Kinetics and Mechanism of MoO$_3$ Reduction. Comments on "In Situ XAS and XRD Studies on the Formation of Mo Suboxides during Reduction of MoO$_3$"

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In this letter, I would like to present some comments on the paper by T. Ressler, R. E. Jentoft, J. Wienold, M. M. Günter, and O. Timpe—"In Situ XAS and XRD Studies on the Formation of Mo Suboxides during Reduction of MoO$_3$"— published in *J. Phys. Chem. B* **2000,** *104,* 6360−6370.

The supposition raised in the paper that Mo$_4$O$_{11}$ is not an intermediate product in the reaction MoO$_3$ → Mo$_4$O$_{11}$ → MoO$_2$ but is formed in the parallel reaction between MoO$_3$ and MoO$_2$ has not been sufficiently documented. This hypothesis is based on the observation that the reaction of MoO$_3$ reduction and the solid-state reaction between MoO$_3$ and MoO$_2$ have comparable rates. The observation does not, however, prove that Mo$_4$O$_{11}$ is not formed in the course of the reduction of MoO$_3$ but merely points to the possibility of formation of the lower oxide on a different competing path. Mo$_4$O$_{11}$ is formed, however, as the first product in the early stage of the reduction, as shown by Ueno et al.[1] as well as by Sloczynski and Bobinski[2] with the use of the XRD technique. This indicates that this suboxide is formed mainly as a result of the reduction of MoO$_3$. Also, in their other paper,[3] the authors claim that Mo$_4$O$_{11}$ is formed as the first product of the reduction of MoO$_3$, which contradicts the findings of the present publication. Furthermore, it should be noted that the reaction between MoO$_3$ and MoO$_2$ leading to the formation of Mo$_4$O$_{11}$ does not involve the reduction of molybdenum, so if Mo$_4$O$_{11}$ were formed along this path, as claimed by the authors, it would have to be reduced to MoO$_2$ with hydrogen, hence Mo$_4$O$_{11}$ would , in fact, be the intermediate product.

The degree of reduction of MoO$_3$ was estimated from the analysis of phase composition during the reduction. This is an indirect method and therefore gives rise to several disputable issues:

(1) In the three-component mixture of solid phases, the content of each component is generally not proportional to the intensities of the reflections in the XRD diagram. The calibration curve shown in the paper refers to the two-component MoO$_3$−MoO$_2$ mixture. Its use in interpreting a three-component mixture may lead to errors. So far the most precise way of determining the actual degree of reduction in the oxide systems as well as the reduction rate has been the direct measurement of the loss of oxygen (e.g., by a gravimetric method). Using gravimetric measurements, as described in refs 2 and 4, the direct rate of reduction was recorded with high accuracy, which revealed more subtle effects such as a minimum and a maximum in the rate depending on the degree of reduction. Such effects are frequently not observed if less accurate, indirect methods are used to measure the rate of reduction.

(2) If one accepts the authors' hypothesis that Mo$_4$O$_{11}$ is formed parallel to MoO$_3$ and MoO$_2$, then the determination of the degree of reduction on the basis of the MoO$_3$ content in the mixture will lead to errors. In this case, the disappearance of MoO$_3$ cannot be a measure of the degree of reduction because MoO$_3$ is consumed in two reactions: reduction by hydrogen and reaction with MoO$_2$ (the latter proceeding without oxygen loss).

The most important problem concerns the proposed mechanism of the reaction. The authors believe that the slowest step, which determines the rate of reduction, is nucleation because their data fit the Avrami−Erofeev equation. This is not a proof because any sigmoidal curve can be described with better or worse accuracy with this equation even if the mechanism of the reaction is different. The authors instead have ignored the following facts that support the autocatalytic mechanism, according to which the dissociative adsorption of hydrogen (or a hydrocarbon as a reducing gas) constitutes the rate-determining step, which is accelerated catalytically by the product of the reaction:

(1) The rate of reduction is proportional to the partial pressure of the reducing gas (hydrogen or a hydrocarbon).

(2) The rate of reduction increases dramatically after adding even very small amounts of metals, thus facilitating the dissociative adsorption of the reducing gas (e.g., Pt or Pd) (a spillover effect).

(3) The rate of the MoO$_3$ reduction increases after adding MoO$_2$, which is the product of the reaction. The parallel reaction mechanism cannot account for this effect.

(4) The rate of reduction brought about by various reducing gases increases in the order H$_2$ < C$_3$H$_6$ < C$_4$H$_8$, which follows the decreasing energy necessary to detach a hydrogen atom from a reducing-gas molecule.

(5) Atomic hydrogen can easily diffuse into the MoO$_3$ structure, as evidenced by the formation of H$_x$MoO$_3$ bronzes at low temperatures. This eliminates the necessity of O^{2-} ion diffusion or of their vacancies through the layer of the product. Water formed as a result of dehydroxylation leads to expansion of the layer of the product and contributes to uncovering new surfaces of MoO$_3$ according to the shrinking core model.

All of these facts supporting the autocatalytic mechanism of the MoO$_3$ reduction were described in my paper[4] on the reduction of MoO$_3$. Also, Arnoldy et al.[5] strongly supported the autocatalytic model on the basis of his investigations of the MoO$_3$ reduction. This is not mentioned either by the authors in their paper. All of the arguments mentioned above are entirely ignored by the authors.

References and Notes

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