

## CHAPTER FIVE

The performance of the effective  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$  catalyst depends on several parameters involved in preparing the catalyst, which includes the method of preparation and activation procedure. Various solids prepared, composing of Mo, V, Te, Nb and oxides of the support, are further characterised to define their structural, thermal and chemical properties. This information would directly contribute to the understanding of catalyst synthesis and the defects properties of the catalyst, which in turn is crucial to a systematic and rational approach in catalyst design.

From the BET surface area result, one can anticipate that the higher surface area catalysts would exhibit higher activity. Hence, the surface area result is one of the major contributive factors governing catalyst activity. Apparently, there is a relationship between pre-calcination temperature and surface area where the surface area increases from  $2.3 \text{ m}^2\text{g}^{-1}$  to  $10.5 \text{ m}^2\text{g}^{-1}$  at 548 K and decrease to  $5.4 \text{ m}^2\text{g}^{-1}$  after that. The use of viscosity enhancers at pre-calcination temperature of 548 K reduces the surface area to only half as compare to the catalyst by standard recipe due to blocking of the accessible pores by these bulky materials. Addition of citric acid during the precursor stage is deleterious to surface area as citric acid is deemed to destroy the catalyst by effects such as leaching, sintering at high temperature and unfavourable precipitation environment (acidic). The addition of various metal promoters (Co, Cr, and Ni) to the bulk contributes to the changes of surface area in different extend. One would expect that when more of such foreign metal being added, more perturb the bulk would be as exhibited by Co. The addition of Cr and Ni somewhat deviates from norm,

which can be seen as experimental repeatability rather than the inherent of the treatment that these systems have been subjected to.

The SEM-EDX analysis has revealed the multi-phase nature of the MoVTe samples. It has further confirmed that the phase formation occurs kinetically after the gas evolution of the ligand removal. In some cases the ligand removal did not happen. The pre-calcination led to a carbon-inorganic composite material with maybe interesting but non-catalytic properties. The promotion had little morphological effect besides separate phase formation of the later transition metal oxides. The EDX analysis in general and the correlation with XRD in particular shows that the pre-calcination step was inadequately conducted within the goal of removing all reducible species prior to catalytic phase formation. The fact that apparently compact oxide crystals still contain large elemental excess of oxygen as water is an indication that there is a hierarchy of structures with the nanostructural details not being seen with the SEM. It can be expected that after high-temperature treatment (e.g. in operation conditions) there will be a significant number of voids and defects present in crystals that appear completely flat and smooth at ambient conditions of SEM observation. In conclusion the thermal treatment of the precursor gel will require much improvement in optimisation of temperature levels, time profiles and chemical composition to allow the idea of converting a ligand-containing gel of the MoVTe composition into a mixed oxide with a majority of material exhibiting the M1 composition and structure.

The XRD investigation revealed all samples contain mainly the hex phase of the target systems with the pentagonal bipyramid motif. The ortho phase is present in some samples as a minority contribution. The literature claim about the assignment of phases using the famous five reflections must be taken with great care as evidenced by the

reference preparation. The phase formation and phase distribution can be affected by changing the redox reactions during pre-calcination and calcination. This indicates the highly metastable character of the catalytically relevant target phases. The admixtures of foreign phase that does not contain the pentagonal bipyramid leads the way to stabilisation of the system. It also appears that the parent phase with the pentagonal bipyramid namely the  $\text{Mo}_5\text{O}_{14}$  phase may be of catalytic relevance. In other catalysts used for oxidation of propene and of acrolein this material is the main catalytic active constituent. XRD is a suitable method to investigate the phase inventory and potentially to infer the kinetics of its formation. There is still much room for improvement in the phase composition of the catalyst taking the literature data of Grasselli as a lead. The analysis has shown how critical the redox chemistry during calcination affects the final structure and how well the systems remember their thermal pre-history. A working hypothesis for the mode of operation of transition metal additives has been found based on the assumption that a structure-activity relationship is valid stating that the ortho phase is the key factor for good catalytic performance in propane oxidation.

The temperature reduction profile shows that at the lowest pre-calcination temperature, structural water was not completely removed and hence allowed the material to be in a stable form and being resistant to chemical reduction. With lower pre-calcination temperature, the material contains too much volatiles and the evolution of these volatiles will continue during reaction giving rise to unwanted and often irreproducible effects. At higher pre-calcination temperature, destruction of phase inventory of these “pre-calcined MoVTe” that is responsible for the reaction process could take place. Thus, as a best compromise from the TPR data one can conclude that the best pre-calcination temperature is at 548 K. Addition of viscosity enhancer, *i.e.* PEG and HEC, contributes adversely to the crystallization process as these excessive

organic additives is preventing the formation of a stable phase inventory during precalcination by severely lowering the oxygen partial pressure. Thus, only amorphous materials were formed. The peak profile gives indications that there is a single-phase decomposition and the resulting product catalyses the deep decomposition of the rest of the material in a diffuse and unresolved process limited by the diffusion out of the inner part of the compact solid. The superimposed peak at higher temperature indicates that the materials that give rise to this feature are not geometrically intermixed with the main phase, consistent with the multiple morphologies seen in the SEM images. The formation of lower valent cations mononuclear 1:2 complexes with the strongly complexing action of citric acid and the subsequent multi-step decomposition pattern lead to the formation of a nanostructured very reactive oxide reducible at 565 K. The fact these samples exhibit no porosity and very compact in their morphology imply that during the precalcination step high temperatures must have been present leading to sintering and even to the decomposition of the oxide structure. By adding promoter, the redox properties of the systems are affected significantly by the increase of reducibility as much as the amount of oxygen removed is concerned. This must have been achieved through alteration of the main structural features giving rise to the allegation that most of the promoter became dissolved in the main matrix. The fact that all promoted samples exhibit significant surface areas indicates that all promoter species seem to stabilize small crystallites and prevent sintering at the main calcinations temperature. It is expected that the promoters act as linkers between supramolecular clusters and so to stabilize a non-dense ("defective") nanostructure making it more difficult for Ostwald ripening to occur at temperatures below the breakdown of the oxygen sublattice. To exploit this reactivity it would be highly desirable to modify the calcinations procedure such as to try to obtain a crystalline precursor after the precalcination.

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. This redox chemistry can be modified by the addition of redox-active transition metal species. It can be recommended that the addition of a very small amount of Cr to the system and appraisal on the optimal calcination process may well bring about a very different catalyst as the solid state transformations will occur at lower temperatures and at a more constant chemical potential without residual auto reduction during the main calcination step will not interfere with the formation of the metastable desired phase mixture M1/M2.