Synthesis and chemistry of chromium in CrAPO-5 molecular sieves

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CrAPO-5 molecular sieves were synthesized hydrothermally starting with different Cr precursors and Cr and template contents. The behavior of Cr was investigated spectroscopically by diffuse reflectance spectroscopy (d.r.s.) and electron spin resonance (e.s.r.). In the gels, Cr^{3+} and Cr^{6+} are present as, respectively, octahedral $Cr(H_2O)_6^{3+}$ and mainly dichromate. Both ions are in the liquid phase of the gels. In all as-synthesized CrAPO-5's, Cr^{3+} is octahedrally coordinated to six oxygen ligands. The corresponding e.s.r. spectra show a broad isotropic signal centered around 1.97, following the Curie–Weiss law. This behavior is comparable with Cr^{3+} impregnated on AlPO-5 and assigned to hexa-aquo Cr^{3+} ions. Upon calcination, this signal decreases in intensity, a new sharp signal of Cr^{5+} is formed, and, in d.r.s., Cr^{6+} is formed at the expense of Cr^{3+}. However, the broad e.s.r. signal of Cr^{3+} does not follow the Curie–Weiss law and is due to Cr^{3+} clusters. Cr^{6+} and Cr^{5+} are easily reduced with CO to octahedral Cr^{3+} and octahedral and tetrahedral Cr^{2+}, whereas recalcination reestablishes the original Cr^{6+} and Cr^{5+} species. All these results support the idea that Cr^{3+} is not incorporated into the framework, but is present as octahedral ions at the surface of the AlPO-5 crystals.

Keywords: CrAPO-5; isomorphous substitution; microporous aluminophosphates; synthesis; d.r.s.; e.s.r.

INTRODUCTION

Metal-substituted aluminophosphate molecular sieves, denoted with the acronym MeAPO's,[1] have received extensive attention from researchers working in the area of molecular sieve science and shape-selective catalysis. Isomorphous substitution of metal ions (Me) in inorganic solids, such as AlPO-5, is an important reaction, which allows control of acidity and cation-exchange capacity.[2] Isomorphic substitution of Al^{3+} and/or P^{5+} has been claimed for a variety of elements such as Ga, Ge, B, As, Si, Ti, Fe, and Co.[3]

In the patent literature,[4] the synthesis of CrAPO-5 has been reported, but the question remains if Cr^{3+} substitutes for Al^{3+} in the framework and to what extent. Isomorphous substitution requires tetrahedral Cr^{3+}, which is difficult to obtain. This is evidenced by the scarcity of tetrahedral Cr^{3+} complexes[5] and the absence of reported inorganic structures with tetrahedral Cr^{3+}.[6] Recently, Rajic et al.[7] studied the possibility of incorporation of Cr^{3+} into a chabazite-type aluminophosphate lattice (SAPO-34), but concluded that no Cr^{3+} was incorporated into the framework. Up to now, no paper has been devoted to a detailed spectroscopic study of this substitution reaction and of the chemistry of CrAPO-n's.

This is the starting point of this research work. We have synthesized series of CrAPO-5 molecular sieves with increasing Cr content and studied the effect of synthesis time, synthesis temperature, and Cr sources. Both as-synthesized and calcined samples were spectroscopically investigated by diffuse reflectance spectroscopy (d.r.s.) and electron spin resonance (e.s.r.). The wet precursor gels were investigated with d.r.s. and the coordination chemistry of Cr was unraveled after calcination, CO reduction, and recalcination.

EXPERIMENTAL

Synthesis procedure

CrAPO-5 was synthesized following a modified method of Flanigen et al.[4] A chromium source was added to a solution of H_3PO_4 (85 wt% sol. in water; *pro* analyze; Janssen Chimica) and bidistilled water under stirring until complete dissolution. Pseudo-boehmite (Capatal alumina; 70% Al_2O_3 and 30% H_2O; Vista) was added under stirring, followed by the dropwise addition of triethylamine (99%; Janssen Chimica). To control the exothermicity of the reaction, all the reagentia were mixed in an ice bath at 273 K. The obtained homogeneous gel was stirred for 1 h and then transferred to a Teflon bottle of 50 ml, which was inserted in a stainless-steel autoclave. The synthesis was performed statically at 423 or 448 K. After synthesis, the light green material was washed five times with distilled water and dried at 333 K.

Four series of CrAPO-5 samples were prepared:

Table 1 Overview of the notations, synthesis conditions, and gel compositions of the samples

Sample name	Gel composition: 0.75 $R \cdot (Cr_xAl_yP_z)O_4 \cdot 20\ H_2O$, with R the template molecule triethylamine			pH of the precursor gel	Synthesis temperature (K)	Synthesis time (h)
	x	y	z			
CrA(III)0.00	0.00	1.00	1.00	2.35	423	168
CrA(III)0.002	0.002	0.998	1.00	2.34	423	168
CrA(III)0.004	0.004	0.996	1.00	2.34	423	168
CrA(III)0.02	0.02	0.98	1.00	2.30	423	168
CrA(III)0.04	0.04	0.96	1.00	2.24	423	168
CrA(III)0.08	0.08	0.92	1.00	1.65	423	168
CrC(III)1	0.02	0.98	1.00	2.30	423	1
CrC(III)2	0.02	0.98	1.00	2.31	423	2
CrC(III)5	0.02	0.98	1.00	2.31	423	5
CrC(III)15	0.02	0.98	1.00	2.30	423	15
CrC(III)30	0.02	0.98	1.00	2.30	423	30
CrC(III)72	0.02	0.98	1.00	2.29	423	72
CrC(III)168	0.02	0.98	1.00	2.30	423	168
CrB(III)0.01	0.01	0.99	1.00	2.32	448	168
CrB(III)0.02	0.02	0.98	1.00	2.30	448	168
Cr(VI)	0.02	1.00	0.98	2.15	423	168

CrA(III) samples, CrB(III) samples, CrC(III) samples, and a Cr(VI) sample. The CrA(III), CrB(III), and CrC(III) samples were prepared with $Cr(NO_3)_3 \cdot 9H_2O$ (*pro* analyze; UCB), whereas the Cr(VI) sample was synthesized with CrO_3 (*pro* analyze, UCB). The synthesis conditions, notations, and gel compositions of all these samples are summarized in *Table 1*. The CrA(III) samples were autoclaved for 7 d at 423 K, whereas the CrB(III) samples were autoclaved at 448 K. The CrC(III) samples were synthesized with a synthesis time in the range 1–168 h at 423 K and the Cr(VI) sample was autoclaved during 7 d at 423 K.

The gels used for the centrifugation procedure (see further) were prepared in the same way as were the gels of the CrA(III) samples: Only the template content (with R = 0.50, 0.75, and 1.25) and the Cr source [$Cr(NO_3)_3 \cdot 9\ H_2O$ and CrO_3] were varied. Reference samples were prepared by impregnation of a $Cr(NO_3)_3 \cdot 9\ H_2O$ solution on pure AlPO-5 (Cr^{3+}/AlPO-5) and mixing of Cr_2O_3 with pure AlPO-5 (Cr_2O_3/AlPO-5).

Pretreatments and techniques

Powder X-ray diffraction (XRD) patterns of the as-synthesized, calcined, and recalcined samples were recorded with an automated Siemens diffractometer, equipped with a Kristalloflex K710 röntgengenerator and a position-sensitive detector of Inel. The as-synthesized samples were granulated and the size fraction 0.25–0.40 mm was loaded in a quartz flow cell with suprasil windows for diffuse reflectance (d.r.s.) and a side arm for electron spin resonance (e.s.r) measurements. E.s.r. and d.r.s. spectra were taken of the as-synthesized and calcined samples and of some reduced samples. The d.r.s. spectra were measured with a u.v.-vis-NIR Cary 5 spectrometer in the range 200–2200 nm against a halon white standard. Some spectra were converted to the Kubelka–

Munk function and plotted as a function of wavenumbers. E.s.r. spectra were taken at 120 and 300 K using a Bruker ER 200 D-SRC instrument in X-band at a microwave power of 200 μW with a double rectangular TE104 mode cavity. Temperature-dependent measurements were done on a Bruker ESP300E equipment in X-band at the same microwave power between 370 and 120 K. Calcination and recalcination (after reduction) were performed at 823 K during 5 h with an O_2 flowrate of 3600 ml/h, whereas reduction was done during 30 min with a CO flow rate of 1800 ml/h at 623 K. D.r.s. spectra were also taken from the wet precursor gels as such and after successive centrifugations (20 min, 5000 rounds/min). *Vacuo* pretreatments were done at 2×10^{-3} Pa at 298 and 473 K overnight.

RESULTS

Spectroscopic characterization of CrAPO-5's as function of the Cr content, synthesis temperature, and the Cr precursor molecule

Figure 1 shows the d.r.s. spectra of CrA(III) samples (see *Table 1*) with increasing Cr content. The spectra of the CrB(III) samples are the same and will not be shown. All the spectra contain two typical bands of octahedral Cr^{3+} at 15,900 and 21,800 cm^{-1},[5,6] which increase in intensity with increasing Cr content. These bands can be assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ (v_1) and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (v_2), respectively. The third band [$^4A_{2g} \rightarrow {}^4T_{1g}(P)$] of octahedral Cr^{3+} occurs around 33,000 cm^{-1}, but is masked by absorptions of the support. The 15,900 cm^{-1} band has two weak shoulders, which are spin-forbidden transitions ($^4A_{2g} \rightarrow {}^2E_g$ and $^4A_{2g} \rightarrow {}^2T_{1g}$).[5,6] In *Figure 2*, the intensities of v_1 are plotted vs. Cr content. There is a relatively good linear relation, suggesting the presence of only one Cr^{3+} species. Replacing the Cr^{3+} salt by CrO_3 in the synthesis mixture results also in the formation of a
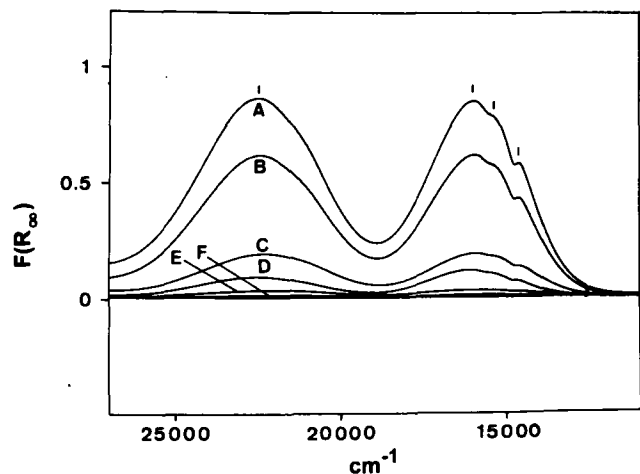
Figure 1 DRS spectra of as-synthesized CrAPO-5 molecular sieves with increasing Cr content: $0.75\, R \cdot (Cr_xAl_yP_z)O_4 \cdot 20\, H_2O$ with x = (A) 0.08, (B) 0.04, (C) 0.02, (D) 0.004, (E) 0.002, and (F) 0.0.

of octahedral Cr^{3+}, whatever the synthesis time. The major change occurs in the n.i.r. region: The overtone and combination bands of water decrease with synthesis time or with increasing crystallinity; overtones of C–H vibrations of the template increase in intensity and are especially visible in the crystalline product.

Spectroscopic analysis of the wet precursor gels

In another series of experiments, the influence of the nature of the Cr precursor and the template content (R) on the retention of Cr in the gel was investigated. The freshly prepared CrA(III) gels with different R contents have a light blue color. *Figure 4* shows the d.r.s. spectra of the Cr(III)–AlPO-5 gels with R = 0.75 before and after centrifugation. The d.r.s. spectra of the gels with other R values are exactly the same. The spectra are characterized by

green material [Cr(VI) sample] with spectra identical to those of *Figure 1*. Therefore, Cr^{6+} is reduced to Cr^{3+} during synthesis.

Time dependence of the synthesis

With the CrC(III) samples, the synthesis was followed as a function of time up to 7 d by taking samples after 1, 2, 5, 15, 30, 72, and 168 h. Some XRD diffractograms are shown in *Figure 3*. The formation of crystalline material starts after 2 h. The only XRD-detectable product after 5 h synthesis is AlPO-H$_3$ (*Figure 3B*). After 15 h, CrAPO-5 could be detected (*Figure 3C*) and longer synthesis times result in increasing amounts of CrAPO-5. After 72 h, no other crystalline phase than CrAPO-5 could be monitored and a highly crystalline material is obtained after 7 d (*Figure 3D*). The XRD pattern of the calcined CrAPO-5 given in *Figure 3E* shows that the material is thermally stable.

The corresponding d.r.s. spectra have characteristic absorption bands of octahedral Cr^{3+} in the d–d region at 629 and 459 nm (15,900 and 21,800 cm^{-1})
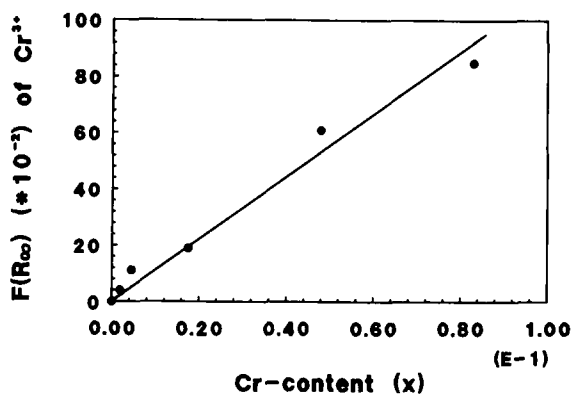

Figure 2 Intensity of the first allowed d–d transition ($^4A_{2g} \rightarrow ^4T_{2g}$) vs. the Cr content of CrAPO-5 molecular sieves.
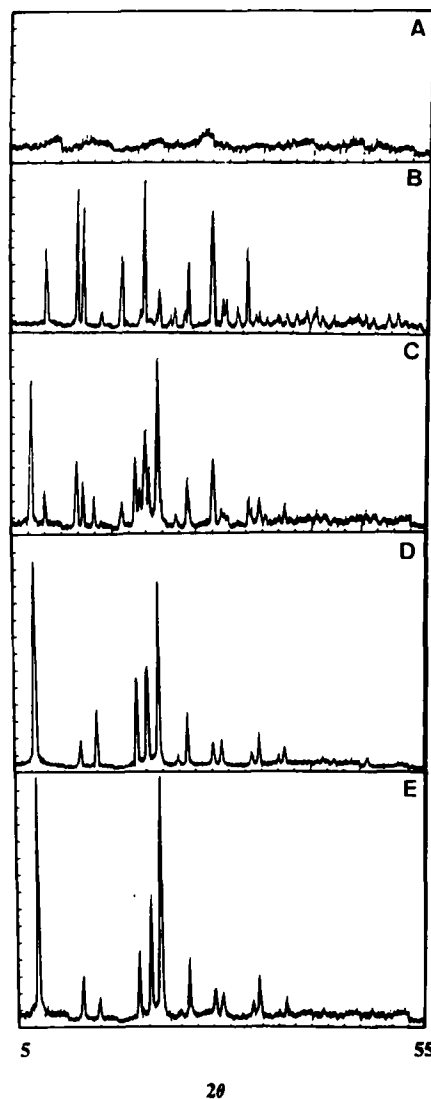

Figure 3 Synthesis of CrAPO-5 as function of time: Evolution of the XRD diffractograms: (A) 1 and 2 h; (B) 5 h; (C) 30 h; (D) 168 h; (E) calcined sample of (D).
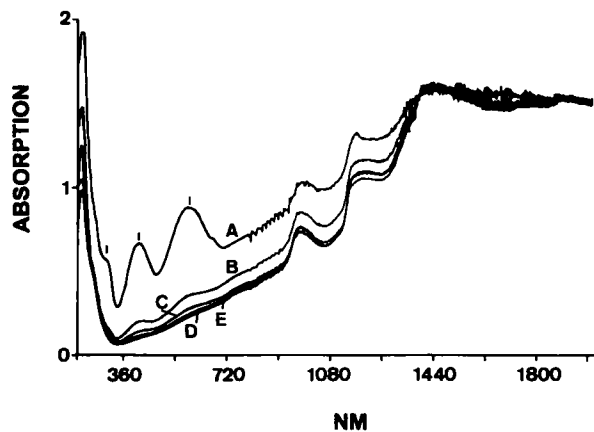
Figure 4 D.r.s. spectra of the Cr(III) gel with R = 1.25: (A) as such; (B) after centrifugation; (C) after 2× centrifugation; (D) after 3× centrifugation; (E) after 4× centrifugation.

three bands at 585, 405, and 297 nm (17,100, 24,700, and 33,700 cm^{-1}), typical for octahedral $Cr^{3+}(H_2O)_6$ complexes.[5,6] After centrifugation, the Cr^{3+} content of the solid decreases and finally disappears almost completely after four washings and centrifugations. This shows that Cr^{3+} is not incorporated into the solid phase, but can be washed off.

The freshly prepared Cr(VI) gels are orange-yellow and the corresponding d.r.s. spectra are shown in *Figure 5*. These spectra are dominated by three intense bands: 444, 370, and 275 nm (22,500, 27,000, and 36,400 cm^{-1}). These bands are typical charge transfers of the type O → Cr^{6+} (Ref. 5) and can be assigned as follows: the symmetry forbidden $1t_1$ → $2e$ (22,500 cm^{-1}) and two allowed transitions $1t_1$ → $2e$ (27,000 cm^{-1}) and $6t_2$ → $2e$ (36,400 cm^{-1}).[8] The 22,500 cm^{-1} band is typically for dichromate species in solution (but absent in chromates).[9] Thus, under the pH conditions of the gel preparation (pH at around 2), Cr is present mainly as dichromate. By centrifugation, almost all Cr is removed from the gel, independently of the Cr precursor and template content. Therefore, there exists no or only a weak interaction between dichromate and the molecular
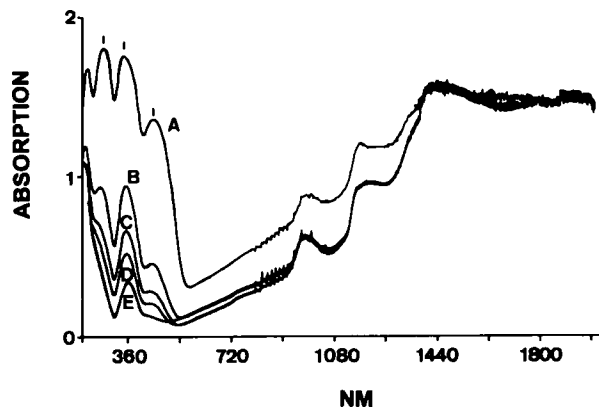

Figure 5 D.r.s. spectra of the Cr(VI) gel with R = 0.75: (A) as such; (B) after centrifugation; (C) after 2× centrifugation; (D) after 3× centrifugation; (E) after 4× centrifugation.
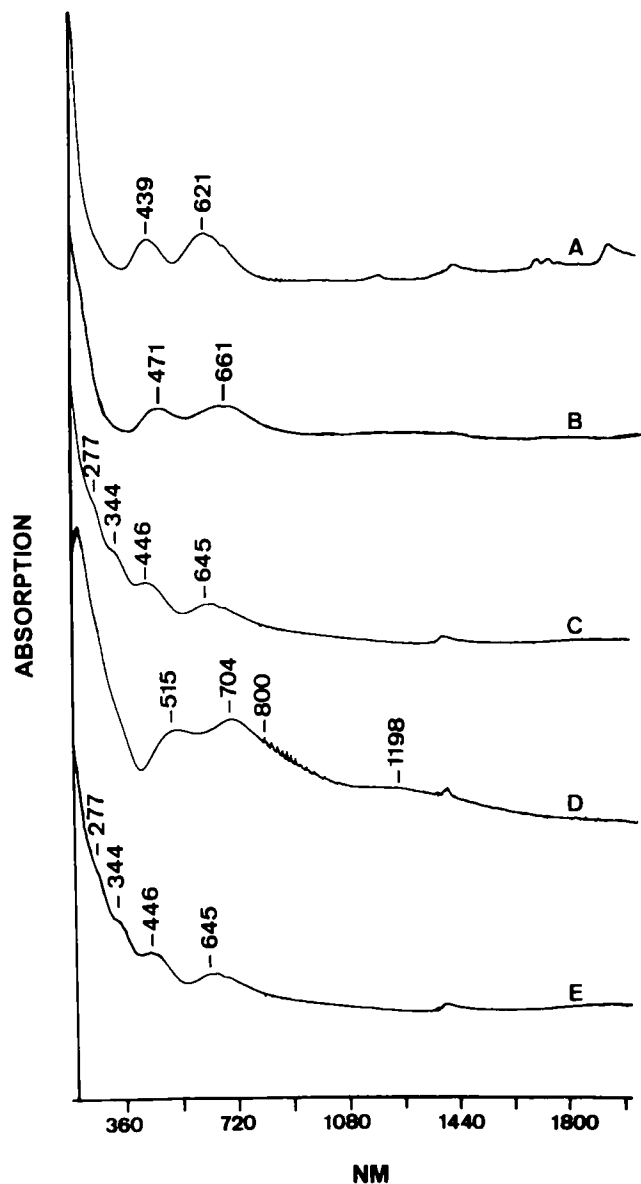

Figure 6 D.r.s. spectra of CrA(III)0.02: (A) as such; (B) after vacuo pretreatment; (C) after calcination; (D) after reduction; (E) recalcination.

sieve gel. Furthermore, the 22,500 cm^{-1} band can be more fully eliminated by the centrifugation procedure than can the two other bands (*Figure 5*). This suggests the presence of dichromate and chromate, the latter interacting more strongly with the gel.

Coordination and chemistry of Cr

Figures 6 and *7* show, respectively, d.r.s. and e.s.r. spectra of CrA(III)0.02, as such, after vacuo pretreatment, calcination, CO reduction, and recalcination. The e.s.r. spectrum of the as-synthesized CrAPO-5 is dominated by an isotropic signal with g = 1.97 and ppw (= peak-to-peak width) = 700 G and a weak, broad signal around g = 4.3. The total intensity follows the Curie–Weiss law. This behavior is comparable with that of Cr^{3+} impregnated AlPO-5. The
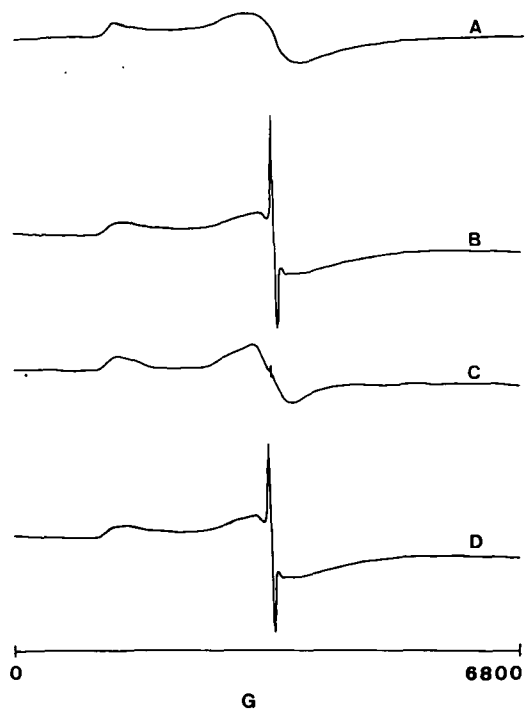
Figure 7 E.s.r. spectra of CrA(III)0.02 (at 300 K): (A) as such and after *vacuo* pretreatment; (B) after calcination; (C) after CO reduction; (D) after recalcination.

d.r.s. spectra show the typical d–d transitions of octahedral Cr^{3+}.

Vacuum pretreatment of the sample at 20°C shifts the d–d transitions of octahedral Cr^{3+} to 638 nm (15,700 cm^{-1}) and 454 nm (22,000 cm^{-1}). At 200°C, these bands shift to 661 nm (14,900 cm^{-1}) and 471 nm (21,100 cm^{-1}), but no new absorption bands at the low energy of tetrahedral Cr^{3+} are observed. The e.s.r. spectra are the same as after synthesis.

After calcination, the color of the sample turns to yellow-green and both e.s.r. and d.r.s. spectra are totally changed. Two new bands in the u.v. appear at 344 and 277 nm (29,100 and 36,100 cm^{-1}) at the expense of the two d–d transitions of Cr^{3+}. These u.v. bands are the two charge-transfer transitions O → Cr^{6+} (d^0). Thus, part of the Cr^{3+} is oxidized to a chromatelike species. The e.s.r. spectra show a new strong and narrow signal with axial symmetry ($g_\perp$ = 1.99 and $g_\parallel$ = 1.90; ppw = 45 G) superimposed on the broad g = 1.97 signal. This signal is ascribed to Cr^{5+},[10,11] and the intensity follows the Curie–Weiss law. The d.r.s. bands of Cr^{3+} are shifted to, respectively, 645 and 446 nm (15,500 and 22,400 cm^{-1}). The intensity of the corresponding e.s.r. spectrum (*Figure 7*) does not follow the Curie–Weiss law. This is mainly due to the broadening of the g = 1.97 signal upon decrease of temperature. Also, the g = 4.3 signal is broadened by the calcination treatment on its high field side, but otherwise not much affected.

After CO reduction, the sample is blue-purple, almost all Cr^{5+} has disappeared, and the e.s.r. spectrum is nearly the same as before calcination. The d.r.s. spectrum is dominated by two bands at 704 and

515 nm (14,200 and 19,400 cm^{-1}), the former asymmetric at lower wavelength (800 nm or 12,500 cm^{-1}). Also, a weak and broad absorption at 1198 nm (8350 cm^{-1}) is visible. The former two bands can be ascribed to (distorted) octahedral Cr^{3+}. The asymmetric shoulder is due to octahedral Cr^{2+}, because octahedral complexes of a high spin $3d^4$, such as Cr^{2+}, show a single spin-allowed d–d transition in that region: $^5E_g \rightarrow {}^5T_{2g}$.[12] The broad and weak band at 1198 nm can be attributed to (distorted) tetrahedral Cr^{2+} complexes.[5] Thus, Cr^{6+} and Cr^{5+} are reduced to Cr^{3+} and minor amounts of Cr^{2+}. Recalcination gives the same spectra as after the first calcination and the color of the sample turns to yellow-green.

DISCUSSION

Chromium in CrAPO-5

In the gels, Cr^{3+} is present as an octahedral aquocomplex, while Cr^{6+} is mainly a dichromatelike species. This chromium has, irrespective of synthesis procedure and Cr precursors, only a small affinity for the gel components and is mainly present in the liquid phase.

Our main goal is to see if Cr can be incorporated into the framework of AlPO-5. The criteria for structural Cr are (1) tetrahedral coordination, (2) a ligand field strength typically for an oxygen environment, and (3) a linear increase of band intensities with the Cr content.

The d.r.s. spectra of the as-synthesized (green) materials are, irrespective of the synthesis time and procedure, typical for octahedral Cr^{3+} and, therefore, the first criterion for structural Cr is not fulfilled. One can use the centers of the band system to calculate the octahedral ligand field strength and the ligand field parameter B with standard procedures.[5,13] The results are shown in *Table 2* and compared with Cr^{3+} impregnated AlPO-5, a physical mixture of Cr_2O_3 and AlPO-5 and literature data of octahedral Cr^{3+} with an oxygen environment. These data show that the ligand field strength of Cr^{3+} in CrAPO-5 is somewhat lower, but similar to those of reference compounds with Cr^{3+} surrounded by six oxygen ligands and, therefore, the second criterion is fulfilled. From *Figure 2*, it follows that the third criterion is obeyed. In the as-synthesized samples, e.s.r. also shows the presence of octahedral hexa-aquo Cr^{3+} ions, which have the same behavior as that of Cr^{3+} ions impregnated on pure AlPO-5.

Thus, during synthesis, there is no indication for a transformation of the octahedral coordination to a tetrahedral one, with an expected absorption around 7500 cm^{-1} [10 Dq(tetrahedral) = (4/9) × 10Dq(octahedral)]. Also, the octahedral Cr^{3+} cannot be transformed to tetrahedral Cr^{3+} by *vacuum* pretreatment. The latter treatment induces a slight shift of the octahedral bands to lower energy. The resulting reduction in ligand field strength (*Table 2*) indicates the change of the environment of the CrO_6 moiety. We have no unambiguous experimental evidence to propose an octahedral lattice Cr^{3+} species. Also, in

Table 2 Ligand field strength, 10 Dq, and Racah's interelectronic repulsion parameter, B, for Cr^{3+} in octahedral environment of oxygen atoms

Compound	10 Dq (cm^{-1})	B	Refs.
As-synthesized CrAPO-5	15,900	577	This work
Vacuum-pretreated CrAPO-5 20°C	15,700	631	This work
Vacuum-pretreated CrAPO-5 200°C	14,900	629	This work
Cr^{3+} impregnated AlPO-5	17,100	712	This work
Mixture of Cr_2O_3 and AlPO-5	16,800	423	This work
α-Al_2O_3 (Cr^{3+})	18,000	643	6
α-Cr_2O_3 (Cr^{3+})	16,650	624	6
Cr_2O_3	16,600	468	6
$MgAl_2O_4$ (Cr^{3+})	18,000	670	6
$MgCr_2O_4$	17,150	633	6
$YCrO_3$	16,450	542	6
$LiCrO_2$	17,300	615	6

dehydrated pure AlPO-5, no octahedral Al^{3+} can be found by n.m.r.

In summary, our results prove that Cr^{3+} is octahedrally coordinated in the initial gel, during synthesis and after synthesis. The question arises why there is no tendency for Cr^{3+} to change to the tetrahedral coordination, necessary for isomorphous substitution in the AlPO-5 molecular sieves. A strong argument can be found in the crystal field stabilization energy (CFSE) of octahedral (224.5 kJ/mol) vs. tetrahedral Cr^{3+} (66.9 kJ/mol).[14] This suggests that a d^3 ion, like Cr^{3+}, has a too strong preference for the octahedral relative to the tetrahedral coordination[15] to be forced in tetrahedral coordination under synthesis conditions.

Chemistry of CrAPO-5

The spectral changes upon calcination are (1) the appearance of two new bands in d.r.s. which are typically for Cr^{6+}; (2) the appearance of a new species, Cr^{5+}, in e.s.r; (3) the shifts of the Cr^{3+} bands in d.r.s. with respect to as-synthesized CrAPO-5; and (4) the nondependence of the 1.97 signal on the Curie–Weiss law. Thus, the oxidation of Cr^{3+} is not complete. Reduction with CO at 623 K is easy with formation of Cr^{3+} and some Cr^{2+}. Oxidation regenerates the initial calcined state. This behavior of CrAPO-5 upon calcination and CO reduction is similar to that of Cr supported on amorphous supports.[8,16]

Cr^{5+} can only be detected in e.s.r. by its axial symmetric signal around $g = 1.97$. The signal can be reversible regenerated by successive calcinations and reduction and the intensity follows the Curie–Weiss law. This signal is attributed to isolated Cr^{5+} and has typical line widths of Cr^{5+} on amorphous supports (γ signal).[10,11] However, the distinction between lattice and extralattice Cr^{5+} cannot be made.

The coordination of Cr^{3+} can be evaluated by d.r.s. and e.s.r. The broad $g = 1.97$ signal in e.s.r. can be assigned to Cr_2O_3 clusters. Although the Neél temperature of α-Cr_2O_3 is 307 K,[17] mostly no clear Neél temperature is observed for supported Cr clusters, indicating amorphous clusters of different particle size. The broadening of the signal with decreasing temperature suggests the presence of Cr^{3+} ions

strongly interacting in a dispersed Cr_2O_3 phase. Thus, the observation of this signal indicates small clusters with properties that deviate from bulk Cr_2O_3 properties, a situation not uncommon for supported metallic and oxidic particles (β-signal on amorphous supports).[10,11,16] The shifts of the octahedral d.r.s. bands of Cr^{3+}, with respect to the as-synthesized CrAPO-5, support this view. Therefore, these signals are due to nonincorporated octahedral Cr^{3+}.

Finally, the $g = 4.3$ signal must be addressed. The pure AlPO-5 also has this absorption, which must be due to Fe^{3+} impurities of the Al source. Thus, pseudotetrahedral Fe^{3+} is the usual assignment, but in view of the work of Nakamura et al.,[18] lattice-substituted Cr^{3+} cannot be excluded. Also, Mosser et al.[19] proved the incorporation of pseudo-octahedral Cr^{3+} in kaolinite, which gives a $g = 4.3$ signal in e.s.r. Furthermore, in the extensive e.s.r. literature on Cr-supported catalysts, a broad absorption in the range $g = 3$–4.5 is reported (δ phase), which is attributed to isolated Cr^{3+}.[16,20,21] Such isolated Cr^{3+} is in (pseudo-)octahedral coordination and located on the surface. Nevertheless, the $g = 4.3$ signal can only be due to pseudotetrahedral Fe^{3+} or pseudo-octahedral Cr^{3+} and is present in small quantities. If it is due to pseudo-octahedral Cr^{3+}, this Cr must be located at the surface, because no octahedral Al sites are available for Cr in dehydrated AlPO-5.

In summary, our results clearly show the following:

1. The affinity of the Cr-ions for the gel is small.
2. No tetrahedral Cr^{3+} can be found.
3. There is spectroscopic resemblance between Cr^{3+} impregnated AlPO-5 and CrAPO-5.
4. The redox chemistry of Cr in CrAPO-5 is similar to that of Cr-supported catalysts.

All this supports the idea of nonincorporation of Cr into the lattice of AlPO-5.

CONCLUSIONS

In the gels of CrAPO-5 molecular sieves, Cr is present as an octahedral Cr–aquo complex (Cr^{3+}) or dichromate (Cr^{6+}). These ions are present in the liquid phase of the gel and can be easily washed off. During

and after synthesis, Cr is present as Cr^{3+} in octahedral coordination to oxygens and this Cr^{3+} cannot be transformed to tetrahedral Cr^{3+} upon *vacuum* pretreatment. Thus, no structural Cr is found in CrAPO-5 molecular sieves. The CFSE of octahedral vs. tetrahedral Cr^{3+} explains why Cr cannot be transformed from octahedral to tetrahedral during synthesis. This Cr^{3+} is partially oxidized by calcination to chromate and Cr^{5+}. CO reduction results in the formation of octahedral Cr^{3+} and octahedral and tetrahedral Cr^{2+}, whereas recalcination restores the Cr^{5+} and Cr^{6+} species.

ACKNOWLEDGEMENTS

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