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Relationships between In situ Bulk Structure and Activity of Molybdenum Oxide based Heterogeneous Catalysts

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Structure-activity relationships constitute important subjects in heterogeneous catalysis research. However, reliable structure-activity relationships can only be obtained from investigating the structure of a catalyst under reaction conditions while simultaneously measuring the catalytic properties of the material. Frequently, the active phase of a catalyst evolves under reaction conditions and is determined by the “real” structure of the catalyst bulk (i.e. under reaction conditions and including all deviations from the ideal structure). In situ bulk structural techniques such as time-resolved X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) possess excellent capabilities to reveal quantitative phase composition and average valence together with the structural evolution of a system under “relevant” (i.e. high T and p) reaction conditions. From a combination of these methods with, for instance, mass spectrometry, reliable relationships between the “real” structure of a catalyst and its function can be obtained. Here, in situ structural investigations of molybdenum oxide based partial oxidation catalysts will be presented aiming, first, at understanding the evolution of the long-range (XRD) and short-range (XAS) structure of the catalyst under reaction conditions and, second, at revealing properties of the system studied not available from investigations under stationary conditions (e.g. reaction intermediates or the solid-state kinetics of the reaction).

Heteropoly oxomolybdates (HPA) with a composition of $Cs_xH_{3-x}[PMo_{12}O_{40}]^*yH_2O$ and $Cs_xH_{4-x}[PVMo_{11}O_{40}]^*zH_2O$ were studied by in situ XAS and in situ XRD under mild reducing conditions (H_2 or propene) and under partial oxidation reaction conditions (propene and O_2). Furthermore, isopoly molybdates and various molybdenum oxides were investigated under propene oxidation reaction conditions. For the HPA it was found that the onset of catalytic activity is correlated to a partial reduction of the Mo and a partial decomposition of the regular Keggin anion under reaction conditions. Apparently, both Mo and V are capable of migrating from the Keggin anions onto free cationic sites in the structure resulting in stable lacunary Keggin anions. The onset temperature of the catalytic activity of the HPA coincides with that of MoO_3 and the



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decomposition products of ammonium heptamolybdate. The latter indicates common features in the various molybdenum oxide based catalysts that will be discussed.