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Genesis of V^{4+} in heteropoly compounds $Cs_xH_{4-x}PVMo_{11}O_{40}$ during thermal treatment, rehydration and oxidation of methanol studied by EPR spectroscopy

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The development and structural changes of V^{4+} and Mo^{5+} centers in caesium salts and the acid form of molybdovanadophosphorus heteropoly compounds $Cs_xH_{4-x}PVMo_{11}O_{40} \cdot nH_2O$ ($x = 0, 3, 4$) of Keggin structure were investigated by electron paramagnetic resonance (EPR) after preparation, thermal treatment in oxygen, reduction by methanol and catalytic oxidation of methanol. The various types of paramagnetic centers are found to characterize the different states and structural transitions of the heteropoly anion. In addition, the EPR spectra reflect well the different reducibility, thermal stability and mobility of vanadium and Keggin ("lattice") oxygen of the Cs_4, the Cs_3H and the H_4 compounds. The V^{4+} centers in the Cs_4 salt are different in structure, lower in concentration and thermally more stable than those in the acid form. The reduction of vanadium during thermal treatment due to the loss and oxidation of coordinated ("lattice") oxygen to O_2 is observed in the acid and the Cs_3H salt only, but not in the Cs_4 compound. As deduced from quantitative EPR measurements and manganometric redox titrations, between 0.5 and 8% of the vanadium is present as V^{4+} after preparation and thermal treatment in oxygen, whereas the majority of vanadium is reduced by reaction with methanol. V^{4+} substitutes Mo atoms in the Keggin unit in the fully exchanged Cs salt (Cs_4). The presence of the bulky caesium counter-cations prevents the removal of vanadium from the Keggin unit to the secondary structure and thus the formation of vanadyl bridged polymers.

1. Introduction

Heteropolyacids and their salts are efficient heterogeneous catalysts for the selective oxidation of several alkanes and aldehydes.[1–3] In various reactions, the partial substitution of molybdenum(VI) by vanadium(V) in the Keggin unit of molybdophosphoric acid has been reported to enhance (or change) catalytic performances. Accordingly, the nature and the role of the vanadium in the catalyst during pretreatment procedures and particularly in the working state is of special interest and has been the subject of several papers.

Because some part of the vanadium introduced is always paramagnetic and the heteropoly compounds are generally amorphous after thermal treatment, EPR is a suitable method to follow structural changes during thermal treatment and catalysis. In several studies, the different types of EPR signals have been found to characterize the different states of the heteropoly acid with sufficient accuracy.[4,5] This conclusion is emphasized on comparing the EPR "transition temperatures" with the thermal analysis transformation points, which indicate structural transitions. Strictly speaking, of course, the structural information is valid only for the paramagnetic part of the vanadium. It is generally assumed that only traces or very minor amounts of V^{4+} are present in $H_4PVMo_{11}O_{40}$ after preparation and after thermal treatment (in oxygen) at higher temperatures, however, the exact V^{4+} quantity was not determined. After catalytic reactions and reduction by organic reactants the majority of the vanadium was found to be present as V^{4+}.[5–7] The paramagnetic centers found after different thermal treatment procedures are mostly the same (concerning EPR parameters) as those observed after catalysis. Their structure could not be deduced directly from the EPR parameters until now. However, mainly during the last few years EPR, NMR and IR investigations have revealed that the vanadium atom in $H_4PVMo_{11}O_{40}$ is eliminated from the Keggin ion to the secondary structure by thermal treatment.[5,7–12]

It is also reported that the secondary structure, stability and catalytic properties of the heteropoly compounds are influenced by the counter-ions.[13–18] These effects are found to be pronounced for partial and complete substitution of H^+ by caesium. In a recent paper, the secondary structures of the salts $Cs_xH_{4-x}PVMo_{11}O_{40} \cdot nH_2O$ were investigated and compared.[15] One could expect that the $Cs_{3/4}$ salts in particular are thermally more stable than the acid form. It should be interesting to compare the thermal behavior and partial reactions of the catalytic cycle of these Cs salts and the acid form monitored by EPR spectroscopy.

The present paper focuses on the EPR investigation of the vanadium(IV) (and molybdenum(V)) species during thermal treatment (including quantitative determination of the number of paramagnetic species) and during catalytic oxidation of methanol over $H_4PVMo_{11}O_{40}$, $Cs_4PVMo_{11}O_{40}$ and $Cs_3HPVMo_{11}O_{40}$. In addition, we investigated the reversibility of the main steps of thermal treatment and catalysis (dehydration–rehydration, decomposition–reconstruction, reduction–reoxidation) with the heteropoly compounds mentioned above.

2. Experimental

Materials and treatment

Detailed preparation procedures for the acid form and the caesium salts of the heteropoly compounds

$Cs_xH_{4-x}PVMo_{11}O_{40} \cdot nH_2O$ used have been reported in the literature.[15] The following nomenclature is used throughout the paper: Cs0V1 for $H_4PVMo_{11}O_{40}$, Cs3V1 for $Cs_3HPVMo_{11}O_{40}$, Cs4V1 for $Cs_4PVMo_{11}O_{40}$, Cs0V0 for $H_3PMo_{12}O_{40}$ and Cs3V0 for $Cs_3PMo_{12}O_{40}$. Thermal treatment of the compounds was performed in an "*in situ*" EPR cell, where the gas streamed through a capillary over the solid catalyst (50 mg, from bottom to top) or in a standard U-tube micro reactor. After the different treatments in the EPR reactor, the system is cooled to room temperature in helium, closed (under He) and directly transferred to the EPR cavity. The composition of the various gas atmospheres (O_2/He, H_2O/He, CH_3OH/He, CH_3OH/O_2/He), the temperature (293–770 K) and duration (in general 30–60 min) of the treatments are given in the text describing the particular experiments (Results section). All experiments are accompanied by corresponding thermoanalytical measurements and the on-line determination of the composition of the product gas phase by a quadrupole mass spectrometer.

EPR spectroscopy

The EPR spectra were recorded on a Varian E-9, a Bruker ESP 300 E, and a Jeol RE2X at X-band frequency at temperatures between 130 and 293 K; microwave frequency about 9.4 GHz, microwave power 5 mW, modulation frequency 100 kHz. The g values were determined with a NMR magnetometer and DPPH as g marker. The EPR parameters were obtained by comparison of experimental and simulated spectra. Simulation was performed according to second-order perturbation theory (programs: Bruker-SIMFONIA and a modified version of ref. 19).

The quantitative determination of the vanadium(IV) content in the heteropoly acids $PVMo_{11}O_{40}$ was performed by EPR spectroscopy and titration. As standards for the quantitative EPR measurements, DPPH (known number of spins) and a series of standard solutions of bis(acetylacetonato)-vanadium(IV) (0.5, 1, 2.5, 5 and 7.5 mmol l^{-1} in CH_2Cl_2) were used. After the thermal treatments the samples were directly transferred to the EPR cell and weighed without contact to air or moisture. The spectra intensity was obtained by numerical double integration of the sample and reference (DPPH) spectra using the corresponding software (ESP300, Bruker; ESPRIT-360, JEOL).

Redox titration

The manganometric titration was performed with an automatic titrator (Metrohm); working electrode: Pt, reference electrode: Ag/AgCl/KCl, 0.1 N $KMnO_4$ solution (0.01 ml s^{-1}). The equivalence point was determined optically as well as electrochemically. After thermal treatment, the catalyst (1 g) was cooled in He and dissolved in doubly distilled water to which sulfuric acid was added. Titrations of vanadium(IV) standard substances confirmed the validity of the technique.

3. Results

To study the influence of the Cs counter-ion on the structure and stability of the different paramagnetic species formed during preparation, treatment and methanol oxidation all investigations were performed in parallel with the acid form (Cs0V1) and the caesium salt (Cs4V1) and selected experiments with Cs3V1, Cs3V0 and Cs0V0. Five different types of well-resolved vanadium(IV) spectra (signals A, B, C, D and strongly broadened vanadium lines without hyperfine structure) and two spectra of Mo^{5+} (E, F) were observed during the various experiments (Tables 1 and 2). Signals C and D were found only for the Cs salts. The other spectral patterns are well known from the literature, although they were not assigned in conformity.

General interpretation of the EPR spectra (before and after treatment)

Figs. 1 and 2 show EPR spectra measured at 130 K (300 K, Fig. 1(a)) of Cs0V1, Cs4V1, Cs3V1 and Cs3V0, respectively, after thermal treatment at different temperatures. The EPR spectra and parameters of the acid are reported in the literature[4,5,7] and will be described briefly. The signal of the acid form after drying at room temperature (dry powder) is due to a tumbling VO^{2+} ion in the water of crystallization. The g_0 and a_0 values are similar to the aqua complex $[VO(H_2O)_5]^{2+}$.[20] At the recording temperature $T_{rec} = 130$ K the tumbling motion is frozen and a "powder" spectrum of remarkably increased intensity is obtained (signal A). This and the spectra described in the following are typical for one unpaired electron ($3d^1$, $S = \frac{1}{2}$) showing a hyperfine interaction (hfi) with the nuclear spin of ^{51}V ($I = \frac{7}{2}$, $\approx 100\%$), and they can be described and simulated by an axially symmetric g and $A(^{51}V)$ hyperfine tensor according to the spin-Hamiltonian

$$H_S = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y).$$

The EPR parameters of the V^{4+} species were deduced from simulation of the spectra (second-order perturbation theory) and are compared to those reported in the literature (Table 1).

Table 1 EPR parameter g and $A(^{51}V/^{95,97}Mo)$ for the different paramagnetic centers observed for various heteropoly compounds (additional parameter see text)[a]

Signal	HPA	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	Ref.[b]
A	Cs0V1, Cs3V1	1.923	1.969	207(186)	78(72)	
	Cs0V1	1.925	1.970	204.6	74.8	4
	$HVOPMo_{12}O_{40}$[c]	1.932	1.978	202	77	5
B	Cs0V1	1.918	1.951	168(150)	44(40)	
		1.926	1.956	163.4	41	4
	$HVOPMo_{12}$[c]	1.930	1.961	165	44	5
	Cs0V1[d]	1.930	1.962	164	40	7
C	Cs4V1	1.925	1.967	162(145)	58(53)	
	$(NH_4)_5[PVMo_{11}O_{40}]$	1.936	1.974	164	57	9
D	Cs3V1	1.927	1.963	152(137)	54(49.5)	
E	Cs0V0, Cs0V1	1.846	1.952	100(86)	45(41)	
F	Cs3V0, Cs4V1	1.940				21, 22

[a] The parameters were obtained by comparison of the experimental and simulated spectra (second-order perturbation theory[19]); hyperfine coupling constants in Gauss (10^{-4} cm^{-1}), estimated errors: $\Delta g = \pm 0.002$ and $\Delta A = \pm 3$ G. [b] All parameters of signals A–F from this work (E, F: Mo^{5+}); literature values obtained for similar treatment or spectra are cited or given for comparison. [c] VO^{2+} as counter-ion to the Keggin anion $H[PMo_{12}O_{40}]^{2-}$. [d] After reduction (catalysis) by isobutane at 623 K.

Table 2 Summary of the assignment of the EPR signals A–F to particular structures or species in the heteropoly compounds based on the results of the present investigations

Signal	Description of the structure	Observed In	Observed After[a]
A	Hydrated V^{4+}, $[VO(H_2O)_5]^{2+}$, as counter-ion to the Keggin unit in the secondary structure	Cs0V1, Cs3V1	Hyd
B	Vanadyl bridges between (outside of the) Keggin units, vanadium coordinated by outer oxygen atoms of the Keggin unit (alternatively: V^{4+} substituting Mo^{6+} in a Keggin unit noticeably distorted by loss of oxygen ligands)	Cs0V1, (Cs3V1)	ThT, Red
C	V^{4+} substituting a Mo^{6+} atom inside the Keggin unit	Cs4V1	Hyd, ThT, Red
D	V^{4+} substituting a Mo^{6+} atom inside the Keggin unit	Cs3V1	ThT, Red
E	Mo^{5+} in a (progressively) distorted Keggin unit (beginning destruction, varying EPR parameter)	Cs0V1, Cs0V0	ThT + Red at high T
F	Unpaired electron delocalized over twelve Mo atoms in an undestroyed Keggin unit	Cs4V1, Cs3V0	ThT at high T
Broad line ($g = 1.96$)	Increased number of V^{4+} species near to each other, showing spin–spin interactions (line broadening), structures as described above	All V^{4+} containing samples	Red

[a] Hydrated form (Hyd); after thermal treatment (ThT), reduction by methanol (Red); high temperature (high T) means at/above the decompositions point of the HPA.

EPR signals after thermal treatment

Heteropoly acid, $H_4PVMo_{11}O_{40}\cdot nH_2O$ (Cs0V1). Signal A (Fig. 1(b)) is observed for all vanadium-containing hydrated molybdophosphoric acids and is reported to be characteristic of a hydrated phase. The well-resolved hyperfine structure ($A_{\parallel}$ and $A_{\perp}$), and the relations $g_{\perp} > g_{\parallel}$, $A_{\perp} < A_{\parallel}$ (Table 1), indicate isolated V^{4+} ions in an axial crystal field (tetragonal distortion) and are typical for a vanadyl ion VO^{2+} with aqua or comparable ligands.[20] Signal A is assigned accordingly to a hydrated vanadyl species outside the Keggin unit (Tables 1 and 2).

Signal B (spectrum in Fig. 1(c)) is obtained after thermal treatment at 573 K in O_2/He. This spectrum is observed between 473 and <773 K under O_2, under reductive conditions and, after catalytic reactions, is partially superimposed by other spectra (Mo^{5+} and/or broad lines[4,5]); it is assigned in the literature to V^{4+} in the secondary structure of the Keggin unit.[5,7,9] Support for this interpretation comes from an investigation of the caesium salt (see below).

Fig. 1(d) shows a spectrum obtained after temperature-programmed desorption (TPD) of water in He up to 773 K. It is very similar to that reported for the treatment in vacuum.[4] It consists of three vanadyl species and a broad (symmetric) line is superimposed. One of these species corresponds to signal B. There was no indication of Mo^{5+} signals.

Fully exchanged caesium salt $Cs_4PVMo_{11}O_{40}\cdot nH_2O$ (Cs4V1). Signal C: The thermal behavior of the Cs salts monitored by the paramagnetic centers is different from the acid form. The V^{4+} signal after thermal treatment of Cs4V1 at 573 K in oxygen (30 min, Fig. 2(a)) is the same as before thermal treatment and is denoted as signal C (Tables 1 and 2). This signal C is observed up to treatment temperatures of nearly 773 K without significant changes (but with progressively reduced intensity). It is assigned to V^{4+} substituting Mo inside the Keggin unit.

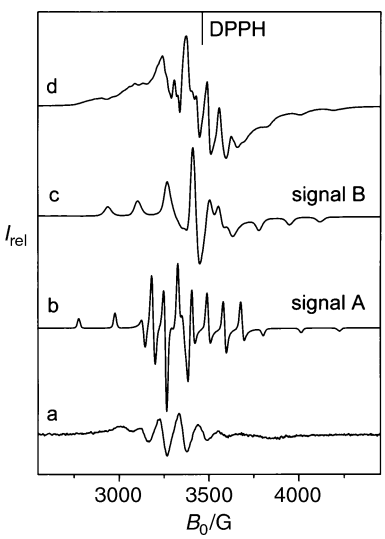

Fig. 1 EPR spectra of $H_4PVMo_{11}O_{40}$ (Cs0V1): without thermal treatment, recorded at (a) $T_{rec} = 300$ K and (b) $T_{rec} = 130$ K; (c) after thermal treatment in O_2(35%)/He at 573 K for 30 min ($T_{rec} = 130$ K) and (d) after TPD (in H_2O/He) up to 773 K ($T_{rec} = 130$ K).

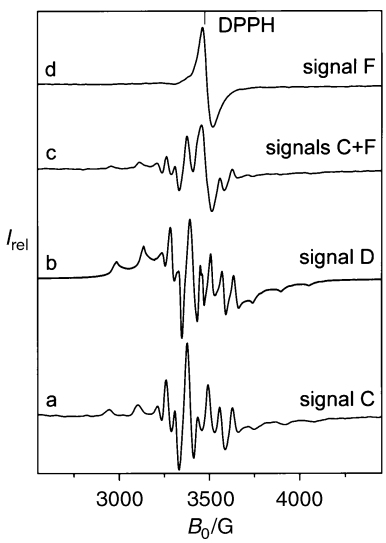

Fig. 2 EPR spectra ($T_{rec} = 130$ K) of Cs salts of heteropoly acids after treatment in O_2(35%)/He: $Cs_4PVMo_{11}O_{40}$ (Cs4V1) at (a) 573 K and (c) 773 K, $Cs_3HPVMo_{11}O_{40}$ (Cs3V1) (b) at 573 K, and $Cs_3PMo_{12}O_{40}$ (Cs3V0) (d) at 673 K.

Signal F: After treatment in O_2/He at and above 673 K an additional signal (F) (Fig. 2(c)) is superimposed on signal C. The same symmetrical signal F at $g = 1.940$ is observed after treatment of Cs3V0 at $T = 643$ K (Fig. 2(d), signal F, Table 1). Indeed, spectrum 2(c) can be simulated by a superposition of (a) and (d) in Fig. 2. The isotropic signal F (Fig. 2(d)) is reported in the literature to represent an unpaired electron delocalized over 12 molybdenum atoms ("hopping") in an undestroyed Keggin unit.[21,22] The signal can be removed by treatment in H_2O/He at room temperature for 30–60 min, however, this treatment did not reproduce the original intensity of signal C. The appearance of signal F indicates the substitution of vanadium by molybdenum in some of the Keggin units. Signal F in Cs4V1 and Cs3V0 is different from that obtained for the acid Cs0V0 after thermal treatment at 673 K (and above), where the Mo^{5+} signal E with $g_\perp = 1.952$, $g_\parallel = 1.846$ and well-resolved ^{95,97}Mo-hfi were observed ($A_\perp = 45$ G and $A_\parallel = 100$ G, not shown[22,23]). The g-anisotropy of the Mo^{5+}-signal is reduced by treatment at higher temperatures (773 K), monitoring a progressive distortion and destruction of the Keggin unit in Cs0V0 and demonstrating the higher thermal stability of the caesium salts.[22,23]

Partially exchanged caesium salt $Cs_3HPVMo_{11}O_{40}\cdot nH_2O$ (Cs3V1). In contrast to Cs4V1, the V^{4+} EPR spectrum of Cs3V1 after treatment in oxygen/He at 573 K (30 min, signal D, Fig. 2(b)) has a very similar spectral pattern as signal C (found for Cs4V1), comparable g values, but different hyperfine coupling constants (reduced ^{51}V hf coupling, Table 1). This indicates that the thermal behavior and the structure after thermal treatment of Cs3V1 are very similar to those of Cs4V1. In addition, small amounts (about 10%) of species B (Cs0V1) are observed in the spectra of Cs3V1, indicating the presence of few small vanadyl bridges between Keggin units (secondary structure).

Quantitative determination of the number of paramagnetic species

The quantitative determination of the vanadium(IV) content by EPR yielded the following results (Table 3). In the untreated heteropoly compounds Cs4V1, Cs3V1 and Cs0V1 about 0.5, 0.7 and 2.3 mol.%, respectively, of the vanadium is present as vanadium(IV) (calculated for 5 (Cs3/4) and 16 (Cs0) H_2O).

After treatment in O_2/He (1 : 2) at 573 K for 30 min 0.2, 2.4 and 5.9 mol.% V^{4+}, respectively, were determined. For Cs4V1 the number of V^{4+} centers determined by EPR is decreased by thermal treatment (oxidation of V^{4+}). The V^{4+} contents obtained by titration methods are generally higher by several percentage points (8 mol.% for Cs0V1 and 4 mol.% for Cs3V1 of the transition metal(s) are reduced by one electron by the thermal treatment). This difference can be explained by the presence of reduced or EPR silent species (V^{4+}-dimers; V^{4+} of tetrahedral symmetry; V^{3+}, although V^{3+} species could not be observed by UV–Vis spectroscopy), and to some extent also by the estimated experimental error ($\Delta_{rel} \leqslant \pm 15\%$),[24] although the reproducibility of all results was very satisfactory.

Reversibility of the structural changes induced by thermal treatment of Cs0V1

We investigated the reversibility of Cs0V1 decomposition in terms of its dependence on the duration of the treatment with H_2O/He at room temperature after treatment at 573, 623 and 673 K for 30 min (4% H_2O/He, 293 K; the temperature $T = 673$ K marks the point immediately before irreversible decomposition of the Keggin unit). Signal A observed for the untreated acid could be reproduced quantitatively in all experiments. During rehydration no additional vanadium species were observed in the EPR spectra. Obviously, no stable paramagnetic intermediates are formed during this process. The dehydration (623 K)—rehydration (293 K) cycle was repeated three times, and the procedure was found to be completely reversible. In the second cycle after oxidative treatment at 673 K a Mo^{5+} signal E (Table 1) was superimposed on the vanadium signal B. This is the first time that the simultaneous presence of these two signals is reported under non-reducing conditions. Signal A could be completely restored by rehydration (*i.e.* the Mo^{5+} signal vanishes); after repeated oxidative treatment the V^{4+} signal B and the Mo^{5+} signal are analogously restored. In no case was a line broadening or temperature behavior indicating a magnetic interaction of the V^{4+} and Mo^{5+} species observed in these experiments. This shows that the V^{4+} and Mo^{5+} centers were never localized in/at the same Keggin unit. The chronological procedure of the rehydration is demonstrated in Fig. 3 (see figure caption). An estimation of the number of paramagnetic centers by double integration of the EPR spectra shows that there is only a slight reduction of the vanadium(IV) content after rehydration.

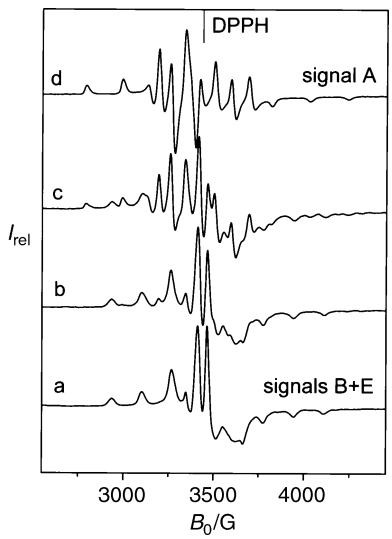

Fig. 3 EPR spectra ($T_{rec} = 130$ K) of $H_4PVMo_{11}O_{40}$ (Cs0V1) during rehydration experiments: (a) after thermal treatment (O_2(35%)/He) at 673 K for 30 min, and after rehydration at room temperature with (b) 5 min H_2O/He, (c) 20 min H_2O/He and (d) 50 min H_2O/He.

Table 3 Degree of reduction of selected heteropoly compounds before and after thermal treatment in O_2(35%)/He at $T = 573$ K (120 min) as determined by EPR (double integration) and redox titration (relative error about 15%)

	EPR		
Compounds	Before treatment	After treatment	Redox titration after treatment
$H_4PVMo_{11}O_{40}$ (Cs0V1)	2.3	5.9	8
$Cs_3HPVMo_{11}O_{40}$ (Cs3V1)	0.7	2.4	4.1
$Cs_4PVMo_{11}O_{40}$ (Cs4V1)	0.5	0.2	—

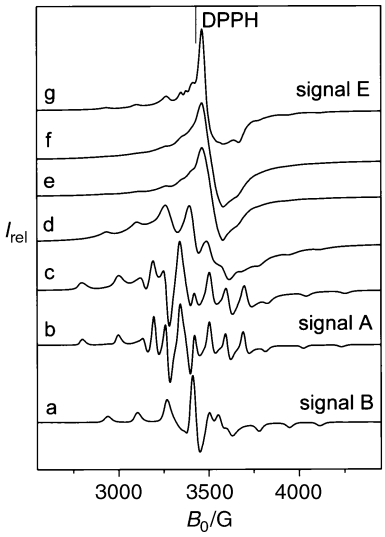

Fig. 4 EPR spectra (T_{rec} = 130 K) of $H_4PVMo_{11}O_{40}$ (Cs0V1) (a) after thermal treatment in O_2(35%)/He at 623 K, (b) after sorption of methanol at 323 K, after treatment (TPD) in He at (c) 373, (d) 473, (e) 573, (f) 623 K and (g) after treatment in O_2(35%)/He at 623 K.

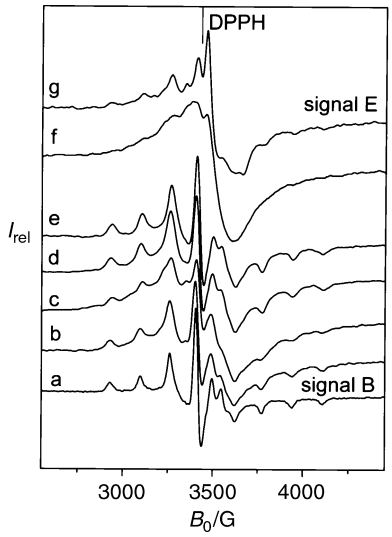

Fig. 6 EPR spectra (T_{rec} = 130 K) of $H_4PVMo_{11}O_{40}$ (Cs0V1) after treatment (a) in O_2(35%)/He at 623 K, (b) methanol/O_2 (1 : 3) at 523 K, (c) in methanol(2%)/He at 523 K, (d) in O_2(35%)/He at 523 K, (e) in O_2(35%)/He at 623 K, (f) in methanol(2%)/He at 573 K and (g) in O_2(35%)/He at 623 K.

Adsorption, desorption and reaction with methanol

Two series of experiments were performed to study the interaction of methanol with the acid and the Cs_4 salt of $PVMo_{11}O_{40}$:

(i) Methanol is adsorbed from a gas stream CH_3OH/He after thermal treatment and the EPR spectra were taken at T_{rec} = 130 K after TPD up to the temperature denoted, followed by treatment at this (constant) temperature for 30 min in He.

(ii) The thermally pretreated heteropoly compounds are treated with a methanol/helium (or methanol/oxygen/helium) stream at different temperatures (30 min) and the reoxidation by O_2/He is investigated.

Adsorption and TPD. For the Cs_4 salt, after all experimental steps of the TPD experiments—activation in O_2/He at 623 K, adsorption of methanol at 323 K, TPD after 473, 573 and 623 K, and after reoxidation in O_2/He at 623 K—only signal C, typical for the Cs_4 salt (Table 2), was observed in the EPR spectra with increasing intensity (by a factor of 5 from room temperature to 623 K). Reoxidation at T = 623 K in O_2/He reproduces the starting intensity of signal C.

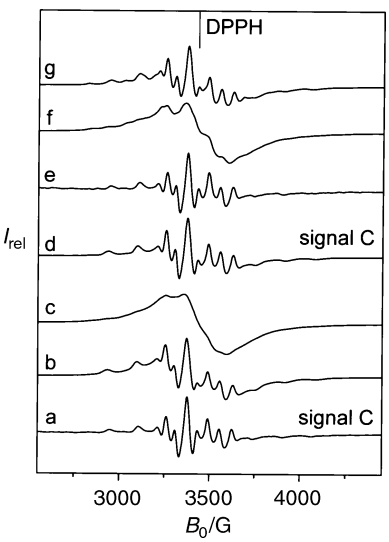

Fig. 5 EPR spectra (T_{rec} = 130 K) of $Cs_4PVMo_{11}O_{40}$ (Cs4V1) after treatment (a) in O_2(35%)/He at 623 K, (b) methanol/O_2 (1 : 3) at 523 K, (c) in methanol(2%)/He at 523 K, (d) in O_2(35%)/He at 523 K, (e) in O_2(35%)/He at 623 K, (f) in methanol(2%)/He at 573 K and (g) in O_2(35%)/He at 623 K.

The EPR spectra obtained under identical conditions for the acid form are shown in Fig. 4. Starting from signal B after thermal treatment, signal A, typical for the untreated, hydrated heteropoly acid, is observed after methanol adsorption at 323 K (Fig. 4(b)). Residues of water in the feed and structural reorganization due to the coordination of methanol to free coordination sites (oxygen vacancies) could be responsible for this reaction. After TPD at increasing temperatures, the EPR lines of signal B appear and increase again, are broadened and superimposed on a broad isotropic line at $g \simeq 1.955$ (line width ΔB_{pp} = 30 mT). This broad line (Table 2) is due to spin–spin interactions between the increased number of V^{4+} centers (shorter distances). After TPD at 573 K, as after reoxidation, the EPR spectrum is clearly dominated by Mo^{5+} signals ($g \simeq 1.924$, ΔB_{pp} = 11.5 mT), indicating partial decomposition of the Keggin unit. This signal is better resolved after reoxidation (signal E, Fig. 4(g), Table 1).

Reaction with CH_3OH/O_2. Treatment of the Cs_4 salt (Cs4V1) by O_2/methanol (Fig. 5) at T = 523 K strongly increases the intensity of signal C typical for the salt superimposed on a broad signal at $g \simeq 1.96$ ($\Delta B_{pp} \approx 25$ mT). After further treatment in methanol/helium the broad signal dominates the spectra (Fig. 5(c)), presumably as a result of strong magnetic interactions between the increased number of paramagnetic V^{4+} centers of the same structure. This signal can be removed nearly completely by reoxidation (O_2/He) at 523 K, although the intensity of signal C is still three times higher than before the treatment series. The starting EPR spectrum (signal C only) is completely restored by reoxidation at 623 K. As shown in Figs. 5(f) and (g) the treatment with methanol at 573 K and reoxidation irreversibly produce an additional V^{4+} species ("$g_{\|/3}$" $\simeq 1.91$, "$A_{\|/3}$" = 205 G) in addition to signal C. This can be interpreted by the presence of a new species with g and A values similar to those of signal C or by rhombic distortion in signal/species C. Treatment in H_2O/He at room temperature for several hours reproduces the original intensity.

During the identical procedure with the acid form (Cs0V1) similarities and differences were observed: catalytic reaction

(CH_3OH/O_2/He) and reduction (CH_3OH/He) increase the intensity and line widths of signal B and the new superimposed broad isotropic signal ($g \simeq 1.955$, $\Delta B_{pp} \approx 25$ mT) to an increasing extent. In comparison to the Cs salt the reoxidation is less complete (remaining broad background signal even after 623 K oxidation over a longer time). After reduction at 573 K and reoxidation at 623 K (Fig. 6(f) and (g)) Mo^{5+} signal E is observed in contrast to the Cs salt. The results indicate the irreversibility of this redox process for the acid and reflect the higher stability of the Cs_4 salt.

4. Discussion

The purpose of this work was to examine the structure of vanadium(IV) and molybdenum(V) species in heteropoly compounds $[PVMo_{11}O_{40}]^{4-}$ formed during dehydration (thermal treatment), during reaction with methanol as stoichiometric organic reductant and during catalytic conversion of methanol with molecular oxygen by EPR spectroscopy. New insights were obtained by the following experiments:

(i) Comparative studies of the acid form and caesium salts of the heteropoly anion (the formation of vanadyl bridges between Keggin units proposed for the acid are impossible for the fully exchanged salt, Cs4V1).

(ii) The quantitative determination of the number of paramagnetic species in the different states of the heteropoly compound.

(iii) Investigation of rehydration after thermal treatment and catalysis.

Although vanadium(V) is present in the starting material only, in all heteropoly compounds described, paramagnetic vanadium(IV) centers could be observed by EPR before and after any thermal treatment. The structure of the paramagnetic species and the degree of reduction, however, strongly depend on the counter-ion, on the treatment temperature and atmosphere (O_2, CH_3OH, He).

The total number of vanadium ions (formally) reduced by one oxidation number during thermal treatment is generally higher in the acid than in the Cs3V1 salt by a factor of 2 to 3 (Table 2). The percentage of V^{4+} relative to the total amount of vanadium is very low in the starting materials ($\leqslant 2\%$). That means, 98% of the vanadium are present as V^{5+}, which has to be taken into account for generalizations of EPR results concerning the whole Keggin structure. Thermal treatment up to 573 K in O_2/He increases the V^{4+} concentration by a factor of three for the acid and the Cs3V1 salt (at least 6% of the vanadium states are present as vanadium(IV) in the acid). Concerning the order of magnitude of the vanadium(IV) content in the HPA it is thus not justified to speak of traces of V^{4+} in the heat-treated (dehydrated) compound.[5] On the other hand, discussing the role and the structure of vanadium in the heteropoly anion, one must carefully distinguish between both oxidation states: V^{4+} and V^{5+}.[7,25] After stoichiometric reduction with methanol and under conditions of catalytic conversion the majority (or even all) of vanadium is present as V^{4+}. Spin–spin interactions between the V^{4+} centers cause broad lines, which prevents the deduction of detailed structural information from these EPR spectra. The reducing agent methanol used can be intercalated into the voids of the crystallites of both the acid form Cs0V1 and the fully exchanged caesium salt Cs4V1. However, different mechanisms must be regarded for the reduction of vanadium during dehydration and catalysis in the acid Cs0V1 and the caesium salt Cs4V1.

The reduction of the transition metal centers (V, Mo) during thermal treatment must be explained by the oxidation of O^{2-} ligands ("lattice oxygen") to molecular O_2, which is lost to the environment (also called autoreduction). This must be connected with structural reorganization (EPR signal A → B) and is—not surprisingly—easier in the acid than in a Cs salt. For the fully exchanged Cs4V1 salt the number of V^{4+} centers did not increase, but actually decreased during the same thermal treatment (Table 3). Salt formation with Cs suppresses the formation of significantly reduced HPA. Loss of "lattice" oxygen (O^{2-} of the Keggin unit) is not possible in Cs4V1. Increasing the treatment temperature (without additional reducing agent), *e.g.* to 773 K, partially deforms Cs4V1, indicated by the Mo^{5+} signal F (Fig. 2(c) and (d)), and does not reduce additional V^{5+}.

A variety of structural models can be found in the literature.[4–6,9,12,22,23] One interpretation assumes[22,23] that the vanadium substitutes molybdenum in the Keggin unit. This vanadium migrates out of the Keggin anion upon thermal treatment, leaving a "lacunary" species characterized by defects in the metal–oxygen octahedra. However, the incorporation of vanadium into the Keggin ion was never proven directly. Signal A, typical for V^{4+} in the hydrated phase of the heteropoly acid, and its parameters are similar to an isolated $VO_{aq}{}^{2+}$ species analogous to the counter-ion in $H[VO(H_2O)_5][PMo_{12}O_{40}] \cdot 23H_2O$,[5] *i.e.* a vanadyl ion in the secondary structure (Table 1). In addition, this EPR signal stands for a very small percentage of the vanadium. However, highly symmetric ^{51}V NMR spectra[25] indicate that even the V^{5+} species, *i.e.* the majority of vanadium, is in the secondary structure for the hydrated acid. Additional support for the assignment of signal A comes from the present results for the fully exchanged Cs salt (Cs4V1). Cs salt formation stabilizes the monomeric Keggin unit against oligomerization and changes the redox properties. The vanadium is expected to be incorporated into the Keggin units in Cs4V1 and cannot move to a bridge-site position due to the bulky Cs counter-ions. Consistently, the EPR spectra of the V^{4+} species in Cs4V1 (signal C) are different from those in the acid (signal A). Consequently we interpret signal C found for Cs4V1 as the V^{4+} center actually substituting Mo^{6+} in a Keggin unit (Tables 1 and 2).

This assignment is further supported by the thermal stability of this species (no changes up to 773 K, Fig. 2(c)) and by the increase in intensity in signal C without a change in the EPR parameters during reduction by methanol. Obviously, this reduction is achieved by an electron transfer without any change in the coordination sphere of the vanadium. A loss of oxygen ligands is not possible and not observed.

Different behavior is expected and observed for the acid form Cs0V1 (and the partially exchanged Cs salt Cs3V1). Signal B, which is also observed, *e.g.*, for $H_4PVMo_{11}O_{40}$,[7] $H[VO(H_2O)_5][PMo_{12}O_{40}]$[5] (Table 1) and $Ce_{0.25}H_3PVMo_{11}O_{40}$ (as monomeric and dimeric species[11]) after thermal treatment and after reduction during catalysis was interpreted as VO^{2+} in the secondary structure. The reduced ^{51}V hyperfine coupling constants $A_{\parallel}$ and $A_{\perp}$ for signal B compared to signal A (Table 1) can be interpreted by a stronger electron delocalization. This can be explained[5] by the displacement of water ligands by the outer oxygen atoms of the heteropoly anions (VO^{2+} bridges different Keggin units). We would like to mention, however, that similar EPR spectra are expected for a distorted V^{4+} substituting a Mo^{6+} inside the Keggin unit. Unfortunately, EPR spectroscopy does not permit the resolution of the small magnetic interactions between the unpaired electron(s) (of V^{4+} and Mo^{5+}) and the nuclear spins of, *e.g.*, ^{31}P, ^{1}H or ^{51}V far from the paramagne tic center, which would be extremely valuable for this structural characterization.

The parameters of signals C and D (Cs salts, Fig. 2) after thermal treatment and reduction by methanol are clearly different from signal B observed for the acid. They are, however, very similar to those of the ammonium salt, $(NH_4)_4[PVMo_{11}O_{40}]$[5,9] (Table 1), where the vanadium ion is assumed to substitute Mo^{6+} in the Keggin structure. On the other side, the similar hyperfine coupling constants of signals B, C and D (Table 1) support the coordination of V^{4+}

mainly to oxygen ions O^{2-} of the heteropoly anions in all cases (inside –Cs4V1– and outside –Cs0V1– of the Keggin unit), and thus the interpretation of signal B in ref. 5. Signals C and D represent a VO^{2+} center within the Keggin structure.

The appearance of signals C and D after thermal treatment at higher temperature reflects the different stability of the acid and the caesium salts. The formation of vandyl bridges between Keggin units is made impossible in the fully exchanged salt. Cs stabilizes the existence of monomeric Keggin units but likewise inhibits the formation of catalytically necessary oligomers, which could easily supply the "lattice oxygen" for selective oxidation of methanol. This is reflected by a remarkably reduced catalytic activity of Cs4V1 compared to Cs0V1 or partially exchanged Cs salts in the selective oxidation of methanol. In Cs3V1 the starting situation after preparation seems to be similar to the acid form: signal A indicates the same environment of the small number of paramagnetic V^{4+} centers. Thermal treatment (and catalysis) produces signal D, similar to signal C of the Cs4V1 salt (and small amounts of signal B), indicating that Cs4V1 and Cs0V1 (minor amounts) are formed from Cs3V1 (restricted number of bridge-positions between Keggin units in Cs3V1).

The structural changes in the acid (Cs0V1) during thermal treatment up to 673 K (signal A → B and formation of Mo^{5+}) are completely reversible by treatment with water (in helium) at room temperature for less than 1 h (Fig. 3(a)–(d)). No stable intermediates (*i.e.* only signal B and A) were observed during this process. One can conclude that the disappearance of signal B (reoxidation of species B and reformation of the starting structure) and the reappearance of signal A (formation of a fully hydrated vanadyl ion) do not take place at the same vanadium atoms.

The narrow line width of the spectra is attributable to the separation of the paramagnetic ions by a heteropoly cage large enough to avoid dipolar broadening. Estimation of the line widths with a simple cubic lattice model[26,27] shows that only (statistically less than) one paramagnetic ion exists in one Keggin anion for all species belonging to signals A–F.

The paramagnetic centers observed after reduction and catalysis are apparently the same as after thermal decomposition: signal B for Cs0V1 and signal C for Cs4V1. The number of vanadium(IV) ions in the system increased remarkably during/after the reaction with such reducing agents as methanol or others, even under a high partial pressure of oxygen. It can be estimated that the majority (or all) of vanadium is present in the +4-state after reduction with, *e.g.*, methanol (2% in He) at $T \geq 520$ K. The degree of reduction is lower ($\approx$20% V^{4+}) under O_2/CH_3OH (3 : 1) gas mixtures than under CH_3OH/He only.

The higher stability of the Cs_4 salt is also reflected by Mo^{5+} signals and the conditions of their appearance: although vanadium is more easily reduced than molybdenum, after thermal treatment, reduction or catalysis of the acid (Cs0V1) above 573 K, Mo^{5+} signals were additionally observed (Fig. 3(a), 4(e) and (f)). The reaction is not reversible by reoxidation in oxygen at 623 K (deformation of the Keggin structure, Figs. 4(g), 6(g)). This is not so for the caesium salt Cs4V1: a Mo^{5+} signal appears above 673 K only. The line widths show that the VO^{2+} and Mo^{5+} centers were never localized in/at the same Keggin unit.

Conclusions

Comparative EPR studies of the heteropoly acid $H_4PVMo_{11}O_{40} \cdot nH_2O$ and the corresponding caesium salts Cs_3H and Cs_4 show that the structure and concentration of paramagnetic V^{4+} (and Mo^{5+}) species strongly depend on the cations (H^+, Cs), treatment temperature and atmosphere (O_2, CH_3OH, He). Possible reducing agents are: (i) O^{2-} ions of the Keggin unit, which are then lost as O_2 to the atmosphere, as well as (ii) organic molecules (CH_3OH). The first mechanism is accompanied by structural reorganization (deformation) of the Keggin structure and is observed in the acid. The Cs_4 salt is more stable and reduction takes place only according to (ii) by "external" reducing agents. V^{4+} substitutes Mo atoms in the Keggin unit in the fully exchanged Cs salt (Cs_4). The presence of the bulky caesium countercations prevents the removal of vanadium from the Keggin unit to the secondary structure and thus the formation of vanadyl bridged polymers. The different structure, stability and redox properties of the acid and the Cs_4 salt correlate with the different catalytic activity of both forms.

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