## IR Spectroscopic Investigation of Heteropolymolybdate Catalysts: Acidic Properties and Reactivity towards Propene

By Friederike C. Jentoft\*, Jutta Kröhnert, and Robert Schlögl

Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin (Dahlem), Germany

Dedicated to Prof. Dr. Helmut Knözinger on the occasion of his 70<sup>th</sup> birthday

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Compounds of the general type  $Cs_xH_{3+y-x}PV_yMo_{12-y}O_{40}$  (x = 0, 2-4 with y = 1, or x = 0, 2 with y = 0) were investigated by IR spectroscopy. After thermal treatment at 473-773 K in vacuum or N<sub>2</sub>, the probe molecules CO (at 77 K, in transmission) or CO<sub>2</sub> (at 298 K, in diffuse reflectance) were adsorbed. On the surface of  $Cs_2H_2PVMo_{11}O_{40}$  and Cs<sub>2</sub>HPMo<sub>12</sub>O<sub>40</sub>, Brønsted acid sites were indicated by a CO band at 2162 cm<sup>-1</sup>. All Cs containing compounds produced CO bands at  $2152 \text{ cm}^{-1}$  or CO<sub>2</sub> bands at  $2341 \text{ cm}^{-1}$ . Additional weak Lewis acid sites of Mo or V in at least two oxidation states were detected after treatment at 673 K. The fraction of the reduced species decreased in the order  $H_4PVMo_{11}O_{40} > Cs_2H_2PVMo_{11}O_{40} > Cs_3HPVMo_{11}O_{40}$ . In situ DRIFT spectra of these three compounds taken during interaction with propene at up to 673 K revealed that the pattern of IR bands typical of the Keggin anion was unaffected at x = 3, altered severely for the acid and to an intermediate extent for x = 2. The changes are consistent with a diminishing of the splitting of the P-O frequency. The Keggin structure represents the initial oxidized state of the heteropoly compound catalysts. Reduction affects but does not destroy the local structure as probed by IR spectroscopy. The more easily reducible  $H_4PVMo_{11}O_{40}$  is active for propene oxidation at 513 K,  $Cs_2H_2PVMo_{11}O_{40}$  only at 617 K.

## **1. Introduction**

Vanado-molybdo-phosphates of the type  $H_{4-x}Cs_xPVMo_{11}O_{40} \cdot yH_2O$  (x = 1-4, "HPA") have been extensively studied as active catalysts for the selective

<sup>\*</sup> Corresponding author. E-mail: jentoft@fhi-berlin.mpg.de

oxidation of several alkanes, aldehydes and acids [1–6]. HPAs are highly attractive as catalytic materials due to their variable structural and synthetic chemistry with the potential to tailor catalysts for demanding processes. The molecular HPA oxides are addressed in the literature as solid acids and redoxactive systems simultaneously. This may explain the enormous academic and industrial attention paid to polyoxo metallates, as they are designated alternatively to HPA, which does not yet correspond to sustained beneficial technical operation of processes [7]. HPAs are interesting for academic research and as models for more complex multi-element oxide systems used in selective oxidation catalysis because their discrete structures allow studying functionality without having to describe the defective structure of strongly bound infinite solids.

HPAs contain networks of  $MO_6$  octahedra, which resemble discrete fragments of metal oxide structures [8]. The Mo and V ions in the popular Mo, V HPA are distributed randomly in the free acid and in its salts, prominently represented by the family of Cs compounds. The polyhedra form the primary structure assembled to a second hierarchy of molecular cluster structures. These clusters, of which the prototype "Keggin" anion  $[M_{12}O_{40}]^{3-}$  is one of the simplest and widely studied examples [6, 9], can be synthesized from a combination of a few oligo-nuclear building blocks to an enormous degree of complexity [10]. The clusters form molecular crystals with a large void system that is filled with stabilizing water molecules. The counter ions of salt species and dynamically exchanging central ion species (V, Nb for Mo) are also located in this void space. The molecular crystals forming the third layer of structural hierarchy are often referred to in the literature as secondary structure [11, 12].

The stabilizing water molecules are present in two distinctly different forms: crystal and structural water. Water is lost under the action of a dry gas stream at 300 K or when the temperature rises. The widths of the distribution of desorption temperatures and their starting points depend on sample composition (structure) and on experimental conditions (kinetics). The structural water persists during the drying of solids and is only removed in a distinct thermal event at about 573 K with substantial variability with chemical composition of the clusters. After the removal of crystal and constitutional water further oxygen evolution takes place and the systems undergo internal redox reaction [13].

Redox catalysis requires the presence of free coordination sites at the transition metals and the availability of free electrons as metallic or radical centers. Both conditions are not fulfilled in the stoichiometric structures of HPAs [14–17], which occur with the transition metals in their highest oxidation states. HPAs exhibit a nano-morphology in which the molecular cluster surface is entirely covered by oxygen atoms, allowing for coordination of protons at bridging sites but giving no access to the transition metal centers. Partial reduction and removal of oxygen are required to enable coordination of labile catalytically relevant species [13, 18]. The balance between the two functions

acidity and redox-activity can be changed by modifying the central metal atom from more redox-active (Mo, V, Nb) to less redox-active (W). This substitution chemistry determines the thermodynamic structural stability of the anions. As the catalytic function seems to be inevitably connected to a defect state of the anion, a complex interplay between electronic and structural effects comes with the apparently simple and versatile chemical flexibility of HPAs.

The filling of the intermolecular void space also affects the structural stability strongly. The presence of water or solvent molecules, salt-forming counter ions and stratification on a support are synthetic and operational variables determining the state of a HPA catalyst under reaction conditions. One key element of structural dynamics of HPA is the tendency of transition metals to migrate out of the anion, leave the anion in a defective "lacunary" state and form a salt [19, 20] with this defective species. The relevance of this solid state transformation that is inhibited by deliberate salt formation (Cs species) or by supporting HPAs for catalytic functions is frequently but controversially stressed in the literature [21–28].

These complex structure–function relationships provoke extensive discussions [24, 29-31], and a variety of *in-situ* studies backed by careful *ex-situ* characterization experiments are needed to resolve controversy. We reported on a series of suitable experiments [32-34] probing certain aspects of structure–function correlations. In the present study we describe spectroscopic and reaction experiments looking at the structural integrity of HPAs and defining boundary conditions for further experiments elucidating the surface electronic structure.

Central to redox catalysis is 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 *in situ* diffuse reflectance UV/Vis/near-IR spectroscopy (DRS) [11, 35], which proved to be a suitable technique for probing both d-d and charge transfer transitions at reaction temperature and under realistic gas compositions [36]. A number of groups have reported *ex situ* optical spectra [25, 26, 37–39]. 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 H<sub>4</sub>PVMo<sub>11</sub>O<sub>40</sub> and Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub> by methanol and ethanol and to correlate structural changes with catalytic data [27].

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 a consequence of the dynamic nature of the activated systems [11, 40]. The multiple redox states of activated HPAs

give rise to band systems strongly overlapping and thus requiring data analysis based on theoretical predictions in order to derive meaningful electronic structural information. It seems thus necessary to apply a surface-sensitive detection method that allows the determination of the electronic structure during catalytic action and as a function of the distance to the surface to evaluate the participation of ionic transport processes in the overall mechanism according to the accepted Mars-van-Krevelen scheme. The information can be obtained from *in-situ* high pressure photoelectron spectroscopy [41]. Its application requires certain boundary limitations in total and partial pressure and the chemical resolution of XPS for molecular structures of hydrocarbon fragments is limited. These limitations preclude a direct structure-function correlation with available data of catalyst performance and with mechanistic concepts all gained at different reaction conditions from those of the intended *in-situ* study. For this reason a combination of infrared spectroscopy and reaction screening is used here to estimate the likely surface species from the wide spectrum of possible structures. The study uses the assumption that all species seen as adsorbates by vibrational spectroscopy are not relevant for the main kinetic reaction channels but represent strongly bound terminal species of slow reaction channels.

Redox transformations of hydrocarbons require acid-base properties for the C-H activation. HPAs exhibit 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 classical methods of probing acid sites have been applied [6, 42] *i.e.* basic probes such as Hammett indicators, ammonia, and pyridine have been adsorbed and analyzed by visual inspection [43], temperature programmed desorption (TPD) [43–47]. IR spectroscopy [47, 48] or calorimetry [44, 49, 50]. The use of Hammett indicators is difficult because HPAs are intensely colored. Polar probes enter the bulk, usually in a number proportional to the amount of protons per formula unit [51]. The reaction with the strongly basic molecules ammonia and pyridine leads to relatively stable ammonium and pyridinium salts; e.g. (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> releases most of its NH<sub>3</sub> at 700 K [44]. Upon heating, pyridinium salts of  $H_{3+x}PMo_{12-x}V_xO_{40}$ release H<sub>2</sub>O, CO, CO<sub>2</sub>, and N<sub>2</sub> besides pyridine, indicating that a substantial fraction of the probe was oxidized, consistent with the inevitably present redox activity. 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 salt formation of the first "probe molecules" offered 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. Bielański et al. [48] detected Brønsted but no Lewis sites on a series of  $H_{3+x}PMo_{12-x}V_xO_{40}$  samples using ammonia as a probe, equally Serwicka et al. [47] found ad(b)sorbed pyridine "predominantly" in its protonated form after adsorption on  $H_{3+x}PMo_{12-x}V_xO_{40}$ . Another probe tested was carbon monoxide, which was adsorbed at 100 K on  $H_3PMo_{12}O_{40}$  and its cesium salts [52]. Again, no Lewis sites were found. However, as HPAs are thought to activate oxygen through a Mars–van-Krevelen mechanism [11, 46], the presence of oxygen vacancies and, thus, Lewis acid sites, *i.e.* coordinatively unsaturated (cus) cations, appears to be compulsory.

The present work re-visits the application of probe molecules after determining the state of the sample in the spectroscopy cell with respect to the loss of water. Infrared spectroscopy probes the structure of a HPA sample in a complementary way to the frequently used diffraction techniques as it "sees" with high resolution the local coordination polyhedron. Small changes in local symmetry, changes of distortions due to modification of redox states and changes of connectivity within the cluster structure are detectable that may be difficult to find in diffraction data that are governed by supramolecular structural features.

## 2. Experimental

## 2.1 Sample preparation

 $H_4PVMo_{11}O_{40}$  was prepared starting from a suspension of MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> in water. The oxides were dissolved through addition of the according amount of  $H_3PO_4$ , and subsequently water was removed [32].  $Cs_xH_{4-x}PVMo_{11}O_{40}$  (x = 2-4) were prepared through addition of a  $Cs_2CO_3$  solution to the heteropoly acid solution in the desired stoichiometry and subsequent water removal. For the preparation of  $Cs_2H_2PVMo_{11}O_{40}$ ,  $CsNO_3$  solution was used alternatively.  $H_3PMo_{12}O_{40}$  and  $Cs_2HPMo_{12}O_{40}$  were prepared according to the procedure reported by Tsigdinos [53].

## 2.2 Transmission FTIR spectroscopy (CO adsorption)

Transmission IR experiments were performed using a Perkin Elmer S 2000 with a liquid nitrogen cooled MCT detector. The spectral resolution was 4 cm<sup>-1</sup> and 200 scans were accumulated. The samples were pressed (at 320 MPa) into self-supporting wafers with an area weight of typically 20 to 30 mg/cm<sup>2</sup>. The wafers were cut into 10 mm × 25 mm pieces and placed in a stainless steel, low temperature infrared cell with CaF<sub>2</sub> windows. The sample was activated *in situ* in the heating zone of the IR cell under vacuum at 523, 673, or 773 K for 2.5 h (subsequent experiments with one sample). After activation the sample was cooled using liquid N<sub>2</sub> in the presence of an inert gas (He, 1 mbar) to 77 K. The CO pressure was increased stepwise from 0.001–6.5 hPa. The IR spectrum measured before CO dosage was used as background. All spectra shown are the difference of the spectrum of the sample in the presence of CO minus the spectrum of the sample in absence of CO.

## **2.3** *In situ* diffuse reflectance FTIR spectroscopy (CO<sub>2</sub> adsorption and propene interaction)

DRIFT spectra were recorded using a Graseby Specac "Selector" attachment with environmental chamber (zinc selenide window) placed in a Bruker IFS 66 spectrometer. The resolution was 1 cm<sup>-1</sup> and 100 scans were accumulated employing an MCT detector. The spectrum of pure KBr (Merck, Uvasol®, dried at 473 K) recorded at room temperature served as background for all measurements. The samples were filled into a gold cup. Gas flows were adjusted with mass flow controllers (Bronckhorst). Heat-treatment was performed in 30 ml/min N<sub>2</sub> (Linde, further purified with Hydrosorb and Oxysorb cartridges) at 473 K and subsequently at 773 K. The sample is heated only from underneath the cup, and the actual temperature, particularly of surface layers, is lower, i.e. 773 K in the DRIFTS cell roughly correspond to 673 K in the transmission cell. Spectra were recorded at the treatment temperatures. After each heat treatment, CO<sub>2</sub> was adsorbed by purging 30 ml/min of pure CO<sub>2</sub> through the cell at 298 K for 30 min. Before spectra were recorded, gas phase CO<sub>2</sub> was removed by purging with N<sub>2</sub> for 30 minutes. For interaction with propene, fresh samples were used, and were first heated to the desired temperature in N<sub>2</sub>, then exposed to a stream of 30 ml/min of propene for 30 min. After subsequent purging for 30 min with N<sub>2</sub>, spectra were recorded. The samples were then heated in N<sub>2</sub> to the next target temperature, and exposed to propene as described above. The cell temperature range was 323–773 K.

## 2.4 Catalysis

Catalytic experiments were performed in a cell designed for in situ UVvis spectroscopy, which has been described elsewhere [36]. Mixtures with SiO<sub>2</sub> (Heraeus, 0.1–0.4 mm) containing 10 wt. % catalyst material were used. The reactor and the SiO<sub>2</sub> itself were inert under reaction conditions. The amount of catalyst in the reactor was 98 mg (for  $H_4PVMo_{11}O_{40}$ ) or 111 mg  $(Cs_2H_2PVMo_{11}O_{40})$ . Deviating from the published arrangement, which allows simultaneous acquisition of UV-vis spectra, the reactor cell was placed in the center of the oven to ensure isothermal conditions. The gas mixture fed to the cell, containing roughly 10% propene and oxygen each, was: 8 ml/min propene (Linde 2.8), 7 ml/min O<sub>2</sub> (Linde) and 57 ml/min He, all at atmospheric pressure. The temperature was increased stepwise at 5 K/min from room temperature to 423, 523, 573, 673, and 723 K (nominal temperatures). As soon as products were detected, the temperature was kept constant for 2 h. Analysis of the effluent gases was performed with two on line gas chromatographs, both equipped with FID and TCD detectors. Oxygen and CO were analyzed using a Perkin Elmer Autosystem with a Carboxen-1000 packed column (2 ft, 45/60 mesh, Supelco). All other products were analyzed using a Perkin Elmer 8700 equipped with a Permabond FFAP capillary column (25 m, Macherey-Nagel).

## 3. Results

#### 3.1 Surface areas

The BET surface areas varied for individual preparations of the same compounds. Surface areas were below 20 m<sup>2</sup>/g, larger values were reached only by  $Cs_2H_2PVMo_{11}O_{40} \approx 35 \text{ m}^2/\text{g}$  and  $Cs_3HPVMo_{11}O_{40} (60-90 \text{ m}^2/\text{g})$ .

# 3.2 DRIFTS: Dehydration of $Cs_xH_{4-x}PVMo_{11}O_{40}$ (x = 0, 2-4) and $H_3PMo_{12}O_{40}$

The dehydration process was followed by DRIFT spectroscopy because with this method interpretable spectra of the acids could be obtained, which was not possible in transmission using self-supporting wafers. Initial spectra taken at room temperature were characterized by OH vibrations, metal-oxygen and phosphorus-oxygen vibrations. Samples with low Cs content (x < 2) gave poorly resolved spectra, which were dominated by absorptions from hydrogen bridging. After dehydrating at 473 K for 1 h, the spectra shown in Fig. 1 were obtained. The strongest OH stretching band in the DRIFT spectra of the series  $Cs_r H_{4-r} PVMo_{11}O_{40}$  (x = 2–4) was positioned at 3445 cm<sup>-1</sup>. The spectra of Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub> and Cs<sub>3</sub>HPVMo<sub>11</sub>O<sub>40</sub> exhibited an additional band at about 3615 cm<sup>-1</sup>. Two very sharp bands at 3693 and 3578 cm<sup>-1</sup> developed with increasing dehydration of  $Cs_4PVMo_{11}O_{40}$ . In the region of OH bending modes, two overlapping bands were detected; the maxima were located at about 1629 and 1611 cm<sup>-1</sup>. The high frequency contribution increased with increasing Cs content. The DRIFT spectra of all samples showed a broad band at about 4025 cm<sup>-1</sup>, which disappeared after treatment at 473 K for the acids, or at 773 K for the Cs salts except for  $Cs_3HPVMo_{11}O_{40}$ . The origin of this band is unclear. Its decrease with increasing temperature suggests it is connected to the presence of water.

After heating to 473 K, the spectra of the acids show only broad and ill-defined absorptions in the region of overtones of metal– and phosphorus– oxygen vibrations. After treatment for 2 h at 773 K, water has been completely removed as can be seen from the absence of the deformation band at around 1600 cm<sup>-1</sup> (Fig. 2). The overtones of the metal– and phosphorus–oxygen vibrations are then clearly visible for all samples. Three pronounced bands are observed for the V-containing samples, and one pronounced and two very weak bands for the V-free acid. The spectra of the acids and the Cs salts differ with respect to the position of the most intense band, which is located at 1925–1930 cm<sup>-1</sup> for the salts and at 1975–1980 cm<sup>-1</sup> for the acids. The spectrum of Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub> has a shoulder towards 1980 cm<sup>-1</sup>, consistent with its proton content. Furthermore, a band at 2034–2038 cm<sup>-1</sup> is present in the spectra of the salts, while for H<sub>4</sub>PVMo<sub>11</sub>O<sub>40</sub> there is a band at 2054 cm<sup>-1</sup>. In the region of the first harmonics of the metal– and phosphorus–oxygen vibrations the spectra were noisy due to low reflectance and band positions could



**Fig. 1.** DRIFT spectra of  $H_{4-x}Cs_xPVMo_{11}O_{40}$  (x = 0, 2-4) and  $H_3PMo_{12}O_{40}$  in the ranges of OH vibrations after activation for 1 h at 473 K in flowing N<sub>2</sub>.

be determined only approximately (not shown). All bands are summarized in Table 1.

#### 3.3 Low temperature CO adsorption – transmission IR spectroscopy

Only Cs-salts could be investigated because the transmittance through selfsupporting wafers of  $H_4PVMo_{11}O_{40}$  and  $H_3PMo_{12}O_{40}$  was too low. The quality of the spectra depended on the amount of CO that could be adsorbed, which in turn depended on the surface area of the samples. It follows that CO was only adsorbed on the external surface. The reproducibility of the complete experiment – wafer fabrication, activation and adsorption – is demonstrated in Fig. 3 using Cs<sub>3</sub>HPVMo<sub>11</sub>O<sub>40</sub>. The band pattern arising from adsorbed CO species was very well reproducible. Slight deviations in absolute intensity were observed between different measurements at similar pressures, but mainly at low pressures. Intensity ratios were well reproducible, allowing for good estimates of the contributions from individual species.



**Fig. 2.** DRIFT spectra  $H_{4-x}Cs_xPVMo_{11}O_{40}$  (x = 0, 2-4) and  $H_3PMo_{12}O_{40}$  in the range of M–O and P–O overtone and combination modes after activation for 2 h at 773 K in flowing N<sub>2</sub>.

For all samples, several bands were observed, independent of the activation conditions. The highest frequency observed for adsorbed CO was  $2162 \text{ cm}^{-1}$ . This band was present in the spectra of two samples, namely  $Cs_2H_2PVMo_{11}O_{40}$  and  $Cs_2HPMo_{12}O_{40}$ , after activation at 523 K in vacuum (Fig. 4). Spectra of other samples such as *e.g.*  $Cs_3HPVMo_{11}O_{40}$  do not show such a band. Furthermore, OH vibrations at  $3270-3230 \text{ cm}^{-1}$  after heat treatment in vacuum are characteristic of the two discussed samples. Heating  $Cs_2H_2PVMo_{11}O_{40}$  to 673 K resulted in the disappearance of a band at  $3270 \text{ cm}^{-1}$  and subsequent CO adsorption did not produce a band at  $2162 \text{ cm}^{-1}$ . The spectrum of  $Cs_2HPMo_{12}O_{40}$  still exhibited a band at about  $3230 \text{ cm}^{-1}$  after heating to 673 K, and at higher CO pressures, a band at  $2162 \text{ cm}^{-1}$  was detected. Although a shift of the band at  $3270-3230 \text{ cm}^{-1}$  through adsorption of CO could not be discerned, it is believed that the band at  $2162 \text{ cm}^{-1}$  arises from CO adsorbed on these OH groups.

Table 1. Metal-	and phosphorus-oxy§	gen vibrations in cm	<sup>-1</sup> from DRIFT spe	ctra recorded af	ter 2 h treatment at	773 K.
$H_4PVMo_{11}O_{40}$	$\mathrm{Cs}_{2}\mathrm{H}_{2}\mathrm{PVMo}_{11}\mathrm{O}_{40}$	$Cs_3HPVMo_{11}O_{40}$	$\mathrm{Cs}_4\mathrm{PVMo}_{11}\mathrm{O}_{40}$	$\mathrm{H_{3}PMo_{12}O_{40}}$	$Cs_2 HPMo_{11}O_{40}$	Range
2121 m	2117 m	$\approx 2145 \text{ w,sh}$ 2113  m	≈ 2145 w,sh 2115 m	2115 w	2118	$2 \times 1075 \cong 2150$
2054 m	2055 sh 2038 m	2034 m	2034 m		2056 sh 2035	$2 \times (1035 - 1030) \cong 2070 - 2060$
1980 s	$\approx 1980  \mathrm{sh}$ 1931 s	1925 vs	1926 s	1975 m	1960 sh 1928 vs	$2 \times (1015 - 990) \cong 2030 - 1980$
1075 vs 1035	1075 vs 1030	1075 vs	1075 vs	1075 vs	1070 vs	P-0
1015 vs 960	1000 vs	1000 vs 945	990 vs 945	1015 vs	$\approx 1000$	Mo=O
910 vs 855 vs	885 vs 835 vs	890 vs 835 vs	broad abs. broad abs.	910 855	$\approx 890$ $\approx 840$	Mo-O <sub>e</sub> -Mo Mo-O <sub>e</sub> -Mo



**Fig. 3.** Difference transmission IR spectra of CO adsorbed on  $Cs_3HPVMo_{11}O_{40}$  at 77 K. Comparison of three different wafers from same batch, activated 2.5 h at 523 K in vacuum.



**Fig. 4.** Difference transmission IR spectra of CO adsorbed on various samples, all activated 2.5 h at 523 K in vacuum. Adsorption temperature 77 K, p(CO) = 0.52 hPa (Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub>), 0.32 hPa (Cs<sub>3</sub>HPVMo<sub>11</sub>O<sub>40</sub>) and 0.71 hPa (Cs<sub>2</sub>HPMo<sub>12</sub>O<sub>40</sub>).

A band at  $2152 \text{ cm}^{-1}$  increased in intensity with increasing Cs content (Fig. 5, spectra normalized to most intense band). The position is also consistent with literature reports on the adsorption of CO on Cs<sup>+</sup> [52]. A band at around 2138 cm<sup>-1</sup> was always observed and is considered unspecific.



**Fig. 5.** Transmission IR difference spectra of samples with different Cs content, normalized to highest intensity. Samples activated 2.5 h at 523 K in vacuum. Adsorption temperature 77 K, p(CO) = 2-6 hPa.

The groups of bands arising from adsorbed CO were fit using Gauss functions. Examples are shown for  $Cs_2H_2PVMo_{11}O_{40}$ ,  $Cs_3HPVMo_{11}O_{40}$ , and  $Cs_2HPMo_{12}O_{40}$ , all activated at 673 K, in Fig. 6a–e. The fits reveal a band at 2146–2148 cm<sup>-1</sup> for  $Cs_3HPVMo_{11}O_{40}$ ; and at higher CO pressure, there is a possibility for another contribution at 2129 cm<sup>-1</sup>. A different picture evolves for  $Cs_2H_2PVMo_{11}O_{40}$ . There is no prominent band at 2148 cm<sup>-1</sup>, but a pronounced band towards lower wavenumbers, specifically at 2133 cm<sup>-1</sup>. Due to the low surface area of  $Cs_2HPMo_{12}O_{40}$ , only spectra at higher CO pressures (Fig. 6e) reveal all species. Besides the bands for CO adsorbed on OH groups and  $Cs^+$ , two bands at 2139 and 2133 cm<sup>-1</sup> are detected. The fit can be improved through addition of a band at 2146 cm<sup>-1</sup>, but this effects a large change in the intensity distribution between 2139 and 2133 cm<sup>-1</sup>. The two bands at 2148–2146 cm<sup>-1</sup> and 2133–2129 cm<sup>-1</sup> represent Lewis acid sites.

#### 3.4 Room temperature CO<sub>2</sub> adsorption – DRIFTS

Acids could not be investigated by transmission spectroscopy. DRIFTS was applied using carbon dioxide as a probe, which is suitable for the detection of redox-labile Lewis acid sites and of basic sites. All samples were exposed to  $CO_2$  at room temperature after activation at 423 K and 773 K. No carbonates were formed, consistent with a low basicity for such large anions with a highly delocalized charge. Spectra in the range of the stretching vibration of lin-



**Fig. 6.** Transmission IR difference spectra of CO adsorbed at 77 K on  $Cs_3HPVMo_{11}O_{40}$  (a,b),  $Cs_2H_2PVMo_{11}O_{40}$  (c,d), and  $Cs_2HPMo_{12}O_{40}$  (e) after activation for 2.5 h at 673 K in vacuum. Fits with Gauss curves.

early adsorbed  $CO_2$  are presented for selected samples after activation at 773 K in Fig. 7.

A band at  $2341 \text{ cm}^{-1}$  present in the spectra of  $Cs_2H_2PVMo_{11}O_{40}$  and  $Cs_3HPVMo_{11}O_{40}$  is assigned to adsorption of  $CO_2$  on  $Cs^+$ . Additional bands indicating Lewis acid sites were observed for these two samples. The slightly higher frequencies at 2353 and 2347 cm<sup>-1</sup> suggest non-reduced metal cations as adsorption sites. For  $H_4PVMo_{11}O_{40}$ , the band at around 2341 cm<sup>-1</sup> is not detected, while a band at 2332 cm<sup>-1</sup> indicates reduced species on the sur-



Fig. 7.  $CO_2$  adsorption at 298 K on  $H_4PVMo_{11}O_{40}$ ,  $Cs_2H_2PVMo_{11}O_{40}$  and  $Cs_3HPVMo_{11}O_{40}$  after activation for 2 h at 773 K.

face. Although the drying temperature of 773 K was nominally higher than the 673 K used for the transmission experiments shown in Fig. 6, we believe that dehydration and reduction did not progress as far, due to temperature gradients in the bed in the DRIFTS cell and the lower water and  $O_2$  partial pressures that can be achieved through evacuation in comparison to purging. Comparison of the spectra in the range of OH vibrations confirms this assumption.

#### 3.5 DRIFT spectra after interaction with propene at 323-673 K

The overtone pattern of  $Cs_3HPVMo_{11}O_{40}$  is not affected after the material has been exposed to propene at temperatures up to 673 K (Fig. 8). There are no additional bands after reaction with propene over most of the temperature range; only interaction at 673 K produces several weak bands, which are located at 2906, 1505, 1435, and 1365 cm<sup>-1</sup>.

Already after contact with propene at 373 K, new bands appear in the spectrum of  $Cs_2H_2PVMo_{11}O_{40}$  (Fig. 9). Very weak bands are detected at 2984 and 2925 cm<sup>-1</sup> in the range of CH stretching vibrations. More intense bands are located at 1693, 1557, 1447 and 1415 cm<sup>-1</sup>. A broad feature is centered around 1365 cm<sup>-1</sup>. The bands at 1693 and 1557 disappear at 473 K, and of the feature at 1365 a band at 1351 cm<sup>-1</sup> remains (not shown). After interaction with propene at 523 K, only bands at 1652, 1423, and 1351 cm<sup>-1</sup> are prominent, while no bands can be discerned in the CH stretching regime.



**Fig. 8.** DRIFT spectra of  $Cs_3HPVMo_{11}O_{40}$  after interaction with propene at increasing temperatures. Propene gas phase removed by 30 min purging with N<sub>2</sub>.



**Fig. 9.** DRIFT spectra of  $Cs_2H_2PVMo_{11}O_{40}$  after interaction with propene at increasing temperatures. Propene gas phase removed by 30 min purging with N<sub>2</sub>.

After exposure to propene at 673 K, the spectrum of  $Cs_2H_2PVMo_{11}O_{40}$  still shows all overtones. The high frequency bands at 2115 and 2035 cm<sup>-1</sup> are weaker than after treatment at 773 K in N<sub>2</sub> (see Figs. 2 and 9). Furthermore, an intense absorption is located at 1423 cm<sup>-1</sup> and a broad feature evolves at *ca*. 1780 cm<sup>-1</sup>.



Fig. 10. DRIFT spectra of  $H_4PVMo_{11}O_{40}$  after interaction with propene at increasing temperatures. Propene gas phase removed by 30 min purging with  $N_2$ .

Interaction of  $H_4PVMo_{11}O_{40}$  with propene at 573 K weakens the highest frequency overtone at about 2260 cm<sup>-1</sup> (Fig. 10). At 673 K, this band and the band at 2115–2120 cm<sup>-1</sup> are no longer present in the spectrum. Concomitantly, the band at 1075 cm<sup>-1</sup> and its shoulder at  $\approx 1130$  cm<sup>-1</sup> disappear. The band at 1015 and its overtone at 1990 cm<sup>-1</sup> appear unaffected.

## 3.6 Propene oxidation catalyzed by $H_4PVMo_{11}O_{40}$ and $Cs_2H_2PVMo_{11}O_{40}$

Propene and oxygen conversion are compared in Fig. 11 for the two tested samples, namely  $H_4PVMo_{11}O_{40}$  and  $Cs_2H_2PVMo_{11}O_{40}$ . An overview of the main products and their selectivities based on propene conversion is given in Table 2. Both catalysts produce isopropanol at low temperatures (323 K). The oxidation activity of H<sub>4</sub>PVMo<sub>11</sub>O<sub>40</sub> sets in at 513 K, which is about 100 K lower than the temperature at which  $Cs_2H_2PVMo_{11}O_{40}$  first starts oxidizing propene. Fig. 11 shows the changes in conversion with the stepwise increase of temperature for each sample. The acid always converts more propene than oxygen, while the Cs salt always converts more oxygen. After 1.5 h at 613 K, the propene conversions are equal for the two catalysts, but the  $O_2$  conversions are 2 and 12%, respectively. The acid produces high amounts of the aldehydes, acrolein and propanal (34 and 30%) and 25% carbon monoxide. The Cs salt yields a slightly lower selectivity towards acrolein (28%) but gives considerably less propanal (16%) and more CO (39%). With increasing reaction temperature, the propensity of the catalysts to deactivate during 2 h under isothermal conditions increases.



Fig. 11. Conversion of propene and oxygen by  $H_4PVMo_{11}O_{40}$  and  $Cs_2H_2PVMo_{11}O_{40}$  at different temperatures. Feed flow: 10%  $O_2$ , 10% propene in He.

## 4. Discussion

## 4.1 Dehydration and dehydroxylation

DRIFT and transmission consistently show a wide range of OH vibrations. The stretching vibrations at *ca*.  $3615 \text{ cm}^{-1}$  and the bending vibration at  $1600 \text{ cm}^{-1}$ seen in the DRIFT spectra show parallel behavior, their intensities are correlated after treatment at 473 K (Fig. 1) and they disappear after treatment at 773 K. These bands are ascribed to the  $v_{as}$  and  $\delta$  vibrations of crystal water. The third characteristic band of crystal water,  $v_s$  at 3545 cm<sup>-1</sup> is not resolved. After heating to a nominal temperature of 773 K, strong OH vibrations are still detected at 3445 cm<sup>-1</sup> with a shoulder towards lower wavenumbers, which varies in intensity depending on the sample and is particularly pronounced for  $Cs_2HPVMo_{11}O_{40}$ . The positions are typical of solid water. However, there are no corresponding bending vibrations to these OH stretching vibrations, i.e. the terms structural or constitutional "water" are somewhat misleading in that internal OH groups are present and not water molecules. Dehydroxylation of OH groups requires migration of two OH groups together, the (intermittent) presence of a coordinatively unsaturated cation and a negatively charged oxygen. During this transition, the Keggin units become reactive but also instable. The "dangling" oxygen cannot be stable because there is no carbonate formation with  $CO_2$ . Hence, either oxo bridges must be formed, the charge must be compensated by a H-bridge with a remaining OH group, or a (partial) charge transfer to a metal cation must occur. If geminal OH groups existed and dehydroxylated only the last reaction would be possible and very soft Lewis acid sites could be formed. Alternatively, on the external surface, H or oxo bridging

Temperature	Products	Products/Sel	lectivity in %
in K		$\rm H_4PVMo_{11}O_{40}$	$Cs_2H_2PVMo_{11}O_{40}$
323	Isopropanol	100	100
513	Acrolein Acetic acid Other products	89 9 Water, Propionic acid	No oxidation products
613-617	Acrolein Propanal Acetone Carbon monoxide Acetic acid Other products	34 30 6 25 4 Water, Acrylic acid, Propionic acid, Isopropanol	28 16 7 39 9 Water, Isopropanol, Propionic acid, Acrylic acid
664–673	Acrolein Propanal Acetone Carbon monoxide Acetic acid Other products	24 24 13 6 29 26 Propionic acid, Acrylic acid, Isopropanol, Water	30 30 33 34 34 9 Water, Isopropanol, Propionic acid, Acrylic acid

to another Keggin unit may not be possible. In earlier UV-Vis experiments [35] it was consistently observed that dehydration was associated with the evolution of inter-valence charge transfer bands without strong changes in the ligand-to metal absorptions indicating the formation of localized reduced species within the Keggin units.

The spectrum of  $Cs_4PVMo_{11}O_{40}$  recorded at 473 K (Fig. 1) shows two sharp bands at 3593 and 3578 cm<sup>-1</sup>. These OH groups disappear at higher temperature. Because of their sharpness, the bands are not associated with vibrations of the heteropoly compound. The OH groups may be from bicarbonates, because for this preparation the highest amount of  $Cs_2CO_3$  is added to the acid solution. However, no typical pattern of carbonates can be discerned; only after activation at 773 K, a band at *ca*. 1790 cm<sup>-1</sup> could indicate C=O vibrations (Fig. 2).

The metal– and phosphorus–oxygen vibrations have been studied extensively at various temperatures and degrees of dehydration [54–61]. Essentially, the Keggin unit is characterized by four types of vibrations, whose frequencies decrease in the order:  $P-O > M=O > M-O_c-M > M-O_e-M$ , with  $O_c$  and  $O_e$  bridging oxygens at corner- or edge-sharing octahedra, respectively. We find the fundamentals of these vibrations shifted to higher wavenumbers in comparison with most of the literature (see Table 1). One reason is the advanced degree of dehydration, and a second is the fact that our spectra were recorded with undiluted samples, *i.e.* the shifts often induced by embedding into a diluent could be avoided [56]. The spectra are noisy in the range of the fundamentals, but the overtones of these vibrations are clearly visible and naturally better separated (Fig. 2). Hence, the DRIFTS method allows monitoring of the state of the Keggin ions during *in situ* experiments using undiluted materials, so that ion exchange and support effects with the diluent can be avoided.

#### 4.2 Surface sites

Adsorption of CO at 77 K did not alter any of the bands of the heteropoly compounds and the intensity of the bands of adsorbed CO increased with increasing surface area. CO oxidation proceeds as a surface-type reaction on heteropoly compounds [6]. It follows that CO adsorption occurs only on the external surface.

At least four types of Lewis acid sites are detected on the samples by CO adsorption at 77 K. The band at 2152 cm<sup>-1</sup> arises from CO adsorption on Cs cations. The band at *ca*. 2138 cm<sup>-1</sup> is always present. Saito *et al*. [52] fit a band at this position with a Lorentzian function and ascribed it to physisorbed CO. In our case, Gauss profiles were found more adequate for all bands than Lorentzian profiles. The band at 2138 cm<sup>-1</sup> formed already at low CO pressures, which is further indication for a stronger interaction than just physisorption. However, these sites are uncharacteristic of any particular sample. The bands at 2148–2146 and 2133–2129 cm<sup>-1</sup> could represent coordinatively unsaturated cations. The position at 2148 cm<sup>-1</sup> is above the gas phase frequency of CO, indicating no  $\pi$ -backbonding from filled *d*-orbitals and thus unreduced species. The positions at 2133–2129 cm<sup>-1</sup> indicate  $\pi$ -backbonding and are consistent with reduced species. V is more easily reduced than Mo [40] and thus a more likely candidate for the low frequency bands, but none of the bands is unique to the V-containing compounds. Zaki et al. [62] published a diagram that correlates the CO vibration frequency with the Mo valence for supported  $MoO_x$  species. According to their diagram, the Mo valence should be between +II and +III to give bands in the range 2125-2150 cm<sup>-1</sup>. On the other hand, reduction with H<sub>2</sub> at 673 K leads to no oxidation state lower than +IV [63], *i.e.* our treatment should not produce the low oxidation states that are derived from Zaki's correlation. It follows that a correlation established for  $MoO_x$  species supported on oxides cannot be transferred to heteropoly compounds. The Mo(VI) and Mo(V) Lewis sites in the supported species are much harder than those in the heteropoly compounds as indicated by their higher CO frequencies (in part >2200 cm<sup>-1</sup>). Hard Lewis acid sites may not so easily release activated oxygen species to form oxygenates. It is concluded that on the surface of heteropoly compounds a unique type of Lewis acid sites is present; these sites are soft despite the moderate degree of reduction of the metal cation. The reactivity of these special Lewis sites may be determined by the fact that they are not defects in a single metal–oxygen polyhedron but are embedded into a larger electronically delocalized unit, the defective Keggin anion.

The fits in Fig. 6 disclose that  $Cs_2H_2PVMo_{11}O_{40}$  exhibits a higher fraction of reduced sites characterized by the band at 2133–2129 cm<sup>-1</sup> than  $Cs_3HPVMo_{11}O_{40}$ . DRIFT spectra of  $CO_2$  adsorbed on these compounds after activation for 2 h at a nominal temperature of 773 K reveal only  $Cs^+$  species on the surface (band at 2341 cm<sup>-1</sup>) and a second type of non-reduced Lewis acid sites. Only  $H_4PVMo_{11}O_{40}$  exhibits reduced surface sites after treatment in flowing  $N_2$  in the DRIFT cell, as indicated by a band at 2332 cm<sup>-1</sup>. Combination of the CO and  $CO_2$  adsorption results allows us to establish an order of reducibility  $H_4PVMo_{11}O_{40} > Cs_2H_2PVMo_{11}O_{40} > Cs_3HPVMo_{11}O_{40}$ , *i.e.* the reducibility decreases with increasing Cs content. The data do not explain the role of V:  $Cs_2HPMo_{12}O_{40}$  has features of both,  $Cs_2H_2PVMo_{11}O_{40}$  and  $Cs_3HPVMo_{11}O_{40}$ , namely Brønsted acid sites (Fig. 4), a considerable fraction of reduced species as well as perhaps some of the species producing the band at 2148–2146 cm<sup>-1</sup> (Fig. 6e).

Low temperature CO adsorption reveals a band at  $2162 \text{ cm}^{-1}$  for  $Cs_2H_2PVMo_{11}O_{40}$  and  $Cs_2HPMo_{12}O_{40}$ . The band is only observed after drying at moderate temperature (523–673 K, Figs. 4 and 6e). The position of the band is typical for CO adsorbed on Brønsted acid sites and is close to the 2165 cm<sup>-1</sup> reported by Saito *et al.* [52] for adsorption of CO on the Brønsted acid sites of 12-tungstophosphoric acid and its Cs salts. The band does not appear in the spectra of Cs rich compounds. On the basis of these three arguments, this band is indicative of Brønsted acidic OH groups. The spectra of  $Cs_2H_2PVMo_{11}O_{40}$  and  $Cs_2HPMo_{12}O_{40}$  show OH bands at about  $3270-3230 \text{ cm}^{-1}$ . The low frequency is consistent with bridging OH groups, which may be acidic as are the bridging OH groups in zeolites. Through treatment at 773 K, these OH groups become dehydroxylated and are no longer detected. CO adsorption causes no detectable shift of these OH bands because they also represent internal OH groups while CO adsorbs only on the fraction present at the external surface.

Although  $Cs_3$ HPVMo<sub>11</sub>O<sub>40</sub> contains one proton per Keggin unit, no acid sites are detected. This may arise from surface enrichment of Cs relative to the bulk formula, a fact for which experimental evidence was obtained [29] by time-resolved dissolution experiments exhibiting a gradient in Cs concentration over samples. Certain acidic sites may only form when the sample is slightly reduced. Reduction is significant for  $Cs_2H_2PVMo_{11}O_{40}$  but not for  $Cs_3HPVMo_{11}O_{40}$  as the analysis of surface cationic centers in Fig. 6 demonstrated. Upon reduction, protons settle on the most highly charged atoms in the Keggin unit, namely the oxygen atoms that connect corner-sharing octahedra [32, 56].

## 4.3 Interaction of Cs<sub>3</sub>HPVMo<sub>11</sub>O<sub>40</sub>, Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub> and H<sub>4</sub>PVMo<sub>11</sub>O<sub>40</sub> with propene at different temperatures

The overtone pattern of  $Cs_3HPVMo_{11}O_{40}$  after exposure to propene at 673 K corresponds to that obtained in inert gas (Figs. 2 and 8). The Keggin structure remains intact not only through heat treatment but also during interaction with propene. New bands indicate the formation of surface species after contact with propene at 673 K. The bands at 2906 and 1365 cm<sup>-1</sup> are typical for the CH stretching and deformation vibrations of methyne groups. The band at 1435 cm<sup>-1</sup> is within the range of CH deformation vibrations, but unspecific. The broad feature at about 1505 cm<sup>-1</sup> is difficult to assign; one possibility is a carboxylate. A second band would then be required, which could be that at 1435 cm<sup>-1</sup>. However, for carboxylates, the two bands are typically further apart, *i.e.* the bands should be at higher and lower wavenumbers, respectively.

Interaction of  $Cs_2H_2PVMo_{11}O_{40}$  with propene at increasing temperature leads to a series of complex spectra. The weak bands detected at 2984 and 2925 cm<sup>-1</sup> already at 373 K are in the range of asymmetric CH stretching vibrations of methyl and methylene groups. Corresponding symmetric stretching vibrations cannot be discerned. However, the band at 1447 cm<sup>-1</sup> matches with the range of CH bending vibrations of methylene groups and the low frequency contribution of the feature at 1365 cm<sup>-1</sup> is explainable by CH bending vibrations of methyne groups. Geminal methyl groups would produce a pair of bands in this range (1385–1365 cm<sup>-1</sup>). Primary and secondary alcohols feature OH bending modes at frequencies up to 1350 cm<sup>-1</sup>, and cannot be excluded. The band at 1415 cm<sup>-1</sup> might arise from vinyl CH vibrations, but stretching vibrations above 3000 cm<sup>-1</sup> are not discernable. The combination of bands is consistent with the adsorption of propene and formation of isopropanol, which is found as a gas phase product in catalytic experiments at low temperatures.

The bands at 1693, 1557, and the high frequency part of the band at 1365 cm<sup>-1</sup> disappear simultaneously at 473 K, indicating that they might belong to the same species.  $\alpha,\beta$ -Unsaturated aldehydes and ketones have C=O and C=C vibrations that could account for the bands at 1693 and 1557 cm<sup>-1</sup>, respectively. Southward *et al.* [57] had assigned a band at 1547 cm<sup>-1</sup> to coke after propene polymerization on salts of 12-tungstophosphoric acid; however, because of the moderate reaction temperature and the decrease of this band with increasing temperature, coke species are not deemed a likely cause in our case. After contact with propene at 523 K, a band at  $1612 \text{ cm}^{-1}$  indicates that water is still present as is the case after treatment in inert gas at 473 K (Figs. 1 and 9). The band that emerges at  $1652 \text{ cm}^{-1}$  at 523 K is assigned to C=C vibrations. The band at  $1418 \text{ cm}^{-1}$  is indicative of vinyl CH in plane bending vibrations and corroborates the presence of unsaturated species. Two more bands at  $1437 \text{ and } 1352 \text{ cm}^{-1}$  are typical of methylene and methyne groups. Without the provision of oxygen, the oxidizing abilities of the material may be exhausted; also the acidic protons may have all reacted to give isopropanol, and acidic polymerization of propene is not observed.

After reaction at 673 K, the spectrum of  $Cs_2H_2PVMo_{11}O_{40}$  shows overtones at 2115 and 2035 cm<sup>-1</sup> that are relatively lower in intensity than after treatment at 773 K in N<sub>2</sub> (see Figs. 2 and 9). The fundamental P–O vibration at 1075 cm<sup>-1</sup> is not affected in a detectable way; however, at such a low reflectance, the intensity may not properly reflect the number of absorbing species. A weakening of the splitting of the P–O band and of the overtone of the main P–O band both indicate an increasing symmetry of the phosphorus environment.

During interaction of  $H_4PVMo_{11}O_{40}$  with propene at elevated temperatures, first the splitting of the P–O vibration is lifted, *i.e.* the high frequency shoulder at  $\approx 1130 \text{ cm}^{-1}$  and its overtone at 2260 cm<sup>-1</sup> disappear similar to observations after treatment in inert gas (Fig. 10, 573 K and Fig. 2, 773 K). This development indicates that the environment of the phosphorous becomes more symmetric. The intensity of the P–O vibration at 1075 cm<sup>-1</sup> is reduced and the band shifts towards lower wavenumbers (673 K). Further evidence for a symmetric environment is provided by the significantly reduced intensity of the P–O overtone at 2115 cm<sup>-1</sup>. The overtone is weak also in the spectrum of the V-free  $H_3PMo_{12}O_{40}$ , which features phosphorous with tetrahedral symmetry (see Fig. 2).

The bands at 1855 and 1780 cm<sup>-1</sup> are believed to be carbonyl bands. Metal–oxygen vibration overtones can be excluded, because the corresponding fundamentals would be missing. A pair of bands at relatively high frequency with a spacing of about  $60 \text{ cm}^{-1}$  (here  $75 \text{ cm}^{-1}$ ) is typical for anhydrides, although for a non-cyclic species, the bands should be of reverse relative intensity or of equal intensity. The absence of a band at around  $1600 \text{ cm}^{-1}$  indicates that the surface is dry at this stage, and the anhydride cannot be converted to acid and be desorbed in this form. Water vapor might be necessary to remove such surface species.

Besides the formation of surface species, the changes to the Keggin ion, expressed by changes to the symmetry of the phosphorus, are most interesting. The spectra reveal a clear trend within the series of samples. For the free acid  $H_4PVMo_{11}O_{40}$ , the splitting is completely resolved. This result suggests that all Keggin units participate and not only surface species. For  $Cs_2H_2PVMo_{11}O_{40}$  the effect is discernable but the reaction is not complete. The Keggin units of  $Cs_3HPVMo_{11}O_{40}$  remain unaffected. One previously suggested interpretation

of the disappearance of the high-frequency shoulder of the P-O vibration is the expulsion of V from the Keggin unit [56]. However, a gap in the Keggin unit would reduce the symmetry around the phosphorous in a similar manner as the inclusion of V. The CO adsorption experiments indicate that the reducibility decreases with increasing Cs content, and propene can act as a reducing agent [33]. Usually, the lower the valence of the metal in an oxo anion, the lower is the oxygen coordination. Once Mo or V are slightly reduced, the PO-M bridges could be weakened, leading to phosphate ions that vibrate almost freely in the center of the Keggin unit and give spectra indicative of tetrahedral symmetry. The interaction between the phosphate core and the surrounding part of the anion is already weak in comparison to other hetero atoms, as indicated by the P-O vibrational frequency, which is almost independent of the nature of the Keggin anion shell [6]. However, without the cohesive force of the central hetero atom, the Keggin ion becomes unstable and may undergo further cage-opening processes creating new under-coordinated cus sites. Multiple lacunary species are well-known from structural studies in which organic ligands were used to stabilize the reactive metal-oxygen clusters [7].

## 4.4 Catalytic activity of H<sub>4</sub>PVMo<sub>11</sub>O<sub>40</sub> and Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub> in propene oxidation

Consistent with their Brønsted acidity, both catalysts produce isopropanol at low temperatures. Propene acts like a drying agent in this case, and water is withdrawn at lower temperature than in inert gas [32]. The presence of oxygen is without effect.

 $H_4PVMo_{11}O_{40}$  becomes active for propene oxidation at much lower temperature than  $Cs_2H_2PVMo_{11}O_{40}$ . This may be explained by the comparably lower stability of the acid in comparison to its salts. Activation of gas phase  $O_2$  may require oxygen vacancies, *i.e.* a defective structure.  $H_4PVMo_{11}O_{40}$  is more easily reduced than  $Cs_2H_2PVMo_{11}O_{40}$  as the  $CO_2$  adsorption data and previous UV-vis spectroscopic investigations show [35]. Alternatively, the low temperature oxidation activity of  $H_4PVMo_{11}O_{40}$  may involve sacrificial consumption of lattice oxygen rather than conversion of gas phase oxygen. The catalytic data show that  $Cs_2H_2PVMo_{11}O_{40}$  produces significant amounts of gas phase oxidation products only at 613 K. The IR spectra give evidence of a variety of adsorbates already after interaction with propene at 373 and 523 K, among them possibly oxygenates. The surface of  $Cs_2H_2PVMo_{11}O_{40}$  is reactive towards propene, but products are desorbed only at higher temperatures.

The two catalysts differ in their oxygen conversion in relation to the propene conversion. The ability of the acid to activate oxygen is low, it always converts more propene. There are no "spacers" in the form of large, non-volatile cations between the Keggin units, and once metal–oxygen bands are broken and reformed, oxo bridges may form between the individual Keggin ions. This interconnecting is not complete in all three dimensions as the remaining Mo=O groups indicate. These bridges ultimately lead to oxide structures. Loss of the open tertiary structure prevents re-oxidation of the bulk of the acid and deactivation is severe.  $Cs_2H_2PVMo_{11}O_{40}$  on the other hand converts significantly more oxygen than propene, evidencing its ability to undergo multiple redox cycles.

## 5. Conclusions

The data show that the catalytic reactivity of HPA compounds is closely related to their structural dynamics. Activation in inert or reactive conditions creates defective anion clusters exhibiting Lewis acid functions. Most interesting is the observation of an apparent increase in local symmetry around the central hetero atom; either a partial liberation of the bonding between the Mo-3 triade to the hetero atom has occurred or in the conventional picture, a hole is broken into the "skin" of the Keggin ion. In both cases the local chemical bonding between Mo and oxygen would be changed, allowing the conclusion that adaptation of the electronic structure may occur during structural re-arrangement of the pristine Keggin anion, and that the Keggin anion is a precursor structure rather than the active species.

Probe molecule adsorption has revealed the weak basicity of the structure which is not to be expected from an oxo-anion, but which indicates the high extent of covalent bonding in the HPA structure.

Indications were found that compositional gradients *e.g.* for the extent of salt formation from the surface into the bulk may strongly affect the catalytic reactivity because the abundance and strength of acid sites is much less developed than expected from the composition of the catalysts. A strong correlation was found between partial reduction and dehydration occurring facile in a reactive atmosphere. This documents that the acidity function and redox function cannot be separated from each other in this class of redox-labile materials.

Analysis of adsorbates shows hydrocarbon species and products of their initial oxidation such as aldehydes or ketones as the most abundant surface intermediates. This would be consistent with a notion that the transformation of an activated hydrocarbon fragment into a partly oxidized species is the difficult step, as more deeply oxidized products can easily desorb and little tendency exists towards coke formation on these, under dry conditions, weakly acidic surfaces.

All these data and observations form valuable guiding information for *in-situ* XPS studies required to directly probe the electronic structure of the reactive surface and to verify the chemical composition of the active form of HPA. The limited chemical resolution of XPS for organic fragments is effectively complemented by the combination of IR-based identification of abundant intermediates and by the reactivity measurements; whereas IR sees long-lived

or dead-end intermediates the product distribution of the reactivity agrees with the absence of expected intermediates which are too reactive or short-lived to be seen by vibrational spectroscopy.

The hypothesis expressed in the introduction that the Keggin structure is not a suitable model for describing the active state of HPA catalysts in gasphase oxidation reactions was clearly established by a method giving local structural information with great chemical resolution, and without having to rely on periodic structures.

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