

Electron Paramagnetic Resonance Study of Chromosilicalite

O. Nakamura

Instituto de Física, Universidade Federal da Bahia, 40210, Salvador, Bahia, Brazil

J. Silvio T. Mambrim, H. O. Pastore and E. J. S. Vichi

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13081, Campinas, São Paulo, Brazil

F. G. Gandra, E. C. da Silva and H. Vargas*

Instituto de Física, Universidade Estadual de Campinas, Caixa Postal 6165, 13081, Campinas, São Paulo, Brazil

J. Pelzl

Institut für Experimentalphysik VI, Ruhr Universität Bochum, P.O. Box 102148, D-4630 Bochum, Federal Republic of Germany

An electron paramagnetic resonance (EPR) study of crystalline chromosilicalite has been presented with the purpose of characterization of the distribution of Cr^{3+} sites in the solid. In addition, a deconvolution process is described whereby the EPR parameters can be analysed.

The catalytic importance of chromium has prompted numerous attempts to introduce chromium cations in zeolites. For example, Naccache and Ben Taarit,¹ Atanasova *et al.*² and Pearce *et al.*³ have investigated the Cr species mainly in A, X, and Y zeolites, whereas Hemidy *et al.*⁴ and Kucherov and Slinkin⁵ reported results for the Cr-mordenite system. In a recent communication⁶ we reported the incorporation of Cr^{3+} in the structural positions of ZSM-5 type zeolites, and recently we have demonstrated the incorporation of oxygen in this zeolite with oxidation of anchored Cr^{3+} to non-interacting Cr^{6+} species.⁷

Here an EPR study of crystalline chromosilicalite is presented with the purpose of further characterizing the distribution of each Cr^{3+} site in the solid. Such characterization is a necessary prelude to establishing the chromosilicalite activity as a catalyst in the production of alkenes. In addition a deconvolution process is described whereby the EPR parameters could be analysed. This method proved to be quite successful, and the results provide evidence that Cr^{3+} ions are at least in two substitutional-like or highly distorted sites and in another one outside the silicon framework.

Experimental

Material and Methods

Synthesis

A mixture of sodium silicate (Riedel de-Haën: 63% SiO_2 , 16% Na_2O and 18% water), ammonium fluoride, chromium nitrate 9-hydrate and water was prepared in the ratio 0.1 : 0.05 : 0.25 : 6.0, for the synthesis of a sample with SiO_2 : Cr_2O_3 ratio of 100 : 1 in the initial mixture. The pH was adjusted to 6.5–7.0 with 48 vol% HF. After 2 h stirring, tetrapropylammonium bromide was added in 40 cm^3 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 chromosilicalite was then filtered, washed until free of F^- and at neutral pH and air dried. The samples were kept in a desiccator over saturated CaCl_2 solution before use. Elemental analysis showed the following composition for the as-synthesized material (in %): SiO_2 , 81.60; Al_2O_3 , 1.00; Cr_2O_3 , 0.90; Fe_2O_3 , 0.02; Na_2O , 2.41. The ratio SiO_2 : Cr_2O_3 is 743.¹¹ The material is a highly crystalline

ZSM-5 molecular sieve, as shown by the ratio of 550 to 450 cm^{-1} absorbances of 0.75 for an as-synthesized sample and of 0.81 for a calcined sample.

EPR

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: DPPH, g -value = 2.0036. The spectra were recorded on samples at room (300 K) and liquid nitrogen (77 K) temperature.

Computational Fittings

The experimental data were fitted to theoretical expressions using an IBM 3090 computer. The expressions used were composed of the superposition of symmetrical line-shapes with powder pattern line-shapes.⁸ The routines used for the fittings are those from Bevington.⁹

Results and Discussion

Fig. 1 shows the spectra of the silicalite material (without chromium) and the effect of its calcination. The EPR spectra prior to calcination, at 300 and 77 K show a broad peak centred at $g \approx 2$. Superimposed on it there is a sharp peak at $g = 1.97$. Also, there is another peak at $g = 4.27$ due to Fe^{3+} ,

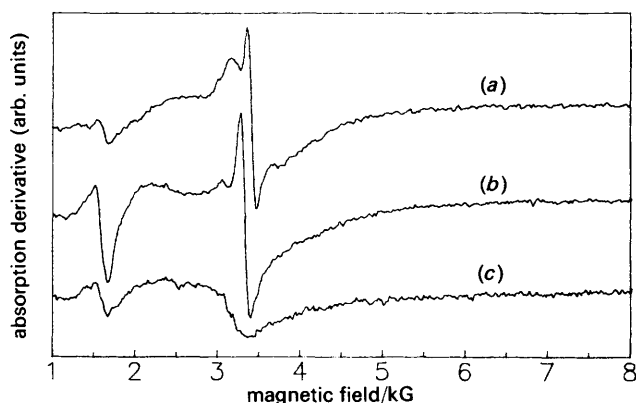


Fig. 1 EPR spectra of a silicalite sample (a) as prepared, at room temperature, (b) at liquid nitrogen temperature, (c) calcined for 24 h at 843 K, at room temperature

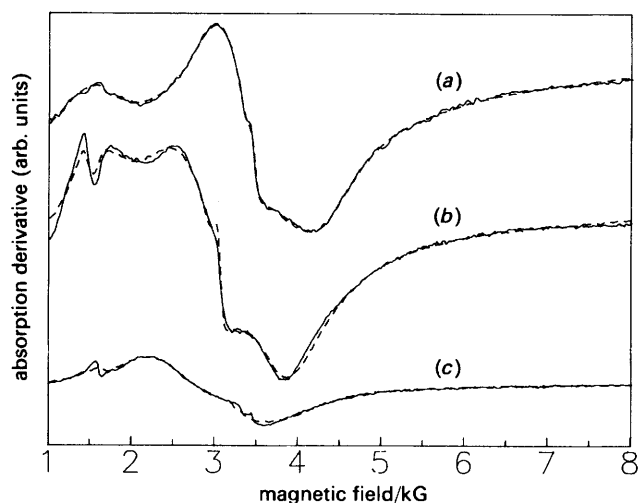


Fig. 2 EPR spectra of crystalline chromosilicalite (a) at room temperature, (b) at liquid nitrogen temperature, (c) calcined for 24 h under oxygen flow. The measurements were carried out at room temperature

an impurity that comes from the silicon source. From the sample calcined at 843 K it can be seen that the broad and the sharp peak signals decreased drastically in intensity. The sharp peak at $g = 1.97$ is due to free radicals formed from organic compounds used as template in the material preparation. These signals described above will serve as background for our EPR chromosilicalite spectra in an effort to elucidate the distribution of Cr^{3+} in the different sites in our zeolite.

Fig. 2 shows the spectra at (a) 300 and (b) 77 K of a highly crystalline zeolitic chromosilicate containing Cr^{3+} both in framework and non-framework positions. The spectra show a distribution of resonances which includes high g -values. To interpret the complex spectra shown in Fig. 2, a deconvolution was made considering the following contributions: one symmetrical line centred on $g \approx 2.0$, the background spectrum and two powder pattern line-shapes. This is shown in Fig. 3. The dashed lines in Fig. 2 correspond to the best fit to the experimental data using the resonance field, linewidth and amplitude as adjustable parameters. The results obtained are presented in Table 1. We assume that the two powder spectra resonances are due to different sites (A and B) in silicon framework positions. Both sites suffer the action of the crystalline field with different cubic symmetry distortions. The symmetrical line (C) centred at $g = 2.0$, has been attributed by several authors³ to the exchange cation $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and is outside the silicon framework. As expected the line centred at $g \approx 2.0$, corresponding to site C, shows an increase in linewidth as the temperature decreases. There is a clear indication of interaction between Cr^{3+} ions for this site out of the silicon framework. Concerning the substitutional sites (A and B) we can see that the linewidth is

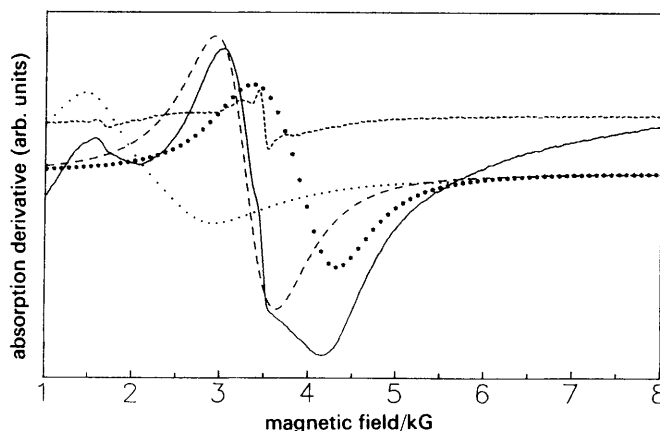


Fig. 3 Deconvolution of the experimental EPR curve of crystalline chromosilicalite at room temperature. (---), Background silicalite; (—), $g = 2$, line C; (· · ·), powder spectrum A; (● ● ●), powder spectrum B; (—), total spectrum

basically constant with temperature considering the complexity of the fitting procedures. This means a lower interaction of the Cr^{3+} ions.

We investigated the changes of EPR spectrum upon calcination of the sample for 24 h at 843 K under oxygen flow. The spectrum is shown in Fig. 2(c). The dashed line corresponds to the fitting of the experimental data. A comparison between Fig. 2(c) and (a) shows a considerable decrease in intensity of the calcined sample spectrum. This can be explained by a decrease in the number of cationic or charge-balancing sites, possibly as a consequence of oxidation of Cr^{3+} to Cr^{6+} . The intensity of substitutional sites A and B also decreases due to ruptures in the zeolite framework resulting from calcination at 843 K. The decrease in intensity of the narrow line centred at $g = 1.97$ is also observed. This line, as discussed previously, is related to free radicals from organic compounds created during the sample preparation. This line has been noted by previous authors¹⁰ and was thought to arise from a small amount of Cr^{5+} . However, we have observed a decrease in the intensity of this line for both the silicalite material (without chromium) and the chromosilicalite upon calcination. Hence, in the present case this decrease is due principally to the annealing and calcination of the free radicals.

The photoacoustic spectrum of the chromosilicalite⁷ is characterized by two bands centred at 440 and 640 nm, respectively, corresponding to ligand field bands of Cr^{3+} . For the level assignment the band centred at 440 nm is interpreted as the ${}^4\Gamma_2 \rightarrow {}^4\Gamma_4$ transition, and the band at 640 nm as the ${}^4\Gamma_2 \rightarrow {}^4\Gamma_5$ transition. After calcination a strong band at 370 nm is clearly seen.⁷ This is assigned to a charge-transfer absorption of Cr^{6+} . The oxidation of $\text{Cr}^{3+} \rightarrow \text{Cr}^{6+}$ accounts for the decrease in the EPR intensity of the line in $g \approx 2.0$ (cationic sites).

Table 1 g -Values for the crystalline zeolitic chromosilicalite obtained from fitting the experimental spectra to the powder spectra and a symmetrical line, as explained in the text; ΔH is the linewidth and A is the relative amplitude

site	g_x		g_y		g_z		$\Delta H/\text{kG}$		A (arb. units)	
	300 K	77 K	300 K	77 K	300 K	77 K	300 K	77 K	300 K	77 K
A	4.49	4.06	2.71	2.19	1.66	2.03	0.60	0.43	1.50	1.04
B	2.00	2.61	1.67	1.75	1.66	1.69	0.66	0.56	5.23	3.66
C	2.08 ^a	1.88 ^a					0.61	1.19	0.14	0.35

^a Total g value.

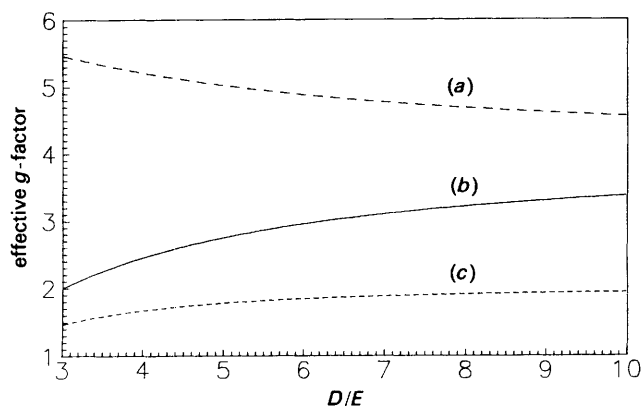


Fig. 4 Theoretical values of effective g -factor in the (b) x , (a) y and (c) z directions as a function of the ratio $E : D$

The positions of the lines of the EPR spectrum can be calculated by solving the spin Hamiltonian.¹¹

$$H = g\beta H \cdot S + D \left[S_z^2 - \frac{S}{3} (S + 1) \right] + E(S_x^2 - S_y^2)$$

provided we can associate an effective $L = 0$ value to orbital ground-state and considering tetragonal distortion from the cubic symmetry of the crystalline field. The parameters D and E represent the axial and rhombic distortion to the octahedron, respectively. The Cr^{3+} ions have the d^3 electron configuration ($L = 3$, $S = 3/2$) and have a larger octahedral site preference energy.¹² Their interaction with the cubic crystalline field is strong and is the principal term determining the energy levels. The spin-orbit interaction and the crystalline field distortions act on the singlet orbital. The Zeeman term will then split the two Kramers doublets and the energy levels will depend on the magnetic field and D and E .¹¹ For each direction of the magnetic field several transitions may occur between the levels and we calculated their resonance field for several values of D and E . Fig. 4 shows the expected g -value as a function of the ratio $D : E$ for a particular transition. For $D : E \approx 6.5$ 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 1). For the site B we could not find any solution with these assumptions.

In order to have a better evaluation of the different contributions of each site, the samples were ion exchanged with aqueous 0.01 mol dm^{-3} HCl for 24 h at $70\text{--}80^\circ\text{C}$. Fig. 5 shows the EPR spectra for samples (a) as synthesized and (b) three times exchanged. It is clear that site B was washed away from the zeolite structure or channels.

Even though site B is not easily oxidized, as would be expected for a channel species, it might be extracted by mild treatments. This leads us to believe that site B is a channel

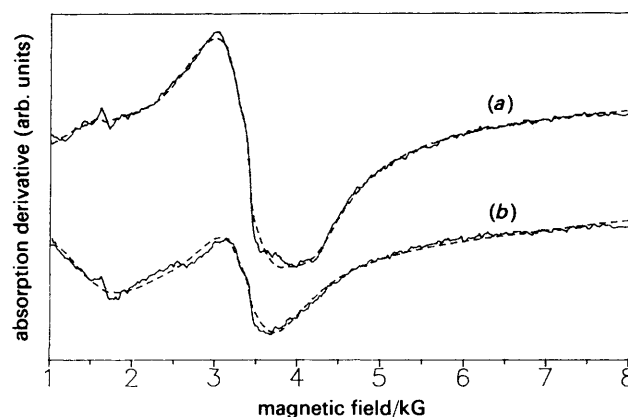


Fig. 5 EPR spectra of chromosilicalite (a) as synthesized and (b) three times ion-exchanged

species, highly distorted. That might be the reason why we were unable to find any solution for the plot of g vs. D/E that satisfied both A and B resonances simultaneously.

The complete characterization of a series of chromosilicalites, including thermal and optical properties will be published in a forthcoming paper.

We gratefully acknowledge FAPESP, CNPq and CAPES for financial support.

References

- 1 C. Naccache and Y. Ben Taarit, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 1475.
- 2 V. D. Atanasova, V. A. Shvets and V. B. Kazanski, *Kinet. Katal.*, 1977, **18**, 1033.
- 3 J. R. Pearce, D. E. Sherwood, M. B. Hall and J. H. Lunsford, *J. Phys. Chem.*, 1980, **84**, 3215.
- 4 J. F. Hemidy, J. M. Goupil and D. Cornet, *J. Chem. Phys.*, 1977, **74**, 74.
- 5 A. V. Kucherov and A. A. Slinkin, *Zeolites*, 1987, **7**, 38.
- 6 H. O. Pastore, E. Stein, C. U. Davanzo, E. J. S. Vichi, O. Nakamura, M. L. Baesso, E. C. da Silva and H. Vargas, *J. Chem. Soc., Chem. Commun.*, 1990, 772.
- 7 J. S. T. Mambrim, E. J. S. Vichi, H. O. Pastore, C. U. Davanzo, H. Vargas, E. C. da Silva and O. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1991, 992.
- 8 C. P. Poole, *Electron Spin Resonance*, Wiley, New York, 1983, ch. 12.
- 9 P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969.
- 10 J. C. Evans, C. R. Owen and C. C. Rowlands, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 4039.
- 11 G. Fuxi and D. He, L. Huiming, *J. Non-Cryst. Solids*, 1982, **52**, 135.
- 12 J. Wong and C. A. Angell, *Glass Structure by Spectroscopy*, Marcel Dekker, New York, 1976, p. 225.