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Active centers in Mo–V–Nb–Te–O_x (amm)oxidation catalysts

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Abstract

The catalytically active centers of the $MoVNbTeO_x$ system for propane ammoxidation to acrylonitrile have been identified. The catalytic system is comprised of three crystalline phases: orthorhombic $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (M1) ($Pba2$: $a = 21.1337$ Å; $b = 26.6440$ Å; $c = 4.01415$ Å; $z = 4$), pseudo-hexagonal $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (M2) ($Pmm2$: $a = 12.6294$ Å; $b = 7.29156$ Å; $c = 4.02010$ Å; $z = 4$) and a trace of monoclinic $TeMo_5O_{16}$ ($P2_{1/C}$: $a = 10.0349$ Å; $b = 14.430$ Å; $c = 8.1599$ Å; $\beta = 90.781°$; $z = 1$). The catalytically active and selective centers reside on the surface of the basal plane of the M1 phase and are 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 structurally isolated from each other (site isolation) by four Nb^{5+} centers, each surrounded by five molybdenum–oxygen octahedra. The V^{5+} surface sites, distinguished through their ($V^{5+}{=}O \leftrightarrow {}^{4+}V^{\bullet}{-}O^{\bullet}$) resonance structure, are the paraffin activating sites capable of methylene-H abstraction; the Te^{4+} sites (lone pair of electrons) for the α-H abstraction of the chemisorbed propylene molecule, once formed; and the adjacent Mo^{6+} sites for the NH insertion into the π-allylic surface intermediate. Herewith, all key catalytic elements needed to transform propane directly to acrylonitrile are contained, strategically arranged and within bonding distance of each other, at the active center of the M1 phase.

Based on the metal site distribution probabilities at the active center 44% of them are computed to be active and selective for propane ammoxidation, 46% inactive for propane but active for propylene ammoxidation and 10% are waste forming sites. A maximum theoretical acrylonitrile selectivity of 81% is predicted on this premise (not achieved as yet experimentally). Under mild operating conditions, the M1 phase alone suffices to effectively convert propane directly to acrylonitrile. Under demanding conditions symbiosis between the M1 and M2 phases occurs, with the latter serving as a co-catalyst or mop-up phase to the former, transforming unconverted, desorbed propylene to acrylonitrile. The M2 phase is incapable of propane activation, lacking V^{5+} sites, but is a good propylene ammoxidation catalyst. A maximum acrylonitrile yield from propane of 61.8% (86% conversion, 72% selectivity at 420 °C) was achieved with a nominal catalyst composition of $Mo_{0.6}V_{0.187}Te_{0.14}Nb_{0.085}O_x$, identified by combinatorial methodology, and is comprised of 60% M1, 40% M2 and a trace of $TeMo_5O_{16}$.

Keywords: Ammoxidation; Propane; Propylene; Acrylonitrile; Catalytically active centers; Site isolation; Phase cooperation; Symbiosis; $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (M1 phase); $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (M2 phase)

1. Introduction

Twenty-five percent of all industrial organic chemicals and intermediates are produced by selective heterogeneous oxidation catalysis. The ammoxidation of propylene to acrylonitrile is one of the most important processes among them and exhibits excellent annual growth. More than 5 billion kg/year of acrylonitrile are produced world wide using the well-known SOHIO/BP process [1,2]. Although this process is very efficient (Table 1) giving >80% acrylonitrile yield on commercial scale [3], significant research efforts are in progress both in industrial and academic laboratories aimed at replacing the olefin feed (propylene) with the more abundant and less expensive paraffin (propane). Promising acrylonitrile yields

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Table 1
Ammoxidation of propylene to acrylonitrile

Current process (SOHIO/BP)

$C_3H_6 + NH_3 + 3/2\ O_2(\text{air}) \xrightarrow{\text{cat.}} CH_2{=}CH{-}CN + 3H_2O$

Catalyst: $(K,Cs)_{0.1-0.2}(Ni,Co,Mn,Mg)_{7.5-9.5}(Fe,Cr)_{2.3-2.5}Bi_{0.5-1.0}Mo_{12}O_x/SiO_2$ (MCM) [4]

Fluid Bed
Conversion: ~100 %
Selectivity: 80+ %
AN Yield: 80+ %

World production: 5.6 billion kg/year (with growth rate of 4%/year)
Uses: nitrile-based synthetic fibers and resins

Future Process

$C_3H_8 + NH_3 + 2O_2(\text{air}) \xrightarrow{\text{cat.}} CH_2{=}CH{-}CN + 4H_2O$

Catalyst:	Sb–V–Al–W–Sn–Te–O_x (SOHIO/BP) [5]	Mo–V–Nb–(Te,Sb)–O_x (Mitsubishi) [6]	VAlON (Prada Silvy) [7]
Fluid Bed			
Conversion	77%	89%	55%
Selectivity	49%	70%	66%
AN Yield	39%	62%	36%
Propane feedstock less expensive than propylene		Save one process step	
Less energy intensive process		Green technology	

of up to 62% have already been obtained on laboratory scale from propane using a Mo–V–Nb–Te–O_x catalyst (Table 1).

It is the objective of this contribution to address the catalytic and structural properties of the Mo–V–Nb–Te–O_x catalyst system and in particular to elucidate the makeup of the active centers, which render this remarkable catalyst, discovered by Mitsubishi Chemical Company [6], so effective for paraffin activation and the selective oxidation of propane to acrylic acid and ammoxidation to acrylonitrile.

2. Experimental

The methods employed for the preparation, evaluation and optimization of catalysts, and for structure determinations have been described earlier [8]. Further details pertaining to the solutions of the M1 and M2 structures are found in Refs. [9–11], respectively.

3. Results

The Mo–V–Nb–Te–O_x catalyst system is comprised of three crystalline phases: orthorhombic $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (M1) (*Pba*2: $a = 21.1337$ Å; $b = 26.6440$ Å; $c = 4.01415$ Å; $z = 4$), pseudo-hexagonal $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (M2) (*Pmm*2: $a = 12.6294$ Å; $b = 7.29156$ Å; $c = 4.02010$ Å; $z = 4$) and a trace of monoclinic $TeMo_5O_{16}$ [8–10]. We have recently discovered [10,11] that the superstructure of the pseudo-hexagonal phase is actually orthorhombic, owing to the complex arrangement of the Te in the hexagonal channels, with its space group being *Pmm*2 rather than *P*6*mm*, thought earlier.

The vital crystollagraphic parameters and the respective structures of M1 [9] and M2 [11], as determined and recently further refined by us on “essentially” pure specimens [10], are shown in Figs. 1 and 2, respectively. The M1 phase having the space group *Pba*2 exhibits twelve crystalographically distinct metal lattice positions. The M2 phase having a *Pmm*2 space group has five crystalographically distinct metal lattice positions (only one of several possible arrangements of V^{4+} in the structure is shown). One of the main differences between the two phases is that the M1 phase contains V^{5+} centers, while the M2 phase does not. This is one of the main reasons why the M1 phase is capable of activating paraffins, while M2 is not. Another significant difference between the two phases is that M1 contains Nb, while M2 contains very little, if any. Nb plays two vital roles in the M1 structure: (i) it spatially separates the active catalytic centers from each other (site isolation) [8,12,13] and thereby imparts this structure its uncanny high selectivity to produce acrylonitrile from propane under ammoxidation conditions; (ii) it stabilizes the overall structure, which is of great importance under catalytic operating conditions.

The ammoxidation of propane was carried out over a set of $Mo_{0.6}V_{0.16-0.213}Nb_{0.055-0.10}Te_{0.10-0.18}O_x$ catalysts. The acrylonitrile yield depends significantly on the Nb/Te ratio of the catalyst and since there is a near-linear relationship between the Nb/Te ratio and the amount of M1 phase in the catalyst, the yield becomes also a function of the M1 phase [8]. Combinatorial methodology was utilized to find the yield optimum. A set of yield curves for $Mo_{0.6}V_{0.187}Nb_xTe_yO_z$ as a function of M1 phase is shown in Fig. 3. Because of the complex phase relationship between M1, M2 and $TeMo_5O_{16}$, a set rather than a single yield curve is obtained as the Te and Nb concentrations are varied independently. The yield max-

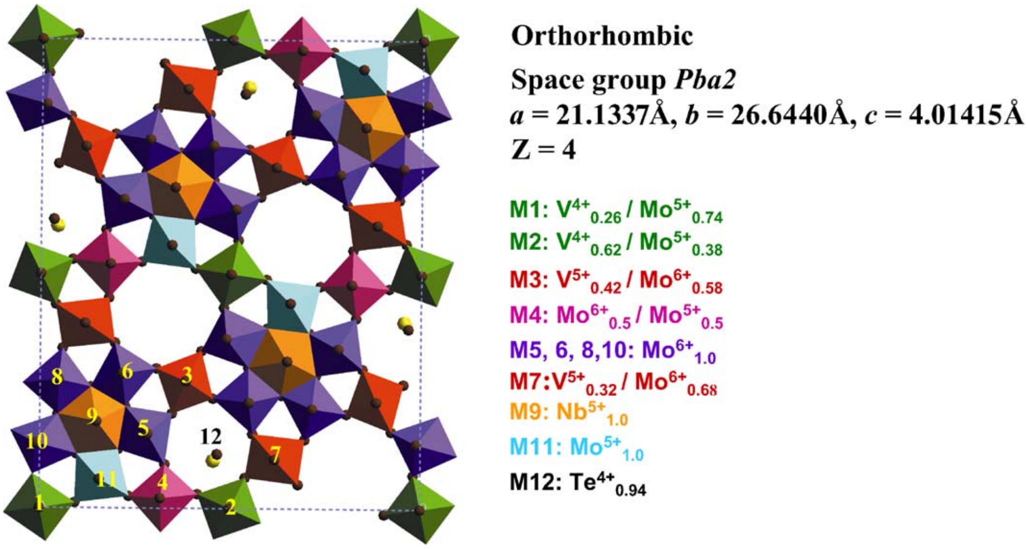


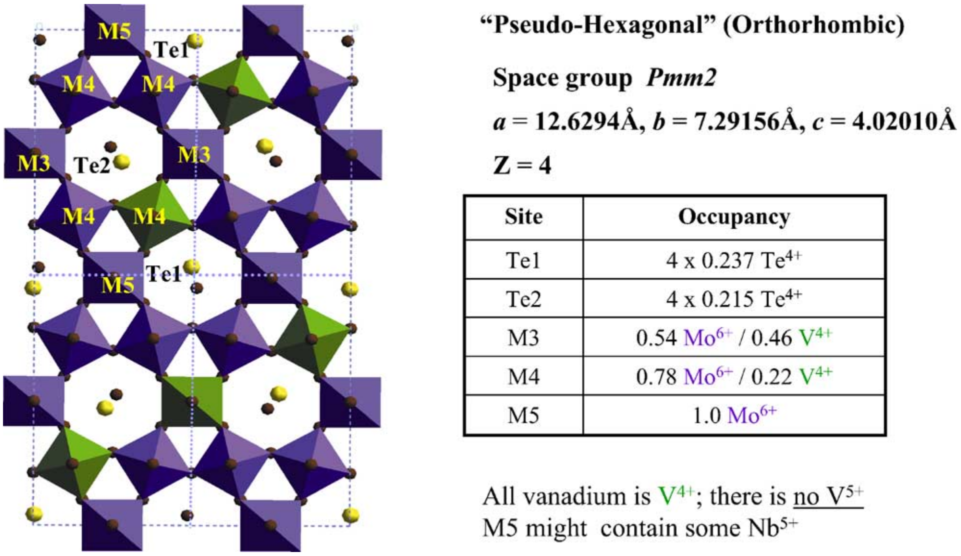
Fig. 1. Structure of $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{29}$ (M1 phase) [8–10].

imum of 61.8% (86% conversion, 72% selectivity, 420 °C) is reached at a composition of approximately 60% M1, 40% M2, and a trace of $TeMo_5O_{16}$. The result implies symbiosis or phase cooperation between M1 and M2 phases, a phenomenon observed already earlier [8,14–16] and discussed in greater detail below.

From the above catalytic results and supporting literature data [17–21], it is apparent that the M1 phase is responsible for the paraffin activation and that the M2 phase is rather ineffective for this reaction. For these reasons it is useful to focus on the structure/activity-selectivity relationships of the M1 phase. From previous work [8,22] it is known, that the M1 phase crystallizes in needles and that grinding of this phase enhances its activity towards acrylonitrile formation from propane. Therefore, it is concluded that the basal plane of the M1 phase is the carrier of the catalytically active and selective centers of this phase, as depicted in Fig. 4 [8].

4. Discussion

The catalytic center (Fig. 4) residing on the surface of the basal plane of the M1 phase is comprised of an assembly of $2V_{0.32}{}^{5+}/Mo_{0.68}{}^{6+}$, $1V_{0.62}{}^{4+}/Mo_{0.38}{}^{5+}$, $2Mo_{0.5}{}^{6+}/Mo_{0.5}{}^{5+}$, $2Te_{0.94}{}^{4+}$ elements, which is stabilized by four Nb^{5+} centers, each surrounded by five molybdenum–oxygen octahedra. As the chemical drawing illustration depicts, all of the key catalytic elements for the conversion of propane in the presence of ammonia to acrylonitrile are contained in the inner metal oxide cluster



Site	Occupancy
Te1	4 x 0.237 Te^{4+}
Te2	4 x 0.215 Te^{4+}
M3	0.54 Mo^{6+} / 0.46 V^{4+}
M4	0.78 Mo^{6+} / 0.22 V^{4+}
M5	1.0 Mo^{6+}

All vanadium is V^{4+}; there is no V^{5+}
M5 might contain some Nb^{5+}

Fig. 2. Structure of $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (M2 phase) [11].

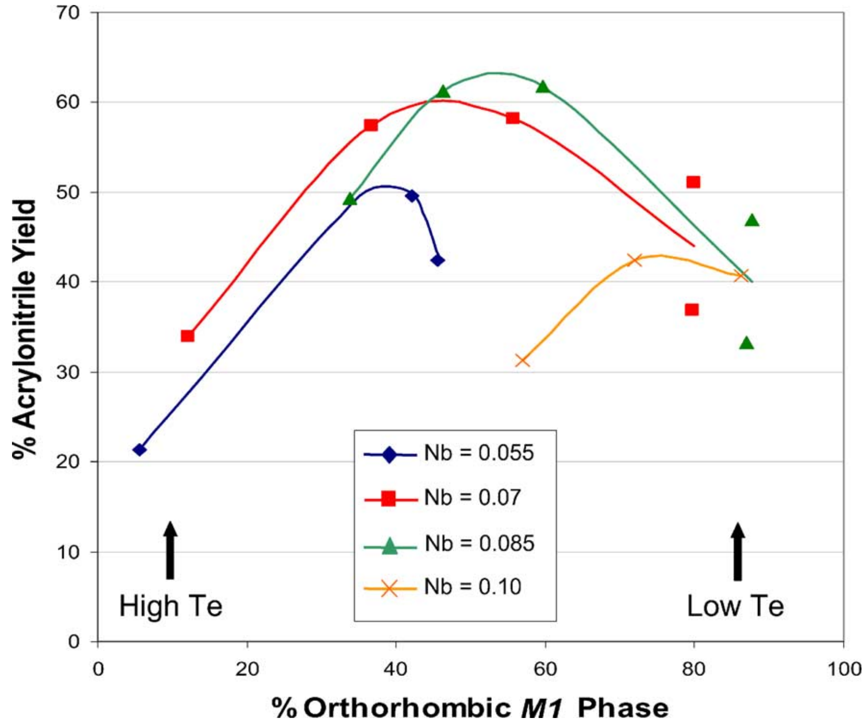
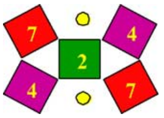


Fig. 3. Acrylonitrile yield vs. % orthorhombic $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{29}$ (M1) phase in propane ammoxidation using $Mo_{0.6}V_{0.185}Nb_xTe_yO_z$ catalysts.

of the active center of this phase. The paraffin activating function of the $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (M1) phase is assigned to the V^{5+} site of the catalytic center. Owing to its resonance structure ($V^{5+}{=}O \leftrightarrow {}^{4+}V^{\bullet}{-}O^{\bullet}$), the oxygen of this site has a partial radical character and can therefore easily abstract a methylene-H from an approaching propane molecule, thereby activating the molecule. A methyl-H abstraction follows with the formation of a surface propylene molecule. This so-formed chemisorbed propylene can react further on the active site without desorption, since two Te^{4+} atoms are strategically positioned within bonding distance of this surface moiety. Thus, an α-H abstraction of the surface adsorbed propylene can easily take place on these neighboring Te^{4+} centers (lone pair of electrons [23]) leading to a π-allyl intermediate, which is bonded to a neighboring Mo^{6+} of the active center. This Mo^{6+} site is also deemed to contain NH surface species and is therefore assigned to be the NH insertion site of the active center. Four Nb^{5+} sites, each surrounded by five molybdenum–oxygen octahedra isolate the active centers from each other (site isolation [12]) thereby stabilizing the structure under reaction conditions and leading to high desired product yields (acrylonitrile). Because of the proximity and strategic positioning of the key catalytic elements at the M1 active center, the conversion of propane to acrylonitrile occurs rather efficiently. Based on these structural and catalytic results and earlier supporting literature [1,24] a detailed reaction mechanism of propane ammoxidation to acrylonitrile has been worked out and is presented elsewhere [8].

Additional information about the ammoxidation reaction pathways over Mo–V–Nb–Te–O_x catalysts can be gleaned by further examining the detailed nature of the M1 active center (Fig. 4). An analysis of the relative elemental distribution probabilities of the M7–M2–M7 sites at the catalytic center (Table 2) leads to the following conclusions: if it is assumed that it takes a single V^{5+} center to activate the paraffin, that the simultaneous presence of two V^{5+} sites at the catalytic center leads to waste products, and that

Table 2
Distribution probabilities of elements at the active site of $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (M1 phase)



M7	M2	M7	Catalytic Properties
V^{5+} (32)	V^{4+} (62)	V^{5+} (32)	0.06 waste
V^{5+} (32)	V^{4+} (62)	Mo^{6+} (68)	0.14 active
Mo^{6+} (68)	V^{4+} (62)	V^{5+} (32)	0.14 active
Mo^{6+} (68)	V^{4+} (62)	Mo^{6+} (68)	0.28 inactive
V^{5+} (32)	Mo^{5+} (38)	V^{5+} (32)	0.04 waste
Mo^{6+} (68)	Mo^{5+} (38)	Mo^{6+} (68)	0.18 inactive
V^{5+} (32)	Mo^{5+} (38)	Mo^{6+} (68)	0.08 active
Mo^{6+} (68)	Mo^{5+} (38)	V^{5+} (32)	0.08 active

M2 and M7 are crystallographic site positions in $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$; numbers in parentheses are % occupancies; numbers in last column are fractions of M7-M2-M7 sites having the composition of a given column. Conclusion: 44% active and selective sites for paraffin conversion, 46% inactive sites for paraffins (active for olefins), 10% waste forming sites. Predicted maximum acrylonitrile selectivity: 81%.

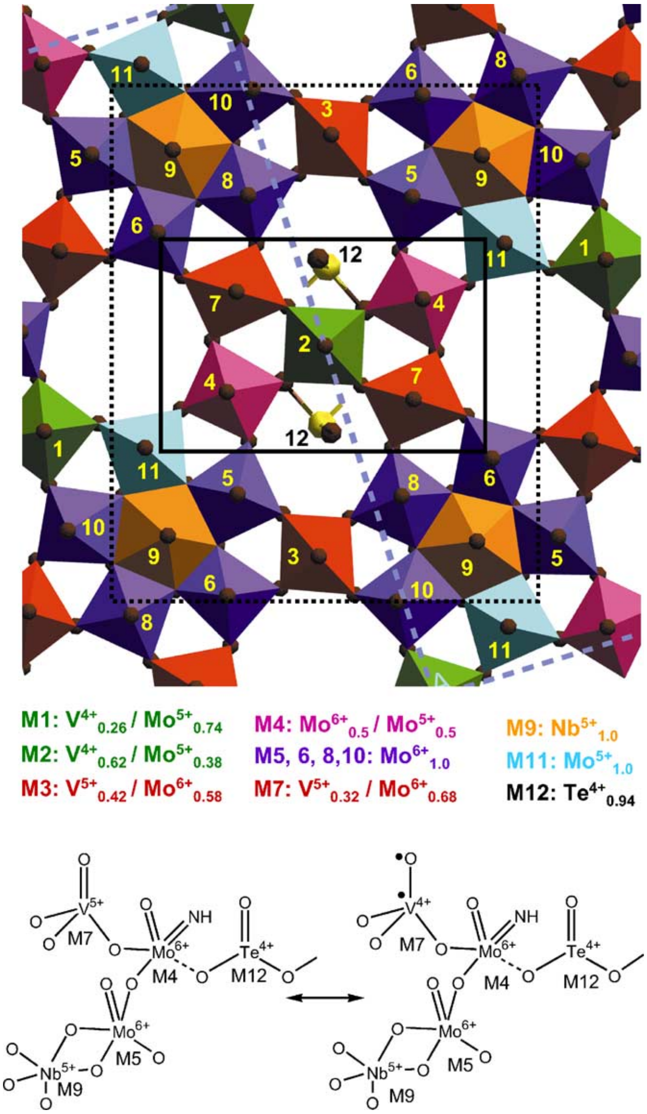


Fig. 4. Catalytically active center of Mo$_{7.8}$V$_{1.2}$NbTe$_{0.94}$O$_{29}$ (M1 phase) in [0 0 1] projection and chemical drawing illustration of the active site [8].

the center is inactive for paraffin activation when no V^{5+} sites are present, an account of active, inactive and waste sites can be computed. Based on this premise, it is concluded that 44% of the sites are active and selective for propane conversion, 46% are inactive and 10% are waste formers. From this analysis a maximum acrylonitrile selectivity of 81% is predicted, which is somewhat higher than the experimental maximum (72%) thus far achieved with these catalysts. The discrepancy between computed and actual selectivity can be interpreted readily on the basis of several scenarios, of which the most likely is premature desorption of propylene from the active site and an encounter of other waste or paraffin activating sites before a selective olefin activating and converting center is reached.

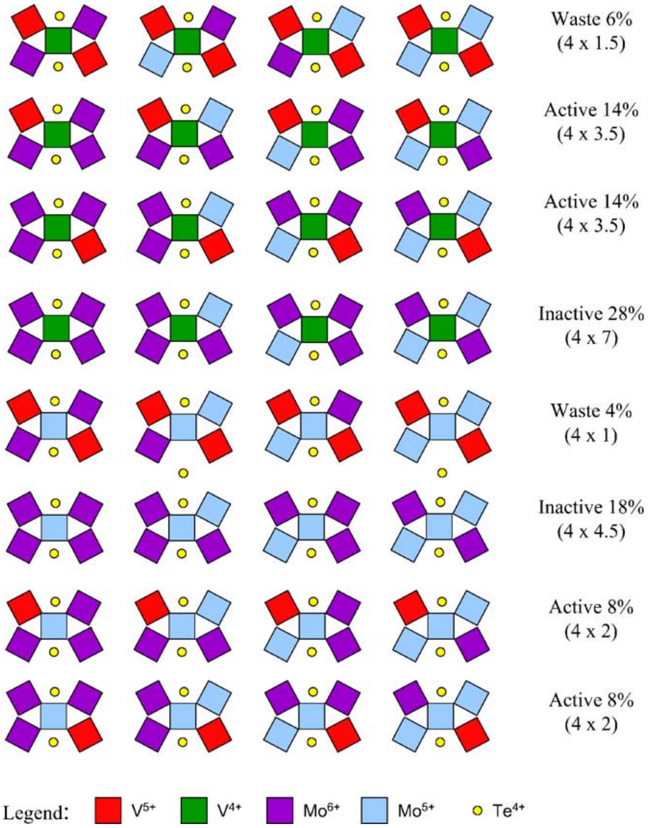
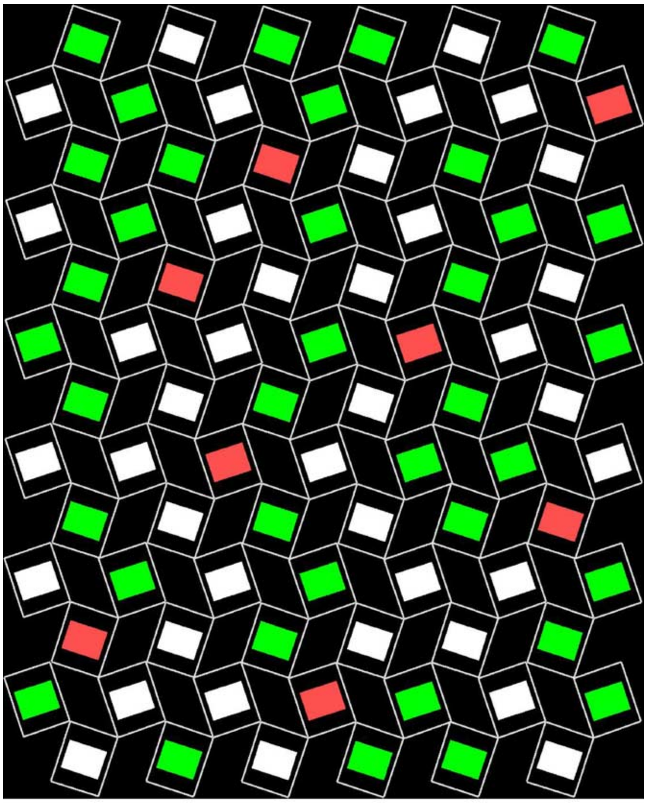


Fig. 5. Probabilities of metal occupancies at the active center of Mo$_{7.8}$V$_{1.2}$NbTe$_{0.94}$O$_{29}$ (M1 phase).

At this point it must be pointed out that the statistics of 44% active/46% inactive/10% waste are a result of the latest refinement [10] of the M1 structure and differ from the 55%/25%/20% values reported earlier [8]. The difference stems from the lower V/Mo ratio of the refined structure as compared to the earlier one, i.e. Mo$_{7.8}$V$_{1.2}$NbTe$_{0.94}$O$_{28.9}$ versus Mo$_{7.8}$V$_{1.2}$NbTe$_{0.94}$O$_{28.2}$ The structure is the same, only the metal occupancies changed. This leads one to realize, because both the M1 and M2 phases are solid solutions [8], that both, but particularly the M1 phase, could be altered to ones catalytic advantage by changing the site occupancies at the active site of this phase through clever synthetic chemistry, isomorphous surface substitution or selective doping. The same would apply to the MoVNbSbO$_x$ system.

A pictorial analysis of the various possible combinations of metal occupancies at the active center of the M1 phase is illustrated in Fig. 5. It clearly depicts the various possible metal arrangements on the basal plane of M1 and the catalytic consequences one can derive following the above postulates. The resulting conclusions as to catalysis are the same as those obtained from the data in Table 2.

Taking the results from Fig. 5 and Table 2, a hypothetical surface grid of active, inactive and waste forming sites can be constructed as shown in Fig. 6. It should be noted that the sites, whether active, inactive or waste forming are site



	For $C_3{}^0$	For $C_3{}^=$	%
🟩	Active	Active	44
⬜	Inactive	Active	46
🟥	Waste	Waste	10

Fig. 6. Distribution of catalytic sites on the surface of the basal plane of $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{29}$ (M1 phase).

isolated from each other owing to the unique structure of M1 as we discussed in an earlier publication [8]. Based on this distribution of sites on the surface of the basal plane of M1, the knowledge that the M2 phase is inactive for propane activation but an effective catalyst for propylene ammoxidation, and the observed symbiosis between M1 and M2, particularly under demanding process conditions (high propane conversion) [8,14–16], a process scheme (Fig. 7) can be proposed for the ammoxidation of propane. We propose that under mild operating conditions (low propane conversion), the M1 phase can perform all functions to convert propane directly to acrylonitrile, without desorption of intermediates. Under such conditions, as shown in the scheme, the active centers convert propane directly to acrylonitrile. The inactive centers are bystanders but can convert desorbed propylene to acrylonitrile if the active centers do not fully attend to this task. The waste centers form CO_x. The M2 phase, if present is a spectator, although if in sufficiently intimate contact with the M1 phase can also convert desorbed propylene to acrylonitrile. Under demanding operating conditions the sites of M1, as depicted in Fig. 7, perform still the same tasks as under mild conditions, although most likely the demand of adjacent propane inactive but propylene active sites to transform unconverted propylene to acrylonitrile increases. The M2 phase ceases to be a bystander and becomes now a co-catalyst or mop-up phase that converts unreacted propylene to acrylonitrile. This observed symbiosis or phase cooperation is effective only if the two phases are in intimate (nanoscale) contact with each other, mere physical mixtures do not appear to exhibit this symbiosis [8].

A possible explanation for symbiosis to be most pronounced under demanding reaction conditions (either high conversion or high throughput) might reside in the following: at high conversion (achieved by increasing the reaction temperature) the M1 phase is less efficient by itself than when in tandem with the M2 phase, because at the elevated temperatures, the paraffin activating ($V^{5+}{=}O \leftrightarrow {}^{4+}V^{\bullet}{-}O^{\bullet}$) sites of the M1 phase regenerate much faster than the α-H abstracting Te^{4+} or NH inserting $O{=}Mo^{6+}{=}NH$ sites. Therefore, the propane activation function continues to work well while the α-H abstracting and NH inserting functions lag behind. This leads to propylene desorption that can now encounter $V^{5+}{=}O$ sites and its combustion; or it must search for a selective propylene to acrylonitrile conversion site, which abound on the M2 phase. At high throughputs (high space velocities and high WWH) the regeneration of Te^{4+} and NH inserting sites will also lag that of the $V^{5+}{=}O$ sites, resulting in some propylene being desorbed before it is converted to acrylonitrile. Conversely, under mild operating conditions, low conversion and throughput, the active center of the M1 phase (Fig. 4) can attend to all of the needs to convert propane directly to acrylonitrile since the regeneration of the α-H abstracting Te^{4+} and NH inserting $O{=}Mo^{6+}{=}NH$ sites can keep up with the regeneration of the paraffin activating $V^{5+}{=}O$ sites.

Although we do not have evidence for epitaxial contact between M1 and M2, if such evidence were forthcoming, then one might wish to consider the possibility that surface or near surface lattice oxygens $[O^{2-}]_{SL}$ from the M2 phase might become accessible to the M1 phase for replenishment of reduced catalytic surface sites. Such transfer would be favorable since the M2 phase contains a larger amount of V^{4+} and Te^{4+} sites than the M1 phase and is thus more amenable to dioxygen dissociation, its incorporation as nucleophilic oxygen into the surface, and ultimate transfer to the catalytically working (paraffin converting) M1 phase. Thus, the observed symbiosis might be caused by two factors: primarily by phase cooperation on the basis of catalytic function (M1 as a superior paraffin activation catalyst cooperating with M2 being a better olefin conversion catalyst) and additionally, possibly to a minor extent on the basis of redox or electronic interactions (M2 being a better oxygen transfer phase feeding lattice oxygen to the M1 phase which is the active paraffin catalyst and thus more easily reduced under reaction conditions). Both phase cooperation modes are known in other complex selective (amm)oxidation catalysts [2].

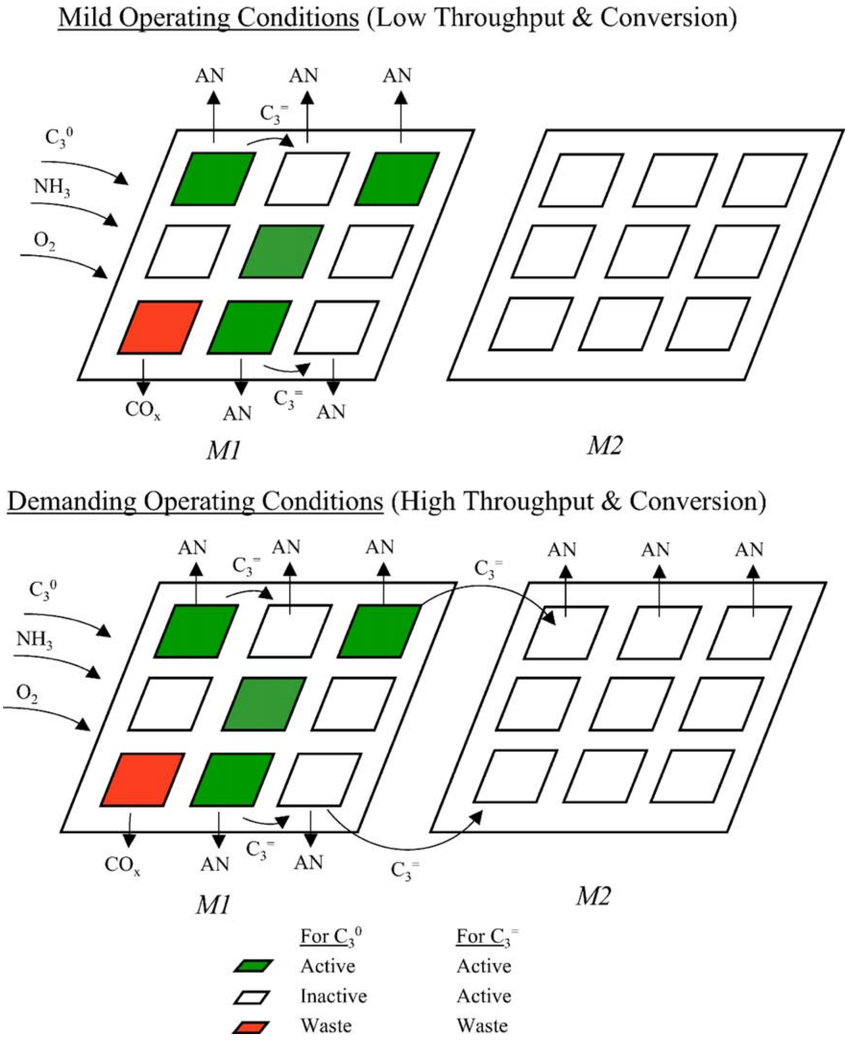


Fig. 7. Schematic of the propane ammoxidation process on MoVNbTeO_x catalysts.

5. Conclusions

The MoVNbTeO_x system is comprised of three crystalline phases: M1, M2 and a trace of $TeMo_5O_{16}$. The structures and metal occupancies of M1 and M2 have been solved and the active and selective catalytic centers assigned.

M1 is the paraffin activating phase containing the key ($V^{5+}{=}O \leftrightarrow {}^{4+}V^{\bullet}{-}O^{\bullet}$) surface centers. M2 lacks these centers and hence cannot activate paraffins.

The active and selective paraffin ammoxidation centers are located on the surface of the basal plane of the M1 phase.

An analysis of the key metal occupancies at the M1 active center suggest a 44/46/10 distribution of active/inactive/waste sites and predicts a maximum attainable acrylonitrile selectivity of 81%. The experimentally obtained maximum thus far is 72%. An explanation for the difference is given.

Under mild operating conditions (low throughput and conversion) the M1 phase suffices to convert propane directly to acrylonitrile. Under severe operating conditions (high throughput and conversion) symbiosis between M1 and M2 phases is observed, with the latter acting as a mop-up phase transforming unreacted propylene to acrylonitrile.

Improvements in catalytic efficiency are envisioned by altering the elemental distribution at the active center of the M1 phase through structure directing synthesis, isomorphous substitution of key elements or surface doping.

For the ammoxidation of paraffins the Sb (and possibly the B:) analogues of MoVNbTeO_x systems will be technically superior to the Te base because of their greatly superior stability under commercial reaction conditions.

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