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Catalytic behavior in propane aromatization using GA-MFI catalyst

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ABSTRACT

Ga–Al–MFI samples were synthesized in hydrothermal conditions from gels of composition $1.08\text{CH}_3\text{NH}_2\text{--}0.134\text{TPABr--}1\text{SiO}_2\text{--}x\text{Al}_2\text{O}_3\text{--}y\text{Ga}_2\text{O}_3\text{--}40\text{H}_2\text{O}$ at 175°C for 7 days, with $x = 0.005$ and 0.0025 , $y = 0.005$, 0.010 and 0.020 . The samples were characterized by XRD, BET measurements, thermal analysis (TGA–DTA) atomic absorption and high resolution solid state MAS ^{27}Al and ^{71}Ga NMR measurements. The aromatization of propane was studied as catalytic test. The activity and selectivity of the catalysts were determined for benzene, toluene and xylenes on the one hand and for methane and ethane on the other hand. The most active sample was obtained with the highest Ga/Al ratio. For this sample, the BTX selectivity obtained by aromatization was always higher than the hydrocracking selectivity leading to methane and ethane. The relative amount of toluene was higher than that of benzene and of xylenes. The samples were deactivated by coke formation that was revealed more severe for the most active sample.

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1. Introduction

Energy consumption increase is one of the issues to be faced in the next twenty years, as a 34% growth is estimated up to 2035 [1]. In this concern, aiming to reduce the fossil fuel consumption rate and mitigate their impact over global sustainability, different alternatives are under investigation such as bio-syngas production [2–4] and CO_2 recycling [5]. Another interesting route to promote rational resource utilization is the production of bio-based additives [6]; among them aromatic compounds from paraffinic fraction aromatization represent a good option because these low-chain hydrocarbons are largely available (for instance from hydrocracking producing bio-diesel and -jet fuel) and their valorization is necessary [7]. In this concern, conversion of lower alkanes to aromatics is a process still receiving a great attention because of the high economic value stemming from the valorization of the $\text{C}_2\text{--C}_4$ paraffinic fraction [8]. The H-ZSM-5 type zeolite modified with gallium is the status of the art catalyst for this reaction, being widely studied in the last two decades [9]. On the other hand, many issues are still open on this matter aiming at optimizing conditions of such a complex process. Excellent reviews deal with the propane aromatization on Ga/H-ZSM-5 catalysts [10] deeply analyzing the current mechanistic understanding for the conversion of propane to aromatic compounds. It also discusses the promotional effect of gallium in terms of the nature of the active sites, together with the new reaction pathways introduced by gallium addition. The experimental results are well discussed in the light of results of theoretical calculations.

Among the large variety of metallic components added to H-ZSM-5 to enhance the dehydrogenation function of these catalysts, gallium has been recognized to give the best performances [10]. The aromatization of liquid petroleum gas (LPG) alkanes to aromatics (mainly benzene, toluene, and xylenes, BTX) on Ga-modified ZSM-5 catalysts is commercialized in the Cyclar process jointly developed by UOP and BP. Specific aspects of catalyst preparation, characterization, kinetic studies, and catalytic function of gallium species on these materials have been discussed in the current literature starting from the 80s. Most gallium modified catalysts are prepared by impregnating, refluxing, or by mechanical mixing of Ga_2O_3 and H-ZSM-5 followed by thermal activation or reduction. The Ga^{3+} cations, irrespective of the preparation technique, are redispersed in as-prepared catalysts under the strongly reducing conditions and high temperature prevalent during aromatization. Derouane and coworkers have studied the migration of gallium in propane aromatization catalysts using XPS, energy-dispersive X-ray (EDX) analysis, ^{71}Ga , ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) and Rutherford backscattering spectroscopy (RBS) of alpha particles [11–13]. During successive reduction–oxidation cycles, either the amount of gallium occupying tetrahedral framework T-sites, cation exchange positions, or the non-dispersed gallium oxide species were quantified by MAS NMR and $\text{NH}_3\text{--TPD}$. Gallium was initially observed as a segregated phase on the outside of the zeolite crystallites, subsequently it undergoes through a migration within the zeolite pores upon reduction and finally it agglomerates on the external surface as a non-dispersed phase during successive regeneration cycles in oxygen and eventually steaming. Moreover, H–Ga–MFI was evaluated to be the best catalyst due to close proximity of extraframework gallium species generated under reaction conditions and Brønsted acid sites of the zeolites [14]. Choudhary and coworkers have found, that increasing

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the Ga/H⁺ content in this material typically enhanced the dehydrogenation function, however, propane conversion did not increase linearly with Ga or H⁺ content implying that a balance between the dehydrogenation and acid function is required for obtaining optimal propane conversion [8,14,15].

A linear correlation was found between the initial rate of propane aromatization and the product when considering the strong Lewis and Brønsted acid site concentration [16]. The effect of calcination temperature on the propane aromatization activity was explained on the basis of the change in the strong acidity of the zeolite ZSM-5 and extraframework Ga content [17]. A highly active Ga/ZSM-5 was prepared by formic acid impregnation enhancing the dispersion of the Ga species and promoting the formation of highly dispersed GaO⁺ species [18]. Once again, the super catalytic behavior was attributed to the synergistic effect between the strong Lewis acid sites and the Brønsted acid sites. Micro-kinetic modeling was studied on propane aromatization on Ga/HZSM-5 catalyst [19]. Monohydric Ga sites, GaH²⁺ are predominant at low Ga/Al ratios and dihydric Ga sites GaH₂⁺ at high Ga/Al ratios. Quite recently it was emphasized that hierarchical bifunctional Ga/HZSM-5 catalysts are excellent solutions for propane aromatization [20,21].

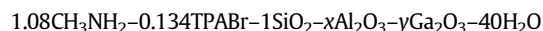
Several mechanisms for alkane activation on the Ga-modified H-ZSM-5 zeolites have been proposed involving the concerted action of H⁺ sites and the non-framework Ga sites. The synergism between these sites could occur at various stages of the activation process, for example, concerted initial C–H bond activation, recombinative desorption of hydride ions and Brønsted acid protons to form molecular hydrogen or during the decomposition of alkyl intermediates bound to Ga species [10]. Several interesting results have been published in terms of Ga/(Ga + Al), revealing how also this parameter is very important in BTX selectivity enhancement. It has been shown [22] that a high propane-to-aromatic activity was exhibited by a Ga-MFI catalyst with a Ga/(Ga + Al) molar ratio below 0.28 with an overall metal content Si/(Ga + Al) equal to 12.8. This sample exhibited a catalytic activity higher than that of the catalyst with the larger bulk Ga content. It was also demonstrated [23,24] that H-GaAlMFI (Si/(Ga + Al) = 31.2 and Ga/(Ga + Al) = 0.33) were performing well in propane aromatization. In the open literature it was reported also that the optimal composition (Ga/(Ga + Al) ratio) is significantly lower than 1 (around 0.25) [23–25].

A final deactivation of the catalyst is due to coking. In this respect, not only the catalytic activity is decreased but also the aromatic selectivity and the dehydrogenation function relative to the cracking one are reduced. The shape selectivity of the zeolite is, however, increased with increasing catalyst deactivation [26–28]. In the present work H-GaAlMFI zeolites were synthesized with various Si/Ga, Si/Al and Si/(Al + Ga) ratios. The samples were characterized by XRD, SEM, BET, thermal analyses, NH₃-TPD analyses and high resolution solid state magic angle spinning ²⁷Al and ⁷¹Ga NMR. The propane conversion and the aromatic selectivity were systematically studied together with the deactivation of the catalysts due to coking in continuous gas-phase reaction test.

2. Materials and Methods

2.1. Sample preparation and characterization

The Ga-MFI samples were prepared starting from a synthesis gel molar composition suggested by Giannetto *et al.* [29] slightly modified as it follows:



CH₃NH₂, aluminum hydroxide (both from Sigma Aldrich) and TPABr (tetrapropylammonium bromide) (Fluka) were added to 2/3 of the total water; then a solution composed by 1/3 of the total water and

gallium nitrate (Ga(NO₃)₃) (Sigma Aldrich 99%) was mixed with the first solution. Eventually, the silica source (precipitated Silica gel) (Merck) was added to the solution leaving the system under stirring for 2 h at room temperature. The crystallization process was investigated at 175 °C in the time range 0–10 days and evidence of high crystallinity (>96%) after 7 days (*vide infra*) suggested this time value for all investigated samples. The sample was filtered, washed, dried and calcined in air at 500 °C in order to eliminate organic molecules and to obtain the acidic form.

All the samples were characterized by X-Ray powder diffraction (APD 2000 Pro) (region 5° < 2θ < 50°, step 0.02(°)·s^{−1}) to verify the obtained catalysts structure; the morphology of the crystalline phase was observed on a scanning electron microscope (FEI model Inspect). The gallium, aluminum and silicon content in the calcined catalysts was measured by atomic absorption (GBC 932 AA). The specific surface area and the micropore volume of the catalyst were obtained by performing a BET and t-plot analysis of porosimetry data (ASAP 2020 Micromeritics) under nitrogen adsorption at 77 K, after a pre-treatment in vacuum at 200 °C for 12 h [30]. The thermoanalytical measurements were performed on the automatic TG/DTA instrument (Shimadzu) under 50 cm³·min^{−1} of air flow (heating rate of 5 °C·min^{−1}).

Surface acidity was measured by NH₃-TPD analysis (TPDRO1100, ThermoFisher) according to the following procedure. Dried sample (100 mg, pellet mesh 90–150 μm) was loaded in a linear quartz micro-reactor and pre-treated at 300 °C in helium flow for 1 h to remove adsorbed water. The sample was cooled down to 150 °C and saturated with 10vol% NH₃/He mixture with a flow rate of 20 STP ml·min^{−1} for 2 h. Ammonia physically adsorbed was removed by purging in helium at 150 °C for 1 h until TCD baseline stabilization. Desorption measurement was carried out in the temperature range of 100–700 °C (10 °C·min^{−1}) using a helium flow rate of 20 STP ml·min^{−1}. A commercial software (PeakFit 4.12, Seasolve-USA) was used for peak analysis and deconvolution.

²⁷Al and ⁷¹Ga NMR spectra were acquired at 130.3 and 152.5 MHz, respectively on a Bruker Avance III-HD 500 (11.7 T), using a 4.0-mm outer diameter probe. Radiofrequency powers were of 54 and 83 kHz, respectively. The pulse length was 3 μs and 4.6 μs for ⁷¹Ga and ²⁷Al, respectively whilst the corresponding angle theta was π/6 and π/4 for ⁷¹Ga and ²⁷Al, respectively. Rotors were spun at 14 kHz and the recycle delay used for both nuclei was 1 s.

2.2. Catalytic tests

Catalyst activity, selectivity and stability in propane aromatization reaction were evaluated by using a lab scale multi-reactor system (AmTech GmbH, Germany) equipped with a stainless steel reactor (I.D. 9 mm, length 205 mm). During test pressure was fixed at 0.3MPa and three values of temperature were investigated (namely 500, 525 and 550 °C). 150 mg of catalyst (300–500 μm) was loaded into the reactor and, after purging by a nitrogen flow, propane was fed mixed with N₂ as carrier (1:3 propane–N₂ molar ratio) by fixing the flow rate at 60 N ml·min^{−1}, resulting in a Weight Hourly Space Velocity (WHSV) of 10.8 g_{propane}·(g_{cat}·h)^{−1}. In order to investigate the effect of contact time on the product distribution, the WHSV was varied in the range 5.4–21.7 h^{−1} by changing the mass of catalyst in the range 50–300 mg_{cat} and keeping at a fixed gas flow rate. The outlet gas stream (mainly containing methane, ethane, propane, benzene, toluene and xylenes) was quantitatively analyzed by an on-line GC (Agilent 7890A) equipped with a specific column (J&W 125-1032) and a FID detector. Three independent repetitions were performed for any test and reported results are the average ± standard error. The amount of coke deposited on the catalyst during the reaction, was measured by thermo-gravimetric analysis from the measured weight loss in the temperature range 250 °C–850 °C following a method described elsewhere [31–33].

3. Results and Discussion

3.1. Sample characterization

The evolution of crystallization of sample with the highest gallium content (sample C) is reported in Fig. S.1 of supplementary information, showing that after 7 days the crystallinity is ca. 96%. The chemical composition of the gel is compared with that of the final Ga, Al MFI samples (Table 1). It is interesting to note that the Si/(Al + Ga) ratio of the samples follows quite closely the composition of the synthesis gel. On the contrary, the incorporation of Al atoms shows a greater efficiency of Al to incorporate on the MFI structure than Ga. Indeed, the Ga/Al ratio on the bulk of the solid is systematically lower than Ga/Al ratio used in the synthesis gel, showing how there is some competition between Ga and Al to incorporate into the structure. In particular, starting from synthesis gel containing similar Al content, the lower is the Si/Ga in the synthesis gel and the more difficult seems to be the Ga incorporation. Indeed, for the samples prepared with similar Si/Al ratios on the gel (sample A and sample C), the Ga incorporation is more difficult for the sample synthesized with the lower Si/Ga ratio (sample C) as the Ga/Al decreases from 8 (on the gel) to 2.7 (on the bulk of the solid) whilst a lower decreasing is observed for the sample synthesized with higher Si/Ga (sample A) as the Ga/Al ratio decreases from 2 (on the gel) to 0.92 (on the bulk of the solid).

Table 1

Chemical composition of the MFI samples and the corresponding gel phases (molar ratios)

	Sample A	Sample B	Sample C
Si/Ga Gel	100	50	25
Si/Ga Bulk	154	47	25
Si/Al Gel	200	100	200
Si/Al Bulk	141	71	69
Si/(Al+Ga) Gel	67	33	22
Si/(Al+Ga) Bulk	74	29	18
Ga/Al Gel	2	2	8
Ga/Al Bulk	0.92	1.5	2.7
Ga/ $\mu\text{mol} \cdot \text{g}^{-1}$	106	343	619
Al/ $\mu\text{mol} \cdot \text{g}^{-1}$	115	226	226
Ga ^{IV} fraction ^① /%	100	100	80
Al ^{IV} fraction ^① /%	100	98	92

^① From NMR analysis.

The XRD spectra of the uncalcined samples all show orthorhombic structure as the 29.3° 2 θ peak is not split (Figs. S.2–S.4 of supplementary section). Fig. 1 shows the XRD diffractogram of calcined samples A, B and C. Sample A (Ga/Al = 0.92) shows the change into monoclinic structure as it can be seen from the doublet at 29.3° 2 θ . Oppositely, for samples B (Ga/Al = 1.5) and C (Ga/Al = 2.7) the structure remains orthorhombic as shown by the singlet at 29.3° 2 θ .

The SEM pictures reported in Fig. 2 show some differences between the three samples. Sample A exhibits well-formed prism-like crystals (typical for MFI) and most of them are intergrowths. Characteristic dimensions are: length 50 μm , width 15 μm and the thickness 7.5 μm . The intergrowths show smaller crystals. Sample B shows similar big crystals with the same dimensions, many intergrowths and many small crystals, the size of which can be estimated to 2–10 μm . Sample C reveals a different structure as only agglomerates of dimensions 20–80 μm can be seen, together with very small crystals of 2–10 μm . This aspect is very important to understand the catalytic behavior exhibited by these samples.

Fig. 3 shows the high resolution solid state magic angle spinning ²⁷Al NMR spectra of samples A, B and C. The aluminum atoms are essentially in tetrahedral position (Al_T), with $\delta = 53.4$ vs Al(H₂O)₆³⁺. The octahedral Al (Al_O) is at $\delta = 0$. The relative quantities are: sample A –

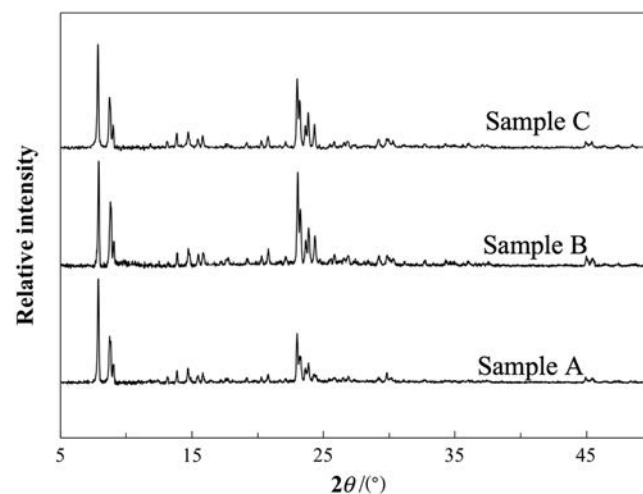


Fig. 1. XRD pattern of calcined samples A, B and C.

Al_T = 100%; sample B – Al_T = 98%, Al_O = 2%; and sample C – Al_T = 92%, Al_O = 8%. Fig. 4 shows the high resolution solid state ⁷¹Ga NMR spectra of samples A, B and C. The gallium atoms are essentially in tetrahedral position (Ga_T) at $\delta = 156$. The octahedral Ga (Ga_O) is at $\delta = 0$ vs Ga(H₂O)₆³⁺. It can be noticed that, in addition to the tetrahedral Ga in a crystalline phase, it also exists in an amorphous phase (Ga_A) shown by the great line width. The relative quantities were obtained by spectral decomposition: sample A – Ga_T = 55%, Ga_A = 45%; sample B – Ga_T = 72%, Ga_A = 28%; and sample C – Ga_T = 55%, Ga_O = 20%, Ga_A = 25%. It can be also noticed that sample C contains also some Ga₂O₃ as this oxide has both tetrahedral and octahedral components [34].

The thermal analysis results are quite revealing and Fig. 5 summarizes the characteristic temperature peaks over DTA analysis as well as TGA test. As the initial gel contained also CH₃NH₂, its presence could also be detected in our samples. Following the reference of Parker *et al.* [35] the temperature of maximum weight loss of physisorbed methylamine is at 180 °C and protonated methylamine counterion to Al negative charge is at 460 °C. The low temperature peak is absent in our samples. On the other hand, it might be that some methylamine could be included in the high temperature peak, but our results are unable to tell the proportion. Therefore, the TGA and DTA peaks can be then attributed solely to TPA⁺ to counterions to SiO[−] defect sites at $T = 417$ °C (sample A) and $T = 447$ °C (sample B) [36], whilst TPA⁺ or protonated methylamine ions are responsible as counterions to Al(OSi)₄[−] and Ga(OSi)₄[−] sites for peaks at $T = 459$ °C (sample A), $T = 465$ °C (sample B) and $T = 483$ °C (sample C). Referring to the total weight loss the following values were computed (wt%): sample A 12%, sample B 10.7%, and sample C 8.9%.

Table 2 includes the textural and acidic properties of the samples. Both the specific surface area B.E.T. and the estimated micropore surface decrease from samples A to C, showing that the bigger crystallites of sample A, have a greater inner surface available, whilst the small crystallites exhibit a smaller inner surface.

NH₃ desorption profiles are reported in Fig. S.5 of supplementary information section. The NH₃-uptake is directly related to overall acid site concentration as effect of the heteroatom presence in the structure and it can be seen that sample C exhibited the highest acidity expressed as equivalent NH₃ (531 $\mu\text{mol} \cdot \text{g}^{-1}$). In order to estimate the strength of observed acid sites, a distinction in weak and strong acid sites, the maximum NH₃ desorption temperatures can be compared [37]. Following this criterion, acid site distribution consists in weak acid sites (desorption temperature below 300 °C) and strong acid sites (above 300 °C). Results reported in Table 2 reveal that a similar acid site distribution is observed for samples B and C even though sample C exhibits an acid strength higher than sample B. In fact, for sample C, maximum desorption temperatures of 241 °C and 425 °C are observed from weak and

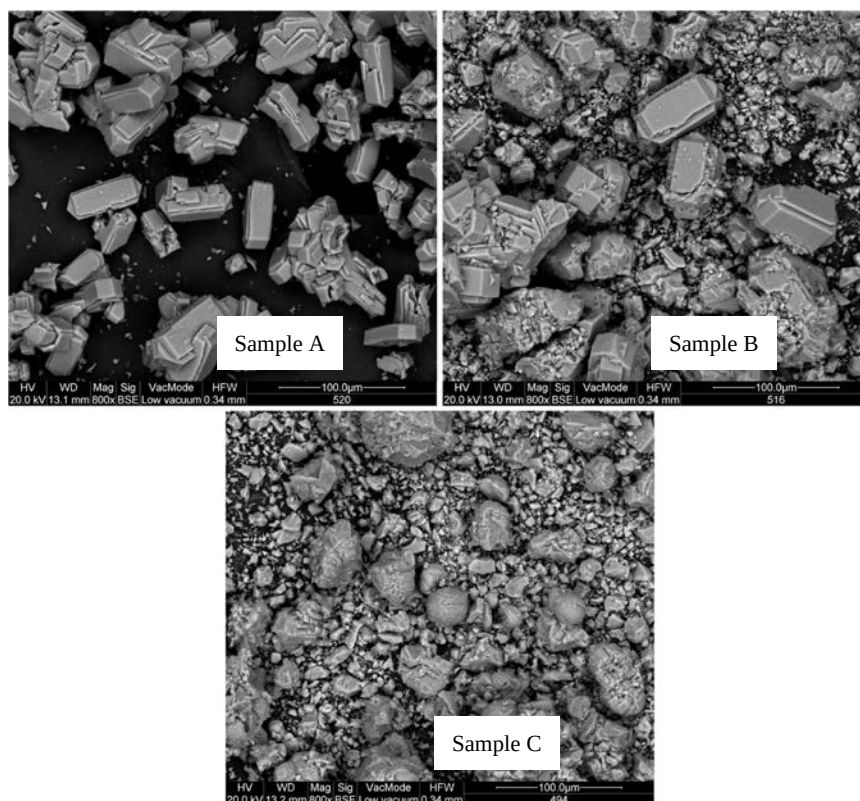


Fig. 2. SEM pictures of samples A, B and C.

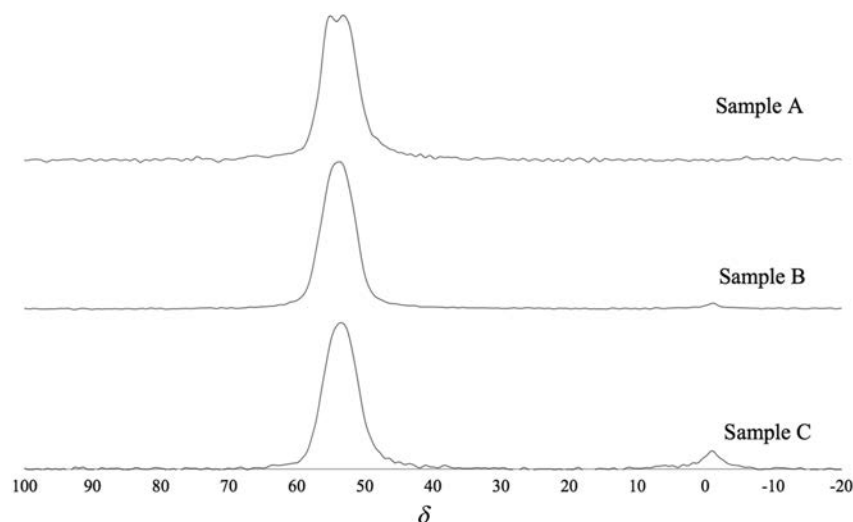


Fig. 3. ^{27}Al NMR spectra.

strong acid sites, respectively. These values are higher than those observed for sample B ($T_{\text{weak}} = 214\text{ }^{\circ}\text{C}$ and $T_{\text{strong}} = 403\text{ }^{\circ}\text{C}$). A different acid site distribution is observed for sample A where both fraction and strength of strong acid sites are higher than those measured for samples B and C.

3.2. Catalytic activity

Catalytic activity of samples is reported in Fig. 6 as propane conversion at any investigated temperature, showing a higher activity when increasing temperature. It can be seen that sample C, with the highest

Ga-content and Al-content, is the most active one whilst the activity of samples A and B is similar. It is found that the catalyst overall acidity promotes the propane conversion, but a Ga-content higher than the Al-content is necessary to promote the formation of aromatics (BTX) rather than propane cracking-hydrogenation leading to smaller alkanes (methane and ethane). This is more clear by estimating BTX selectivity (S_{BTX}) as it follows:

$$S_{\text{BTX}} = \frac{\text{mass of formed BTX}}{\text{mass of converted } \text{C}_3\text{H}_8}$$

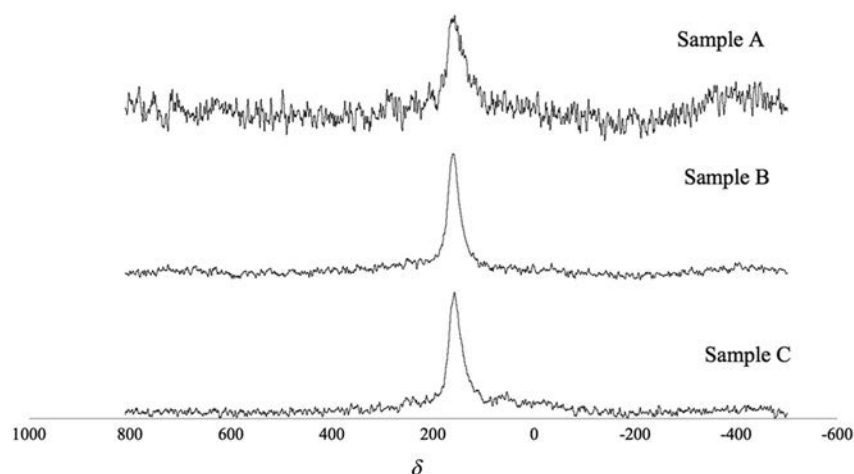
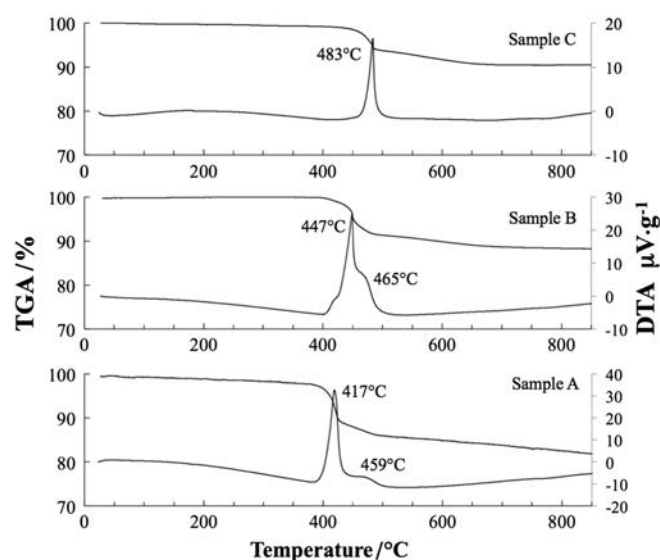
Fig. 4. ^{71}Ga NMR spectra.

Fig. 5. TGA/TDA results of samples A, B and C.

From data of S_{BTX} as a function of temperature (Table 3), it clearly appears that the selectivity for aromatization of propane is greatly influenced by both Ga- and Al-content. Observed data suggest that the presence of gallium species in octahedral coordination is more important than Ga/(Al + Ga) ratio as reported by Matsuoka *et al.* [25] that observed a decrease in terms of propane aromatization activity as Ga/(Al + Ga) increases from 0.25 to 1. In this work, on the contrary, we observed that propane aromatization activity increases when Ga/(Al + Ga) ratio increases from about 0.48 (sample A) to about 0.60 (sample B) and obtaining the highest BTX production for the sample with Ga/(Al + Ga) equals to about 0.73 (sample C). This trend, cannot

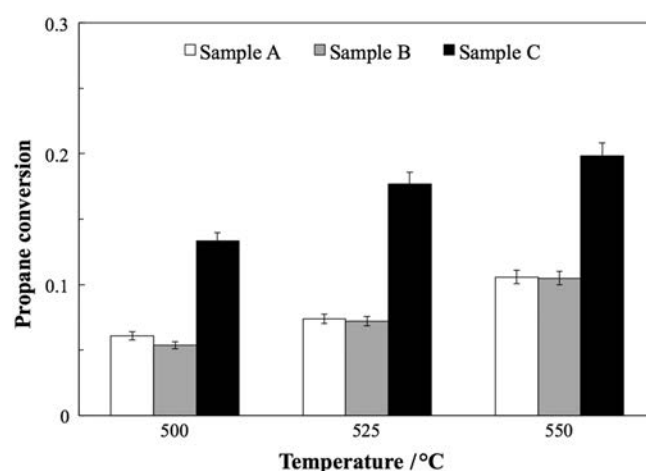


Fig. 6. Effect of temperature and Ga/Al content on propane conversion.

Table 3
BTX selectivity and methane/BTX ratio as a function of temperature

Sample	$S_{\text{BTX}}/\text{wt}\%$			χ		
	500 °C	525 °C	550 °C	500 °C	525 °C	550 °C
A	–	–	–	–	–	–
B	0.2 ± 0.01	3.0 ± 0.2	10.3 ± 0.5	0.01	0.09	0.33
C	40.4 ± 2	38.4 ± 2	36.0 ± 2	2.50	2.24	2.00

be associated with the Ga/(Al + Ga) only, but to the presence of extra-framework gallium species as reported by Montes and Giannetto [23]. This is confirmed by comparing samples with similar aluminum content and acidity (such as samples B and C), where only the sample with octahedral gallium species (sample C) is effective for BTX

Table 2
Textural properties and NH_3 -uptake of samples A, B and C

Sample	B.E.T./ $\text{m}^2 \cdot \text{g}^{-1}$	Micropore area ^① / $\text{m}^2 \cdot \text{g}^{-1}$	NH_3 -uptake/ $\mu\text{mol} \cdot \text{g}^{-1}$	$T_{\text{weak}}^{\text{②}}/\text{°C}$	$x_{\text{weak}}^{\text{③}}$	$T_{\text{strong}}^{\text{④}}/\text{°C}$	$x_{\text{strong}}^{\text{⑤}}$
A	372	214	164	197	0.21	402 and 500	0.79
B	367	162	436	214	0.37	403	0.63
C	344	119	531	241	0.34	425	0.66

① Estimated by t-plot method.

② Temperature of maximum desorption of NH_3 up to 300 °C related to weak acid sites.

③ Weak acid site fraction.

④ Temperature of maximum desorption of NH_3 above 300 °C related to strong acid sites.

⑤ Strong acid site fraction.

production, confirming the role of these species as crucial factor for this process [14,15]. The selectivity of sample A is close to zero, because of a Ga-content lower than the Al-one.

If the selectivity for methane formation S_{CH_4} is defined in an analogous way:

$$S_{CH_4} = \frac{\text{mass of formed } CH_4}{\text{mass of converted } C_3H_8}$$

and the selectivity ratio is calculated as:

$$\chi = \frac{S_{BTX}}{S_{CH_4}}$$

Interesting behavior was found (Table 3). In fact, χ is much higher for sample C than for sample B at 500 °C. As the temperature increases, χ is decreasing for sample C, because the mass percentage of formed CH_4 increases faster. The opposite trend is observed for sample B where this ratio is increasing with increasing temperature, showing that the BTX production is increasing faster than the CH_4 production. This means that the aromatization is favored over the cracking reaction.

Table 4, for sample C with Ga/Al = 2.7, illustrates the selectivity of any of the aromatic compound defined as:

$$S_B = \frac{\text{mass of formed Benzene}}{\text{mass of converted } C_3H_8}; \quad S_T = \frac{\text{mass of formed Toluene}}{\text{mass of converted } C_3H_8};$$

$$S_X = \frac{\text{mass of formed Xylene}}{\text{mass of converted } C_3H_8}$$

$$S_{BTX} = S_B + S_T + S_X$$

Table 4

Selectivity for aromatics as a function of temperature for sample C (Ga/Al = 2.5)

	500 °C	525 °C	550 °C
S_B	0.111 ± 0.003	0.110 ± 0.004	0.106 ± 0.003
S_T	0.230 ± 0.015	0.213 ± 0.005	0.197 ± 0.010
S_X	0.063 ± 0.003	0.062 ± 0.003	0.058 ± 0.002

S_T is significantly higher than S_B and S_X and any parameter is decreasing when increasing temperature. Also from this aspect, despite the similar acidity and aluminum content of sample B and sample C, sample C promotes aromatization more than cracking reaction due to the higher gallium content in octahedral coordination as reported also by Choudhary *et al.* [22]. The relative distribution (in %) of benzene, toluene and xylenes obtained on sample C as illustrated in Fig. 7, reveals that operative temperature does not affect the BTX distribution, despite

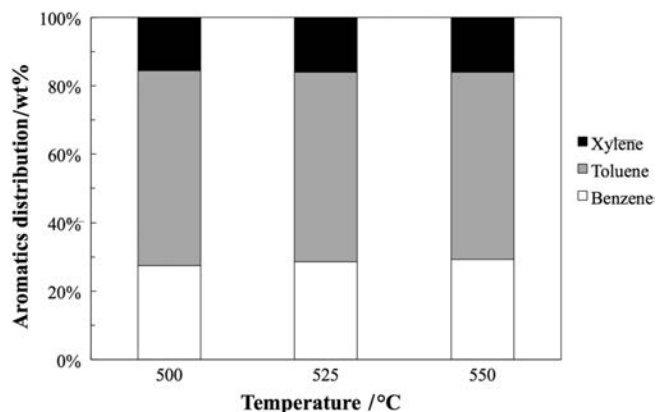


Fig. 7. Relative distribution (in wt%) of benzene, toluene and xylenes in the products obtained on sample C.

the difference in propane conversion. Since the reaction scheme is a complex combination of reactions, also depending on the contact time [38], this parameter was investigated for the catalyst with best catalytic performances, sample C, with the highest Ga/Al ratio. Data of Fig. 8 show that for sample C propane conversion increases as the contact time (calculated as $WHSV^{-1}$) increases, as well as the BTX formation is promoted more than the cracking reaction favorably impacting on the process efficiency. In fact, when increasing contact time, the methane selectivity (wt%) remains constant (around 17%), whilst the BTX selectivity increases from 28% to 44% when the contact time is increased from (0.05 to 0.18) h. As the test is performed over fresh catalyst, the residual product can be assumed as pure ethane ranging from 50% to 40% when increasing the contact time.

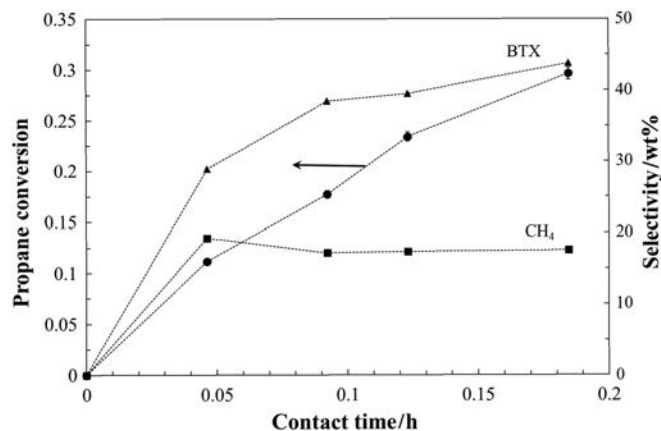


Fig. 8. Propane conversion and BTX/ CH_4 selectivity as a function of contact time for sample C at 525 °C. Dashed lines are reader guideline only.

The methane and ethane selectivities (wt%) were also determined at different temperatures (Fig. 9) for all the investigated samples. Deriving from propane cracking in the presence of hydrogen, it is noteworthy that the methane formation is reduced in sample C with respect to any investigated sample. Similar trend is observed also for ethane and this compound was recognized as the main side product in any condition.

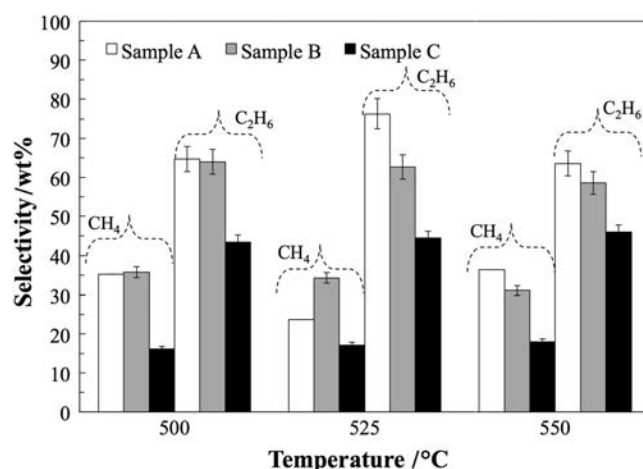


Fig. 9. Methane and ethane selectivity as a function of temperature for samples A, B and C ($WHSV = 10.8 \text{ h}^{-1}$).

Furthermore, also the catalyst stability over time was investigated (Fig. 10) in continuous test. The activity of sample A was very low and it remains nearly constant around a value of 0.07 during 20 h. Except for the early stage of the test, also the activity of sample B remains

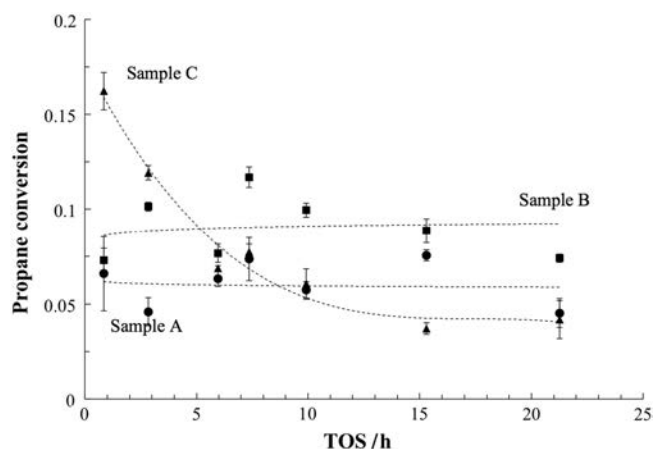


Fig. 10. The conversion of propane as a function of time on stream for samples A, B and C ($T = 525\text{ }^{\circ}\text{C}$, $\text{WHSV} = 10.8\text{ h}^{-1}$). Dashed lines are reader guideline only.

quasi-constant during 20 h, at about 10%, whilst the most significant activity drop was observed for sample C (the most active) from an initial activity of 0.16 to 0.08 after 8 h and further decrease to ca. 0.04 after 20 h, even exhibiting an activity lower than samples B and C due to the deactivation.

The trend observed for propane conversion over time was also found for BTX production. In fact as for sample B propane consumption was quasi-constant as a function of time on stream, so it happens also for the production of BTX (Fig. 11). The production of toluene is always the highest, followed by that of benzene and then by xylenes. Data of sample B reveals a quite stable catalyst as no significant variation in BTX selectivity over time was detected. This is not a surprising result as the overall propane conversion and selectivity are quite low. On the contrary, if the sample more active and selective (sample C) is considered, the production of BTX significantly drops as a function of time on stream as it was already shown for propane conversion with a reduction coefficient of about 54%. The rate of decrease is correlated to the compound molar fraction as the most concentrated product (toluene) exhibited the highest (60%), followed by xylenes (50%) and benzene (45%).

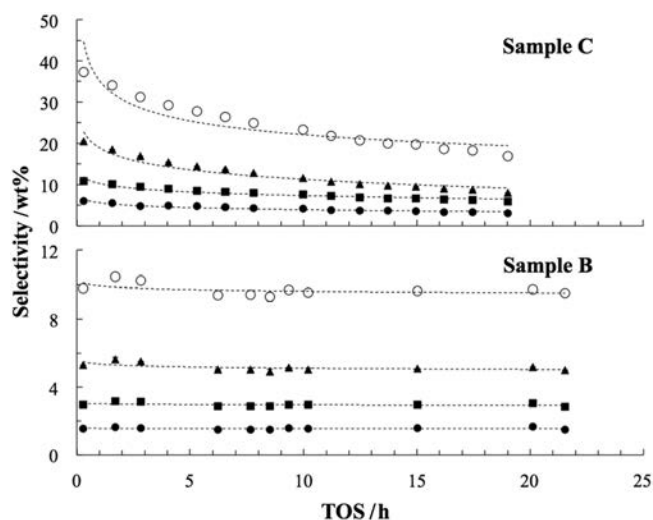


Fig. 11. Selectivity over time for samples B and C. S_{BTX} (open circle), S_{T} (triangle), S_{B} (square), S_{X} (closed circle) ($T = 525\text{ }^{\circ}\text{C}$, $\text{WHSV} = 10.8\text{ h}^{-1}$). Dashed lines are reader guideline only.

Even though the relative amount of any BTX species strongly depends on the specific catalyst features, results of BTX distribution can be justified by some consideration about the reaction mechanism and the activation

energy. Joshi and Thomson have found that 1–6 ring closure to benzene has a $29\text{ kJ}\cdot\text{mol}^{-1}$ higher activation energy compared to toluene and xylenes [39]. Bhan *et al.* have incorporated relative activation energies in their microkinetic model [40] and have successfully predicted the experimentally observed benzene, toluene and xylene production for propane aromatization over HZSM-5 zeolite over a wide range of space time and temperature values. Meriaudeau and Naccache [41] have also found that on bifunctional noble metal zeolite catalysts starting from n-hexane and n-heptane, the major aromatic products were not benzene and toluene, respectively, but were composed of a mixture of benzene, toluene and xylenes. The chemical composition was closer to that expected from thermodynamics, implying that ring closure is not the primary mechanism for production of aromatics, but several fragmentation and C—C bond formation cycle occur prior to ring closure.

In order to verify the impact of the propane conversion-loss on the relative selectivity over time, the selectivity ratio χ between BTX and methane was calculated for sample C at $525\text{ }^{\circ}\text{C}$. The decrease of χ (Fig. 12) indicated that the drop in selectivity is higher for BTX than for CH_4 .

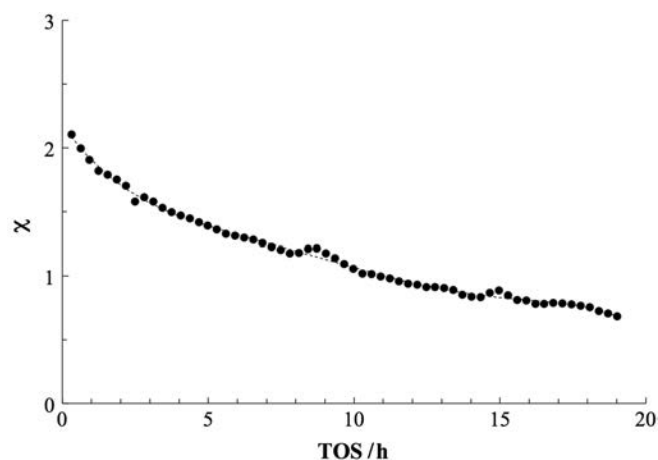


Fig. 12. BTX/methane selectivity ratio as a function of time on stream (sample C, $T = 525\text{ }^{\circ}\text{C}$, $\text{WHSV} = 10.8\text{ h}^{-1}$). Dashed lines are reader guideline only.

In order to understand the decrease of the catalytic activity, the so-formed coke was determined by thermal analysis for samples A, B and C after 20 h of time on stream and data are reported in Table 5. The coke is decomposed at $615\text{--}677\text{ }^{\circ}\text{C}$ depending on the samples. Its amount is quite small (0.79%) on sample A, it increases to 1.13% on sample B and on the most active sample C it is quite high, 6.04%. The increase in the amount of coke on sample C, explains quite well [27] the decrease of activity as a function of time on stream (*vide supra*). About the coke composition, no specific tests were performed even though it was recognized that it is composed of heavy polyaromatic molecules, as it could not be dissolved in CH_2Cl_2 [42].

Table 5

Thermal analysis (TGA and DTA) data of the coke formed on samples A, B and C after 20 h at $525\text{ }^{\circ}\text{C}$

Sample	Coke amount/ $\text{mg}\cdot\text{g}_{\text{Cat}}^{-1}$
A	7.9
B	11.3
C	60.4

4. Conclusions

GaAl-HZSM-5 catalysts were synthesized with various Ga/Al ratios using hydrothermal synthesis. Ga/Al ratio affects strongly either the

bond-strength between the SDA molecules and zeolite or the morphology of the crystal. It was found that effectiveness of aluminum incorporation is higher than gallium one. The presence of gallium in octahedral coordination is important for the dehydrogenation activity whilst the role of aluminum is important for the introduction of Brønsted acid sites. The synergistic effect between these two sites is shown in the propane aromatization reaction. In order to reach both high propane conversion and high BTX selectivity, a Ga/Al ratio higher than 1 is needed. Indeed, the sample with the highest Ga/Al ratio exhibits the highest initial aromatization activity in terms of both propane conversion and BTX selectivity; the superiority of this sample can be reasonably associated with the higher gallium species concentration in octahedral coordination. The aromatic molecules, benzene, toluene and xylenes are not obtained by direct aromatization of dehydrogenated propane but by several fragmentation and C—C bond formation prior to ring closure. As a result, more toluene is formed followed by benzene and xylenes. Their formation is governed by the activation energy of the specific steps. The activity of the catalyst was observed to decrease as a function of time on stream and this was essentially attributed to the formation of coke, the quantity of which is higher on the most active catalyst.

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Supplementary Material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.cjche.2017.04.016>.

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