Synthesis and Characterization of Chromium Silicalite

José Silvio T. Mambrim,† Heloise O. Pastore,*,† Celso U. Davanzo,† Eduardo J. S. Vichi,*,† Osamu Nakamura,†,‡ and Helion Vargas†

Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, Barão Geraldo, 18081-970 Campinas S.P., Brazil, and Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, C.P. 6155, Barão Geraldo, 18081-970 Campinas S.P., Brazil

Received February 20, 1992. Revised Manuscript Received October 12, 1992

Infrared spectroscopy (mid-IR), 29Si and 27Al magic angle spinning nuclear magnetic resonance (MAS-NMR), powder X-ray diffraction (PXRD), electron paramagnetic resonance (EPR), and photoacoustic spectroscopy (PAS), in combination, have produced useful information about a series of crystalline MFI-type chromium silicalite, synthesized in a fluoride medium. Aluminum is an impurity and occupies framework sites, as evaluated by the 27Al MAS-NMR. The mid-IR spectra are very similar to the zeolite ZSM-5 with the addition of a weak band at ~680 cm⁻¹, which we tentatively assign to symmetric stretching of (Cr–O–Si)₅ groups. The samples are crystalline materials and have expanded unit cells, as PXRD measurements pointed out. The as-synthesized sample shows a distribution of Cr sites, detected by EPR, comprising structure and channel occlusion sites; the nonstructural sites being extensively oxidized to Cr(VI) species after calcination in the presence of dioxygen. The changes in the photoacoustically measured physical properties, such as nonradiative relaxation time, the thermal diffusivity and optical absorption coefficient of both calcined and noncalcined chromium silicalite samples are also reported.

Introduction

Zeolitic materials (zeolite-based molecular sieves) containing elements other than aluminum or silicon in the conventional lattice have received increasing attention in recent years,† owing to the possibilities offered by the presence of a heteroelement in the structure. From the catalytic point of view, incorporation of elements other than aluminum in the structure is important since the metallosilicate might have its properties fine-tuned for the selective production of desired compounds.‡ Among the characteristics that determine the selectivity, the structure and dimensions of the system of pores and channels§ (shape selectivity), the Bronsted acidity of sites¶ (quimioselectivity), and the generalised effects arising from differences in the electronegativities of the elements in the structure¶ are the most important. It is well-known that the ZSM-5 structure, with three-dimensional porous network is outstandingly effective in converting methanol to high-octane gasoline.† The final mixture is rich in paraffins and aromatics but very poor in olefins.‡ Incorporation of metal atoms other than aluminum can improve dramatically the selectivity of the molecular sieve toward conversion of methanol to olefins.†,‡,§ This selectivity increasing as the Bronsted sites become less acidic.¶ However, the difficulties in determining the amount of metal incorporated, the thermal stability of the metal in the structure and the difficulty in removing the occluded metallic compounds limit the possibilities of application of these materials in an industrial level.

In this paper, the synthesis, in neutral fluoride medium, of chromium silicalites with MFI structure is described. The products were characterized by chemical analysis, powder X-ray diffraction, infrared spectroscopy, and magic angle spinning nuclear magnetic resonance. The distribution of chromium and its oxidation state were determined by X-ray fluorescence (XRF). The selectivity was studied by gas chromatography (GC) and the physical properties were measured by IR spectroscopy and photoacoustic spectroscopy.


† Instituto de Química.
‡ Instituto de Física Gleb Wataghin.
§ On leave of absence from Instituto de Física, Universidade Federal de Campinas, 20121 Salvador BA, Brasil.

0897-4756/93/2805-0166$04.00/0 © 1993 American Chemical Society
bution and nature of each Cr(III) site in the material, the metal atom redox characteristics as well as its optical, thermal, and magnetic properties were examined using electron paramagnetic resonance and photoacoustic spectroscopy. Preliminary accounts of this work were published previously.12,13

**Experimental Section**

**Synthesis.** A mixture of sodium silicate (Riedel de-Haen: 65% SiO₂, 18% Na₂O, and 18% water), ammonium fluoride, chromium nitrate 9-hydrate, and water, in that order, was prepared in the ratio 0.1 (3.5372 g):0.05 (1.8169) 0.002 (0.6293 g):6.0 (108.09 g), for the synthesis of a sample with SiO₂/Cr₂O₃ ratio of 100 in the initial mixture. The pH was adjusted to 6.5-7.0 with 48 vol % HF. After 2 h of stirring, tetrapropylammonium bromide was added in a 40-mL aqueous solution. The suspension was left to age for 24 h, at 348-353 K, under ambient pressure. The hydrothermal treatment was performed at 443-448 K for 15 days. The crystallized chromium silicalite was then filtered, extensively washed with distilled water until neutral pH, and air-dried. The samples were kept in a desiccator over saturated MgCl₂ solution before the measurements. For ion exchanges the following procedure was used: 1 g of the metallosilicalite was slurried in 12.5 mL of a 0.1 M HCl aqueous solution. After 24 h, the samples were washed with distilled water until neutral pH and then air-dried. Samples were commonly calcined in an open furnace, at 693 K, unless otherwise specified.

**Elemental Analysis.** The silicalites were analyzed for their Si, Al, Cr, Fe, and Na content by atomic absorption after the sample was dissolved in HCl or melts with sodium carbonate. The results obtained by both methods agree within 0.01 % error and are presented in Table I.

**Scanning Electron Microscopy (SEM).** Samples were dispersed over ordinary double-sided tape, glued to the microscope sample holder, and coated with gold. The accelerating voltage was 25 kV, and the image was obtained from secondary electrons. The scanning microscope was a JEOL Model JSM-T300.

**Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR).** These were collected for ⁵⁷Co and ⁵¹V in a Bruker AC300/P with Kel-F rotors, using TMS and an acidic [Al(H₂O)₆]³⁺ solution as references, respectively. The frequencies were 59.628 (Si) and 78.260 MHz (Al), and 1100 (Si) and 40 000 (Al) scans were accumulated. The spinning rate was typically 4500 Hz.

**Powder X-ray Diffraction (PXRD).** The chromium silicalites were analyzed with a Shimadzu diffractometer, Model XD3A (30 kV, 20 mA, 20 2° min⁻¹) using Cu Kα radiation. The samples were highly crystalline phase-pure ZSM-5 molecular sieves. They present orthorhombic symmetry when as-synthesized and an orthorhombic-to-monoclinic phase transition upon calcination at 693 K. This phase transition is expected for these SiO₂/T₂O₃ ratios, where T is the general nomenclature for atoms in the framework of zeolites or zeolithic metallosilicates. For the determination of unit cell volumes, the diffractogram was scanned at 2θ 1° min⁻¹. The (012), (031), (−103), (033), (501), (303), (133), (432), (352), (100), (010), and (0 10) reflections were used to calculate the unit cell volumes for monoclinic samples, while (020), (102), (501), (151), (303), (133), (432), (352), (10 0), and (0 10) were used for orthorhombic ones.

**Infrared Spectroscopy (MID-IR).** Potassium bromide pellets (0.5 wt %) were measured in a Jasco IR 700 spectrophotometer, the ratio of 550 to 450 cm⁻¹ optical densities for as-synthesized (AS) and calcined (C) samples are listed in Table II.

**Electron Paramagnetic Resonance (EPR).** Spectra were obtained using a Varian E-12 spectrometer operating at 9.5 GHz (X-band). The g values of the samples were obtained with reference to a standard mark: diphenylpycrilhydrazine (DPPH), g value 2.0036. The spectra were recorded on samples at the liquid nitrogen (77 K) and at room temperature (300 K).

**Photoacoustic Spectroscopy (PAS).** 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. The thermal properties, the non-radiative relaxation time and the optical absorption coefficients were measured by using instrumentation and techniques described previously.14–16

**Computational Fittings.** The ESR experimental data are fitted to theoretical expressions using an IBM 3090 computer. The expressions used are composed of the superposition of symmetrical line shapes with powder pattern line shapes. The routines used for the fittings are those of Bevington.17

**Results and Discussion**

**Synthesis.** Among the several factors involved in the preparation of metallosilicates, the form in which the trivalent cation is introduced in the synthesis mixture seems to be one of the most critical. In basic medium, where most of the zeolitic alumino-silicates are prepared,18,19 the incorporation of other metals is made difficult owing to formation of less-soluble hydroxido compounds, as in the case of zeolites.

**Table I. Elemental Analysis (wt %) of As-Synthesized (AS) and Ionic Exchanged (IE) Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>SiO₂/Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-100 (AS)</td>
<td>white</td>
<td>81.60</td>
<td>1.00</td>
<td>0.90</td>
<td>0.02</td>
<td>2.41</td>
<td>743</td>
</tr>
<tr>
<td>Cr-50 (AS)</td>
<td>light</td>
<td>82.40</td>
<td>0.64</td>
<td>1.70</td>
<td>&lt;0.01</td>
<td>2.28</td>
<td>492</td>
</tr>
<tr>
<td>Cr-30 (AS)</td>
<td>green</td>
<td>81.30</td>
<td>0.98</td>
<td>1.25</td>
<td>0.04</td>
<td>2.19</td>
<td>165</td>
</tr>
<tr>
<td>Cr-100 (IE)</td>
<td>white</td>
<td>84.5</td>
<td>0.08</td>
<td>0.01</td>
<td>0.04</td>
<td>0.04</td>
<td>20 000</td>
</tr>
<tr>
<td>Cr-30 (IE)</td>
<td>very light green</td>
<td>82.4</td>
<td>0.19</td>
<td>0.79</td>
<td>&lt;0.01</td>
<td>0.07</td>
<td>264</td>
</tr>
</tbody>
</table>

* Cr-100 is a chromium silicalite sample whose SiO₂/Cr₂O₃ ratio in the reactional mixture is 100. The same for Cr-50 and Cr-30. AS = as-synthesized. IE = ion exchanged.

**Table II. Optical Densities Ratios for the Bands at 550 and 450 cm⁻¹, for As-Synthesized (AS) and Calcined (C) Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>AS</th>
<th>C</th>
<th>C</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-100</td>
<td>0.75 0.81</td>
<td>793</td>
<td>796</td>
<td>690 689</td>
</tr>
<tr>
<td>Cr-50</td>
<td>0.79 0.79</td>
<td>788</td>
<td>799</td>
<td>695 691</td>
</tr>
<tr>
<td>Cr-30</td>
<td>0.38 0.38</td>
<td>795</td>
<td>798</td>
<td>695 680</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>AS</th>
<th>C</th>
<th>C</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-100</td>
<td>795 799</td>
<td>793</td>
<td>796</td>
<td>690 689</td>
</tr>
<tr>
<td>Cr-50</td>
<td>788 799</td>
<td>788</td>
<td>799</td>
<td>695 691</td>
</tr>
<tr>
<td>Cr-30</td>
<td>795 798</td>
<td>795</td>
<td>796</td>
<td>695 680</td>
</tr>
</tbody>
</table>

case of iron, or those that do not polycondensate easily as in the case of germanium.\textsuperscript{20} In fluoride medium, the pH can be lowered, and less supersaturated reaction mixtures are formed compared to in an alkaline medium,\textsuperscript{21} leading to less metastable phases which produce more well-formed crystals. The key point is the formation of soluble metal fluoro complexes which are labile enough to provide a more well-controlled nucleation of the zeolite precursors. For different metal incorporation a compromise between pH and F\textsuperscript{-} concentration has to be reached, to optimize the synthesis, due to differences in the stability-lability of the different fluoro complexes. In the chromium silicate synthesis described in this paper, higher ageing times and higher temperatures are required compared to the used for other metallosilicates.\textsuperscript{22} Several pH and F\textsuperscript{-} concentrations were checked before using those described in the synthetic procedure, which allowed some but not varied incorporation. The selection of the template used to direct the construction of the skeletal structure is another critical point since a variety of phases can be produced depending on the nature of the template. The tetrapropylammonium bromide salt used in the synthesis of the chromium silicate described here seems to be the more selective template to direct the construction of MFI-type structures.\textsuperscript{21}

**Chemical Composition and Crystal Morphology.** Apart from the presence of chromium in the samples, the results of the elemental analysis displayed in Table I show that Al\textsubscript{2}O\textsubscript{3} is incorporated in the chromium silicate samples as an impurity, probably coming from the Si source. The location of Al(III) ions in the tetrahedral framework sites is indicated by the\textsuperscript{27}Al MAS-NMR spectra which show a single and characteristic peak at 52.3 ppm.\textsuperscript{23} The presence of Si(OAl) groups in high-silica ZSM-5 structures is confirmed by a peak at -112 ppm in the\textsuperscript{29}Si MAS-NMR spectra.\textsuperscript{23} This peak has shoulders in either higher or lower fields depending on the sample measured, resembling the positions where a high-resolution spectrum would show resolved peaks.\textsuperscript{23} However, due to the high SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio, none of the shoulders at lower field is in the region expected for Si(1Al).\textsuperscript{23} The crystals are rather elongated with sizes varying from 15 to 55 \(\mu\text{m}\) on the longer dimension by 14-\(\mu\text{m}\) width (Figure 1). In Figure 1b it is possible to observe noncrystallized material adhering to the crystal surface and some extent of intergrowth. Treatment with aqueous HCl was inefficient in dissolving this extraneous material. All the samples are homogene ous, i.e., the crystals present the same morphology from one synthesis batch to another and approximately the same dimensions within the same batch.

**Structural Characterization. Unit Cell Expansion.** The co-incorporation of aluminum and chromium in the silicate framework is expected to cause a unit cell expansion to an extent proportional to the quantity of these T atoms per silicate unit cell. Assuming that the T-O-T bond angles do not change with the incorporation of these T\textsuperscript{3+} atoms per Si framework\textsuperscript{24} the unit cell expansion can be calculated using eq 1, where \(V_{\text{Si}}\) is

\[
V_{\text{X}} = V_{\text{Si}} - xV_{\text{Si}}[1 - \left(\frac{d_{\text{Al-O}}}{d_{\text{Si-O}}}\right)^3]
\]

the unit cell volume when \(T = \text{Si}\) only (5298 \(\text{Å}^3\) according to ref 25); \(V_{\text{X}}\) is the unit cell volume of the same lattice where a molar fraction, \(x\), of Si atoms has been replaced by Al atoms; and \(d_{\text{Al-O}}\) and \(d_{\text{Si-O}}\) are the related bond distances (1.71 \(\text{Å}\) and 1.61 \(\text{Å}\), respectively). Table III lists the expected unit cell expansion due to Al incorporation only, along with the PXRD-measured cell volume for as-synthesized, \(V_{\text{AS}}\), and calcined, \(V_{\text{C}}\), chromium silicates. It is clear that for samples Cr-30 and Cr-50, \(V_{\text{AS}}\) is higher, within deviation, than \(V_{\text{C}}\). For sample Cr-100, however, we cannot be sure about chromium(III) incorporation since the expansion might be due solely to aluminum substitution. The same applies to calcined samples: Cr-30 and Cr-50 still have a unit cell volume higher than \(V_{\text{X}}\). The unit cell volume variations are within the range 50–200 \(\text{Å}^3\) in excess of the volume


the length of Cr-O bond in a perfect or distorted silicalite framework, reported in the literature. Since Table I and provide further evidence for the high unit cell expansion obtained here for the chromium materials. After Vedrine et al., a ratio the Cr(II) in the silicalite framework. and those related to the vibrations of the skeleton formed by the tridimensional bonding of those tetrahedra. In zeolites with pentasil structure the bands at absorptions are observed in the IR spectra of zeolites; those vibrations of the secondary building units can be related to the internal vibrations of the TO4 tetrahedron, which include resonances at high temperature, and (c) calcined for 24 h at 693 K.

calculated taking into account the aluminum incorporation only. This is in agreement with values for the unit cell expansion caused by the incorporation of boron, gallium, germanium, and titanium into the silicalite framework, reported in the literature. Since the length of Cr-O bond in a perfect or distorted tetrahedral symmetry is not yet known, the values for unit cell expansion obtained here for the chromium silicalites cannot be discussed further, except that they provide some evidence for the incorporation of some of the Cr(III) in the silicalite framework.

Crystallography of the Material and Skeletal Vibrations. IR spectroscopy has been widely used as a technique for the identification of zeolites. Two types of characteristic absorptions are observed in the IR spectra of zeolites; those related to the internal vibrations of the TO4 tetrahedron, and those related to the vibrations of the skeleton formed by the tridimensional bonding of those tetrahedra. In zeolites with pentasil structure the bands at 450 cm⁻¹, assigned to the internal vibrations of the tetrahedra TO4 (T = Si, Al) and the band at 550 cm⁻¹, assigned to the vibrations of the secondary building units CT⁻T; can be used to evaluate the degree of crystallinity of these materials. After Vedrine et al., a ratio A550/A450 ≥ 0.72 has been widely used as a criterion for high crystallinity of ZSM-5 type zeolites. The A550/A450 values obtained for the chromium silicalite prepared in this work are shown in Table II and provide further evidence for the high crystallinity of these materials. The mid-IR spectra of Cr-100 samples, shown in Figure 2, may also provide some evidence for the incorporation of a small amount of Cr(III) in the silicalite framework. The difference in atomic mass of Si(IV) and Cr(III) in the skeleton is enough to pinpoint contributions of (Si-O-Cr) vibrations to the IR spectra. The bands around 795 cm⁻¹ in Figure 2 are assigned to the symmetric stretching of the (Si-O-Si)n group; the very weak bands around 690 cm⁻¹ are tentatively assigned to the symmetric stretching of the (Si-O-Cr)n group, due to the incorporation of a very small amount of Cr(III) in the framework. These bands are still present in the spectrum after calcination of the material. The frequencies obtained for the samples studied are in Table II. The broadening in the lower wavenumber side of the (Si-O-Si)n of the as-synthesized sample which could be due to asymmetric vibration of the (Si-O-Cr)n groups disappear after calcination. Therefore it may be assigned to Si-F and Si-OH, which are expected to show bands in this region. These may condense and be annealed by calcination.

Distribution of the Cr(III) Species in Chromium Silicalite. The EPR study of the materials shows that the Cr(III) ions are distributed in the solid occupying at least three different sites. The assignment of the sites was made by comparing the EPR spectra of pure silicalite and chromium silicalite samples. Figure 3 shows the effect of temperature and calcination on the spectrum of a pure silicalite sample prepared by the same procedure used for the chromium silicalite, without the Cr(III) source. It contains, therefore, nearly the same amount of Fe(III) and Al(III) found in the chromium silicalite. The as-synthesized sample spectra at 300 and 77 K show a broad peak centered at g = 2.0, superimposed with a sharp signal at g = 1.97 (Figures 3a,b). Calcination at 843 K causes a drastic decrease in the intensity of these signals (Figure 3c), suggesting that the signal at g = 1.97 is probably due to radicals formed during the synthesis or sample workup. The sharp and weak peak at g = 4.27, due to Fe(III) impurities, is not affected by calcination. The spectra of a Cr-30 chromium silicalite sample, at 300 and 77 K, shown in Figure 4, which include resonances at high g values, are interpreted after performing a deconvolution considering the contributions of the symmetrical line centered at g ≈ 2.0, the background silicalite spectra, and two powder patterns. The values obtained for the samples studied are in Table II. The broadening in the lower wavenumber side of the (Si-O-Si)n of the as-synthesized sample which could be due to asymmetric vibration of the (Si-O-Cr)n groups disappear after calcination. Therefore it may be assigned to Si-F and Si-OH, which are expected to show bands in this region.

Figure 2. Mid-IR spectra of (a) Cr-100 as-synthesized and (b) Cr-100 calcined for 24 h at 693 K.

Figure 3. EPR spectra of a silicalite sample (a) as-synthesized at room temperature, (b) as-synthesized at liquid nitrogen temperature, and (c) calcined for 24 h at 693 K.
resonances are due to two sites, A and B, which suffer the action of crystalline fields with different cubic distortions. The symmetrical line C centered at g = 2.0 shows a severe increase in line width as the temperature drops from 300 to 77 K, clearly indicating smaller spin relaxation times. The line widths of the lines A and B are not significantly affected by changes in measurement temperature, indicating, as expected, a lower interaction between the Cr(III) species located in those sites.

Identification of the Cr(III) Species in Sites A and B. Assuming that the Cr(III) species, having an L = 3 electron configuration, as associated to its orbital ground state, are located in cubic crystalline fields tetrahedrally distorted, the positions of the EPR spectrum lines can be calculated by solving the spin Hamiltonian in eq 2, where the parameters D and E represent the axial and the rhombic distortions of the octahedron, respectively. The interaction of the Cr(III) ions, which have d^3 electron configuration (L = 3, S = \( \frac{3}{2} \)), with the cubic crystalline field is strong and is the principal term determining the energy levels. Since the spin–orbit interaction and the crystalline field distortions act on the singlet orbital, the Zeeman term will split the two Kramer doublets and the energy levels will depend on the magnetic field and, consequently, on D and E. Several transitions may occur between the levels for each direction of the magnetic field, and Figure 6 shows the expected g value as a function of D/E ratio for a particular direction of the magnetic field. For D/E = 6.5 and f = 9.54 GHz at room temperature, one finds a set of g values in good agreement with those obtained for site A (see Table IV), confirming that Cr(III) is substituting Si(IV) in the silicate skeleton. The assumptions made in the previous calculations do not provide any solution for site B, indicating that this is not a skeleton site but probably a highly distorted species trapped inside the channels. To distinguish both situations, the as-synthesized samples were ion-exchanged three times with aqueous 0.01 M HCl, for 24 h at 80 °C. The EPR spectra of the ion-exchanged samples, shown in Figure 7, did not display site B peak anymore, showing that the Cr(III) species was washed away. Moreover the line corresponding to site C diminished considerably, making site A even more distinguishable. In line with this observation the weak band at ca. 680 cm^{-1} in the mid-IR spectrum is still present for the ion-exchanged material,

\[
\mathcal{H} = g \beta HS + D[S_z^2 - (S/3)(S + 1)] + E(S_x^2 - S_y^2) \tag{2}
\]

pattern line-shaped spectra, as shown in Figure 5. The dashed lines in Figure 4 correspond to the best fit to the experimental data. For the assignment of the different Cr(III) sites, it was assumed that the powder line shapes are due to two sites, A and B, which suffer the action of crystalline fields with different cubic distortions. The symmetrical line C centered at g = 2.0 is assigned to the ion-exchange cations [Cr(H_2O)_6]^{3+} and to chromium oxide-like compounds occluded in the channels, outside the silicon framework. The EPR parameters for these different sites, shown in Table IV, are obtained by experimental fitting using the line width and the amplitude as adjustable parameters. The Cr(III) species in site C suffer no constraints and are expected to interact, the interaction between them being usually stronger as temperature decreases. In fact, the line centered at g = 2.0 shows a severe increase in line width as the temperature drops from 300 to 77 K, clearly indicating smaller spin relaxation times. The line widths of the lines A and B are not significantly affected by changes in measurement temperature, indicating, as expected, a lower interaction between the Cr(III) species located in those sites.

Identification of the Cr(III) Species in Sites A and B. Assuming that the Cr(III) species, having an L = 3 electron configuration, associated to its orbital ground state, are located in cubic crystalline fields tetrahedrally distorted, the positions of the EPR spectrum lines can be calculated by solving the spin Hamiltonian in eq 2, where the parameters D and E

\[
\mathcal{H} = g \beta HS + D[S_z^2 - (S/3)(S + 1)] + E(S_x^2 - S_y^2) \tag{2}
\]

represent the axial and the rhombic distortions of the octahedron, respectively. The interaction of the Cr(III) ions, which have d^3 electron configuration (L = 3, S = \( \frac{3}{2} \)), with the cubic crystalline field is strong and is the principal term determining the energy levels. Since the spin–orbit interaction and the crystalline field distortions act on the singlet orbital, the Zeeman term will split the two Kramer doublets and the energy levels will depend on the magnetic field and, consequently, on D and E. Several transitions may occur between the levels for each direction of the magnetic field, and Figure 6 shows the expected g value as a function of D/E ratio for a particular direction of the magnetic field. For D/E = 6.5 and f = 9.54 GHz at room temperature, one finds a set of g values in good agreement with those obtained for site A (see Table IV), confirming that Cr(III) is substituting Si(IV) in the silicate skeleton. The assumptions made in the previous calculations do not provide any solution for site B, indicating that this is not a skeleton site but probably a highly distorted species trapped inside the channels. To distinguish both situations, the as-synthesized samples were ion-exchanged three times with aqueous 0.01 M HCl, for 24 h at 80 °C. The EPR spectra of the ion-exchanged samples, shown in Figure 7, did not display site B peak anymore, showing that the Cr(III) species was washed away. Moreover the line corresponding to site C diminished considerably, making site A even more distinguishable. In line with this observation the weak band at ca. 680 cm^{-1} in the mid-IR spectrum is still present for the ion-exchanged material,
Figure 7. EPR spectra of chromium silicalite Cr-100 (a) as-synthesized, and (b) three times ion-exchanged with HCl solution. The dashed lines correspond to the best fit to the experimental curve.

Figure 8. EPR spectra of the chromium silicalite, Cr-30, (a) as-synthesized, (b) calcined at 693 K for 24 h, and (c) calcined for 24 h at 843 K.

Figure 9. Mid-IR spectra showing the effect of calcination at increasing temperatures upon the zeolitic lattice integrity of sample Cr-30 (a) as-synthesized, (b) calcined for 24 h at 693 K, and (c) calcined for 24 h at 843 K.

Figure 10. PA spectra of chromium silicalite Cr-30, (a) calcined at 693 K, (b) as-synthesized, and (inset) after extensive calcination at 693 K (on top). Arrows indicate the presence of two absorbing centers.

Supporting our previous assumption that this band is due to (Si–O–Cr)n group symmetric stretching.

**Oxidation of Extraframework Cr(III) to Cr(VI).**

Calcination of a Cr-30 sample for 24 h, at 693 and 843 K, under oxygen flow, leads to incorporation of oxygen by the sample with oxidation of Cr(III) to Cr(VI) species. A comparison of the EPR spectra of a sample as-synthesized and after calcination at 693 K (Figure 8) shows that they display essentially the same features except by a change in the relative intensities of the peaks within g = 2.08 and 1.66 related to sites C and B, respectively. In spectrum 8b, the relative intensity B/C is higher than for spectrum 8a, showing that Cr(III) species in site C (channels) were oxidized to EPR-silent Cr(VI) species. Calcination at 843 K leads to the complete oxidation of all sites and structure collapse. The effects of calcination in the IR and photoacoustic spectra were also examined. The IR spectra in Figure 9 show that the sample calcined at 693 K retained its MFI structure as determined by the A550/A450 optical density ratio equal to 0.77 for 9a and 0.74 for 9b. However, calcination at 843 K leads to the collapse of the crystal structure of the pentasil zeolite, as shown by the disappearance of the peaks at 550 and 450 cm⁻¹ in Figure 9c. The photoacoustic spectra of the Cr-30, as-synthesized and calcined at 693 K, are shown in Figure 10. The as-synthesized sample shows two bands centered at 440 and 640 nm, assigned to the 4A2 → 4T1(F) and 4A2 → 4T2 transitions, respectively, characteristic of Cr(III) species. After calcination at 693 K a strong band at 370 nm is observed, which is assigned to a charge-transfer absorption of Cr(VI). In Figure 10c it is possible to observe the very weak Cr(III) bands in the presence of Cr(VI), which provides a strong evidence that even after extensive calcination at 693 K some Cr(III) still remains in the chromium silicalite, very likely the ones in Si(IV) substitutional sites. It is interesting to note that Fe(III) species in the silicalite framework are stable to reduction, while Fe(III)-O species housed in the channels are reduced by H2 or CO to EPR-silent Fe(III) species. Therefore, redox cycles involving skeletal transition metal ions might not be as easy as one would expect based on solution chemistry.

**Thermal Characterization.** Apart from providing direct optical spectra, the photoacoustic technique can
also be used in the characterization of thermal properties as well as in the investigation of nonradiative relaxation processes.

**Thermal Diffusivity.** Like the optical absorption, the thermal diffusivity, \( \alpha \), is unique for each material and has been determined for a wide range of them, such as metals, minerals, and biological specimens. Furthermore, \( \alpha \) is extremely dependent upon the effects of compositional and microstructural variables as well as processing conditions as in the case of polymers, ceramics, and glasses. The thermal diffusivities of the as-synthesized and calcined chromium silicates were determined by photoacoustic spectroscopy, PA, using the signal data as a function of modulation frequency, \( f \). By performing a rear-illumination signal amplitude measurement, we have determined that the thermal bending mechanism is the main reason for the detected PA signal in the modulation range of our experiments; i.e., the rear signal amplitude varies as \( f \). This is the expected modulation frequency dependence of the rear signal for a thermally thick sample when the thermoelastic bending dominates the PA signal. In Figure 11 the PA rear-signal amplitude is plotted versus the modulation frequency for a Cr-30 calcined sample. A similar dependence is observed for the as-synthesized sample. The thermal diffusivity is obtained by fitting the front phase signal data to eq 3,

\[
\phi = \phi_0 + \arctan \left[ \frac{1}{(x - 1)} \right]
\]

(3)

where \( x = a(f)^{1/2} \), with \( a = (\pi x/(\alpha f))^{1/2} \), \( f \) being the sample thickness. Assuming \( \phi_0 \) and \( a \) as adjustable parameters, the thermal diffusivity is obtained from the phase data fitting from the parameter \( \alpha \). In Figure 12 the PA signal phase data for the calcined sample is shown as a function of the modulation frequency. The solid curve represents the fitting of the experimental phase data to the theoretical eq 3. The value of \( \alpha \) obtained from the data fitting is \( 0.041 \pm 0.002 \, \text{cm}^2 \, \text{s}^{-1} \). The same procedure was used for the as-synthesized sample, giving a value of \( \alpha \) of \( 0.038 \pm 0.002 \, \text{cm}^2 \, \text{s}^{-1} \).

**Nonradiative Relaxation Processes.** The PA signal also depends upon the light-into-heat conversion efficiency. This means that the PA signal is sensitive to the nonradiative deexcitation process which takes place after the absorption of the incident radiation. Information on the nonradiative deexcitation processes is obtained from the measurements of the PA phase angle as a function of the modulation frequency. For a thermally thick sample, the modulation frequency dependent part of the phase of the PA signal varies as shown in eq 4, where \( \tau \) is the nonradiative relaxation time,

\[
\phi = -\pi/2 - \arctan(\omega \tau) - \arctan \left[ \frac{1}{(2/\omega \tau)^{0.5} - 1} \right]
\]

(4)

Figure 11. PA rear-signal amplitude for the Cr-30 sample as a function of the modulation frequency, showing the \( f \) frequency dependence.

Figure 12. PA rear-signal phase dependence on the modulation frequency for the calcined Cr-30. The solid line corresponds to the data fitting to eq 3.

Figure 13. PA phase versus the modulation frequency at the 440-nm wavelength for the as-synthesized Cr-30. The solid line corresponds to the data fitting to eq 4.
absorption of radiation. For powdered samples, as is the case of the present work, we may have a non-unique relaxation pathway consisting of several successive steps, and the measured lifetime is the average lifetime for heat production. Furthermore, for powdered samples, as is the case of the present work, the relaxation time, \( \tau \), is not expected for the level initially excited but rather for the average lifetime of a variety of states before energy is lost as heat. Thus, we may have a non-unique relaxation pathway consisting of several successive steps, and the measured lifetime is an average lifetime for heat production. Furthermore, for powdered samples, as is the case of the present work, the relaxation time, \( \tau \), also contains a contribution from the heat exchange time between the powder particles and the transducing gas of the PA cell. This heat exchange time depends not only on the shape of the particles but also on their size. The results for each absorption band together with the obtained values of \( \beta \) and \( \tau_B \) are summarized in Table V. Some conclusions might be drawn from the above results. First, the relaxation time, \( \tau \), is not expected for the level initially excited but rather for the average lifetime of a variety of states before energy is lost as heat. Thus, we may have a non-unique relaxation pathway consisting of several successive steps, and the measured lifetime is an average lifetime for heat production. Furthermore, for powdered samples, as is the case of the present work, the relaxation time, \( \tau \), also contains a contribution from the heat exchange time between the powder particles and the transducing gas of the PA cell. This heat exchange time depends not only on the shape of the particles but also on their size. The fact that the average of \( \tau \) for Cr(III) in the as-synthesized sample is equal within the experimental error to the one obtained for the calcined sample shows that the mechanism of relaxation for Cr(VI) is not very different to the one used for Cr(III) to transfer the heat generated upon absorption of radiation.

Table V. Values of the Nonradiative Relaxation Time, \( \tau \), the Characteristic Diffusion Time, \( \tau_B \), and the Optical Absorption Coefficient, \( \beta \), for the Calcined and As-Synthesized Chromium Silicalite Cr-30

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>as-synthesized</th>
<th>calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>440</td>
<td>640</td>
<td>380</td>
</tr>
<tr>
<td>( \tau ) (ms)</td>
<td>2.70 ± 0.35</td>
<td>2.17 ± 0.12</td>
</tr>
<tr>
<td>( \tau_B ) (ms)</td>
<td>0.45 ± 0.05</td>
<td>0.54 ± 0.04</td>
</tr>
<tr>
<td>( \beta ) (cm(^{-1}))</td>
<td>230 ± 19</td>
<td>211 ± 15</td>
</tr>
</tbody>
</table>

Acknowledgment. Financial support from FAPESP, CAPES, and CNPq is gratefully acknowledged. We are indebted to Prof. J. S. Barone for the chemical analysis.