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Thermally and chemically induced structural transformations of Keggin-type heteropoly acid catalysts

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Abstract

Raman characterization revealed that the Keggin anion structure of H4PVMo11O40 is inherentl y unstable upon heat treatment and loss of water. Vanadyl and molybdenyl species are expelled from the Keggin cage and defective Keggin structures are formed. These defective structures further disintegrate to presumably Mo3O13 triads of the former Keggin. These Keggin fragments oligomerize at later stages to molybdenum oxygen clusters comparable to hepta- or octamolybdates. The final disintegration and structural reorganization product is MoO3. This disintegration and recondensation process seems to be strongly affected by the heating rate and hence the presence of water in the sample. Only partial expulsion of V occurred under moderate dehydration conditions. The absence of water during heat treatments stabilizes the intermediate
defective structures. Raman spectroscopy proved that free polyacids are unstable under catalytic partial oxidation conditions. Therefore, it can be suggested that intact Keggin anions are not the active species within an operating partial oxidation catalyst. From this Raman spectroscopy study it may be inferred that the structurally reorganized intermediates are relevant for the catalytic action. The Raman investigations of the HPA decomposition additionally revealed a dependency of the decomposition process on the reactive atmosphere and the presence of Cs. The presence of Cs led to a partial stabilization of the structural disintegration products of PVMo11 and to the formation of the thermodynamically stable, but catalytically inactive Cs3-salt. Cs also inhibited the condensation of MoO3-type oxides. O2 present in the gas phase also led to stabilization of the structural reorganization intermediates. Importantly, the presence of water did not lead to a stabilization of the intact Keggin structure. In contrast, hydrolysis of the Keggin anions seemed to be enhanced compared to the water-free situation. This observation is of high importance because water is added
to the feed in industrial partial oxidation reactions. Hence, under industrial conditions, HPA-derived catalysts are inherently unstable and cannot contain intact Keggin anions at their active surface.
Catalytic partial oxidation conditions even led to a more pronounced structural reorganization and amorphous suboxides of the MoO3-x type seemed to be formed. Hence, heteropolyacids have to be understood only as defined molecular precursor compound.

Keywords: Heteropolyacids; Keggin; Dehydration; Structural disintegration; Lacunary structures; Molybdenyl and vanadyl species; Raman spectroscopy