

In-situ EDXRD investigations of the formation of a new antimonatopolyoxovanadate under solvothermal conditions

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The existing interest in the chemistry of polyoxometallates (POMs) grows not only due to their captivating variety of structures and topologies but also because of their potential applications in areas as photochemistry, catalysis, ion exchange, molecular magnetism and material science [1-6]. A large number of extended solid framework materials based on polyoxometalates have been solvothermally synthesized. Nevertheless, it is not clear what happens during the solvothermal formation of POMs. Time-resolved energy dispersive *in-situ* X-ray diffraction (EDXRD) allows monitoring the growth of crystalline products or intermediates.

During the last years we synthesized several polyoxovanadates, some of them containing germanium or antimony [7-10]. The first investigations with *in-situ* EDXRD of the formation of germanato- and antimonatopolyoxovanadates were done last year at the HASYLAB Beamline F3.

Recently we performed the *in-situ* experiments on the formation of $[\text{Sb}_6\text{V}_{15}\text{O}_{42}(\text{H}_2\text{O})\text{Ni}(\text{C}_5\text{N}_3\text{H}_{15})_2]\{\text{Ni}(\text{C}_5\text{N}_3\text{H}_{15})_2\}_2$ (**I**). This compound is synthesized with Sb_2O_3 , NH_4VO_3 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 2 mL of 50% aepa (*N*-2-Aminoethyl-1,3-propandiamine). Like in the reaction for the formation of $(\text{C}_6\text{H}_{15}\text{N}_3\text{-H}_3)_4[\text{V}_{14}\text{Ge}_8\text{O}_{50}]$ ($\text{C}_6\text{H}_{15}\text{N}_3 = \text{aep} = 1\text{-}(2\text{-aminoethyl})\text{-piperazine}$) (**II**), which was investigated earlier [11], NH_4VO_3 was used for the synthesis of compound (**I**). In both cases vanadium is reduced from V^{5+} to V^{4+} during the reaction. For the synthesis of (**II**) Cu nitrate was used, but Cu is not integrated in the product. On the other hand, Sb and Ni are incorporated in the structure of (**I**) without a change of the oxidation states.

The mechanism of crystallization and the growth kinetics in the formation of (**I**) were explored as function of the temperature, which was varied between 160 and 190 °C. Data analysis showed that the induction time decreases with increasing reaction temperature. At 160 and 170 °C the product crystallized without occurrence of crystalline intermediates. Figure 1 shows a Sharp-Hancock plot for the reflection (011) of (**I**) at 160 °C. Two different regions, $\alpha < 0.65$ and $\alpha > 0.65$, can be distinguished. In the first part of the reaction the exponent m is about 0.47, and for $\alpha > 0.65$ it amounts to 0.58. A comparison of the measured data with different kinetic models is represented in Figure 2. The results suggest that the crystallization of compound (**I**) is a diffusion controlled process under these conditions.

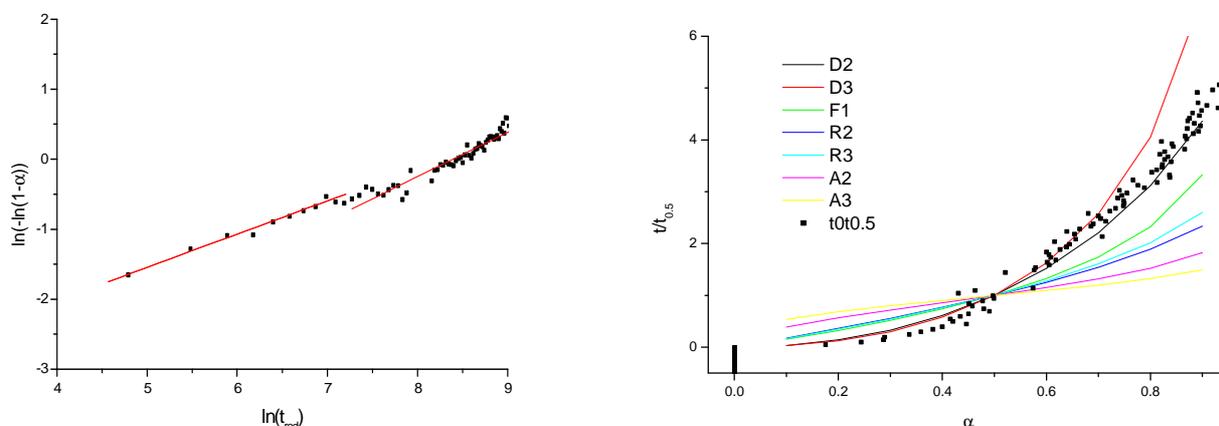


Figure 1: Sharp-Hancock plot of (011) at 160°C. Figure 2: Comparison of different kinetics models at 160°C.

Compound (**I**) can also be prepared by replacing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with other nickel salts. It would be interesting to perform further *in-situ* EDXRD experiments using different nickel salts, since it is not clear which is the role of the different anions of the salts applied for the formation of (**I**) and for the reaction progress.

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