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Selectivity issues in (amm)oxidation catalysis

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Dedicated to Professor Ferruccio Trifiro on his 65th birthday; a fine scientist in the area of catalysis and a very special personal friend. We first met at the Fourth International Congress on Catalysis in Moscow, Russia in 1968 from whence we kept a keen scientific contact, cooperated in research, published together and shared the 2001 Oxidation Catalysis Prize at the Fourth World Congress on Oxidation Catalysis in Berlin, Germany.

Abstract

Selectivity is currently taking center stage in heterogeneous oxidation catalysis as the cost of feed materials escalates. Particularly important and imperative for commercial processes is selectivity at acceptably high conversions. Dealing with this demanding quest we proposed, some 40 years ago, the concept of site isolation, defining one of the key requirements needed to achieve selectivity in oxidation catalysis. This principle continues to be useful in the conceptual design of new selective oxidation catalysts and has successfully described the selectivity behavior of many commercial (amm)oxidation catalysts, including now the MoVNbTeO system for propane ammoxidation to acrylonitrile (or oxidation to acrylic acid). In its catalytically optimum form, this system is comprised of at least two crystalline phases, orthorhombic $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (*M1*) and pseudo-hexagonal $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (*M2*). The *M1* phase is the key paraffin activating and ammoxidation catalyst, its active centers containing all of the key elements V^{5+}, Te^{4+}, Mo^{6+}, properly arranged to catalytically transform propane to acrylonitrile, and four Nb^{5+} centers, each surrounded by five molybdenum-oxygen octahedra, isolating the active centers from each other, thereby preventing overoxidation and leading to the observed high selectivity of the desired acrylonitrile product. Symbiosis between the *M1* and *M2* phases occurs when the two phases are synthesized concurrently in one vessel; or between physical mixtures of the two separately prepared phases provided they are finally divided (≤ 5 μm), thoroughly mixed and in micro-/nano-scale contact with each other. This phenomenon is particularly pronounced at high propane conversion when the *M2* phase begins to serve as a co-catalyst to the *M1* paraffin activating phase, converting extraneous, desorbed propylene intermediate, emanating from the *M1* phase, effectively to acrylonitrile in a phase cooperation mode. The *M2* phase is incapable of propane activation, lacking V^{5+} sites, but is a better propylene to acrylonitrile catalyst than the *M1* phase since it possesses a higher concentration of Te^{4+} sites (i.e., propylene activating sites). Reaction networks for propane (amm)oxidation are proposed for these catalysts.

Keywords: Selectivity; Ammoxidation; Propane; Propylene; Acrylonitrile; Acrylic acid; Catalytically active centers; Site isolation; Phase cooperation; Symbiosis; Reaction mechanisms; $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (*M1*); $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (*M2*); *M1*/*M2* mixtures

1. Introduction

Selectivity plays a central role in heterogeneous oxidation catalysis. It is of utmost importance in industrial catalytic processes, and gaining ever greater importance as the starting hydrocarbons become less abundant and hence more expensive. To develop a successful commercial catalyst it is important that selectivity is also achieved at reasonably high conversions. The importance assigned to achieving high selectivity at reasonable conversions has been recognized by some catalytic researchers already in the forming years of selective heterogeneous light hydrocarbon oxidation and ammoxidation catalysis. Thus, as early as 1963 Callahan and Grasselli [1] put forward their hypothesis of site isolation. This hypothesis states that oxidation catalysts become selective when the number of reacting oxygens at the active centers on the surface of a catalyst is limited and that the active centers must be spatially isolated

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from each other. This site isolation hypothesis has been verified on many catalytic systems since its inception and has served their originators well in the discovery of an array of catalytic solids for the oxidation and ammoxidation of light olefins, several of which have successfully been commercialized, e.g., several generations of catalysts for the ammoxidation of propylene to acrylonitrile and the oxidation of propylene to acrolein and acrylic acid, respectively [2]. The importance of the site isolation hypothesis as we proposed it [1] has been acknowledged already very early by Trifiro, and he was one of the first to recognize and quote our work in the literature, and he adopted and applied it successfully to catalytic systems of interest to him [3].

The site isolation hypothesis can be extended to also include systems such as the MoVNb(Te,Sb)O catalyst for the selective oxidation and ammoxidation of paraffins, e.g., propane conversion to acrylic acid or acrylonitrile, respectively. The latter is the main subject of this contribution. Although the well-known SOHIO/BP process [2,4] for the ammoxidation of propylene to acrylonitrile is very efficient giving 80+% acrylonitrile yield on commercial scale [5], there exists a large incentive, because of the sizable price differential between propane and propylene, to discover an effective propane conversion catalyst so that future commercial ammoxidation processes would become paraffin based. Promising catalyst candidates to achieve this goal are the promoted VSbO and the MoVNb(Te,Sb)O systems, with the latter holding an edge over the former [6].

2. Experimental

The methods employed for the preparation, evaluation and optimization of MoVNb(Te,Sb)O catalysts; and for their structure determinations have been described earlier [7]. Further details pertaining to the solutions of the *M1* and *M2* structures are found in Refs. [8,9] and [10,11], respectively. The preparation, grinding, compacting, sizing, heat treating and catalytic testing of *M1*/*M2* physical mixtures are described in Ref. [12].

3. Results and discussion

Since its inception some 40 years ago, the site isolation hypothesis [1] has been extended and applied successfully over the years from the original CuO catalyst to include such systems as the V_2O_5/KVO_4, $Bi_9PMo_{12}O_{52}$, (K,Cs)(Ni,Co,Mg)(Fe,Ce)(Sb,P)BiMoO, USb_3O_{10}, FeSbO, VSbO, $(VO)_2P_2O_7$, and now also the MoV(Nb,Ta)(Te,Sb)O catalyst systems. The subject has been recently reviewed [13]. In all of the above listed systems, high desired product selectivity can be explained on the basis that the number of reactive oxygens is limited at their respective catalytically active centers and that these centers are spatially separated from each other. The desired site isolation on the surface of the solid catalysts can be achieved either by partial reduction (CuO), by breaking up interconnecting M–O–M (V–O–V) chains (V_2O_5/KVO_4), by phosphate fences $(VO)_2P_2O_7$ or by selected structural makeup of the solids (e.g., the remaining examples listed above).

While selectivity is of utmost importance in oxidation catalysis and drives innovation to which the theme of this symposium attests, it is, however, in itself, not necessarily sufficient as already mentioned, particularly not when a catalyst is sought viable for use in commercial processes. Selectivity by itself cannot be bottled or put into drums and sold! Selectivity must be accompanied by sufficient activity in a catalyst so that reasonable product yields are achieved in once through processes. It is much easier to obtain high catalyst selectivity at low conversions than at high conversions. A catalyst giving 95% of the desired product

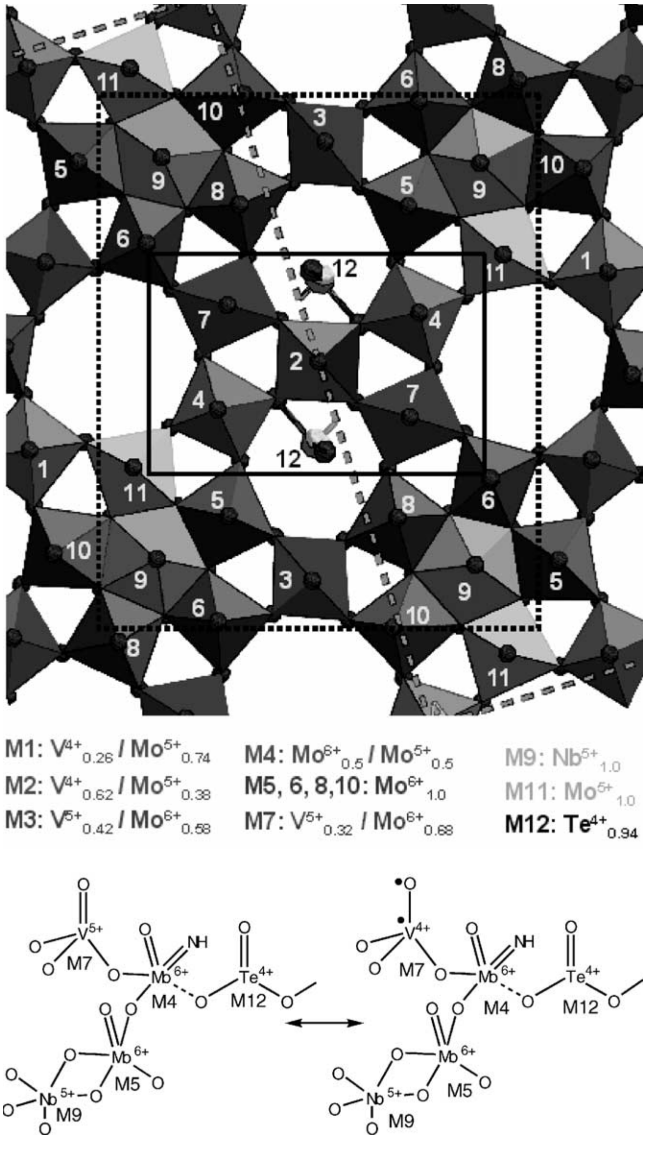


Fig. 1. Catalytically active center of $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{29}$ (*M1*) phase in [0 0 1] projection and ChemDraw illustration of the active site [7].

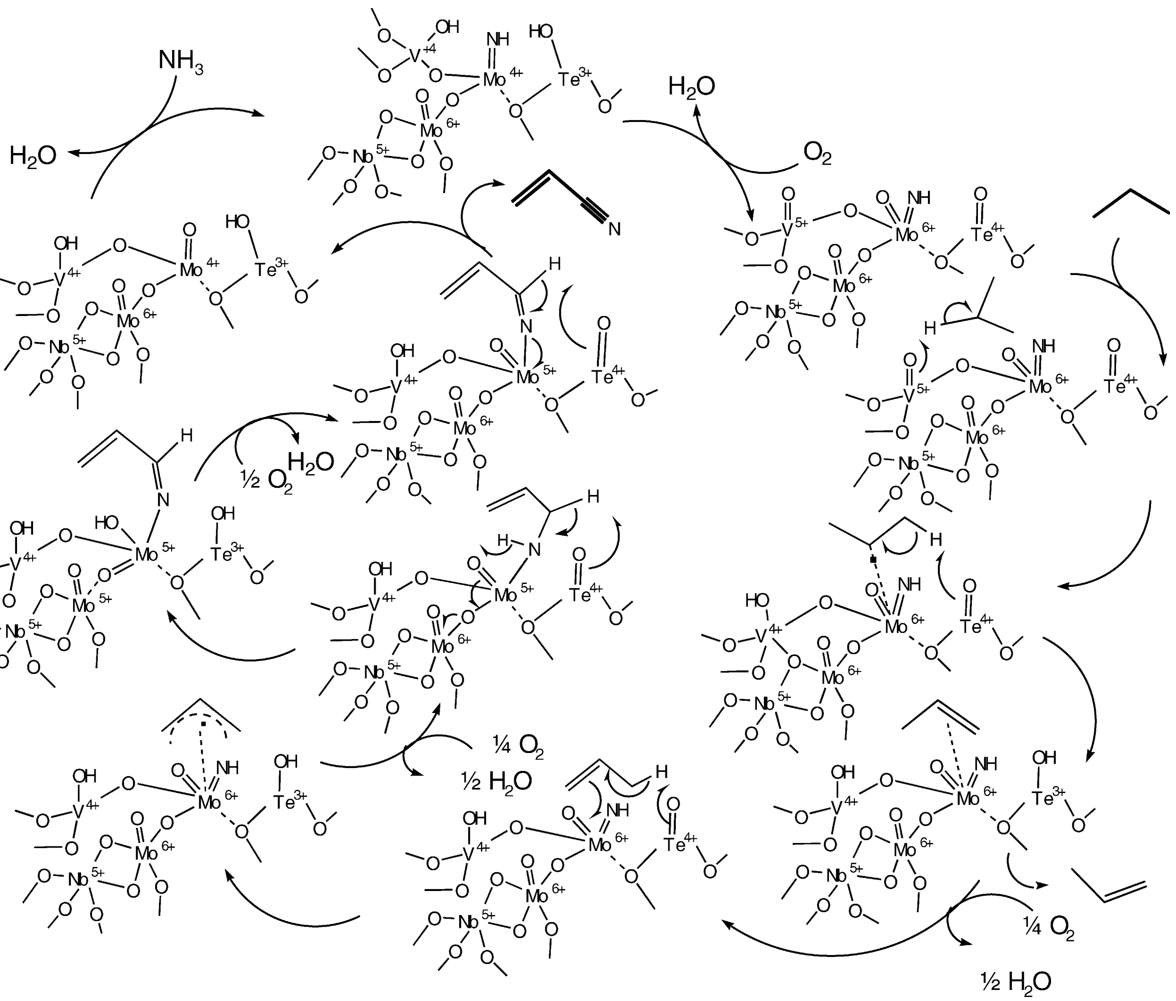


Fig. 2. Proposed propane ammoxidation mechanism over MoVNbTeO catalysts [7].

at 5% conversion will not lead to a successful commercial process since the investment for the plant and feed recycle would be cost prohibitive; certainly a truism for commodity chemicals. For these reasons it is important to discover catalysts which are selective not only at low, but also at high conversions! All of the above listed catalysts, obeying the site isolation hypothesis fall into this category.

Since this contribution deals primarily with the ammoxidation of paraffins, in particular propane, using MoV(Nb,-Ta)(Te,Sb)O catalysts, it is important in addition to the desired acrylonitrile selectivity to also address the question of the source of paraffin activation. It is now well known that most of the heterogeneous catalysts effective for paraffin activation and subsequent selective oxidation or ammoxidation contain vanadium as the key paraffin activating element, be it a VSbO, a MoVNb(Te,Sb)O or a AlVON system [6]. In order to make these systems not only active but also selective at reasonable paraffin conversions and throughputs it is necessary to structurally isolate the paraffin activating vanadium centers from each other (i.e., site isolation). We have recently determined that not all vanadium sites activate paraffins; the presence of V^{5+} sites is mandatory, V^{4+} sites appear to be ineffective for paraffin activation [6,7]. The distortion of the metal octahedra caused by the heptagonal channels of the *M1* structure impose added activity (strain energy) to the V^{5+} sites of the *M1* active centers [7,8].

The maximum acrylonitrile yield from propane is currently obtained with a MoVNbTeO system (~62%) [7], a close second is a MoVNbSbO system (~55+%) [6,14]. Both of these are structurally similar, in both the (V^{5+}=O $^{4+}V^{\bullet}$–$O^{\bullet}$) moiety is the paraffin activating center, while in the first the Te^{4+}–O center is the α-H abstracting moiety activating the once formed chemisorbed (or desorbed) propylene intermediate, while in the second catalyst it is the Sb^{3+}–O center [7].

The MoVNbTeO system discovered by the Mitsubishi Company [15] is comprised of three crystalline phases: an orthorhombic $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (*M1*), a pseudo-hexagonal $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (*M2*) and a trace of monoclinic $TeMo_5O_{16}$ [7–9]. The key paraffin conversion phase is *M1*. This phase contains active centers comprised of an assembly of five metal oxide octahedra ($2V_{0.32}{}^{5+}$/$Mo_{0.68}{}^{6+}$, $1V_{0.62}{}^{4+}$/$Mo_{0.38}{}^{5+}$, $2Mo_{0.5}{}^{6+}$/$Mo_{0.5}{}^{5+}$) and two tellurium-oxygen sites ($2Te_{0.94}{}^{4+}$), which are stabilized and

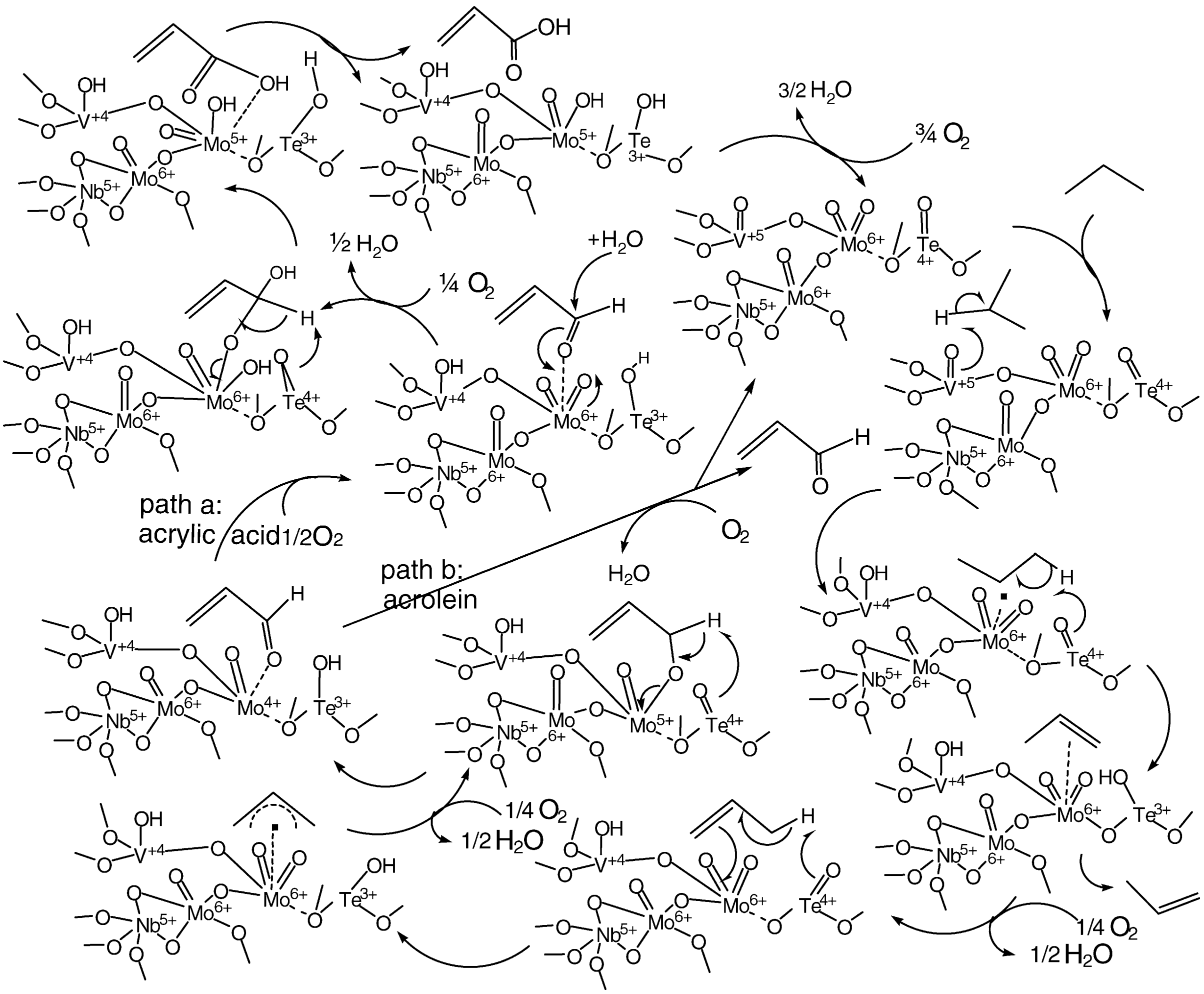


Fig. 3. Proposed propane oxidation mechanism over MoVNbTeO catalysts [17,18].

structurally isolated from each other (site isolation) by four Nb^{5+} centers, each in turn surrounded by five molybdenum–oxygen octahedra (Fig. 1). Although we are well aware [7,9] that the exact elemental composition of the surface will differ somewhat from that in the bulk (e.g., slightly higher Nb and Te and slightly lower V concentrations at the surface of *M1*) and that there are dangling bonds and imperfections on the surface, the surface is nonetheless an extension of the bulk and the structural and spatial arrangements at the surface are deemed not to be significantly different from those of the bulk. Based on these premises, we can reason about the catalytic properties of *M1* and *M2* by meaningfully relying on the intimate knowledge of the structural and compositional makeup of the bulk and the awareness that there will be some differences on the surface. The short range order on the surface will be similar to that in the bulk, although the long range order might be different. These facts will, however, not materially change the interpretation of the overall catalytic behavior.

We conclude that the catalytically active centers of the important *M1* phase are located on the surface of its basal plane (Fig. 1) containing all the necessary key elements within bonding distance of each other to convert propane directly to acrylonitrile with but minimum movement (just a flip) of chemisorbed reaction intermediates about the center. As already mentioned, the $V^{5+}{=}O\ {}^{4+}V^{\bullet}{-}O^{\bullet}$ sites activate the propane by abstracting a methylene hydrogen, the $Te^{4+}{-}O$ sites abstract the α-H of the chemisorbed propylene once formed and the adjacent $O{=}Mo^{6+}{=}NH$ centers insert the NH into the chemisorbed π-allylic intermediate thereby forming the acrylonitrile precursor as shown in Fig. 1. Based on these proposed catalytic steps, derived on the basis of sound classic organic chemistry, theory [16] and an in depth knowledge of the *M1* structure [7–9], a complete ammoxidation reaction mechanism can be written as shown in Fig. 2 [7]. Because of space limitations and its earlier description, it will not be further elucidated here. In complete analogy to the ammoxidation mechanism an oxidation mechanism (Fig. 3) for the selective oxidation of propane to acrylic acid can also be proposed [17] and is discussed fully in another publication [18]. Here, the methylene hydrogen of the propane is again activated and abstracted by the $V^{5+}{=}O\ {}^{4+}V^{\bullet}{-}O^{\bullet}$ sites located at the active centers of the *M1* basal plane, as was the case in ammoxidation. The adjacent Te^{4+}–O sites abstract the α-H of the chemisorbed propylene once formed and the adjacent $O{=}Mo^{6+}{=}O$ centers insert the surface lattice O into the chemisorbed π-allylic intermediate thereby forming a site chemisorbed σ-O-allylic intermediate. This specie could desorb as acrolein, however, the preferred and more likely reaction path is attack by a water molecule leading to a surface bound acrolein hemiacetal intermediate which then readily further oxidizes and desorbs as acrylic acid.

In the context of both above described reaction mechanisms, it might be worth mentioning that the MoVNbTeO catalysts exhibit IR bands in the 875–925 cm^{-1} region [19–21], which attest to higher order Mo–O bonds, namely Mo=O and O=Mo=O. It was Trifiro et al. [22] who first suggested that selective molybdenum based olefin oxidation catalysts exhibit characteristic IR bands in the 900–1000 cm^{-1} region, and assigned these to the asymmetric stretching vibrations of Mo=O bonds. We later determined that these Mo=O moieties and in particular the $O{=}Mo^{6+}{=}O$ sites that under ammoxidation conditions transform to the iso-electronic NH inserting $O{=}Mo^{6+}{=}NH$ centers are respectively responsible for the oxygen insertion into the π-allylic surface intermediate in the oxidation of propylene to acrolein and under ammoxidation conditions for the NH insertion to yield acrylonitrile [7,16,23,24]. We extended this concept to include other molybdate catalysts wherein we noted that the onset of selective oxidation/ammoxidation was first observed when IR bands in the region 893–902 cm^{-1} become visible (assigned to higher order M–O bonds) [25] and extended this concept still further to include also antimony based systems where useful selectivity is observed when IR bands in the region 870–930 cm^{-1} first appear [26]. That M=O moieties (where M = Mo, Sb, etc.) are associated with selective oxidation catalysis [22] and that these moieties can be invoked as the O or NH insertion sites [23,24] appears to be generally applicable to selective molybdenum and antimony based catalysts including now also the MoVNb(Te,Sb)O systems.

Of substantial importance for achieving desired product selectivity is the spatial arrangement and distribution of the various elements of the MoVNbTeO catalyst on the basal plane of the *M1* phase. Fig. 4 reveals that the catalytically active centers are arranged in spatially isolated patterns [7]. This structural arrangement favors high selectivity to acrylonitrile under ammoxidation conditions and acrylic acid under oxidation conditions, respectively by minimizing unwanted overoxidation to CO_x and other waste products. A statistical analysis of the various distribution probabilities of

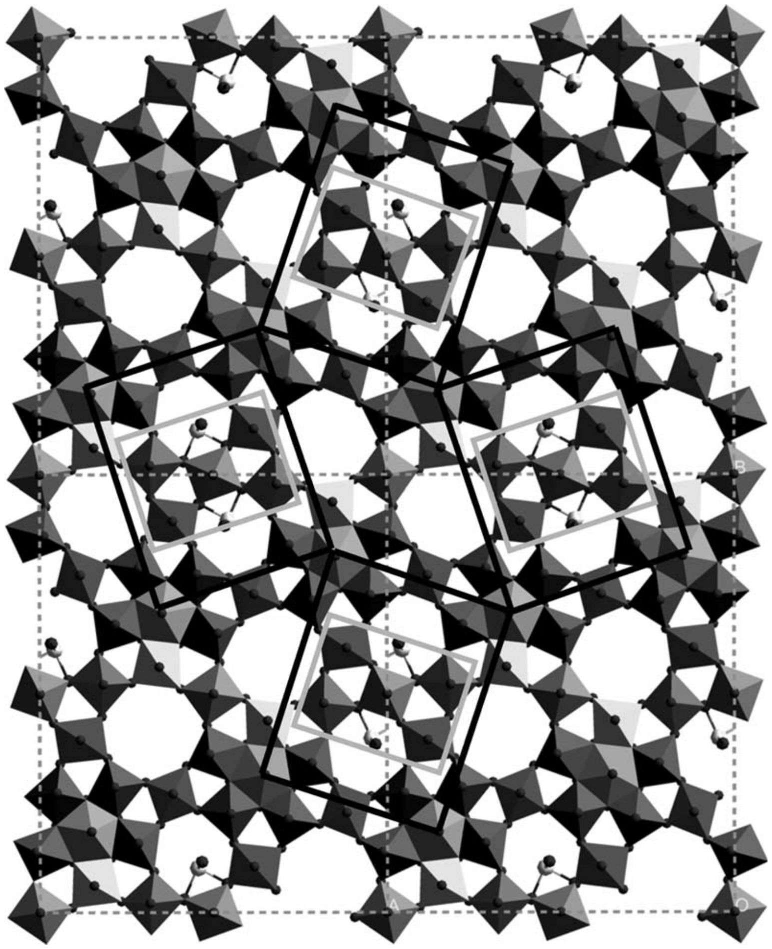


Fig. 4. Site isolation. Four catalytically active centers on *M1* surface in [0 0 1] projection [7].

the key catalytic elements at the active site of *M1* was recently performed [6] and the conclusion derived therefrom is that a maximum attainable acrylonitrile selectivity of 81% should be possible using *M1* as the catalyst. Thus far the maximum experimentally obtained acrylonitrile selectivity is 72% [7]. A possible explanation for this difference might lie in the fact that some propylene desorbs from the *M1* active centers before it has an opportunity to be fully converted to acrylonitrile at these centers; begins to migrate, encounters other V^{5+} sites and combusts. This is a plausible explanation on several counts, not least that unconverted, desorbed propylene is observed as a substantial intermediate product at low propane conversions with neat *M1* as catalyst [27,28] and symbiosis taking place between *M1* and *M2* phases leading to improved acrylonitrile yields at high propane conversions [6,7,12].

The phenomenon of symbiosis (phase cooperation) occurring between the *M1* and *M2* phases by catalytically cooperating with each other in a constructive way has been reported earlier [7,29] and has recently been explored in greater detail by us [12]. While in our earlier study we observed symbiosis when the two phases were simultaneously prepared in one pot, we did not observe it when the two phases were prepared separately and then commingled as a physical mixture [7]. We have now [12] succeeded to demonstrate the desired catalytic symbiotic effect also when the two phases were prepared separately and were then subsequently mixed. However, there are some stringent prerequisites to attain symbiosis. The results are shown in Fig. 5. Symbiosis does not occur if the two separately and thoroughly ground (≤5 μm) *M1* and *M2* phases are separately compacted, separately resized to particles of 250–425 μm and then intermixed to a physical mixture prior to catalytic testing. Symbiosis does, however, occur when these separately and thoroughly ground (≤5 μm) *M1* and *M2* phases are first intimately mixed as powders with each other, compacted, and sized to 250–425 μm. In order to allow for direct comparison of catalytic results between the physical *M1*/*M2* mixtures and neat *M1* phase, the latter was subjected to the identical treatment of grinding (≤5 μm), compacting and sizing to 250–425 μm particles. The symbiotic effect is now clearly observed for a 50 wt.% *M1*/50 wt.% *M2* physical mixture (compacted from ≤5 μm powders) compared to the catalytic performance of the neat *M1* phase, alone (Fig. 5). Its magnitude depends on the severity of reaction conditions, as anticipated [6]. At propane conversions below 5% there is no enhancement in acrylonitrile selectivity or yield of the physical mixture over that obtained with *M1*, alone. However, at higher conversions the enhancement is substantial. For example, at 30% propane conversion a selectivity of 46% is observed with the mixture while the *M1* phase alone exhibits a selectivity of only 33%. One can reason that at the lower propane conversions the classical site isolation principle dictates the selectivity behavior of *M1* [6,7]. At higher propane conversions a substantial amount of propylene that forms on the *M1* phase desorbs as free propylene before it can be directly converted to acrylonitrile at its active center and before it readsorbs on this phase encountering adjacent V^{5+} sites which would lead to combustion. If the particle size of the *M1* phase is sufficiently small (e.g., ≤5 μm) and when these particles are located in the immediate proximity of *M2* phase particles (also ≤5 μm), the free propylene emanating from the *M1* phase can now competitively react on the *M2* phase. Since the *M2* phase does not possess significant amounts, if any, of V^{5+} centers (mainly benign V^{4+} centers), but ample Te^{4+} centers (more than the *M1* phase), these latter centers effectively activate the olefin (α-H abstraction) and convert it to acrylonitrile. Independently, it is well known that *M2* phase is more efficient in converting propylene feed to acrylonitrile than is *M1* phase [12,27].

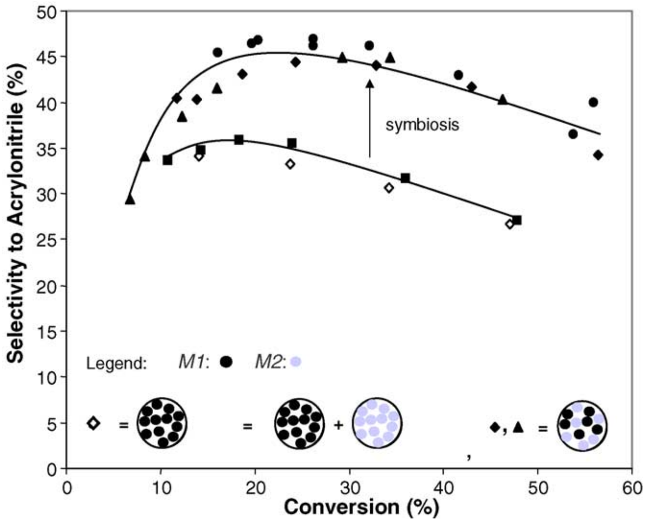
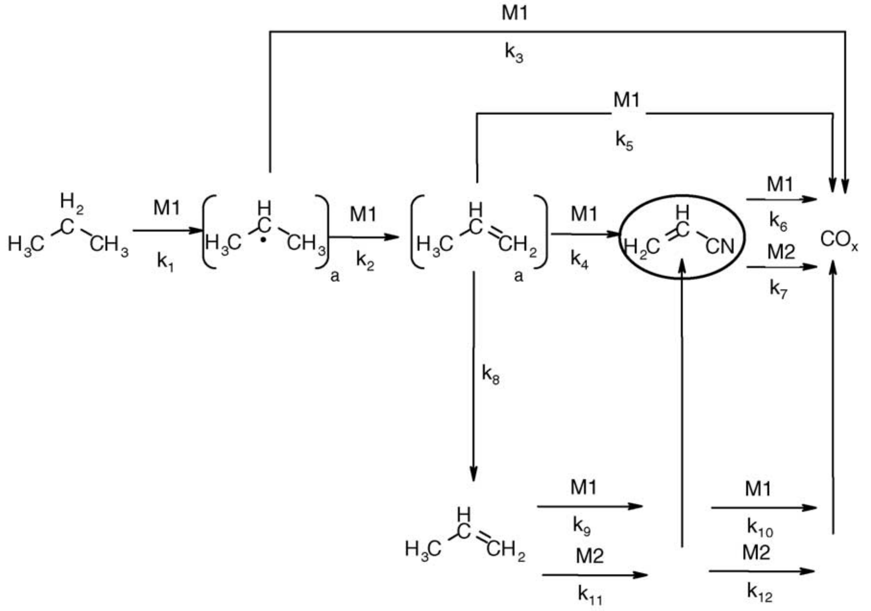


Fig. 5. Symbiosis (phase cooperation) between *M1* and *M2* physical mixtures in propane ammoxidation [12]. Neat *M1* phase ($Mo_{7.8}V_{2.2}Nb_{1.5}$-$Te_{0.9}O_x$), ground to ∼5 μm powder, compacted and sized to 250–425 μm particles; (■) *M1* + *M2* separately ground to ∼5 μm powders, separately compacted and sized to 250–425 μm particles, then mixed; (●) *M1* + *M2* separately ground to ∼5 μm powders, mixed, compacted and sized to 250–425 μm particles; (◆) *M1* + *M2* as in ( ) and additionally heated at 550 °C for 1 h; *M1* + *M2* as in ( ) and additionally heated at 600 °C for 1 h. Physical mixtures = 50 wt.% *M1*/50 wt.% *M2*, with surface area ratio of 4:1; reaction temperature = 380 °C; propane/ammonia/oxygen/argon = 6.1/7.0/18.0/70.2; space velocity = 3.3–26.3 N cm^3/(min g).

Having now conclusively demonstrated that symbiosis occurs in *M1*/*M2* physical mixtures, under the conditions described, we felt that further yield enhancement might be possible, if the physical mixtures of the ≤5 μm powders were additionally calcined. We reasoned that additional calcinations might further increase the contact between the phases and thus enhance their cooperative effect. This did not materialize as is seen from Fig. 5. It is possible that such a yield improvement might be obtained if precursors of the two phases, rather than the already formed phases, be first mixed and then calcined. This concept is currently under study.



k_1 = rate determining
$k_2 >> k_1$
$k_3 < 1/5\ k_2$
$k_4 < k_2$
$k_5 < 1/5\ k_2$
$k_6 <<< k_4$
$k_7 <<< k_4$
$k_8 \sim k_4$
$k_9 \sim k_8$
$k_{10} < 1/5\ k_2$
$k_{11} > k_8 \sim k_9$
$k_{12} < k_{10}$

Fig. 6. Proposed propane ammoxidation network using *M1* and *M2* as catalysts.

As an aside, it should be mentioned here that the *M1* and *M2* phases in the two studies [7,12] while structurally identical are compositionally different. Since both, the *M1* as well as the *M2* phase form solid solutions [7,9] their compositional makeup can vary and is a strong function of preparational variables. In the first study [7] the composition of *M1* is $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ and of *M2* $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$; in the second study [12] the composition of *M1* is $Mo_{7.8}V_{2.2}Nb_{1.5}Te_{0.9}O_x$ and of *M2* $Mo_{4.67}V_{2.52}Te_{2.7}O_x$. This compositional difference leads to an expected difference in the absolute acrylonitrile selectivity and yield of the two base phases in the two respective studies (e.g., the higher vanadium content of *M1* in the second study renders it more active towards propane conversion but also less selective than that of the first study). Only the absolute catalytic values are affected by compositional variations, the general catalytic trends and interactions remain the same. Because the two studies are internally self-consistent, they can be gainfully inter-compared to obtain further insights into the catalytic behavior of these systems. One implication therefrom is that both phases can independently be compositionally manipulated to optimize their respective or combined desired catalytic properties.

We conclude from these studies, that symbiosis between physical mixtures of *M1* and *M2* phases definitely occurs, and that its extent is most pronounced at high propane conversions. At low propane conversions the *M1* phase alone suffices to obtain good acrylonitrile selectivities and yields. For symbiosis to occur, it is imperative that the two separately prepared phases be finally divided (≤ 5 μm) [12], thoroughly mixed and brought into intimate contact with each other. The contact between the two phases must be on a micro-, possibly nano-scale to effectively provide for phase cooperation. If the two phases are prepared simultaneously in one vessel, then the contact between the two phases appears to be automatically sufficient for symbiosis to take place [7].Based on our studies presented here, our earlier studies and related literature, we propose a reaction network pertaining to the ammoxidation of propane using *M1* and *M2* as catalysts (Fig. 6). In this network, *M1* is the sole propane activating phase leading to a surface adsorbed propyl radical $[CH_3CHCH_3]_a$ specie which further reacts on the active site of *M1* to an adsorbed propylene $[CH_3CH{=}CH_2]_a$ specie. This adsorbed propylene specie can now react on the *M1* active site without desorption and with but minimal movement (just a flip) since all key catalytic elements are within bonding distance of the adsorbed specie, directly leading to acrylonitrile (shown in greater detail in Fig. 2). Conversely, the adsorbed propylene specie can desorb, then readsorb on *M1* and further react to give acrylonitrile or CO_x (depending on the site it encounters [6]). If *M2* is also present in close proximity, then the desorbed propylene can also react on this phase to acrylonitrile and/or CO_x. Since the *M2* phase is a more effective propylene to acrylonitrile conversion catalyst than the *M1* phase ($k_{11} > k_9$), it becomes an important propylene mop-up component of the composite *M1* + *M2* catalyst system. As already mentioned, the *M2* phase is completely ineffective for propane conversion. Waste forming pathways are also indicated in the reaction network (Fig. 6).

4. Conclusions

Selectivity in heterogeneous oxidation catalysis plays a very important role in particular as the raw materials used as feeds in commercial petrochemical processes become less abundant and even more expensive.

The desired selectivity of many useful heterogeneous oxidation and ammoxidation catalysts can be explained on the basis of the site isolation hypothesis originally proposed some 40 years ago by Callahan and Grasselli [1].

The selectivity behavior of many model (e.g., CuO; V_2O_5/KVO_4), as well as, well-known commercial catalysts (e.g., $Bi_9PMo_{12}O_{52}$, USb_3O_{10}, $Fe_xSb_yO_z$, $(VO)_2P_2O_7$, (K,Cs)(Ni,Co,Mg)(Fe,Ce)(Sb,P)BiMoO), and now also the leading propane (amm)oxidation catalysts MoV(Nb,Ta)(-Te,Sb)O can be explained on the basis of the above site isolation concept.

The MoVNbTeO system is comprised of three crystalline phases: $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (*M1*), pseudo-hexagonal $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (*M2*) and a trace of $TeMo_5O_{16}$, wherein the *M1* phase is the key paraffin activating and acrylonitrile forming phase.

The active catalytic centers of the *M1* phase have recently been assigned [7] consistent with its structural makeup [8,9] and contain the key elements V^{5+}, Te^{4+} and Mo^{6+} properly spaced and within bonding distance of each other, capable of catalyzing the transformation of propane directly to acrylonitrile under ammoxidation conditions. The active centers are spatially separated from each other by means of Nb^{5+} pentagonal bipyramides, each of which is surrounded by five Mo–O octahedra. The observed high selectivity to acrylonitrile derives from this spatial arrangement of active sites on the surface and is consistent with the site isolation concept [1,2].

At low propane conversions, the *M1* phase by itself suffices to give respectable acrylonitrile yields under ammoxidation conditions and acrylic acid yields under oxidation conditions.

At high propane conversions, symbiosis between physical mixtures of *M1* and *M2* phases is definitely observed provided the two phases are finally divided ($\leq$5 μm) [12], thoroughly mixed and in intimate contact with each other (micro-/nano-scale). Under such conditions a symbiotic effect of enhanced selectivity and yields to acrylonitrile (analogously acrylic acid under oxidation conditions) is observed, as a result of phase cooperation, a concept already well known in oxidation catalysis [2,13].

The demonstrated symbiosis between physical mixtures of two catalysts (*M1* + *M2*) possessing different but complimentary catalytic properties opens up the possibility of applying this concept to many different catalytic combinations and ratios thereof to optimize desired product quality and yield. This overall concept has already been partly, eluded to in earlier publications [30].

While selectivity is a key concept and a key requirement for successful selective oxidation and ammoxidation catalysis, it is not sufficient in itself and must be coupled with acceptable activity, particularly when searching for commercially feasible catalysts. In the quest of this goal, selectivity and activity must be optimized and simultaneously balanced in a catalytic composition. For the rational design of new, yet to be discovered efficient catalysts exhibiting simultaneously high selectivity and activity, the application of the concepts of site isolation [1] and phase cooperation [13] can be gainfully utilized.

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