

UV/Vis/near -IR bands and band gap energies of $H_{4-x}Cs_xPVMo_{11}O_{40}$ ($x=0, 2$) in dependence upon temperature and the atmosphere

S. Klokishner¹, J. Melsheimer², J. Kröhnert², R. Ahmad², F. C. Jentoft², G. Mestl² and R. Schlögl²

¹State University of Moldova, Mateevich Str. 60, 2009 Kishinev, Moldova

²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Quantum mechanical calculations show that the visible part of the spectra in heteropoly acids and Cs-salts is formed by d-d-transitions and intervalent charge transfer bands arising from protonated $VMoO_{11}$ and ill-defined $VMoO_{11-x}$, Mo_2O_{11-y} ($y>2$) species [1]. In heteropolyacids at room temperature (RT) after a certain time on gas flux (He, propene, He/H₂O) the loss of crystal water starts. At this initial stage there is no reduction, the $H_4PVMo_{11}O_{40}$ (HPA) is in the hydrated phase, and the protons are not localized and reside on the bridging water moieties $H_5O_2^+$. The visible part of the spectra originates mainly from the d-d transitions in V^{4+} and Mo^{5+} [2].

At temperatures above RT a modified spectrometer for in situ diffuse reflectance measurements in presence of He, He/H₂O, O₂, propene or propene/O₂, and a new method to determine band gap energies arising from the overlap of the UV and Vis bands, were applied. At higher temperatures (326-371 K) the removal of crystal water is accompanied by the localization of acidic protons. The $VMoO_{11}$ species with protons localized on the bridging oxygens give rise to blue shifted charge transfer bands [1]. To the extent that the number of protonated VMo_{11} species increases with temperature increase in the range of 323-371 K, a gradual blue shift of the Vis peak position and a decrease of the band gap energy is observed. As the temperature continues to rise, „protonic“ water evolves. This water is formed by extraction of an oxygen by two protons, and leads to the formation of ill-defined clusters in which the bridging oxygens are removed. However, the protonic water evolution does not change the degree of reduction. Therefore, at this stage the transformations of the spectra only occur due to the formation of new types of clusters. The theoretical consideration [1] shows that the CT bands arising from $PVMo_{11-x}$ species have maxima higher in energy than those arising from protonated $PVMo_{11}$ ones. As a consequence, a further blue shift of the Vis peak position takes place. Finally, the evolution of molecular oxygen produces a reduction and also promotes a gradual blue shift of the visible band. The number of localized protons on the bridging oxygens at intermediate temperatures and the quantity of released protonic water at very high temperatures is larger for HPA than for the Cs-salt. Therefore the blue shift of the Vis band is not only more significant in HPA, but also proceeds gradually without interruption.

References

1. S. Klokishner, J. Melsheimer, R. Ahmad, F. C. Jentoft, and R. Schlögl, to be published.
2. S. Klokishner, J. Melsheimer, R. Ahmad, F. C. Jentoft, G. Mestl and R. Schlögl, submitted to Spectrochimica Acta, Part A.