

In situ investigations of structure-activity relationships in heteropolyoxomolybdates as partial oxidation catalysts

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Abstract:

The structural evolution of Keggin-type heteropolyoxomolybdates (HPOM) during thermal treatment in propene and in propene and oxygen in the temperature range from 300 to 773 K was investigated by in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS) combined with mass spectrometry. During treatment in propene or hydrogen and at reaction temperatures above 673 K, the initially triclinic $H-3[PMo_{12}O_{40}]-13H(2)O$ is transformed quantitatively into a cubic HPOM (Pn3m, $a=11.853$ Angstrom) exhibiting a long-range structure similar to that of the corresponding cesium salts. The treatment described constitutes the first readily available preparation route for a cubic HPOM without alkali metal ions in the structure. For both $H-3[PMo_{12}O_{40}]$ and $Cs_2H[PMo_{12}O_{40}]$ migration of molybdenum from the Keggin ion onto interstitial sites is proposed to occur in propene or hydrogen at temperatures above about 573 K to give thermally stable, partially reduced lacunary Keggin ions. During activation in propene and oxygen the onset of catalytic activity of $H-3[PMo_{12}O_{40}]$ and $Cs_2H[PMo_{12}O_{40}]$ at about 573 K correlates with partial reduction of Mo and characteristic changes in the local structure of the Keggin ion. The structural changes observed indicate that, similar to the treatment of the HPOM in propene, migration of molybdenum from the Keggin ions onto interstitial sites and formation of lacunary Keggin ions take place. Moreover, the formation of these partially reduced lacunary Keggin ions appears to be a prerequisite for the material to become an active heterogeneous catalyst. Evidently, the undistorted Keggin ion in the as-prepared HPOM has to be regarded as a precursor of the active catalyst.