Reply to "Kinetics and Mechanism of MoO₃ Reduction". Comments on "In Situ XAS and XRD Studies on the Formation of Mo Suboxides during Reduction of MoO₃"

T. Ressler*

Fritz-Haber-Institut der MPG, Department of Inorganic Chemistry, Faradayweg 4-6, D-14195 Berlin, Germany

Previously, Sloczynski et al. (ref 1 and refs therein) reported that the reduction of MoO_3 over the temperature range 733 to 813 K is governed by an autocatalytic mechanism and proceeds according to a two-step process with the suboxide Mo_4O_{11} as an intermediate of the reduction of MoO_3 to MoO_2. In a recent comment to our manuscript "In Situ XAS and XRD Studies on the Formation of Mo Suboxides during Reduction of MoO_3" published in *J. Phys. Chem. B*, **2002**, *106*, 6360, Sloczynski raised several questions that shall be discussed in the following.

Mo_4O_{11} Not an Intermediate of the Reduction of MoO_3 to MoO_2. The conclusion that Mo_4O_{11} is not an intermediate of the reduction of MoO_3 to MoO_2 is not based on the fact that the reduction and the solid-state reaction have comparable reaction rates. Instead, it is based on the fact that during the reduction of MoO_3 to MoO_2 no Mo_4O_{11} is detected at temperatures below ∼700 K. This holds for crystalline phases (XRD, detection limit ∼5 wt %) as well as for amorphous, disordered, or low-concentration phases (XAS, detection limit ∼1 wt %). Mo_4O_{11} is formed only at temperatures above ∼700 K, which coincides with the formation temperature of Mo_4O_{11} from MoO_3 and MoO_2. Furthermore, the evolution of the phases that are present (Figure 13 in ref 2) at temperatures above 700 K clearly shows that Mo_4O_{11} is not an intermediate phase of the reduction of MoO_3.

Whether the formation of Mo_4O_{11} is detected prior to that of MoO_2 during the reduction of MoO_3 depends on the reaction temperature and the hydrogen partial pressure. At high enough temperatures, the reaction of MoO_3 and MoO_2 may be fast enough so that Mo_4O_{11} is indeed detected prior to that of MoO_2. However, this must not be mistaken for the fact that MoO_2 is still being formed prior to the formation of Mo_4O_{11}. From the data shown in the manuscript, it can be seen that MoO_2 is formed in the very early stage of the reduction of MoO_3 and is subsequently consumed by its reaction with MoO_3 to form Mo_4O_{11}.

Furthermore, the conclusion that Mo_4O_{11} is not an intermediate of the reduction of MoO_3 to MoO_2 is also corroborated by the fact that no readily visible structural relationship exists between the orthorhombic layer structure of MoO_3 and the structure of Mo_4O_{11}. Hence, the transformation from MoO_3 to Mo_4O_{11} requires massive structural rearrangements that would be unlikely to happen at temperatures as low as 600 K.

Solid-State Kinetic from In Situ XRD and XAS. The main focus of the manuscript discussed here[2] is the phase identification during the reduction of MoO_3 with hydrogen. The kinetic analysis presented is mostly based on the analysis of the temperature region from 600 to 700 K. In this temperature range, no Mo_4O_{11} is being formed during the reduction of MoO_3, hence

* E-mail: Ressler@fhi-berlin.mpg.de. Tel: (+49) 30 8413 3192. Fax: (+49) 30 8413 4405.

the calibration curve that is presented is very applicable. The limitations of the analysis at temperatures above 700 K, where not only reduction of MoO_3 but also reaction with MoO_2 occurs, have been stated in the manuscript.

Using a bulk sensitive technique and monitoring the structural evolution of a reactant during a solid-state reaction certainly cannot be called an indirect method. With respect to determining the extent of reduction, thermoanalytical techniques may be more accurate than in situ XRD or XAFS. However, thermoanalytical techniques are entirely nonspecific regarding the structural nature of possible intermediates and the structural evolution of the reactants. The loss of oxygen during thermal treatment can never be unambiguously assigned to one particular oxide structure or phase composition. Conversely, in situ structural techniques can provide both extent of reaction curves and structural information on all the phases present. Evidently, neglecting structural information and assuming a reaction mechanism solemnly on the basis of thermoanalytical data have led to the misinterpretation that is discussed here.

Autocatalytic Mechanism for the Reduction of MoO_3. As to the "proofs" of the autocatalytic mechanism as presented by the author, I reply as follows:

(i) In many solid−gas reactions, the rate of reaction is proportional to the partial pressure of the reactant gas. However, this is not conclusive for one particular rate-determining step in one particular solid-state reaction mechanism.

(ii) Without any structural information on the phase composition of a mixture of MoO_3 and Pt or Pd at 800 K, any interpretation of the influence of Pt or Pd on the reaction rate of MoO_3 at this temperature is pure speculation.

(iii) The investigations described by Sloczynski et al. were performed over the temperature range from 733 to 813 K. The author attempted to prove an autocatalytic mechanism by adding MoO_2 to MoO_3 at temperatures above 733 K. However, from temperature-programmed experiments, it is known that the reduction of MoO_3 starts as low as ∼600 K. On one hand, at temperatures below ∼700 K, no accelerating effect of adding MoO_2 to MoO_3 on the rate of reduction can be observed. On the other hand, at temperatures above ∼700 K, the effect of adding MoO_2 on the rate of reduction of MoO_3 by hydrogen or propene cannot be distinguished from the solid-state reaction of MoO_3 and MoO_2 to form Mo_4O_{11}.

(iv) The apparent activation energy, E_a, for the reduction of MoO_3 in hydrogen strongly depends on the hydrogen concentration, whereas this dependence is not observed for the reduction of MoO_3 in propene.[3] Hence, the order in E_a ($H_2 < C_3H_6 < C_4H_8$) is not unique and depends on the reactant concentration. Furthermore, the onset of the reduction of MoO_3 in hydrogen is slightly lower than that in propene ($H_2(∼600 K) < C_3H_6 ≈ He(∼620 K)$) whereas the onset of the reduction is virtually independent of the partial pressure of the reactant.

(v) The formation of H_xMoO_3 bronzes during the reduction of MoO_3 in hydrogen can indeed be observed by in situ XRD and XAS.[4] However, no similar formation of significant amounts of bronzes was detected during the reduction of MoO_3 in propene. The formation of bronzes during the reduction of MoO_3 in hydrogen is certainly part of the reaction mechanism; however, it is not conclusive for a particular rate-determining step.

The increase in crystallite size for both MoO_3 and MoO_2 during the reduction of MoO_3 in hydrogen indicates the presence

of Oswald ripening, which is in agreement with nucleation-growth kinetics. A shrinking-core model can hardly account for the increase in crystallite sizes observed. In studies on the kinetics of solid-state reactions, no particular reaction mechanism can be unambiguously identified by one rate-determining step. Hence, a sigmoidal rate law alone is no proof for any particular reaction mechanism. However, MoO_2 nuclei growth in the MoO_3 matrix appears to be the most likely rate-determining step.

The publications from Sloczynski et al. and from Arnoldy et al. have been referred to in the manuscript. The main focus of the manuscript discussed here is actually not the kinetic analysis but the phase identification during the reduction of MoO_3 with hydrogen (title). Obviously, this does have strong implications for the kinetic analysis as presented in the literature.

Recent Results Supporting Our Previous Conclusions. MoO_3 can be reduced by an extended treatment in helium at elevated temperatures. From temperature-programmed experiments, it can be seen that the onset of the reduction occurs at $\sim$620 K. Evidently, at this temperature, oxygen vacancies become sufficiently mobile in the MoO_3 lattice to permit the reduction of the entire bulk of MoO_3 to MoO_2. The reaction scheme is the same as that of the reduction of MoO_3 in hydrogen; at temperatures below $\sim$700 K, only MoO_2 is detected, whereas at temperatures above 700 K, the MoO_2 that forms reacts with MoO_3 to form the suboxide Mo_4O_{11}. From the temperature-programmed reduction of MoO_3 in hydrogen[2,4] or propene,[3] it can be seen that regardless of the atmosphere used the onset of reduction is at about 600 K and, hence, coincides with the temperature of sufficient oxygen vacancy mobility in MoO_3.

References and Notes

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