In situ XAS and XRD studies on the formation of Mo suboxides during reduction of MoO$_3$

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Abstract:
Reduction of MoO$_3$ with hydrogen (5-100 vol %) in the temperature range from 573 to 833 K was studied by in situ X-ray diffraction and X-ray absorption spectroscopy. The experiments performed focused on elucidating phase composition and evolution with time under isothermal as well as temperature-programmed reduction conditions. At reaction temperatures below 698 K, the reduction of MoO$_3$ to MoO$_2$ is a one-step process without the formation of crystalline intermediates. At reduction temperatures above 723 K and H-2 concentrations higher than 10 vol %, Mo metal is the final product of the reduction of MoO$_3$. In addition, at temperatures higher than 698 K, the formation of Mo$_4$O$_{11}$ was observed. However, Mo$_4$O$_{11}$ is not an intermediate in the reduction of MoO$_3$ but is being formed in a parallel reaction from MoO$_3$ and MoO$_2$ at temperatures above 698 K. It is shown that Mo$_4$O$_{11}$ can be obtained from a reaction of MoO$_3$ and MoO$_2$ at temperatures above 773 K, affording the same phase ratio of monoclinic and orthorhombic Mo$_4$O$_{11}$ as the reduction of MoO$_3$ with hydrogen. Quantitative XRD analysis reveals a sigmoidal shape of the evolution of the MoO$_3$ and MoO$_2$ phases during reduction of MoO$_3$ and an increase in the crystallite size of the phases present. This Oswald ripening indicates that a nucleation-growth kinetic mechanism governs the reduction of MoO$_3$ under the conditions studied. The results presented in this work clearly demonstrate the potential of a combined application of in situ XRD and XAFS to reveal phase composition and kinetics of solid-state reactions.