Investigations of the formation of a new polyoxometallate under solvothermal conditions with in-situ energy dispersive diffraction (EDXRD)

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Polyoxometallates (POMs) are usable for several attractive applications like optical sensing, gas storage and separation, ion exchange, photochemistry and catalysis [1-8]. For this reason, these materials are of great interest and every year several publications appear containing synthesis, structure and applications of POMs. Despite the high interest in POM chemistry, the formation of such compounds under solvothermal conditions has not been studied until now. In heterogeneous reactions like the solvothermal syntheses, many different reaction parameters can influence the formation of the product and these effects are still not well understood. With in-situ EDXRD it is possible to monitor the occurrences of intermediate phase during the formation of POMs without quenching the reaction slurry. Such information can give many hints for the "design" of new and interesting materials.

We started to investigate the formation of the new POMs $[C_6H_{15}N_3\text{-}H_3]V_{14}Ge_8O_{50}$ ($C_6H_{15}N_3$ = 1-(2-aminoethyl)-piperazine) (**I**) and $[C_4H_{10}N_2\text{-}H_2]_4[C_4H_{10}N_2\text{-}H]Ge_8V_{14}O_{50} \cdot H_2O$ ($C_4H_{10}N_2$ = Piperazine) (**II**) in 2008 [9, 10]. These compounds are obtained under solvothermal conditions from a mixture of 2 mmol GeO_2, 3 mmol NH_4VO_3, 1 mmol $Cu(NO_3)_2 \cdot 3\ H_2O$ respectively $AgNO_3$ and 6 mL of an aqueous 75% aep solution. In ex-situ experiments, we observed that under these reaction conditions **I** is obtained at temperatures from 110 to 140 °C whereas **II** crystallizes between 150 and 180 °C. For the formation of **II** the presence of $Cu(NO_3)_2 \cdot 3\ H_2O$ resp. $AgNO_3$ is required and **I** can be obtained also without the metal salts over the whole temperature range. Both **I** and **II** were contaminated with elemental copper/silver when using $Cu(NO_3)_2 \cdot 3\ H_2O/AgNO_3$ while in **II** the 1-(2-aminoethyl)-piperazine molecule is transformed to piperazine during the reaction. During our research in 2008 we were not able to obtain **II** under stirring conditions and we could not explain this unusual observation.

In the last measurement period we focussed the experiments on questions which were still open. First we investigated whether **II** can be obtained under dynamic conditions. Several experiments were performed to crystallize **II** under stirring conditions varying the rotation speed of the stirrer and also the reaction conditions. But we were not able to crystallize the compound indicating that this is an intrinsic property of **II**, i.e. stirring seems to change the composition and/or concentration of the dissolved species thus preventing crystallization. Furthermore, we investigated the influence of the metal salt on the reaction kinetics of the formation of **I** as a function of temperature (120 – 180 °C). The measurements show that **I** crystallizes without any crystalline precursor or intermediate in a one-step reaction. The induction time remains constant, but the crystal growth is much faster at higher temperatures (Figure 1).

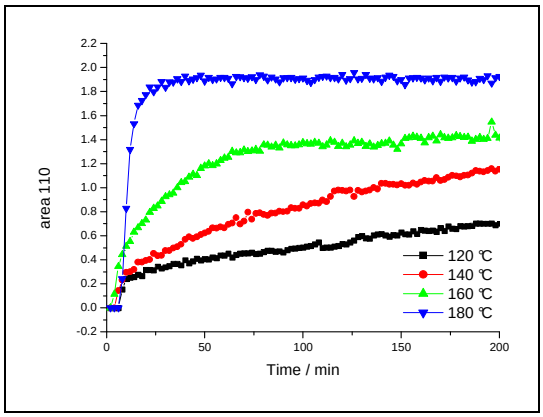

Figure 1: Area of the (110) reflection of **I** vs. time for different temperatures.

The reaction exponent *m* and rate constant *k* depend on the reaction temperature. The reaction mechanism for α = 0 to 0.5 is diffusion-controlled over the whole temperature range. At α = 0.8 the crystallization mechanism slowly changes from a diffusion-control to a first order reaction (Figure 2 left). At 180 °C the product growth is very fast preventing a detailed analysis. From α = 0.8 to 1 the data points steeply increase to very high $t/t_{0.5}$ values (Figure 2 right).

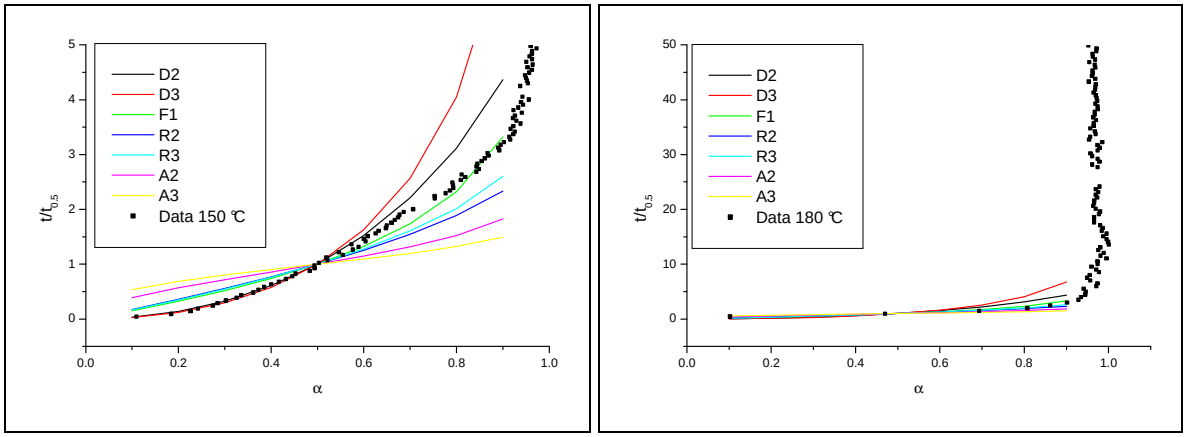

Figure 2: Comparison of the experimental data with different crystallization mechanisms for selected temperatures.

References

[1] M. T. Pope, A. Müller, Angew. Chem. **103**, 56 (1991).
[2] A. Müller, P. Kögerler, A. W. M. Dress, Coord. Chem. Rev. 222, 193 (2001).
[3] M. T. Pope, A. Müller, Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity (1994).
[4] M. T. Pope, A. Müller, Polyoxometalate chemistry: From Topology via Self-Assembly to Applications (2001).
[5] M. B. Zhang, J. Zhang, S. T. Zheng, G. Y. Yang, Angew. Chem. **111**, 2798 (1999).
[6] D. R. Park, H. Kim, J. C. Jung, S. H. Lee, I. K. Song, Catal. Commun. **9**, 293 (2008).
[7] A. Müller, P. Kögerler, C. Kuhlmann, Chem. Commun. 1347 (1999).
[8] C. L. Hill, Chem. Rev. **98**, 1 (1998).
[9] J. Wang, C. Näther, P. Kögerler, W. Bensch, in preparation (2009).
[10] B. Seidlhofer, E. Antonova, N. Pienack, W. Bensch, DESY Annual Report (2009).