Nucleation and Crystal Growth of a $\{V_{14}Sb_8O_{42}\}$ Cluster from a $\{V_{15}Sb_6O_{42}\}$ Polyoxovanadate: *In-Situ* X-ray Diffraction Studies

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Dedication ((optional))

Abstract: The hydrothermal transformation of the heteroatom polyoxovanadate compound $[Ni(en)_3]_3[V_{15}Sb_6O_{42}(H_2O)] \cdot \approx 15H_2O$ in water into $[Ni(en)_2]_2V_{14}Sb_8O_{42} \cdot 5.5H_2O$ was investigated with *in-situ* X-ray diffraction experiments at different temperatures. First, the precursor is amorphized very fast and an induction period is observed depending on the reaction temperature. Crystal growth of the product is completed within 3 h, while higher temperatures lead to an accelerated reaction progress. Evaluation of the kinetics demonstrates that heterogeneous nucleation is the rate-limiting step of the reaction. The activation energies for nucleation and crystal growth are very low compared to data reported in literature for several other chemical systems.

Introduction

The formation mechanisms of crystalline solids from solution are still scarcely understood due to the complexity of chemical reactions during nucleation and crystallization steps.^[1] In the past years the analytic tools for *in-situ* investigations of chemical reactions under real reaction conditions were significantly developed.^[2-13] We and other groups demonstrated that a wealth of information is gained applying *in-situ* X-ray diffraction, *in-situ* total scattering or *in-situ* X-ray absorption spectroscopy during chemical reactions.^[14-30] Despite the increasing efforts to gain insight into mechanisms of chemical reactions, *in-situ* X-ray scattering studies under real reaction conditions are still rarely performed. Several reasons may be responsible preventing a broader application of such experiments: i) special reaction cells must be developed meeting the requirements of the reaction conditions; ii) a high time resolution requires high intensity of X-rays and therefore the experiments are mainly performed at synchrotron radiation facilities. In any case, for direct syntheses of new materials the reaction mechanisms including formation of metastable intermediate phases must be known. Syntheses under solvo- or hydrothermal conditions are widely used for the preparation of new materials. Heteroatom modified high nuclearity polyoxovanadates (POVs) are a class of compounds that can only be prepared under solvothermal conditions. Because the reaction mechanisms are not well understood almost all hetero-POVs were obtained by systematic variation of the reaction conditions. Hetero-POVs with Sb as heteroatom with the general formula $\{V_{18-2n}Sb_{2n}O_{42}\}$ ($n = 2 - 4$)

expanded by e.g. transition metal complexes or organic ammonium cations,^[33, 38-45] leading to an increase in complexity of the chemical reactions. In contrast to polyoxomolybdates or polyoxotungstates no suitable preformed high nuclearity clusters are available for generation of Sb-POVs, which can be regarded as an obstacle for the development of Sb-POV chemistry. In a recent *in-situ* energy dispersive X-ray diffraction (EDXRD) study^[46] we investigated the formation of Sb-POVs in the presence of 1-(2-aminoethyl)-piperazine using an identical ratio for Sb_2O_3 and NH_4VO_3 . The main results of this study were that all $[V_{18-2n}^{IV}Sb_{2n}O_{42}]^{2n-}$ clusters with $n = 2 - 4$ can be obtained by varying the amine concentration, i.e. the amine concentration and consequently the pH value controls the nuclearity of the cluster anion.

During our systematic research into Sb-POV chemistry we were able to prepare a new Sb-POV, $[Ni(en)_3]_3[V_{15}Sb_6O_{42}(H_2O)_x] \cdot \approx 15H_2O$ (I) ($en = \text{ethylenediamine}$, $x = 0$ or 1)^[47] representing the first water soluble hetero-POV. The cluster core is successively transformed within several days in water at room temperature into the Sb-richer $\{V_{14}Sb_8O_{42}\}$ moiety. Using I as synthon in the reaction slurry causes a conversion of the $\{V_{15}Sb_6O_{42}\}$ cluster into $[Ni(en)_2]_2V_{14}Sb_8O_{42} \cdot 5.5H_2O$ (II)^[48] within 3 d containing the β -isomer of $\{V_{14}Sb_8O_{42}\}$ (Figure 1).

Figure 1. Structure of precursor I with the isolated complexes and cluster anions (left) and the structure of product II featuring a 2D layer by interconnection of the anions via V-O-Ni-O-V bridges (right) (C and H atoms are omitted for clarity).

The addition of $[Ni(phen)_3](ClO_4)_2 \cdot 0.5H_2O$ ($phen = 1,10$ -phenanthroline) to an aqueous solution of I afforded crystallization of $[Ni(phen)_3]_2[V_{14}Sb_8O_{42}] \cdot phen \cdot 12H_2O$ (III) with α - $\{V_{14}Sb_8O_{42}\}$.^[49] Performing the reaction in the presence of Sb_2O_3 reduced the reaction time to 1 d. Based on the observation that the $\{V_{14}Sb_8O_{42}\}$ cluster can be obtained with Sb_2O_3 at short reaction times we performed syntheses with NH_4VO_3 with the aim to prepare the V-richest cluster $\{V_{16}Sb_4O_{42}\}$.

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were synthesized and characterized.^[31-37] The clusters can be

Surprisingly, compound **II** could be identified in the reaction product after heating for 1 d. All these intriguing observations encouraged us to investigate the reaction of **I** with *in-situ* X-ray powder diffraction under real reaction conditions.

Results and Discussion

The transformation of a $\{V_{15}Sb_6O_{42}\}$ cluster into $\{V_{14}Sb_8O_{42}\}$ cluster shell proceeds via several structural and chemical changes.^[49] The $\{V_{15}Sb_6O_{42}\}$ cluster with D_3 symmetry contains 15 edge sharing square-pyramidal VO_5 moieties. Two hexagons V_6 composed of six edge sharing VO_5 polyhedra envelop three VO_5 (V_3) units above yielding to the sequence $V_6-V_3-V_6$. The three Sb_2O_5 units bridge the hexagons by Sb-O bonds to the hexagons. The total charge of the anion is 6-. During the formation of the $\{V_{14}Sb_8O_{42}\}$ cluster the chemical composition changes and formally one VO_5 unit is replaced by a Sb_2O_5 moiety. This cluster exhibits a lower charge of 4- and the structure contains two perpendicular V_8 rings formed by edge sharing of VO_5 pyramids. The symmetric arrangement of the four Sb_2O_5 units and of the V_8 rings leads to the symmetry D_{2h} .

Evaluation of the kinetics

The reflection intensities were normalized against the Al (100) reflection caused by the window of the *in-situ* cell to account for beam flux fluctuations ($I_n(t) = I_{exp}/I_{Al}$). The reaction time where the first reflections appeared was set as t_0 (induction period). The real time t_{red} was estimated as $t_{red} = t - t_0$. Evaluation of the crystal growth was done by plotting the extent of reaction $\alpha(t)$ ($\alpha(t) = I_n(t)/I_n(t_\infty)$, t_∞ = end of reaction) versus time. The extent of reaction was analyzed with the JMAK (Johnson-Mehl-Avrami-Kolmogorov) approach^[50-52] according to equation (1):

$$\alpha(t) = 1 - \exp[-(kt_{red})^m] \quad (1)$$

with k = rate constant and m = reaction exponent. Using a Sharp-Hancock (SH) plot^[53] (eq. 2) the parameters m can be derived from the slope and k from the intersection with the y axis and different growth models can be derived.

$$\ln[-\ln(1 - \alpha)] = m \ln(k) + m \ln(t_{red}) \quad (2)$$

It must be noted that the JMAK approach was developed for solid state reactions with severe constraints and one should be careful in interpretation of the kinetic data. Nevertheless, first indications about the dominating reaction mechanism can be obtained by the JMAK analysis. Another approach was established by Gualtieri^[54] for the nucleation and crystallization of zeolites (eq. 3) which seems to be more appropriate for the analysis of kinetic data for crystallization of crystalline solids from solution.

$$\alpha = \{1/(1 + \exp[-(t-a)/b])\} \cdot \{1 - \exp[-(k_g t)^n]\} \quad (3)$$

with α = extent of crystallization and t = time as in equations (1) and (2); a represents the maximum rate of nucleation; b defines the distribution of the probability of nucleation with time; k_g represents the rate constant of the crystal growth and n determines the dimension of crystal growth. The crystal shape is described by n and was set to $n = 3$ based on the rhombohedral particle morphology seen SEM images (Figure S3). Values for b indicate different nucleation models: $b < 15$ heterogeneous; $b \approx 20$ homogenous, and $b > 20$ autocatalytic. If the values a and b are known the nucleation and the crystal growth processes can be separated according to equation (4) describing the time-dependent probability of nuclei development P_N .

$$P_N = \exp\{-(t-a)^2/2b^2\} \quad (4)$$

Results of the kinetics

The *in-situ* XRD patterns displayed in Figure 2 were collected during heating the sample to the desired temperature. Powder patterns were recorded in a fast step rate every 5 s with a heating rate of 1 °C / s obtaining a time resolved set of patterns to follow the evolution of the Bragg reflections of the starting material. At the beginning of heating the Bragg reflections of **I** are clearly visible until they disappear after about 2.5 min ($T = 137$ °C). Similar observations were made at all three reaction temperatures indicating that **I** is either dissolved or transformed to an amorphous state.

Figure 2. X-ray powder patterns (left, $\lambda = 0.4959$ Å) collected every 5 s during heating of the precursor $[Ni(en)_3]_3[V_{15}Sb_6O_{42}(H_2O)] \cdot \approx 15H_2O$ (**I**) to $T \geq 137$ °C. Intensity scale: intensity decreases from red to blue; (right) change of the intensity of the most intense reflection with time plotted as extent of reaction $\alpha(t)$. The red line is a guide for the eyes.

Exemplarily, the evolution of the XRD patterns collected at $T = 144$ °C is shown in Figure 3. After dissolution/amorphization of **I** no reflections could be observed for a period of time t_{red} between about 46.5 min ($T = 144$ °C) and 30.5 min ($T = 164$ °C) until reflections of the product **II** appeared in the powder patterns. Interestingly, during decrease of the reflections of the educt the background at small angles increases indicating the presence of an amorphous phase. With further reaction progress the modulation of the background is successively reduced and disappeared when the product starts to crystallize. After 150 min the reaction seems to be finished because no further increase of the intensities of the Bragg reflections could be detected (Figure 3, top). A comparison of the powder pattern of the final product with that calculated for **II** shows a good agreement (Figure 3, bottom and Figure S1).

For kinetic analyses the most intense (-101) reflection was used for $T = 144, 154$ and 164 °C. The extent of reaction $\alpha(t)$ is shown in Figure 4 demonstrating the temperature dependence of the induction period and the growth of the product. A higher reaction temperature leads to a shorter induction period and accelerates the formation of the product. Once reflections could be detected a fast growth is observed and the reactions are finished depending on the temperature: 144 °C: 150.5 min; 154 °C: 128.5 min; 164 °C: 76.5 min. Please note the signal at $3.00^\circ 2\theta$ is caused by a pixel damage of the detector.

Figure 3. In-situ XRD patterns ($\lambda = 0.4959 \text{ \AA}$) collected during reaction progress of the formation of $[(\text{Ni}(\text{en})_2)_2\text{V}_{14}\text{Sb}_8\text{O}_{42}] \cdot 5.5\text{H}_2\text{O}$ (II). Patterns were recorded every 30 s at 144 °C: top 3D plot and bottom corresponding waterfall plot; colour code: intensity increase in the order blue-green-yellow-red.

In Table S1 the mathematical expressions of different growth models are summarized together with values for m reported in.^[53,55] A plot of these theoretical different growth models together with the experimental data (Figure 5) suggests that a nucleation controlled process dominates the crystal growth (A3, Avrami-Eroféev) (see Supporting Information Figure S4 for the corresponding plots at $T = 144$ and 154 °C).

Figure 4. Extent of reaction $\alpha(t)$ for three different temperatures: 144 (black points), 154 (red points) and 164 °C (blue points) and the fits according to eq. (3) (corresponding coloured lines) based on evaluation of the (-101) reflection. The orange curve shows the fast decrease of the intensity of reflections corresponding to the precursor.

Figure 5. Comparison of the experimental data $t/t_{0.5}$ at 164 °C (points) as a function of $\alpha(t)$ with different kinetic growth models (listed in Table S1).

Using equation (3) and fitting $\alpha(t)$ versus t assuming $n = 3$ (the value 3 indicates three dimensional growth, see SEM picture in ESI) gave values for b indicating heterogeneous nucleation processes for all three temperatures (Table 1). Most likely X-ray amorphous particles formed from the precursor (see discussion above) act as nucleation centers. Evaluation of the data with equation (4) reveals that the nucleation phase and the crystal growth scarcely overlap and give a further proof the observed nucleation processes (Figure 6). Furthermore, the values for k_n and k_g indicate that nucleation is the rate-limiting step at all temperatures, because k_n is slightly lower than k_g ($k_n = 1/a$) (Table 1). Analysis of the full widths at half maximum of the most intense reflection shows only a moderate narrowing with reaction time suggesting that not enough 'monomers' are in solution for further crystal growth. Once the nuclei formed exceed the critical size, these newly formed nanocrystallites consume the 'monomers'.

Figure 6. Temperature depending probability of nuclei development P_N (dotted lines), crystal growth of the (-101) peak (points) and the Gualtieri fit (lines) for the three different reaction temperatures 164 °C (blue), 154 °C (red) and 144 °C (black).

Table 1. Kinetic parameters for the three different reaction temperatures (t_{ed} = induction time, k_n = rate constant of the nucleation process, k_g = rate constant of the crystal growth, adj. R^2 = regression coefficient and a , b = Gualtieri parameters, see text).

T [°C]	144 °C	154 °C	164 °C
t_{ed} [min]	46.5	41.0	30.5
Growth model	A_3 Nucleation	A_3 Nucleation	A_3 Nucleation
k_n [min ⁻¹]	0.01607	0.01967	0.02531
Adj. R^2	0.995		
k_g [min ⁻¹]	0.019(1)	0.024(3)	0.033(1)
Adj. R^2	0.999		
a [min ⁻¹]	62(3)	50(4)	39(5)
b [min ⁻¹]	19(1)	14(1)	7(2)
Adj. R^2	0.995	0.994	0.995

The apparent activation energies for nucleation E_n and crystal growth E_g were calculated using an Arrhenius plot (Figure 7). The values of 34.4 kJ/mol for E_n and 43.8 kJ/mol for E_g are in the lower region of values reported for the formation of MOFs ranging from 50 – 140 kJ/mol^[18,56-60], thioantimonates ca. 42 kJ/mol^[16], or thioantimonates ca. 70 kJ/mol^[21,61], or zeolites ca. 40 – 100 kJ/mol^[62].

Figure 7. Arrhenius plots to determine the activation energies of the nucleation process (red) and of the crystal growth (black).

Conclusions

In-situ XRD investigations were performed during the reaction of a $[V_{15}Sb_6O_{42}]^{6-}$ cluster into the layered compound $[(Ni(en)_2)_2V_{14}Sb_8O_{42}] \cdot 5.5H_2O$. The precursor is either dissolved or amorphized during heating to the desired reaction temperature. The dissolution or amorphization is reflected by an initial increase in intensity of the small-angle region in the X-ray powder patterns followed by a decrease of this signal once crystallization is observable. After disappearance of reflections of the precursor an induction period follows, which becomes shorter with increasing reaction temperature. Kinetic evaluation of the data shows that nucleation is the rate-limiting step at all temperatures. The nucleation process is heterogeneous which may be rationalized by the presence of the X-ray amorphous nanoparticles. The reaction progress depends on the temperature and crystallization is faster at higher temperatures. The activation energies for nucleation and crystal growth are low compared to other groups of compounds. Especially the low nucleation barrier is promising for further investigations concerning the synthesis of new Sb-POVs within short reaction times.

Experimental Section

Materials and Methods

The *in-situ* XRD measurements were performed at DESY in Hamburg, Germany, at the beamlines P07b^[63] and P08^[64]. The data discussed in the manuscript were obtained at P08 and measurements were performed at P07b to ensure reproducibility. A Perkin Elmer XRD1621 Flat Panel detector with a pixel size of 200 x 200 μm and an array size of 2048 x 2048 pixel was used. Laue crystals Si(111) and Si(220) and a single bounce monochromator (SBM) for P07b enabled a maximum beam size of 0.5 x 0.5 mm² with an energy of 87 keV ($\lambda = 0.14235$ Å). And a Laue crystal Si(511) with a large-offset-monochromator for P08 enabled a maximum beam size of 1 x 1 mm² with an energy of 25 keV ($\lambda = 0.4959$ Å). The reactions were performed in Duran®-glass vessels with a maximum volume of ~11 mL. These reaction vessels were heated in a custom-built reactor that was developed at CAU Kiel in collaboration with the beamline staff of beamline P08, PETRA III, DESY, but further details will be published in the near future.

A PTFE coated thermocouple is located inside the reaction vessel monitoring the temperature. The mixtures were stirred using an electromagnetic stirring device. *In-situ* XRD patterns could be collected every 30 s. The data were evaluated with the program "f3tools" which was developed by A. Rothkirch (Hasylab, DESY) which is already well established.^[60,61,65] The compound formed were further characterized by IR spectroscopy measurements (Genesis FTIRTM spectrometer (ATI Mattson)), CHN elemental analysis (EUROEA Elemental Analyzer) and EDX (Philips ESEM XL30 equipped with an EDAX detector). X-Ray powder patterns were recorded on a STOE STADI-P diffractometer equipped with a 1K Mythen detector in transmission geometry using Cu-K α_1 radiation ($\lambda = 1.540598$ Å).

Synthetic details of the *in-situ* experiments

The compound $[Ni(en)_3]_3[V_{15}Sb_6O_{42}(H_2O)_x] \cdot \approx 15H_2O$ (**1**) was synthesized according to literature^[47]. NH_4VO_3 , Sb_2O_3 and

NiCl₂·6H₂O (Merck) and ethylenediamine (Grüssing) were purchased and used without further purification. Reaction times of days are not suitable for *in-situ* XRD studies at synchrotron radiation facilities. Hence, the reaction time must be significantly reduced. In the past, we demonstrated for several solvothermal systems that the reaction time can be drastically reduced by stirring the mixture.^[29,49] During experiments in the laboratory the shortest reaction times were identified for reacting compound **I** (0.045 mmol) with 0.125 mmol of NH₄VO₃ in a glass tube (inner volume 11 mL) and 4 mL distilled water. The syntheses were performed between 144 and 164 °C for **3 h** stirring the slurry (dynamic conditions). X-ray powder diffractometry demonstrated that phase pure **II** is formed in this temperature range. Elemental analysis: C 3.72, H 1.88, N 3.92 %; calc. (C₈H₄₄N₈Ni₂V₁₄Sb₈O_{47.5}): C 3.40, H 1.57, N 3.97 %. EDX analysis: V 40.01, Sb 53.01, Ni 6.99 %; calc. (V₁₄Sb₈Ni₂): V 39.5, Sb 54.0, Ni 6.5 %. For further characterization of the product (PXRD, IR, SEM image) see Supporting Information Figures S1 – S3.

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FULL PAPER

In-situ X-ray diffraction experiments of the transformation of a $\{V_{15}Sb_6O_{42}\}$ cluster containing compound into a layered compound consisting of a $\{V_{14}Sb_8O_{42}\}$ cluster demonstrate a two-step mechanism proceeding via amorphization/dissolution and Avrami nucleation. Activation energies for nucleation and crystal growth are remarkably low.

***In-situ* XRD of a polyoxovanadate transformation reaction**

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