

## 7 CONCLUSIONS

The focus of this research study was the development of an improved catalyst for oxidation propane to acrylic acid. The work presents the study of chemical and phase composition of solid precursor of  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}$  catalyst and phase purification by leaching process. This work also shows the highly complex interaction between the initial compounds ammonium heptamolybdate, ammonium metavanadate, ammonium niobium oxalate and telluric acid. During the mixing process several reactions happened simultaneously and led to an important catalyst precursor for the final structure. Although numerous current literatures describes the multi metal-oxide system concerned, a catalyst precursor formation mechanism can be define that is based on the current literature as well as from data XRD, BET, thermal analysis and SEM/EDX measurements shown in this work.

Whilst the preparation routine of most of the multi metal oxide catalyst shows striking resemblance (solution of molybdate, vanadate, heating to  $80^\circ\text{C}$ , spray drying, calcination in inert gas), to the preparation routine of  $\text{MoVTenbOx}$ , the former procedure leads to well defined single phase material and the latter one to multiphase material, as impressively shown by SEM/EDX images. In combination of molybdenum, vanadium and tellurium ions in solution 1 were identified as Anderson-type heteropoly anion phase  $(\text{TeMo}_6\text{O}_{24})^{n-}$ , formed in samples prepared at pH 3.0-4.5. Addition of niobium oxalate species in a complex solution leads to hydrolyze to hydrated  $\text{Nb}_2\text{O}_5$  precipitate and turn into slurry formation. As the slurry formation is delayed, an effect due to the pH shift alone is unlikely; it is rather believed that Nb itself acts as precipitating agent, after the complex is destroyed in a kinetically controlled step.

In order to increase the surface area of the catalyst, diluents has been added during preparation of the precursor. Aerosil 300 or silica support is most effective diluents that lead to a higher surface area affected by the solid state transformation kinetics and control the catalytic performance. The loading of diluents into the active material is in ratio 50: 50. Oxalic acid was used successfully during catalyst preparation to modify the psychochemical properties of  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}$  catalyst. A comparison shows that the modification not only enhances propane conversion of the catalyst, but also improves its acrylic acid selectivity. This is due to the reductive oxalic acid possesses a suitable redox capacity and increases of surface area of the catalyst.

Spray drying of the slurry preserves its structural and elemental composition. The spray dried material is only a precursor, as the calcination steps lead to formation of the active material. During the pre-calcination step in synthetic air, water and nitric oxides are evaporated, it is crucial that the pre-calcination temperature is below the formation of inactive orthorhombic  $\text{MoO}_3$ . Inert gas calcination forms the final catalyst by formation and separation of many different phases with evaporation of tellurium and molybdenum. Calcination in oxidative atmosphere does not lead to M1, but to a large fraction of orthorhombic  $\text{MoO}_3$  and  $\text{TeO}_2$  whereas calcination in inert atmosphere leads to a multi-phase material, including M1 and M2. In order to increase the surface area of the catalyst, diluents has been added during preparation of the precursor. Aerosil 300 or silica support is most effective diluents that lead to a higher surface area affected by the solid state transformation kinetics and control the catalytic performance. The loading of diluents into the active material is in ratio 50: 50.

From the results, we found out that the drying method and calcination temperature affect the surface area of the catalyst. It will change the morphology of the catalyst particle and the surface will become more porous. It is also further proposed that the calcination temperature will affect the performance of MoVTeNb oxides catalyst, which is very well known to be inactive in propane oxidation if the catalyst leads to the formation of significant amount of MoO<sub>3</sub> during calcination. These suggest that all of the catalysts have a different surface bulk structure or even surface morphology which is in good agreement with the BET surface measurement results. MoVTeNb oxide catalysts that have high surface area correlates well with a high catalytic activity and those that calcination under He contaminated with O<sub>2</sub> led to smaller surface area. An active catalyst should contain at least two major crystal phases that is M1 and M2. It is proposed that phase M1 is active in propane activation but relatively unselective for the acrylic acid formation, while phase M2 is reasonably active for propane activation and fairly selective for acrylic acid formation.

The purpose of leaching of the catalysts is an attempt to remove the *'useless ions'* in the catalysts (non-M1 phase) and to keep the *'useful active component in M1 phase'*. It is also considered to be beneficial to the performance of the surface modification by nanostructuring of active M1 phase. Thus, the present study provides a method for the preparation of a metal oxide catalyst comprising oxides of molybdenum (Mo), vanadium (V), tellurium (Te) and Niobium (Nb) and having a modified surface structure, comprising the steps of

- i) providing a precursor and calcined catalyst material comprising oxides of Mo, V, Te and Nb,

- ii) modification on catalyst preparation
- iii) purification on catalyst material with treating agent i.e.; water, strong acid and base at different time

Some further notification about the potential effect of leaching is depending on the nature of solvent in selectively eliminate components by dissolution of metal-ligand structure in the catalyst. It is predominantly from the surface by kinetically controlled or from the bulk by thermodynamically control. Redeposition of dissolved species to the surface may also occur. The leaching phenomenon can also present a sorption effects from the solvent itself where the solvent molecules can be adsorbed on the surface or even penetrate into the bulk with the chemical interaction that may cause the bond rupture and a structural arrangement on specific sites causing enlargement of a particular crystal axes. The solvent molecules form bonds to the solid and thus facilitate breakage of bonds in the oxide system where a structural arrangement is somehow catalyzed in this way.

This work has defined critical extrinsic variables for a successful synthesis of the stable phases being the kinetics of ligand removal, the control of the cation oxidation state and the active phase of the catalyst. From the BET surface area results, one can anticipate that the higher surface area catalyst would exhibit higher activity. Addition of reductive oxalic acid exhibits high surface area  $5.9 \text{ m}^2/\text{g}$  compared to standard sample only  $3.3 \text{ m}^2/\text{g}$ . Therefore, addition of diluents and oxalic acid also influence in contributing to high surface area about  $28 \text{ m}^2/\text{g}$  for standard catalyst whilst  $37 \text{ m}^2/\text{g}$  for the diluent-modified catalysts. Hence, the surface area result is one of the major contributive factors governing the catalyst activity.

The SEM/EDX analysis has revealed the multi-phase nature and morphology of the MoVTenb catalyst. It has further confirmed that the phase formation occurs kinetically after the gas evolution resulting from ligand removal. The EDX analysis in general and the correlation with XRD in particular shows that the pre-calcination and calcination step was inadequately conducted within the goal of removing all reducible species prior to catalytic phase formation. The morphology of the catalyst shows that the specific character of every sample will be different during drying, calcination or leaching depending on the conditions and media used.

The diffraction pattern for XRD investigation revealed all samples contain mainly the M1 and M2 phases and some other minority phases. The M1 and M2 phases can only be obtained after the sample go through the calcination process. The formation of the crystalline phases M1 (ICSD 55097), M2 (ICSD 55098) indicates in undiluted and diluted  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}$  catalyst. In addition, weak reflection of orthorhombic  $\text{MoO}_3$  (ICSD 05-0508) and  $\text{TeMo}_5\text{O}_{16}$  (ICSD 31874) can be detected from the sample. Rietveld refinement and quantification analysis reveal that ratio of M1 is around 50-60 % and M2 phase about 20-30%. Leaching samples also remains the ratio of M1 and M2 phase as standard samples. This also indicates that when the leaching process occurs in oxide phase, the structure or chemical bonds were strong enough to resist breakage and thus could not be leached out easily.

The thermal analysis data clearly reveal the complex interplay of ligand removal, polycondensation and phase formation occurring in several intertwined processes separated by temperature. The separation is affected by the redox chemistry of the system. It can be recommended that the thermal treatment should follow *in-situ* measurement where the system of kinetic and reaction of MoVTeNb system may well bring the better complex catalytic system with the formation of the metastable desired phase mixture M1 and M2.

In the future the relationship of model development and complex real system can be applied by controlling structure formation using in-situ techniques. In-situ XRD and DSC are the suitable method in order to study the solid state formation. Therefore, the structure and morphology of this complex system also can be improved via extraction technique. The activation after leaching also can improve the structure rearrangement. These might be the key steps for achieving high activity and high phase purity of the catalyst in improving the catalytic activity of propane oxidation to acrylic acid.