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Aiding the Self-Assembly of Supramolecular Polyoxometalates under Hydrothermal Conditions to give Precursors of Complex Functional Oxides

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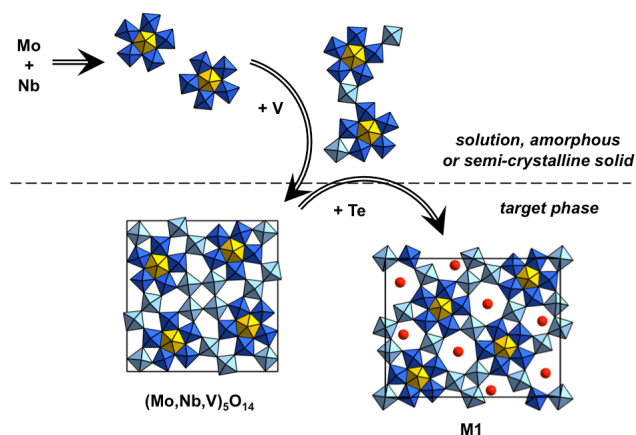
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The activation of small alkane molecules originating from natural gas or renewable resources will offer alternative pathways to functionalized hydrocarbons in a post-petroleum era. Crystalline or nano-crystalline molybdenum-vanadium based multi-metal oxides have been identified as versatile heterogeneous catalysts for selective oxidation of ethane,^[1] propane,^[2] and propene.^[3]

The crystal structures of these oxides show common structural attributes. In the framework of the tetragonal M_5O_{14} -type ($M = Mo, V, W, Ti, Nb$) structure (ICSD 27202),^[4] and in the orthorhombic M1 structure (ICSD 55097) of $MoVTe(Sb)Nb(Ta)$ oxides,^[5] metal-oxide polyhedra are cross-linked in the crystallographic ab plane by sharing corners or edges as shown in Schema 1. Needle-like nano-crystals growth along the crystallographic c axis by linking corners of the polyhedra resulting in a short lattice constant c at 0.4 nm and formation of channels with different sizes typical for oxidic bronzes. The structural motif $\{(M)M_5\}$, ($M = Mo, V, Nb$), which is composed of a pentagonal bipyramidal MO_7 unit that shares the five edges of the planar pentagon with five MO_6 octahedra (Schema 1), is another common feature that is also known as a key constituent of larger structural aggregates appearing in the rich and beautiful chemistry of reduced molybdates in solutions.^[6] Icosahedral molecular systems of the type $\{(Mo^{VI})Mo_5^{VI}\}_{12}(\text{linker})_{30}$, called Keplerates, have been considered as donor of the $\{(M)M_5\}$ building blocks in the M_5O_{14} synthesis^[7] and the hydrothermal synthesis of Mo_3VO_x , $MoVSb$ and $MoVTeNb$ mixed oxides with M1 structure.^[8]

The complexity of the M1 structure provides site isolation, as it is required for a high selectivity in oxidation reactions of C3 and C2 feedstock.^[9] Current synthetic approaches to phase-pure M1 suffer from insufficient repro-



Scheme 1. Representation of the assembly of structural motives during formation of the target phase M1 and the by-product $(Mo,Nb,V)_5O_{14}$.

ducibility,^[10] and apparently similar M1 catalysts may feature very different catalytic behaviour.^[9, 11]

Controlled synthesis of M1 with predictable surface properties requires deeper understanding of the inorganic reactions proceeding during assembly of structural building blocks and crystallization.

In this work, we have studied the formation of mixed MoVTenb oxides under hydrothermal conditions by *in-situ* Raman spectroscopy. The spectroscopic information enabled the design of a new, accelerated and reproducible hydrothermal route towards precursors of phase-pure M1. Modular cross-linking of structural building blocks as outlined in Scheme 1 directs the synthesis towards the desired product avoiding the co-formation of unwanted phases.

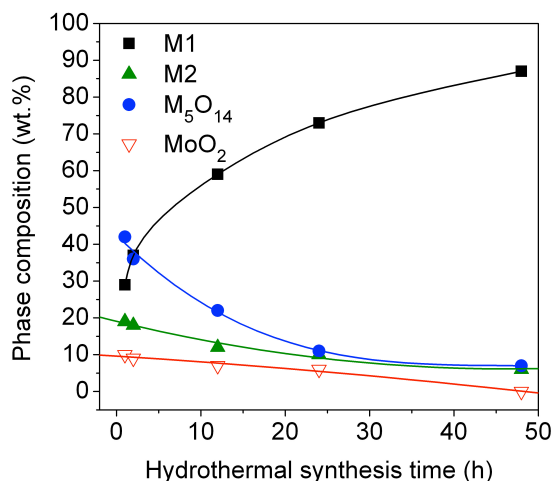


Figure 1. Evolution of phase composition of MoVTeNb oxides as a function of the hydrothermal reaction time at T=448 K, p=14 bar.

In conventional hydrothermal recipes, the synthesis of MoVTeNb oxides is performed starting from suspensions of the oxides or metal salts in water and keeping the mixture for 48 h at T=448 K under autogeneous pressure (Fig. S1A).^[2, 8d] Fig. 1 shows the phase composition of hydrothermal reaction products after crystallization as a function of time. The chemical composition of complementary precipitates and mother liquors are presented in Figure S2 of the Supporting Information. Hydrothermal synthesis for short times yielded a mixture of M₅O₁₄-like oxide (M=Mo, V, Nb), the pseudo-hexagonal M2 phase (ICSD 55098)^[5b], the M1 phase, and a rutile-like phase MO₂ (M=Mo,V). With increasing reaction times, the fractions of M₅O₁₄ and M2 decrease while M1 becomes the main product.

The synthesis was monitored applying *in-situ* Raman spectroscopy. The assignment of the bands is discussed in detail in the Supporting Information. Mixing Mo and V salts at 313 K (Fig. 2) results in the formation of {Mo₇₂V₃₀} Keplerate ions (868, 945 cm⁻¹)^[12] as soon as the acidification of the solution by addition of vanadyl sulfate results in pH<4 (Fig. S3). This observation is in perfect agreement with the recently reported spontaneous formation of {(M)Mo₅}₁₂{Mo₂}₃₀-type Keplerates by addition of preformed {Mo^VO}²⁺ units to an acidified molybdate solution.^[13] These species contain the desired {(M)M₅} structural motives that represent essential building blocks of the M1 structure, and V atoms are already situated in proper linking positions between these pentagonal units. The broad appearance between 1000 and 940 cm⁻¹ indicate the additional contribution of macroisopolyanions [Mo₃₆O₁₁₂]⁸⁻ (Fig. S3).^[14] Subsequent addition of Te and heating to 353 K causes re-dissolution of the pre-formed {Mo₇₂V₃₀} Keplerate clusters and formation of heteropolymolybdate anions [(TeO₃)₂Mo₁₂O₃₆]⁴⁻ (773, 786, 808, 967 cm⁻¹)^[15] which are structurally closer related to the M2 phase and to other undesired crystalline phases like Te-

Mo₅O₁₆. Free telluric acid (644 cm⁻¹)^[16] Anderson-type heteropolyanions [Te(Mo,V)₆O₂₄]ⁿ⁻ (952, 1010 cm⁻¹)^[17] and re-dissolved vanadium species (975, 1050 cm⁻¹) are also present. The final addition of NH₄[NbO(C₂O₄)₂] \cdot xH₂O to the Mo-V-Te solution after cooling to 313 K did not change the Raman spectrum.

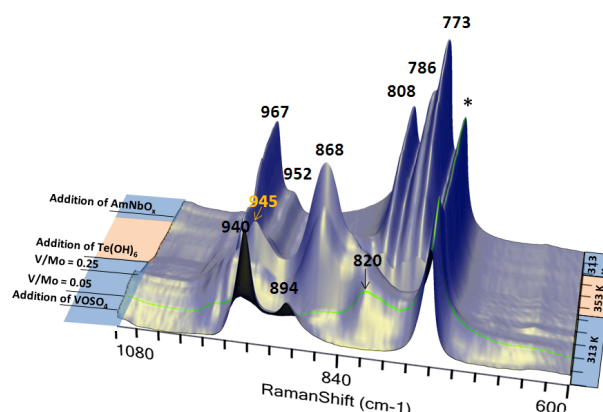


Figure 2. *In-situ* Raman spectra during preparation of the aqueous suspension before hydrothermal synthesis. For details see Supporting Information. Symbol (*) indicates a band of the sapphire window of the Raman probe.

During subsequent heating from 313 K to hydrothermal reaction temperature 448 K (Fig. 3), molybdotellurates are decomposed at T>393 K under intermediate formation of [Mo₃₆O₁₁₂]⁸⁻ ions (988, 952 and 912 cm⁻¹) leading to precipitation of nano-crystalline M₅O₁₄ (M=Mo,V,Nb) oxide (835, 930 cm⁻¹) at T > 418 K,^[18] which is in good agreement with the predominance of this phase in the product obtained after short reaction times (Fig. 1). Since Nb is almost completely incorporated into the solid (Fig. S2), it is assumed that this element plays an important role in the formation of the M₅O₁₄ phase owing to its preference to occupy the MO₇ pentagonal bipyramidal position in the {(M₅)M} units.^[5b]

The spectral changes under isothermal conditions (Fig. S4) become more evident by analyzing the covariance of the observed Raman bands (Fig. 4). The broad contribution between 900 and 800 cm⁻¹, which may indicate {(M)M₅} units in nano-crystals of M₅O₁₄ and M1 (Figs. S6-7),^[7b] and the band at 952 cm⁻¹ for [Mo₃₆O₁₁₂]⁸⁻ anions in solution, remained almost unchanged during the entire reaction. The macro-isopolyanions can be considered as species existing in equilibrium with the solid phase, being responsible for the substantial amount of Mo detected in solution after synthesis. The main changes are related to the growth of bands at 969, 931, 880, 800, 726, and 323 cm⁻¹. Since the resulting product is the precursor of a mixture of M1, M2, M₅O₁₄ and MO₂ phases (Fig. 1), an unambiguous assignment of these bands is not possible.

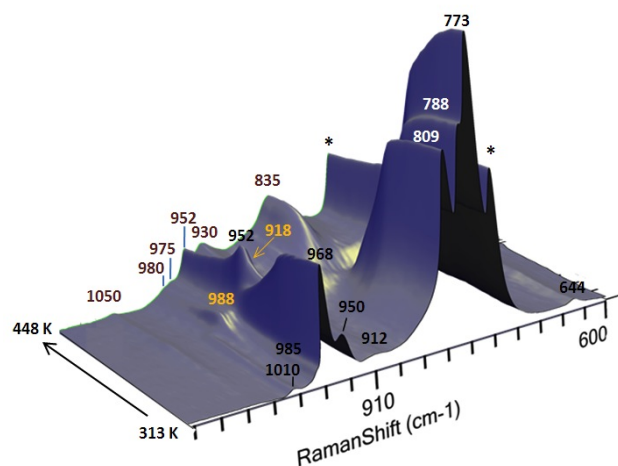


Figure 3. Raman spectra taken during heating from 313 K to 448 K.

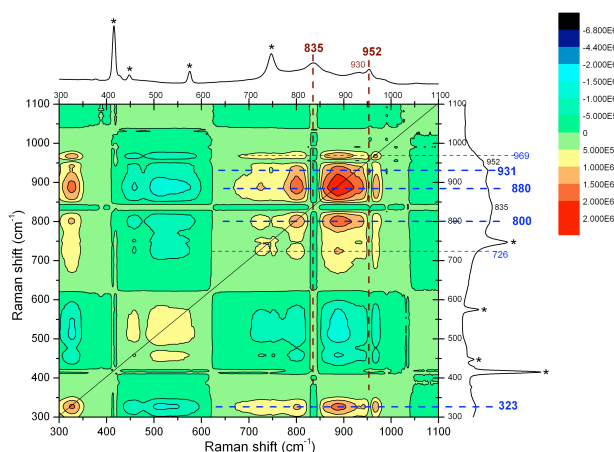


Figure 4. Covariance analysis of *in-situ* Raman bands measured during hydrothermal reaction at 448 K. Initial spectrum shown on top; spectrum after 15h on the right side.

Based on our knowledge acquired by *in-situ* Raman spectroscopy, we conceptually designed a novel, rational synthesis of phase-pure M1 MoVTeNb oxide by stepwise addition of V and Te under pressure (Fig. S1B). At first, a nano-crystalline oxide containing $\{(M)M_5\}$ units (812 cm^{-1}) was formed by hydrothermal reaction of Mo and Nb precursors at 448 K (Fig. S5). At this point, an aqueous solution of VOSO_4 is pumped into the autoclave with the aim to cross-link the pentagonal units with vanadium species, as depicted in Scheme 1. The subsequent introduction of Te as inorganic template is responsible for formation of nano-crystalline M1 ($816, 870(\text{sh}), 919$ and 975 cm^{-1}) with enhanced precursor yield (Tab. S1),

which is of advantage in view of an improved control with respect to the final chemical composition of the solid. The isolated precipitate can be crystallized at 923 K in

argon atmosphere resulting in phase-pure M1 (Figs. S6-7). The surface area of the new M1 is increased as a consequence of controlled initial precipitation of Mo species, which takes place through the decomposition of Mo oxalates (bands at 904 and 951 cm^{-1} in Fig S5). The retarded addition of Te avoids the formation of Te-Mo polyanions in solution, allowing precipitation of higher amount of product in shorter synthesis times at lower temperatures. The new M1 catalyst is characterized by distinguished selectivity to acrylic acid in selective oxidation of propane resulting in an increase in space time yield by a factor of five (Tab. S1).

In summary, it is shown that the simultaneous study of multiple variables during formation of complex nano-structured solids in terms of inorganic systems chemistry^[19] offers a great potential in directing the properties of materials towards desired functionalities.

In-situ investigation of nano-particle synthesis provides insight into molecular processes of self-assembly and precursor formation.^[8a, 8c, 20] Many studies reported so far are focussed on binary and ternary systems.^[20c] However, the complexity of materials required in the field of heterogeneous catalysis necessitates controlled synthesis strategies to create multi-component systems involving structures in the nano- and micro-meter length scale creating surface terminations unexpected from the bulk crystal structure.^[21] The present study of a practical system with substantial chemical complexity exemplifies a new paradigm of inorganic synthetic chemistry. Complex functional materials are assembled by generating sequences of reactions creating each a sub-unit of the target structure. This was enabled by combining the mild reaction environment of solvothermal synthesis with novel analytical capabilities that guide through *in-situ* monitoring of identified intermediates. It allows handling a wide spectrum of chemical elements. We describe here a platform procedure for a systemic synthesis approach aiming at generating complex functionality from structural inorganic concepts using a minimum of unit operations.

Experimental Section

The classical and step-wise synthesis procedures of MoVTeNb oxides are described in detail in the Supporting Information. *In-situ* Raman measurements were performed applying a Kaiser Optics Raman Spectrometer RXN1 equipped with a fiber-optic probe head, using a Laser wavelength of 785 nm . Experimental details of characterization techniques and catalytic tests are summarized in the Supporting Information.

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