

## Studies of UV/Vis/near-IR bands of $H_{4-x}Cs_xPVMo_{11}O_{40}$ ( $x=0,2$ ) compounds in dependence upon temperature and gas atmosphere

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No single technique provides full information about the transformations of the Keggin-type  $H_{4-x}Cs_xPVMo_{11}O_{40}$  ( $x=0,2$ ) compounds with rising temperature over long times on gas stream. Therefore a combination of the UV/Vis/near-IR spectroscopy and quantum-mechanical calculations was used to study these compounds.

Diffuse reflectance spectra were recorded in situ conditions using an improved spectrometer and a suitable microreactor. Visible and near-IR peak intensities, peak positions and the band gap energies were determined from apparent absorption spectra [1]. For both catalysts at temperatures above 300 K a blue shift of the visible and an increase of the near-IR absorption band were detected in the presence of He, the mixture of  $O_2$ /propene, or propene. The observed blue shift of the visible band was stronger under the propene flux than under the He flux (Fig. 1).

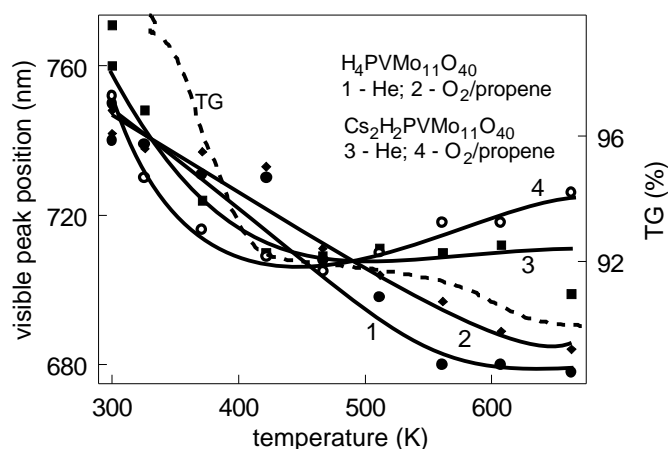


Fig. 1: Visible peak position vs. temperature

The vibronic coupling constants and the crystal field splittings that determine the shape and the positions of the optical bands were calculated in a crystal field model allowing for the covalency effects in the binding of the metal ions to the oxygens in the nearest coordination sphere. The parameters characterizing single-electron transfer between neighboring  $Mo^{5+}$  and  $Mo^{6+}$  (or  $V^{4+}$  and  $Mo^{6+}$ ) ions in the Keggin unit

were shown to be small in comparison with the characteristic vibronic coupling parameters. In this case the problem of calculation of the full optical spectrum of the reduced Keggin unit (intact or defective) reduces to a study of intervalent and d-d transitions in binuclear clusters  $\text{Mo}^{5+}\text{-Mo}^{6+}$  or  $\text{V}^{4+}\text{-Mo}^{6+}$ , in which in dependence upon time on stream and temperature the nearest oxygen surrounding of metal ions may be unimpaired ( $\text{MO}_6$ ) or ill-defined. The composition of very likely species (Fig. 2) was chosen on the basis of thermogravimetric [1], differential thermal, and IMR-MS analyses. Comparison of the results of quantum-mechanical calculations with experimental data allowed to make the conclusion that the lowest energy site of an acidic proton is a bridging oxygen ion ( $\text{O}_b$ ). Species with protons localized on the bridging oxygens or with vacancies of bridging oxygens were shown to give blue shifted charge transfer bands relatively to those arising from intact ones (Fig. 3). In the range of crystal water loss the blue shift of the visible band is provided by species with protons residing on the bridging oxygens. In the range of constitutional water or oxygen evolution species  $\text{Mo}_2\text{O}_{10}$  and  $\text{VMoO}_{10}$  promote the further blue shift of the visible band. The difference in the temperature behavior of the spectra of  $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$  and  $\text{H}_2\text{Cs}_2\text{PVMo}_{11}\text{O}_{40}$  was explained as well.

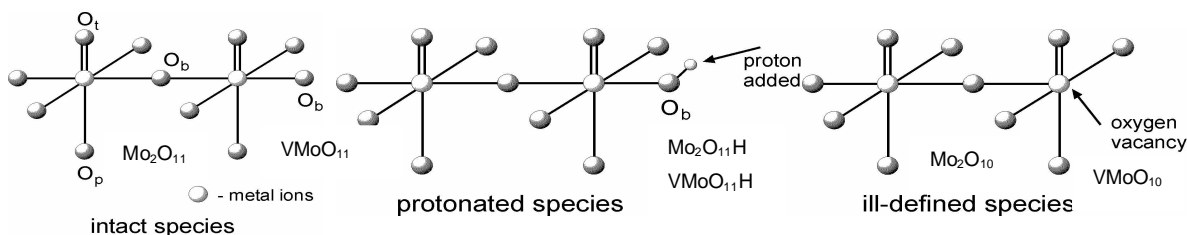


Fig. 2: Schematic representation of species used to calculate charge transfer bands

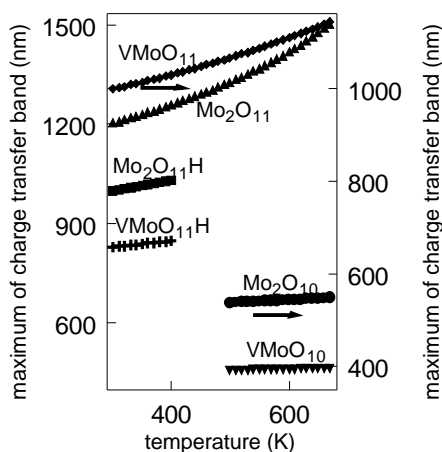


Fig. 3: Calculated maxima of charge transfer band vs. temperature for intact, protonated, and ill-defined species

#### References

1. J. Melsheimer, J. Kröhnert, R. Ahmad, S. Klokishner, F.C. Jentoft, G. Mestl and R. Schlögl, submitted to PCCP.