

Propane Oxidation over Nanostructured Molybdenum-Vanadium Mixed Oxides: In-situ Studies of the Geometric and Electronic Structure

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Introduction

The selective oxidation of propane to acrylic acid over mixed oxides of the type MoVTeX has now reached claimed performances close to the commercialisation limit. Serious problems with reproducibility, stability and the losses of Te compounds make it, however, difficult to see a rapid development of a process technology on the basis of such a catalyst.

The hydrothermal synthesis route developed more recently¹⁾ leads to active and selective systems that are of different structure than the famous M1/M2 active materials and contain not necessarily Te as active component.

These facts and findings challenge our general understanding about the mode of operation of these catalysts²⁾ and lead to the following issues that we address in a collection of in-situ and supporting experiments: 1. How is the M1 structure evolving during the synthesis process? 2. Is the crystalline M1 structure indeed the active phase? 3. What is the origin of the synergy between M1 and M2 phase? Is a mixed material really superior over a single phase oxide? 4. Are there indications for non-crystalline components of relevance for catalysis? 5. What is the functional relation between the M1 phase and the Mo₅O₁₄ structure that is also active? 6. Are there preparative measures to stabilize the M1 structure and to arrive at phase-pure materials?

We consider MoVTeX as end member of a series of catalysts systems with increasing complexity³⁾ ranging from MoO₃ in various forms over Mo₅O₁₄ to the complex oxides. The fact that all three system can in principle selectively oxidize propane shows that there is no fundamental need for the enormous chemical complexity of the systems. It is evident, however, that only the complex systems reveal high performance and stability. This led us to formulate the working hypothesis that MoVTeX is a suitable matrix that brings about under reaction conditions a simplified Mo-V-oxide being the active catalyst. This system is metastable and lead to restructuring in still simpler oxides such as MoO₃ and M2 phase that we find as “synergistic” end products of a dynamical transformation of the pre-catalyst. The abundance of the deactivation products scale with the catalytic efficiency of the system and explain the observation of synergy from phase analysis. Te in such a scenario can have many functions as supporting factor for formation and transformation of the active solid but should not be involved in the organic reactions. This explains the inherent lability of the Te component as well as its beneficial functions by forcing the catalyst to restructure as consequence of the gas phase transport of Te as oxo acid.

Results and discussion

Several in-situ experiments were performed in order to produce facts to support or modify the working hypothesis.

Systems of MoVTeNb oxide with various promoters and diluents were prepared by the standard slurry method and by hydrothermal processing. Phase-pure Mo₅O₁₄ was prepared as model system for complex in-situ analysis according to our previous investigations⁴⁾.

The catalyst synthesis was investigated in the liquid and solidification state by in-situ Raman spectroscopy revealing the formation of a Mo tellurate as the immediate precursor to multinary phase formation.

The calcination process was studied by in-situ DSC and in-situ XRD. The formation of the catalyst can only be coarsely studied under vacuum conditions as at the same temperatures where under atmospheric pressure phase transformations do occur. Also under vacuum the phases do change but different products arise

under different pressures. This highlights the intrinsic metastability of the system being adjusted by the chemical potential of oxygen in a delicate way. The observation explains the critical character of the calcination process and the complex double calcination necessary and gives one hint to the origin of the stability-reproducibility issue. The formation of the M1 phase was observed as multi-step process with the long-range ordering being formed in-plane and out-of plane with respect to the (001) face at different temperatures and with different kinetics. This explains the gross morphology changes of the system seen in in-situ SEM.

In-situ EXAFS and in-situ XRD studies of the crystallisation behaviour of Mo_5O_{14} that is quite similar to that of MoVTeX revealed that a series of discernible polycondensation steps associated with selective ligand abstraction reactions precedes the kinetically very sensitive (holding time in calcination) formation of the complex phase. This process is only possible under conditions of slight oxygen sub-stoichiometry. Too much oxygen leads to binary oxides in high oxidation states, too little oxygen to amorphous products decomposing in crystalline sub-oxides.

Surface analysis and leaching experiments revealed ample evidence together with careful electron microscopy (beam damage problem) that the catalysts are at their surfaces of different chemical composition and ordering than in their bulk. A layer of 1-2 nm thickness is the typical termination situation of well-crystalline MoVTeX systems as well as of highly ordered Mo_5O_{14} . The systems are enriched in non-Mo elements. High pressure in situ XPS experiments with Mo_5O_{14} revealed amongst many other facts the necessity of a strong enrichment in V and a migration of the W component in active catalysts whereas highly crystalline materials without activity terminate with a stoichiometry close to the nominal bulk value.

Conclusions

We find strong evidences for the dynamical nature of the catalysts systems. The instability and volatility are part of the function of the system that cannot perform catalysts in its perfectly crystalline static case. The essential and as yet uncontrolled process finding the optimum between stability (structural perfection) and reactivity (defectation) explains the chemical complexity, the delicacy of the preparation and the reproducibility problems. Nanostructuring with compartmentation of the reactive pre-catalyst may be a solution to the problem allowing to fine-tune the defect structure and to suppress collective dynamical restructuring that leads to non-reactive perfect crystals or to undesired phase-transformations.

References

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