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Abstract

The present study focuses on the evidence about the existence of Keggin ions under various reactive conditions. The stability of the hydrated parent heteropoly acid (HPA) phases is probed in water, by thermal methods in the gas phase, by in situ X-ray diffraction and in situ EXAFS. An extensive analysis of the in situ optical spectra as UV-Vis-NIR in diffuse reflectance yields detailed information about the activated species that are clearly different from Keggin ions but are also clearly no fragments of binary oxides in crystalline or amorphous form. Infrared spectroscopy with CO as probe molecule is used to investigate active sites for their acidity. Besides –OH groups evidence for electron-rich Lewis acid sites was found in activated HPA. All information fit into a picture of a metastable defective polyoxometallate anion that is oligomerised to prevent crystallisation of binary oxides as the true nature of the “active HPA” catalyst. The as-synthesized HPA crystal is thus a pre catalyst and the precursor oxide mixture is the final deactivated state of the catalyst.

Keywords: diffuse reflectance, polyoxometallate, deactivated, in situ, thermal analysis, EXAFS, XRD, UV-vis-NIR spectroscopy, semi-empirical theory, FTIR spectroscopy, CO adsorption

Introduction

Vanado-molybdo-phosphates of the type of \( \text{H}_2\text{PVMo}_{11}\text{O}_{40} \cdot y\text{H}_2\text{O} \) (HPA) and \( \text{H}_{1-x}\text{Cs}_x\text{PVMo}_{11}\text{O}_{40} \cdot y\text{H}_2\text{O} \) (Cs,A, \( x=1-4 \)) have been extensively studied as active catalysts for the selective oxidation of several alkanes, aldehydes and acids [1,2,3,4,5,6]. These compounds contain networks of MO\(_6\) (M=V, Mo) octahedra, which resemble discrete fragments of metal oxide structures [7]. The Mo and V ions are distributed randomly in the mixed HPA and Cs,A compounds. Structural studies revealed that the vanadium may be in the primary structure in the as-synthesized state, but is definitively located in the secondary structure as a vanadyl group after the HPA was used as catalyst [8,9].

HPA crystallize with a large number of water molecules that are present in two distinctly different forms: crystal and structural water. Water is lost under the action of a gas stream at 300 K and/or when temperature rises. The widths of the distribution of desorption temperatures and their starting points depend on sample composition (structure) and on experimental conditions (kinetics). After the removal of crystal and constitutional water further oxygen evolution takes place and the systems undergo internal redox reaction [10]. This complex reactivity that is partly reversible with temperature calls for an in-depth structural study in order to identify the true nature of the catalytically active material. Only then the often-quoted chemical diversity of HPA systems can fully be exploited for catalytic applications. Central to redox catalysis is the knowledge of the electronic structure of the active phase. This can be studied in situ using optical spectroscopy. An essential advance in the studies of optical spectra of catalysts of different stages of their transformation was achieved by applying the in situ diffuse

reflectance UV/Vis/near-IR spectroscopy (DRS) [10,11], which proved to be a suitable technique for probing both d-d and charge transfer transitions at reaction temperature and under realistic gas compositions [12]. A number of groups have reported exsitu optical spectra [13,14,15,16,17]. It is known from these studies that the DRS method detects even small changes in spectral features connected with water loss or chemical reduction. This method was applied to investigate the reduction-reoxidation of HPA and Cs$_3$A by methanol and ethanol and to correlate structural changes with catalytic data [18].

The method exhibits limitations similar to those of other optical methods. The optical bands arising from intra- and interatomic transitions exhibit significant widths and thus limited resolution. Due to strong coupling of outer valence electronic states with the vibrational states of the solid the bands are additionally broadened. A further loss in resolution caused by data acquisition above room temperature has to be accepted as consequence of the dynamic nature of the activated systems [11,19]. The multiple redox states of activated HPA give rise to band systems strongly overlapping and thus requiring data analysis based on theoretical predictions in order to derive meaningful electronic structural information.

The parent structures of HPA that constitute highly active materials for selective oxidation reactions (e.g. methacrolein to methacrylic acid [20]) contain as common motif the Keggin anion. Incompletely salified Cs$_3$A (e.g. Cs$_3$H$_3$,$ PMO$_{12-x}$O$_{40}$ (2 ≤ x < 3), Pn-3m (No. 244), a = 11.85 Å [21]), for instance, is applied on the industrial scale. It has been proposed that the active phase of the HPA under reaction conditions corresponds to the intact and undistorted Keggin structure and, hence, that the catalytic reactivity of the material could be understood based on the initial structure of the HPA [22,23]. Conversely, the stability of the Keggin anions during thermal treatment and under catalytic conditions, the homogeneity of the partially salified HPA, and the correlation of the structure of the HPA and its catalytic activity are under debate [24,25,26,27]. Mixed phases of partially salified HPA have been proposed forming a core-shell system of the Cs$_7$A-salt and the free acid under catalytic conditions [25]. Furthermore, it has been suggested that the molybdenum cations [28] as well as the vanadium cations [29,30] migrate from the Keggin anion to cationic positions in the structure [31,32] and that the heteropoly acids become partially reduced under reaction conditions [33,34].

This migration of cations from the Keggin anion has been speculated to be responsible for the catalytic activity of the heteropoly oxomolybdates with Keggin structure [25,29,30,33,35,36,37]. The result of the migration is a cubic molybdenum autosalified heteropolyacid (Pn-3m, a = 11.853 Å) derived from triclinic H$_2$PMO$_{12}$O$_{40}$*13H$_2$O under reduction conditions with propane and hydrogen at temperatures above 600 K. This way the in situ studies on the electronic structure of the active state of HPA are corroborated by direct in situ geometric structural studies using X-ray diffraction and EXAFS.

Redox transformations require in addition to the availability of electrons (that are absent in stoichiometric parent HPA) certain acid-basic properties of the bi-functional catalysts. A frequently cited property of HPA is their strong acidity that is related to the presence of structural water. As this water may be absent under reaction conditions it is adequate to probe the acid-base properties of activated samples with a suitable method. The acidity of solid heteropoly compounds [38] has been investigated through interaction with bases combined with different methods of analysis: (i) Hammett indicators + visual inspection [39], (ii) ammonia + temperature programmed desorption (TPD) [40,41], IR spectroscopy [42], calorimetry [43,44], and (iii) pyridine + TPD, IR spectroscopy [45,46].

The use of Hammett indicators is difficult because many heteropoly compounds are strongly colored. Not only the surface of heteropoly acids interacts with vapors; many polar molecules enter the bulk, usually in a number related to the amount of protons per formula unit [47] (formation of clathrates?). The reaction with the strongly basic molecules ammonia and pyridine leads to the stoichiometric formation of ammonium and pyridinium salts. This reaction is not easily reversible by evacuation at moderate temperatures. Ammonium salts only start to decompose at higher temperature, e.g. (NH$_4$)$_3$PMO$_{12}$O$_{40}$ releases most of its NH$_3$ at 700 K [41]. Upon heating pyridinium salts of H$_3$PMO$_{12-x}$VO$_x$ in TPD experiments H$_2$O, CO, CO$_2$, and N$_2$ were detected besides pyridine, indicating that a fraction of the pyridine was oxidized. The strong bases ammonia and pyridine can, thus, not be considered as probe molecules for the heteropoly compounds within the definition of acidity as constituting an equilibrium reaction between a conjugated acid-base pair. The heat measured during interaction with the "probe" is actually the heat for the salt formation. It is thus possible to estimate the difference in the enthalpies of formation between the acid and the salt. The often discussed difference in stability can be quantified; as an example (NH$_4$)$_3$PMO$_{12}$O$_{40}$ is about 270 kJ mol$^{-1}$ more stable than the corresponding acid.

The salt formation interferes with the detection of further acid sites, because all additionally offered probe molecules interact with the ammonium or pyridinium salt and not with the original compound. Ammonium and pyridine are thus good to titrate the acidic protons, but all further interpretations are questionable. Bielanski et al. [43] only found Brønsted and no Lewis sites on a series of H$_3$PMO$_{12-x}$VO$_x$ samples using ammonia as a probe, equally Serwicka et al. [47] detected ad(b)sorbed pyridine “predominantly” in its protonated form after adsorption on H$_3$PMO$_{12-x}$VO$_x$.

Another probe tested was carbon monoxide, which was adsorbed at 100 K on H$_3$PMO$_{12}$O$_{40}$ and its cesium salts [48]. The spectra showed three different bands at 2165 cm$^{-1}$, assigned to adsorption on OH groups, 2154 cm$^{-1}$, assigned to adsorption on cesium cations, and 2139 cm$^{-1}$, assigned to physically adsorbed species. Again, no Lewis sites were found. However, as HPA are thought to activate oxygen through a Mars–van–Krevelen mechanism [10,42], the presence of...
oxygen vacancies and, thus, Lewis acid sites, i.e. coordinatively unsaturated (cus) cations, appears plausible.

**Experimental**

**Synthesis**

H$_{52}$P(V)Mo$_{12}$O$_{40}$ was prepared by dispersing MoO$_3$ (and V$_2$O$_5$, both obtained from Merck) in distilled water. Addition of an excess amount of phosphoric acid and refluxing led via dissolution-precipitation to the HPA. Silicon containing HPA were synthesised by dissolving sodium molybdate (and sodium vanadate, both Merck) in distilled water and adding sodium silicate. An alkaline solution was obtained, which was then slowly acidified with hydrochloric acid. From these solutions, the free HPA were extracted with diethyl ether. The heteropoly compounds, H$_2$[PMo$_{12}$O$_{40}$]$_n$13H$_2$O and Cs$_3$H[PMo$_{12}$O$_{40}$], were prepared following the method described by Tsigdinos et al. [49]. All Cs salts of the HPA were obtained by addition of Cs$_2$CO$_3$ to a solution of the appropriate HPA in distilled water. The solution was stirred and subsequently reduced until complete precipitation. The main component that was obtained was Cs$_3$HPmo$_{12}$O$_{40}$. A molybdenum salted HPA was obtained by thermal treatment of H$_3$[PMo$_{12}$O$_{40}$]*13H$_2$O in a flow reactor in the gas phase of 10% propene in helium (100ml/min total flow) up to 673 K (5 K/min). A series of flows with the general composition (NR)$_3$H$_3$[PVMo$_{12}$O$_{40}$]*nH$_2$O was obtained by precipitating the free acid form with alkylammonium bromides. The alkyl group (R) was -H, -methyl, -ethyl, -n-propyl or -n-butyl. All samples were checked for phase purity by X-ray diffraction. A careful study of the intensity distribution and search for amorphous constituents were applied. Only well-crystalline materials were used in the subsequent studies. This way reproducibility of the samples as further checked by thermal analysis was sufficient over the last 10 years that were needed to arrive at the results presented here.

**Analytical**

**Stability in water**

Conductivity was measured with a cell exhibiting a cell constant of 1 cm$^{-1}$ and a WTW device; the Zr(IV) solution was added manually in small quantities and the corresponding conductivity values were noted; the solution was kept at room temperature during the titration.

**TG**

The TG-investigations were carried out using a Seiko SSC 5200; about 20 mg of sample were placed in an Al-pan; the set-up allowed the control of atmosphere and a constant gas-stream of desired composition passing over the heated sample (realized by the use of BRONKHORST mass-flow controllers); the detection of gaseous species was carried out with an IMR-MS (ion-molecule-reaction excitation mass spectroscopy [50]) device connected to the exhaust of the TG-instrument; the heating rate was set to 5 or 10 K/min.

**TPRS**

Experiments were conducted in a tubular glass reactor, inner diameter approximately 7.9 mm; about 20 mg of sample were fixed by glass wool; a stream of He was added to the reactant gases to give a total flow of 100 ml/min; analysis of gaseous compounds downstream of the reactor was realized by a conventional QMS Prisma (BALZERS/PFEIFFER) connected to the exhaust.

**In-situ TG-DSC**

Investigations were performed using a NETZSCH device; the sample was placed in vertical tubular reactor and a gas stream was forced to pass around the sample; the gas flows were regulated by BRONKHORST mass-flow controllers.

**In situ X-ray diffraction**

In situ XRD experiments were performed on a STOE STADI P powder diffractometer (Bragg-Brentano geometry, secondary monochromator, Cu-Kα radiation) equipped with a Bühler HDK S1 high temperature chamber.

**In situ XAS**

In situ transmission XAS experiments were performed at the Mo K edge (19.999 keV) at beamline X1 at the Hamburg Synchrotron Radiation Laboratory, HASYLAB, using a Si(311) double crystal monochromator (measuring time ~ 4.5 min/scan). The measurements were performed in a flow reactor (4 ml volume) in the transmission geometry. Total flow of gases was set to 20 ml/min (10% propene in helium) and a heating rate of 5 K/min was applied. Analysis of the gas phase was performed with a quadrupol mass spectrometer, QMS 200 (Pfeiffer), with a time resolution of ~12 s per selected masses scan. The heteropoly acid was mixed with boron nitride (7 mg HPA, 30 mg BN) and pressed with a force of 1 ton into a 5 mm diameter pellet resulting in an edge jump at the Mo K-edge of $\Delta$E$_0$ ~ 2. Details of the experimental set up can be found in Ref. [50]. XAFS data reduction and analysis were performed using the software WinXAS 2.3, [51].

EXAFS data analysis was performed using theoretical backscattering phases and amplitudes calculated with the ab initio multiple scattering code FEFF7 [52]. EXAFS refinements were performed in R space to magnitude and imaginary part of a Fourier transformed $k^2$-weighted experimental $\chi(k)$ using the standard EXAFS formula (k range from 4.3 to 14.9 Å$^{-1}$, R range 0.7 to 4.2 Å). Structural parameters that are determined by a least-squares EXAFS fit to the experimental spectra are (i) one E0 shift, (ii) Debye-Waller factors for single-scattering paths, (iii) distances of single-scattering paths. Coordination numbers (CN) and S$_0^2$ were kept invariant in the refinement.

**In-situ UV-Vis-near-IR spectroscopy**

A description of the modified UV-Vis-near-IR diffuse reflectance spectrometer, the home-made flow-through microreactor and other experimental details can be found elsewhere [10,12]. All spectroscopic measurements were
carried out with Spectralon® (Labsphere) as reference material. HPA samples (7-19 wt%) were mixed with SiO₂ (Her- aeus, 0.1-0.4 mm). The apparent absorption \( K(\lambda) \) as a function of the wavelength \( \lambda \) was evaluated from the diffuse reflectance data using the Kubelka-Munk rule, which was shown to yield superior results than the intensity scaling with 1 - \( R_{\text{mixture}} / R_{\text{SiO}_2} \).

**IR spectroscopy and CO adsorption**

The IR experiments were carried out on a Perkin Elmer S 2000 spectrometer equipped with a liquid nitrogen cooled MCT detector at a spectral resolution of 4 cm⁻¹ and accumulation of 200 scans. The samples were pressed (at 320 MPa) into infrared transparent, self-supporting wafers (typically 20 to 30 mg/cm²) which were placed in a home-made stainless steel, low-temperature infrared cell with CaF₂ windows. The cell was connected to a vacuum system. The sample was activated in situ in the heating zone of the IR cell under vacuum (final pressure 1x10⁻⁴ hPa) at 523 and 673 K for 2.5 h (subsequent experiments with one sample). The spectra were recorded at 77 K while the CO pressure was increased stepwise in the range of 0.001 – 6.5 hPa. All spectra shown represent the difference between spectra of the sample recorded in the presence and in the absence of CO.

**Results and Discussion**

**Stability**

**Stability in water**

Keggin-type HPA are stable in aqueous solution only at a pH lower than 3. A rise in pH decomposes the complex anion and smaller metallate units are formed. It is argued, that even at low pH the HPA compounds are subjected to dynamic equilibria rather than to permanently stable molecular entities. This can be demonstrated by elimination of \( \text{PO}_4^{3-} \) from a solution of \([\text{PMo}]\) by precipitation with ZrOCl₂ which is known to produce insoluble solids of the approximate composition \( \text{Zr}_3(\text{PO}_4)_4 \) even in very acidic environments. A cloudy precipitate formed instantaneously upon the addition of the first quantities of a 0.01 M ZrO(SO₄)₂ solution to the 0.01 M dissolved \([\text{PMo}]\). After drying at room temperature the isolated solid was a mixture of an amorphous phase and of \( \text{Zr}_3(\text{PO}_4)_4 \) in the XRD characterisation. The action of the precipitating agent on the solution was investigated by the course of the ionic conductivity of the solution during Zr addition. Results are presented in Figure 1. Regardless of the immediate precipitation and the formation of \( \text{Zr}_3(\text{PO}_4)_4 \) the evolution of the conductivity (\( \kappa \)) does not show the characteristic features of the comparative \( \text{H}_3\text{PO}_4 \) titration (inflection point at the stoichiometric ratio \( \text{Zr}:\text{P} = 0.75 \)) but a monotonous increase over the whole range. The HPA is a very strong acid with pKa values below 1 and fully dissociated. The rise in conductivity in parallel to the formation of an insoluble fraction therefore indicates the generation of smaller entities by the degradation of the complex Keggin anion. This simple experiment shows clearly the structural dynamics of Mo-HPA even in water at 300 K.

**Thermal stability of P and Si- HPA**

The decomposition and reduction of HPA under partial oxidation reaction conditions is demonstrated by thermogravimetry. Figure 2 summarises characteristic results. The first two peaks in the DTG can be attributed to loss of crystal water (up to 400K) and subsequent irreversible expulsion of the structural water (up to 640K), which initializes the reduction of the acid itself. Dehydration in hydrogen atmosphere leads, as shown in Figure 3, to three different steps in the TG curve corresponding to three different hydrates. Propene, a model educt for selective oxidation to acrolein and acrylic acid, reacts already at room temperature with the crystal water of the acidic HPA leading to 2-propanol. This way the loss of water of the HPA samples is considerably

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**Fig. 1** The specific conductivity (\( \kappa \)) of a \( \text{H}_3[\text{PMo}_12\text{O}_{40}] \) solution (solid symbols) and \( \text{H}_3\text{PO}_4 \) (open symbols) as response of the addition of \( \text{ZrO(SO}_4)_2 \); the initial concentration of \( \text{H}_3[\text{PMo}_12\text{O}_{40}] \) 7.15 mM and of \( \text{H}_3\text{PO}_4 \) 7.38 mM; the amount of added Zr (IV) is noted in terms of the Zr:P ratio.

**Fig. 2** TG-MS investigation on \( \text{H}_3[\text{PMo}_12\text{O}_{40}] \) in reducing atmospheres: 50 % hydrogen (gray) and 25 % propene (black), heating rate 5 K/min; the DTG-curves are displayed above and the MS traces of carbon dioxide (m/e=44) and 2-propanol (m/e=45) corresponding to the run in propene atmosphere below.

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of reduced P-compounds, e.g. PH
hydrogen atmosphere. It is attributed to the loss of P in form
the loss of structural water under isothermal con-
ous mass loss of the P-containing samples is observed after
seen from the significant effect of its alteration. A contin-
are directly co-ordinated to the heteroatom P or Si as can be
four oxygen atoms. It may be assumed that these four atoms
step is kinetically controlled and corresponds to removal of
moval. The process can be divided into two steps. The first
process relevant for the longer-term stability of the mate-
tures following the linear heating to see kinetically hindered
the one containing silicon. The incorporation of V into the
Keggin cage leads to enhanced destabilization in the case of
Si-HPA. Investigations of the catalytic activity (TPRS) can
be correlated with the TG data. All investigated HPA are
active for the partial oxidation reactions only after they have
lost all their structural water. This catalytic activity de-
creases with time on stream. The active fragments that were
formed from the Keggin anions after loss of structural water
are not stable under “dry” catalytic conditions, i.e. with no
excess water in the feed. Total oxidation increases with the
reactor temperature. For Si-HPA, the total oxidation is the
major reaction path already after the loss of structural water.
From a comparison of the catalytic activities and selectivi-
ties of the different materials it can be concluded that P sta-
bilizes the fragments of the decomposed Keggin anions,
being predominantly active in selective oxidation. The Si-
containing catalysts seem to decompose into fragments more
similar in structure to MoO$_3$ as concluded from the pro-
nounced selectivity to total oxidation.

**Stability of Cs- and ammonium salts in various atmos-
pheres**

The influence of the replacement of the acidic protons by
cesium is demonstrated in Figure 5. It is important to inves-
tigate the isothermal behaviour at typical reaction tem-
peratures following the linear heating to see kinetically hindered
processes relevant for the longer-term stability of the mate-
rials. HPA preparations in which all protons of the HPA
were exchanged by Cs$^+$ ions exhibited a considerably en-
hanced stability toward reduction. The complete salification
suppresses the reduction of the metal oxides as it keeps to-
Salts formed with bulky and instable cations

Replacing Cs⁺ by ammonium ions offers additional opportunities for systematic variation. The availability of alkylammonium species enables the systematic alteration of the cation size and in turn the stability of the HPA-salts. The oxidative sensitivity of organic ligands allows for strong auto-reduction upon thermal treatment and thus for changing the redox state of the HPA without addition of gas phase reagents. Due to the strong propensity of HPA to become reduced and hence defective in their internal structure the entire activation and deactivation scenario in temperature programmed reaction spectroscopy (TPRS) is shortened considerably as compared to Cs salts. The decomposing alkyl-ammonium salt will emit specific fragments depending on the nature of the attached organic residues. These fragments can be detected by mass spectroscopy and used as indicators for the decomposition of the Keggin structure. A series of salts with the general composition (NR₄)₂H₂[PMO₁₁O₄₀]ⁿH₂O is subjected to temperature programmed reaction analysis (R: -H, -methyl, -ethyl, -n-propyl, -n-butyl). Characterization by TG (in inert atmosphere or in 50 % oxygen, heating rate 5 K/min) reveals a distinct dependence of the thermal stability upon the nature of the cation, i. e. upon the residue R. The DTG traces presented in Figure 6 reveal the sample with the bulkiest cation to be the least stable among the alkylammonium salts. The decomposing alkyl-ammonium salt will emit specific fragments depending on the nature of the attached organic residues. These fragments can be detected by mass spectroscopy and used as indicators for the decomposition of the Keggin structure.

Figure 5a shows that the HPA is stabilised by the introduction of Cs. These salts cannot liberate structural water. The decomposition and condensation of the Keggin anion fragments therefore are suppressed. Hence, these Cs salts are catalytically inactive for the partial oxidation. Whilst Cs₃HPVMO₁₁O₄₀ is the most stable of the samples it is also the least active (Fig. 5b). The highest activity is shown by the sample where Cs replaced two protons. Such systems exhibit vacancies in both cationic and anionic sublattices. Salts of this nominal composition precipitate first regardless the ratio of HPA to Cs⁺ in the solution. Mixed solids form with a variable amount of Cs⁺ per Keggin unit. This arrangement is thermally unstable and tends to segregate into a core shell-structure [24,25]. The formal composition of the Cs₂HPA transforms during initial thermal treatment (drying above 473 K) into a nucleus, formed by the stable Cs(3)-salt and a shell of less stable but catalytically active phases of Cs(3-x) salts [24]. This arrangement can be considered as HPA supported on the Cs(3)-salt. The support enlarges the surface area and may stabilize active and metastable phases generated by a partial decomposition of HPA during activation procedures or under reaction conditions. This model is likely to explain the course of the catalytic activity in oxidation reactions along a series of Cs-HPA salts with different numbers of protons replaced by alkali ions.

Figure 5a TG investigation of Cs₃[PMO₁₁O₄₀]; reduction in 50 % hydrogen; different degrees of neutralization: no acid proton replaced (solid line), 2 protons replaced by Cs⁺ (dashed line) and all protons replaced (dotted line); the temperature is increased by 10 K/min to reach the final value of 673 K at 75 min on the relative scale; the relative mass loss for the Cs(x=0) and the Cs(x=2) samples after the expulsion of structural water is noted in the figure.

Figure 5b Temperature-programmed reaction spectroscopy (TPRS) investigation on Cs salts of [PMO₁₁O₄₀]; feed composition: equimolar ratio of propene and oxygen, 10 % in He; the temperature is initially increased to 673 K by 10 K/min and held at this level over the further course of experiment as displayed on the right axis of the panel at the top; traces of gaseous products are detected by an IMR-MS device; top panel water (m/e=18), central panel carbon dioxide (m/e=44) and bottom panel acrolein (m/e=56); the free acid Cs (x=0) is indicated by black lines, the Cs salts by gray lines – Cs(x=1) (solid), Cs(x=2) (dashed), Cs(x=3) (dotted).
Alkylammonium salts of the composition \((\text{NR}_4)_2\text{H}_2\text{[PVMo}_{11}\text{O}_{40}\text{]}\) are subjected to thermal decomposition in He; heating rate: 5 K/min; the organic residue in the ammonium cation are varied. The DTG curves are displayed in the top panel, the corresponding DSC curves are given at the bottom panel.

The decomposition is an endothermic process in inert atmosphere as indicated by the DSC curves. A minor mass loss appears as intermediate event for all samples prior to the main decomposition peak. The underlying process reveals no pronounced energetic characteristic under the given conditions. The corresponding temperature ranges from 550 K for the least stable (R = n-butyl) sample to 650 K for the most stable (R = methyl) one. The analogy with the decomposition scheme shown by the Cs-salts of this HPA allows the identification of this step as the expulsion of structural water. The integrated weight losses corresponding to these DTG signals amount to 1 % and are in reasonable agreement with the assumed abstraction of structural water (note: the molecular mass of the HPA-compounds of concern ranges around 1800 g/mol and one molecule of water released will account for a mass loss of approximately 0,1 %). The loss of structural water is the beginning of the decomposition of the molecular anions. The threshold temperature for the disintegration is strongly affected by the whole salt structure and is not a function of the anion chemistry. This may be understood as kinetic hindrance of the evolution of water by the strength of the cation-anion interaction preventing microstructural disruption of the solid during water evolution.

The decomposition of the alkylammonium salts in reactant feed allows to link the occurrence of product gases and hence the catalytic activity to the degradation of the HPA crystals. The results of TPRS runs with an equimolar ratio of propene to oxygen in the feed are shown in Figure 7a–c for several relevant molecular constituents and in Figure 7d as the conversion of oxygen and propene, respectively. The applied heating ramp was set to 5 K/min. The detection of gaseous compounds downstream the reactor was performed using the highly structure-specific IMR-MS detector allowing the analysis of the products without the usual strong fragmentation [53]. The mass signals for water (18), carbon dioxide (44) and partially oxidized products (59) are displayed. As a general feature the onset temperature for the appearance of these compounds is shifted upwards as the size of the ammonium cation is decreased. The samples are developing their catalytic activity only upon their destruction. The comparison of the calculated conversion in oxygen and propene reveals, that the first, very sharp maximum in carbon dioxide and water for the samples with (-butyl) and
The expulsion of structural water is followed by the decomposition of the (N-propyl) cations. In the presence of atmospheric oxygen, this decomposition is strongly exothermic (note the corresponding DSC peaks and the deviation in the temperature ramp). This is not a single step and gives rise to at least two signals (β and γ). In inert atmosphere, these steps are shifted to higher temperatures and occur as endothermic (β' and γ') reactions, since no external combustion of ligands can occur. Coinciding with step β' (inert atmosphere), water and carbon dioxide were detected (by QMS) in the He stream. Clearly, already during this initial step, the organic residue is partly subjected to internal combustion by autoreduction of the HPA detectable by a corresponding weight loss. If oxygen is available in considerable concentrations (10 %), pronounced oxidation of the organic residue is observed at this initial stage. So far, the sample did not collapse completely. This is what happens at the γ-event, the sample restructures and presumably changes its internal Keggin structure as the counterions disappear. The signal of m/e=58 detected in the inert atmosphere is typically a N-C₃ fragment, released upon the total disintegration of the alkylation ammonium ion. The simultaneous appearance of carbon dioxide and water in the inert atmosphere proves the reduction of the oxides. This assignment agrees with the identification of MoO₃ by XRD in the material after the TPRS experiment.

The conversion of propene in the TPRS run is the highest at point 6. This is seen as the consequence of the initial HPA precatalyst restructuring. The residual mass of the sample decomposed in 50 % oxygen (77.9 %) is in very good agreement with the mass calculated for the formation of MoO₃ and V₂O₅ as final compounds. As observed for other
Keggin-type HPA, a slow process takes place before the reorganization to the final decomposition products occurs. The weight loss of 3% (from 80.9% to 77.9%) corresponds exactly to the abstraction of 4 oxygen atoms per formula unit and most probably indicates the detachment of the triads from the central heteroatom. The triads of octahedra restructure into intermediate states first forming lacunary structures and upon the loss of the “templating” central tetrahedron into binary oxides if sufficient oxygen excess is present. The comparison with the conversion data displayed in the lower part of Figure 8 allows to ascribe the maximum catalytic activity to the partially decomposed (probably lacunary) Keggin ion and the following deactivation to the detachment from the central tetrahedron facilitating the formation of poorly active ordered binary oxides.

In situ structural studies
The previous chapter revealed strong evidence for the view that at least in gas-phase oxidation catalysis the HPA systems are not active in their parent state known from X-ray diffraction studies. The massive dependence of the sequence of events and the complexity of the thermal degradation behaviour that is critically related to catalytic performance require the re-determination of HPA structures under reaction conditions. The powder X-ray diffraction analysis of used catalysts showed binary oxides in their highest or an intermediate oxidation state depending on the chemical potential of the reaction atmosphere. Evidence was presented that the good catalytic performance of these systems is indeed related to a metastable intermediate assigned from weight changes to “lacunary” structures, i.e. to voids in the spherical Keggin motif. For this reason a combination of methods is chosen sensitive either to long-range order and the packing of potentially defective Keggin units or to the local chemical environment of the M-O polyhedra that is sensitive to the partial destruction of the anions.

In situ X-ray diffraction
The evolution of the long-range structure of \( \text{H}_3[\text{PMo}_{12}\text{O}_{40}]^{3+}\text{H}_2\text{O} \) during thermal treatment in 10% propene in helium was measured by in situ X-ray diffraction (XRD). Selected XRD patterns measured at 315 K, 373 K, and 723 K are depicted in Figure 10. At 315 K the 8-hydrate [27,28] is detected together with the anhydrous \( \text{H}_3[\text{PMo}_{12}\text{O}_{40}] \) [54]. The 8-hydrate is formed from the initial 13-hydrate in the temperature range of 300 - 315 K. Between 348 and 573 K the anhydrous phase is observed, while at 598 K a highly disordered and not yet identified phase is formed. The latter is slowly transformed into the cubic HPA (\( Pn-3m \), \( a = 11.853 \) Å) between 600 K and 723 K. At 773 K reduction to MoO\(_3\) is observed. The same evolution of XRD powder patterns was measured during the thermal treatment of \( \text{H}_3[\text{PMo}_{12}\text{O}_{40}]^{3+}\text{H}_2\text{O} \) in 5% \( \text{H}_2 \) in helium. This sequence of events coincides with the thermal analysis data (see Figure 5b) and identifies the cubic structure as the material responsible for selective oxidation activity. In Figure 11 the XRD pattern of a cubic HPA obtained from \( \text{H}_3[\text{PMo}_{12}\text{O}_{40}]^{3+}\text{H}_2\text{O} \) after treatment in 10 % propene in helium (RT - 673 K) is depicted together with two simulated XRD powder patterns using two different structural models. The simulated XRD pattern in Figure 11A was calculated for a potassium salt of a molybdenum heteropoly acid (K\( \text{H}[\text{PMo}_{12}\text{O}_{40}]\) \( \text{H}_2\text{O}, Pn-3m\), [ICSD 209]). For the calculation the potassium ions were omitted and the cell parameter was adjusted to \( a = 11.853 \) Å. Although all peaks in the experimental pattern are accounted for by the cubic HPA phase and all peak positions agree well between experiment and calculation, a considerable deviation in the peak intensities of the two patterns can be seen. The simulated pattern in Figure 11B was calculated for a molybdenum heteropoly acid ([ICSD209]) while a fraction of the molybdenum cations was placed on a cationic site outside the Keggin anion. The position of the cationic site \( x = 0.347; y = 0.713; z = 0.735 \), and the site occupancy factor (SOF) for this site (0.114) and for the molybdenum site in the Keggin anion (0.717) was refined by Rietveld analysis (WinMProf) [55]. The position of the other ions in the unit cell and the
site occupation factors (SOFs) for oxygen and for phosphorus were kept fixed in the refinement. Evidently, by placing a certain amount of molybdenum cations on sites outside the Keggin anions, the agreement between experimental data and simulated powder pattern is considerably improved. Thus, we propose that a cubic molybdenum autosalified HPA is formed from the triclinic free heteropoly acid during thermal treatment in 10 % propene. The lattice constant obtained for the cubic salified HPA ($a = 11.853 \text{Å}$) is very similar to that of the cesium salt of the heteropoly acid ($a = 11.862 \text{Å}$).

It cannot be ruled out that not a naked $\text{Mo}^{6+}$ ion but molybdenyl species or reduced cations are taking the place of the alkali ion. There is no convincing way to determine the local charge distribution, as defects in the surrounding Keggin units have to be assumed. The XRD observations are not specific enough to validate the increase in structural complexity at the extra sites that will bring down further the intensity differences. A complementary local analysis is required to further substantiate autosalification.

**In situ X-ray absorption spectroscopy**

The evolution of the Fourier transformed Mo K edge $\chi(k)$ (pseudo radial distribution function, RDF) during thermal treatment of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]^{+}\text{H}_2\text{O}$ in 10 % propene is depicted in Figure 12A. The initial RDF can be very well simulated by theoretical calculations based on the structure of the undistorted Keggin anion. At ~ 400 K considerable changes in the first Mo – O coordination shell can be observed that indicate distortion compared to the initial Mo – O coordination in the Keggin anion. At ~ 600 K the entire RDF starts to change continuously into what can be assigned to the RDF of the molybdenum salified heteropoly acid (identified in used catalysts by XRD). Interestingly, the same evolution of RDF resulting in the RDF of a molybdenum salified heteropoly acid was observed during thermal treatment of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ in 10 % propene. Conversely, no significant change in the local structure was detected during thermal treatment of $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ under reducing conditions.

In Figure 12B, the Mo K edge-shift corresponding to the structural evolution depicted in Figure 12A is shown. At ~ 600 K strong reduction of the molybdenum in the heteropoly acid is observed that coincides with the formation of the molybdenum salified heteropoly acid (RDF in Figure 12A). From comparison with molybdenum oxide reference compounds [56] an average molybdenum valence of ~ 5.4 is estimated for the resulting molybdenum salified heteropoly acid.

In order to elucidate the short-range order structure of the molybdenum salified HPA, detailed XAFS analysis of the Mo K edge $\chi(k)$ was performed. Satisfying agreement between experimental data and theoretical XAFS calculations was achieved using the Mo – O and Mo – Mo distances and the respective coordination numbers in a Keggin anion as start parameters. This indicates, that to a certain degree the characteristic structure of the Keggin anion is preserved, however, with a considerably altered local geometric and electronic structure. Comparison of the theoretical and the experimental RDF of the molybdenum salified HPA together with the individual scattering paths in the RDF and the RDF of the free heteropoly acid and of ammonium heptamolybdate (AHM) is depicted in Figure 13. The RDF of
the molybdenum salified HPA appears to resemble more closely that of AHM than that of the HPA. The increase in amplitude of the first Mo – O coordination sphere of the HPA compared to HPA is because of a shift of the individual Mo – O shells and a resulting constructive interference of the corresponding XAFS χ(k) functions. The values of the Mo – O distances corroborate the analysis exhibiting a strong reduction in the Mo – O bond to the phosphate group of the Keggin anion. Furthermore, a reduction in the Mo – Mo distance in corner-sharing MoO₆ octahedra was observed, whereas the Mo – Mo distance in edge-sharing MoO₆ octahedra remains approximately the same.

For the Mo – O bond to the phosphate group in the center of the Keggin anion, a strongly reduced Debye-Waller factor is obtained for both the initial HPA and the molybdenum salified HPA. Moreover, taking the Mo – P bond into account in the theoretical XAFS calculations results in a significant improvement of the refinement. Hence, the medium range order resembles that of a Keggin anion. The lengthened Mo – O bond to the phosphate group of the Keggin anion may be indicative for a lacunary Keggin [10, 57] structure with one or more MoO₆ units missing from the initial structure of the Keggin anion. Moreover, the detailed analysis of the local structure based on the Keggin anion structure is in good agreement with the analysis of the long-range order structure, which remains closely related to the cubic structure of a salified heteropoly acid composed of Keggin anions.

Table 1 reports the summary of characteristic structural parameters (coordination number (CN) and distance R of the Mo – O and Mo – Mo coordination shells) of a Keggin anion model structure (based on [ICSD 209]) obtained from a refinement of the model structure to the experimental XAFS functions χ(k) of H₃[PMo₁₃O₄₁₃H₂O] (HPA) and of the Mo salified HPA (HPA⁺) (N_sal = 35, N_par = 14, 7 single scattering paths and 5 multiple scattering paths) (Eₒ (HPA⁺) = -3 eV, Eₒ (HPA) = 1 eV).

Evidently, partially salified heteropoly acids composed of Keggin anions are not thermally stable at temperatures above ~ 600 K and under a reducing atmosphere. Under reaction conditions, a considerably modified local Mo coordination is observed together with a strongly altered electronic structure. The molybdenum salified HPA observed is formed by autosalification as a result of the migration of molybdenum cations from the Keggin to cationic sites in the HPA structure. It seems, that the changes detected in the local structure of the Keggin anions in the heteropoly acid result in the local geometric and electronic structure of the MoO₆ units that resembles that of hexavalent molybdenum in oligomeric molybdates. This change in the local geometric and electronic structure of the HPA under reaction conditions may be a prerequisite for the catalytic activity of heteropoly acids.

We propose that the same structural alterations observed (i.e. migration of Mo cations, partial reduction, modified short-range coordination) also take place under partial oxidation reaction conditions in both the free heteropoly acid and the cesium salt. This structural evolution under reducing conditions may be in agreement with a core-shell model under selective oxidation reaction conditions [26] where the cesium salt acts as nucleus coated by the molybdenum salified HPA. Moreover, taking the Mo – P bond into account in the theoretical XAFS calculations results in a significant improvement of the refinement. Hence, the medium range order resembles that of a Keggin anion. The lengthened Mo – O bond to the phosphate group of the Keggin anion may be indicative for a lacunary Keggin [10, 57] structure with one or more MoO₆ units missing from the initial structure of the Keggin anion. Moreover, the detailed analysis of the local structure based on the Keggin anion structure is in good agreement with the analysis of the long-range order structure, which remains closely related to the cubic structure of a salified heteropoly acid composed of Keggin anions.

Table 1: EXAFS structural parameters of the autosalified HPA (HPA⁺), of the parent free acid (HPA) and of model structures of a Keggin anion (KEG).

<table>
<thead>
<tr>
<th>Pair</th>
<th>CN</th>
<th>R (HPA⁺) (Å)</th>
<th>σ (HPA⁺) (Å)²</th>
<th>R (HPA) (Å)</th>
<th>σ (HPA) (Å)²</th>
<th>R [KEG] (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-O</td>
<td>1</td>
<td>1.73</td>
<td>0.0035</td>
<td>1.69</td>
<td>0.0022</td>
<td>1.698</td>
</tr>
<tr>
<td>Mo-O</td>
<td>2</td>
<td>1.97</td>
<td>0.0025</td>
<td>1.83</td>
<td>0.0044</td>
<td>1.909</td>
</tr>
<tr>
<td>Mo-O</td>
<td>2</td>
<td>2.08</td>
<td>0.0015</td>
<td>1.99</td>
<td>0.0044</td>
<td>1.919</td>
</tr>
<tr>
<td>Mo-O-P</td>
<td>1</td>
<td>2.46</td>
<td>0.0010</td>
<td>2.43</td>
<td>0.0047</td>
<td>2.426</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2</td>
<td>3.52</td>
<td>0.0020</td>
<td>3.41</td>
<td>0.0047</td>
<td>3.417</td>
</tr>
<tr>
<td>Mo-P</td>
<td>1</td>
<td>3.64</td>
<td>0.0009</td>
<td>3.57</td>
<td>0.0009</td>
<td>3.561</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2</td>
<td>3.81</td>
<td>0.0032</td>
<td>3.71</td>
<td>0.0043</td>
<td>3.703</td>
</tr>
</tbody>
</table>
in the packing of the Keggin units become empty and allow the migration of some Mo cationic species into the secondary structure. Upon further thermal load the structural water is lost leaving behind a still three-dimensional M-O oligomer that exhibits significant relaxation of its local environment resembling more that of oligomolybdates than that of the distorted HPA precursor. Two new structures were identified that arrive from restructuring of the hydrated Keggin HPA and that are not amorphous precursors of the parent binary oxides. These oxides only occur at the end of the restructuring process and are irrelevant for good catalytic performance; the reverse synthesis of the HPA is the process of irreversible de-activation in catalysis. To re-activate or to inhibit this process choice of reaction conditions as closely as possible to the synthesis conditions is desirable; here is an explanation for the beneficial effect of a high partial pressure of steam in the feed allowing for local “hydrothermal” synthesis conditions. Such conditions will also relax the chemical stress on the oxides against reduction caused by the hydrocarbon components in the reaction mixture. Evidence from NEXAFS is presented that even without chemical stress the average electronic structure of the metastable intermediates is considerably different from the formal d⁰ valence electronic configurations of cations constituting the parent Keggin structure. Evaluation of the redox states in the active states of the HPA is required.

Electronic Structure by in situ UV-Vis-near-IR Spectroscopy

Summary of typical experimental results
For Cs₃H₅[PVMo₁₁O₄₀]·nH₂O treated in He from RT to 663 K the apparent absorption increases strongly with temperature as can be seen in Figure 14. Simultaneously, the near-IR absorption bands of the crystal water disappear completely. With increasing temperature broad absorptions develop first in the Vis spectral range and at higher temperatures also in the NIR region. Similar behaviour was observed for H₄[PVMo₁₁O₄₀]+nH₂O and Cs₃[H₃PVMo₁₁O₄₀]·nH₂O as shown and discussed in refs. [11,18,19]. Usually, the observed spectra are decomposed into Gauss profiles due to their broadening. This method is simple but quite arbitrary. Therefore, the first moment measuring the mean energy was evaluated in order to obtain more reliable information about the band evolution with increasing temperature and time on stream. The first moment is defined by the following equation:

\[ \bar{\lambda} = \frac{1}{\lambda_1^2} \int_1^2 \lambda K(\lambda) d\lambda = \frac{1}{\lambda_1} \int_1^2 K(\lambda) d\lambda \]  

(1)

Using Eq. (1) the first moments of the spectra acquired at different temperatures were obtained separately for the visible and near-IR spectral ranges. In these two cases the limits of integration have been chosen for the visible range from 500-580 nm (\( \lambda_1 \)) to \( \lambda_2 = 840 \) nm. For the near-IR range these values are 870 nm and 2000 nm. For the visible range, the value \( \lambda_1 \) was varied to minimise overlap between the ligand-to-metal-charge-transfer (LMCT) absorptions and Vis bands arising mainly from intra-atomic d-d-transitions and metal-metal charge transfer. For the full spectra the mean energy can be written as:

\[ \bar{\lambda} = \frac{1}{\lambda_1} \left( \int_1^2 \lambda K(\lambda) d\lambda + \int_1 K(\lambda) d\lambda \right) \]  

(2)

where \( \lambda_1 = 500-580 \) nm.

The resulting values as function of temperature for the two spectral ranges as well as for the whole spectrum are reported in Figure 15A for the free acid H₄[PVMo₁₁O₄₀]+nH₂O and in Figure 15B for Cs₃[H₃PVMo₁₁O₄₀]·nH₂O. The Vis part shifts barely with temperature for the H₄[PVMo₁₁O₄₀]+nH₂O, but it moves considerably for the salt whereas the inverse situation occurs for the near-IR band. The strong contribution of the near-IR band determines the different sensitivity of the whole spectrum to these changes. This result reveals the value of advanced positional analysis that shows the different origins for the phenomenologically same band shifts in the two materials.

Fig. 14 In situ DR UV-Vis-near-IR spectra of Cs₃H₅[PVMo₁₁O₄₀] from RT to 663 K. About 1 g of the HPA/SiO₂ mixture was filled into the cell; a He flow of 100 ml/min and a heating rate of 1 K/min were applied. Only selected spectra of the series are shown. The spectra RT₁ and RT₂ were obtained at 300 K with a drying He stream. The time elapsed between the two spectra was 2 h.
mixed-valence species responsible for the spectral transfor-
V (intact or defective) to the problem of light-induced electron
ating the IVCT band positions of the whole Keggin unit
ground states. This allows us to reduce the problem of calcu-
estimations testify [11] that the transfer parameters are small
different units are taken close to those in HPA. Microscopic
distances between the ions in MO
5+
and near-IR range occur from the transfer of an excess elec-
tron (chemically situated at Mo
4+
and Mo
5+ or V
4+)
and by  parameters characterizing the electron transfer b e-
tween different metal sites of the Keggin molecule [11,19].
As the intensity of an IVCT transition is proportional to the
tween different metal sites of the Keggin molecule [11,19].

Fig. 15 Panel (A): Temperature dependence of the first mo-
ment of the visible, near-IR and total spectra of H
4+[PVMo
6+]O
40 in a He stream. Panel (B): First moment of the
visible, near-IR and total spectra of CsH
3[PVMo
11]O
40 as a function of temperature in a He stream.

Data analysis using semi-empirical theory
The apparent absorption bands in HPA and its salts originate
from d-d transitions in reduced V and Mo ions and from
inter-valence-charge-transfer (IVCT) bands. These bands
designate binuclear metal centers bridged by at least one
oxygen atom in which the formal oxidation states are d
3 and
d
4 for the metals. The shape and the intensity of the IVCT
bands are determined by vibrational coupling parameters
and by parameters characterizing the electron transfer be-
tween different metal sites of the Keggin molecule [11,19].
As the intensity of an IVCT transition is proportional to the
square of the electron transfer parameter, the most intense
charge transfer bands arise from the transitions in which the
only one d
1 electron is excited from its original site to a
neighboring one. Therefore, while calculating the absorption
spectrum of a reduced Keggin unit we only take into account
single-electron transfers between adjacent edge-sharing and
corner-sharing metal sites. IVCT transitions in the visible
and near-IR range occur from the transfer of an excess elec-
tron (chemically situated at Mo
5+ or V
4+ sites) between the
ground states of neighbouring metal centers. While calculat-
ing the transfer and vibrational coupling parameters, the
distances between the ions in MoO
3 units as well as between
different units are taken close to those in HPA. Microscopic
estimations testify [11] that the transfer parameters are small
in comparison with the vibrational coupling constants for the
ground states. This allows us to reduce the problem of calcu-
lating the IVCT band positions of the whole Keggin unit
(intact or defective) to the problem of light-induced electron
transfer between two adjacent metal ions (Mo
5+, Mo
6+ or
V
4+, V
5+). The geometric structure of reduced binuclear
mixed-valence species responsible for the spectral transfor-
mations on different stages of the experiment will be de-
noted as
\[
((O_3)_1(=O)_{2,3}(O_3)_{3,4}(O_3)_{4,5}H_2O)x\]d
1-O
y-d
2((O_3)_{1,2}(O_3)_{3,4}(O_3)_{5,6}H_2O)\]

where d
1 designates the 3d or 4d electron, O
u, O
v are the
bridging and terminal oxygens, O
w stands for the oxygen in
the phosphorus tetrahedral environment, x, y, and z are the
numbers of oxygen ions extracted in the process of constitu-
tional water or oxygen evolution, z
i is the number of protons
localized on the moiety, and a=b or t for protons residing on
the oxygen species O
b or O
v, respectively. The composition
of very likely species was chosen on the basis of TG, DSC
and IMR-MS analysis [11] and using the information pre-
sented in Figures 1-5. Spectral parameters were derived
from studies of MoO
3 [11,58,59]. For sampling of species with
the most probable number of localized protons or oxy-
gen vacancies the methods of probability theory [60] have
also been applied.
The temperature dependence of the maxima of charge-
transfer bands arising from intact and defective binuclear
species is displayed in Figure 16. Two main effects can be
noticed analyzing the curves. Firstly, reduced binuclear spe-
cies MoO
3H
4- (M-metal ion) with protons localized on the
bridging oxygen atoms (O
β) give blue shifted charge transfer
bands relative to those arising from intact ones MoO
3 (com-
pare curves 7, 9, 13 for V
4+-Mo
5+ and 17, 18, 20 for Mo
5+-
Mo
6+ in Fig. 16). Secondly, the removal of bridging oxygen
(species MoO
3o) clearly results in a further blue shift in the

Fig. 16 Summary of semi-empirical calculations for the tem-
perature dependence of the peak positions of the charge
transfer bands arising from ((O_3)_{1,2}(O_3)_{3,4}(O_3)_{5,6}H_2O)\]d
1-
O
y-d
2((O_3)_{1,2}(O_3)_{3,4}(O_3)_{5,6}H_2O)\] to MO
3-MO
4+1.  s
i=1, \ 3, \ 5, \ 8, \ 11, \ 15, \ 17-22 -
Mo
5+-Mo
6+, 1.  s
i=1, \ 3, \ 5, \ 8, \ 11, \ 15, \ 17-22 -
Mo
5+-Mo
6+, 1.  s
i=1, \ 3, \ 5, \ 8, \ 11, \ 15, \ 17-22 -
transition energy (curves 3 and 17). These results obtained allow qualitative explanation for the change in the mean energy for HPA and its salts in the temperature range RT-663 K under helium flux (Fig. 15). Nearly all d-d transitions in the range $\lambda > 400$ nm contribute to the visible part of the spectra (transitions with smaller wavelengths $\lambda < 400$ nm are not considered because they overlap with the LMCT). Besides the d-d transitions a large number of intervalent transitions of the type of

$$\text{Mo}^{5+}-\text{O}_2-\text{Mo}^{6+} \rightarrow \text{Mo}^{5+}(\text{VH}^{5+}\text{O}_2-\text{Mo}^{5+})$$

$$\text{V}^{4+}-\text{O}_2-\text{Mo}^{6+} \rightarrow \text{V}^{5+}(\text{VH}^{5+}\text{O}_2-\text{Mo}^{5+})$$

also occur this spectral range.

**Analysis of the thermal behaviour of HPA**

At 300 K the loss of crystal water begins after a certain time of gas flux in $\text{H}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ [11] and $\text{CsH}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ (Fig. 2 and 14). At this initial stage there is no reduction, the $\text{H}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ and $\text{CsH}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ are partially hydrated, and the protons are not localized and reside on the bridging water moieties $\text{H}_2\text{O}^{2-}$. Thus initially, the spectra should originate from the d-d transitions in the $\text{V}^{4+}$ and $\text{Mo}^{5+}$ ions and the charge-transfer bands arising from reduced $\text{VMoO}_1\text{I}_1$ and $\text{MoO}_2\text{I}_1$ species (Fig. 16, curves 13 and 20). Nevertheless, the intensity of the charge-transfer band induced by intervalent transitions in $\text{MoO}_2\text{I}_1$ clusters at 300 K is lower than that of the band given by $\text{VMoO}_1\text{I}_1$ clusters. The minimum of the adiabatic ground state corresponding to the excess electron localized on the $\text{V}$ site lies considerably lower than that for the excess electron localized on a Mo site. At the same time the d-d transitions yield a much more intense band in the visible spectral range at 300 K than the charge-transfer band from species $\text{VMoO}_1\text{I}_1$. In the hydrated phase the electron transfer is noticeably suppressed due to the high value of the dielectric constant reducing the Coulomb interaction between metal sites facilitating this transfer. Thus we can conclude that at about 300 K the visible spectral range mainly originates from the d-d transitions in $\text{V}^{4+}$ and $\text{Mo}^{5+}$ ions.

With the rise of temperature the crystal water evolves, and the total intensity of the spectra from $\text{CsH}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ and from $\text{H}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ increases due to a rising contribution from the charge-transfer bands. The reason for this is that with water removal the screening of the electrostatic interaction between the metal ions is lifted, the dielectric constant $\varepsilon$ goes down and consequently the transfer parameters increase.

At temperatures from 326 K to 422 K the loss of crystal water is accompanied by the localization of acidic protons, the most preferable sites of which are the bridging oxygen ions. The resulting species $\text{MoO}_2(h_2)$ (M=$\text{V}^{4+}$, $\text{Mo}^{5+}$) displays three d-d bands in the visible range. These transitions are higher in energy than the corresponding transitions in intact $\text{MoO}_2$ (M=$\text{V}^{4+}$, $\text{Mo}^{5+}$) species. In addition, two new binuclear species ($\text{VH}_2\text{MoO}_1\text{I}_1$ (for brevity, we denote the metal ion in whose nearest surrounding a proton resides by $\text{MH}_2$), ($\text{VH}_2$+$\text{MoH}_2$$\text{O}_{11}$) (Fig. 16, curves 7, 9) exhibit IVCT transitions at shorter wavelengths (compare 666 nm, 717 nm, for ($\text{VH}_2$)$\text{MoO}_1\text{I}_1$, ($\text{VH}_2$)$\text{MoH}_2$$\text{O}_{11}$ and 770 nm for $\text{VMoO}_1\text{I}_1$, Fig. 16, curve 13 at 380 K). The reduced less probable $\text{MoO}_1\text{I}_1$ cluster and the cluster $\text{V}(\text{MoH}_2)\text{O}_{11}$ also yield IVCT transitions in the VIS spectra part (Fig. 16, curves 11 and 14). Thus, at temperatures between 326 K and 422 K, the VIS part of the charge transfer band is formed by IVCT transitions in intact and protonated $\text{V}^{4+}$-$\text{Mo}^{5+}$ species. In reduced species ($\text{VH}_2$)$\text{MoO}_1\text{I}_1$, ($\text{VH}_2$)$\text{MoH}_2$$\text{O}_{11}$, $\text{VMoO}_1\text{I}_1$ the positions of the IVCT transitions shift insignificantly in this temperature range as can be seen in Fig. 16. For instance, the peak positions of the IVCT transition in the ($\text{VH}_2$)$\text{MoO}_1\text{I}_1$ cluster are 661 and 670 nm at temperatures 330 and 420 K, respectively. Using probability theory [60], it can be shown for $\text{H}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ that at 422 K, when crystal water is removed, the number of Keggin anions with four acidic protons located only on Mo ions is twice as large as compared to the number of anions with protons distributed between one $\text{V}$ ion (1 proton) and 11 Mo ions (3 protons). Consequently, the number of the IVCT transitions $\text{V}^{4+}$-$\text{Mo}^{5+}$ between neighboring $\text{V}$ and Mo ions in species ($\text{VH}_2$)$\text{MoO}_1\text{I}_1$, ($\text{VH}_2$)$\text{MoH}_2$$\text{O}_{11}$ is small due to the Keggin structure (11 Mo sites at least per polyanion). In addition, the maximum number of d-d transitions from protonated units is 28 per Keggin anion at 422 K for HPA [11] instead of 24 for an undamaged anion. In consequence, for $\text{H}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ the mean energy (first moment) of the VIS spectral part remains practically unchanged in the range 373-422 K, as shown by experiment (Fig. 15A). The high-energy edge of the visible range shifts to higher values. The spectral intensity at these energies is, however, insignificant and does not affect the first moment of the VIS band. The situation is quite similar for $\text{CsH}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ in the range of crystal water removal. It is pointed out that the values of the mean energies are higher in $\text{CsH}_4[\text{PVMo}_11\text{O}_{40}]^4\text{nH}_2\text{O}$ due to the stronger crystal field and the enhanced coupling between electronic and vibrational states caused by the rigid filling of the secondary structure with Cs ions.

As the temperature continues to rise above 423 K, structural water evolves (see TG data in [11]). This water is formed by the extraction of oxygen by two protons and leads to the formation of defective clusters in which bridging oxygen ions are removed. However, the evolution of structural water is experimentally not accompanied by the appearance of new reduced clusters. Therefore, the initial transformation of the visible spectral region has to occur from the dehydration of reduced species of the type of $\text{VMoO}_1\text{O}_{16}$, $\text{MoO}_2\text{O}_{16}$, $\text{VMoO}_1\text{O}_{16}$, $\text{MoO}_2\text{O}_{16}$ (Fig. 16, curves 1-6, 8, 10) and indicates the protonation of these reduced species. It cannot be excluded that the evolution of molecular oxygen from intact non-reduced $\text{VMoO}_1\text{O}_{16}$, $\text{MoO}_2\text{O}_{16}$ moieties [3] could also lead to the above-mentioned reduced fragments. However, in the temperature range 420-670 K the peak positions of the charge transfer bands from species

$(\text{O}_2\text{O}_2(\text{O}_2))\text{Mo}^{5+}-\text{O}_2-\text{Mo}^{5+}(\text{O}_2\text{O}_2(\text{O}_2))$,  
$(\text{O}_2\text{O}_2(\text{O}_2))\text{V}^{4+}-\text{O}_2-\text{Mo}^{5+}(\text{O}_2\text{O}_2(\text{O}_2))$,  

(O\textsubscript{3}O\textsubscript{4}O\textsubscript{5})\textsubscript{2}Mo\textsuperscript{5+}-O\textsubscript{b}-Mo\textsuperscript{6+}(O\textsubscript{3}O\textsubscript{4}O\textsubscript{5}O\textsubscript{5})\textsubscript{2} (Fig. 16, curves 1-3) fall inside the ranges 448-456 nm, 458-472 nm and 532-547 nm, respectively. These positions overlap with the LMCT band and cannot be singled out. Therefore, their contribution to the first moment is not accounted for within the limit for the Vis range.

Other binuclear metal-oxo species exhibiting oxygen defects (Fig. 16, curves 4-6, 8) exhibit characteristic transitions within the window of observation of Figure 15. Likely geometric structures of such species are:

\[
\text{Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5))
\]

\[
\text{Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5\text{O}_5))
\]

\[
\text{Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}_3\text{O}_4\text{O}_5\text{O}_5)
\]

Their relevant band positions are depicted in Fig. 16, curves 4-6, 8, 10. At temperatures from 420-670 K their IVC transitions lie in the ranges 605-620 nm, 660-691 nm, and 710-747 nm, respectively, while the IVC transition in the intact reduced cluster VMoO\textsubscript{4} shifts from 775 to 812 nm. The number of species with oxygen vacancies giving IVC transitions in the visible range is expected to be much smaller than that of intact clusters as no extra feature appears in the expected spectral window. Therefore, at higher temperatures only an insignificant shift in the mean energy of the Vis spectral part is observed (see Figure 15) for H\textsubscript{2}PVMo\textsubscript{4}O\textsubscript{11} and CsH\textsubscript{3}[PVMo\textsubscript{4}O\textsubscript{11}]. The cancellation of two effects of the formation of lacunary and reduced species is responsible for the only apparent insensitivity of the optical spectra to the dynamic transformations. This finding explains the apparent contradiction between structural studies revealing the dynamic behaviour found initially in the thermal analysis data and by optical spectroscopy. It is of utmost importance that this analysis corroborates the formation of defective M-O clusters still within the superstructure of lacunary Keggin ions. The analysis further reveals that these species are a minority fraction of all cluster anions. These defective fragments may thus be good candidates for the active sites in catalysis.

One main trend can be identified in the temperature behaviour of the near-IR spectral part for H\textsubscript{2}PVMo\textsubscript{4}O\textsubscript{11}\textsubscript{40}H\textsubscript{2}O. The first near-IR band originates at 300 K from the homonuclear intervalence transition

\[
\text{Mo}^{5+}-\text{Ob}-\text{Mo}^{6+} \rightarrow \text{Mo}^{6+}-\text{Ob}-\text{Mo}^{5+}
\]

in intact Mo\textsubscript{2}O\textsubscript{11} species (model for reduced triads in the Keggin motif). The intensity of the near-IR spectral range is lower than that of the Vis part. Between 326 K to 420 K the crystal water is removed and the contributions to the near-IR band arise from the same homonuclear

\[
\text{Mo}^{5+}-\text{Ob}-\text{Mo}^{6+} \rightarrow \text{Mo}^{6+}-\text{Ob}-\text{Mo}^{5+}
\]

intervalence transitions in reduced intact and protonated species of the type of

\[
\text{(O}_3\text{O}_4\text{O}_5\text{O}_5\text{)Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5))
\]

\[
\text{(O}_3\text{O}_4\text{O}_5\text{O}_5\text{)Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5\text{O}_5))
\]

\[
\text{(O}_3\text{O}_4\text{O}_5\text{O}_5\text{)Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}_3\text{O}_4\text{O}_5\text{O}_5)(\text{H}_2\text{O})
\]

(Fig. 16, curves 10 and 17, 18). The maxima of the charge transfer bands arising from species with acidic protons localized on bridging oxygen sites (Fig.16, curves 17, 18) are blue-shifted in comparison with those arising from Mo\textsubscript{2}O\textsubscript{11} species. In spite of this, the first moment of the observed near-IR spectral part (Fig. 15) for H\textsubscript{2}PVMo\textsubscript{4}O\textsubscript{11}\textsubscript{40}H\textsubscript{2}O exhibits a red-shift in the temperature range 371-422 K. This is again due to varying spectral weights of the different contributions. The relative spectral weights of reduced species Mo\textsubscript{2}O\textsubscript{11}, (MoH\textsubscript{2})MoO\textsubscript{11} and (MoH\textsubscript{4})MoH\textsubscript{2}O\textsubscript{11} to the full spectra were found to be 18%, 33% and 13%, respectively. Consequently, the total contribution from species Mo\textsubscript{2}O\textsubscript{11} and of (MoH\textsubscript{4})MoH\textsubscript{2}O\textsubscript{11} is of the same weight as for species (MoH\textsubscript{4})MoO\textsubscript{11}. At temperatures of 370 K and 420 K the protonated species (Fig. 16, curves 17, 18) enumerated above exhibit peak positions at 1020 nm, 1036 nm, 1156 nm and 1182 nm, while at the same temperatures in the intact reduced species the charge transfer band exhibit maxima at 1241 nm and 1271 nm (Fig. 16, curve 20). These weighted contributions explain the observed red shift of the first moment of the near-IR band. Due to the smaller number of protons in CsH\textsubscript{3}[PVMo\textsubscript{4}O\textsubscript{11}] the red shift of the near-IR spectra part is less pronounced in this compound.

At higher temperatures the formation of defects also has consequences on the NIR spectral part. The newly appeared reduced, protonated species, for instance of the type of

\[
(\text{O}_3\text{O}_4\text{O}_5\text{O}_5\text{)Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5))
\]

\[
(\text{O}_3\text{O}_4\text{O}_5\text{O}_5\text{)Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5\text{O}_5))\text{H}_2\text{O}
\]

(Fig. 16, curves 21 and 22) exhibit IVC transitions and several d-d transitions in the interval 1240-2200 nm. This explains the growth of the near-IR band to the low energy side at high temperatures. At the same time species of the type of

\[
(\text{O}_3\text{O}_4\text{O}_5\text{O}_5\text{)Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5))
\]

\[
(\text{O}_3\text{O}_4\text{O}_5\text{O}_5\text{)Mo}^{5+}-\text{Ob}-\text{Mo}^{6+}(\text{O}^\text{pp}(\text{O}_3\text{O}_4\text{O}_5))\text{H}_2\text{O}
\]

(Fig. 16, curves 15 and 16) with vacancies in the Op positions exhibit intervalence transitions that fall in the range of 860-930 nm at temperatures between 500-670 K. The lacunary species that appear in the process of the decomposition of the Keggin structure cause the observed increase in the intensity of the near-IR band as well as the expansion of the wavelength range in which this band occurs. As a result, the mean energy of the near-IR band continuously shifts to the red (Fig. 15).

The in-depth analysis of shape and dynamics of the optical spectra thus have brought about not only yet another independent confirmation of the catalytic relevance of oligomeric defective but still superstructured oxo-clusters. In addition detailed structural prototypes requiring as minimum complexity binuclear clusters with defects, chemical reduction and protonation as independent secondary variables were derived from the analysis of the two-dimensional information of spectral weight (position time intensity) versus sample temperature. It became evident that a sample with homogeneous geometric structure is by no means homogeneous at the molecular level. As none of the methods applied so far are truly surface-sensitive there is no information available about the lateral and in-depth distribution of these sites representing on average a cubic packing of Keggin motif.

The function of the HPA systems in selective oxidation phenomenologically requires the presence of strongly acidic
sites that are believed to enable C-H bond activation. In the Introduction it was said that the determination of the acidity of the activated HPA is a non-trivial problem. Thus it is of great relevance to find a sign of acidity as otherwise no solid proof exists for the bifunctional character of HPA. It may well be argued that the acidity of HPA precatalysts is a secondary property over the Keggin structural motif that is clearly required as superstructure for the active sites characterised so far.

**Acid-Base Properties under Relevant Conditions**

A family of heteropoly compounds comprising the acids H$_{3+x}$PMo$_{12-x}$V$_x$O$_{40}$ with $x = 0-2$ and the corresponding salts with partial or complete replacement of the protons by cesium was investigated by adsorption of probes that presumably will not form salts. This usually overlooked deficiency of “typical” acid probes such as ammonia or pyridine hampers previous investigations the same way as the redox-labile character of the probe molecules that tend to reduce HPA. Carbon monoxide was selected because it is an excellent probe for Brønsted and Lewis acid sites [61]. IR spectroscopy was chosen as the method of analysis, because unlike calorimetry or TPD, it gives information on the nature of the sites and with the right probes is fairly sensitive to small energetic differences between sites. IR spectroscopy has been applied extensively for the structural characterization of heteropoly compounds at various temperatures and degrees of dehydration [62,63,64,65,66,67,68,69]. This method in addition delivers information on the structure of a sample after each treatment by investigating the low-frequency range of the IR spectrum.

**Thermal Stability of HPA seen by IR**

Transmittance through the acids (no Cs) was poor and CO adsorption could not be observed. After activation at 523 K, the samples Cs$_x$H$_x$PVMo$_{12}$O$_{40}$ ($x$=2-4) displayed a broad band at 4050 cm$^{-1}$ and a band at 3445 cm$^{-1}$ with a shoulder at approximately 3285 cm$^{-1}$. The intensity of the shoulder decreased from $x = 2$ to $x = 3$, i.e. with increasing Cs content. A weak, narrow band at 3535 cm$^{-1}$ was observed for Cs$_x$H$_x$PVMo$_{12}$O$_{40}$ with $x = 2-4$. After treatment at 673 K, Cs$_x$HPMo$_{12}$O$_{40}$ was devoid of any OH groups, and the spectra of Cs$_x$HPMo$_{12}$O$_{40}$ and Cs$_x$H$_x$PVMo$_{12}$O$_{40}$ were similar in the OH region with a slightly asymmetric band centered at about 3425 cm$^{-1}$. The band at 4050 cm$^{-1}$ disappeared with the treatment at 673 K. The spectrum of Cs$_x$HPMo$_{12}$O$_{40}$ treated at 523 K showed two overlapping bands at approximately 3380 and 3240 cm$^{-1}$. Both bands were weakened after treatment at 673 K and better separated with positions at 3390 and 3230 cm$^{-1}$.

Overtones and combination modes of metal- and phosphorus-oxygen vibrations were observed in the range of 2150–1850 cm$^{-1}$. The spectrum of H$_2$PMo$_{12}$O$_{40}$ exhibited one strong band at 1985 cm$^{-1}$ and a number of ill-defined and weak bands. Three strong bands at 2165, 2130, and 1990 cm$^{-1}$ and one weak band at 2040 cm$^{-1}$ characterized the spectrum of H$_2$PVMo$_{12}$O$_{40}$. For Cs$_x$H$_x$PVMo$_{12}$O$_{40}$ ($x$=2–4) three intense bands were found at 2120 cm$^{-1}$ (s, sh towards higher wavenumbers), 2035 cm$^{-1}$ (s, sh towards higher wavenumbers), and 1935 cm$^{-1}$ (vs, sh towards higher and lower wavenumbers). Depending on the Cs content and the treatment the position of the band varied by ±5 cm$^{-1}$. The general trend was a shift towards higher wavenumbers with increasing treatment temperature. The spectra of Cs$_x$HPMo$_{12}$O$_{40}$ also showed strong bands at similar positions as the other Cs-salts, namely at 2124, 2040, and 1941 cm$^{-1}$. Instead of shoulders towards higher wavenumbers on the bands at 2040 and 1941 cm$^{-1}$, two bands at 2057 and 1975 cm$^{-1}$ were clearly separated. All of these bands remained unchanged within the detection limits during CO adsorption.

The first harmonics of the metal- and phosphorus-oxygen vibrations were not accessible in transmission mode because of the cut-off of the CaF$_2$ windows. These data confirm that thermal treatment modifies the oxo anions but does not lead to expulsion of the central heteroatom and hence preserves the Keggin motif. These findings are in qualitative agreement with all other evidences presented here and indicate that thermal treatment alone without chemical reductive stress does not lead to a complete breakdown of the HPA structure. The loss of –OH groups of all partly salified samples between 573 K and 673 K is a good indication for the similarity of the present sample preparation to the in situ structure-sensitive experiments described above. This result questions the statement about the relevance of Brønsted acidity (acid protons) for the catalytic process that sets in concomitantly with the loss of the –OH groups (compare with Figure 5b).

**Analysis of CO adsorption data**

Representative spectra obtained during CO adsorption following activation at 523 and 673 K are shown in Figure 17.

![Fig. 17 FTIR spectra, difference of spectra of the sample in presence of CO / in vacuum; recorded at 77 K in transmission with self-supporting wafer. Top left: Cs$_x$H$_x$PVMo$_{12}$O$_{40}$ activation at 523 K: p$_{CO}$ = 5.2*10$^{-1}$ hPa; activation at 673 K: p$_{CO}$ = 2.8*10$^{-1}$ hPa. Top right: Cs$_x$HPMo$_{12}$O$_{40}$ activation at 523 K: p$_{CO}$ = 3.2*10$^{-1}$ hPa; activation at 673 K: p$_{CO}$ = 3.5*10$^{-1}$ hPa. Bottom left: Cs$_x$PVMo$_{12}$O$_{40}$ activation at 523 K: p$_{CO}$ = 2.26 hPa; activation at 673 K: p$_{CO}$ = 2.9*10$^{-1}$ hPa. Bottom right: Cs$_x$HPMo$_{12}$O$_{40}$ activation at 523 K: p$_{CO}$ = 7.1*10$^{-1}$ hPa; activation at 673 K: p$_{CO}$ = 3.3*10$^{-1}$ hPa. Pressures were selected to represent spectra of similar intensity.](www.fhi-berlin.mpg.de/ac)
At equal partial pressures, the band intensities were roughly proportional to the surface area of the samples. The best spectra were thus obtained for Cs$_2$H$_2$PVMO$_{11}$O$_{40}$ and Cs$_2$HPVMO$_{11}$O$_{40}$. Often, broad features of overlapping bands were observed. Series of spectra in dependence of the CO partial pressure were thus evaluated and also fit in order to identify all bands. The band positions are given in Table 2.

**Table 2:** IR band positions of CO absorption frequencies for several HPA samples activated at the temperatures given.

<table>
<thead>
<tr>
<th>Sample and activation</th>
<th>Band positions in cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$<em>2$H$<em>2$PVMO$</em>{11}$O$</em>{40}$, 523 K</td>
<td>2162</td>
</tr>
<tr>
<td>Cs$<em>2$H$<em>2$PVMO$</em>{11}$O$</em>{40}$, 673 K</td>
<td>2152</td>
</tr>
<tr>
<td>Cs$<em>2$HPVMO$</em>{11}$O$_{40}$, 523 K</td>
<td>2154</td>
</tr>
<tr>
<td>Cs$<em>2$HPVMO$</em>{11}$O$_{40}$, 673 K</td>
<td>2154</td>
</tr>
<tr>
<td>Cs$<em>2$PVMO$</em>{11}$O$_{40}$, 523 K</td>
<td>2153</td>
</tr>
<tr>
<td>Cs$<em>2$PVMO$</em>{11}$O$_{40}$, 673 K</td>
<td>2155</td>
</tr>
<tr>
<td>Cs$<em>2$HPMO$</em>{12}$O$_{40}$, 523 K</td>
<td>2164</td>
</tr>
<tr>
<td>Cs$<em>2$HPMO$</em>{12}$O$_{40}$, 673 K</td>
<td>2153</td>
</tr>
</tbody>
</table>

According to the literature [48] the band at 2162-2164 cm$^{-1}$ can be assigned to CO adsorbed on OH groups. The best evidence of CO adsorption on OH groups is a shift of the OH band parallel to the development of the corresponding CO band; no such shift was observed in our case. Other arguments though suggest adsorption of CO on OH groups: (i) the band position is typical of OH-coordinated CO, (ii) the band is observable after treatment at 523 K but not after treatment at 673 K, it is consistent with dehydroxylation, and (iii) the band is not observed for the Cs-rich and thus H-poor compounds. It appears that the shift of the OH groups could not be observed because the quality of the spectra in this range is poor and/or only a fraction of the OH groups is acidic enough for interaction.

The band at 2152-2155 cm$^{-1}$ has been assigned previously [48] to the adsorption of CO on Cs. This band, which was typically rather narrow, was found for all Cs-containing samples and the relative intensity increased with increasing Cs content.

It has been suggested that the band at 2137-2140 cm$^{-1}$ arises from "physisorbed or liquid-like CO" [48]. Not always but frequently are such bands only formed at high CO coverage, and Saito et al. [48] fitted the band with a Lorentzian line profile. We detected this band already at CO pressures <10$^{-3}$ hPa, and the line profile was not Lorentzian. However, as we observed this band for all samples, it might indeed be unspecific adsorption, not meriting further interpretation at the current state of investigation.

Most interesting are two additional bands that were not reported before: the band at 2144-2147 cm$^{-1}$, which is present in the spectra of Cs$_2$HPVMO$_{11}$O$_{40}$ and Cs$_2$PVMO$_{11}$O$_{40}$, and the band at 2130-2135 cm$^{-1}$, which is present in the spectra of Cs$_2$H$_2$PVMO$_{11}$O$_{40}$ and Cs$_2$PVMO$_{11}$O$_{40}$. Besides the OH-groups and Cs cations, other sites may also interact with the CO. Lewis acid sites could be created by defects (oxygen vacancies) in the Keggin units of the heteropoly compounds or through fragmentation of Keggin units. Coordinatively unsaturated Mo or V cations could represent such Lewis sites. Single bands at these positions are not typical of CO adsorption on Mo cations. Only bands in band pairs, indicating geminal CO species at Mo$^{5+}$ and Mo$^{6+}$ species, respectively, have been reported at these positions [70]. Neither did we observe band pairs nor are Mo$^{5+}$ species expected, because XPS measurements [71] have shown that, e.g., Mo in H$_2$PMO$_{12}$O$_{40}$ is reduced to Mo(IV) only through extensive treatment in H$_2$ at 623 – 673 K and under milder reduction conditions Mo(VI) or becomes Mo(V). We generated reference data by adsorbing CO on mechanically activated MoO$_3$ and V$_2$O$_5$. Among the features observed for both compounds were bands at ca. 2145 and 2130 cm$^{-1}$, indicating that these band positions are possible for CO adsorbed as well on Mo as on V cations. The two bands observed for various heteropoly compounds can thus be assigned to coordinatively unsaturated metal cations, i.e. Lewis acid sites; but neither of the two bands is characteristic of a particular metal cation. Most likely, the cations are reduced with respect to the original oxidation state, and the band with the lower frequency represents less positively charged species and thus a softer Lewis acid.

No assignment can be made yet for the band at 2150 cm$^{-1}$, which appears only in the spectra of Cs$_2$PVMO$_{11}$O$_{40}$. As mentioned before, the intensity of the CO bands depends roughly on the BET surface area of the sample, suggesting that CO interacts only with the surface. The bands representing the overtones and combination modes of the metal- and phosphorus oxygen vibrations did not change upon CO adsorption. Either only a small surface fraction of the sites interacts and the changes are below detection limit, or these bands represent only intact Keggin units, which do not interact with CO.

The following picture evolves from our experiments: the stability of Cs$_2$HPVMO$_{11}$O$_{40}$ is also manifested in the CO...
adsorption data; it is the only compound that yields the same CO band pattern after activation at 523 K and 673 K. All other samples undergo significant changes when heated to the higher temperature. The Mo/V cations in Cs$_3$HPMo$_{12}$O$_{40}$ are also not reduced as much by the activation procedure as in Cs$_3$HPVMo$_{12}$O$_{40}$ and Cs$_3$PVMo$_{12}$O$_{40}$. The investigated heteropoly compounds provide more surface sites than just OH-groups and Cs cations, i.e. different types of Lewis sites. The observation of such sites is consistent with the partial decomposition of the Keggin units. The probe molecule adsorption study was intended to discuss the presence of –OH groups on activated samples. The main result was, however, the detection of adsorption sites developing only after activation of the HPA that were not described earlier as other studies addressed the chemisorption properties of the parent HPA. It may be speculated that only the reduced species of lacunary Keggin units that were identified by DRS spectroscopy and that contribute to the Mo K-edge NEXAFS shift produce sites that adsorb CO at 2130 cm$^{-1}$. These sites are redox active and may be able to provide enough electrons (two electrons per molecule and site) to bind and cleave molecular oxygen. These sites are not unique to V-substituted HPA as the band at 2130 cm$^{-1}$ may also be present in Cs$_3$HPMo$_{12}$O$_{40}$.

Conclusions

The set of complementary in situ studies focused on one family of molybdenum-based HPA has produced clear evidence that neither the parent Keggin ions nor their perfect salt crystals are the catalytically active phase. Already in water the ionic crystals dissolve and the Keggin ions deprived of their stabilizing secondary structure hydrolyze and set free their templating central heteroatom. In gas-phase reactions activity sets in abruptly after, again, the removal of the secondary structure by evaporation of water or decomposition of counterions. If the secondary structure is completely non-volatile (fully salified) then no catalytic activity is observed at all. The loss of the secondary structure is connected to the formation of defective void structures of the Keggin ion (lacunary species). If these species are partially reduced and exhibit sites of substantial local electron density, then they may behave as active sites for redox catalysis. The openings in the Keggin ions may not grow above a critical size. Then, under the action of either water or reducing gas-phase species the central templating heteroatom is lost as phosphate or PH$_3$. The presence of this template is vital for the function of the catalyst as was also shown by replacing P by Si which is much less stable. In the absence of the template the molybdate species restructure into fragments of binary oxides that are “at best” active in total oxidation catalysis (concept of site isolation in selective oxidation).

The ultimate use of the present family of HPA in catalysis is limited despite their great chemical variability, by their metastable nature that can only be overcome by stabilizing its secondary structure that hinders the formation of active sites. The dynamic nature of the defective active phase limits the predictability of the behavior of intermediate completion of the secondary structure that tends to disintegrate in core-and-shell states of complete and empty secondary structures.