

In Situ Investigations of Structure–Activity Relationships in Heteropolyoxomolybdates as Partial Oxidation Catalysts

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Abstract: The structural evolution of Keggin-type heteropolyoxomolybdates (HPOM) during thermal treatment in propene and in propene and oxygen in the temperature range from 300 to 773 K was investigated by in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS) combined with mass spectrometry. During treatment in propene or hydrogen and at reaction temperatures above 673 K, the initially triclinic $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ is transformed quantitatively into a cubic HPOM ($Pn\bar{3}m$, $a = 11.853 \text{ \AA}$) exhibiting a long-range structure similar to that of the corresponding cesium salts. The treatment described constitutes the first readily available prepara-

tion route for a cubic HPOM without alkali metal ions in the structure. For both $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ and $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ migration of molybdenum from the Keggin ion onto interstitial sites is proposed to occur in propene or hydrogen at temperatures above about 573 K to give thermally stable, partially reduced lacunary Keggin ions. During activation in propene and oxygen the onset of catalytic activity of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ and

$\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ at about 573 K correlates with partial reduction of Mo and characteristic changes in the local structure of the Keggin ion. The structural changes observed indicate that, similar to the treatment of the HPOM in propene, migration of molybdenum from the Keggin ions onto interstitial sites and formation of lacunary Keggin ions take place. Moreover, the formation of these partially reduced lacunary Keggin ions appears to be a prerequisite for the material to become an active heterogeneous catalyst. Evidently, the undistorted Keggin ion in the as-prepared HPOM has to be regarded as a precursor of the active catalyst.

Keywords: EXAFS spectroscopy · heterogeneous catalysis · polyoxometalates · structure–activity relationships · X-ray diffraction

Introduction

Heteropolyoxomolybdates (HPOMs), also frequently denoted as heteropoly acids (HPAs), are highly active heterogeneous catalysts for partial oxidation of alkenes and alkanes (e.g., methacrolein to methacrylic acid).^[1] Cubic Cs salts of heteropolyoxomolybdates composed of Keggin ions (Figure 1, top) (e.g., $\text{Cs}_x\text{H}_{3-x}[\text{PMo}_{12}\text{O}_{40}]$ ($2 \leq x \leq 3$), $Pn\bar{3}m$ (No. 244), $a = 11.85 \text{ \AA}$)^[2], Figure 1, bottom) are applied as oxidation catalysts on an industrial scale, and therefore their structure and catalytic properties have been extensively studied in the past. However, to further improve the catalytic behavior of HPOMs by, for instance, selecting suitable substituents, replacing the heteroatom, or selecting appropriate activation procedures, detailed knowledge about correlations between the structure of the material under reac-

tion conditions and the catalytic activity are required. Therefore, structural investigations on HPOMs must be combined with measurements of the activity and selectivity of the material under the reaction conditions employed. Only structure–activity relationships elucidated under relevant reaction conditions (i.e., in situ) will eventually enable targeted preparation of and rational activation procedures for catalytically improved heteropolyoxomolybdates.

With respect to the structure of the active HPOM under reaction conditions, two alternatives can be envisaged and are controversially discussed in the literature. First, the active phase of the HPOM under reaction conditions may correspond to the intact and undistorted Keggin structure, and hence the catalytic reactivity of the material could be understood on the basis of the initial structure of the HPOM.^[3–6] Second, the Keggin ions may not be stable during thermal treatment and under catalytic conditions, and partial reduction of the heteropolyoxomolybdates may occur under reaction conditions.^[7,8] Alkali metal salts of HPOM that exhibit a considerable inhomogeneity have been proposed,^[9–14] as well as mixed phases of alkali metal salts of HPOM with various degrees of substitution of the acidic protons by alkali metal ions, which form a core–shell

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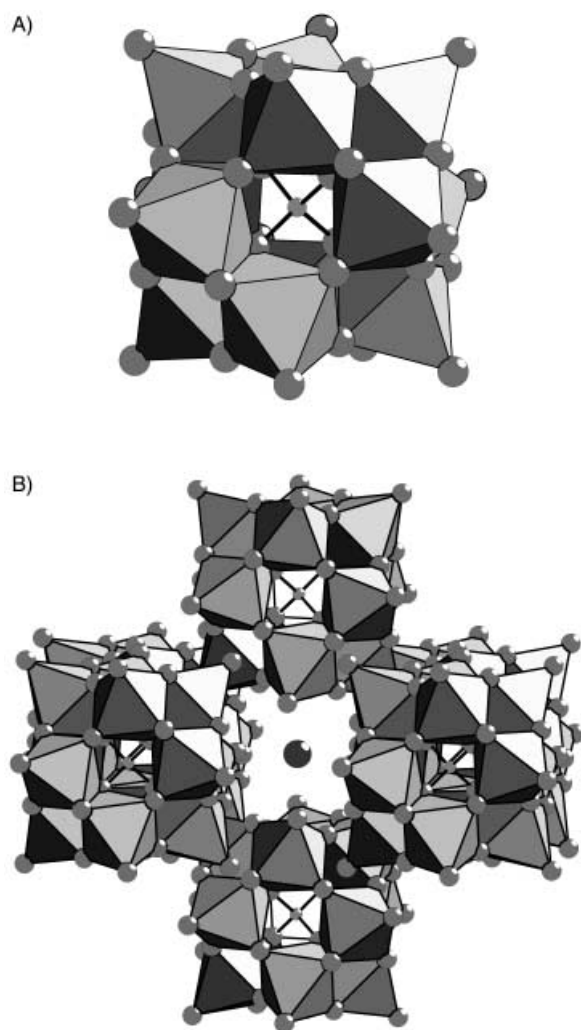


Figure 1. Schematic structural representations of the Keggin anion in heteropolyoxomolybdates (top) and the arrangement of Keggin anions in the cubic structure of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ (bottom).

system of the Cs_3 salt and the free acid under catalytic conditions.^[13] In addition, migration of molybdenum addenda ions^[14–20] or vanadium addenda substituents^[14,16,21–25] from the Keggin anion onto interstitial sites in the HPOM structure^[15,20,21,22] has been suggested, with or without reconstruction of the Keggin ion.

Because the “real” structure of heteropolyoxomolybdates (i.e., the structure of the material under reaction conditions) has not yet been fully elucidated, the reliable structure–reactivity relationships for HPOMs that are needed for rational improvement of their catalytic properties are lacking. According to the literature, the thermal instability and dynamic behavior of the Keggin anion in the HPOM has been observed, and it has been proposed that this instability may be important for understanding the functionality of the material as a heterogeneous catalyst. However, open questions remain such as 1) what is the thermal and chemical stability of intact or partially decomposed Keggin ions, 2) is the onset of the structural instability of the Keggin ion correlated to the onset of catalytic activity, 3) is the structure of the activated HPOM related to that of the original Keggin

ion or rather to that of a bulk molybdenum oxide MoO_{3-x} , and 4) what are the potential driving forces for a structural rearrangement of the Keggin ions in HPOM at elevated temperatures?

Here we report on in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy investigations of the thermal treatment (i.e., activation) of various heteropolyoxomolybdates under reducing (propene or hydrogen) and catalytic (propene and oxygen) reaction conditions. Under reducing conditions the formation of partially reduced lacunary Keggin ions was observed that may serve as a reference material for the catalytically active phase in future studies. Under partial oxidation conditions structural changes in the Keggin ions occur that are very similar to those detected under reducing conditions and thus indicate that during activation of HPOM the onset of catalytic activity is closely correlated to partial reduction and decomposition of the material.

Experimental Section

X-ray diffraction: In situ XRD experiments were performed on a STOE STADI P powder diffractometer equipped with a secondary monochromator ($\text{Cu}_{K\alpha}$ radiation, Ge secondary monochromator) and a scintillation counter operated in a stepping mode. The in situ cell consisted of a Bühler HDK S1 high-temperature diffraction chamber. The gas-phase composition at the cell outlet was analyzed on line with a Pfeiffer Prisma 200 quadrupole mass spectrometer in a multiple-ion detection mode. In situ XRD measurements were conducted under atmospheric pressure in flowing reactants (flow rate of 100 mL min^{-1}). Gas-phase compositions of 10% propene in helium, 5% hydrogen in helium, and 10% propene and 10% oxygen in helium were employed. XRD patterns were measured every 25 K in the temperature range from 315 to 773 K, resulting in an effective heating rate of 1.31 K min^{-1} . A detailed description of the setup used can be found in reference [26]. Ex situ XRD measurements were performed on a STOE STADI P theta-theta diffractometer ($\text{Cu}_{K\alpha}$ radiation, Ge secondary monochromator) in the range of $2\theta = 5\text{--}100^\circ$ with a step width of $2\theta = 0.01^\circ$ and a measuring time of 10 s per step.

X-ray absorption spectroscopy: 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 an Si(311) double-crystal monochromator (measuring time ca. 4.5 min/scan). The storage ring operated at 4.4 GeV with injection currents of 150 mA. The in situ experiments were conducted in a flow reactor^[27] at atmospheric pressure in flowing reactants (ca. 30 mL min^{-1} , temperature range from 300 to 773 K at 5 K min^{-1} , subsequently held at 773 K). The gas-phase composition at the cell outlet was continuously monitored with a mass spectrometer in a multiple-ion detection mode (QMS200, Pfeiffer). The HPOMs were mixed with boron nitride (7 mg HPA, 30 mg BN) and pressed with a force of 1 t into a pellet 5 mm in diameter, which resulted in an edge jump at the Mo K-edge of $\Delta\mu_x \approx 1.5$. Details of the experimental setup can be found in ref. [26]. X-ray absorption fine structure (XAFS) analysis was performed using the software package WinXAS v2.3^[28] following recommended procedures from the literature.^[29] Background subtraction and normalization were carried out by fitting linear polynomials to the pre- and post-edge regions of an absorption spectrum, respectively.

The extended X-ray absorption fine structure (EXAFS) $\chi(k)$ was extracted by using cubic splines to obtain a smooth atomic background $\mu_0(k)$. The radial distribution function $\text{FT}[\chi(k)]$ was calculated by Fourier transforming the k^3 -weighted experimental $\chi(k)$ function, multiplied by a Bessel window, into the R space. EXAFS data were analyzed by using theoretical backscattering phases and amplitudes calculated with the ab initio multiple scattering code FEFF7.^[30] Single and multiple scattering paths in the Keggin ion model structure were calculated up to 6.0 \AA with

a lower limit of 2.0% in amplitude with respect to the strongest backscattering path. EXAFS refinements were performed in R space to magnitude and imaginary part of a Fourier transformed k^3 -weighted experimental $\chi(k)$ by using the standard EXAFS formula (k range from 3.4–15.1 \AA^{-1} , R range 0.7–4.1 \AA).^[31] Structural parameters that are determined by a least-squares EXAFS refinement of a Keggin model structure to the experimental spectra are 1) one overall E_0 shift, 2) Debye–Waller factors for single scattering paths, 3) distances of single scattering paths, 4) one-third cumulant for the Mo–O distances in the first coordination shell and one-third cumulant for all remaining scattering paths. Coordination numbers (CN) and S_0^2 were kept invariant in the refinement.

Sample preparation: The heteropolyoxomolybdates $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$, $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$, and $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ were prepared according to the method described by Tsigdinos et al.^[32] Phase purity was verified by ex situ X-ray diffraction. A cubic HPOM was obtained by thermal treatment of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ in a flow reactor in 10% propene in helium (100 ml min^{-1} total flow) in the temperature range from 300 to 673 K with a heating rate of 5 K min^{-1} .

Results

The evolution of the structure of the heteropolyoxomolybdates $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ (HPOM), $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ (Cs_2 -HPOM), and $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ (Cs_3 -HPOM), during thermal treatment in 5% hydrogen or 10% propene in helium (reducing conditions) and 10% propene and 10% oxygen in helium (catalytic partial-oxidation conditions) was determined by in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS) combined with mass spectrometry.

In situ X-ray diffraction: The evolution of XRD patterns measured during thermal treatment of HPOM in 10% propene in helium in the temperature range from 300 to 773 K is depicted in Figure 2. At 315 K the octahydrate^[9,11] is detected together with anhydrous $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$.^[33] The octahydrate is formed from the initial tridecahydrate in the temperature range from 300 to 315 K. Between 348 and 573 K the anhydrous phase is observed, while at 598 K a highly disordered phase, not yet identified, is formed. The latter is transformed into a cubic HPOM ($Pn\bar{3}m$, $a = 11.853 \text{ \AA}$) between 600 and 723 K. Eventually, at 773 K, the cubic

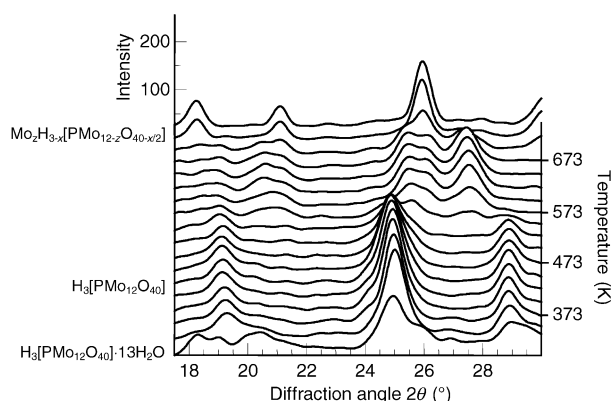


Figure 2. Evolution of XRD patterns measured during the thermal treatment of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ in 10% propene in helium in the temperature range from 300 to 773 K. The various phases observed are indicated.

HPOM slowly decomposes into MoO_3 , which is subsequently reduced to MoO_2 (not shown). A very similar evolution of XRD powder patterns was measured during the thermal treatment of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ in 5% H_2 in helium, which also resulted in the formation of the cubic HPOM. During the thermal treatment of Cs_2 -HPOM in 10% propene in helium a characteristic change in the intensity ratios of various XRD lines was observed, in agreement with similar reports in the literature.^[17]

Figure 3 shows the XRD pattern of a cubic HPOM obtained from $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ after treatment in 10% propene in helium (300–673 K) together with two simulated XRD powder patterns. The simulated XRD patterns in

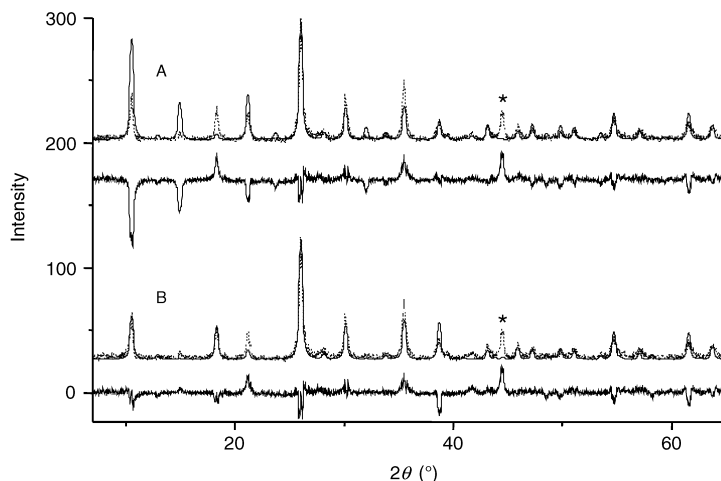


Figure 3. Experimental XRD patterns of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ treated in 10% propene at a temperature of 673 K (dotted line, A) together with the calculated pattern of an “ $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ ” HPA based on structural data given in [ICSD 209] ($Pn\bar{3}m$, $a = 11.853 \text{ \AA}$; solid line), and B) together with a calculated pattern based on [ICSD 209] with molybdenum on a cationic site. * indicates a reflection from the sample holder used. The differences between the experimental and the calculated patterns are shown for clarification.

Figure 3 were calculated for a potassium salt of a heteropolyoxomolybdate ($\text{K}_2\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot \text{H}_2\text{O}$, $Pn\bar{3}m$, [ICSD 209]^[34]). For the calculation the potassium ions were omitted, and the cell parameter was adjusted to $a = 11.853 \text{ \AA}$. Although all peaks in the experimental pattern in Figure 3 A are accounted for by the simulation, and all peak positions agree well between experimental and calculated patterns, a considerable deviation in the peak intensities of the two patterns can be seen. The simulated XRD pattern in Figure 3 B was calculated for the structural model of $\text{K}_2\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot \text{H}_2\text{O}$, in which in addition to omitting the potassium ions, a fraction of the molybdenum cations was placed on a cationic site outside the Keggin anion. The position of the cationic site and the site occupancy factor (SOF) for this site and for the molybdenum site in the Keggin anion were determined by a Rietveld refinement (WinM-Prof^[35], Table 1). The positions of the other ions in the unit cell and the SOFs for oxygen and phosphorus were kept invariant in the refinement. It can be seen from Figure 3 B that by placing a certain number of molybdenum ions out-

Table 1. Lattice constant and atom coordinates in the unit cell of HPOM treated in 10% propene in He obtained from a Rietveld refinement of a structure model ([ICSD 209], space group $P4_2/n \bar{3} 2/m$ (22), cell choice 2, $a = 11.852(9)$) with molybdenum cations on a cationic site. The isotropic temperature factors B_{iso} for Mo2 and Mo1 were refined in the same wa.

Atom	Wyckhoff	x	y	z	SOF	B_{iso}
Mo1	24k	0.4670	0.4670	0.2587	0.717(8)	1.57
O1	24k	0.6528	0.6528	0.0060	1.000	1.56
O2	24k	0.0689	0.0689	0.7670	1.000	2.07
O3	24k	0.1233	0.1233	0.5398	1.000	1.81
O4	8e	0.3273	0.3273	0.3273	1.000	1.01
P	2a	0.2500	0.2500	0.2500	1.000	1.15
Mo2	48l	0.347(7)	0.713(7)	0.735(1)	0.114(2)	1.57

side the Keggin anions, the agreement between experimental data and simulated powder pattern is considerably improved.

In situ X-ray absorption spectroscopy: The experimental EXAFS Mo K-edge $\chi(k)$ of $\text{Cs}_2\text{-HPOM}$ at 300 K is shown in Figure 4. The sufficient signal-to-noise ratio up to about

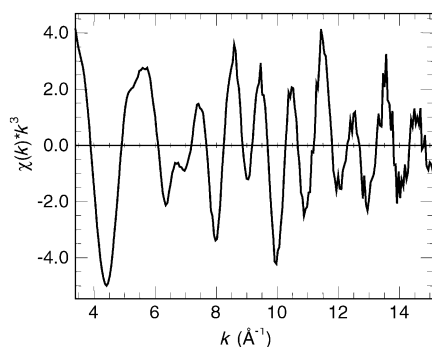


Figure 4. Experimental Mo K-edge $\chi(k)$ of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ measured at 300 K with a measuring time of 4.5 min.

15 \AA^{-1} enables a reliable structural analysis of changes in the local structure of the Keggin ion under reaction conditions. The evolution of the Fourier-transformed Mo K-edge $\chi(k)$, $\text{FT}[\chi(k)]$, during thermal treatment of $\text{Cs}_2\text{-HPOM}$ and HPOM in 10% propene in the temperature range from 300 to 773 K is depicted in Figure 5 A and B, respectively. Significant changes in the local structure of the Keggin anion in both materials can be seen at temperatures above about 600 K. The Mo K-edge spectrum measured at 773 K can be assigned to that of the cubic HPOM observed by in situ XRD (Figure 2). A similar evolution of the local structure of the Keggin anion was observed during treatment of HPOM and $\text{Cs}_2\text{-HPOM}$ in 50% hydrogen in helium. Conversely, the changes detected in the Mo K-edge $\text{FT}[\chi(k)]$ of $\text{Cs}_3\text{-HPOM}$ during thermal treatment in propene or hydrogen (Figure 6) correspond solely to the effect of the increasing reaction temperature rather than changes in the local structure. The evolution of Mo K-edge $\text{FT}[\chi(k)]$ during thermal treatment of $\text{Cs}_2\text{-HPOM}$ in 10% propene and 10% oxygen in helium (Figure 7) shows minor changes, mostly at-

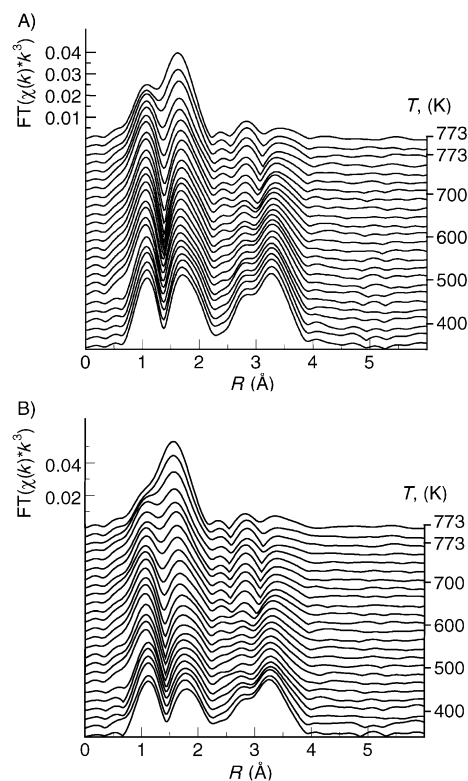


Figure 5. Evolution of Mo K-edge $\text{FT}[\chi(k)]$ measured during treatment of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ (A) and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ (B) in 10% propene in helium in the temperature range from 300 to 773 K.

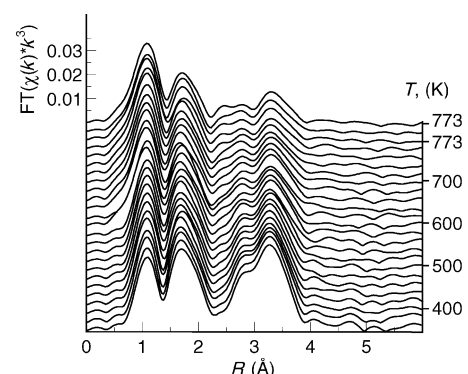


Figure 6. Evolution of Mo K-edge $\text{FT}[\chi(k)]$ measured during treatment of $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ in 10% propene in helium in the temperature range from 300 to 773 K.

tributable to the increasing reaction temperature. At 773 K, the treatment of HPOM in propene and oxygen resulted in complete decomposition of the Keggin structure and formation of orthorhombic MoO_3 .

Local structural evolution under reaction conditions: To elucidate the evolution of the short-range-order structure of the HOPMs under reducing and partial-oxidation conditions, a detailed XAFS analysis of the measured Mo K-edge $\chi(k)$ data was performed. Figure 8 shows good agreement between the experimental $\text{FT}[\chi(k)]$ of HPOM and an XAFS refinement using theoretical phases and amplitudes calculat-

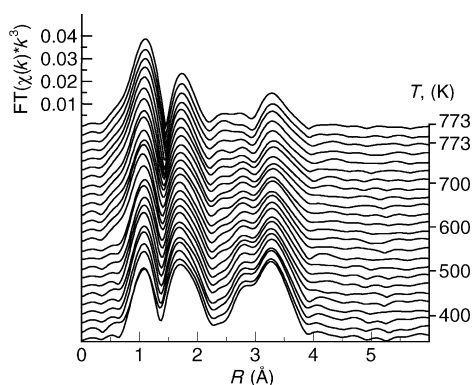


Figure 7. Evolution of Mo K-edge $FT[\chi(k)]$ measured during treatment of $Cs_2H[PMo_{12}O_{40}]$ in 10% propene and 10% oxygen in helium in the temperature range from 300 to 773 K.

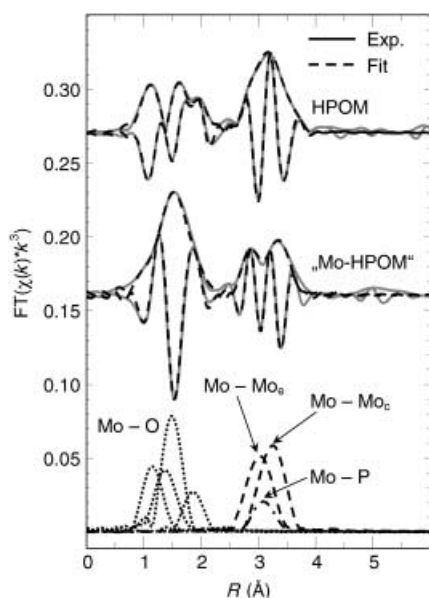


Figure 8. Experimental (Exp., solid; measured in situ during treatment of HPA in 10% propene at 773 K) and theoretical (Fit, dashed) Mo K-edge $\chi(k)$ of $H_3[PMo_{12}O_{40}] \cdot 13H_2O$ (HPOM, top) and $Mo_2H_{3-x}[PMo_{12-x}O_{40-x/2}]$ (Mo-HPOM); traces are arbitrarily shifted for clarity. Selected single scattering paths in cubic "Mo-HPOM" are shown (bottom).

ed for the Keggin ion in the structure of $K_2H[PMo_{12}O_{40}] \cdot H_2O$ ($Pn\bar{3}m$, [ICSD209]^[34]). Similar results for the corresponding XAFS refinements were obtained for Cs_2 -HPOM and Cs_3 -HPOM. Figure 9 shows a schematic representation of part of the Keggin structure. The Keggin ion consists of four triads, each built up by three edge-sharing MoO_6 units (A in Figure 9). The three MoO_6 units share a common oxygen atom that is connected to the central heteroatom in the Keggin ion (B in Figure 9). The four triads in the Keggin anion are linked together by common corners of the corresponding

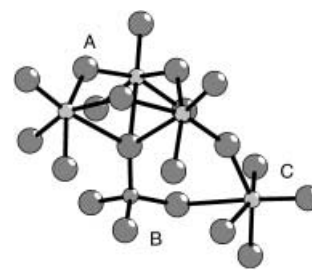


Figure 9. Schematic structural representation of a section of the Keggin anion showing a triad consisting of three edge-sharing MoO_6 units (A) connected to the central PO_4 tetrahedron (B) and by corner-sharing to an MoO_6 unit of a neighboring triad (C).

MoO_6 units (C in Figure 9). The individual shells that can be clearly distinguished in the $FT[\chi(k)]$ of the heteropolyoxomolybdates correspond to the Mo–O distances in the MoO_6 units (1.69–2.43 Å), the triads (3.41 Å, edge-sharing), and the triads (3.71 Å, corner-sharing). From the absence of higher shells in $FT[\chi(k)]$ of the heteropolyoxomolybdates investigated, it is deduced that neither backscattering from the Cs counteranions in Cs_x -HPOM nor from neighboring Keggin anions is detectable in the Mo K-edge XAFS signal at temperatures above 300 K. Additionally, Figure 8 displays the experimental $FT[\chi(k)]$ of the cubic HPOM obtained from treatment of HPOM in propene (Figure 5B) and a XAFS refinement using the same phases and amplitudes as described above. A good agreement between the experimental spectrum of the cubic HPOM and the theoretical XAFS calculations was achieved by using the Mo–O and Mo–Mo distances and the respective coordination numbers in the Keggin ion as starting parameters. The Mo–O, Mo–P, and Mo–Mo distances in the Keggin anion of HPOM and the cubic HPOM obtained from the XAFS analysis are given in Table 2. Apparently, treatment of HPOM and Cs_2 -HPOM in propene results in slightly modified Keggin anions with elongated Mo–O and Mo–Mo distances.

Figure 10 shows the evolution of selected Mo–O and Mo–Mo distances in the Keggin anions of Cs_2 -HPOM and Cs_3 -HPOM during treatment in 10% propene in the temperature range from 300 to 773 K (Figure 5). Above about 573 K an increase in the Mo–O and Mo–Mo distances in Cs_2 -HPOM can be seen, and this is most pronounced for the Mo–Mo distance between edge-sharing octahedra in the Keggin anion (within the triads). Eventually, at 773 K the

Table 2. Structural parameters (coordination numbers (CN) and distances R of Mo–O and Mo–Mo coordination shells) of a Keggin anion model structure (based on [ICSD209]) obtained from a refinement of the model structure to the experimental XAFS functions $\chi(k)$ of $H_3[PMo_{12}O_{40}] \cdot 13H_2O$ (HPOM) and the resulting cubic HPOM (HPOM*) ($N_{ind}=25$, $N_{free}=14$, 7 single scattering paths and 5 multiple scattering paths); $E_0(\text{HPOM}^*)=-3$ eV, $E_0(\text{HPOM})=1$ eV).

	CN	$R(\text{HPOM}^*)$ [Å]	$\sigma(\text{HPOM}^*)$ [Å]	$R(\text{HPOM})$ [Å]	$\sigma(\text{HPOM})$ [Å]	$R_{\text{theor}}[\text{HPOM}]$ [Å]
Mo–O	1	1.73	0.0035	1.69	0.0022	1.698
Mo–O	2	1.97	0.0025	1.83	0.0044	1.909
Mo–O	2	2.08	0.0015	1.99	0.0044	1.919
Mo–O–P	1	2.46	0.001	2.43	0.0014	2.426
Mo–Mo	2	3.52	0.0020	3.41	0.0047	3.417
Mo–P	1	3.64	0.0009	3.57	0.0009	3.561
Mo–Mo	2	3.81	0.0032	3.71	0.0043	3.703

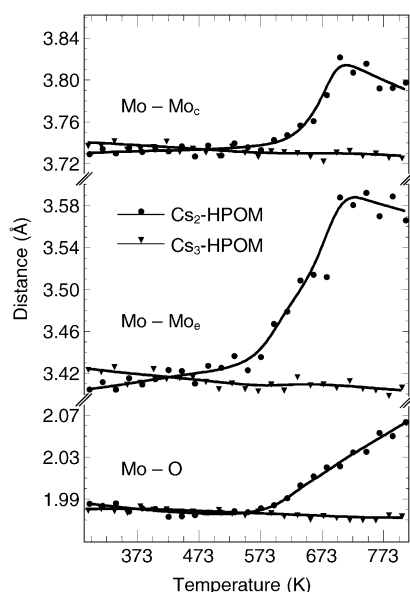


Figure 10. Evolution of selected Mo–O and Mo–Mo distances in the Keggin structure of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ and $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ during treatment in 10% propene in helium in the temperature range from 300 to 773 K.

treatment results in the formation of the characteristic local structure of the Keggin ion of the cubic HPOM structure (Figure 8, Table 2). Conversely, no changes in the Mo–O and Mo–Mo distances in Cs_3 -HPOM can be detected during treatment in propene. With respect to the other Mo–O distances in the Keggin structure, except for the Mo–O distance of 2.44 Å, which exhibits a monotonous increase over the temperature range, all Mo–O distances showed an increase at a reaction temperature of about 573 K.

Figure 11 illustrates the evolution of selected Mo–O and Mo–Mo distances in the Keggin anion of Cs_2 -HPOM during treatment in 10% propene and 10% oxygen in the temperature range from 300 to 773 K (Figure 7). Above about 573 K an increase in the Mo–O and Mo–Mo distances in Cs_2 -HPOM can be noticed. The onset of the structural changes in the Keggin ion of Cs_2 -HPOM are correlated to the onset of catalytic activity of the material, as can be seen from the increasing concentration of the partial-oxidation product acrolein in the gas phase. It can be seen from Figures 10 and 11 that the onset temperature and the relative amplitude of the lengthening of the Mo–O and Mo–Mo distances in the Keggin anion of Cs_2 -HPOM under catalytic reaction conditions coincide with the formation of the cubic HPOM during the treatment of Cs_2 -HPOM and HPOM in propene. During the thermal treatment of HPOM in propene and oxygen a similar evolution of characteristic Mo–O and Mo–Mo distances in the Keggin structure was observed. In contrast to the treatment of Cs_2 -HPOM in propene and oxygen, during treatment of HPOM in propene and oxygen at 773 K the Keggin structure of HPOM decomposed rapidly with formation of orthorhombic MoO_3 .

The evolution of the average valence of Mo in the Keggin anion of Cs_2 -HPOM and Cs_3 -HPOM during thermal treatment in 10% propene, and of Cs_2 -HPOM and HPOM during thermal treatment in 10% propene and 10% oxygen,

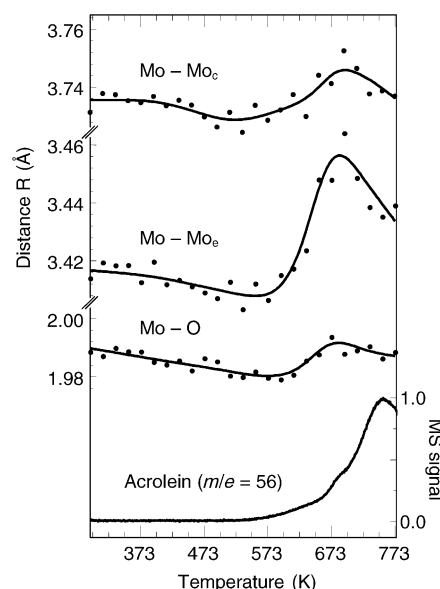


Figure 11. Evolution of selected Mo–O and Mo–Mo distances in the Keggin structure of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ during treatment in 10% propene and 10% oxygen in helium in the temperature range from 300 to 773 K together with the acrolein concentration in the gas phase, measured by MS.

is depicted in Figure 12. The average Mo valence was obtained by comparing the position of the Mo K-edge of the heteropolyoxomolybdates to those of various molybdenum oxide reference compounds.^[36] At reaction temperatures above about 573 K, the Mo in the Keggin anions of Cs_2 -HPOM is significantly reduced, and this coincides with the structural changes in the Keggin anions observed in this temperature range. Conversely, molybdenum in the Keggin

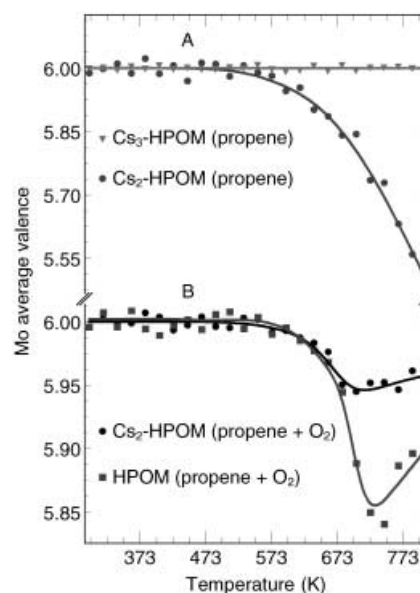


Figure 12. Evolution of Mo average valence obtained from the Mo K-edge position of A) $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ and $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ during treatment in 10% propene in helium and B) of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ during treatment in 10% propene and 10% oxygen in helium in the temperature range from 300 K to 773 K.

anions of $\text{Cs}_3\text{-HPOM}$ remains at an average valence of +6 over the entire temperature range, which agrees with the structural invariance of the material during treatment in propene. Under catalytic reaction conditions (propene and oxygen) both $\text{Cs}_2\text{-HPOM}$ and HPOM exhibit a slight reduction at temperatures above about 573 K. The increase in the average Mo valence in the partially reduced HPOM at a temperature of ~ 773 K correlates with the decomposition of the Keggin structure and the formation of orthorhombic MoO_3 .

Figure 13 illustrates the evolution of the Debye–Waller (DW) factor of the XAFS scattering path corresponding to the Mo–Mo distance of 3.71 Å in the Keggin structure during treatment of $\text{Cs}_2\text{-HPOM}$ in propene and in propene and oxygen, and of $\text{Cs}_3\text{-HPOM}$ in propene, in the tempera-

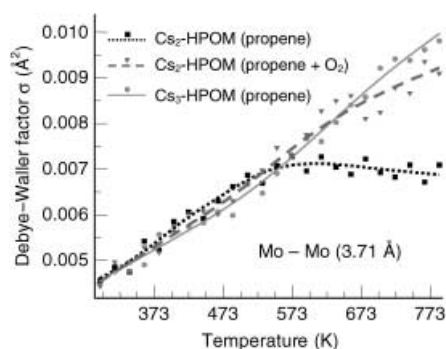


Figure 13. Evolution of the Debye–Waller factor of the Mo–Mo scattering path at an original distance of 3.71 Å of $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$ during treatment in 10% propene in helium and in 10% propene and 10% oxygen, and of $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ during treatment in 10% propene in helium in the temperature range from 300 to 773 K.

ture range from 300 K to 773 K. The increasing DW factors in the temperature range below 573 K are indicative of increasing thermal disorder in the Keggin structure during thermal treatment. However, at about 573 K during the treatment of $\text{Cs}_2\text{-HPOM}$ in propene DW decreases relative to the DW factor of the Mo–Mo distance in the Keggin structure of $\text{Cs}_3\text{-HPOM}$. The decrease in the DW factor corresponding to $\text{Cs}_2\text{-HPOM}$ above about 573 K coincides with the partial reduction of Mo, the elongation of Mo–Mo and Mo–O distances, and the formation of the cubic HPOM. The DW factor corresponding to $\text{Cs}_3\text{-HPOM}$ in Figure 13 appears to exhibit a change in slope at about 573 K, with a larger slope above this temperature. A similar increase in the DW factors of other scattering paths in the Keggin structure of $\text{Cs}_3\text{-HPOM}$ during treatment in propene is shown in Figure 14. This relative change was most pronounced for the Mo–O distances of 1.69 Å and 1.99 Å, while the Mo–Mo distance of 3.71 Å exhibited the largest absolute increase in the DW factor with temperature. Other scattering paths in the Keggin structure of $\text{Cs}_3\text{-HPOM}$ showed no discernable change in the slope of the increase of the corresponding DW factor with temperature.

In addition to investigating the structural evolution of various as-prepared HPOMs under temperature-program-

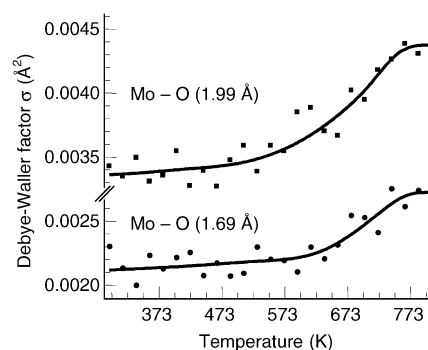


Figure 14. Evolution of the Debye–Waller factors of two Mo–O scattering paths at original distances of 1.69 Å and 1.99 Å of $\text{Cs}_3[\text{PMo}_{12}\text{O}_{40}]$ during treatment in 10% propene in helium in the temperature range from 300 to 773 K.

med reaction conditions, the cubic HPOM prepared from HPOM and $\text{Cs}_2\text{-HPOM}$ at 673 K was subjected to extended treatment in propene and oxygen at 673 K in a conventional tubular glass reactor. Under these reaction conditions, the cubic HPOM exhibited higher catalytic activity than HPOM, $\text{Cs}_2\text{-HPOM}$, and orthorhombic MoO_3 . Furthermore, under the propene-oxidation conditions employed (including a considerable partial pressure of water resulting from oxidation of propene) the cubic HPOM had remarkable long-term stability: no changes were detectable in the cubic structure of the activated HPOM after more than 12 h on stream. The improved catalytic activity is in good agreement with the results described by Mariosi et al. for an activated $\text{Cs}_2\text{-HPOM}$.^[17] Details of the catalytic and structural studies performed on the cubic HPOM under partial oxidation conditions will be presented in a forthcoming publication.

Discussion

Structural changes in heteropolyoxomolybdates during thermal treatment in propene: The evolution of the short-range-order structure of the Keggin anion in heteropolyoxomolybdates (Figure 1A) was investigated under reactive atmospheres at elevated temperatures. The experiments described focused on the stability of partially decomposed Keggin ions and correlations between the structural changes of the Keggin ion and the catalytic activity in the partial oxidation of propene. From the in situ XRD experiments performed during the thermal treatment of HPOM in propene, it was found that, up to a reaction temperature of ~ 573 K, the structural evolution of HPOM during treatment in propene corresponds to that described in the literature[9,11,33] (Figure 2). However, at 573 K the formation of a cubic phase is observed that has a structure with similar long-range order to the known cubic cesium salts of the HPOM (i.e., $\text{Cs}_2\text{-HPOM}$ and $\text{Cs}_3\text{-HPOM}$; Figure 1B). A Rietveld refinement of a structural model consisting of a cubic arrangement of Keggin anions under the assumption that a certain number of the molybdenum ions had migrated onto sites between the Keggin anions resulted in significantly im-

proved agreement between experimental data and theoretical calculation (Figure 3, Table 1). The improvement in the structural refinement obtained is in good agreement with that reported by Marosi et al.^[17]. These authors observed similar changes in the intensity of the diffraction pattern of a cubic Cs₂-HPOM under catalytic reaction conditions and interpreted them as the result of the migration of Mo ions onto interstitial sites.

In analogy to the migration of vanadium or iron addenda substituents from the Keggin ion onto interstitial sites, however, it is more or less explicitly assumed in the literature that the Keggin ions reconstruct after the loss of the addenda ions. To investigate the local structural changes in the Keggin ion during thermal treatment (i.e., activation) in reducing and oxidizing atmosphere, and hence the stability of the partially reduced and decomposed Keggin ion that may form under these conditions, we performed in situ XAS measurements on various heteropolyoxomolybdates.

Local electronic and geometric structure of a lacunary Keggin ion:

The changes in the Mo K-edge FT[$\chi(k)$] of Cs₂-HPOM and HPOM (Figure 5) indicate significant alterations of the local structure in these materials under reducing conditions. Apparently, the local structural changes in HPOM exceed those observed in Cs₂-HPOM, whereas no significant structural changes are observed in the FT[$\chi(k)$] of Cs₃-HPOM (Figure 6). The FT[$\chi(k)$] of the cubic HPOM and Cs₂-HPOM with Mo on interstitial sites indicate a remarkable degree of order in the partially reduced and decomposed Keggin ions. A complete decomposition of a few Keggin ions while the majority either remains in the original state or reconstructs after partial decomposition should result in an unaffected FT[$\chi(k)$], contrary to the structural changes observed. The local structure of the HPOM probed by XAFS corresponds to the local arrangement of edge- and corner-sharing MoO₆ units in the Keggin anion (Figure 9). Both the structure of the original HPOM and the structure of the cubic HPOM obtained after treatment in a reducing atmosphere can be simulated by theoretical XAFS calculations based on the structure of the Keggin anion (Figure 8). For the former, the Mo–O and Mo–Mo distances obtained from the XAFS refinement agree well with those obtained from single-crystal structure analysis^[34], whereas for the latter a significant lengthening of the Mo–O and Mo–Mo distances in the Keggin anion is obtained.

Evidently, the medium-range order of the cubic HPOM resembles that of a Keggin anion, while the changes in the local geometric and electronic structure are indicative of a lacunary Keggin^[8,37] structure in which one or more MoO₆ units are missing from the initial structure of the Keggin anion. A schematic representation of a partially decomposed Keggin ion with a Mo cation located on an interstitial site and coordinated to the remaining MoO₆ units of the Keggin ion is presented in Figure 15. Moreover, detailed analysis of the local structure of the cubic HPOM is in good agreement with the analysis of the long-range-order structure, which remains closely related to the cubic structure of a Cs salt of a heteropolyoxomolybdate composed of Keggin anions (Figure 8).



Figure 15. Schematic representation of a partially decomposed Keggin anion (lacunary Keggin anion) as a model for the catalytically active species in heteropolyoxomolybdate partial oxidation catalysts.

Figure 10 shows that the onset of the structural changes in the Keggin anion of Cs₂-HPOM is at about 573 K. In comparison, no significant structural changes were observed in Cs₃-HPOM over the temperature range studied (Figure 10). The same holds for the evolution of the average Mo valence of the Keggin anion, for which no changes were observed during treatment of Cs₃-HPOM in propene or hydrogen. Conversely, partial reduction of molybdenum in Cs₂-HPOM was detected at temperatures above 573 K (Figure 12), which coincides with the local structural changes observed at this temperature. The average Mo valence of about 5.4 of the resulting cubic HPOM at 773 K is in good agreement with thermogravimetric measurements on the treatment of HPOM in propene, which showed a loss of about four oxygen atoms per Keggin ion in the temperature range from 573 to 773 K (av Mo valence of 5.33).^[38]

Here we describe for the first time a straightforward route for the preparation of a cubic heteropolyoxomolybdate (*Pn* $\bar{3}m$, $a=11.853$ Å; Figure 1) from triclinic H₃[PMo₁₂O₄₀] \cdot 13H₂O under reducing conditions with propene and hydrogen at temperatures above about 600 K. The lattice constant obtained for the cubic HPOM is very similar to that of the cesium salt of the heteropolyoxomolybdate ($a=11.862$ Å). From the evolution of the scattering background in the in situ XRD patterns measured under reaction conditions, it can be concluded that the majority of the sample remains crystalline. Furthermore, the preparation route indicates considerable stability of the cubic HPOM or Cs₂-HPOM with Mo ions on interstitial sites, and hence a considerable tendency of the Keggin ion to partially decompose at elevated temperatures. Thus, it appears likely that a similar partial decomposition of Keggin ions takes place during activation of HPOM under partial oxidation conditions, and this would make the cubic HPOM a suitable material for future studies on structure–reactivity relationships of HPOM.

Driving force for the formation of lacunary Keggin ions:

The driving force for the formation of a lacunary Keggin anion may be relaxation of the Keggin structure at elevated temperatures, possibly accompanied by formation of links

between the Keggin ions and thus more stable extended oxide structures. Accordingly, this would explain the migration of Mo cations from the Keggin anion onto interstitial sites that is described here for the treatment of HPOM and Cs₂-HPOM in propene and that has also been observed during treatment of Cs₂H₂[PVMo₁₁O₄₀] in propene^[39]. The intact Keggin anion may be strained and energetically less favorable at elevated temperatures, and thus partial decomposition and relaxation of Mo–O and Mo–Mo bonds in the Keggin anion occur on heating. The considerable decrease in the DW factor of the Mo–Mo distances above about 573 K during treatment of Cs₂-HPOM in propene (Figure 13) appears to corroborate a relaxation of the partially reduced Keggin anion on migration of Mo ions onto interstitial sites. Moreover, the decreasing DW factor (Mo–Mo distance of $R=3.71$ Å) observed during treatment of Cs₂-HPOM in propene (Figure 13) makes a complete decomposition of the Keggin ion into fragments of solely edge-sharing MoO₆ units unlikely. This decomposition has been suggested in the literature,^[14] but complete decomposition of Keggin ions would result in a strong increase in the DW factor, particularly that of the Mo–Mo distance of 3.71 Å, because of a decrease in coordination number.

With respect to the thermal treatment of Cs₃-HPOM in propene, the change in the slope of the evolution of the DW factor of the Mo–Mo distance at $R=3.71$ Å corresponds to the onset of the partial reduction and decomposition of Keggin anions during treatment of Cs₂-HPOM in propene (Figure 13). Evidently, even in the Keggin anions of Cs₃-HPOM an increase in the static disorder (Mo–O DW factors in Figure 14) is observed at temperatures above about 573 K. Two alternatives can be discussed for the stability of Cs₃-HPOM under reducing and catalytic reaction conditions. First, because all available interstitial sites are occupied by bulky Cs ions, no sites are available for migration of Mo ions. Therefore, the local structure of the partially reduced lacunary Keggin anion does not develop (Figure 10 and Figure 12), and hence no catalytic activity is detectable. Second, the Cs₃-HPA salt does not contain constitutional water that can be released at elevated temperature with partial reduction of the Keggin anion. In contrast to the layer structure of orthorhombic MoO₃,^[36,40] no readily available oxygen diffusion pathways exist in the secondary structure of the HPOM. Thus, also in contrast to the behavior of MoO₃, no partial reduction of Cs₃-HPA is observed during treatment in propene, and neither partially decomposed Keggin ions are formed nor is catalytic activity developed under reaction conditions.

Structural changes in HPOM during activation in propene and oxygen:

Under partial-oxidation conditions in propene and oxygen, the evolution of the local structure of Cs₂-HPOM in the temperature range from 300 to about 700 K indicates that the structural characteristics of the Keggin anion are mostly preserved (Figure 7). This is in agreement with the structural evolution of Cs₂-HPOM during thermal treatment in propene. In situ XRD experiments performed during extended treatment of Cs₂-HPOM in propene and oxygen showed the formation of MoO₃ at temperatures

above about 700 K. During treatment of HPOM in propene and oxygen, eventually complete decomposition of the Keggin structure and formation of orthorhombic MoO₃ was observed at about 670 K. Apparently, both HPOM and Cs₂-HPOM decompose in propene and oxygen to form MoO₃, whereas during treatment of HPOM and Cs₂-HPOM in propene, complete decomposition and reduction to MoO₂ is observed only at temperatures above about 750 K and with extended treatment times.

The local structural changes observed in the Keggin ion of Cs₂-HPOM during treatment in propene and oxygen, which coincide with the onset of catalytic activity, are in good agreement with those observed during treatment in propene. Both onset temperature and changes in the Mo–O and Mo–Mo distances during treatment in propene and oxygen indicate that, similar to the treatment of Cs₂-HPOM in propene, in both HPOM and Cs₂-HPOM partial decomposition of the Keggin ion (i.e., migration of Mo cations and modified short-range coordination) takes place at temperatures above about 573 K. The same holds for the onset temperature for reduction of molybdenum in HPOM and Cs₂-HPOM in propene and oxygen, which coincides with that of the reduction observed during treatment of HPOM and Cs₂-HPOM in propene (Figure 12).

Evidently, HPOM and Cs₂-HPOM exhibit a considerable activity and selectivity for the partial oxidation of propene, whereas no catalytic activity can be detected for Cs₃-HPOM. It seems that the partial decomposition of the Keggin ion and the formation of a lacunary Keggin ion, and possibly the formation of extended (condensed) oxide structures, are prerequisites for the onset of catalytic activity of the material (Figure 11). For the reasons discussed above those structural changes cannot occur in Cs₃-HPOM, and hence no catalytic activity is observed on this material.

Similar to Cs₂-HPOM (Figure 11), the onset of the catalytic activity of HPOM is correlated to the partial decomposition and reduction of the material under reaction conditions (Figure 12). However, in contrast to Cs₂-HPOM, HPOM decomposes readily at temperatures above about 700 K to form orthorhombic MoO₃. Apparently, in the structure of the HPOM too many sites are available for the migration of molybdenum cations from the Keggin ion. This can be seen in the reduction of molybdenum in HPOM under reaction conditions (Figure 12) which proceeds much further than the reduction of molybdenum in Cs₂-HPOM. Evidently, the lacunary Keggin anions formed during treatment of HPOM in propene and oxygen become destabilized to a degree that facilitates complete decomposition to form extended oxide structures and eventually MoO₃. Conversely, because of the bulky Cs cations in the Cs₂-HPOM structure, only a limited number of sites are available for migration of Mo cations from the Keggin ions. Hence, the remaining lacunary Keggin anions become less destabilized compared to those in HPOM, and the active structure of Cs₂-HPOM is more stable than that of HPOM.

In explaining the structural changes in Cs₂-HPOM^[12] under reaction conditions, a core–shell model assuming a mixture of Cs₃-HPOM and HPOM was suggested in the literature. However, according to the structural data presented

here this model cannot account for the structural changes observed in Cs₂-HPOM during activation in propene. If a significant amount of Cs₂-HPOM was transformed into a mixture of Cs₃-HPOM and largely disordered or even completely decomposed HPOM, the local structure, as observed by means of FT[$\chi(k)$], would resemble that of the original Keggin anion, and hardly any changes should be noticeable. This is certainly not in agreement with the experimental data, which indicate that a major fraction of the Keggin anions in the structure is transformed into lacunary Keggin ions. Furthermore, the complete decomposition of the HPOM and the formation of molybdenum oxides that has been observed during extended treatment under reaction conditions reveal the thermal instability of heteropolyoxomolybdates.^[14] However, interpreting the molybdenum oxides formed as the catalytically active species in activated HPOM may be misleading. The results presented here indicate that the formation of the lacunary Keggin ion correlates with the onset of catalytic activity and that the more readily detectable MoO₃ and other molybdenum oxides are products of the proceeding decomposition of the HPOM rather than the catalytically active phase.

The magnitude of the local structural changes (i.e., distances and average valence) observed in Cs₂-HPOM during treatment in propene is considerably larger than that in the Keggin ions of Cs₂-HPOM treated in propene and oxygen. Two reasons may be responsible for this effect. First, under more oxidizing reaction conditions, reduction of the molybdenum cations in the Keggin ion may be less than in a more reducing atmosphere, so that shorter Mo–O and Mo–Mo distances result. The difference in the number of oxygen atoms that are missing in each Keggin ion under reducing atmosphere (ca. 4) and under catalytic conditions (ca. 1) may represent the oxygen atoms available for activation of the propene during partial oxidation reaction. Second, under oxidizing reaction conditions the number of Mo cations migrating from Keggin anions onto interstitial sites may be smaller, and thus fewer partially decomposed Keggin ions are formed. The former reason may be corroborated by the smaller degree of reduction observed in Cs₂-HPOM in propene and oxygen compared to Cs₂-HPOM in propene (Figure 12), whereas the latter appears to be corroborated by the higher catalytic activity of “activated” cubic HPOM that was previously treated in propene and contains a larger amount of lacunary Keggin ions. To further address these questions, structure–activity correlations of the “activated” polyoxomolybdate, in particular during isothermal periods under partial-oxidation, conditions, will be the subject of future investigations.

Structure–activity relationships in heteropolyoxomolybdates: Elucidating relationships between the structure of a material and its reactivity requires detailed knowledge about the structure of the material under the reaction conditions applied (in situ). More often, the initial geometric and electronic structure of the material at room temperature in air (ex situ) is not identical to the structure present under reaction conditions. For heteropolyoxomolybdates under reaction conditions, “structure” does not refer to the undistur-

bed Keggin structure of the initial material but rather to the electronically and geometrically distorted structure of partially reduced lacunary Keggin ions (Figure 15). It seems that a certain instability of the structure of the heteropolyoxomolybdates is a prerequisite for obtaining an active catalyst under reaction conditions. Partial decomposition of the Keggin anion, partial reduction of molybdenum, and migration of molybdenum cations onto interstitial sites generate the particular sites in the lacunary Keggin ion required for activation of oxygen and propene. Evidently, the correlation between the structural changes described during activation of HPOM and the onset of catalytic activity indicates that the original Keggin structure should be regarded as the precursor for the structure of the partially decomposed active catalyst. With respect to the onset temperature of catalytic activity at about 573 K, the correlation with the onset of structural changes in the Keggin ion that indicate a certain instability of the Mo–O bonds at that temperature agrees well with similar results obtained for the partial oxidation of propene on orthorhombic MoO₃^[40]. It may be deduced that similar “active sites” for the partial oxidation of propene are formed on the structure of the lacunary Keggin ion and on MoO₃ under reaction conditions.

Conclusion

The structural evolution of Keggin-type heteropolyoxomolybdates (HPOM) during thermal treatment in propene and in propene and oxygen in the temperature range from 300 to 773 K was determined by in situ XRD and XAS experiments combined with mass spectrometry. Under a reducing atmosphere (propene or hydrogen) migration of molybdenum cations from the Keggin ion onto interstitial sites takes place at temperatures above about 573 K to give thermally stable partially reduced lacunary Keggin ions. During treatment in propene or hydrogen and at reaction temperatures of about 673 K, the initially triclinic H₃[PMo₁₂O₄₀]·13H₂O is transformed quantitatively into a cubic heteropolyoxomolybdate with a long-range structure very similar to that of the cesium salts. The driving force for the partial decomposition of HPOM and Cs₂-HPOM may be thermal strain or increased disorder in the Keggin ions at elevated temperatures, possibly together with the formation of extended molybdenum oxide structures. Because in the Cs₃-HPOM the configurational water is completely exchanged and all interstitial sites are occupied by the bulky Cs cations, no partial reduction or decomposition with increasing temperature was observed.

Under catalytic oxidation conditions (propene and oxygen) in the temperature range from 300 to 773 K, the onset of catalytic activity of HPOM and Cs₂-HPOM at about 573 K correlates with partial reduction of Mo and characteristic changes in the local structure of the Keggin ion. The structural changes observed indicate that, similar to the treatment of HPOM and Cs₂-HPOM in propene, migration of Mo ions from the Keggin ions onto interstitial sites and formation of lacunary Keggin ions takes place. Moreover, the formation of these partially reduced and decom-

posed Keggin ions appears to be a prerequisite for the material to become an active heterogeneous catalyst. Evidently, the undistorted Keggin ion in the as-prepared heteropolyoxomolybdates should be regarded as a precursor of the active catalyst. Reliable structure–activity relationships of HPOM must take into account the structural changes in the material under reaction conditions. Hence, the function of the HPOM as a partial oxidation catalyst should be correlated to the partially decomposed structure of the lacunary Keggin ions observed under reaction conditions.

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