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THE REDUCTION / OXIDATION BEHAVIOUR OF MnAPO-5 AS STUDIED BY ESR SPECTROSCOPY

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It is shown by ESR spectroscopy that Mn^{2+} ions in MnAPO-5 are oxidized to Mn^{3+} during calcination at $T \geqslant 475$ K. Mn^{2+} occupies variously distorted tetrahedral positions within the framework and in extra-lattice sites. Octahedrally coordinated Mn^{2+} presumably located in the channels becomes detectable after adsorption of water. The ESR spectra of reduced MnAPO-5 show line-narrowing due to spin exchange interactions. The material behaves reversible in redox cycles at temperatures near 500 K.

Keywords: $AlPO_4$-based molecular sieve, MnAPO-5, ESR-spectroscopy, redox chemistry, hydration/dehydration, Mn-location, Mn-coordination

1. Introduction

During the last few years, the family of $AlPO_4$-based molecular sieves has been considerably extended. Among the new materials are SAPOs, MeAPOs, MeAPSOs, ElAPOs, ElAPSOs and the MCM-type molecular sieves [1–3]. Some of them can be synthesized from gels containing transition metal ions such as Mn^{2+} or Co^{2+} and it is assumed that these cations are incorporated into tetrahedrally coordinated lattice positions during hydrothermal crystallization of the molecular sieves. In fact, data obtained by Goldfarb [4] using ^{31}P and ^{27}Al MAS-NMR-spectroscopy and ESR-spectroscopy for the characterization of MnAPO-5 suggest that at least part of the Mn^{2+}-cations occupy framework positions. However, it is proposed that there are also non-framework manganese cations in the channels of MnAPO-5 which presumably compensate for the negative charge of the framework. Such materials may have potential applications as catalysts for redox reactions. However, to the best of our knowledge reports on the redox behaviour of manganese cations in MeAPO molecular sieves have not yet been published.

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Therefore, we made an attempt to characterize the oxidation state of manganese cations in MnAPO-5 after treatment at different temperatures and in different atmospheres.

2. Experimental

MnAPO-5 was synthesized according to a method adopted from the patent literature [5]. The exact procedure was as follows: 70 g H_2O and 42 g H_3PO_4 (85 wt.%) are added to 24.1 g pseudo-boehmite (Condea, Pural SB) with stirring. To this mixture, 1.13 g $MnCl_2$-$4H_2O$ dissolved in 50 g H_2O are added dropwise under continuous stirring. After homogenizing for 30 minutes 28.4 g triethylamine are added. After homogenizing for an additional 30 minutes, the mixture is filled in a stainless steel autoclave and heated for 24 hours at 437 K under agitation to achieve crystallization. The crystalline product is thoroughly washed with distilled water and dried overnight at 393 K in air. The crystallinity and phase purity of the synthesized sample was checked by X-ray powder diffraction. The $(Al + P)/Mn$ ratio of the material is 140.

As-synthesized MnAPO-5 samples were calcined in a flow of dry O_2 in steps of 100 K in the temperature range 375–875 K for 16 h each. The material obtained after calcination at 875 K was subsequently reduced for 16 h in flowing dry H_2 at 326, 373, 421, 450, 473, 573, 675, and 775 K. After reduction at 775 K, the sample was subjected to a second oxidation sequence under conditions identical to those mentioned above. Water adsorption was carried out by exposing MnAPO-5 samples to an O_2 flow saturated with 2.7×10^3 Pa H_2O vapour for 2 h at room temperature. The samples were kept under oxygen-free argon in 4 mm (o.d.) pyrex ESR-tubes for the measurements.

ESR measurements were performed on a Varian E-Line spectrometer operating at X-band. Spectra were recorded at either room temperature or 93 K. DPPH (diphenyl picryl hydrazine) was used as an external standard.

3. Results and discussion

Mn^{2+} (d^5) has a $^6S_{5/2}$ ground state. Its ESR spectrum is thus readily observed, the g-values being isotropic and close to the free-spin value of 2.0023 [6]. In contrast, ESR signals for Mn^{3+} (d^4) ions remain undetectable at room temperature (especially in tetrahedral and distorted octahedral environment) due to high relaxation rates and great zero-field splittings.

As-synthesized MnAPO-5 was a white powder and gave an ESR signal (fig. 1a) at $g = 2.027$ showing six resolved hyperfine lines ($I = 5/2$) with a 95 G splitting which corresponds to octahedral Mn^{2+} [6,7]. Upon calcination in a flow of dry O_2, the colour of the material changes with increasing calcination temperature

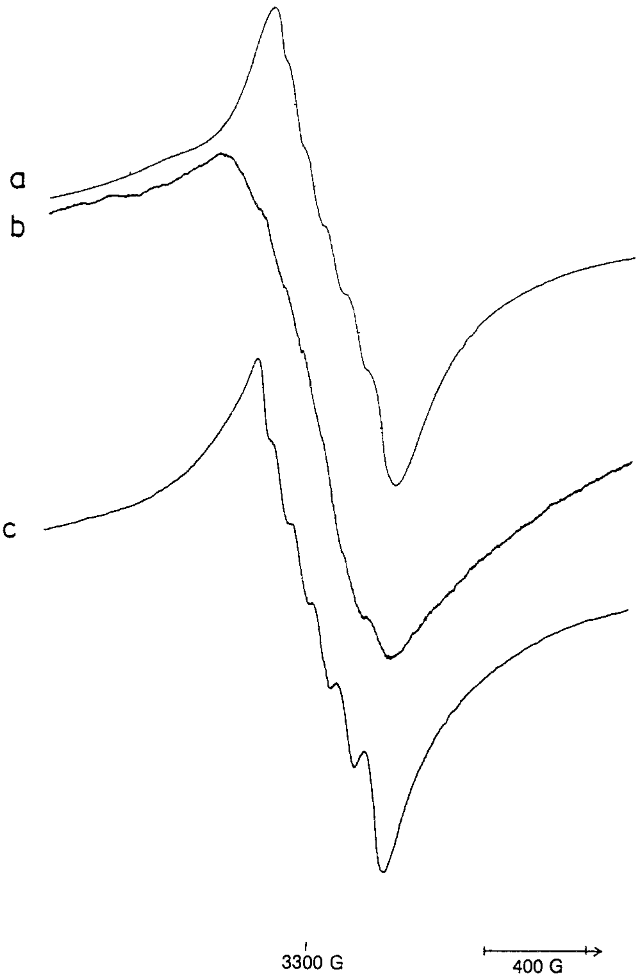

Fig. 1. ESR spectra (measured at room temperature) of as-synthesized and calcined MnAPO-5: (a) as-synthesized; (b) MnAPO-5 after calcination at 875 K in a flow of dry O_2; (c) calcined MnAPO-5 after exposure to 2.7×10^3 Pa H_2O vapour at room temperature.

from white through brownish (probably due to thermal decomposition of the template) to violet. The corresponding ESR signal after calcination at 875 K (see fig. 1b) is broadened and does not show hyperfine splitting even when measured at 93 K. Its intensity is reduced to approximately one third that of the as-synthesized sample. This decrease in signal intensity has to be attributed to a partial oxidation of Mn^{2+} to non-detectable Mn^{3+}. With no other signal appearing even at 93 K, an oxidation to Mn^{4+} can be ruled out. Goldfarb [4] reported evidence for the existence of non-structural in addition to structural (tetrahedrally coordinated) manganese ions. The non-structural manganese ions are supposed to be located in the channels of the MnAPO-5 structure and to probably compensate for the negative framework charge induced by the structural manganese. It is tempting to assume that in the absence of water non-structural Mn^{2+} ions (probably as $[Mn(OH)]^+$ complexes for reasons of local charge compensation) build up distorted tetrahedral coordination spheres with oxygen atoms of the framework. The broad ESR-signal of fig. 1b is therefore assigned as a superposition of at least two unresolved signals of structural and non-structural Mn^{2+} in variously distorted tetrahedral oxygen environments. It should be noted that Goldfarb [4] also observed a loss of hyperfine structure on calcination/dehydration of her MnAPO-5 samples. In contrast to the present results, however, she found a significant line narrowing on calcination. This discrepancy is most probably due to the much lower Mn content in our sample having a $(Al + P)/Mn$ ratio of 140 as compared to 21 and 67 of Goldfarb's samples. Spin exchange interactions were assumed to be responsible for this line narrowing, which may not occur to a significant extent in our sample at least when a certain percentage of the Mn is present as Mn^{3+}in the calcined state.

Readsorption of water at room temperature led to a colour change from violet to pale pink and the ESR signal became narrower with the hyperfine splitting being resolved (fig. 1c). Colour and ESR signal were identical when a MnAPO-5 sample was calcined in a flow of moist oxygen. Changes in colour and ESR signal were entirely reversible when hydration/dehydration cycles were carried out. The ESR signal observed in the hydrated state (fig. 1c) is therefore believed to represent a superposition of a signal due to tetrahedrally coordinated framework Mn^{2+} and a signal of octahedrally coordinated non-structural Mn^{2+} (most likely $Mn^{2+}(H_2O)_6$). The latter species gives rise to the observation of the six hyperfine lines with $A_{iso} = 95$ G.

No changes in colour or ESR signal were observed, when the samples obtained after calcination at 875 K in dry or moist O_2 were exposed to a flow of dry H_2 at $T \leqslant 450$ K. However, the powder turned white when the reduction temperature reached 475 K and a comparably narrow and intense ESR signal was observed at $g = 2.008$ (fig. 2a). Mn^{3+} ions present in the calcined sample are reduced to Mn^{2+} under these conditions, thus leading to an intense signal. The larger concentration of extraframework Mn^{2+} in the channel system may now also lead to more pronounced spin exchange interactions [8] and thus account for the narrow line width.

When water is readsorbed on the reduced sample, the original ESR signal is resolved into three lines at room temperature (fig. 2b). The six hyperfine lines with $A_{iso} = 95$ G of octahedrally coordinated Mn^{2+} become clearly resolved when the spectrum is measured at 93 K (fig. 2c). As in the case of the hydrated calcined sample (fig. 1c) we interpret this spectrum as a superposition of two signals from tetrahedral framework Mn^{2+} and from octahedrally coordinated extralattice Mn^{2+} aquo complexes.

Oxidation/reduction cycles showed the reversibility of these processes. Exposure of a reduced sample to flowing O_2 at $T \leqslant 375$ K did not lead to any colour change of the white powder and the narrow ESR signal characteristic of the

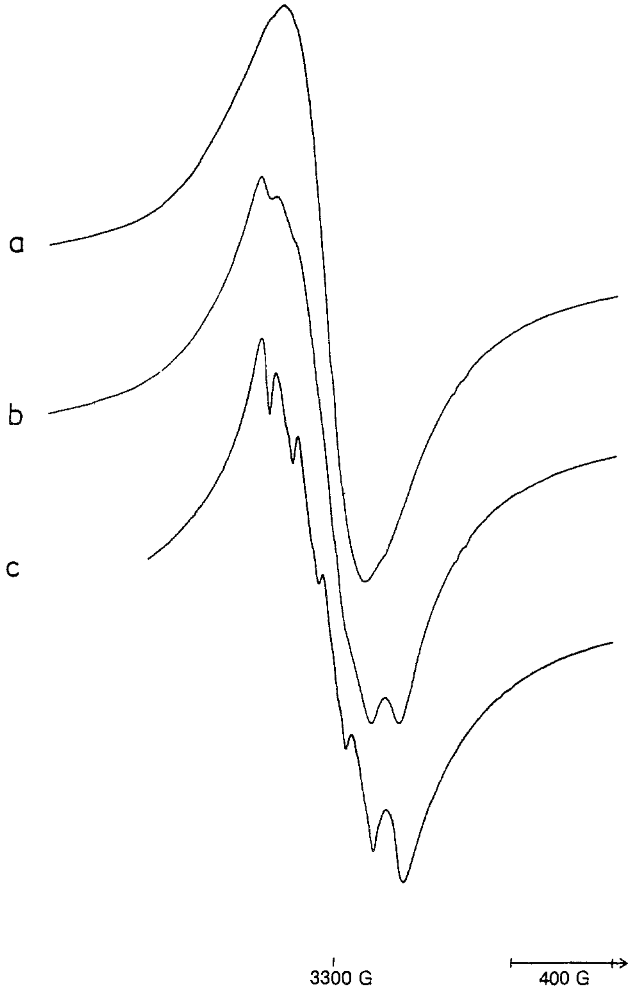

Fig. 2. ESR spectra of reduced MnAPO-5: (a) MnAPO-5 (calcined at 875 K) after reduction at 475 K in flowing H_2; (b) sample (a) after exposure to 2.7×10^3 Pa H_2O vapour at room temperature (measured at 297 K); (c) same as (b), measured 93 K.

reduced state (fig. 2a) was observed. The colour turned to violet on oxidation at $T \geqslant 475$ K and the broad ESR signal was measured which was also found for the calcined sample (fig. 1b). Hyperfine splitting became evident when this reoxidized material was rehydrated.

4. Conclusions

The present ESR study of a MnAPO-5 sample with low Mn concentration (ratio $(Al + P)/Mn = 140$) provides evidence for the existence of structural as well as non-structural Mn^{2+}. In contrast to Goldfarb [4], no irreversible changes involving migration of Mn^{2+} out of the framework during high temperature treatment of samples containing greater Mn concentrations could be detected. O_2 treatment led to partial oxidation of presumably non-structural Mn^{2+} to Mn^{3+}. Reduction/oxidation cycles were reversible as were also hydration/dehydration cycles of both oxidized and reduced materials. The results emphasize the potential usefulness of MnAPO-5 as a catalyst for redox reactions.

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