EXAFS studies on MFI-type gallosilicate molecular sieves

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EXAFS spectroscopy shows that gallium atoms incorporated into the framework of MFI-type ZSM-5 gallosilicates have a typical Ga–O bond length of 1.82 ± 0.01 Å corresponding to a tetrahedral coordination. Accordingly, the coordination number, N, was found to take the value $N = 4.2 \pm 0.3$. Template burning (at 773 K) causes little disturbance to the zeolite framework, and most of the gallium remains tetrahedrally coordinated. However, after a heat treatment at 923 K the apparent coordination number was found to decrease, as well as the corresponding Ga–O bond length. These results were interpreted in terms of formation of extra-framework gallium oxide species which appear to be EXAFS silent. The thermal stability of the gallosilicate framework was found to increase with increasing Si/Ga ratio.

Keywords: EXAFS spectroscopy, gallosilicate, molecular sieves, zeolites

1. Introduction

Zeolite frameworks are constructed from corner-sharing TO_4 tetrahedra, where T is Si or Al. Isomorphous substitution of the T atom by other tetrahedrally coordinated elements (e.g., Fe, Ga or Ti) provides a means to enhance catalytic behaviour of the zeolite in specific chemical processes. Interest in gallium-containing MFI-type zeolites stems from their high selectivity to aromatics in the catalytic conversion of olefins and paraffins following the so-called Cyclar process [1–6], and also from their high catalytic activity for vapour-phase conversion of phenol and ammonia mixtures into aniline [7]. There is evidence that enhanced aromatization on gallium-containing zeolites is the result of a bifunctional catalytic process involving both framework and extra-framework gallium atoms [8–11].

The gallosilicate GaZSM-5, which has the MFI-type structure, can be prepared by template-assisted hydrothermal synthesis [12,13]. Incorporation of gallium into the zeolite framework has been confirmed by means of powder X-ray diffraction, solid-state NMR and IR spectroscopy [13,14]. Template burning and subsequent thermal treatments can lead to partial disruption of the gallosilicate framework followed by migration of some gallium atoms into an extra-framework position, thus giving rise to a bifunctional catalyst. The aim of the present work is to analyse both incorporation of gallium into tetrahedral framework sites and partial de-galliation upon thermal treatments by means of EXAFS, which is a very powerful technique in this context. Parallel EXAFS studies on TiZSM-5 and FeZSM-5 have recently been reported [15–18].

2. Experimental

Three Na–GaZSM-5 zeolite samples having Si/Ga ratios of 25, 50 and 75 were prepared by template-assisted hydrothermal synthesis, using appropriate amounts of sodium silicate, gallium nitrate and tetrapropylammonium bromide solutions (Aldrich Chemicals, 99.99%). Thermal decomposition of the organic template was achieved by calcination at 773 K for 5 h, using at the end of the calcination period an oxygen flow to burn off traces of residual coke. Ionic exchange with a 1 M ammonium nitrate solution led to the ammonium forms of the zeolites, which were then thermolysed at 723 K to yield the corresponding protonic H–GaZSM-5 forms. The resulting materials were characterized by powder X-ray diffraction and IR spectroscopy, and found to be highly crystalline MFI-type gallosilicates. Details on synthesis and characterization were given elsewhere [14]. Samples will be hereafter designated GaZSM-5(x), where x denotes the Si/Al ratio. To investigate the effect of a high-temperature treatment, portions of each sample were heated in a dynamic vacuum (residual pressure smaller than 10^{-2} Pa) for 2 h at 923 K.

EXAFS studies (Ga K-edge X-ray absorption measurements) were performed [19] by using the synchrotron radiation of the EXAFS13 station at LURE (Orsay, France) which was equipped with a Si(111) double-crystal monochromator detuned to $1/2$ to avoid harmonics. The storage ring (DCI) was operated at 1.85 GeV and 315–250 mA. EXAFS measurements were carried out in the transmission mode, at 300 K, and with sampling steps of 2 eV and integration time of 2 s per point. Both incident and transmitted photon fluxes were measured using air-filled ionization chambers. Pressure inside the transmitted beam ionization chamber was adjusted so as to optimize the detector signal.

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Homogeneity of the samples was checked by radiographic methods. A specifically designed sample cell [18] connected to a vacuum line allowed to outgass the samples *in situ*, to a residual pressure of 10^{-3} Pa, before EXAFS measurements.

For each sample three spectra were recorded (under the same experimental conditions) and the corresponding $\chi(k)$ functions were averaged before EXAFS data analysis, which was carried out using computer software developed by Michalowicz [20] and following standard procedures [21]. For extracting the experimental $\chi(k)$ values, a linear background fitting the pre-edge region was extrapolated to the higher energy region and subtracted from absorption data. Atomic-like contributions were estimated by a polynomial fit (fifth degree) and subtracted from experimental data following Lengeler and Eisenberger [22]; the result was normalized to edge height.

The most stable phase of gallium oxide, β-Ga_2O_3, has a complex structure [23] where Ga^{3+} ions occupy the centre of both distorted tetrahedra and distorted octahedra, and there are three non-equivalent anion sites. Therefore, experimental phase and amplitude values extracted from β-Ga_2O_3 cannot be directly used to fit the first coordination shell of gallium atoms in the gallosilicate. For this reason, we used the phase and amplitude functions derived according to McKale et al. [24], after checking them on the spectrum of β-Ga_2O_3. This check, shown in figure 1, was performed by simulating an average first coordination shell of Ga in β-Ga_2O_3 as composed of two sub-shells having coordination numbers and average Ga–O distances fixed to the corresponding crystallographic values, and by fitting two energy shift parameters, ΔE_1 and ΔE_2, two Debye–Waller factors, σ_1 and σ_2, and the mean free path parameter, γ, of the photoelectron. The value of γ thus obtained was used as a fixed parameter to fit the spectra of all gallosilicate samples using McKale's theoretical phases and amplitudes. Note that, in order to limit the number of fitting parameters, grouping of bond distances is usually done for EXAFS studies of materials exhibiting sub-shell splitting [25].

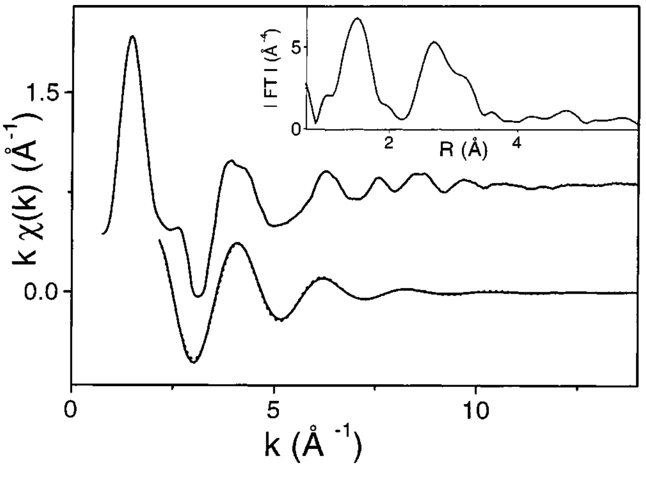

Figure 1. EXAFS results for β-Ga_2O_3. Upper curve: experimental data. Lower curves: first-shell fit obtained using McKale's functions (the dashed line represents the experimental data and the full line is the simulated spectrum). Inset shows the k^3-weighted Fourier transform radial function (no phase correction was applied).

3. Results and discussion

Figure 2 shows the raw experimental $k\chi(k)$ data for all gallosilicate samples. Corresponding k^3-weighted Fourier transform data, in the range 4.0–14.6 Å^{-1}, are reported in figure 3. First-shell contributions to the EXAFS spectra were back-FT transformed into k-space (1.0–1.8 Å range) and modelled as Ga–O contributions using McKale phases, as described in section 2, the fits thus obtained are shown in figure 4. Quantitative first-shell data obtained from these EXAFS fits are summarized in table 1.

The samples still containing the organic template give a gallium coordination number $N = 4.2 \pm 0.3$ and a Ga–O bond length of 1.82 ± 0.01 Å. These results indicate tetrahedral coordination of gallium atoms and consequent incorporation into the zeolite framework, which is in agree-

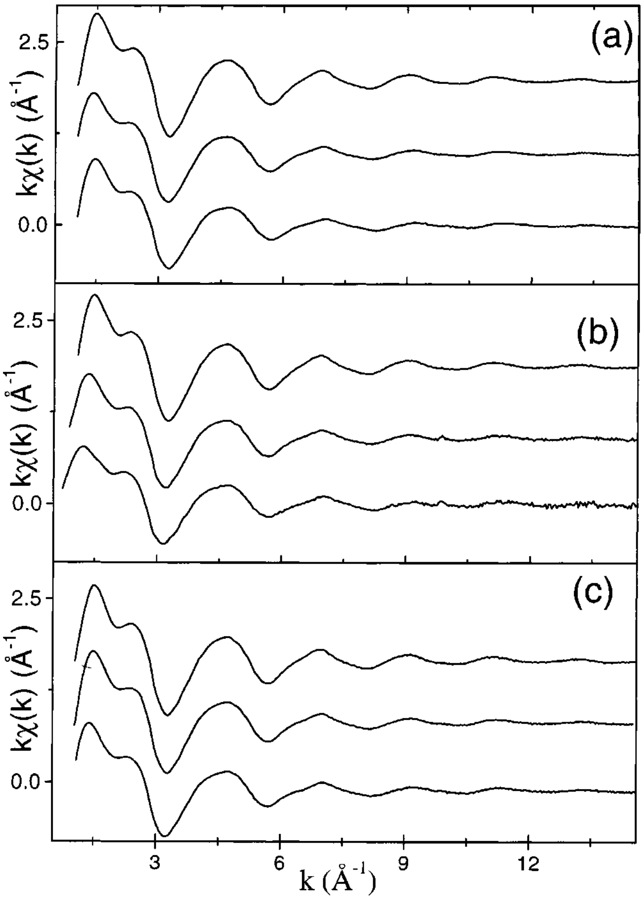

Figure 2. Experimental $k\chi(k)$ data averaged over three spectra for each sample. (a) GaZSM-5(25), (b) GaZSM-5(50) and (c) GaZSM-5(75). In each of the three sets the upper spectrum corresponds to the samples having the template agent, the middle spectrum was obtained after template removal at 773 K, and the lower spectrum after heating the sample at 923 K.

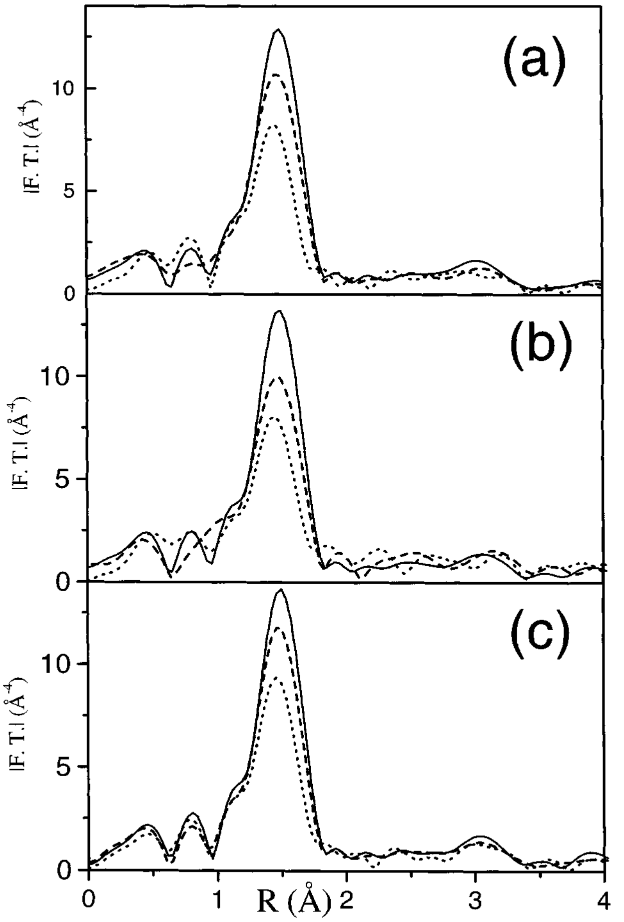

Figure 3. The k^3-weighted Fourier transform of the EXAFS functions reported in figure 2. No phase correction was applied. Sets (a), (b) and (c) as in figure 2. Full lines: samples containing the template agent. Dashed lines: after template burning at 773 K. Dotted lines after heating at 923 K.

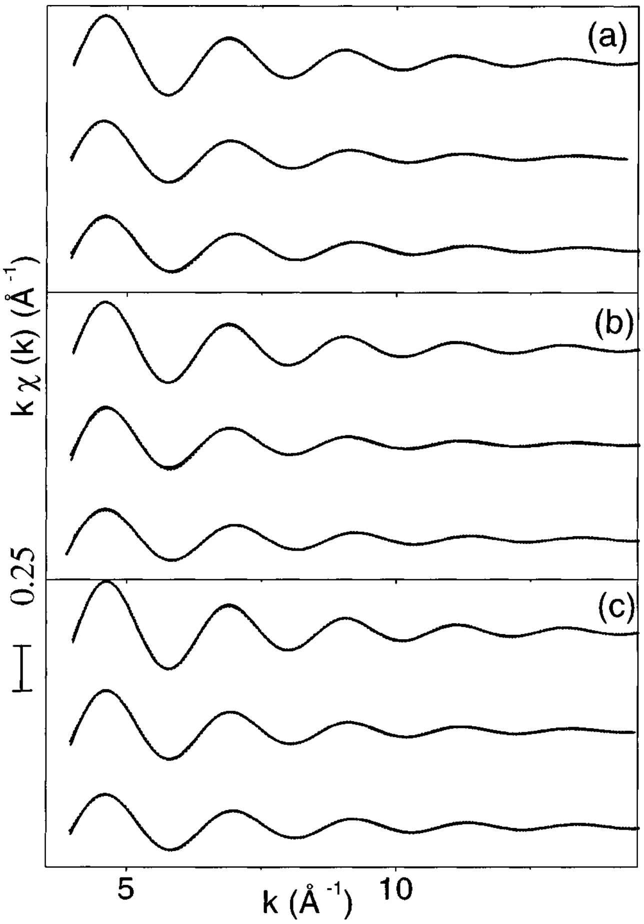

Figure 4. Back-FT of the radial distribution functions reported in figure 3, filtered over the first coordination shell (dashed lines). Full lines represent the fits obtained using McKale's functions. Sets (a), (b) and (c) as in figure 2.

Table 1
Gallium coordination number (N), Ga–O bond length (R), Debye–Waller parameter (σ) and energy shift of the Ga K-edge (ΔE) for the different gallosilicate samples.

Sample	Treatment[a]	N	R (Å)	σ ($\times 10^{-2}$ Å)	ΔE (eV)
GaZSM-5(25)	1	4.2 ± 0.3	1.82 ± 0.01	5 ± 1	10 ± 2
	2	3.4 ± 0.3	1.80 ± 0.01	6 ± 1	8 ± 2
	3	2.5 ± 0.3	1.78 ± 0.02	5 ± 2	8 ± 2
GaZSM-5(50)	1	4.2 ± 0.3	1.82 ± 0.01	5 ± 1	10 ± 2
	2	3.6 ± 0.3	1.81 ± 0.01	7 ± 1	8 ± 2
	3	2.6 ± 0.3	1.77 ± 0.02	6 ± 2	10 ± 2
GaZSM-5(75)	1	4.2 ± 0.3	1.82 ± 0.01	5 ± 1	10 ± 2
	2	3.9 ± 0.3	1.80 ± 0.01	6 ± 1	10 ± 2
	3	2.9 ± 0.3	1.78 ± 0.02	5 ± 2	8 ± 2

[a] 1 – as prepared (containing the template), 2 – after template burning at 773 K and 3 – after heating *in vacuo* for 2 h at 923 K.

ment with previous results from X-ray diffraction [14], ^{71}Ga MAS NMR [26,27] and IR spectroscopy [14]. Note that in β-Ga_2O_3 gallium atoms situated at (distorted) tetrahedral sites are surrounded by one oxygen atom at 1.80 Å, two at 1.83 Å and a fourth one at 1.85 Å; this gives an average Ga–O bond distance of 1.83 Å [23] which coincides (within experimental error) with our result of 1.82 ± 0.01 Å. For octahedrally coordinated gallium atoms in β-Ga_2O_3 the average Ga–O bond length is 2.00 Å [23]. A previous EXAFS report on GaZSM-5 [28] gives 1.78 ± 0.01 Å for the Ga–O bond length and $N = 4.6$ for the coordination number of gallium.

Template burning, at 773 K, causes a slight decrease of both the Ga–O bond length and the gallium coordination number (table 1). This behaviour can be interpreted as an indication that a small fraction of gallium atoms have migrated into extra-framework positions (see below). Note that for GaZSM-5(75) the gallium coordination number remains at $N = 3.9$ (very close to 4.2 in the sample before template burning), while for GaZSM-5(50) and GaZSM-5(25) corresponding values are $N = 3.6$ and 3.4, respectively (table 1). This is in agreement with previous IR work [14] which showed that thermal stability of gallosilicates increases with increasing Si/Ga ratio.

Samples heat-treated at 923 K show a further decrease of both gallium coordination number and Ga–O bond length. The low coordination numbers observed, $N = 2.5$–2.9, can be explained in terms of formation of extra-framework gallium oxide species having a large heterogeneity of environments around the gallium atoms. This structural disorder would lead to a large contribution of the static component to the Debye–Waller factor and attendant incoherent EXAFS signals [29–31]. Therefore, the observed EXAFS oscillations are due exclusively to the fraction of gallium atoms remaining (tetrahedrally coordinated) in the gallosilicate framework, and the derived values of coordination number are anomalously low because of the presence of silent gallium atoms which form heterogeneous extra-framework aggregates. Note that these gallium atoms do contribute to the edge jump in the measured μx spectrum to which the corresponding $\chi(k)$ function was normalized (see section 2). In conclusion, gallium coordination numbers significantly lower than $N = 4$, as obtained for samples treated at 923 K, have to be interpreted as a clear indication of formation of extra-framework species containing gallium. In agreement with our EXAFS results, Bayense et al. [26] reported a ^{71}Ga MAS NMR study showing that a large fraction of gallium is removed from the framework of MFI-type gallosilicates upon steaming at 923 K. More recent IR spectroscopic studies [14] also proved the same behaviour of GaZSM-5 molecular sieves.

Finally, the apparent shortening of the Ga–O bond length in the samples treated at 923 K (table 1) can also be explained in terms of structural disorder of extra-framework gallium oxide species. The effect of a large disorder is equivalent to a system having an asymmetrical radial distribution function, which can lead to an apparent contraction of bond length in the usual analysis of EXAFS data [32,33].

4. Conclusions

In agreement with previous reports, our EXAFS studies show that by means of hydrothermal synthesis, using gels of appropriate chemical composition, Ga^{3+} ions can be incorporated (at regular tetrahedral sites) into the framework of MFI-type silicates. The gallosilicates thus obtained are not much disturbed by template burning at 773 K; most of the gallium present remains in the framework. However, further heating at 923 K (*in vacuo*) causes removal of a substantial part of the framework gallium, with concomitant formation of extra-framework gallium oxide particles. These small particles appear to have a high degree of structural disorder, which leads to incoherent EXAFS signals. Extra-framework gallium is indirectly detected by EXAFS; its presence is reflected in the anomalously low values of the coordination number and Ga–O bond length obtained for gallium atoms remaining in the zeolite framework.

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