Multifunctionality of Active Centers in (Amm)oxidation Catalysts: From Bi–Mo–O x to Mo–V–Nb–(Te, Sb)–O x

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Active centers, catalytic behavior, symbiosis and redox properties of MoV(Nb,Ta)TeO ammoxidation catalysts

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Selective as well as waste forming active centers were defined for MoVNbTeO and MoVTaTeO catalysts in the ammoxidation of propane to acrylonitrile and all catalytic functionalities were assigned to specific elements at the respective active centers. Symbiosis between *M1* and *M2* phases of these catalysts was observed, with phase cooperation being more extensive in the Nb than Ta containing compositions. The difference in catalytic effectiveness arises most likely because contact and surface area exposure of the two respective, cooperating phase pairs are not equal. The *M1* phase of the catalysts is reducible by propane and ammonia in the absence of dioxygen and is regenerable to its original, fully oxidized state by dioxygen (air). No structural collapse is observed even after 120 C_3H_8 + NH_3 reduction pulses. The so induced reduction of the catalyst extends up to 70 layers deep. The product distribution over the first few pulses is very similar to that under catalytic conditions, supporting the concept that lattice oxygen is involved in the catalytic ammoxidation process. Therefore, the ammoxidation of paraffins is a redox process, as is of course the well-known olefin ammoxidation process.

KEY WORDS: ammoxidation; propane; acrylonitrile; symbiosis; redox; MoV(Nb,Ta)TeO; (MoW)VTeO

1. Introduction

(Amm)oxidation of propane to acrylonitrile and acrylic acid, respectively are two important processes still awaiting improvement in yields, before they can be commercialized and replace the well established olefin based processes [1]. The desirability for such a switch is the far greater availability and substantially lower cost of the paraffin feed. To achieve the desired goal it is important to understand the intricacies of the paraffin based catalytic processes so that the catalysts can be altered and thereby be improved. One promising approach is to identify the active centers of the catalytic materials and to pinpoint the respective functionalities associated with the various metals of these centers [2]. Such endeavors should ultimately lead to catalyst improvements through judicious metal substitutions at the active centers or their immediate surroundings.

Among the most promising catalysts for propane ammoxidation is the MoV(Nb,Ta)(Te,Sb)O system [2–7]. It is generally agreed that the catalyst is comprised of at least two phases (*M1* and *M2*) and that *M1* is the paraffin-activating phase while *M2* is the olefin conversion phase [2,8–13]. All catalytic functionalities of the active centers of the two phases have been assigned [2,11]. Symbiosis between the two phases occurs and

thereby leads to significantly improved acrylonitrile yields [2,10–16]. Recently we have also explored the redox properties of these compositions, showing that the catalysts are reducible by propane and ammonia in the absence of dioxygen and that the reduced solids can again be reoxidized by dioxygen (air) to their original, oxidized and catalytically active, state [17].

2. Experimental

2.1. Catalyst preparation

A series of catalytic materials for the ammoxidation of propane were prepared with the general precursor composition $Mo_1V_xNb_yTe_zO_n$ using published methods [3,4,18]. A first solution was prepared by dissolving ammonium heptamolybdate, ammonium vanadate, and telluric acid in water at 60 °C. This solution was allowed to cool to room temperature. A second solution was prepared by dissolving niobic acid in oxalic acid at 60 °C and allowing the solution to cool to room temperature. The Nb concentration of the final solution was 0.4 M and the oxalate/Nb ratio was 3. The appropriate amount of the first and second solutions were mixed and then dried by rotary evaporation. The solid product was dried at 120 °C for 12 h and calcined at 600 °C for 2 h under N_2. A series of catalytic materials with the precursor composition $Mo_1V_xTa_yTe_zO_n$ were prepared as above except

a Ta oxalate solution was used. The Ta oxalate solution was prepared by dissolving $Ta(OEt)_5$ in aqueous oxalic acid at 60 °C. The final Ta concentration was 0.4 M and the oxalate/Ta ratio was 3. The nominal compositions of the catalysts were $Mo_1V_{0.31}Nb_{0.1}Te_{0.23}$ (optimal), $Mo_1V_{0.31}Nb_{0.125}Te_{0.2}$ (*M1*), $Mo_1V_{0.31}Nb_{0.04}Te_{0.37}$ (*M2*), $Mo_1V_{0.31}Ta_{0.1}Te_{0.22}$ (optimal), $Mo_1V_{0.31}Ta_{0.12}Te_{0.22}$ (*M1*) and $Mo_1V_{0.3}Ta_{0.06}Te_{0.37}$ (*M2*). These catalysts were tested as described below and their performance as a function of the amount of orthorhombic (*M1*) phase is illustrated in Section 3.3.

2.2. Catalyst testing

The above-prepared materials were tested for catalytic activity in multi-channel fixed bed reactors [19]. The reaction conditions were: 150 mg catalyst charge to each channel, atmospheric pressure, 420 °C, WHSV = 0.25 to 0.1 h^{-1}, feed ratio $C_3H_8/NH_3/O_2/He = 1/1.2/3/12$. The effluent of the reactor was analyzed by gas chromatography using a plot-Q and a molsieve column with FID and TCD detectors, respectively. Conversion, selectivity, and yield are defined as: Conversion = (moles C_3H_8 consumed/moles C_3H_8 charged)×100, Selectivity = (moles product/moles C_3H_8 consumed)× (# C atoms in product/3)×100, Yield = (moles product/moles C_3H_8 charged)×(# C atoms in product/3)× 100.

X-ray powder diffraction was carried out on a Philips X'Pert Pro diffractometer using a Cu K_α source (λ = 0.15406 nm) in 0.01° steps. The SEM images were taken on a Hitachi S-4300 instrument.

2.3. Symbiosis

In the study of symbiosis, neat *M1* and *M2* phases, as well as physical mixtures of them, were prepared as described earlier [14] and had the following compositions:

(*M1*) $MoV_{0.30}Nb_{0.17}Te_{0.14}O_x$ (5.2 m^2/g), (*M2*) $MoV_{0.54}Te_{0.59}O_x$ (1.3 m^2/g) and (*M2*−W) $Mo_{0.3}W_{0.7}V_{0.54}Te_{0.59}O_x$ (2.1 m^2/g). Each of the neat phases was prepared separately, ground separately to ≤5 μm powders, compacted to 0.25–0.425 mm particles and tested. Physical mixtures were prepared from separately prepared neat phases, ground seperately to ≤5 μm powders, then thoroughly mixed and then compacted to 0.25–0.425 mm particles. The physical mixtures were blended as 50/50 by weight which resulted in a surface area ratio of: *M1/M2* = 4:1 and *M1/M2*−W = 2.5:1. The activity measurements were conducted at 380 °C, feed ratios: propane/ammonia/oxygen/Ar = 6.1/7.0/18.0/70.2 and with a space velocity varying in the range 3.3–26.3 Ncm^3 min g by varying either the flow rate or the amount of catalyst. From the obtained results the selectivity to acrylonitrile versus conversion was plotted as illustrated in Section 3.4.

2.4. Redox pulse experiments

Redox experiments were conducted as described earlier [17] by pulsing propane + ammonia in the absence of gaseous oxygen over *M1* phase of composition $MoV_{0.25}Nb_{0.12}Te_{0.11}O_x$ (surface area 14.2 m^2/g). The product distribution as a function of pulse number (reduction) was recorded. From that data and the knowledge of the compositional makeup of selective and waste forming centers on the basal (001) plane of *M1* [2,11] it is possible to calculate the degree of reduction at the various stages of reduction. Thus reduction levels at 6, 12 and 120 pulses were calculated and are discussed in Section 3.5 below.

3. Results and discussion

3.1. The active centers of M1 and M2 of MoVNbTeO catalysts

In earlier work [2,8] we have identified the active centers of both, *M1* and *M2* phases (Figures 1, 2) and note distinct differences between them. The *M1* phase contains V^{5+} sites, which the *M2* phase does not; they are considered the paraffin activating sites. The presence of V^{5+} sites is, however, not sufficient for useful catalysis; the sites must be located adjacent to a heptagonal channel which the paraffin to be activated at least partially enters in the activation process [12,20]. The *M1* phase, by virtue of its unique structure possesses the
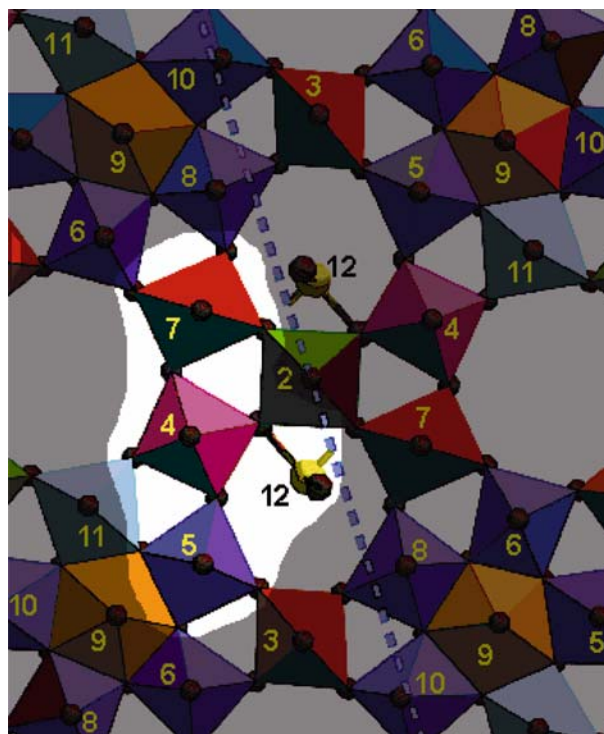

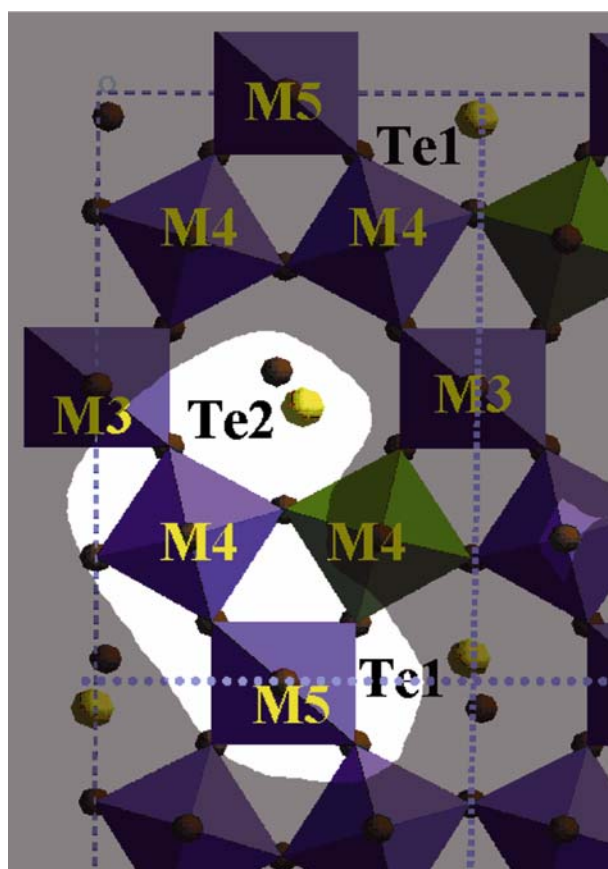Figure 1. Active center on the basal plane (001) of *M1* phase of MoVNbTeO catalysts.

Figure 2. Active center on the basal plane (001) of *M2* phase of MoVTeO catalysts.

desired heptagonal channels and the V^{5+} sites are spatially strategically located along these channels. The *M2* phase possesses neither V^{5+} sites nor heptagonal channels and is therefore not capable of activating paraffins.

The active centers of *M1* are located on the surface of their basal planes (001) and contain all needed key catalytic functionalities properly arranged within bonding distance of each other to convert propane directly to acrylonitrile (Figure 1). The V^{5+} site (M7) is the paraffin-activating site, Te^{4+} (M12) the α-H abstracting site, Mo^{6+} (M4) the NH inserting site and another adjacent Mo^{6+} (M5) the acrylonitrile finishing site. In this $8e^-$ oxidation process four surface lattice oxygen's $[O]_{LS}$ are involved in the overall reaction.

Four Nb sites surrounded by 5 Mo atoms form "pinwheels"; these delineate each active center on the surface of the basal plane and separate them spatially from each other. The thereby achieved spatial separation provides for the necessary site isolation [21,22] of the active centers, leading to the desired selectivity properties of the *M1* phase towards acrylonitrile formation [2,13].

The *M2* active center (Figure 2) is comprised of a Te^{4+} (Te1 or Te2) site responsible for the α-H abstraction of the olefin (propylene), an adjacent Mo^{6+} (M4)

site responsible for the NH insertion, and a spectator Mo^{6+} (M3, M4 or M5) site, which finishes off the acrylonitrile reaction. As already mentioned this center, lacking the appropriate V^{5+} sites, is not capable of paraffin activation and is therefore inactive for propane conversion. However, it is an excellent catalyst for the conversion of propylene to acrylonitrile and superior to *M1* for this reaction [10, 11, 13, 14]. Among others, the excellent olefin conversion lies in its rather high concentration of α-H abstracting Te^{4+} sites; the olefin (propylene) activating sites. Therefore, the *M2* phase can serve as a useful mop-up co-catalyst to the *M1* phase in mixtures of the two, complimenting each other under certain reaction conditions. This matter will be more thoroughly discussed below in the section pertaining to symbiosis (Section 3.4).

The overall process of converting propylene to acrylonitrile is a $6e^-$ oxidation. The reaction mechanism of this process is similar to that over BiMoO catalysts [2]. The function which Bi^{3+} provides in BiMoO systems is provided here by Te^{4+} of the *M2* phase (e.g. lone pair of electrons). The functions of the adjacent Mo^{6+} and its spectator Mo^{6+} are, respectively identical in the two catalyst systems.

3.2. The active centers of M1 and M2 of MoVTaTeO catalysts

The *M1* phase of MoVTaTeO system is structurally essentially identical to that of MoVNbTeO described above. We note already in the synthesis of the Ta *M1* phase that it is more easily formed than the Nb equivalent and that less Ta is required in solution to form the *M1* phase. This is also consistent with the early synthetic and structural work of Ekström et al. [23,24] using Group V elements as structure directing moieties in the synthesis of complex molybdenum oxides. He found that complex open structures of molybdenum oxides were stabilized with Group V elements in the order Ta > Nb > V. While the stability of the crystalline materials is governed by thermodynamics, the synthesis process is governed by kinetics of the nanoparticles as they form and assemble in solution [25]. Therefore, it is understandable why Ta dominates the inclusion process over Nb or V. We observe [26] that in corresponding *M1* crystals less Ta than Nb is occupied by the pentagonal bipyramides and that Ta can occupy various Mo^{6+} or V^{4+} positions. The V^{5+} positions remain essentially the same in either specimen. This results in an *M1* active center that is structurally virtually the same as that of its Nb cousins, but for the variance in the chemical makeup as described. Therefore, some difference in catalytic behavior between the two might be expected, although as will be seen below (Section 3.3) this difference is not very large.

The *M2* phase of MoV(Ta)TeO should by definition be identical to that of MoV(Nb)TeO since neither

should contain any Nb or Ta. The phase should be simply MoVTeO. In actuality, small amounts of Nb and Ta do enter the *M2* phase if it is synthesized in the presence of either Nb or Ta ions, as is the case in the *in situ* one container preparations of the respective optimal catalytic compositions, both lying in the range of about 60% *M1* and 40% *M2*.

3.3. Comparison of MoVNbTeO and MoVTaTeO catalysts

The XRD's of the Nb and Ta *M1* and *M2* phases, as well as, the optimum catalytic *M1* + *M2* phases are shown, respectively in Figures 3 and 4. As can be seen there are no obvious structural differences indicated between the Nb and Ta containing systems.

The SEM images of representative *M1*, *M2*, and optimum catalytic *M1* + *M2* mixtures of MoVNbTeO and MoVTaTeO systems, respectively are depicted in Figures 5 and 6. The samples are ground and are identical to those used in catalytic tests. In general the *M1* phase is somewhat more needle like in its habitat than is *M2*, which is more platelet like. Both of these observations have been made already earlier for the MoVNbTeO system [2,27]. The *M1* phase of the MoVTaTeO system appears to be somewhat less needle like than that of MoVNbTeO system. However, overall the differences of the habitat are rather minor between these two systems.

The catalytic behavior of the two families of catalysts is illustrated in Figure 7. Acrylonitrile (AN) yield is plotted against the percent of the *M1* orthorhombic phase. It is apparent that in both families the *M2* phase is ineffective for paraffin conversion as expected, based on their compositional makeup, as discussed above. The neat *M1* phase of the Nb containing system is slightly superior (43% AN) to that of the Ta system (41% AN). The difference is rather small and could be caused by many minor compositional or topological differences.
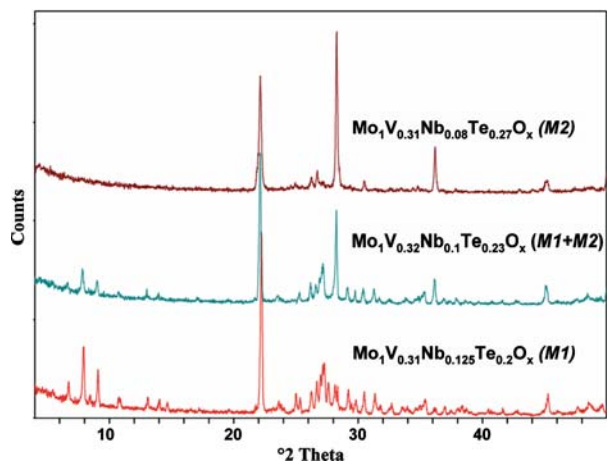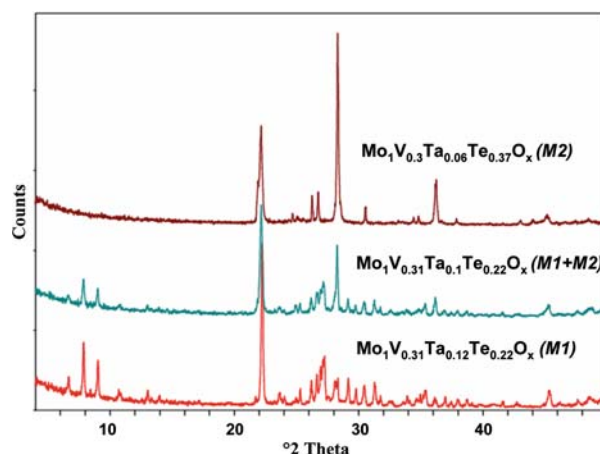

Figure 4. XRD of *M1*, *M2*, and *M1* + *M2* (catalytic optimum) of MoVTaTeO catalysts.

Remarkable is the large difference in the symbiotic behavior of the two respective optimal compositions around 60% *M1* + 40% *M2* phase. The Nb containing system yields a symbiotic acrylonitrile yield of about 62% AN while the Ta system yields only about 42% AN. Why this large difference? The two *M1* phases give almost the same AN yields and both *M2* phases show inactivity towards paraffins and are expected to exhibit essentially identical behavior towards olefins (propylene). The only obvious explanation of this large difference in symbiotic performance lies probably in a difference in surface areas and contact behavior of the respective phase pairs, depending on whether the optimal composition was prepared from Nb or Ta containing precursors. SEM images show no obvious differences of texture between the respective optimal pairs. Additional studies are needed to arrive at a more exact explanation of the observed catalytic difference.

3.4. Symbiosis between M1 and M2 phases

Several investigators [2,5,6,11,15,16] have reported improvement in product yields as a result of the cooperation of two or more phases in the MoVNbTeO system. In these studies, the optimal catalytic compositions were prepared in an *in situ* one-pot synthesis, whereby the two phases (*M1* and *M2*) or precursors thereof formed already in solution had ample opportunity to intermingle. More recently [10,13,14] we also clearly demonstrated the existence of the symbiotic effect between these phases (*M1* and *M2*), when they were prepared separately (two pot synthesis), ground separately and mixed subsequently for catalytic testing. These combined studies permitted us to define the boundaries and limitations of the symbiotic effect. The catalytic synergy exhibits itself when both phases have a maximum particle size of ≤5 *μm* and that they are thoroughly intermixed. For optimal catalytic effectiveness, the two phases must be microcrystalline

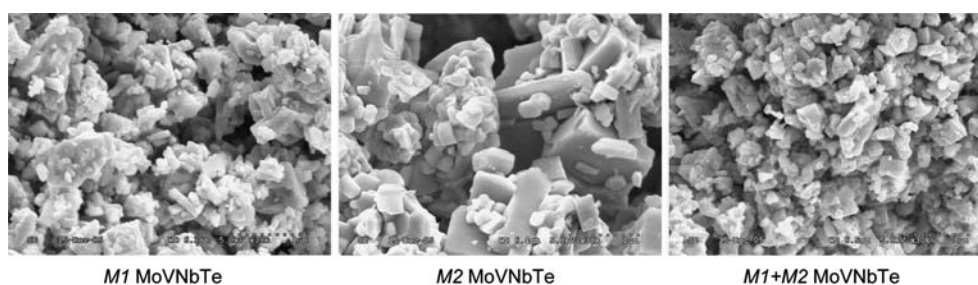Figure 3. XRD of *M1*, *M2*, and *M1* + *M2* (catalytic optimum) of MoVNbTeO catalysts.
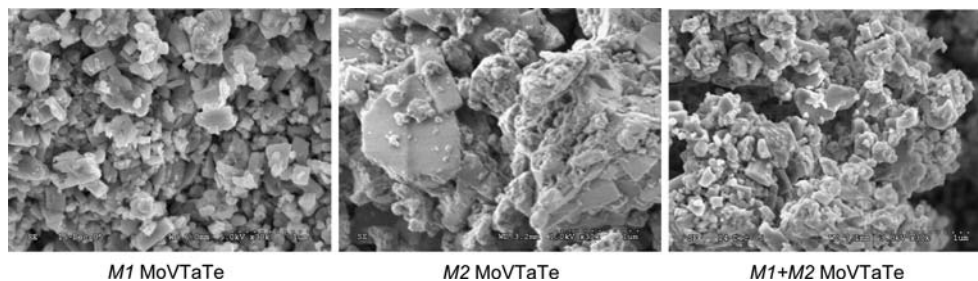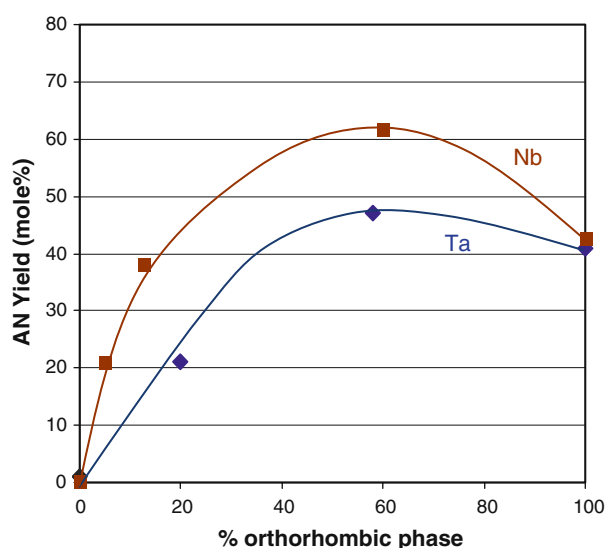
Figure 5. SEM of *M1*, *M2*, and *M1 + M2* (catalytic optimum) of MoVNbTeO catalysts.

Figure 6. SEM of *M1*, *M2*, and *M1 + M2* (catalytic optimum) of MoVTaTeO catalysts.

Figure 7. Catalytic behavior of MoVNbTeO and MoVTaTeO systems.

[2,15,16,22,28]. When they are amorphous, lacking long-range order, they are catalytically much less effective and lack long term stability [2].

Complimentary to the single-pot *in situ* prepared *M1/M2* mixtures showing symbiosis [2], physical mixtures of *M1 + M2* prepared and ground separately and mixed subsequently were now investigated for phase interaction. As a typical example of this type of interaction, separately prepared *M1* phase of composition $MoV_{0.30}Nb_{0.17}Te_{0.14}O_x$ was combined with a separately prepared *M2* phase having the composition of $MoV_{0.54}Te_{0.59}O_x$ [14]. In a second set of experiments, the same *M1* phase was commingled with a tungsten substituted *M2* (*M2*−W) phase of composition $(Mo_{0.3}W_{0.7})V_{0.54}Te_{0.59}O_x$. The cooperative phase behavior of both sets of catalysts is illustrated in Figure 8. In both instances, symbiosis is observed only under the already earlier observed requirements of small particle size (≤5 μm) and intimate mixing of phases [13,14]. The symbiotic effect at a 20% conversion level manifests itself in a 47% AN selectivity for the former mixture of phases vs. 34% for neat *M1* and a 37% AN selectivity for mixtures of *M1 + M2* particles exceeding the 5 μm limitation. Using the tungsten substituted (*M2*−W) catalyst as one of the phase pairs, the observed symbiotic AN selectivity at 20% conversion is essentially the same as that for the unsubstituted (*M2*) base pair mixture, namely 48%. Thus, the enhancement due to symbiosis for physical mixtures of *M1 + M2* or *M1 + M2*−W with particle size of ≤5 μm is about 38% over neat *M1* (also ≤5 μm particle size) and 27% over *M1 + M2* particles having a too large grain size (i.e., >5 μm). Aside from the symbiosis effect it is worthy to note that an *M2* catalyst having 70% of its Mo content substituted by W (*M2*−W) behaves catalytically very similar to its all Mo parent; i.e., as a mop-up catalyst in *M1/M2* mixtures converting propylene to acrylonitrile. This implies that a rather large amount of the molybdenum moieties in the *M2* phase of the MoV(Nb,Ta)TeO catalysts are not involved in the catalytic process. In a parallel study [29] we explore the
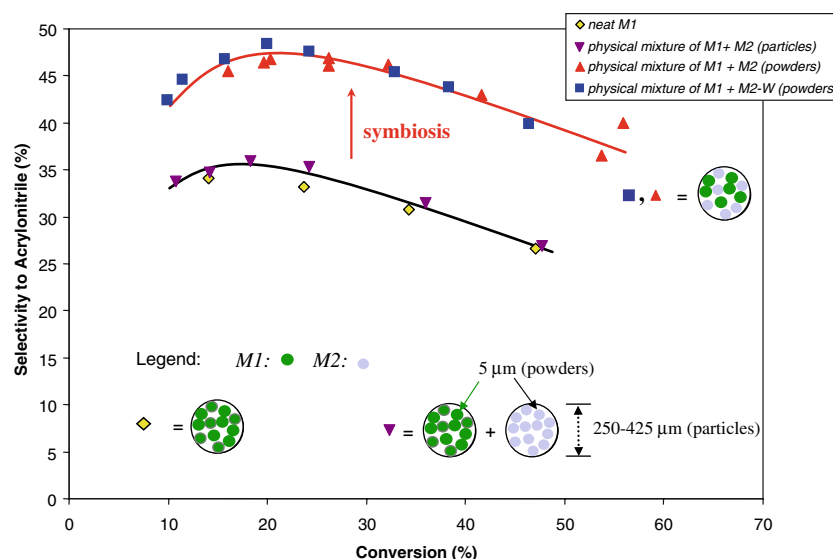
Figure 8. Symbiosis between $M1 + M2$ and $M1 + M2-$W physical mixtures of (Mo,W)VNbTeO catalysts in propane ammoxidation.

subject of substitutions, where preliminary results suggest a fruitful area of study with the promise of discovering more efficient catalysts. Thus an optimization of the Mo/W ratio in $M2$ compositions strongly influences not only the activity but also the selectivity towards acrylonitrile [29].

With symbiosis illustrated between $M1$ and $M2$ phases for the MoVNbTeO and MoVTaTeO systems comprising $M1 + M2$ mixtures prepared in a one-pot *in situ* synthesis and for physical mixtures of $M1 + M2$ phases of diverse chemical compositions synthesized separately and subsequently mixed, expands the knowledge and scope of the phase cooperation phenomenon. It still remains to be demonstrated that symbiosis occurs between any paraffin activating and olefin converting catalyst pairs. Probably some limitations will present themselves, namely lack of proper contact between the phases or chemical incompatibility of phases.

3.5. Redox behavior of MoVNbTeO catalysts

MoV(Nb,Ta)(Te,Sb)O catalysts exhibit redox properties in the catalytic cycle of the (amm)oxidation reaction. This behavior is demonstrated here on the $M1$ phase of MoVNbTeO catalyst. An essentially pure $M1$ sample (trace of $M2$) prepared by hydrothermal synthesis and having a composition of $MoV_{0.25}Nb_{0.11}Te_{0.17}O_x$ or equivalently written as $Mo_{7.8}V_{1.95}Nb_{0.86}Te_{1.33}O_x$ was investigated as a representative sample of this catalyst family [17]. Redox experiments were conducted by pulsing propane and NH_3 over the catalyst (Figure 9). The experimental range was 1–120 pulses. Indeed the catalyst can be reduced by propane and ammonia in the absence of dioxygen, confirming that the ammoxidation process

over this catalyst family and more narrowly over the $M1$ phase of the MoVNbTeO catalyst is truly a redox process involving the lattice oxygen of the solid. Further, it is significant that the product distribution in the early pulses is similar to that obtained under catalytic conditions in the presence of gaseous oxygen (air). This is further support for lattice oxygen being involved in the actual catalytic process.
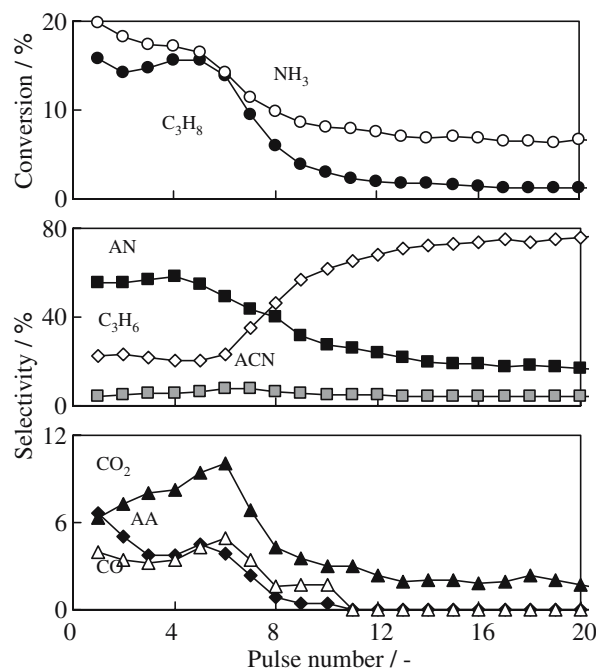

Figure 9. Conversion and product selectivity vs. $C_3H_8 + NH_3$ pulse number passed over an $M1$ phase of a MoVNbTeO catalyst [17]. Acrylonitrile (AN), Acetonitrile (ACN), Acrylic acid (AA).

From the pulse reduction experiments it becomes apparent that a substantial amount of lattice oxygen $[O]_L$ can be removed from the *M1* phase without structural collapse. Even after 120 C_3H_8 + NH_3 pulses the lattice parameters of the investigated phase are virtually unchanged [17]. From the pulse data it can be calculated that after 120 C_3H_8 + NH_3 pulses up to 70 layers of the *M1* crystals are involved in the reduction process. The assumptions for this calculation are that the reduction occurs only from the basal planes of the *M1* crystals and that the catalytic site distribution on the surface of the *M1* basal plane of MoVNbTeO proposed earlier [11] holds, namely being 44% active, 10% waste and 46% inactive. It is further assumed, based on this model, that conversion of propane and ammonia to acrylonitrile occurs exclusively on these selective surface centers removing 4 $[O]_{LS}$ from it per catalytic event. Similarly, the conversion of propane to CO_x occurs on the waste forming centers removing 10 $[O]_{LS}$ per catalytic event. It is further assumed that the respective selective and waste forming surface sites, once reduced become reoxidized by the underlying $[O]_L$, from within the crystal. It is further assumed in this calculation that the composition of the underlying layers is identical to that of the surface. Thus only lattice oxygens from equivalent, underlying sites are involved in the reoxidation. In this manner reduced channels ensue below the active center which remains oxidized until the reoxidation process from within cannot keep up with the reduction of the surface center and at which point the reaction stops. This model certainly oversimplifies the true redox process, because there will be "crosstalk" between the reduced and oxidized areas of the catalyst; it is simply a model which allows pondering about the catalyst's intrinsic properties.

We envision the reduction process of the selective catalytic center (Figure 1) [2,11], which comprises the oxidation process of the propane and ammonia molecule to acrylonitrile, to involve 1M7, 1M4, 1M12 and 1M5 site, each giving up 1[O] and $1e^-$. Since the ammoxidation process is an $8e^-$ process it is necessary to dispense of additional $4e^-$. We propose that this occurs by involving the second half of the active center, namely the complimentary set of 1 M7, 1M4, 1M12 and 1M5 sites. In this manner eight elements of the center are reduced, each by $1e^-$ as seen in Figure 10, thereby distributing the charge over the entire center. In this process, 4 $[O]_{LS}$ were removed producing one acrylonitrile. The center now awaits its reoxidation, which is proposed to occur through diffusion of $[O]_L$ from within the crystal towards the surface.

In a manner similar to the selective process, the waste forming process is thought to occur on the waste forming centers of the basal plane of the *M1* crystals. In this process 10 $[O]_{LS}$ are involved per catalytic event. And according to our active center site description [11] there are 10 surface lattice oxygens available at the waste
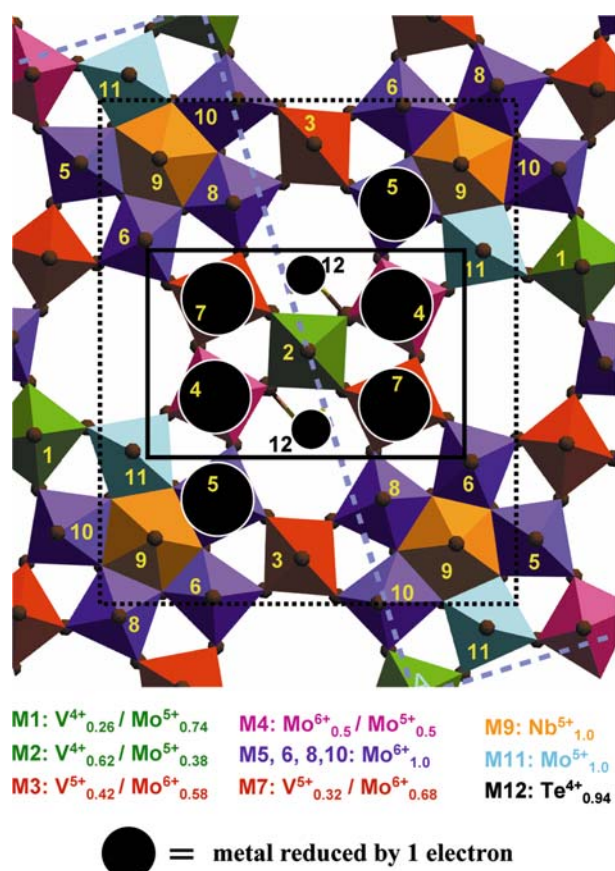

Figure 10. Reduced selective active center on the basal plane of an *M1* crystal of a MoVNbTeO catalyst.

forming center as follows: 2M7, 2M4, 2M12, 2M5 and 2M8. As already discussed [2], two V^{5+} sites per active center in respective M7 positions create a waste forming center (see Figure 1 and distribution probabilities in [11]). The waste forming process requires $20e^-$, therefore another 10 elements must be identified where the remaining charge can be distributed. Likely candidates in the proximity are: 2M3, 4M6, 2M10 and 2M8. A reduced waste forming center with its 10 surface lattice oxygens removed and the reducing charge of 20 e- disbursed over the entire active center is shown in Figure 11. Again, it is assumed that underlying lattice oxygens regenerate the surface center in the pulse experiments until the process exhausts itself and the reaction stops. This actually did not occur in its entirety even after 120 pulses since some waste still continues to form even at this deep reduction level of the solid.

Another interesting conclusion can be drawn from the analysis of the product distribution over the first six reduction pulses (Figure 9). At this point, 0.46% of the total lattice oxygen is removed with the reduction proceeding 14 layers deep; accepting our proposed reduction assumptions mentioned above. It is noted that over these six pulses the selectivity to AN is relatively constant at about 55% and that to propylene about 22%. Thereafter, the selectivity to AN drops dramatically and
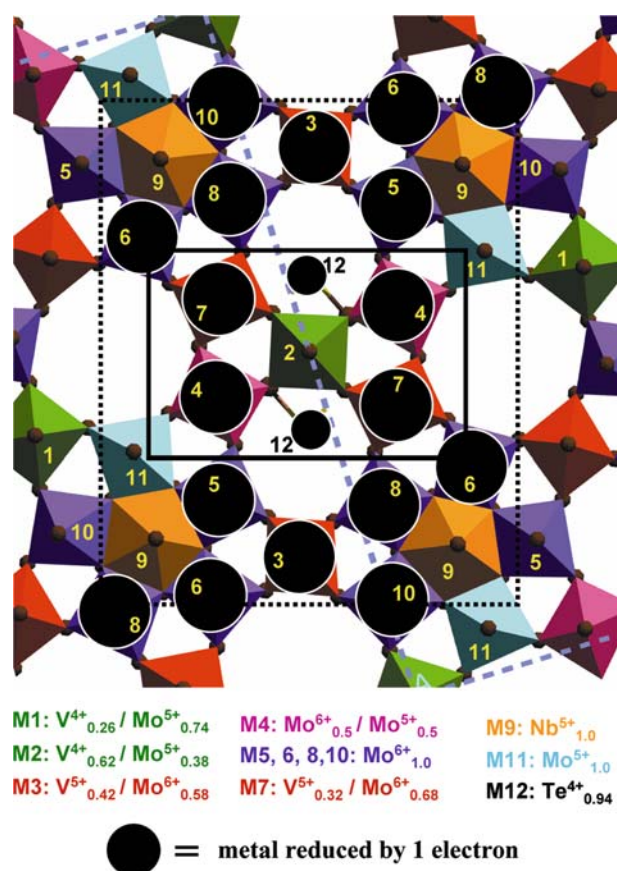
M1: $V^{4+}_{0.26}$ / $Mo^{5+}_{0.74}$ M4: $Mo^{6+}_{0.5}$ / $Mo^{5+}_{0.5}$ M9: $Nb^{5+}_{1.0}$
M2: $V^{4+}_{0.62}$ / $Mo^{5+}_{0.38}$ M5, 6, 8,10: $Mo^{6+}_{1.0}$ M11: $Mo^{5+}_{1.0}$
M3: $V^{5+}_{0.42}$ / $Mo^{6+}_{0.58}$ M7: $V^{5+}_{0.32}$ / $Mo^{6+}_{0.68}$ M12: $Te^{4+}_{0.94}$

● = metal reduced by 1 electron

Figure 11. Reduced waste forming center on the basal plane of an *M1* crystal of a MoVNbTeO catalyst.

M1: $V^{4+}_{0.26}$ / $Mo^{5+}_{0.74}$ M4: $Mo^{6+}_{0.5}$ / $Mo^{5+}_{0.5}$ M9: $Nb^{5+}_{1.0}$
M2: $V^{4+}_{0.62}$ / $Mo^{5+}_{0.38}$ M5, 6, 8,10: $Mo^{6+}_{1.0}$ M11: $Mo^{5+}_{1.0}$
M3: $V^{5+}_{0.42}$ / $Mo^{6+}_{0.58}$ M7: $V^{5+}_{0.32}$ / $Mo^{6+}_{0.68}$ M12: $Te^{4+}_{0.94}$
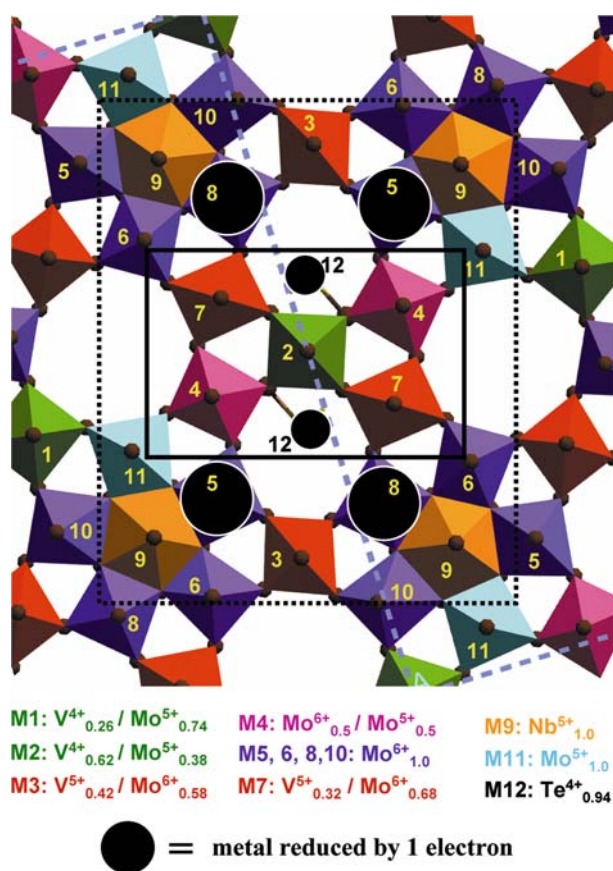
● = metal reduced by 1 electron

Figure 12. Partially reduced selective active center on the basal plane of an *M1* crystal of a MoVNbTeO catalyst. This center is capable of oxidizing propane to propylene and NH_3 to N_2, but not propane + NH_3 to acrylonitrile.

that to propylene increases significantly. This suggests that at this reduction level of the catalyst Te^{4+} is reduced to $Te^{(3+)}$ or Te^{2+} impairing the α-H abstraction of the adsorbed propylene molecule and hence indirectly impairing the NH insertion function. The production of AN ceases. However, the center is still able to produce propylene, meaning that the propane activating function of V^{5+} (M7) is still in tact. From first principles of redox chemistry it can be reasoned that the regenerability of the elements involved in the reduction of the active center will be $V^{4+/5+} \sim Mo^{5+/6+} > Te^{2+/(3+)/4+}$, with V^{5+} being restored first, followed by Mo^{6+}, followed by Te^{4+}. Thus, a partial regeneration of the selective center by accepting one $[O]_L$ from the bulk and thereby transferring $2e^-$ to the bulk, creates a surface active center still capable of oxidizing propane to propylene, but not further to AN. Such a partially reoxidized center is illustrated in Figure 12. It is envisioned that the 1st H abstraction from propane occurs again on a V^{5+} (M7) site, just like in the selective ammoxidation process when the active center is fully oxidized [2]. However, since now Te^{4+} is absent, the 2nd H abstraction is performed by a Mo^{6+} (M6 or M4) site yielding a propylene molecule which desorbs without further transformation to AN, at the center. The H abstraction by a Mo^{6+} moiety results in a Mo^{5+} mono-oxo species, which has a triply-

bonded Mo = O character, known as the "spectator oxo" effect proposed by Goddard and Rappe [30]. This constellation is estimated to add about 13–18 kcal/mole of driving force to the 2nd H abstraction reaction on Mo^{6+} di-oxo centers [31]. However, since the process only involves a $2e^-$ oxidation, any combination of adjacent V^{5+} - Mo^{6+} - $Mo^{6+/5+}$ moieties should be able to perform this task. The same, partly reoxidized active centers (Figure 12) are deemed also capable of oxidizing NH_3 to N_2.

Beyond the first six pulses, the activity of the catalyst (Figure 9) declines significantly. Both, the conversion of propane as well as that of ammonia decline in tandem, with propane conversion dropping faster. Although more (3) lattice oxygens are required to convert NH_3 to N_2 than are to convert propane to propylene (1) the reactivity at this catalyst reduction level does not follow the simple stoichiometric oxygen requirement of the reaction. Presumably the higher basicity of the NH_3 molecule over propane dictates the reaction sequence through preferential chemisorption on the active center of the partly reduced catalyst. The abrupt drop in activity further portends that the reoxidation of the surface centers through the bulk lattice oxygens slows

down substantially once a few (e.g. 14) layers of the catalyst have become partly reduced.

Significant amounts of lattice oxygen can be removed without structural collapse from the *M1* structure [17]. According to our estimate after 6 (C_3H_8 + NH_3) pulses 14 layers of the crystal are reduced, which is equivalent to 0.46% of the total lattice oxygen having been removed. After 12 pulses 19 layers are reduced (0.62% $[O]_L$ removed) and after 120 pulses 70 layers (2.4% $[O]_L$ removed). If a catalyst, reduced by 120 C_3H_8 + NH_3 pulses, is reoxidized with pulses of gaseous dioxygen (air) then the calculated number of reduced layers is 56, equivalent to 1.9% of the total lattice oxygen. This apparent discrepancy, 70 vs. 56 layers is not unusual, since it is essentially impossible to completely reoxidize a significantly reduced oxidation catalyst with a limited number of oxygen (air) pulses. To achieve complete reoxidation it is necessary to expose the catalyst to a flow of oxygen (air) for about 15 min at reaction temperature or shorter at a somewhat higher temperature. Therefore, the 70-layer estimate is considered a more realistic assessment of the 120 pulse (C_3H_8 + NH_3) reduction than the 56-layer estimate.

In sum, the ammoxidation process of propane to acrylonitrile over MoVNbTeO catalysts is a redox process, most likely following a Mars van Krevelen [32] mechanism, or a modification thereof.

4. Conclusions

1) Through judicious analysis of XRD, ND, HREM, SEM data, as well as, application of sound chemical concepts, theory and analysis of catalytic data, the structure and composition of the active centers of *M1* and *M2* phases of MoV(Nb,Ta)TeO catalysts were determined. All catalytic functionalities of the active and selective centers, as well as, waste forming centers, could be assigned to specific metals.

2) Symbiosis between *M1* and *M2* mixtures was demonstrated for propane ammoxidation and conditions for its occurrence defined. Phase cooperation occurs with one-pot *in situ* synthesized phase mixtures, as well as with separately prepared phases that are physically mixed post synthesis.

3) Redox behavior of MoVNbTeO catalysts was observed and defined. Redox driven interactions of the active centers between the surface and the bulk could be ascertained and mechanistically interpreted. *M1* crystals could be reduced with C_3H_8 + NH_3 pulses, whereby up to 70 layers were involved in the reduction process. The *M1* crystallites could be restored to their original fully reoxidized state and without structural collapse using dioxygen (air) pulses.

4) A moderately reduced MoVNbTeO catalyst (*M1* phase), produces propylene as its major useful product under anaerobic ammoxidation conditions.

This observation could be developed further, leading ultimately to the discovery of a useful propane to propylene oxydehydrogenation process.

5) The possible role which dislocations, if at all present, might play in the catalysis of MoV(Nb,Ta)(Te,Sb)O solids remains unanswered at this junction. Additional TEM experiments employing spherically corrected electron optics are warranted.

6) A focused, well thought out and intelligent combinatorial methodology program should be initiated with the aim of scanning substantial regions of the periodic table to identify new chemical compositions for selective paraffin activation and their subsequent selective (amm)oxidation. If combinations of elements are chosen based on sound chemistry, structural considerations and experience-rich intuition, new catalytic systems of interest should be identifiable.

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