

Speciation of Molybdates under Hydrothermal Conditions

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In situ Raman spectroscopy was applied to investigate the speciation of molybdates under hydrothermal conditions in 0.2 M aqueous solution in the temperature range between 20°C and 200°C and at pH values between 7 and 1. The nature and abundance of molecular and supra-molecular species differs significantly compared to the distribution of species under ambient conditions at the same pH. Whereas heptamolybdate $\text{Mo}_7\text{O}_{24}^{6-}$ dominates under ambient pressure at 25°C in the pH range between 6 and 5, at 170–190°C, chain-like or molecular structures of dimolybdates $\text{Mo}_2\text{O}_7^{2-}$ and trimolybdates $\text{Mo}_3\text{O}_{10}^{2-}$ are preferentially formed.

In acidic solutions ($\text{pH} < 2$), supramolecular species, like $\text{Mo}_{36}\text{O}_{112}^{8-}$, which generally predominate at 25°C, do not occur at $T > 100^\circ\text{C}$. Instead, $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ is the final molecular precursor of precipitation reactions that was detectable by Raman spectroscopy. The structural type of the solid phase formed through addition of vanadyl sulfate under hydrothermal conditions is sensitively controlled by the nature of the molecular precursor, which is adjusted by the pH. In acidic medium, *hex.* MoO_3 (ICSD 80290) is formed, while at $\text{pH} = 5.8$ nano-crystalline M1 (ICSD 55096) was obtained.

Introduction

Hydrothermal synthesis gives access to various material families including oxides, carbides, nitrides, open-framework and hybrid structures, metallics and intermetallics, and carbons. Proper choice of reaction conditions, and the addition of complex-forming, capping or structure-directing agents lead to solid particles characterized by different morphology and render the controlled synthesis of hierarchical pore structures possible. Hydrothermal routes benefit from kinetic control that facilitates the formation of metastable phases, which often comprise the desired functionality.^[1] This benefit is accompanied by the disadvantage that predictions of product properties are oftentimes quite difficult. Spectroscopic and analytical studies of inorganic syntheses are particularly important to understand the mechanisms behind the complex reactions under hydrothermal conditions and to rationally

design experiments for the synthesis of new phases exhibiting designated properties.^[1d, 2] We have developed an analytical autoclave (Figure 1) that enables the synthesis of comparatively large batches of oxides according to a new concept that implies a guided synthesis based on spectroscopic information obtained online during the entire experiment.^[3] The synthesis is performed automated according to a pre-assigned sequence of reaction steps and the reaction parameters, such as temperature, pressure, power intake of the stirrer, and pH are measured and recorded.

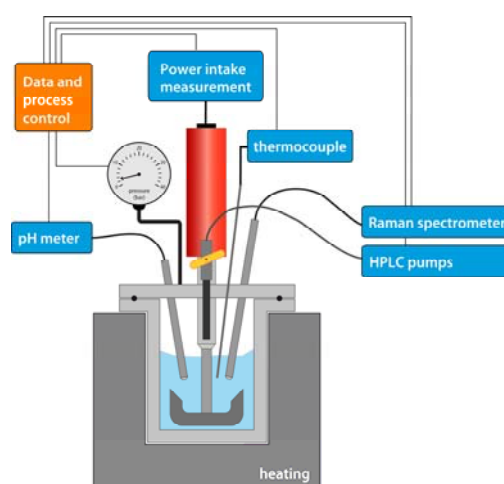


Figure 1. Analytical autoclave used for the *in situ* investigation of the molybdate chemistry under hydrothermal conditions at various pH. Technical details are described in the experimental section.

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The analytical autoclave set-up allows for the *in situ* investigation of species appearing during the reaction, *e.g.* polyoxometalates, by Raman spectroscopy and enables the

directed synthesis to desired phases by adjusting the reaction parameters accordingly, *e.g.* through addition of reactants or changing the pH by using the HPLC pumps. Other analytical tools, such as IR and UV-vis spectroscopy or other scattering techniques to investigate the chemical changes and dissolution or phase formation behavior under hydrothermal conditions can also be applied in that set-up.

The nature of metal oxide clusters is not only of importance for understanding the mechanisms of phase formation in the synthesis of metal oxides but also in the contrary process, meaning the dissolution of minerals that occur under extreme conditions in our earth's crust. Molybdate species have been investigated by XANES in aqueous solutions in presence of chloride, iron and manganese ions.^[4] Also the dipole properties of water are significantly changed under high temperatures and pressures, which has an impact on the dissolution behavior of minerals.^[5]

Polyoxometalates with different compositions and structures have been investigated for decades by now with the prospects of various applications and have been subject of several review articles.^[6] Giving a broad overview on the coordination chemistry of the different transition metals, their existence under the reaction conditions applied in the synthesis of metal oxide catalysts has to be further investigated. Previously, we reported the directed synthesis of complex Mo-based mixed oxides through subsequent addition of the required structural building units.^[3] With the aim to systematically broaden our knowledge concerning intermediates present under hydrothermal conditions during the synthesis of transition metal oxides, the current study is devoted to the speciation of isopolymolybdates at elevated temperature and pressure and their impact on solid formation upon the addition of vanadium as a second transition metal ion. The objective is to study the speciation of polyoxometalates under conditions that are close to the hydrothermal synthesis of molybdenum oxides and mixed MoV oxides, meaning that the experiments were performed in pure water in the absence of buffer solutions or alkali salts. The physical and chemical properties of water change significantly under hydrothermal conditions with increasing temperature and pressure, in particular the negative logarithm of the ionic product of water K_w decreases from 14 to 11.3 under autogenous pressure from 25°C to 200°C.^[7] For this reason, the ionic strength is not constant during the *in situ* spectroscopic experiments at variable temperature. The influence of proton concentration and temperature under the conditions of hydrothermal synthesis of MoV-based oxides will be discussed.

Results and Discussion

The structure of molybdates in aqueous solution is manifold and strongly depends on parameters such as concentration, ionic strength, pH, counter ion, solvent and temperature. The reversible transformation of isopolymolybdates in aqueous solution occurs through hydrolysis and condensation in consequence of changing pH, that is, in contrast to tungstates, a spontaneous process.^[8] The degree of polymerization of the individual species can be expressed by calculation of the Z^+ -value, which is described by the ratio of protons consumed per molybdenum atom in the condensation reaction (Equation 1, in which v

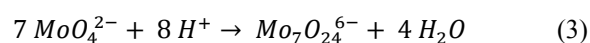
corresponds to the stoichiometric coefficient). The Z -value of the solution, taking into account the initial H^+ concentration (C_{H^+}), the equilibrium concentration of protons (c_{H^+}) and the autodissociation of water under the given reaction conditions (Equation 2), indicates the species to be expected at certain pH.^[9]

$$Z^+ = |v_{H^+}| / |v_{MoO_4^{2-}}| \quad (1)$$

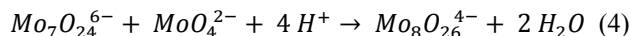
$$Z = (C_{H^+} - c_{H^+} + K_w/c_{H^+}) / c_{MoO_4^{2-}} \quad (2)$$

In solution, mostly a mixture of different species exists at the same time. The speciation of molybdates and the effect of concentration and pH value on the transformation at normal pressure have been investigated thoroughly by potentiometric measurements,^[10] UV/vis spectroscopy,^[11] electrospray mass spectrometry,^[12] and Raman spectroscopy.^[10a, 13] In Figure 2, the Raman spectra in the range of the characteristic Mo=O vibrations of 0.2 M molybdate solutions at different pH values from 7.0 to 1.0 are compared for experiments conducted at 25°C and ambient pressure (Figure 2a), and at 175°C and autogenous pressure of 891 kPa (Figure 2b). The entire range of the spectra from 200 to 1200 cm^{-1} is shown in the Supporting Information (Figures S1-S2). The comparison of those two experiments reveals significant differences in the distribution of molybdate species at identical pH values but different temperatures and pressures. Please note, that the bands for the individual species observe a slight shift towards lower wavenumbers due to thermal effects. The center of the band at 749 cm^{-1} from the sapphire window of the probe, which is used as reference, exhibits a temperature shift of ~4 cm^{-1} (Figure S3, Supporting Information) in the temperature range between 20 and 190°C, which is also expected for the molybdate species.

In the experiment performed at 25°C, the starting pH of the molybdate solution was adjusted to 9.0 by addition of ammonium hydroxide solution resulting in the preferential occurrence of tetrahedrally coordinated MoO_4^{2-} anions characterized by Mo-O stretching vibrations at 896 and 839 cm^{-1} and a band at 316 cm^{-1} (Figure S1, Supporting Information). At pH values above 7 and $T=25^\circ C$, the tetrahedral MoO_4^{2-} is the only stable form, which is sequentially polymerized upon acidification (Figure 2a). The condensation reaction is thermodynamically driven by the formation of Mo-O-Mo bonds and the release of H_2O . Accordingly, the resulting structures should be composed of edge-sharing octahedra with a minimum of terminal oxygen atoms.^[10f] At room temperature, the first step is the direct transformation of monomeric MoO_4^{2-} to heptamolybdate ($Z^+=1.14$) that can be followed with Raman spectroscopy by the continuous decrease of the MoO_4^{2-} band at 896 cm^{-1} and parallel appearance of a band due to the formation of $Mo_7O_{24}^{6-}$ at 939 cm^{-1} (Figure 2a).^[10a, 13g, 14] Although, according to Equation 3, a number of 7 molybdate ions and 8 protons are required in total, no indications for stable intermediates with less complexity have been found by Raman spectroscopy and reported so far. The pH range dominated by heptamolybdate is between 6 and 5 in which $Mo_7O_{24}^{6-}$ always coexists with other species, such as remaining MoO_4^{2-} , $Mo_3O_{10}^{2-}$, and its protonated form $HMo_7O_{24}^{5-}$.^[14]



Upon continuing addition of acid, the Raman band maximum of the heptamolybdate shifts to 948 cm^{-1} at $\text{pH}=4.0$ due to formation of trimolybdate ($Z^+=1.33$) with the most intense $\text{Mo}=\text{O}$ band at 950 cm^{-1} as also found by Himeno *et al.*,^[13a] or protonation of heptamolybdate,^[14] and finally decreases in intensity. Subsequently, new bands at 958 and 969 cm^{-1} arise, indicating the formation of α - and β - $\text{Mo}_8\text{O}_{26}^{4-}$ ($Z^+=1.5$), respectively. Formally, the octamolybdate can be obtained by the addition of MoO_4^{2-} to heptamolybdate consuming four additional protons according to Equation 4.



The α -form is constituted by six edge-sharing MO_6 -units forming a six-membered ring with each side of the plane being capped by two MO_4 -tetrahedra. A more dense structure, comprising only edge-sharing MO_6 -octahedra is then formed in the β -octamolybdate by reconstruction. The γ - $\text{Mo}_8\text{O}_{26}^{4-}$ has been reported as intermediate species in the transformation from the α - to the β -form,^[15] but has not been found in noticeable concentrations as for its thermodynamic and kinetic instability.^[13a]

ammonium heptamolybdate solution with $Z=1.14$ (Figure 3) at autogenous pH values and the thermal decomposition of Mo_{36} ions in aqueous solution (Figure 4) which serve as reference experiments.

During heating of an aqueous solution of ammonium heptamolybdate from 20°C to 190°C the speciation is found to change significantly, which is reflected in the variation of the $\text{Mo}=\text{O}$ Raman vibrations (Figure 3a). The relative amount of each species, under the reasonable assumption of identical scattering cross-sections of all the species involved,^[13a] are visualized in Figure 3b. The spectra have been simulated using Gaussian functions after subtraction of the background and correction for thermal shift of the respective bands. The species considered in the spectral deconvolution have been restricted to the species expected in the Z -range of the solution and taking into account the different bands in that spectral range with fixed relative intensities (Table S1, Supporting Information).

As the pH value changes only slightly between 5.4 and 6, these effects can be attributed to changing equilibria of the different stable species under the given temperature. This is

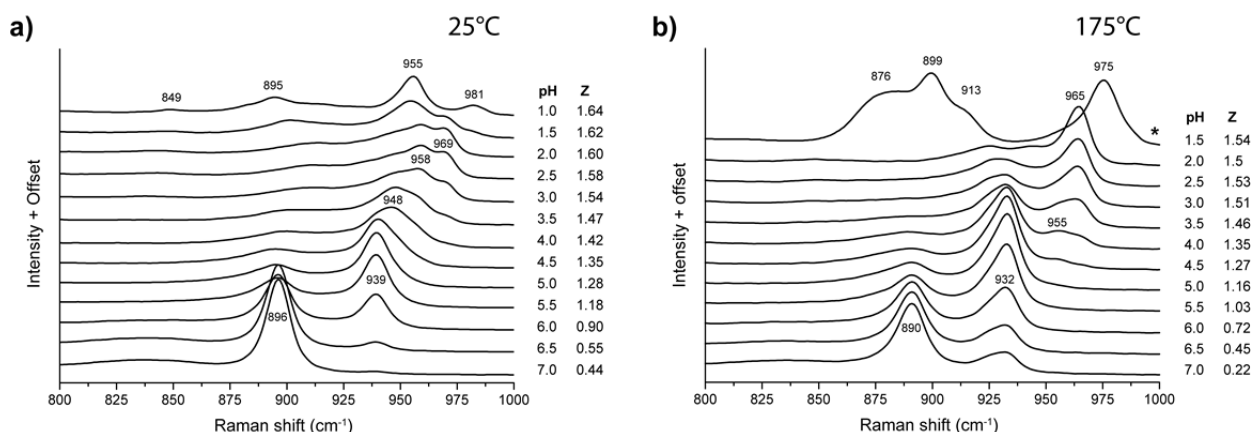


Figure 2. Raman spectra of molybdate solutions (starting concentration 0.25 M, final concentration 0.2 M) at different pH values from pH 7.0 to 1.0 for 25°C (a) and pH 7.0 to 1.5 for 175°C (b) with the corresponding Z -values of the solutions; the spectrum marked with * has been scaled by the factor of 0.5.

In the more acidic regime with Z -values above 1.64, formation of the even more complex isopolymolybdate ion $\text{Mo}_{36}\text{O}_{112}^{8-}$ ($Z^+=1.78$) can be observed at 25°C evident by the appearance of bands at 981 , 955 , 895 , and 849 cm^{-1} ,^[13d] which is the only stable phase at pH below 1.0. This Mo_{36} ion can be described as a centrosymmetric dimer of Mo_{18} subunits in which two of the Mo atoms become seven-coordinate and form a pentagonal bi-pyramidal unit surrounded by edge-sharing MO_6 -octahedra. This motif is also found in other highly condensed solid phases, such as the so called Mo_5O_{14} -type,^[16] and M1 phases.^[17] Finally, molybdic acid is precipitated from that solution as a white solid at a pH below 1. Bands reported for H_2MoO_4 in solution^[18] at 919 cm^{-1} are not detected under the present experimental conditions because of the very fast condensation reactions to polymolybdates. The observations made in the experiment at 25°C (Figure 2a) are consistent with the literature^[10a, 13a, 13d, 13e] and provide the basis for further variation of the experimental parameters. To understand the differences observed when the same experiment was performed at 175°C (Figure 2b), we first discuss the speciation during heating of a 0.2 M aqueous

also underlined by the fact, that the reaction is fully reversible; no chemical changes can be observed afterwards. The auto-dissociation of water at elevated temperatures as well as the pH changes have no significant influence on the Z -value of the investigated molybdate solution and cannot be attributed to the observed changes (Table S2, Supporting Information). A 0.2 M solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ has a pH value of 5.4 at 20°C , and exhibits a mixture of MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$ as derived from the bands at 895 and 939 cm^{-1} , while the heptamolybdate species predominates in agreement with the previous experiment (Figure 2a). The slight anisotropy of the band at 939 cm^{-1} to higher wavenumbers and the difference in the sum of Z^+ -values of MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$ to the initial 1.14 gives reason for the presence of trimolybdate under these conditions, which is also found by Himeno *et al.* as a minor species under similar conditions.^[13a]

When heating that solution under autogenous pressure, the band of the orthomolybdate at 896 cm^{-1} gradually decreases and the band due to heptamolybdate originally at 939 cm^{-1} apparently shifts towards higher wavenumbers as a result of strong overlap with the increasing band of trimolybdate at

950 cm^{-1} . That is also accompanied by the increase in the pH value from 5.4 to 5.7 indicating changes in the nuclearity of the molybdates. The spectral deconvolution (Figure 3b) shows, that both are transformed to other species and completely disappear at 130°C. At the same time, another band around 956 cm^{-1} arises together with a peak at 965 cm^{-1} , which is first seen as a shoulder of the main feature and becomes more dominant at higher temperatures. The latter two bands can be attributed to α - and β - $\text{Mo}_8\text{O}_{26}^{4-}$, respectively which are both not observed under ambient conditions at pH values above 4.0 in considerable amounts. At 25°C, octamolybdate occurs in the pH range between 3.5 and 1.5 (Figure 2a). The band intensity of the α -modification shows a maximum around 130°C and decreases thereafter for the benefit of the formation of β - $\text{Mo}_8\text{O}_{26}^{4-}$ which proves to be more stable at elevated temperatures under autogenous pressure. The pH reaches a maximum at $T=130^\circ\text{C}$ in agreement with progressive condensation, but decreases slightly at higher temperatures suggesting depolymerisation. This is also reflected by the development of a new band at 932 cm^{-1} that appears for the first time as a shoulder in the spectrum at 80°C when heptamolybdate is already substantially decomposed and continuously gains in intensity, finally dominating the spectrum at 190°C. Since the Z-value of the solution marginally changes during the heating experiment, the formation of octamolybdate ions must go in line with

In summary, a 0.2 M aqueous solution of molybdates under autogenous pressure at temperatures between 170 and 190°C contains mainly dimolybdate species together with tri-, tetra-, and octamolybdates.

Figure 4 illustrates the thermal stability of $\text{Mo}_{36}\text{O}_{112}^{8-}$ ions in a 0.2 M solution obtained by adjusting an aqueous molybdate solution to a pH value of 1.5. The spectrum of the initial $\text{Mo}_{36}\text{O}_{112}^{8-}$ solution exclusively exhibits the characteristic bands of the supramolecular species at 981, 955, 895 and 849 cm^{-1} . During heating of that solution the band structure is changed, explicitly from about 50°C on an additional band at 969 cm^{-1} appears and slowly shifts towards higher wavenumbers while the other bands weaken and finally disappear at 70°C. The formation of the hexagonal- MoO_3 phase (ICSD 80290)^[21] is well observed by the very intense bands at 973 and 901 cm^{-1} with shoulders at 878 and 911 cm^{-1} . Obviously, the $\text{Mo}_{36}\text{O}_{112}^{8-}$ ion is decomposed at quite low temperature to form the bulk *hex.*- MoO_3 phase. This also goes in line with the loss of structural features, such as the pentagonal bipyramidal units of the Mo_{36} -unit and formation of a loose network of edge- and corner sharing MO_6 -units with large pores. The experiment shows that the supramolecular species $\text{Mo}_{36}\text{O}_{112}^{8-}$ can be excluded as intermediate under hydrothermal conditions ($T>100^\circ\text{C}$).

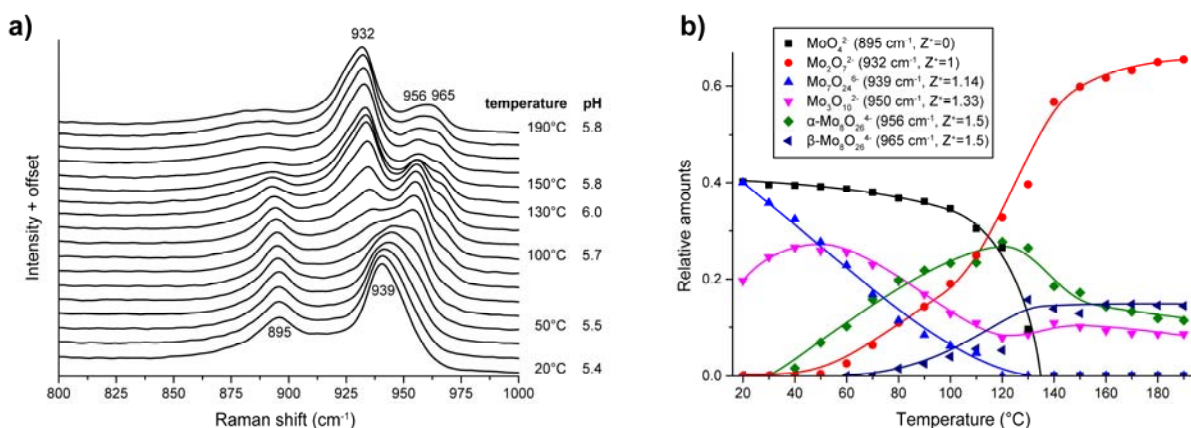


Figure 3. *In situ* Raman spectra recorded during heating of a 0.2 M ammonium heptamolybdate solution from 20 to 190°C with the corresponding pH values (a) and species distribution plot derived from spectral deconvolution of the Raman spectra (b). The Z-value remains constant at 1.14 during the entire experiment (see Table S2, Supporting information).

depolymerisation and release of the required protons. Following this argument and considering the spectral shift of the $\text{Mo}=\text{O}$ vibration towards lower wavenumbers, this newly formed species with a peak maximum at 932 cm^{-1} requires a degree of polymerisation between ortho- and heptamolybdate. Dimolybdates, which are constituted either by corner-sharing tetraedra in a dimeric or by corner- and edge-molybdate units in the polymeric form, are found in literature with a $\text{Mo}=\text{O}$ band in the spectral range from 925 to 939 cm^{-1} ,^[19] are the only stable molybdates to be expected with a Z^+ -value lower than heptamolybdate. At $T>100^\circ\text{C}$, a shoulder to the band at 932 cm^{-1} becomes visible resulting in a pronounced tail towards lower energy ($\sim 925 \text{ cm}^{-1}$) at 190°C. In addition, a new broad band is observed at 889 cm^{-1} . These trends may be interpreted in terms of ongoing restructuring and the formation of more open, chain-like structures, like in $[\text{Mo}_3\text{O}_{10}]^{2-}$,^[13a] or $[\text{Mo}_4\text{O}_{13}]^{2-}$.^[20]

Those findings now help with the interpretation of the spectra obtained from the experiment of Figure 2b done at different pH at a temperature of 175°C. In the neutral regime, the orthomolybdate is the dominant species, characterized by the band at 890 cm^{-1} . On addition of HNO_3 , this band decreases and the band at 932 cm^{-1} with a shoulder clearly visible at 925 cm^{-1} , which are missing at 25°C, increase in intensity. The band at 925 cm^{-1} , which persists until $\text{pH}=2.5$, may indicate the presence of chain-like, oligomeric structures like in trimolybdates.^[13a, 22] As discussed in the heating experiment of heptamolybdate, the band at 932 cm^{-1} can be attributed to dimolybdate species. This is the first example showing its presence in solution at $\text{pH}=7$. While at low temperatures, α -octamolybdate is formed at pH 3.0 (band at 958 cm^{-1}), at 175°C it is only observed as a broad shoulder around 955 cm^{-1} indicating an accelerated transformation into the β -modification of the octamolybdate (965 cm^{-1}). The breaking of bonds and structural rearrangement in the transformation from the α - to the β -

modification of the octamolybdate has been discussed by Wang *et al.* to be enhanced by the formation of hydrogen bonds with ammonium in the solution.^[23] From this point of view, acidification of the solution and temperature increase

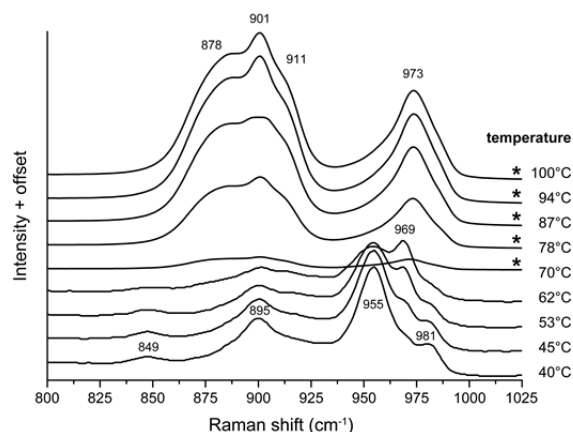


Figure 4. *In situ* Raman spectra recorded during heating of a $\text{Mo}_{36}\text{O}_{112}^{8-}$ solution (initial pH=1.5) and formation of the hexagonal- MoO_3 phase; due to the high scattering cross-section the spectra recorded at temperatures from 70-100°C marked by * have been scaled by a factor of 0.1.

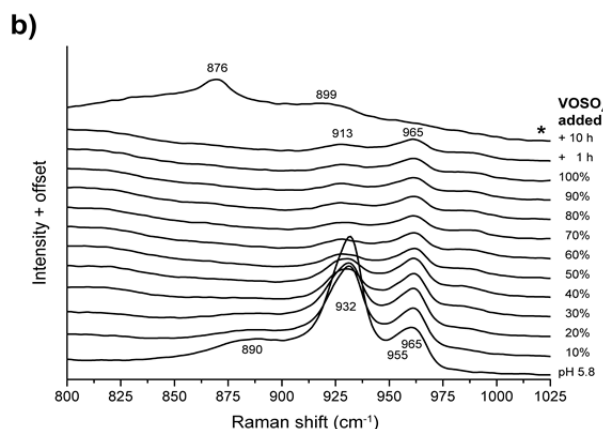
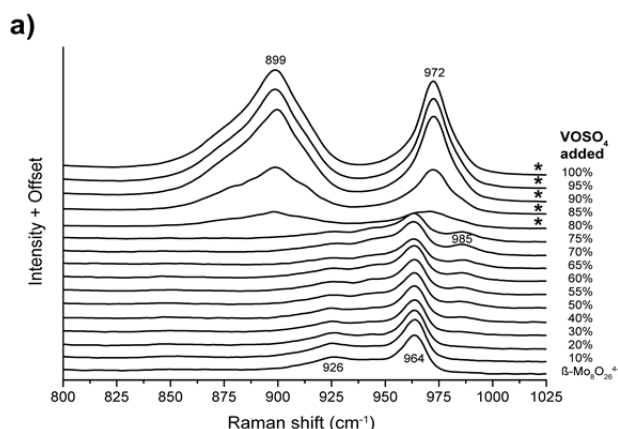


Figure 5. *In situ* Raman spectra recorded during the addition of a vanadyl sulfate solution at 0.5 ml/min to a solution of $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ at pH 2.1 at 175°C (a) and a molybdate solution at pH 5.8 at 200°C (b). Bands marked with * have been scaled for better comparison by the factors of 0.1 for (a) and 2 for (b).

should benefit the formation of $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ in agreement with our experimental results. The spectra between pH 3.0 and 2.0 at 175°C mainly exhibit the bands of $\beta\text{-Mo}_8\text{O}_{26}^{4-}$. Instead of bands due to $\text{Mo}_{36}\text{O}_{112}^{8-}$, which has been shown to be instable at high temperatures (Figure 4), the characteristic bands of the hexagonal MoO_3 phase are observed at pH 1.5 and below,^[24] which precipitates from the solution as a fine yellowish powder. The formation of the phase was confirmed by XRD (Figure S4, Supporting Information). At normal pressure, the hexagonal MoO_3 phase is precipitated at lower pH value (pH=1) and lower temperatures.^[25]

In summary, the speciation of molybdates in 0.2 M aqueous solution under hydrothermal conditions differs substantially from the speciation at room temperature at comparable pH values. This has been shown for the pH range between 7 and 1 at 175°C (Figure 2b) and for a solution of molybdates under autogenous pH and pressure between 170 and 190°C (Figure 3), temperatures and

concentration typically applied in hydrothermal synthesis protocols of molybdenum-based mixed oxides. Our results clearly show that it is not useful to consider the fairly well known speciation at ambient conditions as a basis for discussion of phase formation under hydrothermal conditions. Furthermore, it becomes obvious that the pH value is an important controlling parameter also under hydrothermal conditions.

The impact of the pH on the formation of the ternary metal oxides is illustrated in the two comparative experiments shown in Figure 5. In the experiment presented in Figure 5a, vanadyl sulfate was pumped into the autoclave at 175°C to a molybdate solution that preferentially contains octamolybdate species. The pH has been adjusted by preceding addition of nitric acid until pH=2.1. Raman spectroscopy confirms the predominance of $\beta\text{-Mo}_8\text{O}_{26}^{4-}$ under these conditions. The addition of vanadyl ions under pressure at 175°C triggers the precipitation of hexagonal MoO_3 in which molybdenum is partially substituted by vanadium. During addition of the vanadyl sulfate solution, the pH is found to drop from 2.1 to 1.0 which is the previously found pH range of the phase formation. The precipitation of hex.- MoO_3 gets obvious by intense bands with maxima at 899 and 972 cm^{-1} and is also confirmed by XRD measurements (Figure S5, Supporting Information).

The more open, chain-like structures of di- and trimolybdates that prevail in molybdate solution at a pH of 5.8 (see Figure 3) show differing reactivity. The higher temperature of 200°C was applied to maximise the occurrence of dimolybdate species in the solution (Figure 3b). As it becomes apparent from Figure 5b, the reaction with vanadyl sulphate added at 200°C preferentially consumes these species. The intensities of the octamolybdate bands are hardly affected by vanadyl sulfate addition, which finally results in the formation of a nanocrystalline material mainly composed of the bronze-like “M1” structure at a final pH of 3.0 (ICSD 55097; Figure S6, Supporting Information) indicated by the peaks at 776 and 899 cm^{-1} .^[3]

Conclusions

The speciation of molybdates under hydrothermal conditions differs significantly from the speciation under

ambient conditions at comparable pH values basically due to the thermal stability of the species involved in the equilibria in aqueous solution. At temperatures usually applied in hydrothermal syntheses (170-200°C), less dense, chain-like structures are preferentially formed in the pH range between 6 and 5 (autogenous pH). In acidic solutions (pH < 2), supramolecular species, like $\text{Mo}_{36}\text{O}_{112}^{8-}$ do not occur. Instead, octamolybdate is the final molecular precursor of precipitation reactions that was detectable by Raman spectroscopy. The different precursor species show differing reactivity with vanadyl sulfate resulting in the formation of mixed MoV oxides with either hexagonal or bronze-like structure.

The current work clearly demonstrates the power of *in situ* spectroscopy as a tool to improve our understanding of the inorganic reactions occurring under hydrothermal conditions. Elucidation of nucleation and growth of solid particles requires first of all knowledge about the molecular and supra-molecular precursors occurring under the applied conditions in solution. The present work shows that the broad knowledge concerning the speciation of polyoxometalates in aqueous solution under ambient conditions cannot be transferred to the situation inside an autoclave at high temperatures. The synthesis of mixed MoV oxides starting from different molecular precursors illustrates that based on *in situ* spectroscopy, an interactive synthesis is possible that opens up new prospects in controlled fabrication of nano-structured materials.

Experimental Section

The experiments were done in MiliPore® water with the use of commercially available chemicals: ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ (Merck), vanadyl sulfate ($\text{VOSO}_4 \cdot 4 \text{H}_2\text{O}$ (Acros Organics)) ammonia (20 %, Fluka) and HNO_3 (20 %, Merck).

The autoclave setup used for these experiments has been designed together with Premex reactor AG for allowing simultaneous analysis of the reaction by Raman spectroscopy, pH measurements and power intake of the stirrer at temperatures up to 210°C. Two different reactor vessels with a total volume of 400 ml have been used, fabricated in one case of corrosion resistant stainless steel (1.4435) and in the other case of Hastelloy C-22 (2.4602). The vessels are heated through an external thermostat using silicon oil with a heat-rate of approx. 3 K/min. The solution is stirred by an anchor type stirrer with a rotation speed of 50-600 rpm. Beside measurement of the temperature and pressure inside the vessel, the used reactor allows for the insertion of a Raman probe (RAMANRXN1, immersion optic 1/4"OD (HC-276); Kaiser Optical Systems) and pH probes (ZrO₂ probe Model A2 and Ag/AgCl reference electrode, both with a 1/2" outer tubing made from C-276; Corr Instruments), and is equipped with valves to add reactants into the vessel at any given time by use of an HPLC pump (Smartline pump 1050; Knauer). The Raman spectra were automatically recorded each 60 s at a wavelength of 785 nm with an exposure time of 30 s, while the nitric acid was pumped inside the reactor at 0.25 ml/min. The pH probes were calibrated by use of four buffer solutions at the given reaction temperatures prior to the experiments.

The deconvolution of the Raman spectra has been performed with the program Fityk^[26] allowing for the species with similar Z-values to be expected in the solution. The peak positions and relative

intensities of the peaks were taken as in Table S1 (Supporting Information). Since the temperature shift is non-linear for all the bands of the sapphire probe, the shift of the Mo=O vibrations has been allowed in the same range as for the band at 750 cm⁻¹, which is the closest to the bands of interest.

For the pH dependent experiments, 9.18 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ were dissolved in 200 ml H₂O, giving a clear 0.25 M solution with a pH of 5.4. Approximately 9 ml ammonia were added to adjust the pH to 9.0 at room temperature. The solution was then transferred to the autoclave reactor and the temperature set to 25 or 175°C, respectively. After reaching the target temperature, the acid was slowly dosed reaching a final volume of 260 ml (final concentration 0.2 M).

In the heating experiment, 9.18 g heptamolybdate were dissolved in 260 ml of water to give a 0.2 M solution and slowly heated to 190°C at a heat-rate of 3 K/min.

The reactivity investigation of molybdates at different pH on the addition of VOSO_4 has been carried out using a solution of 9.18 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ in 230 ml H₂O at pH 2.1 and 5.8 at temperatures of 175 and 200°C, respectively and slowly pumping a solution of 3.3 g $\text{VOSO}_4 \cdot 5 \text{H}_2\text{O}$ in 30 ml H₂O at a pump rate of 0.5 ml/min. The hydrothermal product obtained in the experiment shown in Figure 5b has been washed with oxalic acid (0.25 M) at 60°C for 30 min and thermally treated at 400°C in argon for 2h afterwards.

Acknowledgement

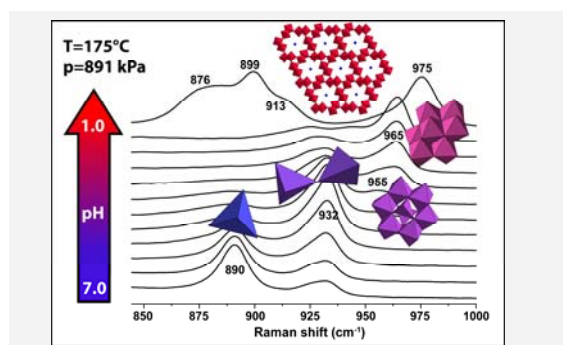
Financial support by the BASF is gratefully acknowledged. The authors thank Dr. Frank Girgsdies, Jasmin Allan, Stephen Lohr, and Mateusz Jastak for scientific discussions and experimental support.

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