

## Synthesis and Spectroscopic Characterization of Cr<sup>III</sup> in Crystalline Zeolitic Silicates

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The incorporation of Cr<sup>III</sup> into the framework of high content silica zeolite is confirmed by electron spin resonance and photoacoustic spectroscopies.

The newest effort in the chemistry of zeolites is the synthesis, characterization, and applications of materials where aluminium or silicon in the conventional lattice are completely or partially replaced isomorphously by other elements which assume tetrahedral co-ordination.

Isomorphous substitution of elements such as germanium,<sup>1</sup> phosphorus,<sup>2</sup> boron,<sup>3</sup> and gallium<sup>4</sup> for silicon or aluminium in zeolite frameworks has been reported. Germanium, phosphorus, and gallium, which have ionic radii close to those of Si<sup>4+</sup> and Al<sup>3+</sup>, are expected to replace the latter ions in the zeolite lattice. However, the incorporation of transition metal ions into the zeolite framework is more difficult owing to their differences in ionic radii to silicon and aluminium. Recently pentasil-type zeolites with iron substituted at silicon sites have been unambiguously characterized.<sup>5–10</sup> Here, we report on the synthesis and characterization of pentasil-type zeolites with chromium substituted at silicon sites in the lattice. Our samples have been studied by electron spin resonance (ESR,  $\nu = 9.53$  GHz) and photoacoustic spectroscopy (PAS), which reveal direct information on the state of the chromium atoms in the lattice.

Initially we tried conventional procedures for the synthesis of ZSM-5 zeolites,<sup>11</sup> changing the aluminium source for a chromium one. The green powder obtained showed, in the IR and X-ray diffraction spectra, the presence of a highly crystalline zeolitic structure. The Cr<sup>III</sup> ESR spectrum of this

sample [Figure 1(a)] consisted of a single symmetric line, centred at  $g = 2$ . This spectrum is attributed to Cr<sup>III</sup> ions outside the silicon skeleton, probably linked to oxygen atoms to form oxides similar to Cr<sub>2</sub>O<sub>3</sub>. After changes in the experimental procedure, e.g., changing the reactants molar ratios [SiO<sub>2</sub>, 0.005; Cr<sub>2</sub>O<sub>3</sub>, 0.04 (TPA)<sub>2</sub>O (TPA = tetrapropylammonium)], and lowering the pH (6.0–6.8), we obtained a very light-green powder, highly crystalline as judged by X-ray diffraction analysis. The elemental analysis of the as-synthesized sample showed the presence of aluminium (0.61%, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 228), iron (0.05%, SiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> = 4650), and chromium (0.41%, SiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> = 540). Figure 1(b) shows the ESR spectrum of this sample. The spectrum shows a distribution of resonances which includes high  $g$  values. These resonances are associated with Cr<sup>III</sup> in cubic symmetry (octahedral or tetrahedral co-ordination), probably with low symmetry distortions in the silicon substitutional positions. The line with  $g = 4.3$  is due to iron(III), an impurity that came through the silicon source. Washing this silicate three times with dilute hydrochloric acid caused no change to the ESR spectrum.

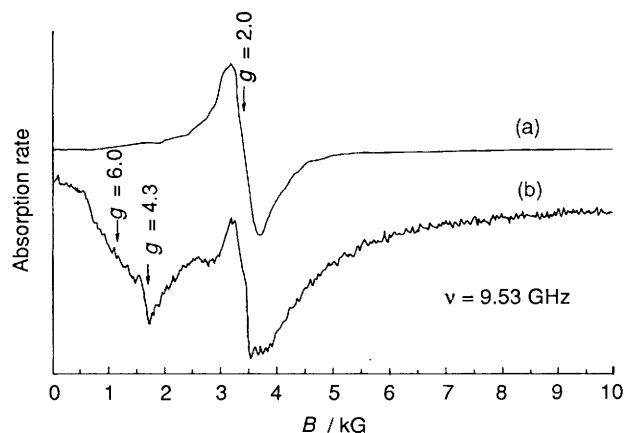
The optical absorption measurements were carried out at room temperature in the wavelength range 300–700 nm using an EDT model OAS-400 photoacoustic spectrometer.<sup>12,13</sup> The spectrum for the Cr<sup>III</sup> in the zeolitic silicate shown in Figure 2 is characterized by two bands centred at 440 and 640 nm. For the level assignment<sup>14</sup> the band observed at 440 nm is identified as the  $^4\Gamma_2 \rightarrow ^4\Gamma_4$  (F), and the band at 640 nm is interpreted as the  $^4\Gamma_2 \rightarrow ^4\Gamma_5$  transition. The resulting energy-level values are given in Table 1.

The values obtained for Cr<sup>III</sup> in this silicate are comparable with reported values for Cr<sup>III</sup> in soda-lime silica glass.<sup>15</sup> After washing the sample showed the same PAS spectrum.

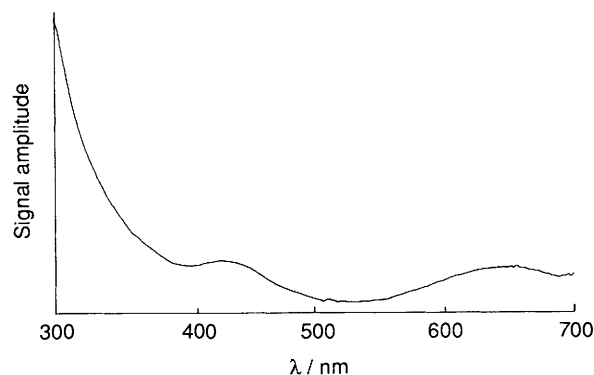
Although previous reports have appeared in the literature,<sup>16,17</sup> the ESR and PAS spectra shown in this communication give unambiguous evidence that Cr<sup>III</sup> is present in substitutional sites, co-incorporated with aluminium in the zeolite, for the first time. Complementary work including OH-IR spectroscopy is now in progress.

**Table 1.** Calculated and measured energy levels (nm) for Cr<sup>III</sup>.

Transition	$^4\Gamma_2 \rightarrow ^4\Gamma_4$	$^4\Gamma_2 \rightarrow ^4\Gamma_5$
Calculated	448	650
Experimental	440	640



**Figure 1.** ESR spectra of Cr<sup>III</sup> in chromium silicate, (a) in cationic positions only, (b) in silicon substitutional sites and in cationic sites.  $1G = 10^{-4}$  T.



**Figure 2.** Photoacoustic spectra of Cr<sup>III</sup> in chromium silicate at a modulation frequency of 10 Hz.

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