Propane as alkylating agent for alkylation of benzene on HZSM-5 and Ga-modified HZSM-5 zeolites

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Abstract

Alkylation of benzene with propane has been studied under continuous-flow condition at atmospheric pressure. Ga-modified HZSM-5 zeolites have shown to be very efficient catalysts for alkylation of benzene with propane. Toluene and ethylbenzene are formed as major products and cumene and *n*-propylbenzene are also produced at low reaction temperatures in small amounts. The product formation pathways on HZSM-5 and Ga-modified HZSM-5 have been discussed and suggest that acid-catalyzed cracking of propane predominates on HZSM-5, leading to the formation of toluene and ethylbenzene. Over Ga-modified HZSM-5, a bifunctional pathway is noted and cracking of propane and propane dehydrogenation are controlled by Lewis (Ga^{x+})/Brönsted (H^+) acid sites ratio. The effect of oxidative and reductive treatments on catalytic activity has been studied and shown that the catalytic activity and the selectivity to toluene of the Ga-modified HZSM-5 zeolite catalysts are enhanced after H_2/O_2 treatment due to the increase in gallium dispersion.
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Keywords: Benzene alkylation; Propane; HZSM-5; Ga-modified HZSM-5; Reaction pathways; Toluene; Ethylbenzene; Cumene

1. Introduction

Benzene alkylation with olefins or alcohols is an important industrial step in the formation of intermediates for chemical products. Alkylation of benzene with propylene, the conventional alkylating agent used for the chemical industry, was extensively studied to produce cumene, which is an important intermediate for the co-production of phenol and acetone. Cumene production is currently based on the use of solid phosphoric acids or Friedel–Crafts catalysts. However, these processes present serious environmental problems. Much effort was devoted to finding alternative catalysts to overcome these drawbacks. Among them, new cumene processes based on Y, modified mordenite, ZSM-5 and other zeolites were developed [1–10]. Other studies already showed the potential application of BEA and MWW zeolites for benzene alkylation [11–17] and a liquid phase industrial process using β-zeolite is indeed in operation [11–16]. Despite the advantages of β-zeolites, reaction control is difficult due to the high activity of protonated zeolites,

and it was shown by in situ ^{13}C NMR study that the reaction was complete even at $-80\,^{\circ}C$ [16,17]. On the other hand, the oligomerization of propylene at low temperature leads to strong coke formation which deactivates the catalysts.

Recently, several studies have shown that propane could be activated on Ga-MFI materials [18]. Using propane as an alkylating agent for benzene alkylation could be a great interest for economic reasons. Nevertheless, only a few studies concerning alkylation of benzene with propane have been reported [19–22]. The possible catalytic formation of highly valuable alkylaromatics from alkanes and benzene was disclosed by Schmerling and Vesely in 1973 using Friedel–Crafts catalysts [23]. Two years after, Olah et al. have described in detail that benzene alkylation with propane occurred over anhydrous fluoroantimonic acid even at ambient temperature and cumene was reported as the major reaction product [24]. Likewise, using Ga-MFI zeolite, cumene is formed at the reaction temperatures lower than $350\,^{\circ}C$ and other alkylated aromatics appear with increasing temperature to $440\,^{\circ}C$ as revealed by an in situ FT-IR study [19]. Ivanova et al. have found using ^{13}C MAS NMR techniques that toluene and ethylbenzene are formed as the primary products of reaction at $300\,^{\circ}C$ on Ga-modified HZSM-5

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[20]. However, all the above studies on zeolites were performed under static conditions. Recent studies made by Bigey and Su [21] and Smirnov et al. [22] on a series of modified MFI zeolites under flow conditions have shown also that higher reaction temperatures favor the production of toluene and disfavors that of ethylbenzene both on HZSM-5 and Ga-modified HZSM-5 catalysts and that the reaction atmosphere and the incorporation of Pt in catalyst systems can result in significant modification in selectivity of products [21,22].

Very recently, a series of Ga-modified or bimetal (Ga, Pt)-modified HZSM-5 catalysts were prepared. The effect of pretreatment conditions on the acidity and the chemical state of Ga species and the confinement of benzene molecules in the nanocavities of catalysts was studied by FT-IR technique [25]. The present work, which is a continuation of our research in this field, is to clarify the catalytic behavior of Ga-modified ZSM-5 in the alkylation of benzene with propane under continuous-flow operating conditions. We try to establish at a molecular level a correlation between the catalyst pretreatment atmospheres (chemical state of Ga species) and the activity and selectivity of catalysts and reaction pathways in order to develop the efficient and highly selective catalysts for alkylbenzene production using propane as alkylating agent.

2. Experimental

2.1. Catalyst preparations and characterization

HZSM-5 (Si/Al ratio $\cong 21$) and Ga-modified HZSM-5 zeolites were prepared as described in [25]. Samples containing different amounts of Ga were obtained by successive ion-exchange leading, respectively, to Ga1,HZSM-5 (0.57 wt.% Ga), Ga2,HZSM-5 (1.24 wt.% Ga) and Ga3, HZSM-5 (1.81 wt.% Ga) materials.

Bulk chemical compositions of materials were obtained by elementary analysis. IR spectra in the framework vibration region were recorded (FT Spectrum 2000, Perkin-Elmer) using the KBr wafer technique. SEM (Philips XL 20 microscope) was used to study the crystal morphology and crystal size. X-ray diffraction (XRD) patterns were collected on a Philips P.W. 1349/30 diffractometer using Cu Kα radiation. Unit cell parameters were evaluated with changing Ga composition by using $d(1\,0\,1)$, $d(5\,0\,1)$ and $d(0\,5\,1)$ reflections. The crystallinity of the solids was determined as indicated in [25]. Crystallite sizes were also evaluated using the Debye–Sherrer relation taking into account the well-resolved $d(1\,0\,1)$ reflection. Specific surface areas and porosities were measured by nitrogen adsorption using a Micrometrics ASAP 2010 apparatus. Solid state ^{27}Al, ^{29}Si and ^{71}Ga MAS NMR spectra were collected on a Bruker MSL 400 MHz NMR spectrometer. TMS, Al and Ga nitrate solutions were used as external references. Prior to ^{71}Ga NMR analysis and to minimize quadrupolar

effects, samples were exchanged with an aqueous solution of NH_4NO_3 and re-equilibrated [26].

2.2. Catalytic testing

2.2.1. Catalytic device

Catalytic activity of the samples was evaluated using a continuous-flow unit at atmospheric pressure. N_2 and propane flows were regulated by mass flow controllers. Benzene (HPLC grade 99.0%, Sigma–Aldrich) was introduced by bubbling N_2 in a saturator–condensator device where the temperature was regulated by a cryostat. One hundred milligrams of catalyst were placed in a quartz reactor. In order to prevent condensation of products, all feed lines were heated. After reaction, the products were analyzed on line by gas chromatography equipped with a 30 m AT-WAX capillary column and flame ionization detector. Gases (N_2, O_2 and H_2) for GC were purified by gas clean filter system in order to remove traces of moisture and/or oxygen.

2.2.2. Operating conditions

Prior to catalytic tests, the samples were calcined in a pure O_2 flow at 550 °C (3 °C/min, 50 cm^3/min) for 10 h followed by a treatment under a flow of moisture-free N_2 at 550 °C for 2 h (standard treatment). All catalytic measurements were obtained for a benzene/propane molar ratio (Bz/C3) and WHSV, respectively, fixed at 0.24 and 10.3 h^{-1}. The effect of reaction temperature on the catalytic activity of samples was first studied in a temperature range of 350–550 °C after standard treatment. Between two catalytic measurements, samples were maintained under pure N_2 flow at the reaction temperature. Influence of time on stream on the zeolite activities and selectivities was determined at 500 °C under a continuous flow. The effect of reductive–oxidative treatment at 550 °C was studied as follows: the samples were treated under standard treatment (O_2) followed by a reduction under H_2 at 550 °C for 5 h (O_2/H_2) and finally were subjected to a re-oxidation under O_2 at 550 °C for 10 h ($O_2/H_2/O_2$). Between the various treatments, catalysts were maintained at 550 °C and the catalytic device was purged under N_2 after each treatment. In order to avoid coke deposition, all the data were collected at only 5 min on stream.

3. Results and discussion

3.1. Catalyst characterization

Materials were well crystallized according to scanning electron micrographs (Fig. 1). Crystallite shapes are hexagonal, about 420–740 nm in size. Gallium incorporation seems not induce changes in morphology. Crystallite sizes and crystallinities deduced from X-ray diffraction and IR data are reported in Table 1. XRD patterns (not shown) are closely similar to those published elsewhere for ZSM-5 materials and confirm the orthorhombic structure. XRD and FT-IR
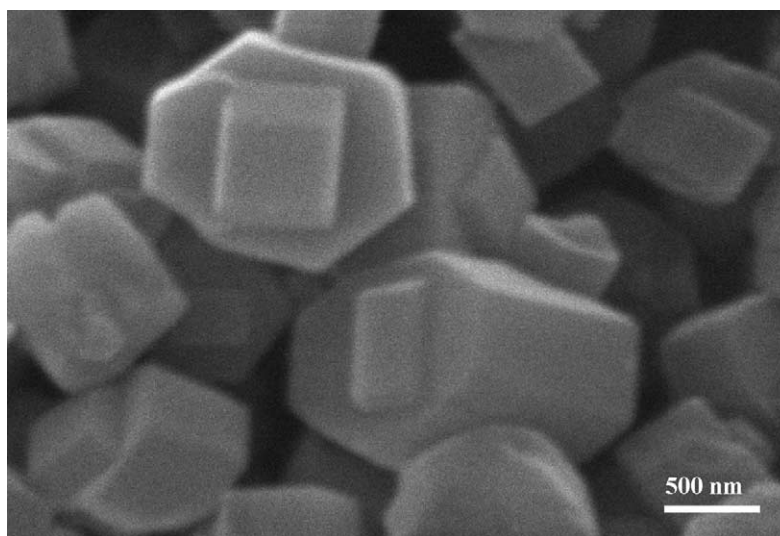
Fig. 1. Scanning electron micrographs of HZSM-5 zeolite.

Table 1
Physicochemical characterization of materials

Samples	Relative cristallinity[a]	Cristallite sizes (Å)[a]	I_{450}/I_{550}[b]	$V_{u.c.}$ (Å^3)[a]	Pore size (Å)	BET (m^2/g)
HZSM-5	100	65	0.70	5139	5.37	367
Ga1,HZSM-5	100	78	0.78	5118	5.34	384
Ga2,HZSM-5	95	61	0.76	5150	5.43	328
Ga2,HZSM-5	91	69	0.78	5215	5.58	355

[a] Deduced from XRD patterns.
[b] Ratio of the optical density of the bands located at 450 and 550 cm^{-1} ($I_{450}/I_{550} = 0.8$ for 100% crystallinity).

results confirm that materials are highly crystalline. However, it seems that gallium incorporation slightly affects the crystallinity and expands the unit cell values. Expansion of the unit cell is commonly used as proof of the incorporation of Ga into the framework [26]. Adsorption isotherms of N_2 (not reported here) are typical of microporous materials. No significant change in the mean pore sizes and in specific surface areas with gallium incorporation is observed (Table 1). Chemical compositions by elemental analysis and NMR techniques for HZSM-5 and Ga-modified HZSM-5 are collected in Table 2. ^{29}Si NMR spectra exhibit two signals at above −113 and −106 ppm which were assigned to Si–(OSi)$_4$ and Si–(OSi)$_3$(OAl) groups. Si/T (with T = Al, Ga or defect OH) ratio deduced from the ^{29}Si NMR spectra is in good agreement with chemical analysis in the case of

Table 2
Chemical characterization of materials

Samples	Ga (wt.%)[a]	Si/Al[a]	Ga/Al[a]	Si/T[b]	T/u.c.[b]
HZSM-5	–	20.46	–	21.4	3.8
Ga1,HZSM-5	0.57	20.31	0.11	25.2	3.7
Ga2,HZSM-5	1.24	20.54	0.24	24.5	3.8
Ga2,HZSM-5	1.81	20.44	0.37	23.5	3.9

[a] Elementary analysis (precision: ±0.01).
[b] NMR results (precision: ±0.1).

HZSM-5 zeolite. The Si/T ratio obtained for Ga-modified HZSM-5 materials exhibit higher values. This could be attributed to defects in the unit cell leading to a decrease of the intensity of the band at −106 ppm or due to Ga incorporation in the framework inducing a dealumination during acidic ion-exchange of the parent HZSM-5 zeolite with Ga(NO$_3$)$_3$. In all samples, ^{27}Al NMR spectra show a major signal at 54 ppm corresponding to framework tetrahedral Al. Signals at 0 and 25–30 ppm are, respectively, due to the octahedrally and pentacoordinated Al species. The intensity of the signal at 0 ppm is lower for the HZSM-5 zeolite. According to Si/T ratios, these observations confirm the presence of a small amount of extra-framework aluminum, probably resulting from dealumination during the acidic ion-exchange [25].

In all Ga-modified HZSM-5 samples, one ^{71}Ga NMR signal with quite low intensity (Fig. 2) is observed at 156–160 ppm assigned to the tetrahedrally coordinated framework Ga according to literature [26]. Ga extra-framework (GaO(OH)) and Ga hexacoordinated species giving rise, respectively, to a signal at around 50 and 0 ppm are not observed. However, this does not provide evidence that there is no extra-framework or no non-framework Ga species. Indeed, no signals were observed on ^{71}Ga MAS NMR spectra of samples without ion-exchange with NH$_4$NO$_3$, and it has been previously shown that non-framework gallium species were undetectable by ^{71}Ga NMR experiments. These species
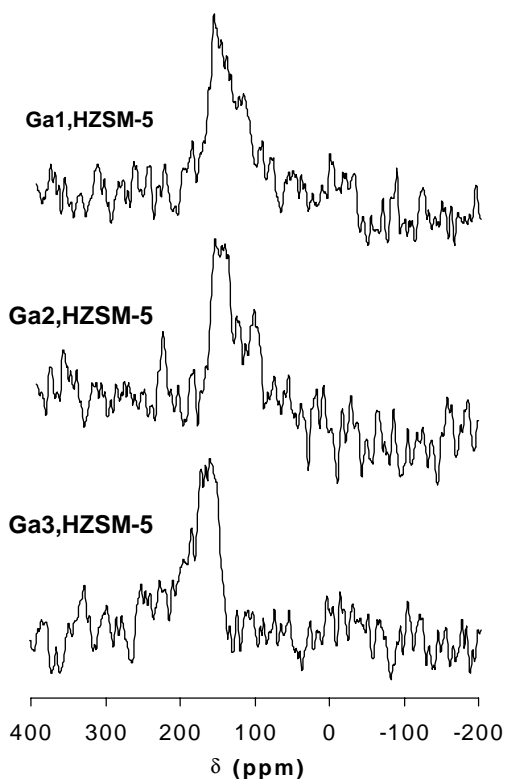
Fig. 2. ^{71}Ga MAS NMR spectra of Ga-modified HZSM-5 zeolites.

Fig. 3. Catalytic activity of HZSM-5 and three Ga-modified HZSM-5 zeolites as a function of reaction temperature.

are mainly localized in an environment of low symmetry which is characterized by a strong quadrupolar effect. With regards to these observations, Other than gallium atoms incorporated in T vacancies, Ga is mainly present as poorly dispersed extra-framework species $(Ga_2O_{3-x}(OH)_x)$ as revealed by our recent FT-IR study [25].

3.2. Catalytic activity evaluation

Catalytic activities were investigated on Ga-modified HZSM-5 samples and compared with those obtained with Ga-free zeolite. Percent conversion (conv.%) is defined as the number of moles of benzene converted (alkylated) over the number of moles introduced multiplied by 100. The product selectivity (%) is expressed as the percentage of this product among all products.

3.2.1. Influence of the reaction temperature

In Fig. 3 is reported the evolution of catalytic activities in the range of 350–550 °C. Almost no activity is observed on HZSM-5 below 500 °C. The conversion remains lower than 5% even at 550 °C. The low benzene alkylation activity is mainly due to thermodynamic factors that propane dehydrogenation is strongly endothermic and temperatures above 800 °C are required to favor its activation. On the contrary, at 400 °C, Ga-modified HZSM-5 materials show already some activities which increase with temperature. The addition of Ga increases thus considerably the benzene conversion. In-
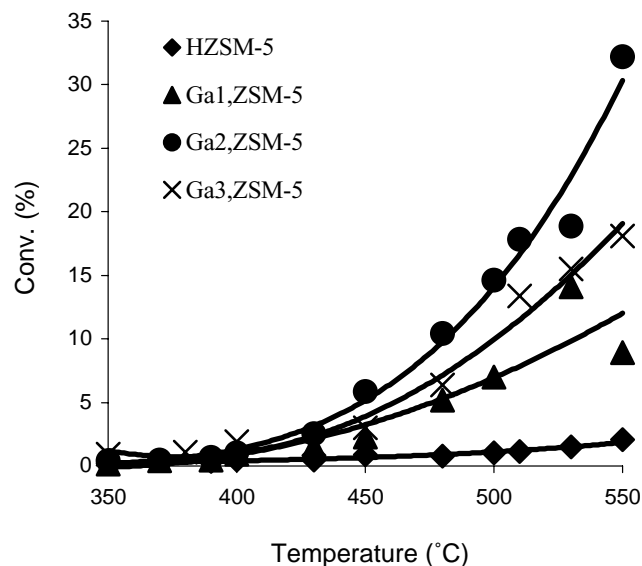
deed, the conversion of benzene on Ga doped HZSM-5 is 3–10 times higher than the parent HZSM-5 zeolite. Our observations confirm that the addition of Ga to HSZM-5 facilitates propane activation as proposed previously by Ivanova et al. in the case of propane aromatization [20] and consequently the alkylation of benzene. However, it appears that catalytic activity is not a function of the Ga loading. Indeed, the highest activity is obtained on the Ga2,HZSM-5 zeolite. Ga1,HZSM-5 and Ga3,HZSM-5 show comparable behavior with lower activities. The difference in activity could be ascribed to various Ga species dispersions.

It is possible that different Ga species coexist, and as suggested from MAS NMR results, some of them do not participate to propane activation. Guisnet and Gnep have previously concluded that, in the case of MFI gallosilicates, tetrahedral gallium species (in framework vacancies) were inactive in the dehydrogenation reaction [27]. Table 3 reports the product distributions obtained for 450 and 550 °C over four catalysts studied here. Toluene and ethylbenzene (Et-Bz) are main products. However, Et-Bz is predominantly produced on HZSM-5 in spite of the very low conversion and toluene on Ga,HZSM-5 zeolites. The general trend is that the toluene quantity increases with reaction temperature. Cumene and n-propylbenzene (nPr-Bz) are also formed in low quantities at 450 °C and disappear at elevated temperatures as the conversion increases. Xylenes, tri- and tetramethylbenzenes (t + T Me-Bz) are formed in small quantity. p/m-Xylene ratios show that the formation of p-xylene is slightly favored against m-xylene. o-Xylene is practically no observable. We noted also the formation of other alkylated aromatics (C_9–C_{10}–C_{11+} and polyalkylated aromatics: ethyltoluene, condensed aromatics including naphthalene and methylnaphthalene). These products are only formed on Ga-containing samples, being in very low quantities in

Table 3
Catalytic activities and product selectivities obtained at 450 and 550 °C

|	HZSM-5		Ga1,HZSM-5		Ga2,HZSM-5		Ga3,HZSM-5	
	450 C	550 °C	450 °C	550 °C	450 °C	550 °C	450 °C	550 °C
Conversion (%)	0.9	2	2	21	6	32	3	18
Toluene (wt.%)	7	31	48	68	51	79	43	58
Et-Bz (wt.%)	82	55	22	5	24	4	27	5
Xylenes (wt.%)	0	5	6	11	8	9	5	12
Cumene (wt.%)	4	0	3	Traces[a]	2	Traces	2	Traces
nPr-Bz (wt.%)	7	2	6	Traces	3	Traces	2	Traces
t + T Me-Bz (wt.%)	0	5	3	3	3	Traces	4	3
Other C_9–C_{10}–C_{11+}	–	–	15	12	9	2	15	20
p/m-Xylene	∞	1.1	1.6	1.0	1.1	0.9	1.2	1.6

[a] Products detected are lower than 1%.

the case of the more active Ga2,HZSM-5 catalyst but in significant quantities on Ga1,HZSM-5 and Ga3,HZSM-5.

Our results indicate that introduction of Ga improves the catalytic activity of HZSM-5 toward benzene alkylation and influences strongly the selectivity. The difference in activity and in selectivity observed between HZSM-5 and Ga-modified HZSM-5 suggests that the activation of propane occurs very likely in the first case via a monofunctional acid mechanism and in the second case via a bifunctional mechanism. The distribution of products for the HZSM-5 sample shows that acid-catalyzed cracking of propane leading to methane (or CH_3^+) and ethane (or $C_2H_5^+$) dominates over propane dehydrogenation. This explains that toluene and ethylbenzene are mainly formed and that only small quantities of cumene and n-propylbenzene are observed. A schematic representation of propane activation involving a carbocation species (carbonium or carbenium ions) on HZSM-5 sample is given in Scheme 1. The propane is protonated first on Brönsted acid sites of HZSM-5 to give a proponium ion. This ion is further decomposed in three different ways to CH_4 and $C_2H_5^+$ via β-scission, to $C_3H_7^+$ and H_2 via dehydrogenation or to CH_3^+ and C_2H_6. The reaction of CH_3^+, $C_2H_5^+$ and $C_3H_7^+$ carbenium ions with benzene leads to toluene, ethylbenzene and propylbenzene and cumene in small amounts, respectively. The low amount of cumene observed could also be due to the fast secondary transformation of cumene to other products.

The main reaction products obtained by Isaev et al. [28] for benzene alkylation with propane were toluene, xylenes and condensed aromatics. Olah et al. claimed that cumene was the major reaction product obtained over anhydrous fluoroantimonic acid [24]. On the other hand, an in situ ^{13}C MAS NMR study investigating benzene

alkylation with propane over Ga-modified HZSM-5 catalysts has shown that toluene and ethylbenzene were the major primary products [20] as observed in our present continuous-flow operating conditions. The lower amount of cumene observed at very low reaction temperatures confirms our previous in situ FT-IR study [19] that cumene can be formed in small amount only at reaction temperatures lower than 350 °C and that higher temperatures led to the formation of other alkylated aromatics. Nevertheless, our observation differs somewhat from previous results on propane aromatization showing that propane dehydrogenation dominated over acid-catalyzed cracking upon addition of gallium [9,29]. According to our present results, it appears that the operating conditions as well as the nature of zeolitic materials play a significant role in the reaction mechanism. The parent HZSM-5 zeolite used here has a low Si/Al ratio, i.e. a high concentration of Brönsted acid sites with respect to HZSM-5 with a very high Si/Al ratio, i.e. low concentration of Brönsted acid sites, used by Ivanova et al. Moreover, it is important to mention that in our case, the high reaction temperatures used probably induces the conversion of individual propane and benzene reactants leading to complicated reaction routes. In the case of Ga,HZSM-5 zeolite, a bifunctional mechanism involving double acidic sites: Ga^{x+} species acting as Lewis sites and protonic sites (Brönsted sites) should be considered [20,30]. We suggest here therefore the formation of a protonated pseudo-cyclopropane adsorbed species. The most likely reaction pathways for the benzene alkylation with propane on Ga-modified HZSM-5 catalysts in our operating conditions are illustrated in Scheme 2. The course of reaction pathway ((1, 2) or (3, 4)) strongly depends on the zeolite acidity and consecutively on the Lewis/Brönsted balance (Ga^{x+}/H^+).
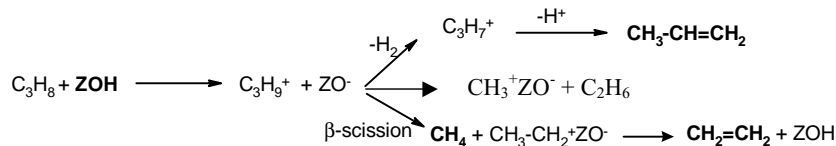
Scheme 1. Schematic representation of propane activation on HZSM-5 catalyst.
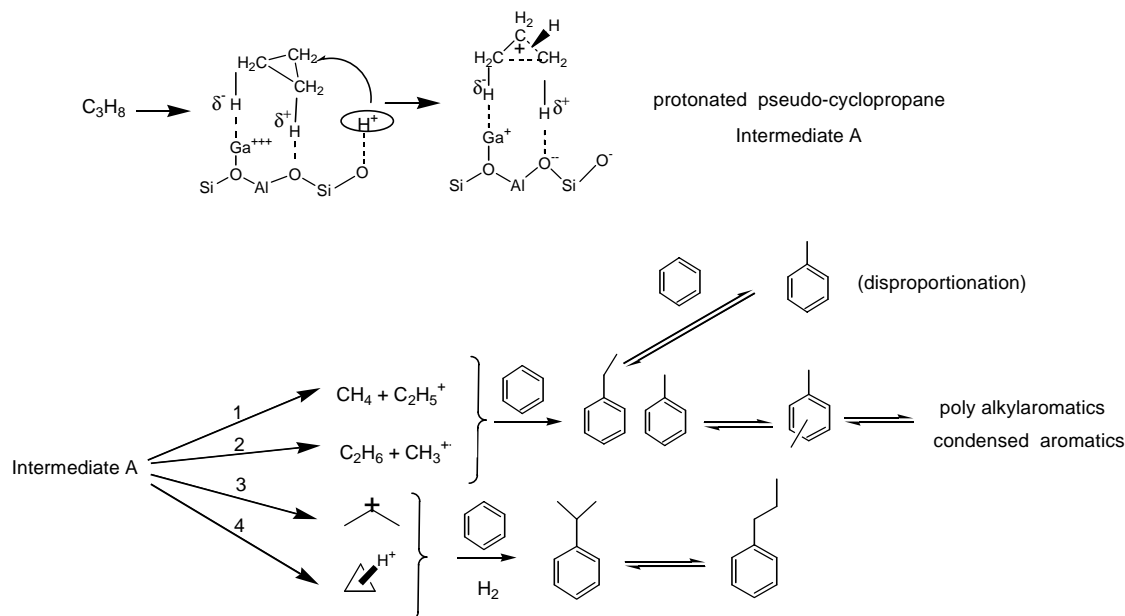
Scheme 2. Schematic reaction pathways for benzene alkylation with propane on Ga-modified HZSM-5 materials.

In our case, cracking activity (paths 1 and 2) is favored over dehydrogenation, probably due to a high density of strong H^+ acidic sites. The differences observed in toluene/Et-Bz ratio are probably due to ethylbenzene disproportionation. This is in accordance with the product distributions showing an increase in toluene percentage with the temperature. The almost absence of cumene and *n*-propylbenzene at elevated temperatures could also be ascribed to secondary reactions giving fragmentation to toluene and ethylbenzene. To favor the formation of direct addition products, i.e. to favor the propane dehydrogenation, the high Si/Al ratio of HZSM-5 (low concentration of Brönsted acid sites) and low reaction temperatures should be used.

3.2.2. Evolution of catalytic properties versus time on stream (Bz/C3 = 0.24)

Fig. 4 shows benzene conversion over HZSM-5 and Ga-modified HZSM-5 catalysts at 550 °C versus time on stream. As mentioned previously, HZSM-5 zeolite exhibits a very low activity. The conversion on this zeolite remains constant as a function of time on stream. In the case of Ga-containing samples, the high initial benzene conversion decreases quickly with time on stream in the same way for all the catalysts. All Ga-modified HZSM-5 catalysts deactivate rapidly. After 15 h on stream, all the catalysts exhibit activities similar to that observed for HZSM-5. These experiments point out the fact that gallium species as active sites are preferentially deactivated than protonic sites.

The selectivities at 550 °C versus time on stream for HZSM-5 and Ga-modified HZSM-5 are reported in Fig. 5. For the HZSM-5 zeolite, the product distribution shows a slight modification with time on stream that the percentage of toluene and ethylbenzene increases and that

of *n*-propylbenzene decreases. Concerning Ga-modified HZSM-5 catalysts, more drastic changes in the product distributions are observed with time on stream. A decrease in toluene and xylene percentages and the formation of large amounts of undesired products (C_9–C_{10}–C_{11+}) can be noted. After 20 h, reaction on these catalysts leads predominantly to the formation of byproducts (polyalkylated aromatics, condensed polyaromatics, etc.) which are more abundant for Ga2,HZSM-5 and Ga3,HZSM-5 reaching above 60%, while lower than 45% in the case of Ga1,HZSM-5.

These observations confirm that deactivation of gallium species results from carbonaceous residues mainly due to
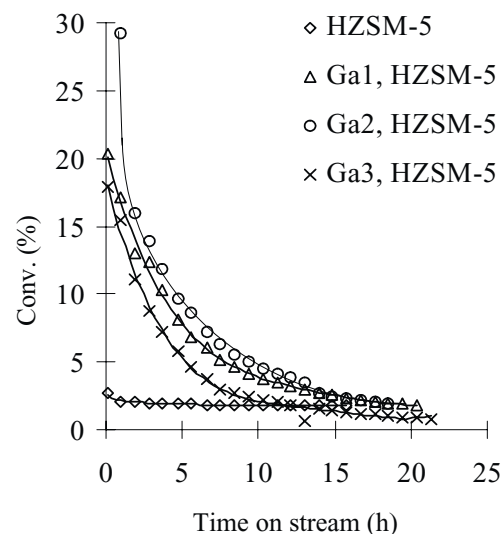

Fig. 4. Evolution of catalytic activities HZSM-5 and three Ga-modified HZSM-5 zeolites at 550 °C vs. time on stream.
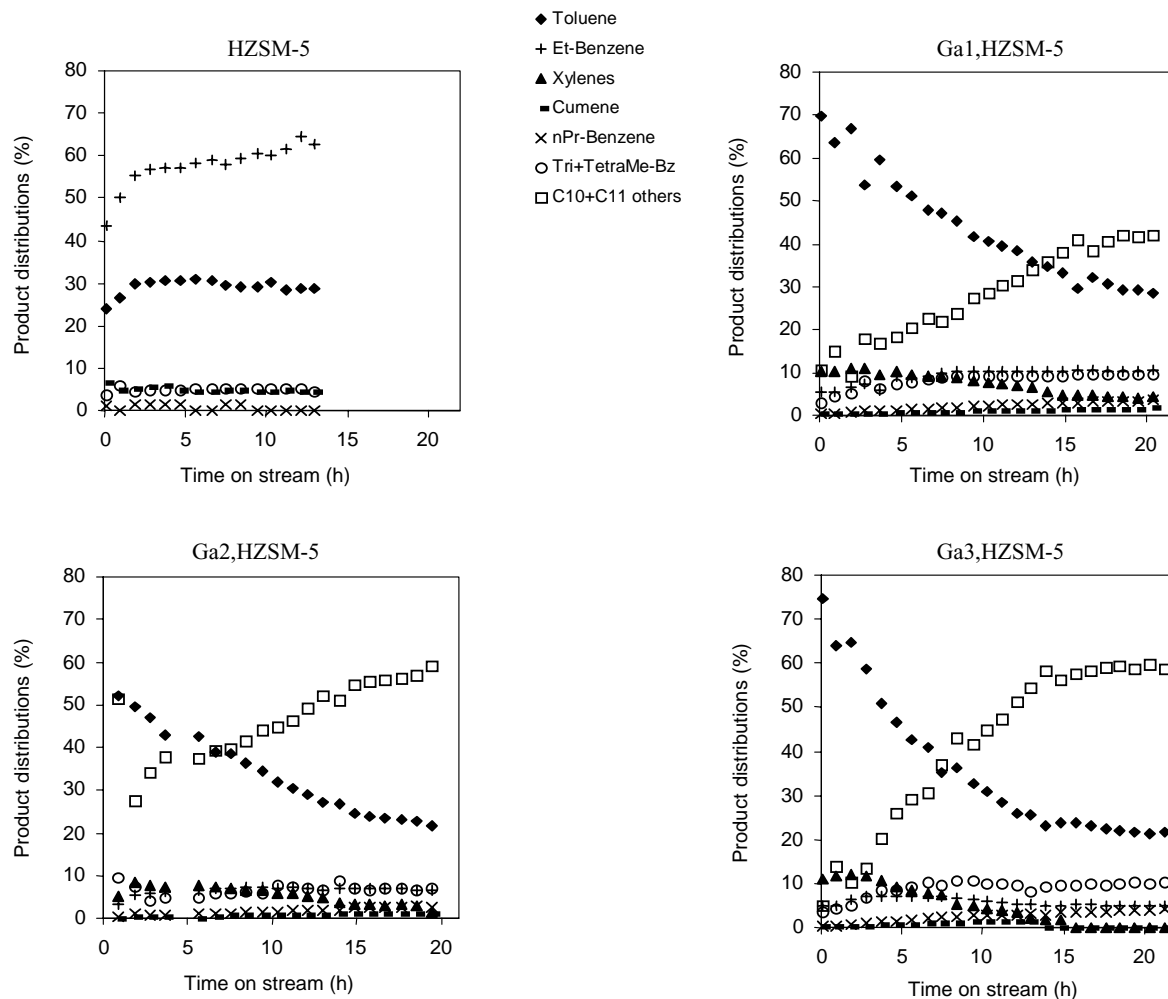
Fig. 5. Evolution of the selectivities of HZSM-5 and three Ga-modified HZSM-5 zeolites vs. time on stream at 550 °C.

deposition of condensed aromatics. Such behavior has been previously observed for propane aromatization over Ga-MFI catalysts [27,31,32]. These authors claimed also that a better dispersion of Ga significantly decreased coke formation by increasing the rehydrogenation of coke precursors [14]. We can deduce that the sample containing the lower Ga content (Ga1,HZSM-5) would be better dispersed than the others because of the delayed appearance of polyalkylated and condensed aromatics in this catalyst. Deactivation also strongly influences the *p*/*m*-xylene ratios, especially in the case of the Ga2,HZSM-5 and Ga3,HZSM-5 samples. We noted an increase of *p*/*m*-xylene ratio with time on stream until *m*-xylene is no longer detected. This observation suggests a shape selectivity owing to deactivation by coke deposition and indicates that coke is partly located inside the zeolite channel. It is important to mention that catalytic properties for Ga-containing samples are partially recovered after oxidation at 550 °C for 10 h. These results [33] suggest that the coke deposits consist of hard coke as proposed by Choudhary et al. [32].

3.2.3. Influence of oxidative and reductive treatments

Our recent FT-IR study showed clearly that the pretreatment conditions can influence strongly the acidity of catalysts [25]. This could induce a modification in catalytic behavior of catalysts. Oxidative and reductive treatments were investigated in order to clarify the nature of active gallium species. Fig. 6 displays the comparison of the conversion and the product distribution obtained for all catalysts after an oxidation treatment (O_2) followed by reduction (O_2/H_2) and a second oxidation ($O_2/H_2/O_2$). The results show that reduction and oxidation treatments have no effect on the catalytic properties of HZSM-5 catalyst. On the contrary, with Ga-HZSM-5 zeolites we note after reductive treatment (O_2/H_2) an enhancement of the conversion, which is more pronounced in the cases of samples containing lower Ga loadings. These changes are accompanied by an increase of toluene formation and a decrease of ethylbenzene production. The formation of xylene isomers remains unchanged on Ga1,HZSM-5 and Ga2,HZSM-5, but decreases on Ga3,HZSM-5. After re-oxidation ($O_2/H_2/O_2$),
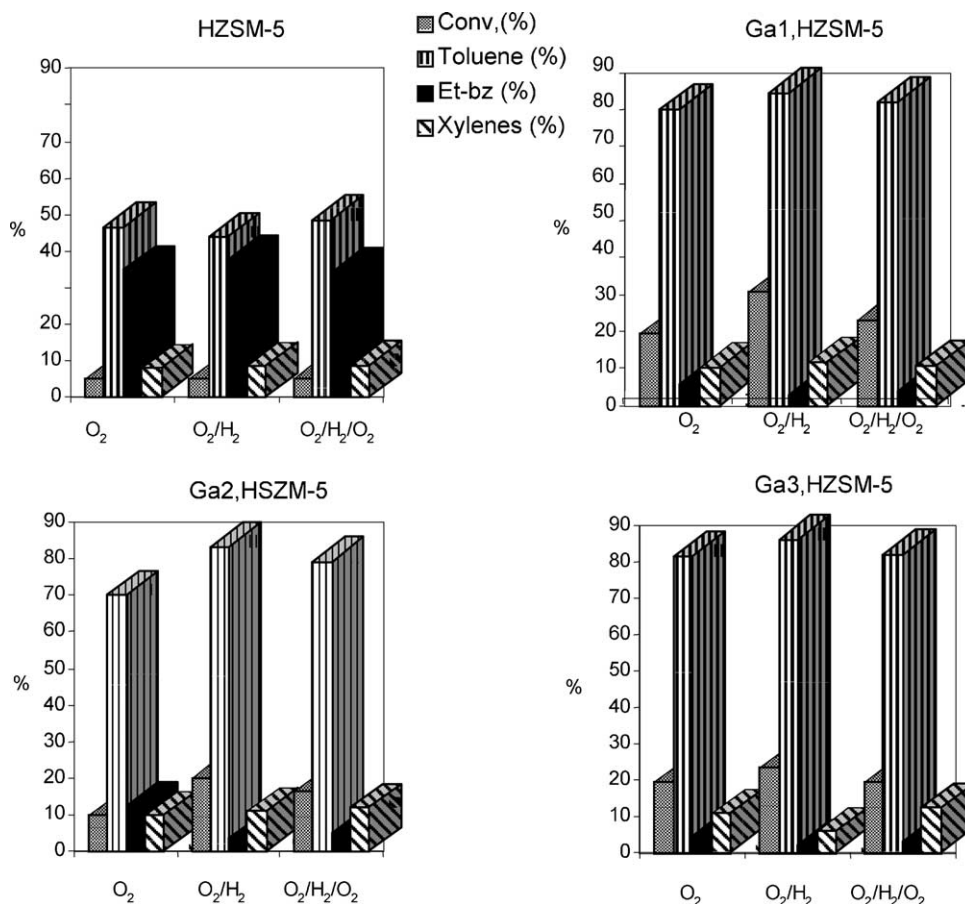
Fig. 6. Influence of oxidation/reduction treatments on catalytic properties of HZSM-5 and three Ga-modified HZSM-5 zeolites.

the results are similar to those obtained after a standard oxidation (O_2), suggesting that the modifications induced by the reduction are practically reversible even if the conversion remains slightly higher.

Consecutively of what is observed after reduction treatment, we attribute the gain in activity to a modification of the nature of gallium species. On the basis of recent FT-IR results [25] and literature [26,30,33,34], we suggest that gallium species are mainly present as non-framework ionic exchanged Si–O(Ga^{x+})–Al species. Our FT-IR investigations provided evidence that after thermal treatment, the dehydroxylation of $Ga_2O_{3-x}(OH)_x$, which is present in as-prepared catalyst, produces an oxide form such as Ga_2O_3. The reduction of Ga_2O_3 species, easily reducible between 500–800 °C, initially gives Ga_2O. Then these species will interact with zeolite Brönsted sites (OH groups), decreasing the number of these sites (intensity of OH groups in FT-IR spectra) to give Si–O(Ga^{x+})–Al. After re-oxidation, gallium species are mainly re-oxidized to Ga_2O_3 and partly to the gallyls species $[GaO]^+$. This procedure will increase gallium dispersion. It is clear that $O_2/H_2/O_2$ treatment can enhance the catalytic activity by increasing the dispersion of Ga species. One may propose that the tetrahedrally coordinated framework Ga can migrate from framework toward extra-framework after reduction treatment, these excess Ga

extra-framework species will modify the catalytic properties of catalysts. If this the case, after a re-oxidation ($O_2/H_2/O_2$) treatment), the catalytic properties of catalysts should be different from those after only a standard oxidation treatment. What we observed is the reversible catalytic properties. The tetrahedrally coordinated framework Ga species should be very probably inactive in the present reaction as observed by Guisnet and Gnep in the dehydrogenation reaction [27]. The present and previous FT-IR work shows clearly that reduction atmosphere modifies really the state of the Ga extra-framework species. This modification can further influence the catalytic activity properties of catalysts.

4. Conclusion

Ga-modified HZSM-5 zeolites are efficient catalysts to alkylate benzene with propane leading to toluene and ethylbenzene. Other alkylated products such as xylene, cumene and n-propylbenzene are also produced in lower quantities. Propane activation for benzene alkylation is favored on Ga-doped HZSM-5 zeolites acting as bifunctional catalysts containing Lewis and Brönsted acidic sites. The gallium species active for propane activation are initially Ga_2O_3 clusters after oxidation. Si–O(Ga^{x+})–Al species (due to the

interaction of Ga_2O and OH groups) are probably formed after O_2/H_2 treatment leading to a significant increase in activity by increasing gallium dispersion. The reaction pathway would be strongly dependent on the (Lewis and Brönsted) acidity of zeolite and also on the Ga^{x+}/H^+ ratio. The most active catalyst is obtained for a 1.24 wt.% Ga and the less sensitive catalyst toward coke deposition is obtained for a 0.57 wt.%. The coke deposition probably occurs in the zeolite channel resulting from condensed polyaromatics. A series of works using different highly dealuminated and Pt or bimetal (Ga, Pt)-modified HZSM-5 catalysts are being undertaken to improve the activity and selectivity of catalysts [33].

Acknowledgements

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