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In Situ X-ray Absorption Study of the Genesis and Nature of the Reduced Gallium Species in Ga/HZSM5 Catalysts

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ABSTRACT: *In situ* gallium K edge XAFS spectroscopy experiments were performed with GaZSM5 catalysts containing two different gallium loadings (2 and 4%) under hydrogen or propane in the 703−823K temperature range. It was found that, irrespective of the gallium loading and reducing gas, linear correlations were found between the coordination numbers of both the first (Ga−O scattering legs) and second (Ga−Ga scattering legs) gallium coordination spheres estimated from EXAFS and the degree of reduction estimated by XANES. The results showed that the reduction proceeds from Ga^{3+} binuclear species 4-fold coordinated to oxygen to an isolated Ga^+ ion coordinated to a single oxygen atom.

In Situ XAFS Correlations in Ga/HZSM5 Catalysts
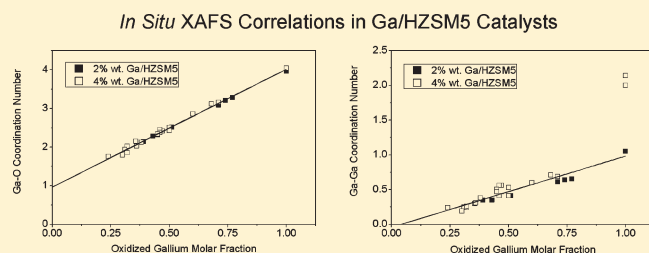
■ INTRODUCTION

The aromatization of light hydrocarbon gases (C_2-C_4) has been investigated for more than two decades, due to its economical and strategic importance for the exploitation of natural gas reserves and valorization of light hydrocarbons obtained from petroleum refining. Commercially, reactions using gallium modified ZSM5 zeolite catalysts are known as the "Cyclar" process, developed jointly by UOP and BP.[1]

Determining the role of gallium species in these reactions has proven difficult, as the nature of the active species remains unclear, mainly because the active gallium species is highly dispersed and only present under reaction (reductive) conditions.[2−6] In this sense, X-ray absorption techniques are extremely useful as they allow the detection of dispersed and even isolated species and were already used in the literature in order to study this system.[2,4−13] However, the data analysis has been generally limited to qualitative interpretation of the XANES (qualitative correlations between edge shifts and oxidation state of gallium atoms) and EXAFS spectra (qualitative conclusions about the dispersion of gallium species). In particular, we found no attempt in the literature to quantitatively correlate the dispersion of the gallium species, obtained from EXAFS measurements, and their state of oxidation, obtained from XANES measurements in the same experiments.

In a previous publication[14] we established quantitative correlations between dispersion, acidity, and reducibility of the oxide form of GaZSM5 catalysts of varying composition (zeolite silica-to-alumina ratio and gallium loading) and their propane aromatization activity. It was found that isolated oxidic gallium species exist in the catalysts, along with condensed species, but their proportion decreases with increasing Ga/Al ratio. Gallium incorporation, besides decreasing the density of Brønsted acid sites as compared to the pure zeolites, caused the appearance of strong Lewis acid sites, capable of retaining adsorbed pyridine up to 673 K. This strong Lewis acidity was related to the presence of highly dispersed oxidic gallium species. These species, perhaps on account of their strong Lewis acidity, are more easily reduced than the condensed gallium species present in the zeolite channels. A fairly linear correlation was found between the initial rate of propane aromatization at 703 K and the product of strong Lewis and Brønsted acid site concentrations, which pointed toward the need for the simultaneous existence of Lewis and Brønsted acid sites in the oxidized form of the catalysts for good alkane aromatization activity. As it is generally assumed that the active gallium species is in a reduced state, rather than attributing this correlation to the cooperative action of Lewis and Brønsted acid sites in the reaction mechanism, we proposed that the reducibility of the strong Lewis acid species facilitates the formation of the reduced gallium species that are supposed to be the actual active sites in alkane activation.

In this paper, we attempt to correlate quantitative in situ XANES and EXAFS results on Ga-HZSM5 catalysts in different states of reduction, in order to obtain data on the structure of reduced gallium species under propane aromatization conditions.

■ EXPERIMENTAL SECTION

Catalysts containing 2 and 4 wt % gallium, supported on an HZSM5 zeolite with silica-to-alumina ratio (SAR) of 35, were prepared by incipient wetness impregnation with a gallium nitrate solution and were activated by two successive reduction−oxidation cycles. Catalysts prepared this way with 2 and 4% wt. of gallium were named, respectively, T2GaZ35 and T4GaZ35. For more details on catalyst preparation and the naming scheme see ref 14.

X-ray absorption measurements at the gallium K edge were made using the XAFS2 beamline facility of the LNLS storage ring

(Campinas-Brazil), operating at 1.37 GeV with a maximum beam current of 250 mA. Monochromatization of the incident beam was accomplished using a double Si(111) crystal. Energy calibration of the beam was done with β-Ga$_2$O$_3$, which was chosen as the standard reference. The intensities of the incident and transmitted beams were monitored by Ar-filled ionization chambers, and the analyses were carried out between 10 260 and 11 350 eV.

Samples were analyzed, pressed as wafers, in a tubular quartz reactor with Kapton windows and atmospheric pressure gas flow of 100 cm^3 min^{-1}. The gases used were helium, 5% vol hydrogen in helium, and 2% vol propane in helium. Spectra were obtained at different times and temperatures, and gaseous products were monitored online by an Omnistar quadrupole mass spectrometer.

■ RESULTS

Figure 1 shows propane conversion on the catalysts as function of time on stream and reaction temperature. All curves for each catalyst were obtained in a single continuous experiment. The curves show that both catalysts were able to convert propane under the reaction conditions employed. Products obtained were hydrogen, methane, ethylene, ethane, propylene, and benzene showing that the aromatization reaction was indeed occurring during the XAS measurements.

The XANES spectra of gallium modified catalysts show no pre-edge peaks. Two distinct white lines can be observed in the region of the absorption edge, which vary in intensity and in edge position, indicating the presence of gallium species with different charge densities during reduction with hydrogen and reaction with propane. Figure 2 shows the XANES spectra of sample T4GaZ35 at different temperatures and times under a hydrogen atmosphere. The presence of two isosbestic points, marked with vertical straight lines in Figure 2, suggests that only two species are contributing to the overall spectra, Ga^{3+} (E_0 = 10 372 eV) and Ga$^+$ (E_0 = 10 368 eV).

As only the Ga^{3+} XANES spectrum was available, from the samples in oxide form, an iterative alternating least-squares (ALS) method[15−17] was used in order to extract the Ga$^+$ XANES spectrum and the molar fractions of each species (Ga^{3+} and Ga$^+$) from the spectra of partially reduced catalysts. The restrictions applied to the alternating least-squares problem were the following: (1) positive molar fractions and absorptivities, (2) normalized sum of molar fractions, and (3) a difference between the Ga^{3+} simulated and experimental XANES spectra of less than 2%.

Convergence was achieved after 63 iterations, with 99.64% (R^2) of the covariance explained. The optimized spectra of both gallium species are shown in Figure 3, where isosbestic points are again marked with vertical straight lines. Also, calculation of the feasible band boundaries[18,19] showed errors of less than 0.02 in molar fractions. It is interesting to notice that the results were the same, irrespective of whether the ALS method was used with data from experiments with hydrogen or propane or with all data available.

Table 1 shows the main conditions of the XAS measurements (reducing gas, temperature, and starting time of each spectrum), together with the corresponding amount of Ga^{3+} species deduced from the XANES portion of the spectra with the least-squares fitting procedure just described. As expected, the degree of reduction increased markedly with increasing reduction
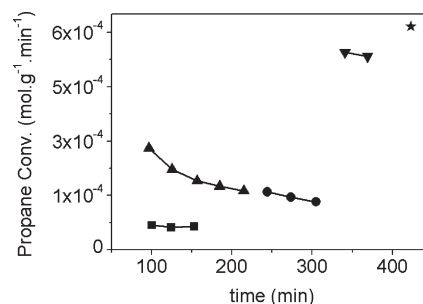
Figure 1. Propane conversion of the catalysts as function of time on stream and reaction temperature: (■) T2GaZ38-703K, (▲) T4GaZ38-703K, (●) T2GaZ38-773K, (▼) T4GaZ38-773K, and (★) T4GaZ38-823K.
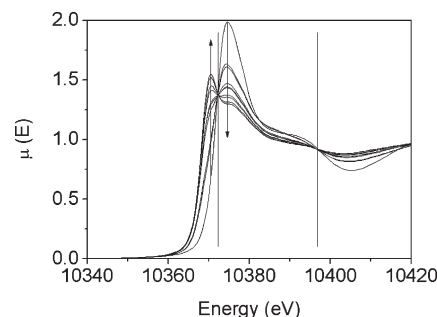
Figure 2. XANES spectra of sample T4GaZ38 at different temperatures under reductive (hydrogen) atmosphere. The arrows indicate the progress of the catalyst reduction, and the isosbestic points are marked with vertical lines.
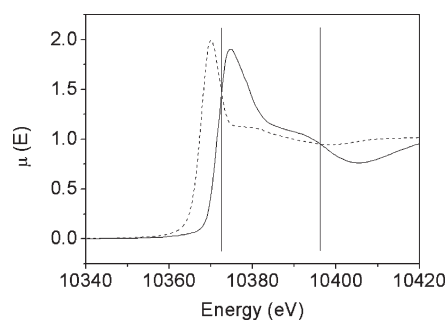
Figure 3. Optimized spectra of oxidized (—) and reduced (---) gallium species. Isosbestic points are marked with vertical lines.

temperature and also with time at each temperature. This last fact indicates that, strictly speaking, the XAS spectra, which were each collected in 15 min, were changing during the collection period, but as shown in Table 1, the small changes in reduction degree among the spectra obtained at any given temperature indicate that most of the increase in reduction degree occurred during the heating period between temperatures. Therefore, changes in reduction degree and their effect on spectral shape during collection of a single spectrum are ignored in the following analysis.

The EXAFS spectra were analyzed by a standard procedure of data reduction and least-squares fitting using the IFEFFIT code[17] with phase and amplitude functions calculated using the FEFF 8.20 code.[21,22] Simulations were made in R-space using $k = 2−12$ Å^{-1}, d$k = 2$, and $k_{weight} = 3$ using a first coordination sphere of

4750

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Table 1. Description of *in Situ* XAFS Spectra Collection Conditions under Reductive Atmosphere and Gallium Oxidized Species Molar Fractions χ (Ga^{3+})

T (K)	time (min)	χ (Ga^{3+})^a
	T2GaZ35 with 2% v/v C$_3$H$_8$/He	
298		1.00
703	9	0.77
703	33	0.74
703	62	0.71
773	153	0.51
773	182	0.43
773	214	0.39
	T4GaZ35 with 2% v/v C$_3$H$_8$/He	
298		1.00
703	4	0.60
703	32	0.50
703	64	0.47
703	92	0.46
703	122	0.45
773	248	0.32
773	276	0.31
823	330	0.24
	T4GaZ35 with 5% v/v H$_2$/He	
298		1.00
703	13	0.71
703	51	0.68
783	104	0.50
783	133	0.46
783	154	0.45
823	209	0.38
823	238	0.36
873	297	0.32
873	327	0.30

^{a} Molar fractions error is ±0.02 units.

Table 2. Mean Bond Distances, Debye–Waller Factors, and First Coordination Sphere Third Cumulant

parameter	value (error)
σ^2 Ga–O (Å^{-2})	0.0102 (6)
C_3 Ga–O (Å^{-3})	0.0015 (2)
R Ga–O (Å)	1.93 (1)
σ^2 Ga–Ga (Å^{-2})	0.0156 (5)
R Ga–Ga (Å)	2.97 (2)

Figure 4. Graphical result of the simulation of sample T4GaZ38 under propane flow at 703 K: (left) Fourier transform magnitude, (right) Fourier transform imaginary part; (—) experimental spectra, (O) simulated spectra.
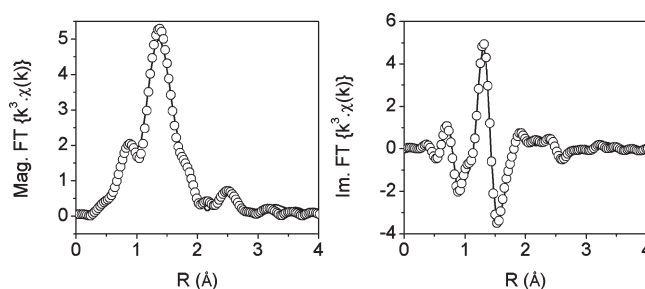
oxygen atoms and a second coordination sphere of gallium atoms, where the mean coordination numbers were determined in each case.

The mean results of bond distances, Debye–Waller factors, and first coordination sphere's third cumulant along with their associated errors are shown in Table 2. As no trend was observed, values shown in this table are an average from all partially reduced catalysts, and errors were calculated according to Student distribution within 95% confidence limits. In the EXAFS simulations of all studied catalysts a third cumulant was used to account for the asymmetric peak shapes observed. The third cumulant is the first term of a power series correction for the Debye–Waller factor in the EXAFS equation in order to account for the anhamonicity of the potential which is more severe at higher temperatures. All values of R_{factor} obtained were below 3% which is considered very good in this kind of work. As a representative example, the graphical result of the simulation of sample T4GaZ38 under propane flow at 703 K can be seen in Figure 4.

It is apparent that the Debye–Waller factors found here for the first gallium coordination sphere are almost twice those obtained before for the catalysts in oxidized form at room temperature.[5,14] This can be due to the combined effect of

thermal disorder due to the high temperature of the in situ XAS experiments and the fact that, as clearly apparent from the XANES data, at least two gallium species in different states of reduction, presumably with different Ga–O distances, contribute to the spectrum and only one first neighbor Ga–O scattering path was used in the fitting procedure.

Table 3 shows individual simulation results for three spectra: one for catalyst T4GaZ35 in oxide form at room temperature, one for the same catalyst at its highest degree of reduction at 823 K under a flow of 2% v/v C$_3$H$_8$/He, and one for the reduced catalyst after cooling under this same flow to room temperature. It is apparent that the main reason for the large DW factors obtained with the partially reduced catalysts was the high temperature at which the spectra were collected, since after cooling to room temperature, the DW factor returned to the value obtained with the oxidized catalyst at the same temperature.

It is also observed from Tables 2 and 3 that first sphere Ga–O distances were considerably larger with the partially reduced catalysts at high temperature than with the catalysts in oxide form at room temperature. From Table 3 it is seen that the Ga–O distance for the partially reduced catalyst decreased after cooling to room temperature, but did not reach the value obtained with the catalyst in oxide form. Therefore, the large average Ga–O distances obtained for the partially reduced catalysts are the combined effect of high temperature and change in the nature of the gallium species.

It is possible to correlate the percentages of Ga^{3+} and Ga$^+$ obtained by XANES with the Ga–O and Ga–Ga coordination numbers obtained by EXAFS. Figures 5 and 6 show the results for these two sets of data. Both graphs contain data for the two series of catalysts and, with catalyst T4GaZ35, for reduction under both hydrogen and propane. A good linear dependence was found between coordination number and gallium oxidation state, in the case of the first coordination sphere, as shown in Figure 5. By extrapolation of the data to 0% of Ga^{3+}, it can be

Table 3. Individual Simulation Results for Catalyst T4GaZ35 in Oxide Form at Room Temperature (RT), Reduced at 823 K under a Flow of 2% v/v C_3H_8/He after Cooling under This Same Flow to Room Temperature

sample	σ^2 Ga—O (Å^{-2})	C_3 Ga—O (Å^{-3})	R Ga—O (Å)	σ^2 Ga—Ga (Å^{-2})	R Ga—Ga (Å)
T4GaZ35 oxidized	0.007	0.0010	1.83	0.013	3.00
reduced at 823 K	0.012	0.0021	1.91	0.014	2.96
cooled to RT	0.006	0.0009	1.86	0.010	2.98
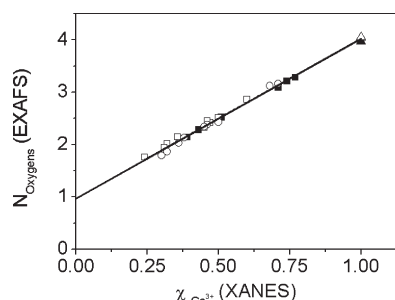
Figure 5. Correlation between the percentages of Ga(III) and Ga(I) obtained by XANES and gallium first sphere (oxygen) coordination numbers obtained by EXAFS: (■, □) reduced in propane; (●, ○) reduced in hydrogen; (▲, △) oxidized samples. Filled symbols represent T2GaZ35; hollow symbols represent T4GaZ35.
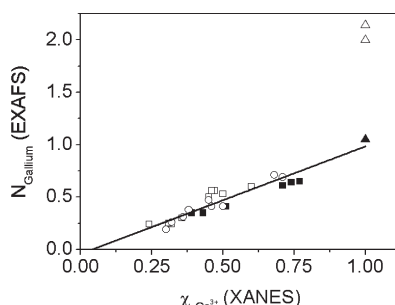
Figure 6. Correlation between the percentages of Ga(III) and Ga(I) obtained by XANES and gallium second sphere (gallium) coordination numbers obtained by EXAFS: (■, □) reduced in propane; (●, ○) reduced in hydrogen; (▲, △) oxidized samples. Filled symbols represent T2GaZ35; hollow symbols represent T4GaZ35.

seen that the reduced species has one oxygen atom in the first coordination sphere (the fitting line intercepts the ordinates axis at 0.97 ± 0.03, and correlation coefficient was $r^2 = 0.995$).

In Figure 6, a line may be fitted to the points pertaining to the partially reduced catalysts. The best-fit line extrapolates essentially to zero Ga—Ga coordination number (intercept −0.01 ± 0.040, and correlation coefficient $r^2 = 0.84$) for 0% Ga^{3+}. These results clearly demonstrate that the reduced gallium species which, according to the literature,[2−4,6,9,11−13] is the active phase in these catalysts, is an isolated gallium species. This isolated gallium species is most probably located as a charge compensation cation in the MFI zeolite, but from the XAFS results, it is not possible to exclude the presence of hydride ligands to the gallium atoms, because hydrogen has a very low photoelectron backscattering amplitude giving almost zero EXAFS signal.

Figures 5 and 6 demonstrate that the same type of reduced gallium species is produced independently of the nature of the reducing gas, hydrogen or propane.

Our previously published EXAFS results on GaZSM5 catalysts supported on different ZSM5 samples and containing varying

gallium loadings[14] showed that oxidized gallium species are 4-fold coordinated to oxygen in all catalysts. This, taken together with the linearity of the graph in Figure 5, strongly indicates that spectra in the partially reduced catalysts may be explained by the coexistence of oxidized 4-fold-coordinated gallium species with monocoordinated reduced gallium species.

On the other hand, the line in Figure 6 is striking. This line extrapolates to very close to a 1.0 sphere coordination number as the reduction degree approaches zero (100% Ga^{3+}). This implies that, irrespective of the gallium loading of the zeolite and reducing atmosphere, the reduction seems to proceed from an oxidized gallium species with a single gallium atom at its second coordination sphere, i.e., a binuclear oxidic gallium species. Yet, the second sphere coordination number for catalyst T4GaZ35 before the reduction was close to 2. It must be concluded that, during the initial stages of the reduction, more condensed oxidized gallium species are converted to binuclear ones, since already at ca. 25% reduction of Ga^{3+} the experimental points are close to the regression line.

■ DISCUSSION

In order to speculate on the processes occurring during reduction of the GaZSM5 catalyst, we have to revisit some of our previously published data on their oxidized form. The required data are shown in Table 4 and include the amounts of gallium (from X-ray fluorescence), framework aluminum (from ^{27}Al and ^{29}Si solid state NMR), Brønsted acid sites, and strong Lewis acid sites (from FTIR spectroscopy of adsorbed pyridine), all in a per gram of catalyst basis, and the percentage of octahedrally coordinated Al (from ^{27}Al solid state NMR) for the two Ga/HZSM5 catalysts and their respective parent zeolites, as described in ref 14 (oxide form). Also included in the table is the proportion of $[Si(SiO_4)_2(AlO_4)_2]$ and $[Si(SiO_4)_3(AlO_4)]$ units in the zeolite framework, i.e., the proportion of silicon atoms with, respectively, two aluminum atoms and those with one aluminum atom at the second coordination sphere measured by ^{29}Si solid state NMR.

The X-absorption spectra for the oxidized catalysts shown here and in our previous publications were obtained with catalysts that had been equilibrated with atmospheric air, and therefore, the gallium species in them were presumably hydrated or hydroxylated. On the other hand, strong Lewis acidic sites were found in the catalysts after evacuation at 673 K.[14] Recent work has computed the energetics of carbon monoxide adsorption on Lewis acid sites associated with oxidic gallium clusters of different structures and numbers of gallium atoms.[23] Strong Lewis acidity was only found with fully dehydrated clusters containing gallium atoms with less than 4-fold coordination to oxygen, with the exception of a $Ga_2O_2^{2+}$ cluster that requires association with two ion-exchange sites at the same five-membered ring of the MFI structure. This necessarily implies, due to Löwenstein's rule, the existence of silicon atoms connected to two framework aluminum atoms through oxygen bridges ($[Si(SiO_4)_2(AlO_4)_2]$ units). According to our [29]Si solid-state

Table 4. Some Characterization Data for Catalysts T2GaZ35 and T4GaZ35

catalyst	Si/Al[a]	Ga[b]/mmol g⁻¹	Al[c]/mmol g⁻¹	B[d]/mmol g⁻¹	L[e]/mmol g⁻¹	% Al_{oct}[f]	% SiAl[g]	% $SiAl_2$[h]
TZ35	19.4		0.823	0.877	0	5.6	19.5	0.61
T2GaZ35	20.1	0.287	0.774	0.580	0.107	8.2	17.2	1.26
T4GaZ35	21.2	0.717	0.705	0.426	0.160	16.4	16.7	1.35

[a] Framework Si/Al ratio, average between ^{29}Si and ^{27}Al NMR results. [b] Determined by X-ray fluorescence. [c] Framework aluminum atoms, determined by XRF and ^{27}Al NMR. [d] Brønsted acid sites, determined from FTIR of adsorbed pyridine after evacuation at 473 K. [e] Strong Lewis acid sites, determined from FTIR of adsorbed pyridine after avacuation at 673 K. [f] Percentage aluminum in octahedral coordination, measured by ^{27}Al NMR. [g] Percentage of silicon with one aluminum atom as second nearest neighbor measured by ^{29}Si NMR. [h] Percentage of silicon with two aluminum atoms as second nearest neighbors measured by ^{29}Si NMR. Experiments described in ref 14.

NMR results, the proportion of such units with respect to total silicon atoms is around 1.3% in the catalysts of the present study. This, multiplied by the Si/Al framework ratio gives the number of $[Si(SiO_4)_2(AlO_4)_2]$ units per framework aluminum, and it is found that this number is 0.26 for catalyst T2GaZ35 and 0.28 for catalyst T4GaZ35. The proportion of silicon atoms with three aluminum atoms in the second coordination sphere is negligible.

Characterization by FTIR of adsorbed pyridine displayed in Table 4 showed that the ratio of strong Lewis acid sites created due to gallium incorporation, defined as those capable of retaining adsorbed pyridine up to an evacuation temperature of 673 K, to framework aluminum in catalyst T2GaZ35 (L/Al_{FW}) is 0.14. So, there seems to be plenty of $[Si(SiO_4)_2(AlO_4)_2]$ units to accommodate $Ga_2O_2^{2+}$ clusters, in case these are really formed and are responsible for the strong Lewis acidity.

At the same time, we were able to measure the decrease in Brønsted acidity due to gallium incorporation by FTIR, from both the intensity of the bridged hydroxyl band in the OH stretching region of the spectra and that of the skeletal vibrations of adsorbed pyridine. Both methods gave very similar results. Part of this decrease in Brønsted acidity must have arisen from the dealumination that accompanies gallium incorporation and subsequent reduction/reoxidation cycles. Knowledge of the increase in the proportion of extra-framework aluminum during catalyst preparation as compared to the parent zeolite from ^{27}Al NMR measurements allows one to estimate the decrease in Brønsted acidity due solely to the exchange of protons by gallium-containing cations. We estimated this value from the following calculation

$$\Delta B_{exc}/Al_{FW} = (\Delta B_{tot}/Al_{FW}) - (x_{oct} - {}^0x_{oct})/(1 - x_{oct}) \quad (1)$$

where $\Delta B_{exc}/Al$ is the decrease in Brønsted acidity due to cation exchange, $\Delta B_{tot}/Al$ is the total decrease in Brønsted acidity, both expressed on a per framework aluminum basis, and x_{oct} and ${}^0x_{oct}$ are the fractions of octahedral to total aluminum in a given catalyst and in the parent zeolite, respectively. It should be noticed that XRF analysis showed a negligible difference in total aluminum content between the catalysts and the respective parent zeolites, so any aluminum removed from the framework remained in the catalysts as extra-framework aluminum (EFAL).

By this method we estimate that the decrease in Brønsted acidity due to exchange with gallium cations ($\Delta B_{exc}/Al_{FW}$) in T2GaZ35 is 0.22 per framework aluminum. This is considerably more than the Lewis acidity, which indicates that some of the replacement of protons by gallium atoms does not lead to Lewis acid sites. This means either that $Ga_2O_2^{2+}$ units do not count as two Lewis acid sites each or that they do so, but there are other charged species that do not contribute to Lewis acidity.

In catalyst T2GaZ35 in its oxidized form the second sphere coordination number is close to 1.0, as apparent from Figure 6, so

this catalyst is probably rich in binuclear oxidic gallium species. At the same time, the ratio of gallium to framework aluminum (Ga/Al_{FW}) is 0.38. If we make the simplifying assumption that only binuclear oxidic gallium species are present in this catalyst, three conditions must be simultaneously met: $Ga/Al_{FW} = 0.38$, $L/Al_{FW} = 0.14$, and $\Delta B_{exc}/Al_{FW} = 0.22$. It is next assumed that uncharged, singly charged, and doubly charged binuclear oxidic gallium species may exist in the catalyst and further that each unit charge corresponds to the consumption of a Brønsted acid site. Furthermore, it is assumed that only charged species can act as Lewis sites. Then, a system of three equations with three unknowns may be set up inter-relating the number of each of the binuclear species per framework aluminum, n_0, n_1 and n_2, where the subscript corresponds to the charge on each species. There are two possibilities to solve this system: (1) assuming that each charged species, either singly charged or doubly charged, counts as one Lewis acid site; (2) only doubly charged binuclear species contribute to Lewis acidity and count as two acid sites each.

According to hypothesis 1, the system is as follows:

$$n_0 + n_1 + n_2 = 1/2Ga/Al_{FW} \quad (2.1)$$

$$n_1 + n_2 = L/Al_{FW} \quad (2.2)$$

$$n_1 + 2n_2 = \Delta B_{exc}/Al_{FW} \quad (2.3)$$

For hypothesis 2, the following system applies:

$$n_0 + n_1 + n_2 = 1/2Ga/Al_{FW} \quad (3.1)$$

$$2n_2 = L/Al_{FW} \quad (3.2)$$

$$n_1 + 2n_2 = \Delta B_{exc}/Al_{FW} \quad (3.3)$$

Both hypotheses lead to valid solutions for the system, and the present data do not allow us to distinguish between them. However, alternative hypotheses, such as assuming that uncharged species also contribute to the Lewis acidity or that only doubly charged species are Lewis acid sites and count as one site, do not lead to valid solutions (negative value for some species). Hypothesis 1 leads to $n_0 = 0.05$, $n_1 = 0.055$, and $n_2 = 0.08$ binuclear species, and hypothesis 2 leads to $n_0 = 0.04$, $n_1 = 0.08$ and $n_2 = 0.07$ binuclear species per framework aluminum. In both cases, n_2 is smaller than the number of $[Si(SiO_4)_2(AlO_4)_2]$ units per framework aluminum estimated from ^{29}Si NMR.

Of course there is a large uncertainty in these simple calculations due to the accumulated errors of the experimental methods and the simplifying assumptions used. However, they do show that the presence of $Ga_2O_2^{2+}$ species is required to explain our data, but are not the only type of binuclear oxidic species in this
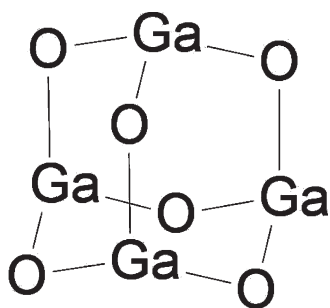
Figure 7. Structure of a hypothetical Ga_4O_6 cluster with a 3 second sphere coordination number for each gallium atom.

catalyst and are not necessarily solely responsible for its strong Lewis acidity.

We must now turn our attention to catalyst T4GaZ35. In this catalyst, the second sphere coordination number is close to 2.0. This means that there are oxidic gallium species in this catalyst with more than 2 gallium centers. This considerably complicates any analysis, since one may have a distribution of oxidic gallium species of different sizes and charges. In an attempt to simplify the problem, we recall that, in a previous publication with another series of Ga/HZSM5 catalyst, that differed from the present one by the fact that a broader range of Ga/Al ratios and at most one reduction/oxidation cycle during catalyst preparation was used, the EXAFS data could be adequately simulated by assuming a mixture of β-Ga_2O_3 and either binuclear species or a gallium species containing three gallium atoms as second nearest neighbors, depending on gallium loading and pretreatment procedure.[5] It was also concluded from molecular modeling calculations for gallium clusters using a universal force field (UFF) that a Ga_4O_6 cluster, such as the one shown in Figure 7, fits snugly inside the MFI zeolite channels and satisfies the requirement of coordination number 3 for the second coordination sphere of gallium atoms.[5]

With the present catalysts, no evidence was found for the formation of β-Ga_2O_3[14], and in order to simplify the problem, we assume that only binuclear and tetranuclear species exist in this catalyst. The fraction of the framework aluminum present as binuclear species in this catalyst may then be calculated from eq 4 below:

$$X_2 = (3 - N_{Ga})/2 \qquad (4)$$

If this is so, essentially half of the gallium in catalyst T4GaZ35 must be present in binuclear and the other half in tetranuclear oxidic form. Since the gallium to framework aluminum mole ratio is 1.02 in T4GaZ35, there will be ca. 0.25 binuclear species (0.51/2) and 0.13 tetranuclear species (0.51/4) per framework aluminum in this catalyst.

At the same time, from Table 4, the number of strong Lewis acid sites per framework aluminum is 0.23 and the decrease in Brønsted acidity due to proton exchange with gallium, again per framework aluminum, is 0.27 in this catalyst. Thus, as compared to T2GaZ35, the increase in Lewis acidity is 0.09 and the decrease in Brønsted acidity is 0.05. This is to be compared with a 0.06 increase in the amount of binuclear species (0.19 to 0.25) and a 0.13 increase in the amount of tetranuclear species (0 to 0.13). Therefore, the amount of tetranuclear species produced by increasing the gallium content would be in large excess compared to the decrease in Brønsted acidity. In its turn, the decrease in Brønsted acidity would be comparable to the estimated increase in the amount of binuclear species. Therefore, the tetranuclear species are probably uncharged, and all of the decrease in

Brønsted acidity would be due to the formation of charged binuclear species.

It is also seen that the increase in Lewis acidity due to the increase in gallium content is nearly twice the decrease in Brønsted acidity, but considerably smaller than the estimated amount of tetranuclear species produced. Furthermore, surely there must be an important contribution from the formation of new charged binuclear species to the increase in Lewis acidity, so the tetranuclear species cannot be solely responsible for the increase in Lewis acidity, if at all. The larger increase in Lewis acidity as compared to the decrease in Brønsted acidity could also be explained by a replacement of $Ga_2O_2^{2+}$ units by singly charged binuclear oxidic gallium species with the increase in gallium content, within the hypothesis that both doubly charged and singly charged binuclear species may act as one Lewis site each.

It should also be considered that the results of the present work (cf. Figure 6) strongly suggest that more condensed oxidic gallium species decompose to produce binuclear species at the early stages of the reduction. From the previous discussion, these binuclear species are probably neutral and with low Lewis acidity. This could explain the fact that we found an inverse correlation between the strong Lewis acidity and the degree of aggregation of the oxidic gallium species (as measured by the second sphere coordination number of the gallium in oxidized, atmosphere-equilibrated samples[14]). This might also explain the linear correlation observed between reducibility of the gallium and strong Lewis acidity,[14] since strong Lewis acid sites may be responsible for hydrogen dissociation during the reduction process.

We must also recall that one of the catalysts studied in ref 14 had a second sphere coordination number significantly smaller than 1, implying that monomeric oxidic gallium species may exist at low Ga/Al_{FW} ratios. This catalyst was also the one with the highest Lewis acidity per gallium atom and the highest reducibility. This means that monomeric gallium species, presumably gallyl ions (GaO^+) coordinated to exchange sites of the zeolite framework, may also act as strong Lewis acid sites.

The linearity of Figure 5 strongly suggests that the Ga^{3+} species in our catalysts are 4-fold coordinated to oxygen, irrespective of the degree of reduction that increases markedly with reduction temperature. At the same time, it was found that strong Lewis acid sites are generated upon evacuation at 673 K. Since, as already mentioned, the X-ray absorption spectra of fully oxidized catalysts were obtained with atmosphere-equilibrated samples, it is likely that the gallium species in these samples are hydrated or hydroxylated. Upon evacuation at 673 K, the gallium species in the atmosphere-equilibrated catalyst are likely to be dehydrated to produce coordinatively unsaturated gallium ions responsible for the Lewis acidity. Some likely possibilities for 4-fold-coordinated charged and uncharged binuclear gallium species and their dehydration products are shown in Figure 8. Dotted lines in this figure represent coordination of the gallium ions to oxide ions at the zeolite channel walls, and the aluminum ions belong to the zeolite framework. The dehydrated species in Figure 8c is the same $Ga_2O_2^{2+}$ unit proposed by Zhidomirov et al. to be mainly responsible for the strong Lewis acidity of Ga/HZSM5.[23] It should be noticed that all of the proposed species are 4-fold coordinated to oxygen, in agreement with the EXAFS data.
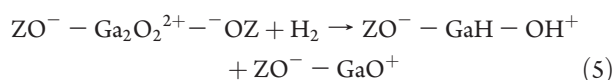
So a picture that is consistent with the body of our data envisages the existence of a range of binuclear oxidic gallium species with different charges, as shown in Figure 8. The Lewis acidity of these species is expected to increase with increasing charge. Their reducibility is then also expected to increase with
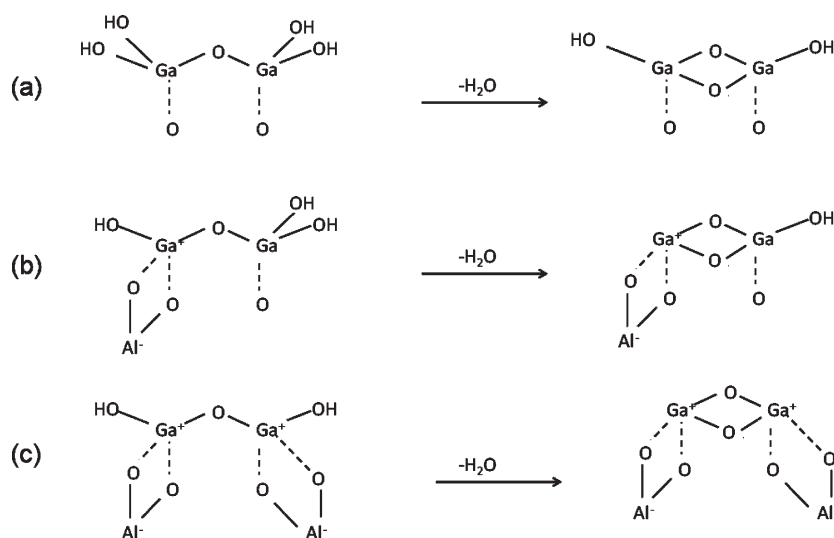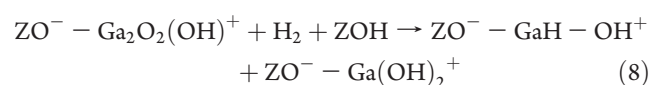
Figure 8. Possible (a) uncharged, (b) singly charged, and (c) doubly charged hydrated and dehydrated gallium binuclear species.

increasing charge, as strong Lewis acidity may be expected to favor hydrogen or propane dissociation at an acid−base pair. Some likely reactions to be occurring with doubly charged binuclear species are as follows, where ZO^- represents an ion exchange site at the zeolite framework:

$$ZO^- - Ga_2O_2{}^{2+} - {}^-OZ + H_2 \rightarrow ZO^- - GaH - OH^+$$
$$+ ZO^- - GaO^+ \qquad (5)$$

$$ZO^- - GaH - OH^+ \rightarrow ZO^- - Ga^+ + H_2O \qquad (6)$$

$$ZO^- - GaO^+ + H_2 \rightarrow ZO^- - Ga^+ + H_2O \qquad (7)$$

Reaction 7 may also occur with gallyl cations that exist in catalysts with low Ga/Al ratios. Reactions 5−7 may also involve propane instead of hydrogen, producing propene in addition to water.

Similar processes may be envisaged for singly charged species such as the ones depicted in Figure 8:

$$ZO^- - Ga_2O_2(OH)^+ + H_2 + ZOH \rightarrow ZO^- - GaH - OH^+$$
$$+ ZO^- - Ga(OH)_2{}^+ \qquad (8)$$

$$ZO^- - Ga(OH)_2{}^+ \rightarrow ZO^- - GaO^+ + H_2O \qquad (9)$$

Reactions 6 and 7 above would then complete the production of Ga^+ species.

It is observed from Figures 5 and 6 and Table 1 that, even by heating at 873 K, a significant portion of the gallium is not reduced. This more difficult to reduce fraction probably represents neutral binuclear species originally present in the catalysts or produced by decomposition of more condensed species. Reduction of these neutral species may involve the formation of volatile Ga_2O that has been long held responsible for the migration of gallium species from the external to the internal surface of zeolites:

$$Ga_2O_3 \cdot xH_2O + 2H_2 \rightarrow Ga_2O + (2+x)H_2O \qquad (10)$$

$$Ga_2O + 2ZOH \rightarrow 2ZO^- - Ga^+ + 2H_2O \qquad (11)$$
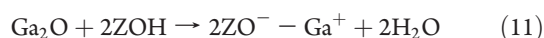
In eq 10, the $Ga_2O_3 \cdot xH_2O$ species is supposed to be a dehydrated or hydroxylated binuclear species with x between 0 and 2.

The nature and fate of the more condensed oxidic gallium species are less clear. This species is probably related to the neutral Ga_4O_6 cluster shown in Figure 7, but in the proposed structure gallium is 3-fold coordinated to oxygen, and for 4-fold coordination to be achieved, it would have to be assumed that each gallium atom in the cluster is coordinated either to a water molecule or to an oxygen atom of the zeolite framework. As pointed out by Zhidomirov et al.,[23] such a species is expected to have a Lewis acidity nearly as strong as that of the $Ga_2O_2{}^{2+}$ cluster, so it is presumably hydrated when equilibrated with the atmosphere and might decompose upon dehydration, either thermally or by reaction with water, hydrogen, or propane. The hydration water of the species itself or that produced by dehydration of other species could be the source of the hydrolysis reaction. Reduction with hydrogen or propane could lead to Ga_2O, which then generates Ga^+ species by reaction 11. However, it should be noticed from Figure 6 that already at 25% reduction of the gallium, the points pertaining to catalyst T4GaZ35 are close to the regression line, meaning that the condensed species have already been completely decomposed. Within the assumption used before that only tetranuclear and binuclear species are present in the oxide form of T4GaZ35, we concluded that about half of the gallium should be in the tetrameric species. Even if we consider that this reduction is partial, leading to Ga_2O and an oxidized dimeric species, 25% of the total gallium should be reduced to the +1 state when the tetranuclear species is completely consumed. This would mean that up to 25% reduction degree only the tetranuclear and none of the binuclear species would have been reduced in our catalyst, which appears rather unlikely. Therefore, if one hypothesis is to be favored, that would be that the decomposition of the tetranuclear species does not involve reduction. Many possible reactions may be envisaged, and the generic reaction 12 below is a reasonable possibility:

$$Ga_4O_6 + 2xH_2O \rightarrow 2Ga_2O_3 \cdot xH_2O \qquad (12)$$

Here, as before, $Ga_2O_3 \cdot xH_2O$ represents a dehydrated or hydroxylated binuclear oxidic gallium species with x between 0 and 2, and the Ga_4O_6 species could itself contain hydration water.

CONCLUSION

Comparison between gallium K edge XANES and EXAFS results showed that reduced gallium species, generally held responsible for aromatization activity in gallium modified ZSM5 catalysts, are indeed isolated gallium atoms (Ga^+) probably at zeolite ion exchange positions, bound to a framework oxygen atom ($Si-O-Al$). The fact that a linear correlation was found between the gallium second sphere coordination number and the Ga^{3+} content of all partially reduced catalyst, which extrapolates to a coordination number of 1 for 100% Ga^{3+}, strongly suggests that, at the early stages of the reduction, more condensed oxidic gallium species present in the completely oxidized catalysts are converted to binuclear species. Consideration of the changes in Brønsted and Lewis acidity of the zeolites upon gallium incorporation suggests that binuclear species with charges between 0 and +2 may be produced and the charged species are responsible for the strong Lewis acidity of the GaZSM5 catalysts. Perhaps on account of that fact, the charged species are more easily reduced than the neutral ones.

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