

SYNTHESIS AND CHARACTERISATION OF TRANSITION-METAL SUBSTITUTED KEGGIN-TYPE POLYOXOMETALATES

Maximilian J. Poller, Jan-Christian Raabe, and Jakob Albert

Institute of Technical and Macromolecular Chemistry, Universität Hamburg,
Hamburg, Germany

Polyoxometalates (POMs) have been proven particularly useful for catalytic applications. They have a high Brønsted acidity in their protonated form, which makes them suitable for acid catalyzed reactions.[1] By substituting the framework metal with a redox active element, they can also function as redox catalysts. A prominent example is the application of $H_8PV_5Mo_7O_{40}$, as a catalyst for the oxidative conversion of biomass to formic acid.[2] It is nonetheless necessary to tune the molecular properties of the POM to tailor the catalyst to the desired functionality in order to enable a broader range of catalytic applications.

We work on the incorporation of different transition metals into the framework of Keggin phosphomolybdates and phosphotungstates and on the analytical characterisation of the resulting compounds. We have successfully employed two different strategies for the synthesis of transition metal substituted Keggin POMs: ab-initio self-assembly, where all precursors are added during the initial formation of the POM,[3,4] and the substitution of a framework atom via the formation of a lacunary structure.[4,5] In order to overcome the problem in separating the POM from the counter ions of its precursors, we have successfully employed an adapted membrane nanofiltration procedure, which was originally developed for catalyst recycling.[5,6] Employing those methods, we succeeded in synthesizing a number of Keggin-type POMs containing different transition metals (e.g. Mn(II), Nb(V), V(V)) with varying degrees of substitution, that were confirmed by elemental analysis (ICP-OES) and infrared spectroscopy.[3–5] Additionally, we have comprehensively characterised these newly discovered compounds using a wide range of analytical methods including UV-Vis spectroscopy, NMR spectroscopy, x-ray diffraction, and electrochemical measurements. Correlation of these results with the catalytic activity (which is currently being investigated in the Albert research group), will provide a solid foundation for the future development of tailor-made catalysts.

[1] Inumaru, K.; Ishihara, T.; Kamiya, Y.; Okuhara, T.; Yamanaka, S. *Angew. Chemie - Int. Ed.* **2007**, *46* (40), 7625.

[2] Voß, D.; Kahl, M.; Albert, J. *ACS Sustain. Chem. Eng.* **2020**, *8* (28), 10444.

[3] Raabe, J.-C.; Albert, J.; Poller, M. *J. Chem. – A Eur. J.* **2022**, *28* (49).

[4] Raabe, J.; Aceituno Cruz, J.; Albert, J.; Poller, M. *J. Inorganics* **2023**, No. 11, 138.

[5] Raabe, J.-C.; Esser, T.; Jameel, F.; Stein, M.; Albert, J.; Poller, M. *J. publication in preparation*.

[6] Esser, T.; Huber, M.; Voß, D.; Albert, J. *Chem. Eng. Res. Des.* **2022**, *185*, 37.