

In situ Structural Evolution of Molybdenum Heteropoly Acids

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Introduction

Polyoxometalates of the Keggin type are known for their redox properties and are employed for numerous applications.^[1] The Cs salt of the Keggin type heteropoly acids (HPA) are used as catalyst, for instance, for the oxidation of methacrolein to methacrylic acid on an industrial scale.^[2] Despite the numerous studies on the catalytic reactivity of Keggin type HPA, the question remains whether the intact Keggin anion is the catalytically active species^[3] or if a modified structure is formed under catalysis reaction conditions.^[4] Here, the evolution of the Keggin anion during thermal treatment under different conditions is investigated by in situ X-ray absorption spectroscopy (XAS) and in situ X-ray diffraction (XRD).

Results and Discussion

Under mild reducing conditions at 700 K the formation of a cubic (*Pn3m*) molybdenum salt from the free acid ($\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$) is observed by in situ XRD. The molybdenum salt is also formed from the free acid under oxidizing conditions together with various bulk molybdenum oxides. The structure of the molybdenum salt consists of partially destroyed Keggin anions and molybdenum ions on cationic sites outside the Keggin anions. This structure results from the migration of molybdenum atoms under reaction conditions and, hence, the formation of the molybdenum salt can be denoted as autosalification. The structural alteration of the Keggin anion under reaction conditions is identified by detailed analysis of the XAS spectra. The same alteration on the short range order scale as detected for the free acid, is also observed for the Cs salt ($\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$), while in contrast to the free acid, the Cs salt shows no changes on the long range order scale. Catalytic tests of the molybdenum salt show an increased activity in partial oxidation of light alkenes.

References

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