

## EPR study of chromium centres in CrAPO-5 molecular sieves

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The X-band EPR spectra of CrAPO-5 molecular sieves exhibiting high or low sorption capacities for nitrogen and benzene, signed HS and LS samples, respectively, were studied at 300 and 77 K. The EPR spectra of the as-synthesized HS and LS samples consist of a broad intense signal ( $g_{\text{eff}} = 1.971 \pm 0.001$ ,  $\Delta H_{pp} \cong 500$  G) with a positive lobe at  $g_{\text{eff}} = 5.15 \pm 0.01$ , assigned to  $\text{Cr}^{3+}$  ( $3d^3$ ,  ${}^4F_{3/2}$ ) ions with a rhombic distorted octahedral coordination. Calcined samples show an additional narrow EPR signal of axial symmetry with  $g_{\parallel} = 1.971 \pm 0.001$  and  $g_{\perp} = 1.959 \pm 0.001$ , also assigned to  $\text{Cr}^{5+}$  ( $3d^1$ ,  ${}^2D_{3/2}$ ) ions in an octahedral coordination. HS samples heated under vacuum exhibit a decrease in the intensity of the  $\text{Cr}^{3+}$  lines as well as several new signals. Two of them are characterized by an axially symmetric  $g$  factor and belong to  $\text{Cr}^{5+}$  centres in square pyramidal and tetrahedral coordination. The third signal may be assigned to  $\text{Cr}^{3+}$  ( $3d^5$ ,  ${}^6S_{5/2}$ ) ions. The EPR spectra of LS samples heated under vacuum show a strong decrease in the intensity of  $\text{Cr}^{3+}$  lines and only the two signals of  $\text{Cr}^{5+}$  centres in the same coordination. Their  $g$  factors are similar to those in the HS samples. Thermal treatment under oxidative ( $\text{O}_2$ ) and reductive ( $\text{H}_2$ ) atmospheres reveal the reproducible redox properties of  $\text{Cr}^{5+}$  ions and a high stability of  $\text{Cr}^{3+}$  ions, especially in the HS samples.

Key words: CrAPO-5; chromium centres; EPR;  $g$  factor; redox properties

### 1. Introduction

The incorporation of transition metals into the framework sites of aluminophosphate molecular sieves by isomorphous substitution for  $\text{Al}^{3+}$  or  $\text{P}^{5+}$  is a useful method

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for modifying the properties of such materials. Transition metals, however, which can easily form ions of various valences and coordination states, e.g. V, Cr, Mo, W, etc., have generally supplied substantial difficulties for such incorporation. Chromium belongs to the group of catalytically interesting metals. For example,  $\text{AlPO}_4\text{-5}$  containing Cr has been used as a recyclable catalyst for the auto-oxidation of hydrocarbons, polymerisation of ethylene, etc. Therefore there have been many efforts to incorporate chromium into the frameworks of aluminophosphates in order to create isolated redox centres.

A possible introduction of Cr into silicates was reported more often than into aluminophosphate molecular sieves, and some authors have postulated an isomorphous substitution of Cr into the framework positions of silicate zeolites. Weckhuysen and Schoonheydt [1, 2] reported on extensive spectroscopic (EPR and diffuse reflectance spectroscopy) studies of Cr in  $\text{AlPO}_4\text{-5}$  and in various silicates. They concluded that Cr cannot be substituted into the framework positions but that it is anchored at the surface, which is mainly due to a strong preference of the  $\text{Cr}^{3+}$  ions for octahedral coordination. Sheldon et al. [3–6] postulated a framework substitution of both  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  ions in octahedral and tetrahedral coordination on the basis of catalytic behaviour, in spite of the fact that  $\text{Cr}^{6+}$  species can easily be washed out from their calcined materials. Radaev et al. [7, 8] investigated large crystals of  $\text{CrAPO-5}$  synthesized via the fluoride method and concluded that Cr occurs as an extra-framework species. A spectroscopic study of Cr-containing SAPO-5 showed pseudo-octahedrally coordinated  $\text{Cr}^{3+}$  ions [9]. From EPR, electron spin echo modulation, and UV-Vis spectroscopy investigations of CrAPSO-11, Kevan et al. [10] postulated that  $\text{Cr}^{3+}$  can be incorporated in small amounts in the initial as-prepared materials, but that after calcination it is transformed into  $\text{Cr}^{5+}$  located at  $\text{P}^{5+}$  framework sites. The same authors maintained to provide evidence for the framework substitution of small amounts of  $\text{Cr}^{3+}$  and  $\text{Cr}^{5+}$  ions in CrAPSO-5 from similar EPR and electron spin echo modulation spectroscopy investigations [11].

Our method of synthesis [12] has for the first time allowed stable substitution of larger amounts of  $\text{Cr}^{3+}$  for  $\text{Al}^{3+}$  in the framework of  $\text{AlPO}_4\text{-5}$ , i.e. producing  $\text{CrAPO-5}$  material with high sorption (HS samples) properties typical of AFI structures. Other synthesis procedures similar to those reported in the above cited literature have regularly yielded materials with low or very low sorption (LS samples) properties, though most of the other features were similar for both groups [12]. Though the applied characterisation methods [12], especially UV-Vis spectroscopy, seemed to indicate explicitly the framework incorporation of chromium, the final determination of the valence state and geometry of the local environment of Cr ions in both types of  $\text{CrAPO-5}$  has appeared to be difficult. Therefore, we performed detailed EPR examinations in order to study the features, local symmetry, and stability of chromium in  $\text{AlPO}_4\text{-5}$ , as well as the behaviour of incorporated Cr ions during thermal treatment under oxidizing ( $\text{O}_2$ ) and reducing ( $\text{H}_2$ ) atmospheres. The results of these investigations were first presented in [13]. Some results obtained by EPR spectroscopy are presented in this paper.

## 2. Experimental

The CrAPO-5 samples were synthesised following the general procedure for growing large crystals given in [14–16] and modified as described elsewhere [12, 13]. The obtained crystals had dimensions within the range 20–80  $\mu\text{m}$  and morphologies of single hexagonal prisms typical of the AFI structure type [12]. All the prepared CrAPO-5 samples had an intense green colour after synthesis. The obtained samples were calcined under a slow stream of air at 773 K for at least 48 h. After calcination and template removal, the samples synthesised from pseudoboehmite Al compound were coloured green-yellow (samples 1 and 2) and the others (from amorphous Al compounds) greenish-grey or dirty grey (samples 3 and 4). The green-yellow colour of samples 1 and 2 could change to violet and reversibly to green-yellow depending on the state of hydration, while the grey colour of samples 3 and 4 was stable and independent of any treatment.

The synthesised samples differed distinctly in their sorption properties. The green-yellow samples showed an adsorption capacity for water typical of the AFI structure type and a high sorption capacity for benzene and nitrogen (HS samples 1 and 2) [12, 13]. The grey samples adsorbed hardly any nitrogen or benzene, and their sorption of water was also somewhat reduced (LS samples 3 and 4) [12, 13]. This behaviour indicates a normal open state of the channels in the HS materials and clogged channels in the LS materials.

The redox processes of the samples were carried out in special tubes from Varian using the Balzers–Pfeifer vacuum system, high purity oxygen and hydrogen, and an automatic electric furnace controlled by a computer. The oxidation (reduction) process of the CrAPO-5 samples included heating them to 773 K and exposing to an oxygen (hydrogen) atmosphere ( $P = 10$  mbar) for 12 h at 773 K.

X-band EPR measurements of the CrAPO-5 samples were carried out at room and liquid nitrogen temperatures using a computer controlled RADIOPAN SE/X-2544 spectrometer with RCX 660 cylindrical  $\text{TM}_{110}$  cavity, operating in the high-frequency (100 kHz) magnetic field modulation mode. The EPR spectra of the CrAPO-5 polycrystalline samples were recorded in closed high-pure quartz tubes from Varian in air and vacuum. The  $g$  values of EPR lines were determined from experimental spectra using the resonance relationships and BRUKER computer simulation program „SimFonia”. The microwave frequency in each specific case was determined by means of a polycrystalline diphenylpicrylhydrazyl (DPPH) frequency marker ( $g = 2.0036 \pm 0.0001$ ) and the EPR line of the coke radicals ( $g = 2.0032 \pm 0.0001$ ).

## 3. Results and discussion

### 3.1. EPR spectra of as-synthesised and calcined CrAPO-5 samples

Typical X-band EPR spectra measured at 300 K for the as-synthesised HS (Fig. 1, spectrum 1) and LS samples (spectrum 3) are similar. The spectra recorded at liquid

nitrogen temperature were similar as well and consisted of a broad line, A ( $g_{\text{eff}} = 1.971 \pm 0.001$ ,  $\Delta H_{pp} \cong 500$  G), of Lorenz shape and a positive lobe, B ( $g_{\text{eff}} = 5.15 \pm 0.01$ ). The intensities of A and B vary strongly between the samples (Fig. 1). Similar EPR spectra have been observed earlier for Cr in alumina [17], silica [18], chromosilicate [19], molecular sieves of the AEL [10, 20] and AFI [11] types, and a number of other compounds with a disordered structure, particularly in Cr-doped glasses of different compositions [21–23]. Both observed signals have been assigned to  $\text{Cr}^{3+}$  ( $3d^3$ ,  ${}^4F_{3/2}$ ) ions.

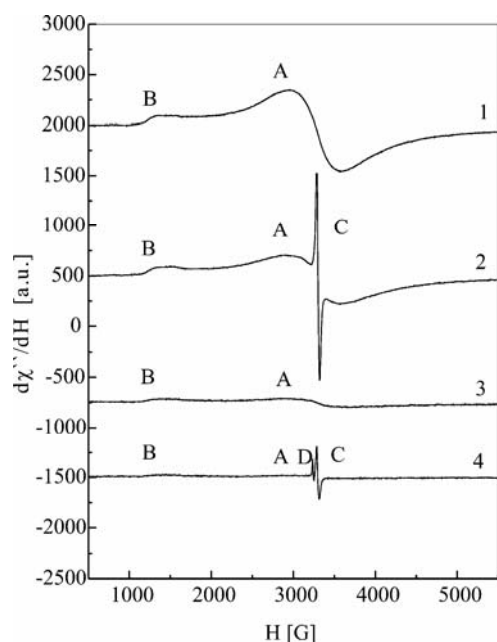


Fig. 1. Typical complete EPR spectra of HS (1, 2) and LS (3, 4) CrAPO-5 samples: 1, 3 – as-synthesised, 2, 4 – calcined samples (recorded at 300 K)

The A and B lines of  $\text{Cr}^{3+}$  ions were originally interpreted [18] by an analysis of the spin Hamiltonian:

$$H = \beta HgS + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) \quad (1)$$

where  $D$  and  $E$  are the axial and orthorhombic crystal field terms, respectively, and  $\beta$  is the Bohr magneton. Such an interpretation of the EPR spectra of the  $\text{Cr}^{3+}$  ions in disordered systems has been confirmed in several studies [11, 20–23] and supported for CrAPSO-5 based on of computer simulation [11]. In particular, the best fit has been obtained for the following parameters of the spin Hamiltonian:  $g_{\perp} = 1.98$ ,  $g_{\parallel} = 1.80$ ,  $D = 0.50 \text{ cm}^{-1}$ ,  $E/D = 1/3$ , and a peak-to-peak derivative linewidth of  $\Delta H_{pp} = 300$  G. The simulated EPR spectrum of the  $\text{Cr}^{3+}$  ions showed a weak line at  $g_3 = 0.98$  in addition to the two well-known lines at  $g_1 = 5.20$  and  $g_2 = 2.00$ . This weak line has been found in the experimental spectra of CrAPSO-5 [11], whereas in the EPR spectra of our CrAPO-5 samples this line was not observed.

A significant broadening of the EPR lines of  $\text{Cr}^{3+}$  in CrAPO-5 samples ( $\Delta H_{pp} \cong 500$  G) with respect to the same lines for CrAPSO-5 materials with very low contents of Cr ( $\Delta H_{pp} = 300$  G) [11] can be related to a dipolar interaction of the  $\text{Cr}^{3+}$  ions [23–25]. We observed similar EPR spectra of isolated and dipolar-coupled  $\text{Cr}^{3+}$  ions in Cr/ $\text{Al}_2\text{O}_3$  samples, which were used as a simple model system in our investigations.

Comparing our experimental data with those reported in [17–23], the observed EPR spectra of the as-synthesised HS and LS samples can be assigned to  $\text{Cr}^{3+}$  ions at sites with strongly (maximum) rhombic distorted ( $|E/D| = 1/3$ ) octahedral coordination. Therefore, we may assume that chromium ions occur in the CrAPO-5 framework mainly as  $\text{CrO}_{4/2}^-$  units complemented by two  $\text{H}_2\text{O}$  molecules from the pores, thus achieving a distorted octahedral coordination. This coordination gives the intense green colour to the species, which replace  $\text{AlO}_{4/2}^-$  tetrahedra in the framework [12, 13]. The EPR lines of  $\text{Cr}^{3+}$  are much more intense (over 10 times) for the HS than for the LS samples (Fig. 1), despite much smaller differences in Cr content. The differences in the intensities suggest that some of the chromium may be retained during synthesis as ions with higher valence that may also be attached to the framework. This result correlates with UV-Vis spectroscopy, which shows that LS samples have a higher content of  $\text{Cr}^{6+}/\text{Cr}^{5+}$  and a lower content of  $\text{Cr}^{3+}$  centres than the HS samples [13]. One can notice that the concentration of the  $\text{Cr}^{5+}$  centres in the as-synthesised HS and LS samples is negligible and that their EPR spectra were not observed. Therefore, in the as-synthesised CrAPO-5 samples the  $\text{Cr}^{6+}$  ions, in general, are attached to the framework.

The EPR spectra of calcined HS and LS samples show a new narrow signal of chromium (denoted as C in spectra 2 and 4 of Fig. 1). The C signal is identical in all calcined HS and LS samples and consists of two weakly resolved lines (Fig. 2, spectra 1–4), which were not better resolved at liquid nitrogen temperature. The spectra of the calcined LS samples, however, show an additional isotropic symmetrical line, D, with  $g = 2.0032 \pm 0.0001$  and  $\Delta H_{pp} = (7.5 \pm 1.0)$  G (Fig. 1, spectrum 4 and Fig. 2, spectra 3–4). This D line was observed exclusively in the LS samples and was assigned to coke radicals [26], which formed in the channels from organic template molecules during the calcination process. A small amount of coke in the LS samples could provide an internal reference for determining the  $g$  values.

The parameters obtained from the experimental spectra have offered the possibility of simulating the C signal observed in calcined samples (Fig. 2, spectra 1–4). The computer simulation was performed using standard methods for disordered (polycrystalline or powdered) samples. The best fit of the simulated spectra to the experimental ones was obtained assuming a Lorenz line shape, with  $\Delta H_{pp} = (16.5 \pm 1.0)$  G. The corresponding  $g$  factor values are given in Table 1. The  $g$  factors obtained for the C signals (Table 1) are similar to those of the octahedrally-coordinated  $\text{Cr}^{5+}$  ions in silica-alumina and alumina [17, 27–30]. It should be noted that the EPR spectra of  $\text{Cr}^{5+}$  in silica-alumina with low  $\text{Al}_2\text{O}_3$  content (3 wt. %) are characterised by an anisotropic  $g$  factor and linewidth similar to that of Cr/ $\text{SiO}_2$  ( $g_{\perp} = 1.98$ ,  $g_{\parallel} = 1.90$ ,  $\Delta H_{pp} = 15$  G).

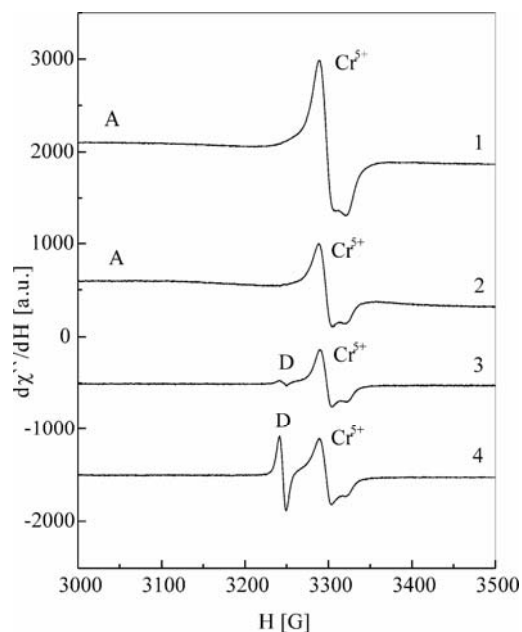


Fig. 2. Central region of the EPR spectra recorded at 300 K for the HS (1, 2) and LS (3, 4) CrAPO-5 samples calcined at 773 K. EPR signal C is attributed to  $\text{Cr}^{5+}$  ions

An increase of the  $\text{Al}_2\text{O}_3$  content to 10 wt. % leads to a change in the spectral parameters of  $\text{Cr}^{5+}$  ( $g_{\perp} = 1.97$ ,  $g_{\parallel} = 1.95$ ,  $\Delta H_{pp} = 20$  G). In result, the  $\text{Cr}/\text{Al}_2\text{O}_3$  system is characterised by an isotropic symmetric line with  $g_0 = 1.96$  and  $\Delta H_{pp} = 44$  G. An isotropic symmetric EPR line of  $\text{Cr}^{5+}$  ions with  $g_0 = 1.972 \pm 0.001$  and  $\Delta H_{pp} = 47.0 \pm 1.0$  G has also been observed by us in the model system  $\text{Cr}/\text{Al}_2\text{O}_3$  calcined in air at 700 K. These changes in the EPR spectra are caused by the transformation of the coordination of  $\text{Cr}^{5+}$  from tetrahedral (local symmetry –  $T_d$ ) in  $\text{SiO}_2$  to square pyramidal with a short chromyl bond (local symmetry –  $C_{4v}$ ) in  $\text{Al}_2\text{O}_3$  [27, 30]. The adsorption of  $\text{H}_2\text{O}$  results in the transformation of the tetrahedral and square pyramidal coordinations of  $\text{Cr}^{5+}$  to an octahedral one in  $\text{Cr}/\text{SiO}_2$ ,  $\text{Cr}/\text{SiO}_2\text{-Al}_2\text{O}_3$ , and  $\text{Cr}/\text{Al}_2\text{O}_3$  systems and leads to an increase of the  $g_{\parallel}$  value from 1.90 to 1.95, i.e., to a “symmetrization” of the EPR spectra [31, 32].

Table 1. The  $g$  factors for the C signals of the calcined CrAPO-5 samples, obtained as the best fit of the spectra recorded at 300 K and simulated EPR spectra

| Cr ion           | $g$ factor | HS samples        |                   | LS samples        |                   | Notes   |
|------------------|------------|-------------------|-------------------|-------------------|-------------------|---|
|                  |            | 1                 | 2                 | 3                 | 4                 |   |
| $\text{Cr}^{5+}$ | $g_{xx}$   | $1.970 \pm 0.001$ | $1.971 \pm 0.001$ | $1.972 \pm 0.001$ | $1.972 \pm 0.001$ | $g_{xx} = g_{yy} = g_{\perp}$<br>$g_{zz} = g_{\parallel}$ |
|                  | $g_{yy}$   | $1.970 \pm 0.001$ | $1.971 \pm 0.001$ | $1.972 \pm 0.001$ | $1.972 \pm 0.001$ |   |
|                  | $g_{zz}$   | $1.959 \pm 0.001$ | $1.959 \pm 0.001$ | $1.959 \pm 0.001$ | $1.959 \pm 0.001$ |   |

Similar anisotropic EPR signals, with  $g_{\perp} = 1.97$  and  $g_{\parallel} = 1.95$ , for octahedrally-coordinated  $\text{Cr}^{5+}$  ions have been observed in hydrated zeolites of the ZSM-5 type

[33, 34]. During the oxidation process,  $\text{Cr}^{5+}$  ions are stabilised in the channels of ZSM-5 as  $\text{CrO}_2^+$  particles with part of the non-framework  $\text{O}^{2-}$  ligands [33, 34]. These isolated ions in the zeolite structure may be considered to be coordinatively non-saturated surface ions, which define the catalytic activity of the material [34].

Therefore, signal C has been identified to correspond to isolated  $\text{Cr}^{5+}$  ions at axially-distorted octahedral sites. This signal appears during calcination and indicates that a certain part of the  $\text{Cr}^{3+}$  ions are oxidized to  $\text{Cr}^{5+}$  at sites with a more symmetric octahedral coordination.

### 3.2. EPR spectra of CrAPO-5 samples under vacuum heat treatment

Heat treatment at 773 K under vacuum ( $2.4 \times 10^{-7}$  mbar) for 12 h led to the dehydration of the calcined HS samples and lowered the coordination of the Cr ions. In result, the lines of  $\text{Cr}^{3+}$  (A and B lines in Fig. 1) and  $\text{Cr}^{5+}$  (C line in Fig. 2) vanished and several new EPR signals of Cr appeared (Fig. 3). Instead of the former  $\text{Cr}^{3+}$  signals, an extremely broad ( $\Delta H_{pp} \cong 2500$  G) and intense signal appeared, with  $g = 2.55 \pm 0.01$ , attributed to  $\text{Cr}^{3+}$  as well and described in [13].

New narrow signals were three EPR signals originating from  $\text{Cr}^{5+}$  centres for the dehydrated HS (1) sample as well as two signals of  $\text{Cr}^{5+}$  and two signals of  $\text{Cr}^+$  centres for the dehydrated HS (2) sample (Fig. 3, spectra 1 and 2). The identification of the new Cr centres was made on the basis of literature data for other Cr-containing oxide compounds, such as silica, silica–alumina, and alumina [10, 11, 27–34]. The assignments,  $g$  factors, and possible coordinations for Cr centres in all investigated samples after such treatment are presented in Table 2.

Table 2. Assignments and  $g$  factors of the experimental EPR signals, obtained at 300 K, for chromium ions in CrAPO-5 samples after heating at 773 K under vacuum ( $2 \times 10^{-7}$  mbar) for 12 h, and the corresponding coordination of the Cr centres

| Cr ion               | $g$ factor       | HS samples   |              | LS samples   |              | Coordination                |
|----------------------|------------------|--------------|--------------|--------------|--------------|-----------------------------|
|                      |                  | 1            | 2            | 3            | 4            |                             |
| $\text{Cr}^{5+}$ (1) | $g_{\parallel}$  | 1.962±0.001  | 1.960±0.001  | 1.962±0.002  | 1.961±0.002  | Square pyramidal            |
|                      | $g_{\perp}$      | 1.974±0.001  | 1.969±0.001  | 1.975±0.002  | 1.974±0.002  |                             |
| $\text{Cr}^{5+}$ (2) | $g_{\parallel}$  | 1.943±0.002  | 1.951±0.002  | 1.930±0.002  | 1.930±0.002  | tetrahedral                 |
|                      | $g_{\perp}$      | 1.990±0.002  | 1.982±0.002  | 1.991±0.002  | 1.991±0.002  |                             |
| $\text{Cr}^{5+}$ (3) | $g_{\parallel}$  | 1.951±0.002  | not observed | not observed | not observed | tetrahedral                 |
|                      | $g_{\perp}$      | 1.999±0.002  |              |              |              |                             |
| $\text{Cr}^+$ (1)    | $g_{\text{iso}}$ | not observed | 2.005±0.001  | not observed | not observed | near to $\text{P}^{5+}$ ion |
| $\text{Cr}^+$ (2)    | $g_{\text{iso}}$ | not observed | 2.005±0.001  | not observed | not observed | unknown                     |

The EPR signals of  $\text{Cr}^{5+}$  ( $3d^1$ ,  ${}^2D_{3/2}$ ) ions in the dehydrated HS (1) sample are characterised by axially symmetric  $g$  factors and belong to centres in square pyramidal ( $\text{Cr}^{5+}$  (1) lines) and tetrahedral ( $\text{Cr}^{5+}$  (2) and  $\text{Cr}^{5+}$  (3) lines) coordinations. The

axially symmetric EPR signals of the HS (2) sample similarly belong to  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) centres in square-pyramidal and tetrahedral coordinations, respectively. The EPR signal of  $\text{Cr}^{3+}$  ( $3d^5$ ,  ${}^6\text{S}_{5/2}$ ) ions, consisting of a single narrow ( $\Delta H_{pp} \cong 9$  G) line (for  $\text{Cr}^{3+}$  (2) centres) and two symmetric satellites (for  $\text{Cr}^{3+}$  (1) centres) is characterised by an isotropic  $g$  factor ( $g_{\text{iso}} = 2.005 \pm 0.001$ ). In our opinion, the two satellite lines are caused by the superhyperfine (SHF) interaction (the isotropic SHF constant  $a_{\text{iso}} \cong 21$  G) of  $\text{Cr}^{3+}$  (1) centres with one nucleus of the  ${}^{31}\text{P}$  isotope (nuclear spin being  $I = 1/2$ , and natural abundance 100%).

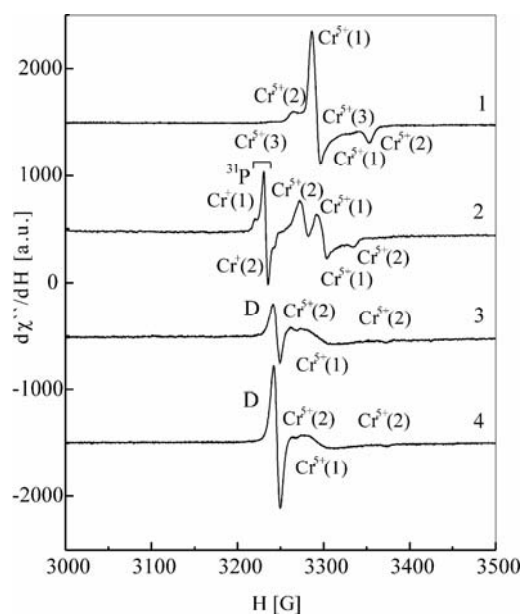


Fig. 3. Central region of the EPR spectra, recorded at 300 K, of HS (1 and 2) and LS (3 and 4) CrAPO-5 samples after heating at 773 K under vacuum ( $2 \times 10^{-7}$  mbar) for 12 h

Vacuum heat treatment of the calcined LS samples under the same conditions as for HS samples led to a strong decrease of the  $\text{Cr}^{3+}$  lines (A and B in Fig. 1) and to a full disappearance of the octahedral  $\text{Cr}^{5+}$  centres (signal C in Fig. 2). Instead of the former  $\text{Cr}^{5+}$  signals, two new EPR signals appeared, which were attributed to  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) centres with square-pyramidal and tetrahedral coordinations, respectively (Fig. 3, spectra 3 and 4), and with  $g$  factors similar to those of the HS samples (Table 2). In the LS samples after vacuum heat treatment, only traces of the A and B  $\text{Cr}^{3+}$  signals (Fig. 1, spectra 3 and 4) were observed, whereas the characteristic of HS samples broad  $\text{Cr}^{3+}$  signal, with  $g = 2.55 \pm 0.01$ , was not observed. Together with a grey colour, these spectral features indicated that only a small amount of  $\text{Cr}^{3+}$  ions could be substituted into the framework positions of the LS samples.

The observed new forms of  $\text{Cr}^{5+}$  and  $\text{Cr}^{3+}$  centres may be created from the extra-framework (or surface)  $\text{Cr}^{6+}$  and  $\text{Cr}^{2+}$  ions, respectively, under vacuum heat treatment. Some type of disproportionation reaction of  $\text{Cr}^{5+}$  or/and  $\text{Cr}^{3+}$  ions may also be imagined.

### 3.3. Redox behaviour of CrAPO-5 samples

The stability of the observed  $\text{Cr}^+$ ,  $\text{Cr}^{3+}$ , and  $\text{Cr}^{5+}$  ions in CrAPO-5 was studied by applying redox processes to the calcined HS and LS samples, pre-treated in vacuum. Heat treatment in oxidative and reductive atmospheres did not considerably affect  $\text{Cr}^{3+}$  ions in either the HS or LS materials, but strongly influenced  $\text{Cr}^+$  and  $\text{Cr}^{5+}$  centres.

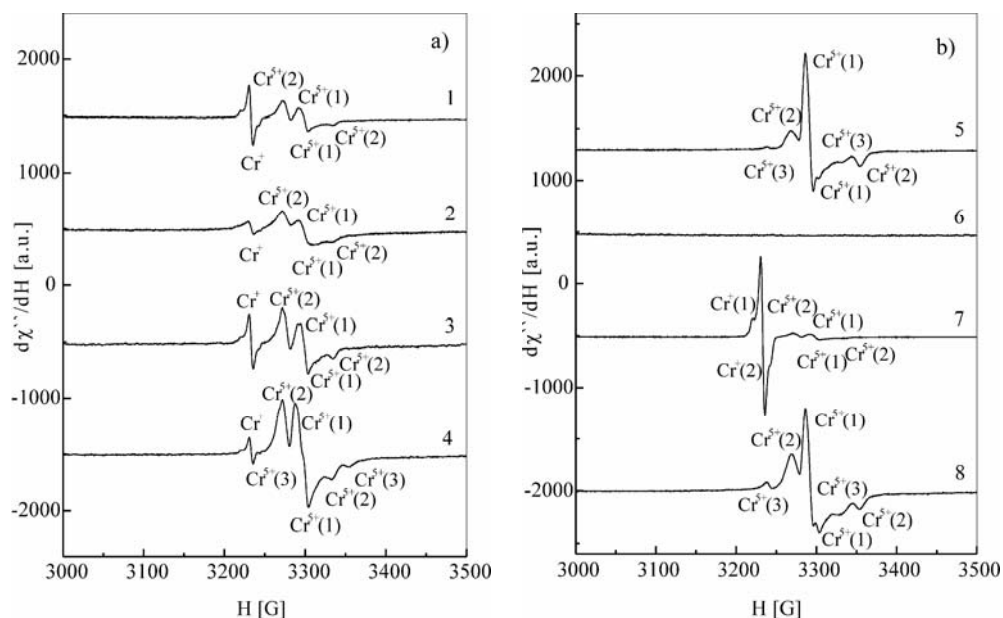


Fig. 4. Central region of the EPR spectra, recorded at 300 K, of the calcined HS (2) sample after the following treatments: a) heating at 773 K under vacuum ( $2 \times 10^{-7}$  mbar) for 12 h (1), exposure to air (10 mbar) at 300 K for 85 h (2), adsorption of  $\text{O}_2$  (10 mbar) at 300 K and evacuation (3), heating at 573 K under vacuum ( $8.9 \times 10^{-6}$  mbar) for 1 h (4); b) heating at 773 K in  $\text{O}_2$  (10 mbar) for 12 h and evacuation (5), heating at 773 K in  $\text{H}_2$  (10 mbar) for 12 h and evacuation (6), exposure to air (10 mbar) for 4 h (7), heating at 773 K in  $\text{O}_2$  (10 mbar) for 12 h and evacuation (8)

Changes in the EPR spectra of sample HS (2) after various oxidative and reductive treatments are shown in Fig. 4. It should be noted that the spectrum of  $\text{Cr}^+$  centres was unstable and that its intensity decreased strongly after exposition to air at room temperature, whereas the intensities of the  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) spectra were only slightly reduced under the same conditions (Fig. 4a, spectra 1, 2). The adsorption of  $\text{O}_2$  at 300 K with further evacuation of residual gas led to an increase of the intensity of  $\text{Cr}^+$  lines and to an improvement in the resolution of the  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) lines (Fig. 4a, spectrum 3). The observed differences between exposure to air and pure  $\text{O}_2$  at room temperature may be connected to the adsorption of water from air, i.e. the hydration of sample. Heat treatment at 573 K in vacuum led to a decrease in the intensity of the  $\text{Cr}^+$  signal and to an increase in the intensity of the  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) EPR signals. This heat treatment also led to an appearance of an additional signal of

$\text{Cr}^{5+}$  (3) (Fig. 4a, spectrum 4), with  $g$  factors ( $g_{\parallel} = 1.951 \pm 0.002$  and  $g_{\perp} = 1.999 \pm 0.002$ ) similar to those of the  $\text{Cr}^{5+}$  (3) signal for the vacuum pre-treated HS (1) sample (Table 2). Oxidation of the HS (2) sample in an  $\text{O}_2$  atmosphere at 773 K led to a full disappearance of the  $\text{Cr}^+$  EPR lines and to the appearance of a complex spectrum (Fig. 4b, spectrum 5) similar to that for the HS (1) sample pre-treated in vacuum (Fig. 3, spectrum 1). This complex spectrum belongs to the  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) centres, which are characterised by axially-symmetric  $g$  factors similar to those for the same  $\text{Cr}^{5+}$  centres in the HS (1) sample (Table 2). The reduction of the HS (2) sample with hydrogen at 773 K led to the full disappearance of all EPR lines (Fig. 4b, spectrum 6). Exposure to air at 300 K restored the initial  $\text{Cr}^+$  and  $\text{Cr}^{5+}$  EPR spectra (Fig. 4b, spectrum 7). Reoxidation in an  $\text{O}_2$  atmosphere at 773 K led to the full disappearance of  $\text{Cr}^+$  spectra and restored the well-resolved complex EPR spectrum (Fig. 4b, spectrum 8) similar to that of the HS (1) sample (Fig. 3, spectrum 1) and the HS (2) sample after the first oxidation (Fig. 4b, spectrum 5).

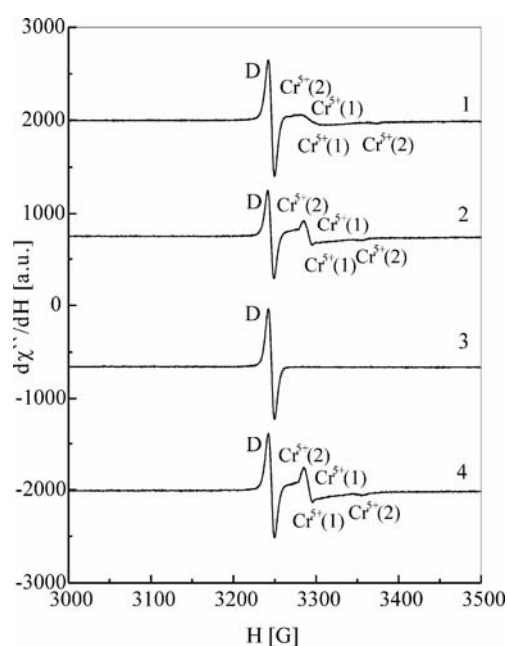


Fig. 5. Central region of the EPR spectra, recorded at 300 K, of the calcined LS (4) sample after heating at 773 K for 12 h: 1 – under vacuum ( $2 \times 10^{-7}$  mbar), 2, 4 – in oxidising atmosphere ( $\text{O}_2$ , 10 mbar), 3 – in a reducing atmosphere ( $\text{H}_2$ , 10 mbar)

The CrAPO-5 LS samples revealed redox properties similar to those of the HS samples. Figure 5 shows the changes in the EPR spectra of the LS (4) sample calcined and pre-treated in vacuum (spectrum 1), after oxidation in oxygen (spectra 2, 4) and after reduction in hydrogen (spectrum 3). The oxidation of the LS (4) sample led to an insignificant change in the linewidth of the  $\text{Cr}^{5+}$  (1) centres and in the  $g_{\parallel}$  value of the  $\text{Cr}^{5+}$  (2) centres (Fig. 5, spectrum 2). Hydrogen reduction of the LS (4) sample led to the full disappearance of  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) lines (Fig. 5, spectrum 3). Reoxidation in oxygen gave the same EPR spectra of  $\text{Cr}^{5+}$  (1) and  $\text{Cr}^{5+}$  (2) centres as after the first oxidation (Fig. 5, spectrum 4). A decrease in the linewidth of  $\text{Cr}^{5+}$  (1) centres and

anisotropy of the  $g$  factor for  $\text{Cr}^{5+}$  (2) centres in the LS (4) sample after oxidation may suggest partial healing of the structure under oxidative treatment [35], in the sense Cr incorporating into CrAPO-5 framework positions. The almost constant line intensity of coke radicals (Fig. 5, line D) observed for the LS (4) sample during redox, however, indicated that a considerable part of chromium still remained as an extra-framework species in the channels. This part made the complete removal of organic carbonaceous residuals impossible.

#### 4. Conclusions

Cr occurs in the HS samples mostly as  $\text{Cr}^{3+}$  in the octahedral form  $[\text{CrO}_4/2\text{L}_2]^-$ , as a framework species. A certain amount of  $\text{Cr}^{6+}$  and/or  $\text{Cr}^{5+}$ , seen with UV-Vis and/or EPR spectroscopy, seems to be either a framework species substituted for P or, more likely, a type of surface species anchored to the framework and not hindering diffusion and sorption in channels. In LS samples,  $\text{Cr}^{6+}$  and/or  $\text{Cr}^{5+}$  share to a distinctly higher extent, which most likely results in the clogging of pores.

In vacuum pre-treated calcined HS materials, Cr remains mostly as  $\text{Cr}^{3+}$  and two forms of  $\text{Cr}^{5+}$  appear: square pyramidal (five coordinated) chromyl groups and tetrahedrally coordinated  $\text{Cr}^{5+}$  centres. The latter may be an extra-framework species. In vacuum pre-treated calcined LS materials mainly tetrahedral extra-framework  $\text{Cr}^{5+}$  species occur, and  $\text{Cr}^{3+}$  exists in small amounts only. The LS samples also show a strong signal from carbon, which is extremely resistant against oxidation. Thus, the vacuum heat treatment of the calcined samples confirms the occurrence of  $\text{Cr}^{3+}$  in strongly prevailing amounts in the HS materials and indicates that only small amounts of  $\text{Cr}^{3+}$  exist in the LS materials. The formation of a small amount of  $\text{Cr}^{5+}$ , which does not hinder adsorption in the HS samples, may suggest that these ions can be substituted for P.

Oxidative and reductive treatments reveal reproducible redox properties of  $\text{Cr}^{5+}$  centres in square-pyramidal and tetrahedral coordinations in both HS and the LS calcined CrAPO-5 samples pre-treated in vacuum. These treatments do not considerably influence the EPR spectra of the  $\text{Cr}^{3+}$  ions in the samples. Results reveal a high stability of the  $\text{Cr}^{3+}$  ions, especially in HS CrAPO-5 materials, which can be justified only by framework incorporation.

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