

# Chemistry and spectroscopy of vanadium in VAPO-5 molecular sieves

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VAPO-5 molecular sieves were synthesized hydrothermally starting with different vanadium, phosphorus, and template contents and with different templates as a function of time. The crystallization process was followed by X-ray diffraction and scanning electron microscopy; the coordination of vanadium was investigated by diffuse reflectance spectroscopy (d.r.s.) and electron spin resonance (e.s.r.). In the gels, vanadium is present as an octahedral ion and can be washed off easily. The crystallization process is retarded by increasing the vanadium content and gel (V + Al)/P ratios different from 1. Good crystalline materials were obtained by using tripropylamine, triethylamine, and tetrapropylammoniumhydroxide as template and synthesis times between 48 and 120 h. In the as-synthesized samples, isolated (pseudo-)octahedral  $V^{4+}$  is detected by e.s.r. and d.r.s. This vanadium is accessible by ammonia and comprises only 10% of the total vanadium content. Upon calcination,  $V^{4+}$  ions are oxidized to tetrahedral  $V^{5+}$ , which can only be reduced partially to  $V^{4+}$ . On this basis, no unambiguous evidence is found for isomorphous substituted vanadium in AIPO-5 molecular sieves.

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

## INTRODUCTION

Metal-substituted aluminophosphate molecular sieves (MeAPOs) possess interesting catalytic properties; this topic has been reviewed by Bellussi and Rigutto.<sup>1</sup> CoAPO-5s are active in the autoxidation of *p*-cresol and cyclohexane,<sup>2-4</sup> whereas CrAPO-5 catalysts oxidize secondary alcohols.<sup>5</sup> VAPO-5 molecular sieves catalyze the ammoxidation of alkanes, epoxidation of alkenes and allylic alcohols, and oxidation of aromatic compounds.<sup>6-9</sup>

The isomorphous substitution of these metal ions (Co, Cr, and V) in crystalline aluminophosphates is a matter of debate.<sup>1</sup> In CoAPO-5s, tetrahedral  $Co^{2+}$  substitutes for  $Al^{3+}$ , at least at low cobalt loadings; and, depending on the synthesis conditions, CoAPO-5 and CoAPO-34 can be obtained.<sup>10-12</sup> As synthesized CrAPO-5 crystals possess only octahedral  $Cr^{3+}$ , indicating no isomorphous substitution,<sup>13</sup> whereas VAPO-5 molecular sieves contain isolated square pyramidal  $V^{4+}$  and oxidic V ( $V_2O_5$ -like phase).<sup>6-8</sup> According to Montes et al.<sup>7</sup> and Jhung et al.,<sup>8</sup> substitutes for  $P^{5+}$ ; Rigutto and van Bekkum<sup>6</sup> suggested the replacement of  $Al^{3+}$  by  $V^{4+}$ . Two questions remain unsolved. (1) Is vanadium substituting for phosphorus or aluminum and to what extent? (2) What is the effect of the synthesis conditions on the coordination and oxidation state of vanadium?

These issues can only be solved by a systematic study of the synthesis process and of the crystalline materials by a combination of characterization techniques. In the present study, we have synthesized series of VAPO-5 molecular sieves with increasing vanadium, phosphorus, and template contents. The effects of synthesis time and template were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The coordination chemistry of vanadium was studied by a combination of electron spin resonance (e.s.r.) and diffuse reflectance spectroscopy (d.r.s.) of the initial gels and of the as-synthesized, calcined and reduced samples.

## EXPERIMENTAL

### Synthesis procedure

VAPO-5 was synthesized following a modified method of Flanigen et al.<sup>14</sup> Vanadyl(IV) sulfate (Fluka) was added to a solution of  $H_3PO_4$  (85 wt% solution in water; pro analysis, 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). The reaction mixture was prepared in an ice bath at 273 K. The obtained homogeneous gel was stirred for 1 h and inserted in a Teflon-lined autoclave. The synthesis was performed at 448 K. After synthesis, the material was

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washed three times with distilled water and dried at 333 K for 24 h.

Five series of VAPO-5 samples were prepared: A samples (as a function of vanadium content); B samples (as a function of synthesis time); C samples (as a function of template content); D samples (as a function of phosphorus content); and E samples (as a function of the template molecule). The A, B, C, and D samples were prepared with triethylamine; the E samples were synthesized with different template molecules. The synthesis conditions, notations, and gel compositions of all these samples are summarized in Table 1. A reference sample was prepared by impregnation of AlPO-5 with  $\text{VOSO}_4$  ( $\text{V}^{4+}/\text{AlPO-5}$ ).

### Pretreatments and techniques

The samples were granulated, and the size fraction 0.25–0.40 mm was loaded in a quartz flow cell with Suprasil windows for d.r.s. and a side arm for e.s.r. measurements. e.s.r. and d.r.s. were taken from the as-synthesized samples, after drying in He at 70°C, after calcination, reduction, and recalcination; and from vacuum-treated samples. The d.r.s. spectra were measured with a u.v.-vis-n.i.r. Cary 5 spectrometer in the range 200–2,500 nm and against a Halon white standard. The spectra were converted to the Kubelka-Munk function and plotted as a function of wavenumbers after subtraction of a baseline. e.s.r. spectra were taken in the range of 120–370 K using a Bruker ESP300E equipment in X-band at a microwave power of 200  $\mu\text{W}$  with a double rectangular TE104 mode cavity. The spectra were simulated by a program, based on matrix diagonalization and second-order perturbation for superhyperfine splitting, developed by Mabbs and Collison.<sup>15</sup> Quantitation of V in the e.s.r. spectra was performed after double integration using a  $\text{Cu}(\text{acac})_2$  (Strem Chemicals) diluted in KCl standard. Calcination and recalcination (after reduction) were performed at 823 K for 12 h with an oxygen flow rate of 3,600 ml/h; reduction was done for 30 min with a CO flow rate of 1,800 ml/h at 573 K. d.r.s. spectra were also taken from the wet precursor gels of the A-type samples as such and after

successive centrifugations (20 min, 5,000 rounds/min). Vacuum pretreatments were done at  $2 \times 10^{-3}$  Pa at 298 and 473 K overnight. Some samples were treated after drying at 70°C with ammonia for 15 min at 423 K. Powder XRD patterns of the as-synthesized, calcined, and recalcined samples were recorded with a Philips PW 1012/30 powder diffractometer. SEM on the as-synthesized samples was performed on a Jeol Superprobe 733.

## RESULTS

### Spectroscopy of the wet precursor gels

The precursor gels were light blue or blue, depending on the V content. The coordination and retention of V in these gels were investigated by d.r.s., as shown in Figure 1. The retention of V was tested by washing the gel with bidistilled water followed by centrifugation. The spectra of a fresh gel showed at least five  $d-d$  transitions of  $\text{V}^{4+}$  in the region 10,000–20,000  $\text{cm}^{-1}$ . After one washing, most of the V was removed; by washing further the amount removed was rather small. The residual  $\text{V}^{4+}$  spectrum contained three broad bands, the relative intensities of which were different from those of the initial spectrum. This suggests the presence of at least two  $\text{V}^{4+}$  species; both are, however (pseudo-) octahedral.<sup>16</sup>

### Synthesis of VAPO-5

Figure 2 shows the XRD diffractograms of the A samples (see Table 1) with increasing V content. The spectra are typical for AlPO-5, but the relative intensities of the peaks in Figure 2 (especially between 19.5 <  $2\theta$  < 22.5) depend on the V content. The XRD diffractogram of the A-0.08 sample contains four extra peaks near 13, 18, 38, and 44°, indicative of a second crystalline phase. Furthermore, with increasing V content, the formation of VAPO-5 from pseudo-boehmite required a longer synthesis time. This is evidenced by the weak XRD line intensities of A-0.08-48 h in Figure 2. Table 2 summarizes the composition of the initial gel and the corresponding

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

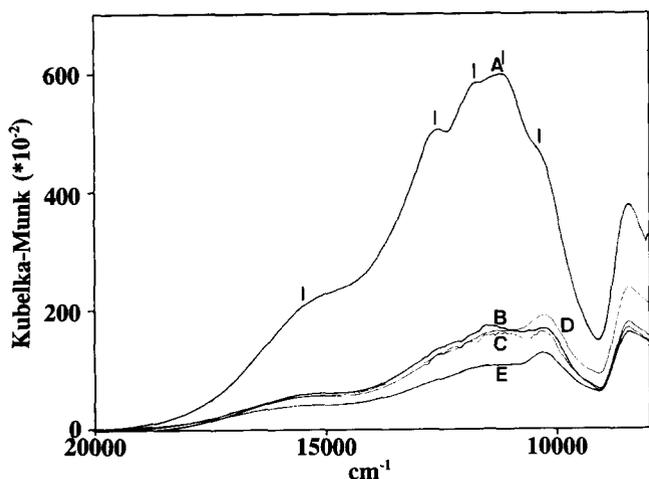
Sample name	Gel composition: $r\text{R} \cdot (\text{V}_x\text{Al}_y\text{P}_z)\text{O}_4 \cdot 16.7\text{H}_2\text{O}$						pH	Synthesis time (h)
	r	R	x	y	z			
A-0.01	0.74	$\text{Et}_3\text{N}$	0.01	0.99	1	3.76	2, 24	
A-0.02	0.74	$\text{Et}_3\text{N}$	0.02	0.98	1	4.26	48	
A-0.04	0.74	$\text{Et}_3\text{N}$	0.04	0.96	1	3.70	48	
A-0.08	0.74	$\text{Et}_3\text{N}$	0.08	0.92	1	2.90	48	
B-0.02	0.74	$\text{Et}_3\text{N}$	0.02	0.98	1	4.26	2, 4, 24, 48, 72, 96, 120, 144, 168	
C-1	0.5	$\text{Et}_3\text{N}$	0.02	0.98	1	3.03	24, 72	
C-2	1.0	$\text{Et}_3\text{N}$	0.02	0.98	1	6.06	24, 72	
C-3	1.25	$\text{Et}_3\text{N}$	0.02	0.98	1	6.75	24, 72	
D-1	0.74	$\text{Et}_3\text{N}$	0.02	0.98	0.72	5.84	72	
D-2	0.74	$\text{Et}_3\text{N}$	0.02	0.98	1.67	2.30	2, 24, 72	
E- $\text{Pr}_3\text{N}$	0.74	$\text{Pr}_3\text{N}$	0.02	0.98	1	5.76	24, 72	
E- $\text{Pr}_2\text{NH}$	0.74	$\text{Pr}_2\text{NH}$	0.02	0.98	1	3.49	24, 72	
E-TMAOH	0.74	TMAOH	0.02	0.98	1	1.99	24, 72	
E-TPAOH	0.74	TPAOH	0.02	0.98	1	2.99	24, 72	

**Table 2** Chemical analysis of as-synthesized VAPO-5 materials

Sample name	Vanadium content in initial gel	(V + Al)/P ratio of the as-synthesized materials
VAPO-0.01-24 h	0.01	1.03
VAPO-0.02-48 h	0.02	1.09
VAPO-0.04-48 h	0.04	1.68
VAPO-0.08-48 h	0.08	1.29

synthesis time was between 48 and 120 h. The B-0.02-120 h sample, as shown in the SEM in *Figure 3*, contained two different kinds of crystals: hexagonal, with a size between 5 and 10  $\mu\text{m}$ , and needle-shaped, with a length of 2–10  $\mu\text{m}$ . The amount of needles increased with decreasing synthesis time. The crystals from the B-0.02-168 h sample formed agglomerates. The hexagonal and needle-shaped structures were still present.

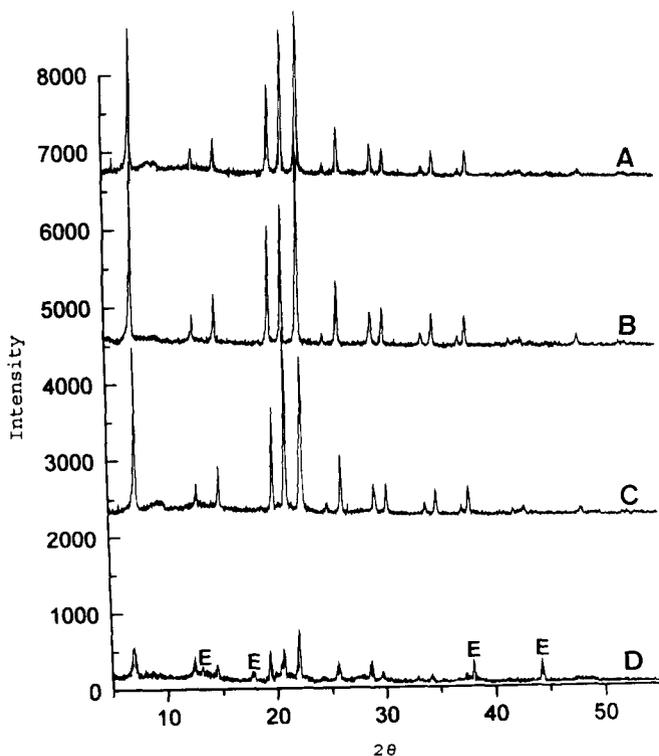
In other experiments, the influence of the template (R) content and phosphorus content on the synthesis of VAPO-5 was investigated. The optimal template content for the C samples (see *Table 1*) synthesized for 24 h was 0.5  $\text{Et}_3\text{N}/[(\text{Al},\text{V})\text{O}_2 + \text{PO}_2]$ . Above 0.74  $\text{Et}_3\text{N}/[(\text{Al},\text{V})\text{O}_2 + \text{PO}_2]$ , additional lines appeared in the XRD diffractograms. After a synthesis time of 72 h, the typical AlPO-5 pattern was observed, whatever the template content. The phosphorus amount seems critical for the synthesis of VAPO-5. With an excess of phosphorus [ $(\text{Al} + \text{V})/\text{P} < 1$ ], VAPO-5 was synthe-



**Figure 1** d.r.s. spectra of the wet precursor gel (A-0.02 sample) (A) and of the gel after one (B), two (C), three (D) and four (E) washings.

chemical analysis of the as-synthesized VAPO-5 samples. At low V content, the (V + Al)/P ratio was close to 1, whereas at higher loadings it deviated from 1. This suggests excess V and/or Al in VAPO-5, the excess increasing with amount of V.

With the B samples, the synthesis was followed as a function of time, changing between 2 and 168 h. Samples B-0.02-2 h and B-0.02-4 h are amorphous, and only after 24 h, could the typical XRD lines of AlPO-5 be detected. No crystalline phase other than VAPO-5 appeared, even after 168 h. The optimal



**Figure 2** XRD diffractograms of the A samples as function of the vanadium content: (A) A-0.01-24 h; (B) A-0.02-48 h; (C) A-0.04-48 h; (D) A-0.08-48 h.



**Figure 3** SEM of the B-0.02-120 h sample.

sized initially, but at longer synthesis time (24 or 72 h) other crystalline phases were formed. When the (Al + V)/P ratio largely exceeded 1, only a few crystals were formed, even after 72 h of synthesis.

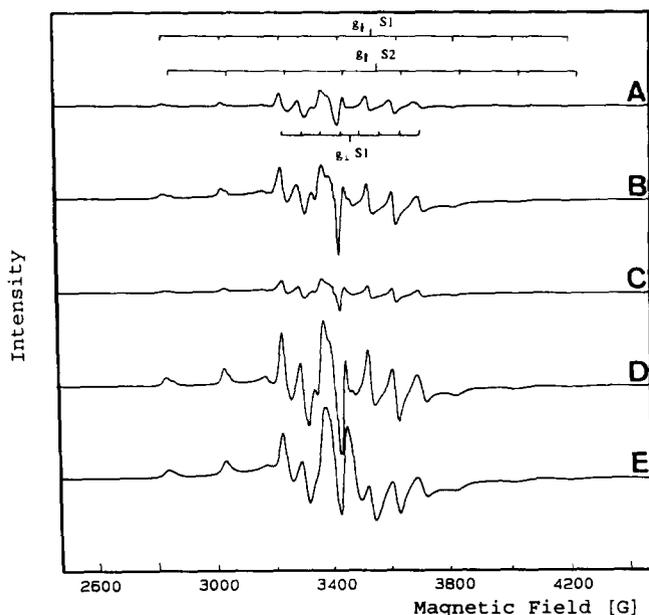
The XRD diffractograms for VAPO-5 samples synthesized with different template molecules showed a pure AFI phase for tripropylamine and triethylamine after 24 h; with tetrapropylammoniumhydroxide a VAPO-5 phase was formed after 72 h of synthesis. With tetramethylammoniumhydroxide and dipropylamine, no pure VAPO-5 samples could be obtained.

## Chemistry and spectroscopy of VAPO-5

### As-synthesized VAPO-5

The e.s.r. spectra of VAPO-5 as a function of the vanadium loading are shown in *Figure 4*. The spectra are characterized by two axially symmetric signals with hyperfine splitting. Such spectra are typical for vanadium(IV), with  $d^1$  configuration and  $I = 7/2$ , and are usually designated as  $S_1$  and  $S_2$  signals.<sup>6,7</sup> These signals possess slightly different  $g$  and  $A$  values (see further). At higher V contents an additional broad signal is formed with  $g$  around 2. At low loadings, the total integrated intensity of the spectrum follows the Curie-Weiss law in the measured temperature range of 120–370 K. This is not the case at high V content. This observation supports the idea that  $S_1$  and  $S_2$  are due to magnetically isolated  $V^{4+}$  ions, whereas the broad signals can be assigned as oxidic V. In any case, the calculated spin densities correspond to less than 10% of the V, independent of the V content.

*Figure 5* shows a simulation of the e.s.r. spectrum of the A-0.01 sample, which is performed by using a



**Figure 4** e.s.r. spectra of the A samples as function of the vanadium content: (A) A-0.01-24 h measured at 120 K; (B) A-0.02-48 h measured at 120 K; (C) A-0.02-48 h measured at 300 K; (D) A-0.04-48 h measured at 120 K; and (E) A-0.08-48 h measured at 120 K.

rhombic symmetric Hamiltonian with hyperfine splitting. The procedure consists of three steps: (1) a separate simulation of the  $S_1$  and  $S_2$  signals; (2) a summation of both simulated spectra with appropriate weight factors; and (3) comparison with the experimental spectra and possible reevaluation of the starting variables and reiteration. It can be deduced from *Figure 5* that a good resemblance is obtained between the experimental and calculated spectrum. The obtained  $g$  and  $A$  values are summarized in *Table 4* and compared with some literature data. The spectral parameters of  $S_1$  and  $S_2$  are typical for a distorted octahedral  $V^{4+}$ .

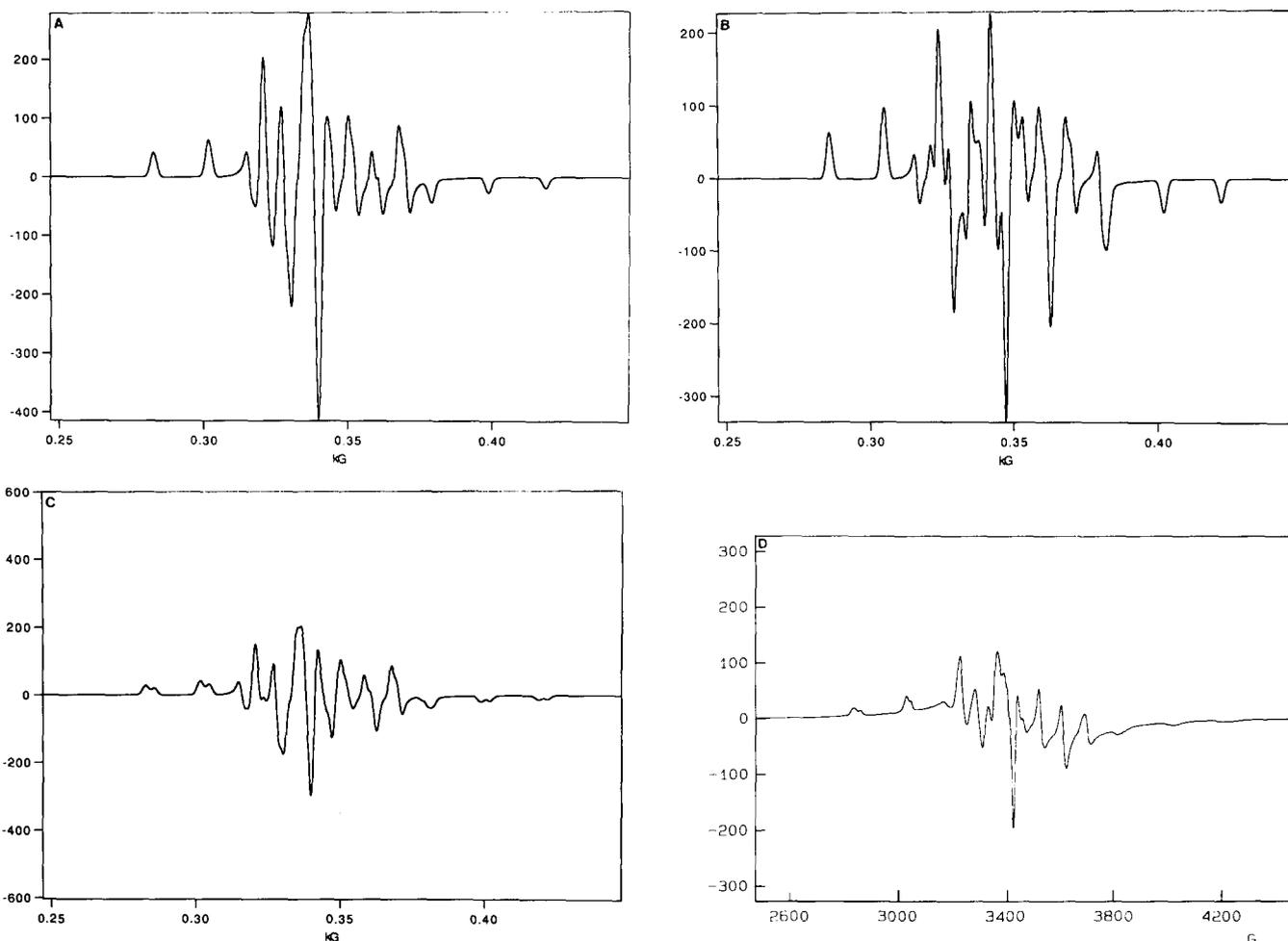
The corresponding d.r.s. spectrum (*Figure 6*) shows two absorption bands in the 10,000–20,000  $\text{cm}^{-1}$  region: at 13,100  $\text{cm}^{-1}$  with a low field shoulder and at 16,500  $\text{cm}^{-1}$ . The intensity increases with increasing V content. These values can be compared with absorption bands of reference compounds summarized in *Table 3*. The observed absorptions are typical for (pseudo-) octahedral vanadyl species.

The d.r.s. and e.s.r. spectra are similar for the syntheses performed as a function of time. The e.s.r. intensity attains its maximum after 72 h of synthesis, whereas the d.r.s. bands decrease with increasing synthesis time. This means that different V species are probed by these techniques. No systematic influence of the template content on the spectroscopic features could be observed. However, the kind of template molecule strongly influences the e.s.r.-spectra: with  $\text{Pr}_3\text{N}$  and  $\text{Et}_3\text{N}$  the typical  $S_1$  and  $S_2$  signals are formed, whereas for the other templates only the  $S_1$  signal superposed on a broad signal is detected.

### Oxidized and reduced VAPO-5

The e.s.r. spectra as a function of treatment conditions are given in *Figure 7A*. After helium treatment at 70°C, the  $g$  and  $A$  values change slightly, and the distinction between  $S_1$  and  $S_2$  is more clearly resolved (see *Table 4*). Oxygen treatment at 110°C changes only color, whereas the spectra remain unchanged. By calcination at 550°C, the sample is yellow, and the e.s.r. signal has almost completely disappeared. After CO reduction, the color changes to purple-gray, and the  $S_1$  and  $S_2$  signals are reestablished; however, the relative intensity of  $S_1$  is lower than that of  $S_2$ . The measured spin density is then about 60% of the original value before calcination (*Figure 7B*). Simulation of the e.s.r. spectra of the reduced samples was possible by taking into account only signal  $S_2$  and axial symmetry. The obtained  $g$  and  $A$  values are given in *Table 4*. The parameters are typical for (pseudo-) octahedral  $V^{4+}$ . Recalcination restores the situation after initial calcination.

The d.r.s. spectra remain unchanged after helium and oxygen treatment at 70 and 110°C, respectively. After calcination at 550°C an intense band around 36,000  $\text{cm}^{-1}$  appears (*Figure 6*) which is due to the  $\text{O} \rightarrow \text{V}^{5+}$  ( $d^0$ ,  $T_d$ ) charge transfer of tetrahedral  $\text{V}^{5+}$  (see *Table 3*). Reduction results in the disappearance of this band and the formation of a strong band at 12,400  $\text{cm}^{-1}$  and a weak one around 16,500  $\text{cm}^{-1}$ .



**Figure 5** Simulation procedure of the e.s.r. spectrum of as-synthesized A-0.01 sample. (A), simulation of  $S_1$ ; (B), simulation of  $S_2$ ; (C) summation of simulated  $S_1$  and  $S_2$  (with  $S = 0.65 \cdot S_1 + 0.35 \cdot S_2$ ); and (D) the experimental e.s.r. spectrum.

The latter is reminiscent of the original pseudo-octahedral  $V^{4+}$ . The former is probably also due to  $V^{4+}$ .

#### Vacuum- and ammonia-treated VAPO-5

Vacuum treatment was performed at room tem-

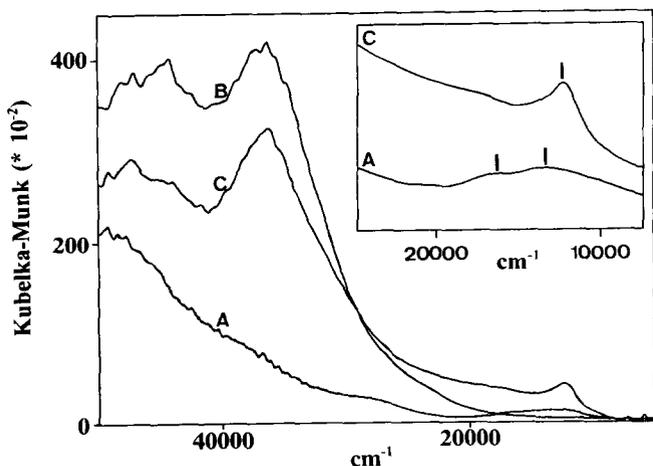
perature and 100°C. The e.s.r.  $S_1$  and  $S_2$  do not change significantly, except that their intensities decrease upon heating. The d.r.s. spectra are unchanged up to a vacuum treatment at 100°C (not shown for brevity). Ammonia treatment at 150°C on as-synthesized samples results in the disappearance of the  $S_1$  and  $S_2$  signals, and a new octet signal becomes visible in e.s.r. (see Table 4); the d.r.s. spectra remain unchanged except for the overtones of NH at 6,300  $cm^{-1}$ .

#### DISCUSSION

This work is a systematic study of the synthesis of VAPO-5 molecular sieves, and the synthesized materials are spectroscopically characterized by a combination of d.r.s. and e.s.r.

#### Synthesis of VAPO-5

The optimum conditions of VAPO-5 are the same as those of AlPO-5, as far as nature and amount of template are concerned.<sup>17</sup> At a constant synthesis temperature and time, the crystallinity of the products, as observed from the XRD patterns, decreases



**Figure 6** d.r.s. spectrum of the A-0.02-48 h sample (A) as-synthesized; (B) calcined at 500°C in  $O_2$ ; and (C) reduced at 300°C in CO.

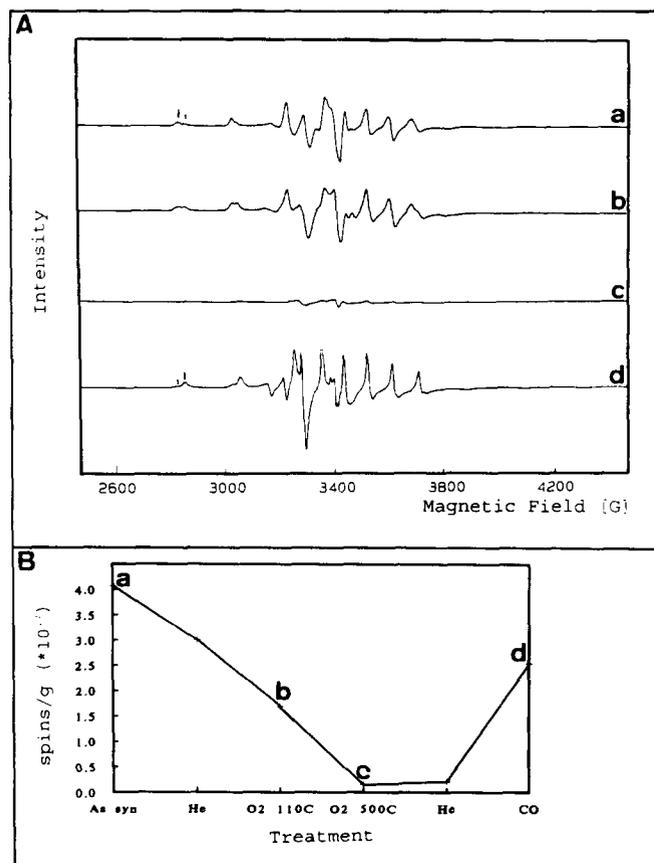
**Table 3** d.r.s. absorption bands of some reference compounds (15,18–20)

Reference compound	Absorption bands (cm <sup>-1</sup> )	Assignment
V(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	11,800; 11,300	A <sub>2g</sub> → T <sub>2g</sub> ; A <sub>2g</sub> → T <sub>1g</sub> (F)
V(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	17,200; 25,200	T <sub>1g</sub> → T <sub>2g</sub> ; T <sub>1g</sub> → T <sub>1g</sub> (P)
VO <sup>2+</sup> (0.5 M HClO <sub>4</sub> )	13,100; 16,000	B <sub>2g</sub> → E <sub>g</sub> ; B <sub>2g</sub> → B <sub>1g</sub>
VOSO <sub>4</sub> · 5H <sub>2</sub> O	13,000; 16,000	B <sub>2g</sub> → E <sub>g</sub> ; B <sub>2g</sub> → B <sub>1g</sub>
VO <sub>4</sub> <sup>3-</sup>	37,000–43,000	1t <sub>1</sub> → 2e
V <sup>3+</sup> /Al <sub>2</sub> O <sub>3</sub>	17,450; 25,200; 31,200	<sup>3</sup> T <sub>1g</sub> → <sup>3</sup> T <sub>2g</sub> ; <sup>3</sup> T <sub>1g</sub> (P) → <sup>3</sup> A <sub>2g</sub>
VO(H <sub>2</sub> O) <sub>5</sub> <sup>2+</sup>	13,000; 15,900; 28,600	B <sub>2g</sub> → E <sub>g</sub> ; B <sub>2g</sub> → B <sub>1g</sub> ; charge transfer

with increasing V content. Thus, V retards the synthesis. As the V loading increases, the synthesis time increases. At  $x = 0.08$  no pure AFI phases can be obtained. Equally important for obtaining pure AFI phases is the (V + Al)/P ratio of 1. Any deviation gives mixtures or phases or incomplete crystallization. This suggests that, if V substitutes into the lattice, it will take the Al<sup>3+</sup> site. This idea is in agreement with that of Rigutto and van Bekkum<sup>6</sup> but not with Montes et al.<sup>7</sup>

### Spectroscopy of VAPO-5

As far as gel chemistry is concerned, most V=O<sup>2+</sup> is loosely bound to the synthesis gel. A small fraction only is bound as a pseudo-octahedral species. This is



**Figure 7** (A), e.s.r. spectra of the A-0.01 sample as function of pretreatment: (a) as-synthesized; (b) dried at 110°C in O<sub>2</sub>; (c) calcined at 500°C in O<sub>2</sub>; and (d) reduced at 300°C in CO. (B), spin densities as function of pretreatment.

analogous to the situation of Co<sup>2+</sup>.<sup>12</sup> In the as-synthesized VAPO-5 V is present as V<sup>4+</sup>. No spectroscopic evidence is found for other oxidation states. d.r.s. and e.s.r. do give complementary information about this V<sup>4+</sup>. Thus, whereas the d.r.s. spectra are characteristic of the total V content, present as V<sup>4+</sup>, e.s.r. reveals the magnetically diluted fraction, which is less than 10% of the total V<sup>4+</sup> content and is not resolved in the d.r.s. spectrum. Both d.r.s. and e.s.r. spectra are indicative for pseudo-octahedral V<sup>4+</sup> with up to six oxygens in the first coordination sphere.

Three types of pseudo-octahedral V<sup>4+</sup> exist: minor quantities giving the e.s.r. signals S<sub>1</sub> and S<sub>2</sub>, and an extralattice oxidic phase characterized by the broad  $g = 2$  signal. Although they make up at maximum 10% of the total V<sup>4+</sup> content, it cannot be excluded that the weak  $g = 2$  signal is representative of the other 90% of V<sup>4+</sup> too. If one assumes that this 90% is also present in the form of oxidic V<sup>4+</sup> clusters of various sizes, then magnetic interactions among V<sup>4+</sup> may account for the weakness of the signal at 110 K. This also means that the majority of V<sup>4+</sup> is extralattice and that the d.r.s. spectra are representative of oxidic V<sup>4+</sup> clusters. S<sub>1</sub> and S<sub>2</sub> have been observed in other crystalline and amorphous materials<sup>21–27</sup> (Table 4). In addition, the lack of spectroscopic features of tetrahedral V<sup>4+</sup> excludes true isomorphous substitution. At best, S<sub>1</sub> and S<sub>2</sub> are atomically dispersed, pseudo-octahedral V<sup>4+</sup> species, anchored to the surface, most likely at an Al<sup>3+</sup> site. Possible models have been proposed by Rigutto and van Bekkum,<sup>6</sup> but others may be envisaged. Thus, NH<sub>3</sub> interacts with the V<sup>4+</sup> species giving the signals S<sub>1</sub> and S<sub>2</sub>. This indicates that either they have a free coordination site, or NH<sub>3</sub> substitutes for water in the coordination sphere. This is shown schematically in Figure 8. No change is observed in the d.r.s. spectrum, suggesting that V is present in extralattice clusters.

### Chemistry of VAPO-5

Upon oxidation all V is recovered in the form of V<sup>5+</sup> with the typical O → V<sup>5+</sup> charge transfer band of VO<sub>4</sub><sup>3-</sup>. Such a tetrahedral environment is typical for atomically dispersed V<sup>5+</sup> and is also found for supported V catalysts.<sup>25–28</sup> Therefore, its presence is not sufficient evidence for isomorphous substitution as claimed by Jhung et al.<sup>8</sup> By CO reduction, (pseudo-)octahedral V<sup>4+</sup> is partially regenerated (as a S<sub>2</sub> signal), whereas the sharp absorption band at 12,500 cm<sup>-1</sup> in d.r.s. is probably due to (pseudo-)octahedrally coordinated V<sup>2+</sup> (Table 3).

**Table 4** e.s.r. parameters of VAPO-5 molecular sieves after different pretreatments and of some reference compounds

Sample name	$T_{\text{meas}}$ (K)	Signal	$g_{xx}$	$g_{yy}$	$g_{zz}$	$A_{xx}$ (G)	$A_{yy}$ (G)	$A_{zz}$ (G)	Reference
A-0.01 as-synthesized	120	S <sub>1</sub>	1.977	1.993	1.947	74.2	74.2	196	This work
		S <sub>2</sub>	1.975	1.992	1.930	74	74	195	
A-0.01 helium at 70°C	120	S <sub>1</sub>	1.976	1.992	1.953	75	75	192	This work
		S <sub>2</sub>	1.976	1.993	1.941	75	75	191	
A-0.01 reduced with CO	120	S <sub>2</sub>	1.982	1.982	1.915	79	79	207	This work
A-0.02 treated with ammonia	120		1.975	1.975	1.938	63	63	190	This work
V silicalite with a high V content (octahedral V <sup>4+</sup> )	77	S <sub>1</sub>				80	80	203	21
V silicalite with a low V content (octahedral V <sup>4+</sup> )	77	S <sub>1</sub>	1.9827	1.9827	1.9355	80	80	203	21
V silicalite with a low V content after reduction (tetrahedral V <sup>4+</sup> )	77	S <sub>2</sub>	1.9117	1.9117	1.9117	68	68	154	21
V <sub>2</sub> O <sub>5</sub> -ZSM-5 hydrated	293		1.981	1.981	1.946	77	77	180	22
V <sub>2</sub> O <sub>5</sub> -ZSM-5 vacuum treated	300		1.990	1.990	1.928	81	81	206	23
VO <sup>2+</sup> -ZSM-5 hydrated	300		1.990	1.990	1.949	73	73	186	24
V <sup>4+</sup> in ThGeO <sub>4</sub> (V <sup>4+</sup> in tetrahedral coordination)	77		1.980	1.980	1.831	35	35	191	18
VOPO <sub>4</sub> · 2H <sub>2</sub> O (V <sup>4+</sup> in octahedral coordination)	300		1.981	1.981	1.938	70	70	194	18
VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> (after oxidative dehydrogenation)	298		1.982	1.982	1.919	70	70	190	25

In summary, this study shows that independently of the synthesis time, template, phosphorus, and vanadium content, vanadium in VAPO-5 molecular sieves is present as isolated V<sup>4+</sup> and oxidic V. Under all conditions of the present investigation V is in (pseudo-)octahedral coordination. Calcination results in the formation of tetrahedral V<sup>5+</sup>, whereas reduction partially regenerates V<sup>4+</sup> ions. No spectroscopic evidence is found for true isomorphous substitution of V<sup>4+</sup> into the lattice of AlPO-5 molecular sieves, that is, V<sup>4+</sup> tetrahedrally coordinated to four lattice oxygens.

## CONCLUSIONS

Pure VAPO-5 molecular sieves can be synthesized hydrothermally starting with different V and template content and with different templates as a function of time. In the gels, V is present as an octahedral ion and can be largely washed off from the gel. The crystallization process is retarded by increasing the V content and gel (V + Al)/P ratios different from 1. Good crystalline materials were obtained by using tripropylamine, triethylamine, and tetrapropylammonium-hydroxide as template and synthesis times between 48 and 120 h. With e.s.r. only the atomically dispersed V<sup>4+</sup> is visible; d.r.s. shows the total amount. Both spectroscopic techniques reveal that V is present as oxidic and/or anchored V<sup>4+</sup> ion. Isolated, anchored V<sup>4+</sup> is accessible by ammonia, indicating a free coordination site. V<sup>4+</sup> is oxidized to V<sup>5+</sup>. This V<sup>5+</sup> is reducible to V<sup>n+</sup> (with  $n < 5$ ). No unambiguous evi-

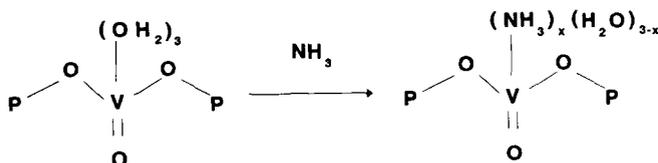
dence is found for isomorphous substituted V in AlPO-5 molecular sieves.

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**Figure 8** Proposed structure of the anchored vanadium species in VAPO-5 and the interaction with ammonia.

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