Formation of Bronzes during Temperature-programmed Reduction of MoO$_3$ with Hydrogen - An In situ XRD and XAFS Study

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Abstract
The temperature-programmed reduction of MoO$_3$ from 300 K to 773 K in 50 vol-% hydrogen in He (10$^5$ Pa) at different heating rates (0.1, 0.2, and 5 K/min) was investigated by in situ XRD and XAFS. At heating rates of ~ 0.1 and ~ 0.2 K/min the formation of the molybdenum bronze H$_{0.34}$MoO$_3$ was observed by in situ XRD in the early stage of the reduction of MoO$_3$. At a heating rate of 5 K/min the formation of a more disordered bronze (H$_x$MoO$_3$ with x ~ 0.07) prior to the detection of the product phase MoO$_2$ was observed by in situ XAFS. In both studies the consumption of the bronze was found prior to the complete reduction of MoO$_3$. A simplified mechanism for the temperature-programmed reduction of MoO$_3$ in hydrogen is proposed that includes (i) incorporation of H$_2$ in the MoO$_3$ bulk and formation of a more or less ordered bronze, (ii) consumption of the bronze and formation of nucleation site for MoO$_2$, (iii) nucleation of MoO$_2$ and nuclei growth.

Keywords: molybdenum oxide, TPR, reduction, bronze, in situ, XRD, XAFS

Introduction
Molybdenum oxide based systems are highly active heterogeneous catalysts for the selective oxidation of hydrocarbons [1, 2]. Because the catalytically active phase appears to be neither MoO$_3$ nor MoO$_2$ but rather a partially reduced molybdenum oxide, the reduction of MoO$_3$ or molybdenum mixed oxides with hydrogen or light alkenes has been investigated in great detail in the past [3, 4]. Recently, we reported the formation of the molybdenum suboxide Mo$_4$O$_{11}$ from a parallel reaction of MoO$_3$ and MoO$_2$ during reduction of MoO$_3$ with hydrogen [5]. However, no crystalline intermediate phase was detected and the reduction of MoO$_3$ to MoO$_2$ was concluded to be a one step process. Nucleation-growth kinetics were found to govern the reduction of MoO$_3$ with hydrogen over a large range of reaction temperatures and H$_2$ partial pressures. Interestingly, the apparent activation energy of the reduction of MoO$_3$ with hydrogen was found to decrease with increasing hydrogen concentrations with no apparent change in the rate-determining step.

However, despite the number of studies on phase evolution and kinetics of the reduction of MoO$_3$ to MoO$_2$ much less is known about the early stage of the reduction of MoO$_3$ prior to the formation of crystalline products. Thöni and Hirsch [6] and Gai [7] proposed that oxygen vacancies originating in the course of reduction resulted in the formation of shear-planes in molybdenum trioxide. In order to further elucidate the early stage of the reduction of MoO$_3$ with hydrogen, in particular structural changes in MoO$_3$ or the evolution of phases prior to the formation of MoO$_2$, we have performed in situ XRD and XAFS studies on the temperature-programmed reduction of MoO$_3$. The potentials of in situ X-ray absorption spectroscopy for structural studies especially in conjunction with in situ X-ray diffraction have been described in a recent publication [5]. In this work the two complementary techniques were employed to elucidate both phase compositions and detailed structural changes in the phases present under reaction conditions. Therefore, both the near-edge structure and the extended fine structure of Mo K edge spectra are analyzed in detail. The former can yield quantitative phase composition and the average Mo valence, the latter affords the evolution of the local structure of the nearest neighbor shells around the Mo absorber. Here, a new approach to the analysis of XAFS data of phase mix-
ures, particularly important for in situ studies in solid state chemistry is presented.

Experimental

MoO₃ preparation

Molybdenum trioxide (MoO₃) was prepared by thermal decomposition of ammonium heptamolybdate (AHM), (NH₄)₂MoO₃·3H₂O (Aldrich Co.), in flowing synthetic air (RT ~ 773 K, 2 K/min) [5]. Specific areas were calculated by applying the BET method to the nitrogen adsorption isotherms obtained at liquid nitrogen temperature on samples outgassed at 473 K using a Quantachrom adsorption instrument. A BET surface area of ~ 5 m²/g was determined for MoO₃ prepared from AHM. Peak profile analysis of XRD patterns yields an average crystallite size of ~ 75 nm.

X-ray diffraction

In situ XRD experiments were carried out in Bragg Brentano scattering geometry on a STOE STADIP P diffractometer equipped with a secondary monochromator (Cu Kα, radiation) and a scintillation counter operated in a stepping mode. The in situ cell consisted of a Bühler HDK SI high temperature diffraction chamber. Typically, 15 mg of sample are uniformly spread on the heating band. The gas phase composition was analyzed by mass spectrometry. XRD measurements reported here were conducted under atmospheric pressure in flowing reactants (~ 100 ml/min total flow). The in situ XRD set-up used is described in more detail in [5]. Calculation of theoretical X-ray powder patterns and lattice constant refinements were done using the software PowderCell v2.1 [8].

In situ X-ray Absorption Spectroscopy

For in situ XAFS experiments molybdenum oxide was mixed with boron nitride (ratio 1:3) and 30 mg of the mixture was pressed with a force of 1 ton into a 5 mm in diameter self-supporting pellet. The absorption jump, ΔI/I, at the Mo K edge was ~ 1.5. In situ XAS experiments were carried out in a flow-reactor at atmospheric pressure. Temperature programmed reduction experiments were conducted in flowing reactants (40 ml/min) at a constant heating rate of 5 K/min. The composition of the gas phase was continuously monitored using a mass spectrometer (QMS200 from Pfeiffer). The in situ XAS set-up used is described in more detail in [5]. In situ XAS experiments were performed at the Mo K edge (19.999 keV) at beamline X1.1 at the Hamburger Synchrotron Radiation Laboratory, HASYLAB, using a Si(311) double crystal monochromator. The storage ring operated at 3.6 GeV with injection currents of 150 mA.

X-ray absorption fine structure (XAFS) analysis was performed using the software package WinXAS v2.0 [9] following recommended procedures from the literature [10]. Background subtraction and normalization were performed by fitting linear polynomials to the pre-edge and the post-edge region of an absorption spectrum, respectively. The Mo K edge absorption threshold was determined from the first root in the first derivative of the near-edge region (XANES) (in the following edge shifts are reported relative to the first inflection point in the Mo metal K edge XANES at 19999 eV). Reduction or oxidation of Mo causes a shift in the Mo K absorption edge to lower or higher photon energies, respectively, and, hence, the edge shift can be used to identify changes in Mo valence during reaction.

Principal component analysis (PCA) of the Mo K edge XANES was used to identify Mo oxide phases present during the reduction of MoO₃. Given a library of molybdenum reference spectra, PCA can identify number and type of phases present in a set of experimental XANES spectra. Subsequently, a least-squares fitting procedure is applied to obtain the evolution of the amount of each reference phase during the reaction. Hence, XANES analysis can afford information on low concentration or amorphous phases not readily available with XRD. More details on PCA analysis of XAFS spectra can be found in Ref. [11].

For the absorption fine structure (EXAFS) analysis, a smooth atomic background, Iₒ(k), was obtained using cubic splines. The radial distribution function FT(€(k)) was obtained by Fourier transforming the k²-weighted experimental €(k) function, multiplied by a Bessel window, into the R space. EXAFS data analysis was carried out using theoretical backscattering phases and amplitudes calculated with the ab-initio multiple-scattering code FEFF7 [12]. Single scattering and multiple scattering paths in the employed model structures were calculated up to 5.0 Å with a lower limit of 2.0 % in amplitude with respect to the strongest backscattering path. EXAFS fitting and simulation were performed using the standard EXAFS formula (k range from 3.5 to 15 Å⁻¹, R range 0.9 to 4.4 Å). For mixtures of MoO₂ and MoO₃, the ratio of the two corresponding theoretical XAFS functions was set to the ratio of MoO₂ and MoO₃ as determined by the XANES analysis. Structural parameters that are determined by a least-squares EXAFS fit to experimental spectra are (i) one E₁ shift for all paths in the MoO₃ structure and one E₂ shift for those in the MoO₂ structure, (ii) one Debye temperature for oxygen backscatterer, and one for molybdenum in MoO₂ and one for molybdenum in MoO₃, (iii) selected Mo-O and Mo-Mo coordination shell distances (Table 1), (iv) third cumulants for MoO₂ and MoO₃, Coordination numbers (CN) were kept invariable in the refinement. These restrictions were necessary to reduce the number of free running parameter (N_free) to less than the number of independent parameters (N_ind) in the experimental data used. EXAFS refinements reported here were carried out in R space to magnitude and imaginary part of a Fourier transformed k²-weighted experimental €(k). More details about the XAFS fitting procedure employed can be found in reference [13].

Results

Figure 1a and b depict XRD patterns measured in situ during temperature programmed reduction of MoO₃ in 50 vol-% H₂ (in He) with an effective heating rate of 0.2 K/min and 0.12
K/min, respectively. At a heating rate of 0.2 K/min the formation of MoO$_3$ can be seen at ~ 613 K. In addition, diffraction peaks that can not be assigned to MoO$_3$ or MoO$_2$ were observed at this temperature (* in Figure 1a). Upon further heating these additional peaks disappear and all peaks present can be assigned to either MoO$_3$ or MoO$_2$ (Figure 2). Eventually, at 773 K the TPR results in the formation of molybdenum metal (* in Figure 1a). At a heating rate of 0.12 K/min additional diffraction peaks that do not belong to MoO$_3$ or MoO$_2$ were also observed (* in Figure 1b), even more pronounced than in Figure 1a, and prior to the formation of detectable amounts of MoO$_2$ at 603 K. From a comparison with known references (Figure 2) the additional diffraction peaks observed (* in Figure 2 (D)) were assigned to the molybdenum bronze H$_{0.34}$MoO$_3$ [14]. Nearest neighbor shell distances and lattice constants for MoO$_3$ and H$_{0.34}$MoO$_3$ at elevated temperature are given in Table 1. A structural model of H$_{0.34}$MoO$_3$ is depicted in Figure 3. In this bronze the orthorhombic layer structure of MoO$_3$ is retained and hydrogen is located in the layers at oxygen atoms of corner-sharing MoO$_6$ units along the [100] direction.

In Figure 4 the evolution of Mo K edge XANES spectra measured during TPR of MoO$_3$ in 50 vol-% H$_2$ (in He) at (a) 0.2 K/min and (b) 0.12 K/min. Peaks indicated with an * correspond to H$_{0.34}$MoO$_3$. * denotes molybdenum metal.

depicted. At ~ 673 K a transition from the distinct near-edge structure of MoO$_3$ to that of MoO$_2$ can be seen. Principal component analysis of the spectra in Figure 4 revealed two major phases (MoO$_3$ and MoO$_2$) to be sufficient to reconstruct the experimental data. A refinement of the sum of MoO$_3$ and MoO$_2$ reference spectra to the experimental spectra afforded the quantitative evolution of the two phases during TPR of MoO$_3$ as shown in Figure 5. In addition, the shift in photon energy of the Mo K edge during TPR was determined (Figure 5). Already prior to the formation of detectable amounts of MoO$_2$ at temperatures between 473 K and 673 K a slight shift of the Mo K edge towards lower photon energies can be observed. This indicates a reduction of molybdenum in this region that is not accompanied by the formation of an additional phase, which is sufficiently ordered for detection.

![Figure 1](image1.png)

**Figure 1**: Evolution of XRD patterns measured during TPR of MoO$_3$ in 50 vol-% H$_2$ (in He) at (a) 0.2 K/min and (b) 0.12 K/min. Peaks indicated with an * correspond to H$_{0.34}$MoO$_3$. * denotes molybdenum metal.

![Figure 2](image2.png)

**Figure 2**: Comparison of theoretical powder patterns (A and B) of orthorhombic MoO$_3$ (Pbnm, {5-508}) and H$_{0.34}$MoO$_3$ (Cmcm, {34-1230}) [14], and XRD patterns measured in situ during TPR of MoO$_3$ (Figure 1a). (C) MoO$_3$ at 593 K. (D) mixture of MoO$_3$, H$_{0.34}$MoO$_3$ (denoted by *), and MoO$_2$ at 613 K. (E) mixture of MoO$_3$ and MoO$_2$ at 633 K.

![Figure 3](image3.png)

**Figure 3**: Structural model of orthorhombic H$_{0.34}$MoO$_3$ (Cmcm [14]) (small circles: hydrogen, medium circles: oxygen, large circles: molybdenum). Orthorhombic MoO$_3$ possesses a very similar layer structure without the hydrogen atoms.
The evolution of the Fourier transformed EXAFS \( ?(k) \) obtained from the spectra in Figure 4 is shown in Figure 6. At a temperature of 673 K a transition from the FT(\( ?(k) \)) of MoO\(_3\) to that of MoO\(_2\) can be seen. The considerable reduction in amplitude of the Mo-Mo shells in Figure 6 is mainly caused by the increasing temperature. However, the evident change in the shape of the "Mo-O" peaks in Figure 6 can not solely be ascribed to a temperature effect and, thus, indicates a change in the short-range order around the Mo absorber at temperatures between 473 K and 673 K. To further elucidate this change in the short-range order of MoO\(_3\) during TPR with hydrogen, a refinement of theoretical EXAFS functions to the experimental spectra was performed. As an example, Figure 7 shows the fit of a sum of the EXAFS functions of MoO\(_3\) and MoO\(_2\) to the experimental FT(\( ?(k) \)) of a mixture of MoO\(_3\) and MoO\(_2\) at 733 K. The structural parameters refined are given in Table 2. The most prominent single and multiple scattering paths present in the two structures are depicted in Figure 7 underlining the complexity of the system studied. However, by employing constraints on the refinement as described above, reliable information about the structural changes that MoO\(_3\) undergoes during TPR can be obtained. Moreover, in the work presented here, the relative evolution of the nearest neighbor distances around the Mo absorber is more important than their absolute values to interpret the structural modification observed in terms of a reaction mechanism.

### Table 1. Nearest neighbor shell distances in MoO\(_3\) at different temperatures and in H\(_2\)MoO\(_3\) at 593 K.

<table>
<thead>
<tr>
<th>Shell</th>
<th>MoO(_3) (300 K, Å)</th>
<th>MoO(_3) (593 K, Å)</th>
<th>MoO(_3) (748 K, Å)</th>
<th>H(_2)MoO(_3) (593 K, Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo - O</td>
<td>1.671</td>
<td>1.698</td>
<td>1.716</td>
<td>1.696</td>
</tr>
<tr>
<td>Mo - O</td>
<td>1.735</td>
<td>1.742</td>
<td>1.748</td>
<td>1.938</td>
</tr>
<tr>
<td>Mo - O</td>
<td>1.948</td>
<td>1.952</td>
<td>1.954</td>
<td>1.938</td>
</tr>
<tr>
<td>Mo - O</td>
<td>1.948</td>
<td>1.952</td>
<td>1.954</td>
<td>1.959</td>
</tr>
<tr>
<td>Mo - O</td>
<td>2.251</td>
<td>2.260</td>
<td>2.268</td>
<td>1.959</td>
</tr>
<tr>
<td>Mo - O</td>
<td>2.332</td>
<td>2.370</td>
<td>2.395</td>
<td>2.459</td>
</tr>
<tr>
<td>Mo - Mo</td>
<td>3.438</td>
<td>3.477</td>
<td>3.504</td>
<td>3.529</td>
</tr>
<tr>
<td>Mo - Mo</td>
<td>3.696</td>
<td>3.699</td>
<td>3.701</td>
<td>3.724</td>
</tr>
<tr>
<td>Mo - Mo</td>
<td>3.963</td>
<td>3.978</td>
<td>3.992</td>
<td>3.882</td>
</tr>
</tbody>
</table>

### Table 2. Structural parameters of a mixture of MoO\(_3\) and MoO\(_2\) at 733 K in 50 % H\(_2\) (Figure 7) obtained from a refinement of a sum of theoretical EXAFS functions calculated for an orthorhombic MoO\(_3\) structure and a monoclinic MoO\(_2\) structure (k = 3.0 to 15.3 Å\(^{-1}\), R = 0.7 to 4.2 Å, N\(_{int}\) = 29, N\(_{int}\) = 19, 16 single scattering paths and 20 multiple scattering paths). Parameters refined are (i) for MoO\(_3\), ?(O) = 1360 K, ?(Mo) = 373 K, E\(_p\) (MoO\(_3\)) = -1.9, (ii) for MoO\(_2\), ?(O) = 520 K, ?(Mo) = 373 K, E\(_p\) (MoO\(_2\)) = -3.4 (\(\Delta\) Debye temperature). The fit residual amounted to 4.6.

<table>
<thead>
<tr>
<th>Shell</th>
<th>MoO(_3)</th>
<th>MoO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>R, (Å)</td>
<td>?(^2), (Å(^{-1}))</td>
</tr>
<tr>
<td>Mo-O</td>
<td>1 (^{\ddagger})</td>
<td>1.693 (^{+})</td>
</tr>
<tr>
<td>Mo-O</td>
<td>1 (^{\ddagger})</td>
<td>1.725 (^{+})</td>
</tr>
<tr>
<td>Mo-O</td>
<td>2 (^{\ddagger})</td>
<td>1.982 (^{+})</td>
</tr>
<tr>
<td>Mo-O</td>
<td>1 (^{\ddagger})</td>
<td>2.275 (^{+})</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2 (^{\ddagger})</td>
<td>3.421 (^{+})</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2 (^{\ddagger})</td>
<td>3.696 (^{+})</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2 (^{\ddagger})</td>
<td>3.921 (^{+})</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2 (^{\ddagger})</td>
<td>3.802 (^{+})</td>
</tr>
</tbody>
</table>

\(^{+}\) indicates parameters that were fixed in the refinement, \(^{-}\) denotes parameters that were correlated to other parameters in the fit.
Figure 6: Evolution of Mo K edge FT(\(\delta (k)\)) during TPR of MoO\(_3\) in 50 vol-% H\(_2\) (Figure 4). The first peak (~1.5 Å) corresponds to Mo-O backscatterer, the second peak at ~3.5 Å corresponds to Mo-Mo backscatterer. (x) denotes the formation of edge-sharing octahedra in the distorted rutile structure of MoO\(_2\). Three regions are indicated (i) MoO\(_3\), initial material, (ii) H\(_{0.34}\)MoO\(_3\), mixture of MoO\(_3\) and H\(_{0.34}\)MoO\(_3\), (iii) MoO\(_2\), mixture of MoO\(_2\) and MoO\(_3\).

Figure 7: Refinement of a sum of theoretical EXAFS functions of MoO\(_3\) and MoO\(_2\) to an experimental FT(\(\delta (k)\)) at 733 K in 50 vol-% H\(_2\) (Figure 6). The phase composition was obtained from a XANES analysis. Thin dashed lines correspond to prominent single backscattering paths in the MoO\(_3\) structure, thin dotted lines to those in the MoO\(_2\) structure. Structural parameters obtained from the fit are given in Table 2.

Figure 8 shows the evolution of selected Mo-O and Mo-Mo distances in the MoO\(_3\) structure during TPR in 50 vol-% H\(_2\) (Figure 6). In the temperature region from 473 K and 673 K significant deviations from the expected linear thermal expansion of MoO\(_3\) can be noticed. Interestingly, prior to the detection of MoO\(_2\) at 673 K, the Mo-O and Mo-Mo distances return to the values expected for MoO\(_3\) at this temperature. For comparison, the evolution of selected Mo-O distances in MoO\(_3\) during heat treatment in He is depicted in Figure 9. The different slopes of the three traces in Figure 9 confirms an anisotropic thermal expansion of MoO\(_3\) (increased expansion perpendicular to the layers in Figure 3) that is evident from the structural parameters of MoO\(_3\) at different temperatures given in Table 1. The good agreement of the XRD and XAFS data on the structural evolution of MoO\(_3\) at elevated temperatures confirms the reliability of the EXAFS analysis approach taken in this work.

Discussion

In situ XRD and XAFS studies on the temperature-programmed reduction of MoO\(_3\) were performed to elucidate structural changes in the early stage of the reduction prior to the formation of detectable amounts of MoO\(_2\) (limits ~5 % for XRD and ~1 % for XAFS). Heating rates of ~0.2 K/min
resulted in the formation of an additional crystalline phase (in situ XRD, Figure 1) which was identified to be similar to the molybdenum bronze H$_{3-x}$MoO$_3$ (Figure 2 + 3). Figure 2 indicates that at a heating rate of 0.2 K/min H$_{3-x}$MoO$_3$ is formed in the early stage of the reduction to MoO$_2$ and is consumed prior to the complete reduction of MoO$_3$ to MoO$_2$. However, under isothermal reduction conditions at temperatures above 623 K or at heating rates of about 2 K/min no crystalline molybdenum bronzes were detected [5].

The in situ XAFS results presented also indicate a slight reduction (Figure 5) and local structural changes in MoO$_3$ prior to the formation of detectable amounts of MoO$_2$ (Figure 6 + 8). However, a heating rate of 5 K/min evidently does not permit the formation of sufficiently ordered H$_{3-x}$MoO$_3$ that could be identified as a third phase in addition to MoO$_3$ and MoO$_2$ (Figure 5). Nearest neighbor shell distances for MoO$_3$ and H$_{3-x}$MoO$_3$ at 593 K are given in Table 1, with those shells highlighted that exhibit the largest differences in the two otherwise similar structures (Figure 3). It can be seen now from Figure 8 that between 473 K and 573 K the Mo-O shell at R = 1.74 Å (increase) and the Mo-Mo shells at R = 3.70 Å (increase) and at 3.96 Å (decrease) deviate from the expected linear increase with temperature in a way that coincides with the structural differences between MoO$_3$ and H$_{3-x}$MoO$_3$ (Table 1). Apparently, also at a heating rate of 5 K/min, hydrogen is incorporated into the MoO$_3$ bulk prior to the formation of MoO$_2$. However, the molybdenum bronze formed seems to be rather disordered which can, for instance, be noticed from the Mo-O shell at R = 2.25 Å that does not exhibit the expected decrease while going from MoO$_3$ to H$_{3-x}$MoO$_3$. Because the complete reduction of MoO$_3$ to MoO$_2$ (valence from +6 to +4) leads to a shift of the Mo K edge of 2.1 eV, an edge shift of ~ 0.07 eV in the early stage of the reduction (Figure 5, T ~ 600 K) indicates an average Mo valence of about +5.93 (assumes a linear relationship between average valence and Mo K edge shift). This would correspond to a bronze with an estimated chemical formula of H$_3$MoO$_3$ (with x ~ 0.07) at ~ 600 K in 50 vol-% H$_2$.

In both the in situ XRD (Figure 2) and the in situ XAFS experiments (Figure 8) it appears, that the bronze formed is consumed at the expense of the formation of MoO$_2$ prior to the complete reduction of the MoO$_3$ bulk. In addition, although between 573 K and 673 K the local structure appears to return to that of MoO$_3$ (Figure 8) no shift of the Mo K edge to higher photon energies is observed. This indicates that the average valence of Mo does not change although the H$_3$MoO$_3$ formed seems to be consumed. This can be interpreted such that with increasing reaction temperature the incorporated hydrogen reacts with the MoO$_3$ bulk and forms "MoO$_{3-x}$" that eventually serves as nucleation site for the reduction product MoO$_2$. The structural nature of the "MoO$_{3-x}$" formed prior to the detection of bulk MoO$_2$ (for instance, very small MoO$_2$ nuclei or shear structures) will be the subject of future investigations.

A schematic representation of the mechanism of the temperature-programmed reduction of MoO$_3$ in hydrogen is given in Figure 10. At a temperature of about 470 K hydrogen is incorporated into the MoO$_3$ bulk. During this step the orthorhombic layer structure of MoO$_3$ is retained and appears to be only slightly distorted. With increasing temperature (~ 600 K) the hydrogen in the MoO$_3$ bulk is consumed and nucleation sites for MoO$_2$ are being formed. Eventually, at lower hydrogen concentrations (for instance 5 vol-%) the reduction of MoO$_3$ may be sufficiently delayed to permit the formation of Mo$_3$O$_{11}$ prior to the complete reduction to MoO$_2$ [5]. Furthermore, the results presented offer a suitable explanation for the H$_2$ concentration dependence of the apparent activation energy of the reduction of MoO$_3$ with hydrogen as reported previously [5]. Evidently, hydrogen is incorporated into the MoO$_3$ bulk and, hence, can thereby assist in the formation of MoO$_2$ nuclei. Because the nucleation of MoO$_2$ is the rate-determining step at this stage of the reduction, an increased concentration of hydrogen in the gas phase and, thus, in the bulk may lead to a decreased apparent activation energy of the reduction process.

Concluding remarks

In this work the temperature-programmed reduction of MoO$_3$ from 300 K to 773 K in 50 vol-% hydrogen at different heating rates (0.1, 0.2, and 5 K/min) was investigated by in situ XRD and XAFS. At heating rates of 0.1 and 0.2 K/min the formation of the molybdenum bronze H$_{3-x}$MoO$_3$ was observed by in situ XRD in the early stage of the reduction of MoO$_3$. At a heating rate of 5 K/min the formation of a more disordered bronze (H$_3$MoO$_3$ with x ~ 0.07) prior to the detection of the product phase MoO$_2$ was observed by in situ XAFS. In both studies the consumption of the bronzes was found prior to the complete reduction of MoO$_3$. A simplified mechanism for the temperature-programmed reduction of MoO$_3$ is proposed that includes (i) incorporation of H$_2$ in the MoO$_3$ bulk and formation of more or less ordered bronzes, (ii) consumption of the bronze and formation of sites for nucleation of MoO$_2$, (iii) nucleation of MoO$_2$ and nuclei growth.

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