Chapter 1

Introduction

INTRODUCTION

The economy of Malaysia is largely built on their vast resources of petroleum and palm oil. The profit for petrochemical processing could be substantially increased if suitable catalyst material could be developed, that would turn them into products of higher value, e.g. acrolein or acrylic acid. Molybdenum oxide based catalysts are good candidates for such types of reaction as they show high rates and superior selectivity for many selective oxidation reactions. Empirical optimisation through doping with various cations has already reached a high level again stressing the huge potential of such catalysts. Mitsubishi has recently patented a material with the approximate composition of $Mo_1V_{0.33}Te_{0.22}Nb_{0.11}O_x$. [1, 2, 3, 4]. Thorough characterisation of this material has led to the identification of two phases displayed in Figure 1.1. The first one (M1) is orthorhombic and isostructural of $Cs_{0.7}(NbW)_5O_{14}$ [5] and consists of pentagonal bipyramides and hexagonal and heptagonal channels as the main structural motifs. The second phase (M2) is pseudo hexagonal [6]. There is an ongoing debate about the nature of the active sites, however, it is generally accepted that highly specific local electronic structures of the active metal sites are essential for the catalytic performance [7]. Figure 1.2 illustrates the variation of terminal Mo-O bond distance as measure for the local electronic structure in Mo^{VI} and Mo^{V} polyhedra [8, 9, 10, 11]. The variation in bond distance, reflecting modifications of the d-states hybridisation, is achieved *through variation of the connectivity of oligo-molybdates comprising octahedra in* differing relations and combinations of octahedra with other polyhedra [12].

As simple Mo oxides contain only a small selection of these distances, it is easy to understand that surface defects that inevitably will alter the local connectivity are the tool by which the optimisation of the catalyst is performed [13].

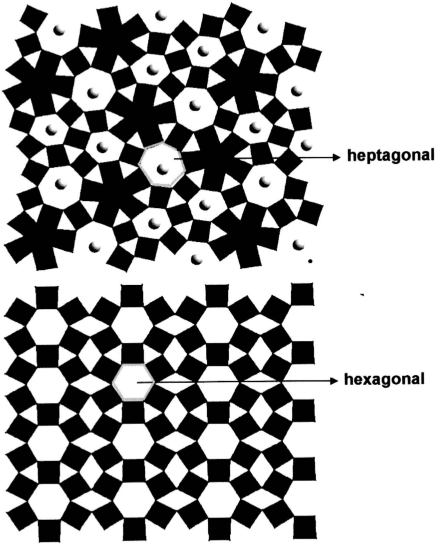

Figure 1.1 The two phases of $Mo_1V_{0.33}Te_{0.22}Nb_{0.11}O_x$, *M1 (above) and M2 Phase (below)*

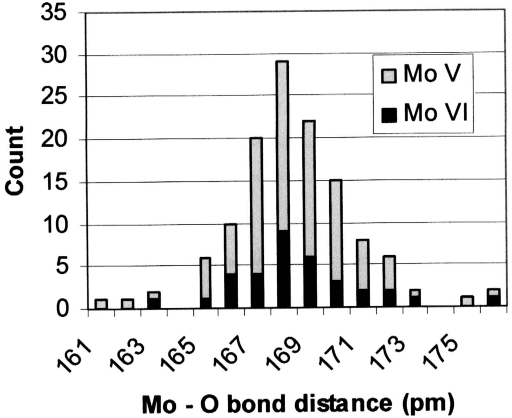

Fig 1.2 Typical Mo-O bond distances in Mo Oxides

The major route of defect introduction is currently the incorporation with foreign atoms although the high chemical complexity of such systems makes understanding and control of catalyst formation extremely difficult. An alternative way is to reduce the chemical complexity by maintaining the same high structural complexity. Nanotechnology is a suitable tool for making specific oligo anions by carefully connecting MoO_6 octahedra. (Bottom Up Approach).

The current preparation routine for MoVTeNb Oxides mentioned above is the "slurry method" in which a mixture of solid and liquid phases (slurry) is spray-dried and calcined. Such procedure is extremely undefined and will therefore lead to inhomogeneous material. Precipitation, however, is a method that is much more understood and can be carried out in a much more controlled way. There is still a multitude of variables that affect the precipitation, as seen in Figure 1.3. The mentioned parameters have to be fully understood and controlled in order to achieve reproducibility of the solids prepared.

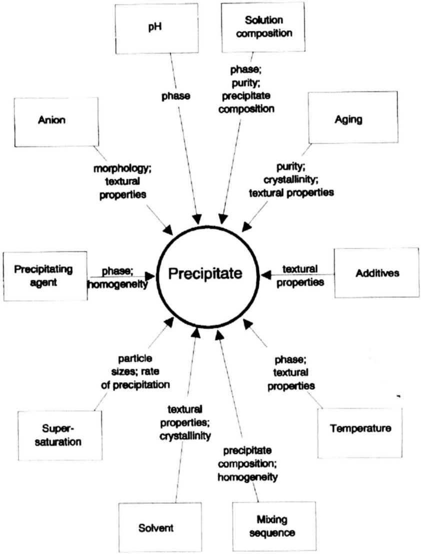

Fig 1.3 Parameters affecting precipitation taken from Weitkamp et al. [53].

After precipitation the catalyst generally undergoes further post precipitation treatment, such as washing, drying, calcination and activation. The same high amount of control has to be maintained throughout each step of such processes (Figure 1.4).

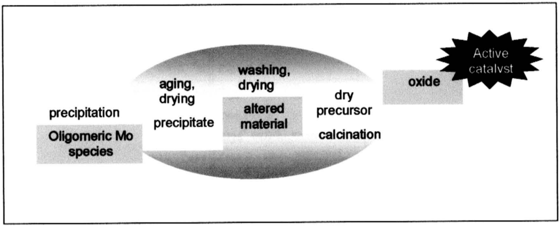

Fig 1.4 Post precipitation process for the preparation of active Mo catalyst

In this, the chemical complexity of the catalyst system is kept as low as possible, e.g. the synthesised catalyst material only contains molybdenum and oxygen.

Many studies about polymolybdates in solution have been carried out by Tytko [20, 51]. Figure 1.5 shows a summary of species that were observed at relevant pHs. It is already known that such procedures led to a variety of precipitates [14, 15, 16, 17, 18, 19, 20, 21, 22]. The first prominent compound of this type was reported by Böschen *et al.* [18] for $K_4Mo_{36}O_{112}\cdot 8H_2O$ [23, 24, 25]. Like in the M1 phase mentioned above, this material contains pentagonal bipyramides which Müller discribes as important building block [26] for large polymolybdates (keplerates, >500 atoms). Even in the photochemical molybdenum blues reaction this motif is discussed [27].

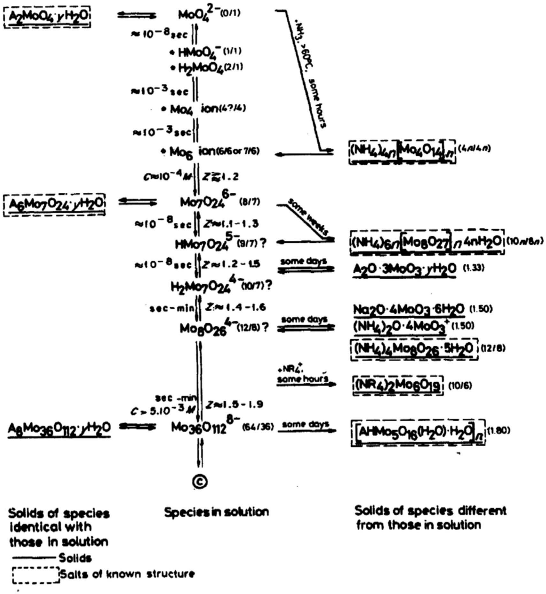

Fig 1.5 Molybdenum species in solution at different pH (decreasing pH application) taken from Tytko and Glemser [20].

1.1 Effect of various synthesis parameters on Molybdenum phases

Counter ions play an important role in the formation and the structure of polymolybdates which precipitated from aqueous solution. Conditions favourable for the precipitation of some polymolybdates from aqueous solution with the cations, NH_4^+, $[(NH_2)_3C]^+$, $[(CH_3)_4N]^+$, and $[(n\text{-}C_4H_9)_4N]^+$ have been determined [46]. Four types of counter-ion are used, that is ammonium, potassium, lithium and sodium. From these series of counter ions, different structures were obtained by varying the acid concentration, molybdenum concentration and precipitation temperature. Depending on the counter-ion and conditions, four different structural types of polymolybdates were investigated namely supramolecular $Mo_{36}O_{112}^{4-}$ (supramolecular phase), hexagonal molybdenum oxide (h-MoO_3), trimolybdate ($K_2Mo_3O_{10}$) and orthorhombic molybdenum oxide (o-MoO_3). Ammonium counter-ion produced supramolecular $Mo_{36}O_{112}^{4-}$ and hexagonal molybdenum oxide, while by using potassium as counter-ion, supramolecular like-phase and trimolybdate were obtained. Smaller counter ions, such as lithium and sodium however, resulted in one phase each, orthorhombic and hexagonal molybdenum oxide respectively. Raman Spectroscopy has been chosen as the additional techniques to identify the polymolybdates obtained [46].

Figure 1.6 shows the characteristic XRD pattern and Raman spectrum of the supramolecular phase. Supramolecular-like phase can only be observed using ammonium and potassium as counter-ions. The identification of supramolecular-like phase by powder XRD revealed peaks at lower angle with a characteristic peak which appears always at 7° in all patterns [41, 43]. Raman spectrum revealed bands at: 960, 893, 373 and 237 cm^{-1} which appear at all supramolecular spectrum indicated Mo_{36} as revealed by Tytko [37].

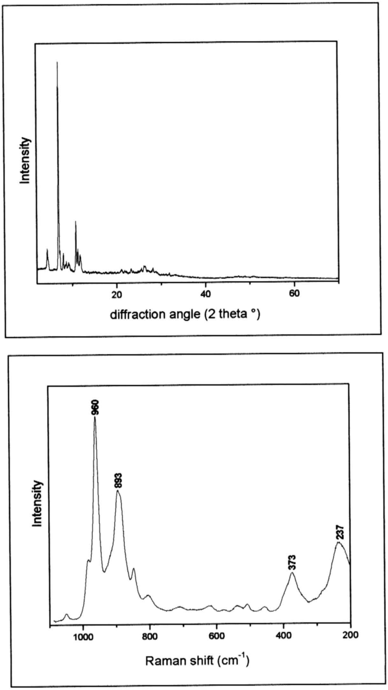

Fig 1.6 XRD pattern and Raman spectrum of supramolecular- like phase.

Supramolecular $Mo_{36}O_{112}^{4-}$ phase structure has been reported by Müller *et al.* [42], Krebs et al [43], and Zhang et. al [41] as a large molybdenum compound obtained by acidification of molybdate solution. The structure of the 36-molybdate ion in the supramolecular phase consists of 18-molybdate subunits combined via four common oxygen atoms to form a ring around the b-axis. Some of the cations and the molecules of crystal water are in the middle of this ring as shown in Figure 1.7. The anion contains two compact groups of five mainly edge-sharing MoO_6 octahedra. Groups of corner-sharing octahedra and H_2O molecules bound to Mo were also found, which are characteristic of the polymeric compounds. The anion has also two remarkable features, the MoO_7 polyhedra and the H_2O molecules which are simultaneously co-ordinated to two Mo atoms.

The MoO_7 polyhedra can be viewed as pentagonal bipyramids. Zhang *et al.* [41] investigated another supramolecular Mo_{36} compound. There are mainly 32 edge-sharing MoO_6 octahedra and 4 $Mo(NO)O_6$ pentagonal bipyramids to form a large ring in the centre containing six H_2O molecules, which was claimed to be the most interesting features. Zhang claimed that the formation of this supramolecular phase can be obtained in a moderate acidity of the aqueous mediums, not in the extremely acidic or non-acidic aqueous media. Tytko *et al.* [37] reported the aggregation of polymolybdates species. They determined many possibilities through the formation of Mo_{36} by dimerisation, trimerisation, and tetramerisation of molybdates ion. Tytko [51] again reported $Mo_7O_{24}^{6-}$ as the initial major product or as starting nucleus for the formation mechanisms of polymolybdates.

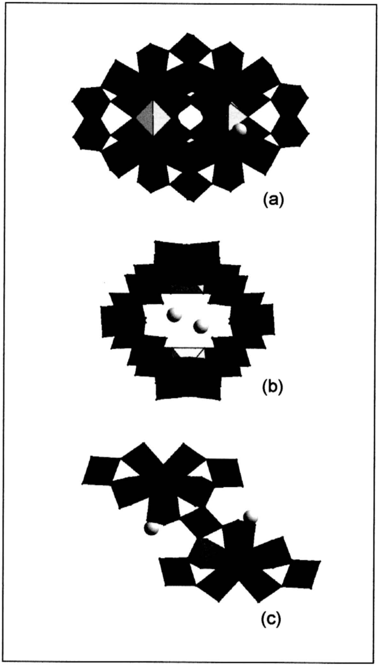

Fig 1.7 Three orthogonal views of the cluster molecule in the supramolecular phase with potassium as cation. The gray spheres represent potassium atoms that are located inside the cluster.

Figure 1.8 shows the XRD pattern and Raman spectrum of hexagonal molybdenum oxide. The hexagonal phase is obtained from ammonium, potassium and sodium counter-ions. In principal, hexagonal phase can be obtained as the temperature is raised during the precipitation in the aqueous solution. Bands situated at 976, 904, 691, 494, 400, 256 and 224 cm^{-1}, are attributed to hexagonal molybdenum oxide in Raman spectrum.

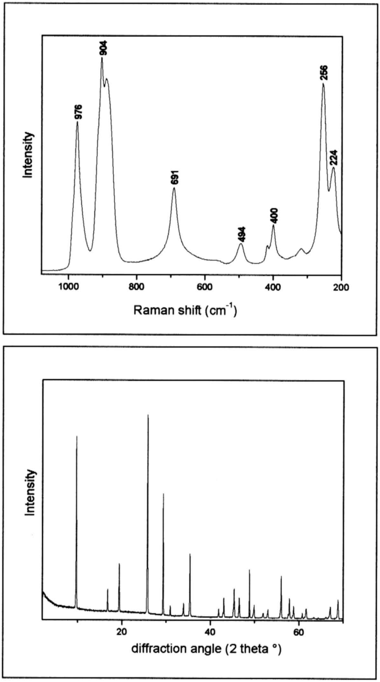

Fig 1.8 XRD pattern and Raman spectrum of hexagonal molybdenum oxide.

Hexagonal molybdenum oxide structure has been reported by several authors. Hexagonal molybdenum oxide is another form of molybdenum trioxide other than monoclinic and orthorhombic. The structure was synthesised by Krebs and Paulat-Böschen [38] for the potassium molybdate $KMo_5O_{15}OH{\cdot}2H_2O$. The structure consists of double chains made of edge sharing, strongly distorted MoO_6 octahedra, the same zig-zag chains as those found in α-MoO_3 (Figure 1.9). The double chains are linked by common corners. Along the short c-axis the polymeric structure forms tunnels in which cations such as ammonium, potassium and sodium are located. McCarron *et al.* [43] studied the cation exchange properties of the hexagonal molybdate system using Na, Rb, Cs, and K. They revealed that the structure of Na molybdates differs from that of the isostructural K, Cs, Rb and NH_4 molybdates in the positioning of the alkali metal within the channel structure. For larger cation molybdates, the potassium cation occupies an octahedral site with higher bond distances compared to smaller cation, sodium. This indicates that the size of counter-ion does influence the bond distance in the channel. In this work (referring to author's work), NH_4 and K would be larger cations than Li and Na. It is believed that larger cation in the tunnel will stabilise the structure. Due to its microporosity and possible catalytic activity, there has been considerable interest in obtaining a hexagonal molybdenum oxide with empty tunnels. There were already several reports which claimed the successful preparation of the hexagonal structure containing empty tunnels with only molybdenum in the lattice [59].

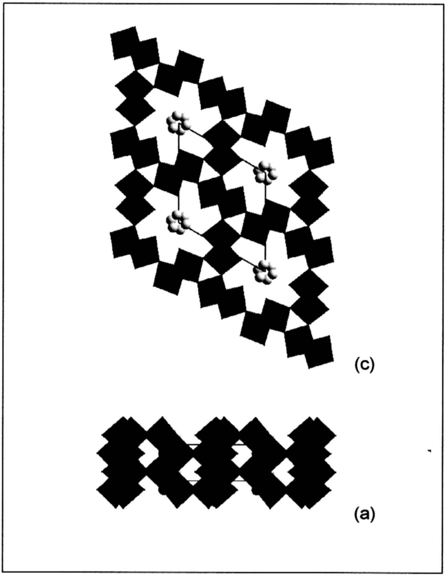

Figure 1.9 Structure of hexagonal molybdenum oxide (sodium counter-ion), view along c (top) and a (bottom). The grey spheres are sodium atoms, which are disordered on alternative positions inside the hexagonal channels (in the ammonium phase, the ammonium ions would be located in the centre of the channels).

Figure 1.10 shows the XRD pattern and Raman spectrum of trimolybdate which can only be obtained when potassium is used as counter-ion at high temperature and high molybdenum concentration. The XRD pattern shows many peaks and trimolybdate is one of the major phases observed in this compound. The minor phases are unknown and probably consist of other kind of polymolybdates in the structure. Raman bands correspond to trimolybdate display bands at 949, 940, 912, 612, 372, and 217 cm^{-1}. There are several types of trimolybdates available as reported by few researchers. Gatehouse [39] discovered anhydrous trimolybdate with monoclinic system, while Lasocha [40] synthesised anhydrous trimolybdate with orthorhombic system.

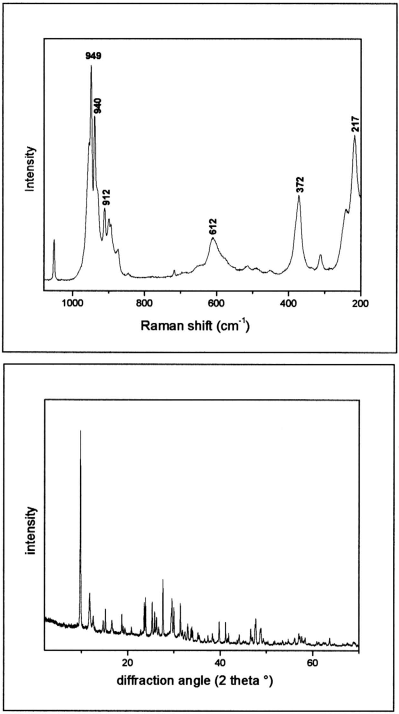

Fig 1.10 XRD pattern and Raman spectrum of trimolybdate

The observed trimolybdate (referring to author's work) corresponds to the trimolybdate observed by Lasocha [40]. The structure consists of infinite zig-zag chains of distorted edge and vertex shared MoO_6 octahedra parallel to the c axis. Pairs of octahedra joined by an edge create Mo_2O_{10} units. Each unit shares four vertices with adjacent units and form infinite ribbons with formula Mo_2O_8 to which MoO_6 octahedra are attached alternately to both sides of this ribbon, forming chains with formula Mo_3O_{10} (as shown in Figure 1.11). Adjacent chains have no common oxygen atoms and are held together by potassium ions and water molecules. The potassium ions occupy interchain positions in irregular eightfold coordination.

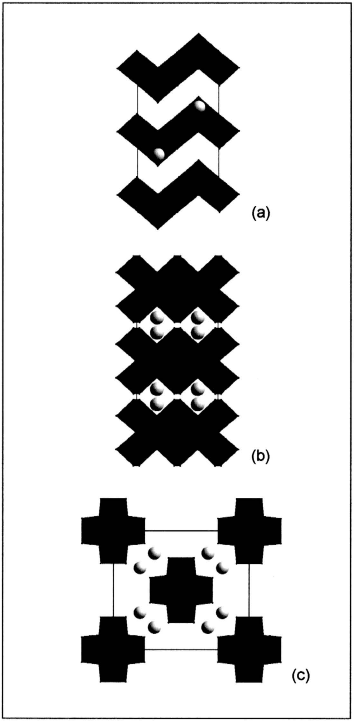

Figure 1.11 Crystal structures of potassium trimolybdate along a, b and c directions respectively.

Figure 1.12 shows the XRD pattern and Raman spectrum of molybdenum oxide orthorhombic (α-MoO_3) which can only be obtained when lithium is used as counter-ion at high temperature. The XRD pattern is a mixture of narrow and broad peak which maybe due to disorder of the unit cell in the structure. Raman spectrum shows characteristic bands at 997, 824, 668, 380, 338, 291, and 247 cm^{-1}.

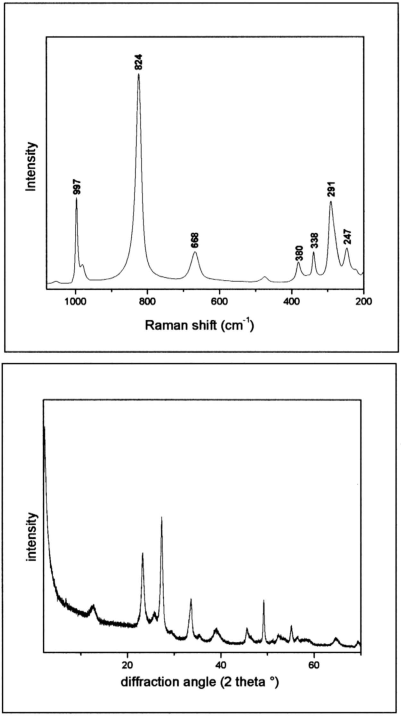

Figure 1.12 XRD pattern and Raman spectrum of orthorhombic MoO_3.

α -Molybdenum trioxide (MoO_3) is one of the most stable phases. It commonly has a layered structure in which each layer is built up of MoO_6 octahedra at two levels connected in one direction (c), by common edges and corners so as to form zig-zag rows (Figure 1.13). The rows are mutually connected by corners to layers, which are placed on top of each other. Three of the six oxygen atoms surrounding every molybdenum atom are thus common to three MoO_6 octahedra, two of them belonging to two octahedral and the sixth one being unshared.

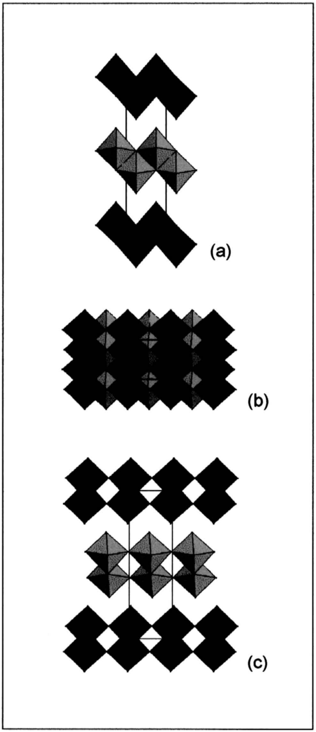

Fig 1.13 Structure of orthorhombic MoO_3*, seen along a (top), c (middle), and b (bottom).*

1.2 Outline of work.

The aim of this work is to synthesise molybdenum oxide with a variety of structural features by employing preparative nanotechnology. As discussed above formation of such structures is affected by a wide array of parameters that requires a multitude of characterisation techniques to be used. The work conducted focussed on Powder XRD as a major technique applied while Raman spectroscopy and Electron Microscopy (TEM and SEM) were used as auxiliary technique to study the molybdenum oxide. Structural measurements using X-ray diffraction and Raman spectroscopy reveal the unfolding structural changes. As such materials undergo electronic changes during catalytic reactions we will also present an *in-situ* UV/Vis/NIR study on the different families of molybdenum oxide (MoO_x) catalysts. The catalysts were prepared by the group before sending for further characterisation. Synthesis of the compounds and analyses by UV-Vis, FTIR and BET are largely covered by Abdullah. N [61] while Basher. Q [62] is focusing on the calcination process by TG and DSC experiments.