

CHAPTER TWO

2.1 Catalytic Oxidation

2.1.1 Selective Oxidation Reaction

Oxidation reactions play an important role in modern chemicals industry because more than 60% of products obtained by catalytic route are products of oxidation [17]. The reason is that oxygen (pure or in air) is cheap and processes the high reactivity necessary to activate saturated hydrocarbon to valuable and economical products [18]. Ethylene oxide, acrolein, acrylic acid, acetic acid and maleic anhydride are which produced from saturated or non-saturated C_2 to C_8 hydrocarbons are obtained by heterogeneous selective oxidation on metal oxide [19]. The oxidation reaction has been studied in the last 30 years and the main components of catalyst used in these reactions are listed in Table 2.1, 2.2 and 2.3 [20].

Oxidation processes are defined as conversion of compounds under the influence of various oxidizing agent in organic chemistry. A distinction is made between complete combustion, which leads to the formation of CO , CO_2 , and H_2O and partial oxidation, which is important because it produces valuable intermediate oxygenated products [18].

2.1.2 Types of Selective Oxidation Reaction

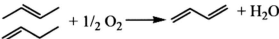
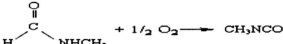
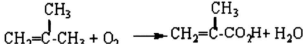

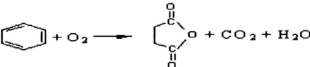
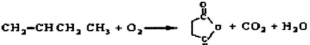
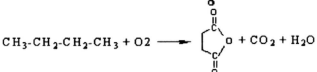
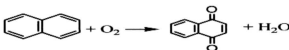
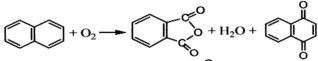
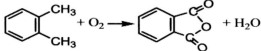
There are two categories of selective oxidation reaction, one involves only dehydrogenation and the other involves both dehydrogenation as well as oxygen insertion into the hydrocarbon molecule [21].

The reaction where a hydrocarbon molecule is converted into a more unsaturated hydrocarbon by breaking C-H and forming C=C are known as dehydrogenation reactions. The hydrogen is a by-product in the absence of oxygen. These reactions are operated at high temperature (normally more than 723 K) because the thermodynamic equilibrium normally favors the reactant at low temperature. At the high temperature (more than 723 K), undesired coking take place readily and water is usually added to reduce cooking. The water provides the thermodynamic driving forces for the reaction and thus the reaction can be conducted at lower temperature than without oxygen, and deactivation due to coking is less severe. The carbon skeletons of the hydrocarbons molecules are not broken in this dehydrogenation reaction [21].

The second type of selective oxidation is dehydrogenation and oxygen insertion reactions. Oxygen is needed as oxidant both for incorporation into the hydrocarbon molecule and in the formation of water in the dehydrogenation steps. The common features of this reaction are that C-H bonds are broken and C-O bonds are formed, except for oxidation of ethylene oxide where C-H bonds are not broken, as well as ammoxidation reactions such as propane to acrylonitrile in which C-N bonds are formed. In these dehydrogenation and oxygen insertion reactions, there are some cases that the carbon skeleton is broken such as the oxidation of benzene to maleic anhydride, while the others carbon skeleton remains intact. The selectivity is determined by the ability of oxide to catalyse the formation of C-O bonds without breaking only desired number of C-C bonds due to excessive breaking of C-C bonds which lead to combustion [21].

1

Table 2.1. Selective oxidation reaction of hydrocarbon [20]

PRODUCT	REACTION	CATALYSTS
Intramolecular oxidative dehydrogenation		
Butadiene		Fe ₂ O ₃ , Cr ₂ O ₃ , Cu (Ni) ₃ (PO ₄) ₂
Methylisocyanate		Ag
Intermolecular oxidative dehydrogenation		
Vinyl Acetate	CH ₂ =CH ₂ + CH ₃ COOH + 1/2 O ₂ → CH ₂ =CH-O-CO-CH ₃	Pd/CH ₃ COONa
Allyl Acetate	CH ₂ =CH-CH ₃ + CH ₃ COOH + 1/2 O ₂ → CH ₂ =CH-CH ₂ -O-CO-CH ₃	Pd/CH ₃ COONa
Oxidation		
Ethylene oxide	CH ₂ =CH-CH ₃ + O ₂ → CH ₂ =CH-CHO + H ₂ O	Pd/CH ₃ COONa
Acrolein	CH ₂ =CH-CHO + O ₂ → CH ₂ =CH-COOH + H ₂ O	Mo-Bi-Fe-O
	CH ₂ =CH-CH ₃ + O ₂ → CH ₂ =CH-CHO + H ₂ O	Mo-V-O
Acrylic Acid	CH ₂ =CH-CH ₃ + O ₂ → CH ₂ =CH-CHO + H ₂ O	Mo-V-Te-Nb
	CH ₂ =CH-CHO + O ₂ → CH ₂ =CH-COOH + H ₂ O	Mo-V-Sb-Nb
Methacrylic Acid		i). Mo-Bi-O
		ii). Mo-V-P-O (Heteropolyacid)
Maleic anhydride		Mo-V-O
		(VO) ₂ P ₂ O ₇
		(VO) ₂ P ₂ O ₇
Naphthoquinone		V ₂ O ₅ + promoter
Phthalic Anhydride		V ₂ O ₅ /Al ₂ O ₃
		V ₂ O ₅ /TiO ₂

2.2 The Chemistry of Selected Metal Catalysts systems

2.2.1 Active Compound

a). Molybdenum

Molybdenum is one of the elements in the group VIB (6) and has a ground state electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^1$. These elements have typically metallic bcc structures and in the massive state are lustrous, silvery, and fairly soft (when it is pure). This metal is refractive in nature and for this reason this metallic Mo is fabricated by the techniques of powder metallurgy and, in consequence, many of their bulk physical properties depend critically on the nature of their mechanical history. As in the preceding transition-metal groups, the refractory behavior and the relative stabilities of the different oxidation states can be explained by the role of the $(n-1)$ d electrons [22].

The oxidation states of molybdenum can range from +6 down to +2. In contrast, clusters and multiple bonded species, which, particularly in the case of molybdenum, has produced an effusion of publications in recent years, dominate the chemistry of molybdenum in oxidation states +5 to +2. This is due not only to the intrinsically interesting chemistry involved but also because of molybdenum's role in biological processes and, catalytically, in the hydrodesulfurization (HDS) process for removing S-compounds from petroleum feedstocks. In the lower oxidation states, found in compounds with π -acceptor ligands, the metals are quite similar. Pure molybdenum, which finds important applications as a catalyst in a variety of petrochemical processes and as an electrode material, can be obtained by hydrogen reduction of ammonium molybdate [22].

Table 2.2 shown some physical properties of the molybdenum. Coordination numbers as high as 12 can be attained, but those over 9 in the cases of Mo involve the presence of the peroxo ligand or π -bonded aromatic rings systems such as $\eta^5\text{-C}_5\text{H}_5^-$ or $\eta^6\text{-C}_6\text{H}_6$ [22].

b). Vanadium

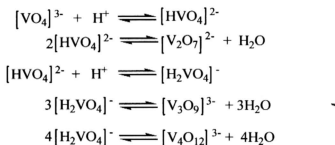
Vanadium is one of element in Group IVB (5) and has a ground states electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$. This element is shiny, silvery metals with typical metallic bcc structures and slightly less electropositive. The extra d electron again appears to contribute to stronger metal metal bonding in the bulk metals, leading in each case to a higher mp, bp and enthalpy of atomization. Indeed, these quantities reach their maximum values in this and the following group. In the first transition series, vanadium is the last element before some of the $(n-1)$ d electrons begin to enter the inert electron-core of the atom and are therefore not available for bonding. As a result, not only is its mp the highest in the series but it is the last element whose compounds in the group oxidation state are not strongly oxidizing [23].

Table 2.2 shown the physical properties of vanadium. The stability of IVB (5) decreases as the group is descended. Formal oxidation states for vanadium are from +5 and down to -3. The most stable oxidation states for vanadium under normal condition are +4 and even the +3 and +2 oxidation states (which are admittedly strongly reducing) have well-characterised cationic aqueous chemistry. Table 2.2 shown some physical properties of vanadium. Four principal oxides formed of vanadium +5 (V_2O_5), +4 (VO_2), +3 (V_2O_3) and +2 (VO), a number of other phases of intermediate composition have been identified and the lower oxides in particular have a wide range

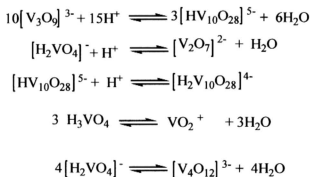
of homogeneity. V_2O_5 is an orange yellow colour when it is pure (due to charge transfer) [23].

V_2O_5 is amphoteric. It is slightly soluble in water and gives a pale yellow colour in an acidic solution. It dissolves in acids producing salts of a pale yellow dioxovanadium (V) ion, $[VO_2]^{2+}$, and in alkalis producing colourless solutions, which, at high pH, contain the orthovanadate ion (VO_4^{3-}). At intermediate pH a series of hydrolysis polymerization reactions occur yielding the isopolyvanadates. Figure 2.1 show how the existence of the various vanadate species depending on the pH and on the total concentration of vanadium [24]. Their occurrence can be accounted for items of protonation and condensation equilibria such as the following:

In alkaline solution:



In acid solution:



In these equilibria the site of protonation in the species $[HVO_4]^{2-}$, $[H_2VO_4]^{-}$ etc., is an oxygen atom (not vanadium); a more precise representation would therefore be $[VO_3(OH)]^{2-}$, $[VO_2(OH)_2]^{-}$ etc. However, the customary formulation is retained for convenience (cf. HNO_3 , HSO_4^{-} , H_2SO_4 , etc.) [23].

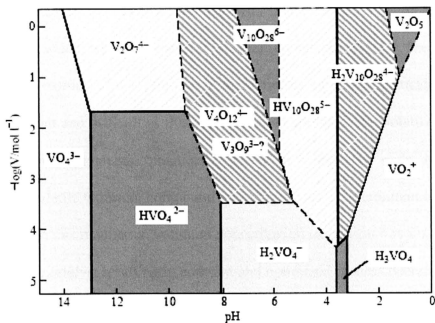


Figure 2.1: Occurrence of various vanadate and polyvanadate species as a function of pH and total concentration of vanadium [23].

c). Tellurium

Tellurium is one of elements in the Group VIA (16) and has a ground states electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^4$. Tellurium is often added as a promoter to enhance selectivity of a desired product. The oxidation states of Te are +4, +5 and +6. Table 2.2 shown some physical properties of Tellurium. In the +4 oxidation states its role is that of hydrogen abstraction and in the +6 oxidations state that of selective oxygen or nitrogen insertion. It also suppresses by-product formation of unwanted cracked intermediates as well as COx [25].

The major drawback of using tellurium-containing catalysts is tellurium volatility when in its lower oxidation states of +4 generated under the redox conditions of the catalytic operations. Unless immediately reoxidized to the +6 oxidation states, it volatilized and is lost from the catalyst with a concomitant loss of its beneficial properties originally imparted to the base catalyst. To minimize the losses of tellurium

+6 from the catalyst surface an intercalysts redox stabilization of tellurium +6 is strategically added with of powerful reoxidation couple (V, Cu, Fe or U) in the immediate proximity of the tellurium in the lattice of a given catalytically active phase [25]. As elegant and difficult as this approach is, it alleviates the volatility problem not entirely. A more pragmatic, practical approach in commercial scale operation is the addition of volatile tellurium compound on a continuous or intermittent basis directly to the reactor. In this manner an optimum concentration of tellurium is maintained on the surface of the catalyst resulting in constant and optimized process operation [25]. Table 2.2 summarized of the physical properties of tellurium.

d). Niobium

Niobium is one of elements in the Group IVB and has a ground states electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$. This element has typically metallic bcc structure and slightly less electropositive. Generally this element will react with most non-metals, giving product, which is frequently interstitial and nonstoichiometric. The formal oxidation states of niobium are from +5 to -3 and the most stable, under normal condition is a +4 oxidation state, which is best, represented by their halides [23]. Table 2.2 depicts physical properties of niobium.

The Nb +4 ions have only slightly smaller radii and have 8 coordination numbers. In the +5 states, Nb is sufficiently active in this coordination number with ligand than bidentate ones with very small “bites” such as peroxo group and this element provides no counter-part to the cationic chemistry of vanadium in the +3 and +2 oxidation states. Nb form a series of “cluster” compound based on octahedral

Nb_6X_{12} units. The occurrence of such compound is largely a consequence of the strength of metal-metal bonding in this part of the periodic table (as reflected in high enthalpies of atomization) [23].

Niobium is not so extensive or well characterized as that vanadium and niobium pentoxide is relatively much more stable and difficult to reduce. The structure is extremely complicated and Nb_2O_5 in particular display extensive polymorphism. High temperature reduction of Nb_2O_5 with hydrogen gives the bluish-black dioxide NbO_2 that has a distorted rutile structure. Between Nb_2O_5 and NbO_2 there is a homologous series of structurally related phase of general formula $\text{Nb}_{3n+1}\text{O}_{8n-2}$, with $n = 5, 6, 7, 8$ (c.i Nb_8O_{19} , $\text{Nb}_{19}\text{O}_{46}$, $\text{Nb}_{11}\text{O}_{27}$ and $\text{Nb}_{25}\text{O}_{62}$). In addition, oxide of formula $\text{Nb}_{12}\text{O}_{29}$ and $\text{Nb}_{47}\text{O}_{116}$ has been reported: the numerical relationship to Nb_2O_5 is clear since $\text{Nb}_{12}\text{O}_{29}$ is $(12\text{Nb}_2\text{O}_5-2\text{O})$ and $2 \text{ Nb}_{47}\text{O}_{116}$ (or $\text{Nb}_{49}\text{O}_{232}$) is $(47 \text{ Nb}_2\text{O}_5-3\text{O})$. Further reduction produces the gray monoxide NbO that has a cubic structure and metallic conductivity and that its composition range is only $\text{NbO}_{0.982}$ to $\text{NbO}_{1.008}$. The structure is a unique variant of the rock salt NaCl structure in which there are vacancies (Nb) at the eight corners of the units cell and an O vacancy at its center (Figure 2.2). The structure could therefore be described as a vacancy-defect NaCl structure $\text{Nb}_{0.75\pm0.25} \text{O}_{0.75\pm 25}$, but as all the vacancies are ordered it is better to consider it as a new structure type in which both Nb and O form 4 coplanar bonds. The central feature is a 3D framework of Nb_6 octahedral cluster. The structure is reminiscent of the structure-motif of the lower halides of Nb and the retention of Nb_6 clusters rather than the adoption of the ionic NaCl -type structure (a similarly be related to the high heat of sublimation of Nb and neighboring metal [23]).

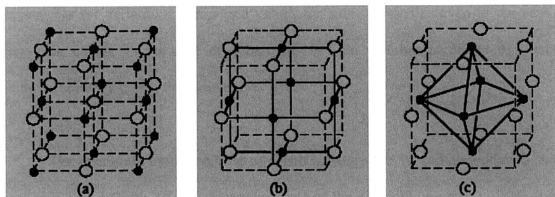


Figure 2.2: (a) NaCl(MgO) showing all sites occupied by M(●) and O (○). (b) NbO showing planar coordination of Nb (and O) and vacancies at the cube corners (Nb) and center (O). (c) NbO as in (b), but emphasizing the octahedral Nb₆ cluster (joined by corner sharing to neighboring unit cells) [23].

2.2.2 Promoter

The addition of a fifth component as a promoter in this mixed metal oxide catalyst is widely used in order to enhance activity and/or selectivity. In the case of promoter metal it is a simple procedure to add small amounts of a metal during the alloy preparation stage. Although other metals have been used in the laboratory studies, the most common transition metals used as promoters are Co, Cr, Ni, etc.

a). Cobalt

Cobalt is one of the elements of VIII (9) Group and has a ground states electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$. This element has an allotrope (the β -form) with hcp α -form structure where it is more stable than the bcc structure. However, the transformation between these allotropes is generally slow and the β -form, which can be stabilized by the addition of a few percent of iron, is often present at room temperature. This, of course, has an effect on physical properties and is no doubt

responsible for variations in reported values for some properties even in the case of very pure cobalt. In the case of cobalt this is ^{59}Co , but bombardment by thermal neutrons converts this to the radioactive ^{60}Co .

The maximum oxidation state of cobalt is from -3 to +4 and no oxidation states for Co is found above +4 and the summarised of the physical properties of this metal shown in the table 2.2. The most common oxidation states for Co are +2 and +3. Table 2.2 shows some physical properties of cobalt. The $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ are both known but the latter is a strong oxidizing agent and in aqueous solution, unless it is acidic, decomposes rapidly as Co^{III} oxidizes the water with evolution of oxygen. Consequently, in contrast to Co^{II} , Co^{III} provides a few simple salts, and those, which do occur, are unstable. However, Co^{III} is unsurpassed in the number of coordination complexes, which it forms, especially with *N*-donor ligands. Virtually all of these complexes are low-spin, the t_{2g}^6 configuration producing a particularly high CFSE. The effect of the CFSE is expected to be more marked in the case of the heavier elements because for them the crystal field splitting is much greater [26].

b). Chromium

As a typical transition element, chromium has the ground state electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. Table 2.2 shows some physical properties of chromium. Chromium compounds exist in an unusually large number of oxidation states (-4 to +6). The extremely low ones are stabilized by π -acid ligands; therefore, the -2, -1, 0, and +1 state are formal oxidation states held by chromium compounds such as carbonyl nitrosyls and organometallic complexes [22].

The most common oxidation states of chromium in inorganic compounds are +II, +3, and +6. Complexes of divalent chromium are usually strongly reducing and are often susceptible to air oxidation. The most stable oxidation state of the element is +3 and so the largest number of its coordination compounds exists in this state. The oxidation states +4 and +5 are relatively rare. The few compounds that have been isolated rapidly disproportionate to chromium (+3) and chromium (+6) compounds. Chromium (+4) and chromium (+5) species are, however, important in chromium (+6) induced oxidations, since they always occur as transient intermediates. In its highest oxidation state (+6) chromium forms compounds, which are all oxo compounds, but the number of coordination compounds representing it is rather limited. Hexavalent chromium is a powerful oxidant and the use of chromium based oxidants in organic synthesis [27 and 28] goes back well over a century.

Chromium oxidations have been widely explored and are still of interest due to the wide variety of oxidizable functions by the proper choice of reagents. A large number of chromium reagents and procedures have been described in reviews and books [29 and 30]. These methods imply either the use of stoichiometric quantities or large excess of chromium reagents. Apart from the fact that chromium reagents are toxic, the cost of using stoichiometric amounts of reagents makes these procedures less attractive. In addition, the metallic by-products are also toxic and their presence makes the reaction work-up cumbersome. Due to the above cost and environmental factors, it is advantageous to use chromium-catalyzed oxidations instead [31]. Table 2.2 shown the summerised of physical properties of this metal.

c). Nickel

Nickel is a one of elements in the group VIII (10) that has a ground states electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$. Table 2.2 shows physical properties of nickel. The range of oxidation states of nickel only reaching +4 and for +2 oxidation states is undoubtedly the most common and provides the most extensive aqueous chemistry. In the divalent state nickel exhibits a wide, interesting variety of coordination numbers and stereochemistries, which often exist simultaneously in equilibrium with each other [32].

For oxide, only NiO is reasonably well characterised. The formation of NiO is realised by heating the metal in oxygen. It is difficult to achieve a complete conversion while grey to black colours probably arise from slight nonstoichiometry. It is best prepared as a green powder with the rock-salt structure by heating the hydroxide, carbonate or nitrate. Nickel hydroxide $Ni(OH)_2$ is a green precipitate obtained by adding alkali to aqueous solutions of Ni^{II} salts and, like NiO, is entirely basic, dissolving easily in acids. Nickel sulfides are very similar to those of cobalt, consisting of NiS_2 (pyrites structure), Ni_3S_4 (spinel structure) and the black, nickel-deficient $Ni_{1-x}S$ (NiAs structure), which is precipitated from aqueous solutions of Ni^{II} by passing H_2S . There are also numerous metallic phases having compositions between NiS and Ni_3S_2 [32]. Table 2.2 shown the summerised of physical properties of this metal.

Table 2.2 Physical properties of Group5 (V and Nb), Group 6 (Cr and Mo), Group 9 (Co), Group 10 (Ni) and Group 16 (Te).

Property	V	Nb	Cr	Mo	Co	Ni	Te
Atomic number	23	41	24	42	27	28	52
No. of naturally occurring isotopes	2	1	4	7	1	5	
Atomic weight	50.9415 (1)	92.9064 (2)	51.9961 (6)	95.94 (1)	58.9332 (9)	58.6934 (2)	127.6
Electronic configuration	[Ar] 3d ³ 4s ²	[Kr] 4d ³ 5s ²	[Ar] 3d ⁵ 4s ¹	[Kr] 4d ⁵ 5s ¹	[Ar] 3d ⁷ 4s ²	[Ar] 3d ⁸ 4s ²	[Kr] 4d ¹⁰ 5s ² 5
	1.6	1.6	1.6	1.8	1.8	1.8	
Electronegativity							
Metal radius (12-coordinate) / pm	134	146	128	139	125	124	
Ionic radius (6-coordinate) / pm	V) 54 IV) 58 III) 64 II) 79	V) 64 IV) 68 III) 72 II) -	VI) 64 V) 68 IV) 72 III) 61.5	VI) 59 V) 61 IV) 65 III) 69	V) - IV) 53 III) 54.5 (1s) 61 (hs) II) 65 (1s), 74.5 (hs)	V) - IV) 48 III) 56 (1s), 60 (hs) II) 79	
MP/°C	1915	2468	1900	1620	1495	1455	450
BP/°C	3350	4758	2690	4650	3100	2920	990
ΔH _{fus} /kJmol ⁻¹	17.5	26.8	21 (±2)	28 (±3)	16.3	17.2 (±0.3)	
ΔH _{vap} /kJmol ⁻¹	459.7	680.2	342 (±6)	590 (±21)	382	357 (±17)	
ΔH _f (monatomic) /kJmol ⁻¹	510 (±29)	724	397 (±3)	664 (±13)	425 (±3)	429 (±13)	
Density	6.11	8.57	7.14	10.28	8.90	8.908	6.24
Electrical resistivity (20°C) / μohm cm	~25	~12.5	13	~5	6.24	6.84	

2.3 Literature Review of Multimetal Oxides Catalysts (MMO) System.

The application of multimetal oxides type catalysts in propane oxidation to acrylic acid only started in the 1990s, although M-V-Nb mixed oxides, the basis for these high performing propane selective oxidation catalysts was initially developed in the 1970s for the oxidation of ethane to ethene and acetic acid [33]. This Mo-V-Nb oxide catalyst was also reported to be capable of activating propane at 300°C but producing only acetic acid, acetaldehyde and carbon dioxides [6]. Most of the applications of multimetallic oxides catalysts are mentioned in patents. Table 2.3 lists some of the multimetallic oxides catalysts systems for propane oxidation to acrylic acid.

Generally all of these multimetal oxide catalysts are Mo-based and most of them also contain V as a major component. Most patents claim that Mo is an essential element of commercial catalyst for propylene oxidation to acrylic acid while V is another essential element used as commercial catalyst for acrolein oxidation to acrylic acid [6]. Mixed oxide catalyst lacking V is very active for propylene oxidation [42, 43 and 44] and is not very active for propane oxidation [35 and 36].

The potential of Mo and V based mixed oxide catalyst in propane oxidation was reported by Bartek et al. [34]. However, the most effective catalysts to date for propane oxidation to acrylic acid are those Mo-V-Te-Nb-O catalysts reported by Ushikubo et al. [37] and Lin and Linsen [6]. In fact, a catalyst with the same four components was first found to be effective for propane ammoxidation to acrylonitrile process [45]. It has been quite unexpected that the same catalyst can function so well for two different reactions without needs future for compositional modification. Although the two reactions, propane oxidation and propane ammoxidation may share some fundamental

reaction steps, such as propane activation and propane oxidative dehydrogenation, there are significant different between the two [6]. For instance, ammonia activation and addition steps for nitrile formation are unique to propane ammoxidation acrylonitrile and do not exist in propane oxidation. Furthermore, acrylonitrile and acrylic acid differ significantly with respect to the acidity and thermal stability. Nonetheless, this Mo-V-Te-Nb mixed metal oxide catalyst was shown to be remarkably robust and efficient for both reactions (Table 2.4) [46].

The performance of Mo-V-Te-Nb-O catalysts for propane oxidation to acrylic acid has been shown to be significantly better than that of any other multi-component metal oxides (*MMO*) type of catalysts, or any *VPO* or *HPC* type of catalysts. However, it is difficult to prepare active Mo-V-Te-Nb-O catalysts that exhibit the claimed performance in either propane ammoxidation to acrylonitrile or propane oxidation to acrylic acid [9]. In this case, not only the composition of the catalyst is of importance, but also the preparation method also greatly gives varying effectiveness of the catalyst of essentially the same composition. For example, the performance of $\text{Mo}_1 \text{V}_{0.3} \text{Te}_{0.23} \text{Nb}_{0.1} \text{O}_n$ catalysts can vary from very poor (no yield) [6, 47], mediocre (14% acrylic acid yield) [41], to excellent (more than 40% acrylic acid yield) [6, 47]. These performance differences reflect different structure of the catalysts prepared under different preparation conditions [6, 47 and 48].

Manhua et.al. reported the reaction-pathways in selective oxidation of propane over a mixed metal oxide catalyst. He showed some the catalytic properties of a Mo-V-Te-Nb-O metal oxide catalyst in the selective oxidation of propane and its corresponding partial oxidation immediate. He proposed that different catalysts gives

different oxidation pathway. Mo-V-Te-Nb-O catalysts showed direct oxidation pathway of propylene to CO_x as well [49].

Védrine et.al in his study of Mo-V-Sb-Nb mixed metal oxide catalysts for selective oxidation process found that the effectiveness of this catalyst is influenced by activation methods. Proposed that the propane oxidation reaction mechanism has a relationship with the physical properties of the Mo-V-Sb-Nb mixed oxide catalyst, which is determined by the calcinations and activation procedures. The catalyst performance closely follows the presence of specific crystalline phase. The activity and selectivity of acrylic acid improve, in order, from air-calcined sample, to nitrogen-calcined samples activated in O_2/He , to nitrogen-calcined sample activated in He. This is assigned to the diminishing presence of more oxidised phases, where MoO_3 is major phase [50].

Nieto et.al. reported that the catalytic behavior of MoVTenbO catalysts prepared by hydrothermal synthesis and they characterized the catalysts by using XRD, FTIR, SEM-EDX and XPS. In this way, several crystalline phases have been observed in the active and selective catalysts, i.e. $\text{TeMo}_5\text{O}_{16}$, $(\text{Mo}_{0.93}\text{V}_{0.07})_5\text{O}_{14}$, $3\text{MoO}_2\text{Nb}_2\text{O}_5$ and/or $\text{Nb}_{0.09}\text{Mo}_{0.91}\text{O}_{2.8}$ and new TeVMo oxide crystalline phases. In this study he found that vanadium is the key element in the activation of propane and the selective achievement of acrylic acid while V- and/or Nb- doped MoTe-containing crystalline phases are related to the selective transformation of propene to acrylic acid or acrolein. Nb-containing MoVTe presents both high activity and high selectivity to acrylic acid [51].

Nobuo et.al. studied nickel molybdate modified with telluromolybdate for selective oxidation of propane to acrylic acid and acrolein. He observed synergistic effect between nickel molybdates and telluromolybdate, and the selectivity of acrylic acid and acrolein are 87%. It was achieved at 9% weight loading of telluromolybdate. Sb-modified nickel molybdate was also found to be effective for this reaction, although the yield was low compare with Te-modified catalysts [52].

Millet et.al. reported the behavior of tellurium in MoVTaNbO catalysts for propane oxidation to acrylic acid. They found that the oxidation state and the local geometry of tellurium in MoVTaNbO catalysts would be affect the selectivity of acrylic acid for selective oxidation of propane. They characterised catalysts by using X-ray absorption, Mössbauer and XPS. They showed that only Te^{+4} are present in the bulk while Te^{+5} are detected on the surface. EXAFS experiments showed that MoVTaNbO catalysts have two phases M1 and M2. The stoichiometry of these M1 and M2 phases are $\text{TeM}_3\text{O}_{10}$ and $\text{Te}_2\text{M}_{20}\text{O}_{57}$ with M equal to Mo, V, and Nb, respectively [53].

Table 2.3

Mixed metal oxide type catalysts for propane oxidation to acrylic acid

<i>Catalyst example</i>	<i>Feed</i> (C3=propane)	<i>Temperature</i> (C°)	<i>Conversion</i> (%)	<i>Yield</i> (%)	<i>Selectivity</i> (%)	<i>Reference</i>
Mo ₁ V _{0.4} Nb _{0.04} Bi _{0.08} Sb _{0.08} K _{0.08} O _n	C3/O ₂ /H ₂ O	400	19	6	29	[34]
MoSnO _n	C3/O ₂ /N ₂	360	4	2	48	[35]
Mo _{1.51} Ni ₁ Te _{0.01} P _{0.02} O _n	C3/O ₂ /H ₂ O/He	460	12	3	23	[36]
Mo ₁ V _{0.3} Te _{0.23} Nb _{0.12} O _n	C3/air/H ₂ O	380	80	48	60	[37]
Mo ₁ V _{0.3} Sb _{0.16} Nb _{0.05} O _n	C3/air/H ₂ O	380	50	16	32	[38]
Mo ₁ V _{0.3} Sb _{0.25} Nb _{0.11} O _n	C3/O ₂ /H ₂ O/N ₂	400	21	12	61	[39]
Mo ₁ V _{0.3} Sb _{0.25} Nb _{0.12} K _{0.013} O _n	C3/O ₂ /H ₂ O/N ₂	420	39	25	64	[40]
Mo ₁ V _{0.3} Te _{0.23} Nb _{0.12} O _n	C3/air/H ₂ O	390	71	42	59	[6]
Mo ₁ V _{0.3} Te _{0.23} Nb _{0.12} O _n	C3/O ₂ /H ₂ O/He	350	23	14	61	[41]

Table 2.4

Mo-V-Te-Nb catalyst in propane (Amm) Oxidation

<i>Catalyst</i>	<i>Reaction</i>	<i>Temp (C°)</i>	<i>Conv (%)</i>	<i>Selectivity (%)</i>	<i>Yield (%)</i>	<i>Ref.</i>
Mo ₁ V _{0.3} Te _{0.23} Nb _{0.12} O _n	Oxidation	380	80	60 (acrylic acid)	48(acrylic acid)	[37]
Mo ₁ V _{0.3} Te _{0.23} Nb _{0.12} O _n	Ammoxidation	420	89	64 (acrylonitrile)	58(acrylonitrile)	[42]