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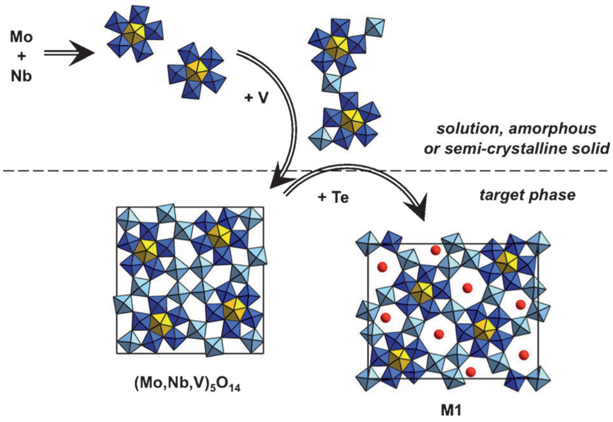
Aiding the Self-Assembly of Supramolecular Polyoxometalates under Hydrothermal Conditions To Give Precursors of Complex Functional Oxides**

*Maricruz Sanchez Sanchez, Frank Girgsdies, Mateusz Jastak, Pierre Kube, Robert Schlögl, and Annette Trunschke**

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 nanocrystalline molybdenum–vanadium-based multimetal 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 structure (M = Mo, V, W, Ti, Nb; 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 (Scheme 1). Needle-like nanocrystals grow 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, which are 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 (Scheme 1), is another common feature that is also known as a key constituent of larger structural aggregates that are observed for reduced molybdates in solutions.[6] Icosahedral molecular systems of the type $\{(Mo^{VI})Mo_5^{VI}\}_{12}(\text{linker})_{30}$, which are 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]



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

The complexity of the M1 structure provides site isolation, as it is required for a high selectivity in oxidation reactions of C_3 and C_2 feedstock.[9] Current synthetic approaches to phase-pure M1 suffer from insufficient reproducibility,[10] and apparently similar M1 catalysts may feature very different catalytic behavior.[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.

Herein, we present studies of 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 to the desired product, thereby avoiding the co-formation of unwanted phases.

According to 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 (Supporting Information, Figure S1 A).[2,8d] Figure 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 M_5O_{14}-like oxide (M = Mo, V, Nb), the pseudo-hexagonal M2 phase (ICSD 55098),[5b] the M1 phase, and

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[*] Dr. M. Sanchez Sanchez, Dr. F. Girgsdies, M. Jastak, P. Kube, Prof. Dr. R. Schlögl, Dr. A. Trunschke
Department of Inorganic Chemistry
Fritz-Haber-Institut der Max-Planck-Gesellschaft e.V.
Faradayweg 4–6, Berlin (Germany)
E-mail: trunschke@fhi-berlin.mpg.de
Homepage: http://www.fhi-berlin.mpg.de/acnew/welcome.epl

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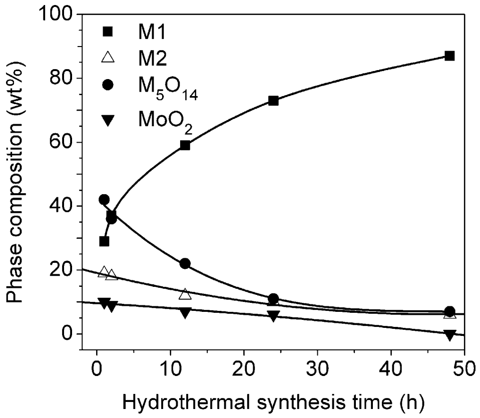


Figure 1. Evolution of the phase composition of MoVTeNb oxides as a function of the hydrothermal reaction time at $T = 448$ K, $p = 14$ bar.

MoO_2. With increasing reaction times, the fractions of M_5O_{14} 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 (Figure 2) results in the formation of $\{Mo_{72}V_{30}\}$ Keplerate ions (bands at 868, 945 cm^{-1})[12] as soon as the acidification of the solution by addition of vanadyl sulfate results in a pH value of less than 4 (Supporting Information, Figure S3). This observation is in perfect agreement with the recently reported spontaneous formation of $\{(Mo)Mo_5\}_{12}$-$\{Mo_2\}_{30}$-type Keplerates by addition of preformed $\{Mo^VO\}^{2+}$ units to an acidified molybdate solution.[13] These species contain the desired $\{(M)M_5\}$ 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 $[Mo_{36}O_{112}]^{8-}$ (Supporting Information, Figure S3).[14] Subsequent addition of Te and heating to 353 K causes re-dissolution of the pre-formed $\{Mo_{72}V_{30}\}$ Keplerate clusters and formation of heteropolymolybdate anions $[(TeO_3)_2Mo_{12}O_{36}]^{4-}$ (773, 786, 808, 967 cm^{-1}),[15] which are structurally more closely related to the M2 phase and to other undesired crystalline phases, such as $TeMo_5O_{16}$. Free telluric acid (644 cm^{-1}),[16] Anderson-type heteropolyanions $[Te(Mo,V)_6O_{24}]^{n-}$ (952, 1010 cm^{-1}),[17] and re-dissolved vanadium species (975, 1050 cm^{-1}) are also present. The final addition of $NH_4[NbO(C_2O_4)_2]\cdot x\,H_2O$ to the Mo-V-Te solution after cooling to 313 K did not change the Raman spectrum.

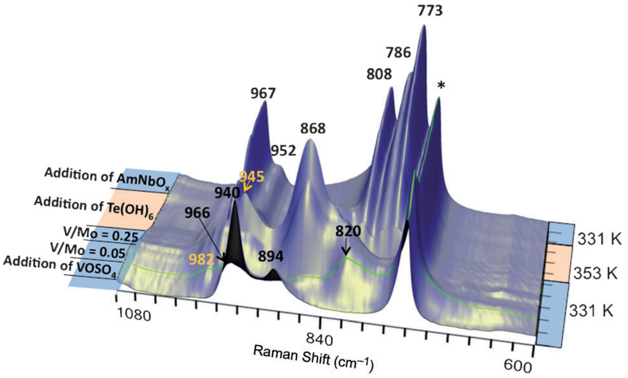


Figure 2. In situ Raman spectra recorded during preparation of the aqueous suspension before hydrothermal synthesis. For details, see the Supporting Information. The asterisk indicates a band of the sapphire window of the Raman probe.

During subsequent heating from 313 K to hydrothermal reaction temperature 448 K (Figure 3), molybdotellurates are decomposed at $T > 393$ K under intermediate formation of $[Mo_{36}O_{112}]^{8-}$ ions (988, 952, 912 cm^{-1}), leading to precipitation of nanocrystalline M_5O_{14} oxide (M = Mo, V, Nb; 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 (Figure 1). As Nb is almost completely incorporated into the solid (Supporting Information, Figure S2), it is assumed that this element plays an important role in the formation of the M_5O_{14} phase owing to its preference to occupy the MO_7 pentagonal bipyramidal position in the $\{(M_5)M\}$ units.[5b]

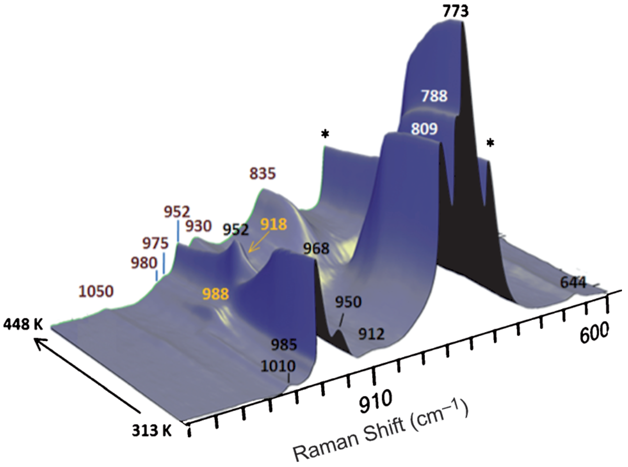


Figure 3. Raman spectra taken during heating from 313 K to 448 K.

The spectral changes under isothermal conditions (Supporting Information, Figure S4) become more evident by analyzing the covariance of the observed Raman bands (Figure 4). The broad contribution between 900 and 800 cm^{-1}, which may indicate $\{(M)M_5\}$ units in nanocrystals of M_5O_{14} and M1 (Supporting Information, Figures S6, S7),[7b] and the band at 952 cm^{-1} for $[Mo_{36}O_{112}]^{8-}$ 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, which are 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}. As the resulting product is the precursor of a mixture of M1, M2, M_5O_{14}, and MoO_2 (Figure 1), an unambiguous assignment of these bands is not possible.

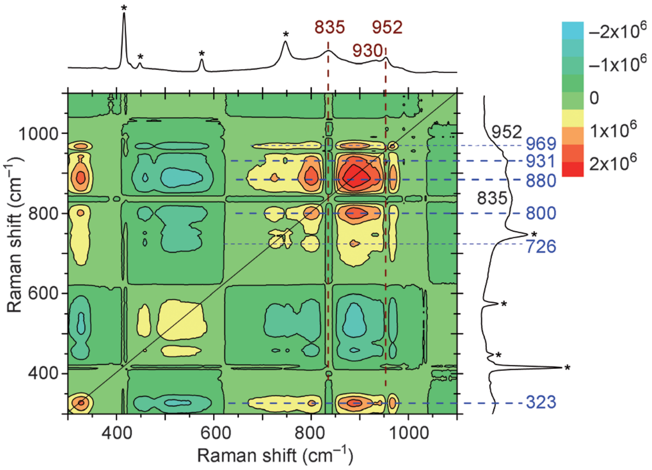
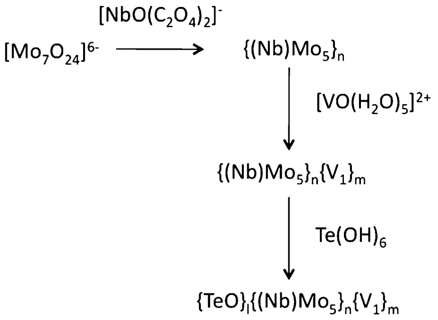


Figure 4. Covariance analysis of in situ Raman bands measured during hydrothermal reaction at 448 K. The initial spectrum is shown at the top; the spectrum acquired after 15 h is shown on the right-hand side.

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 (Scheme 2; Supporting Information, Figure S1B). At first, a nanocrystalline oxide containing {(M)M$_5$} units was formed by hydrothermal reaction of Mo and Nb precursors at 448 K (Supporting Information, Figure S5; band at 812 cm^{-1}). 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 nanocrystalline M1 (Supporting Information, Figure S5; bands at 816, 870(sh), 919, 975 cm^{-1}) with enhanced yield of precursor (Supporting Information, Table 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 an argon atmosphere, resulting in phase-pure M1 (Supporting Information, Figures S6 and S7). 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 Figure 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 high selectivity to acrylic acid in selective oxidation of propane, resulting in an increase in space–time yield by a factor of five (Supporting Information, Table S1).



Scheme 2. Stepwise synthesis of phase-pure M1 precursors.

In summary, it is shown that the simultaneous study of multiple variables during formation of complex nanostructured 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 nanoparticle synthesis provides insight into molecular processes of self-assembly and precursor formation.[8a,c,20] Many previously reported studies have focused on binary and ternary systems.[20c] However, the complexity of materials required in the field of heterogeneous catalysis necessitates controlled synthesis strategies to create multicomponent systems involving structures in the nano- and micrometer 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 subunit of the target structure. This was enabled by combining the mild reaction environment of solvothermal synthesis with novel analytical capabilities that guide by 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 that aims at the generation of complex functionality based on structural inorganic concepts using a minimum of unit operations.

Experimental Section

The classical and stepwise 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 probehead, 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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