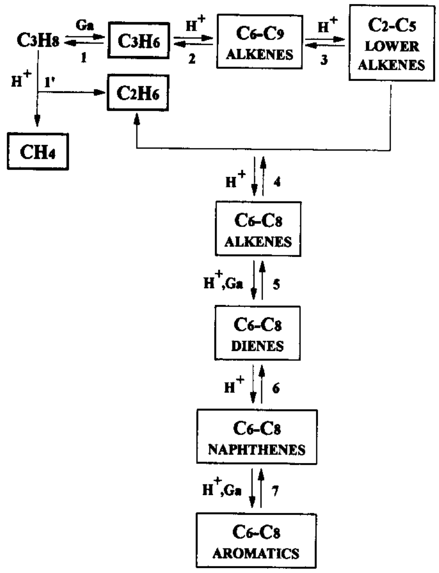
4. Discussion

When the physicochemical characterization of solids shows that the calcination temperature, only produces small changes in crystallinity (Fig. 1, Table 1), the ^{27}Al and ^{71}Ga MAS NMR show that calcination temperatures between 530°C $\leq T_c \leq$ 550°C only led to decomposition of organic compounds used for the zeolite synthesis. Meanwhile calcination temperatures $T_c \geq$ 600°C led to changes in the chemical framework composition of the zeolite due to degalliation and/or dealumination of the zeolitic support (Table 1). In Fig. 2, the degree of degalliation and dealumination, for a given calcination time, is plotted as a function of T_c and, as can be seen, the degalliation process is more sensitive to the calcination temperature than the dealumination one. The degalliation is observed to start at 600°C while the dealumination at 650°C. Moreover, a comparison of both processes within the temperature range 650 to 800°C, shows that the first is about 2.2 times faster than the second. Thus, in the case of GaAl-800 the original framework gallium species are almost totally lost, meanwhile about 57% of the original aluminum atoms are still present (Fig. 2, Table 1). This degalliation rate is similar to the observed for pure gallosilicate MFI-type zeolites synthesized by the same method [35]. The fact that degalliation is faster than dealumination could be attributable to the Ga^{3+} ion size, which is grater than that of the Al^{3+} ion [41].

The effect that T_c has over the as-synthesized solid, TPA,$MeNH_3$-[$Ga_{0.99}Al_{1.90}$]-ZSM-5 (organic compound decomposition and/or degalliation and/or dealumination) leads to the "real catalysts" reported in Table 2. This assumes that the extraframework aluminum species formed by dealumination do not participate in the catalytic transformations.

Due to the fact that, by calcination in the range 530°C $\leq T_c \leq$ 550°C, only the decomposition of organic compounds used for the zeolite synthesis take place (Table 1), it is logical to expect that the catalysts obtained have almost the same activities in acid catalyzed reactions (Table 2). However, when the calcination temperature is grater than 550°C, besides the organic compound decomposition, also take place a decrease in the number of Ga/u.c. and/or Al/u.c. (Tables 1 and 2). These atoms, when in framework positions, are responsible for the Brönsted acidity of catalysts. Hence, when their contents decrease by degalliation and/or dealumination, a decrease of activity in acid catalysis must be expected [35] (Table 2).

The degalliation and afterwards formation of EFGS explain why catalysts with lower activities in acid catalyzed reactions are more active and selective for propane aromatization. The presence of EFGS produces changes in the reaction mechanism, from a pure acid one, as in the case of GaAl-530 and GaAl-550, to a bifunctional one for GaAl-700, GaAl-750 and GaAl-800 [3,4,6,15]. As has been previously reported, the change in the reaction mechanism is produced by the dehydrogenation activity of those EFGS which catalyze the propane dehydrogenation step (Scheme 1, step 1, reaction rate limiting step), and the dehydrogenation of naphthenic intermediates toward aromatics products (Scheme 1, step 7) [3,4,6,14–16]. The EFGS participation in the first reaction is responsible for the overall increase in the reaction rate, meanwhile their participation in the second reaction increases the selectivity toward aromatics. Thus, as the amount of EFGS increase, the catalyst activities increase reaching a maximum at T_c = 800°C (Table 2). The temperature at which this maximum was found, differ from that found for gallosilicates synthesized and calcined following the same procedure [32,33,36]; in which case was 750°C [35]. This behavior is due to the fact that at 800°C both zeolitic supports are almost completely degalliated, but in the case of galloaluminumsilicates, an important



Scheme 1. Main reaction scheme for propane transformation over bifunctional catalysts.

fraction of framework aluminum atoms still remain, making then available enough acidic sites (Table 2) to catalyze the necessary reactions for the aromatization of olefins formed by dehydrogenation of propane (Scheme 1). Due to the high degalliation degree of solids calcined at 800°C, the amount of remaining acidic sites in solids obtained from gallosilicates is low enough to produce a decrease in activity, even when the EFGS content is higher than that found for solids obtained from galloaluminumsilicates. The catalytic behavior of GaAl-600 lies between both ends: the same activity but a slightly higher selectivity toward aromatics than GaAl-530 and GaAl-550. It is due to the low degree of degalliation (Table 2, Fig. 2).

As expected, because of the presence of EFGS, 1.5Ga/GaAl-530 is more active than GaAl-530 [3,4,6,15]. This bifunctional catalyst, prepared using the conventional method, shows an activity in propane transformation which is 1.44 and 1.16 times lower than that observed for GaAl-800 and GaAl-750, even when its acidity in acid catalyzed reactions is 2.5 and 2.1 times higher, respectively (Table 2). As for gallosilicates, this behavior could be attributed to a better EFGS distribution [35]. In fact, XPS studies show that EFGS introduced by ion exchange and/or impregnation are mainly located in the outer surface of the crystallites, meanwhile those formed by degalliation show a better distribution throughout the zeolite crystal [39,42].

As we said before, the increase in the selectivity toward aromatics is also related to the calcination temperature effect on the as-synthesized TPA,MeNH$_3$-[Ga$_{0.99}$Al$_{1.99}$]-ZSM-5. While acidic solids (GaAl-530 and GaAl-550), not affected by degalliation, show low selectivity toward aromatics (BTX/light products ≈ 0.25) and present H$_2$/BTX ratios typical of acidic catalysts [15] (H$_2$/BXT = 2.5), solids calcined at $T_c \geq 700$°C, with a high degree of degalliation, are highly selective toward aromatics (BTX/light products = 1.20) and present H$_2$/BTX ratios typical of bifunctional catalysts [15], which are very similar to those of the conventional 1.5Ga/GaAl-530 catalyst. This confirm that the straightforward calcination of galloaluminumsilicates, synthesized without inorganic cations, leads directly to bifunctional catalysts which, sometime, are more active and as selective as those prepared by conventional methods.

Changes in the naphthenes APD (Tables 3 and 4) also confirm the formation of EFGS [35].

In our reaction conditions, cyclohexane and cyclohexene transformations over α-Ga$_2$O$_3$ only lead to the formation of benzene. Nevertheless, on acidic catalysts the main product is toluene (Tables 3 and 4), and the APD is very similar to the APD obtained for propane and *n*-hexane transformations. It is due to the fact that on acidic catalysts naphthene transformations go through an initial ring opening followed by cracking [16]. The presence of EFGS (added by ion exchange and/or by impregnation or produced by degalliation) allow that both reactions, the direct aromatization by dehydrogenation of naphthenes and the conventional acidic and/or bifunctional one, take place on the same catalyst, the importance of each one depending on the ratio of EFGS to the acidic sites (EFGS/H) [35].

The exclusive acidic character of GaAl-530 and GaAl-550 and the absence of EFGS is supported by their APD, very similar to that obtained with conventional acidic zeolites, H-[Al]-ZSM-5 and H-[Ga]-ZSM-5 (Tables 3 and 4) [35].

In the presence of an important number of EFGS and of acidic sites, as in the case of GaAl-700 (EFGS/H = 0.42), GaAl-750 (EFGS/H = 0.58) and GaAl-800 (EFGS/H = 0.85), the APD is similar to that obtained with bifunctional catalysts prepared by conventional methods.

The similarity of the APD obtained by the transformation of cyclohexane and cyclohexene when the same catalyst is used, suggest that any both reactants can be used as model molecules.

5. Conclusions

The straightforward calcination of galloaluminumsilicate MFI-type zeolites, synthesized from alkali-free media, leads to the production of acidic or bifunctional catalysts with catalytic properties, for the propane, cyclohexane and cyclohexene transformations, almost identical to those shown by catalysts obtained by conventional methods. The degalliation process begin at a calcination temperature lower than the dealumination one. The goodness of cyclohexane or cyclohexene transformation as a model reaction to detect the presence of EFGS, is also demonstrated.

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