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Inhibition of Propylene Oxidation to Acrylic Acid by Amorphous Overlayers on MoV(Nb)TeO Based M2 Catalysts

Robert K. Grasselli · Claus G. Lugmair ·
Anthony F. Volpe Jr. · Arne Andersson ·
James D. Burrington

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Abstract One of the most effective catalysts for the selective oxidation of propane to acrylic acid (AA) and ammoxidation to acrylonitrile (AN) is the MoV(Nb,Ta)(Te,Sb)O system, comprised of two phases, with M1 the major catalyst and M2 the co-catalyst in symbiosis with M1, converting intermediately formed propylene to the respective desired end products. An improvement in either phase should enhance the overall desired yields of a combined M1/M2 conglomerate. The current study concentrates on the M2 phase (variously substituted and/or doped) where depending on composition and preparation technique crystalline materials or crystalline materials with amorphous overlayers are obtained. Crystalline M2 catalysts without amorphous overlayers are vastly superior to those encumbered with overlayers. In a comparative study the former give a maximum AN yield of ~45% in propylene ammoxidation, the latter ~24%. In the selective oxidation of propylene to acrylic acid, the difference in performance between the two types of catalysts becomes enormous: The crystalline M2 catalyst gives a maximum AA yield of ~34% while the Te–molybdate overlayered M2 a meager ~3%. Doping of crystalline M2 phase with P significantly enhances AA yields over the base and should be seriously considered in future attempts to improve M1/M2 propane/propylene catalyst systems.

Keywords Propylene · Acrylic acid · Acrylonitrile · Selective oxidation · Ammoxidation · MoVTeO catalysts · M2 phase · Amorphous overlayers

1 Introduction

Many studies have been undertaken and much has been written about the MoV(Nb,Ta)(Te,Sb)O based catalysts in both, primary and patent literature over the past 20 years [1–21]. These catalysts are, thus far, the most effective systems for the conversion of propane to acrylic acid and acrylonitrile, respectively [22, 23]. As is well known, they are comprised of two phases: M1 (orthorhombic) $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ and M2 (pseudo-hexagonal) $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$, usually employed in a 60/40 molar ratio to optimize desired yields [17, 18]. In this configuration, the M1 phase performs the principal catalytic functions needed for the conversion of propane to acrylic acid or acrylonitrile, while the M2 phase is a co-catalyst in symbiosis with M1 performing a mop-up operation converting free intermediately formed propylene to the respective desired end products, AA or AN. This mop-up operation takes place particularly under demanding operating conditions (e.g. high conversions) [17, 19–21].

R. K. Grasselli (✉)
Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716, USA
e-mail: rkgrasselli@yahoo.com

R. K. Grasselli
Department of Chemistry, Technische Universität München, Garching 85748, Germany

C. G. Lugmair · A. F. Volpe Jr.
Symyx Technologies Inc, 3100 Central Expressway, Santa Clara, CA 95051, USA

A. Andersson
Department of Chemical Engineering, Lund University, Chemical Center, P.O. Box 124, 22100 Lund, Sweden

J. D. Burrington
The Lubrizol Corporation, 29400 Lakeland Boulevard, Wickliffe, OH 44092, USA

In an effort to further improve the overall performance of the base MoV(Nb,Ta)(Te,Sb)O system, it should be possible to achieve this by improving the performance of either of the two (M1 or M2) phases. We have made several attempts to verify this postulate. Thus, partial substitutions were made of V, Te and Mo with Ti, Ce and W, respectively in the M2 phase, with the substituted compositions exhibiting modestly enhanced activity and selectivity over the base in the ammoxidation of propylene to AN [24, 25]. In another study we doped M1 and M2 phases with measured (minute) amounts of acidic elements (e.g. P, B, W) for the selective oxidation of propane and propylene to AA. We reasoned that acidic additives would enhance the reaction channel to acrylic acid over that to acrolein (desorbed), which is what actually takes place. Yield improvements in AA of 5–10% (i.e., improvement in AA selectivity at constant propylene conversion), were obtained; and that, importantly under commercially relevant conditions, which is a substantial achievement [26].

The main aim of the study reported here is to show that the catalytic behavior of M1 and M2 catalysts is greatly influenced by the method of catalyst preparation and whether the resulting catalysts are crystalline and free of unwanted overlayers, or if they are encumbered with amorphous overlayers. Thus, we show that M2 catalysts containing amorphous overlayers of Te–molybdate [24], while reasonably good ammoxidation catalysts for the conversion of propylene to AN, fail substantially in the selective oxidation of propylene to AA. We also show that M2 catalysts which are crystalline and contain no amorphous overlayers perform splendidly in both ammoxidation to AN, and selective oxidation to AA.

2 Experimental

The preparation and characterization of the M2 catalysts discussed here has been reported earlier. The amorphously overlayered materials and their characterization are reported in [24, 25]. The crystalline materials without overlayers are reported in [19–21, 23, 26]. Some additional systems, in particular P doped M2's (with no amorphous overlayers) were prepared as follows:

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 solution, second solution, and a H_3PO_4 (1.0 M) solution 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.

Both sets of catalysts, with and without amorphous overlayers, were tested for catalytic activity in a tertiary screening six-channel reactor module [27, 28]. A specific weight of catalyst (200 mg) was diluted with SiC (about 3x volume of catalyst) to establish a consistent bed height. The reaction conditions for propylene oxidation were: atmospheric pressure, 290–370 °C, WHSV = 0.07–0.12 h^{-1}, and feed ratio $C_3H_6/O_2/He/H_2O = 1/2/8.4/2.8$. For propylene ammoxidation the reaction conditions were: atmospheric pressure, 400–430 °C, and feed ratio $C_3H_6/NH_3/O_2/He = 1/1.4/3/12$. The effluent of the reactor was analyzed by gas chromatography using a plot-Q and a molsieve column with TCD detectors. Conversion, selectivity, and yield are defined as: Conversion = (moles C_3H_6 consumed/moles C_3H_6 charged) × 100, Selectivity = (moles product/moles C_3H_6 consumed) × (number of C atoms in product/3) × 100, Yield = (moles product/moles C_3H_6 charged) × (number of C atoms in product/3) × 100.

3 Results

3.1 Catalytic Results

We present and compare catalytic results of variously prepared and substituted and/or doped M2 compositions for the selective oxidation and ammoxidation of propylene to AA and AN, respectively. It is well known that both M1 and M2 phases form solid solutions within their respective unique structures, so that the chemical composition of either can vary over fairly wide ranges of compositions [17], and that certain elements of either structure can be substituted by select other elements [19, 24–26].

The first set of M2 phases discussed here was prepared in Andersson's laboratory (Table 1) [24, 25] and these catalysts are deemed to contain amorphous overlayers on top of the microcrystalline M2 "support". The amorphous overlayers are thought to be compositionally comprised of essentially Te–molybdate as deduced from HREM and XPS data [24]. The base composition has an empirical formula of $MoV_{0.54}Te_{0.59}O_x$ and has been also variously substituted with W, Ti and Ce.

The second set of M2 compositions (Table 2), prepared at Symyx Technologies, is microcrystalline in nature and contains no amorphous overlayers. The empirical formula of this set of catalysts is $MoV_{0.31}Nb_{0.06}Te_{0.37}O_x$. The base composition has also been doped with various amounts of P in an attempt to enhance performance (particularly to AA).

Table 1 M2-a overlayer catalysts with W, Ti, and Ce added to synthesis mixture. (Prepared in Andersson Laboratory [24, 25])

Sample no.	Mo	W	V	Te	Ti	Ce
M2-a	1	0	0.54	0.59	0	0
MW-30	0.7	0.3	0.54	0.59	0	0
MW-50	0.5	0.5	0.54	0.59	0	0
MW-70	0.3	0.7	0.54	0.59	0	0
MW-100	0	1	0.54	0.59	0	0
TC-30	1	0	0.54	0.41	0	0.18
VT-30	1	0	0.38	0.59	0.16	0
VT-50	1	0	0.27	0.59	0.27	0

Table 2 M2 catalysts with P added to synthesis mixture. (Prepared in Symyx Laboratory)

Sample no.	Mo	V	Nb	Te	P
M2-1	1	0.31	0.06	0.37	0
M2-2	1	0.31	0.06	0.37	0.0005
M2-3	1	0.31	0.06	0.37	0.001
M2-4	1	0.31	0.06	0.37	0.005

Table 3 Comparison of Propylene Ammoxidation Data obtained originally in Andersson Laboratory (Lund, Sweden) [24, 25] and the same catalysts (Te–molybdate overlayered M2-a's) run currently in Symyx Technologies Laboratory (California, USA) reaction conditions: reaction temperature 420 °C feed composition $C_3H_6/NH_3/O_2/He = 1/1.4/3/12$ WHSV = 0.1–0.2 h^{-1}

Anderson notation [24, 25]	Anderson data [24, 25]			Symyx data		
	Selectivity %					
	AN	ACR	Sum	AN	ACR	Sum
15% Propylene conversion						
M2-a, M-O	64	10	74	73	6	79
MW-30				72	3	75
MW-50				57	1	58
MW-70						
MW-100						
TC-30	71	–	71	66	1	67
VT-30	62	15	77			
VT-50	67	9	76			
Average	66	11	75	67	3	70
30% Propylene conversion						
M2-a, M-O	52	27	79			
MW-30	57	23	81			
MW-50	67	14	81			
MW-70	80	3	83	58	1	59
MW-100	70	0	70			
TC-30	–	–	–			
VT-30	56	16	72	61	17	78
VT-50	52	23	75	64	14	78
Average	62	15	77	61	11	72

3.1.1 Ammoxidation of Propylene to AN

3.1.1.1 M2 Compositions with Amorphous Surface Overlayers The ($MoV_{0.54}Te_{0.59}O_x$) catalysts containing amorphous overlayers prepared in Andersson's laboratory are reasonably good ammoxidation catalysts converting propylene to acrylonitrile in the range of 15–30% at a selectivity of up to about 70% [24, 25]. The propylene ammoxidation results as reported in this literature are summarized in Table 3.

In order to establish a common base for comparative studies of the two sets of catalysts, it was important to establish that the overlayered catalysts give similar results in the ammoxidation of propylene to AN in both laboratories. For these reasons the original Andersson catalysts were secured and run at Symyx in a tertiary screening six-channel reactor for propylene ammoxidation. The results are shown in Fig. 1. We report not only AN (acrylonitrile) and ACR (acrolein) data, but also acetonitrile, HCN and CO_x in order to close the material balance. From these results we extract the pertinent data and compare them in Table 3 to the originally reported literature results [24, 25]. It is apparent that the agreement is very good. For example, at 15% propylene conversion the average AN selectivity is 66% as measured by Andersson and 67% as measured now at Symyx; at 30% conversion the corresponding values are 62% and 61%, respectively.

With the above results in hand, we can comfortable state that we are looking at the same overlayered catalysts in both laboratories and that we can proceed with our intended study, comparing overlayered catalysts to non-overlayered microcrystalline M2's for the production of AN and later on also AA.

As an aside it might be worth mentioning that the overlayered catalysts produce rather large amounts of acrolein under ammoxidation conditions (in both laboratories), implying that in addition to Te–molybdate, there must be some extraneous V-centers on the surface, which increase undesired NH_3 combustion, thereby lowering the AN selectivity.

3.1.1.2 Microcrystalline M2 Compositions without Amorphous Surface Overlayers We have prepared some standard, crystalline M2 compositions ($MoV_{0.31}Nb_{0.06}Te_{0.37}O_x$) and some P doped analogues thereof having no amorphous overlayers. The ammoxidation results are shown in Fig. 1.

It is apparent that the microcrystalline compositions, base and doped, are much more active at comparable selectivity levels than the overlayered compositions.

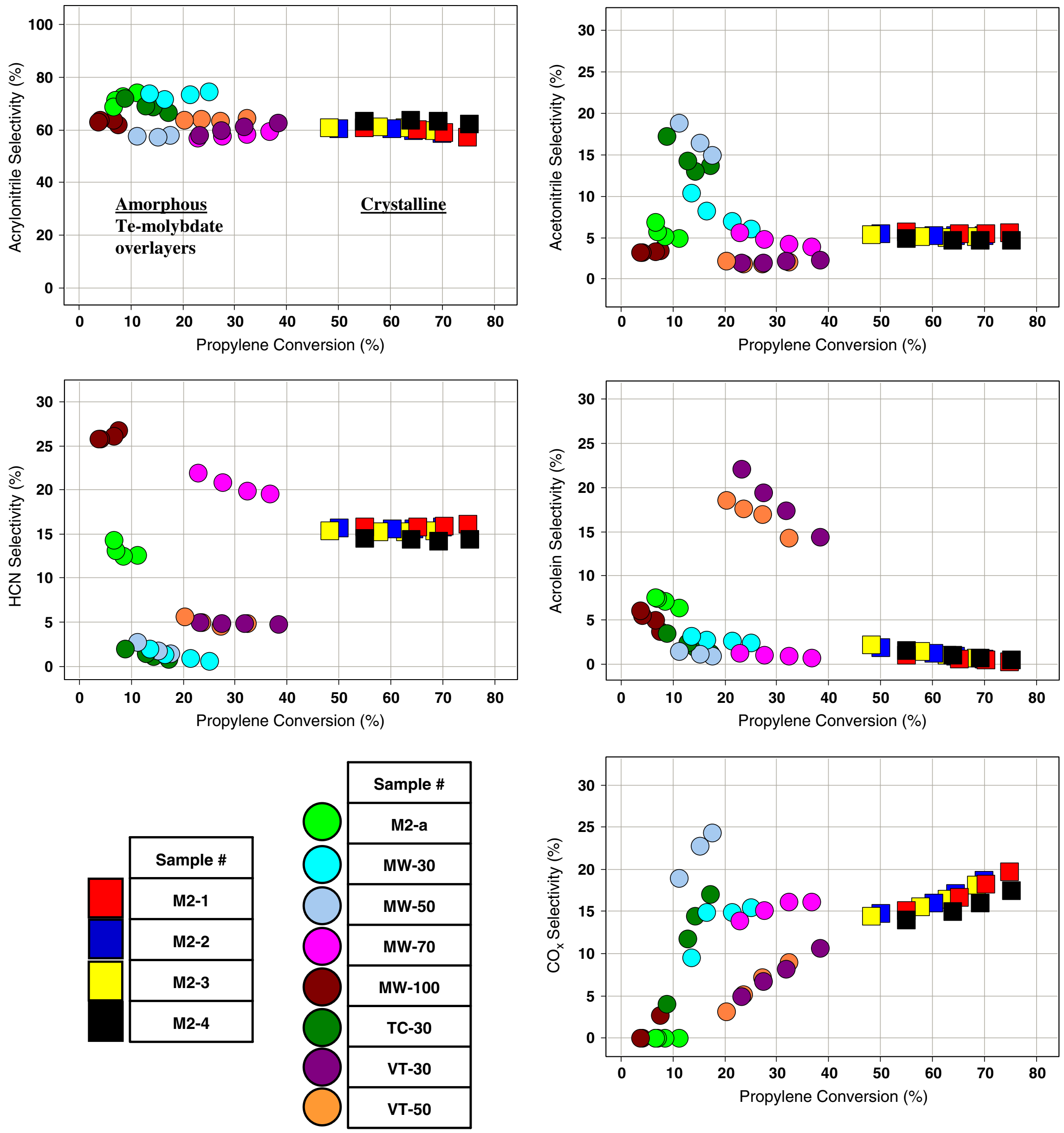

Fig. 1 Propylene ammoxidation over M2-a (Andresson) and M2 (Symyx) catalysts. Reaction temperature 420 °C, feed composition $C_3H_6/NH_3/O_2/He = 1/1.4/3/12$, WHSV = 0.1–0.2 h^{-1}

Although the surface area of the microcrystalline compositions is somewhat larger (~1.7 m^2/g) than the overlayered catalysts (~1.1 m^2/g), the former are much more efficient in catalyzing the desired ammoxidation reaction than the latter. If an attempt is made to push the conversion of the overlayered catalysts beyond about 40%, waste conversion overshadows any hoped for gains in AN yield.

From Fig. 1 the maximum AN yields for both sets of catalysts can be deduced, being ~24% for the overlayered catalysts and ~45% for the microcrystalline catalysts; the latter systems being about twice as efficient as the former.

As one of our theses has been for some time [19–21] that an improvement over the base of either M1 or M2 catalysts should lead to an overall improvement in the yield of the desired product when the two phases are combined and work in concert, we undertook the doping of the M2 phase (primarily with P) [26] to improve AA yields, which we succeeded to achieve. We observe here, that the doping with P also enhances the AN yield over and above the base as seen in Fig. 2. The improvement is not overwhelming (not as large as will be seen later in Section 3.1.2. for AA formation), but there is a definitive increase of AN selectivity from 59% to 64% as the P level is increased in the

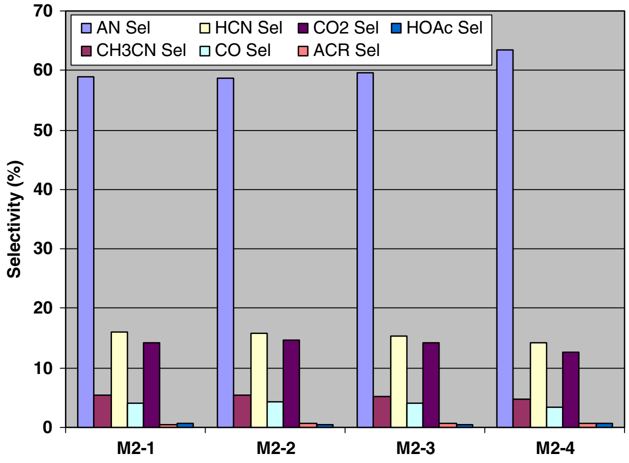

Fig. 2 Propylene ammoxidation over P doped M2 (Symyx) catalysts. Selectivities at 70% propylene conversion. Reaction temperature 420 °C, feed composition $C_3H_6/NH_3/O_2/He = 1/1.4/3/12$

composition, with a concomitant decrease in byproducts HCN, acetonitrile and CO_x, as measured at a 70% propylene conversion level. Although there is no obvious reason why P doping should enhance AN selectivity, it is possible that NH_3 utilization is improved (better adsorption).

3.1.2 Oxidation of Propylene to AA

With the realization that amorphous overlayers apparently exist on top of some crystalline M2 bulk compositions and that these surface layers are comprised essentially of Te–molybdate, we reasoned that if this were to be true, these compositions would be poor catalysts for the conversion of propylene to acrylic acid. This prediction is based on the well known fact that Te–molybdate, while a respectable AN catalyst is a very poor AA catalyst [22]. The same is true of Bi-molybdate and is anticipated to be true also for a Bi-molybdate amorphous overlayer, if such were to be prepared on top of M2 or any other microcrystalline support.

3.1.2.1 M2 Compositions with Amorphous Surface Overlayers As we predicted, the Te–molybdate overlayered M2 compositions essentially fail in AA synthesis as seen from Fig. 3. The selectivities to AA lie below 10% over the complete range of conversions studied with these catalysts, giving a meager maximum AA yield of ~3%. While at the lower propylene conversion levels of 5–15% primarily acrolein is formed, as expected (these catalysts can activate an olefin by abstracting an α-H from propylene and inserting an oxygen to form acrolein; as they were able to insert a nitrogen to form AN, seen above in Section 3.1.1.1.) these catalysts are incapable of transforming the so formed acrolein to acrylic acid. Instead, side reactions to acetic acid and acetone begin to dominate the reaction path as propylene conversion is increased (Fig. 3). An explanation for this behavior is given below in Section 3.1.2.3.

3.1.2.2 Microcrystalline M2 Compositions without Amorphous Surface Overlayers In contrast to the overlayered catalysts, catalysts possessing no amorphous overlayers, exhibit excellent AA selectivities, even at high propylene conversions and they produce low amounts of undesired acetic acid and acetone byproducts (Fig. 3). For example, at 47% propylene conversion the base composition gives an AA selectivity of 52% and increases with P doping up to 68% at the highest P dopant level studied (Fig. 4). At the same time the already low unwanted byproduct selectivities of acetic acid, acetone and particularly CO decrease. This comprises a significant improvement in the AA yield over and above the base, rising from 24% to 32% by introducing phosphorous into the M2 catalyst composition.

3.1.2.3 Mechanistic Considerations The mechanisms for propane and propylene ammoxidation over M1 and M2 phases have been discussed earlier [17] and are applicable, as originally proposed, to the catalysts discussed here.

A generic mechanism of propane oxidation based on that in [26], expanded to show M1 and M2 sites is presented in Fig. 5. Therefore, Nb^{5+} in the formerly referenced M1-catalyst mechanism has been replaced in the figure with M^{n+}, which can be Nb^{5+}, Ta^{5+}, or $Mo^{6+/5+}$. In the MoV(Te,Sb)(Nb,Ta)O group of compositions, comprised of M1 and M2 structures, only M1 is capable of catalyzing both the activation of propane to propylene (surface structures No. 1–No. 4) and its subsequent conversion to acrolein and AA (surface complexes No. 4–No. 12). M2, while incapable of activating the paraffin, can however catalyze the propylene transformations to acrolein and AA (No. 4–No. 12) as does M1. Note the differently highlighted areas in Fig. 5.

We have already reported on the beneficial effects of P doping [26] and our view that the enhanced ability of so-doped M2 compositions is primarily due to two enhancements: a) that of the proton donating properties of Te–OH induced via P or directly through an adjacent P–O–H moiety at the reaction complex number 8, and b) that of the acidic properties of Mo^{6+} in complex number 9, which strengthens its binding of the organic fragment thereby facilitating the hydrolysis reaction of this surface complex on its path towards AA formation.

Te–molybdate overlayers on top of M2 lead to unwanted products, of which the major components are acetone and acetic acid. In fact these unwanted products exceed the yields of the desired acrylic acid (Fig. 5). Acetone is likely formed by interaction of propylene with fully oxidized acid

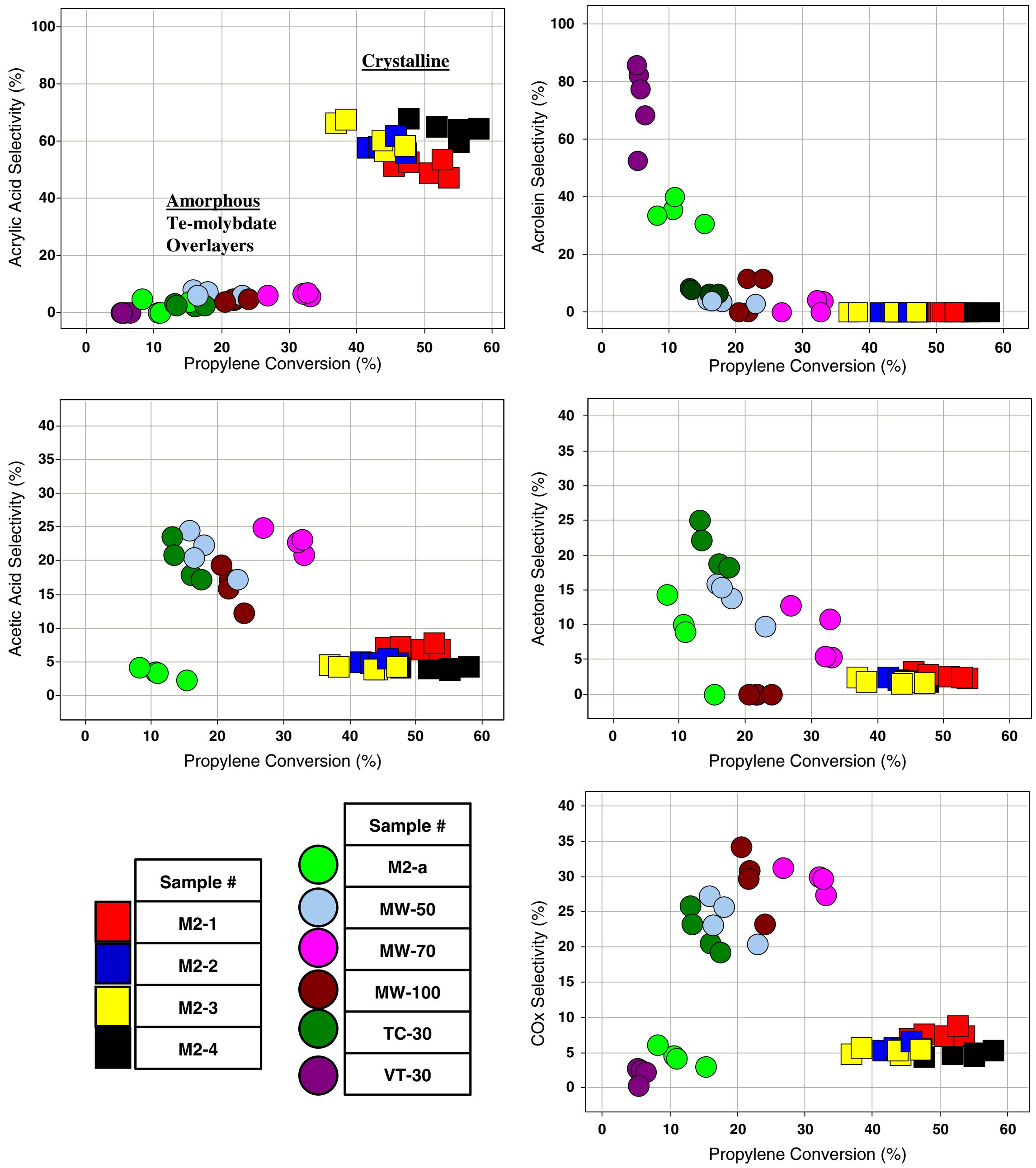

Fig. 3 Propylene oxidation over M2-a (Andersson) and M2 (Symyx) catalysts. Reaction temperature 350 °C, feed composition $C_3H_6/O_2/He/H2O = 1/2/8.4/2.8$, WHSV = 0.07–0.12 h^{-1}

sites no. 4, whereby an acid site such as Te^{5+}–OH is formed. This site (No. 4a in Fig. 6) could transfer an H^+ to form a carbonium ion that would compete with allyl formation and ultimately lead to acetone, as shown. The second major unwanted product is acetic acid**,** which could arise from the reduction in the rate of desorption of acrylic acid from surface site no. 10 due to decreased reoxidation of Te–molybdate in the M2 overlayer, leading to further oxidation to acetic acid and CO_x, as suggested in Fig. 7.

With crystalline M2 compositions, doped or undoped, the mechanistic channels leading to acetone and acetic acid are minimized. However, in the Te–molybdate overlayered M2 compositions they appear to be prominent and successfully compete with the mechanistic channel leading to AA.

3.2 Characterization of Catalysts

The characterization of the M2 compositions discussed here has been already previously reported: those containing amorphous overlayers of Te–molybdate [24] and those without amorphous overlayers [18, 19, 26].

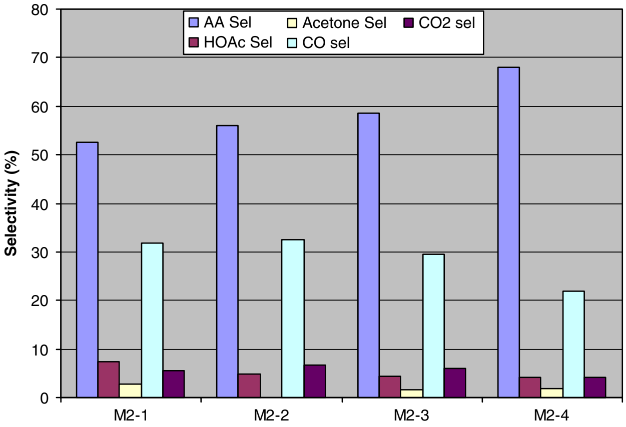

Fig. 4 Propylene oxidation over P doped M2 (Symyx) catalysts. Selectivities at 47% propylene conversion. Reaction temperature 350 °C feed composition $C_3H_6/O_2/He/H_2O = 1/2/8.4/2.8$

4 Discussion

Our overall thesis for the study reported here was that amorphous overlayers on the surface of crystalline catalysts in general, and more specifically if comprised of unwanted compositions for a specific reaction, will be deleterious to the desired catalytic process. Thus, we reasoned that systems of the M2 ($MoV_{0.54}Te_{0.59}O_x$) phase when covered with amorphous overlayers of Te–molybdate will impede the conversion of propylene to acrylic acid; the reaction will stop at acrolein at best, and be beset by unwanted side reactions. This conviction has its roots in the early research of propylene selective oxidation and ammoxidation at SOHIO. While it was possible to use a one catalyst system (e.g. Bi-molybdate) to commercially ammoxidize propylene to AN [23], it became readily apparent that it was necessary to use a two catalyst system to commercially produce AA from propylene. Namely, if Bi-molybdate (or Te–molybdate) was chosen as the catalyst for the conversion of propylene to acrolein, a second more acidic catalyst, for example *P*-molybdic acid (on SiO_2) was needed to convert the intermediately formed acrolein to AA. The result was a two stage process that is still practiced today; of course with more sophisticated improved catalysts in both stages [22].

With this backdrop, we predicted that the recently investigated Te–molybdate overlayered M2 systems

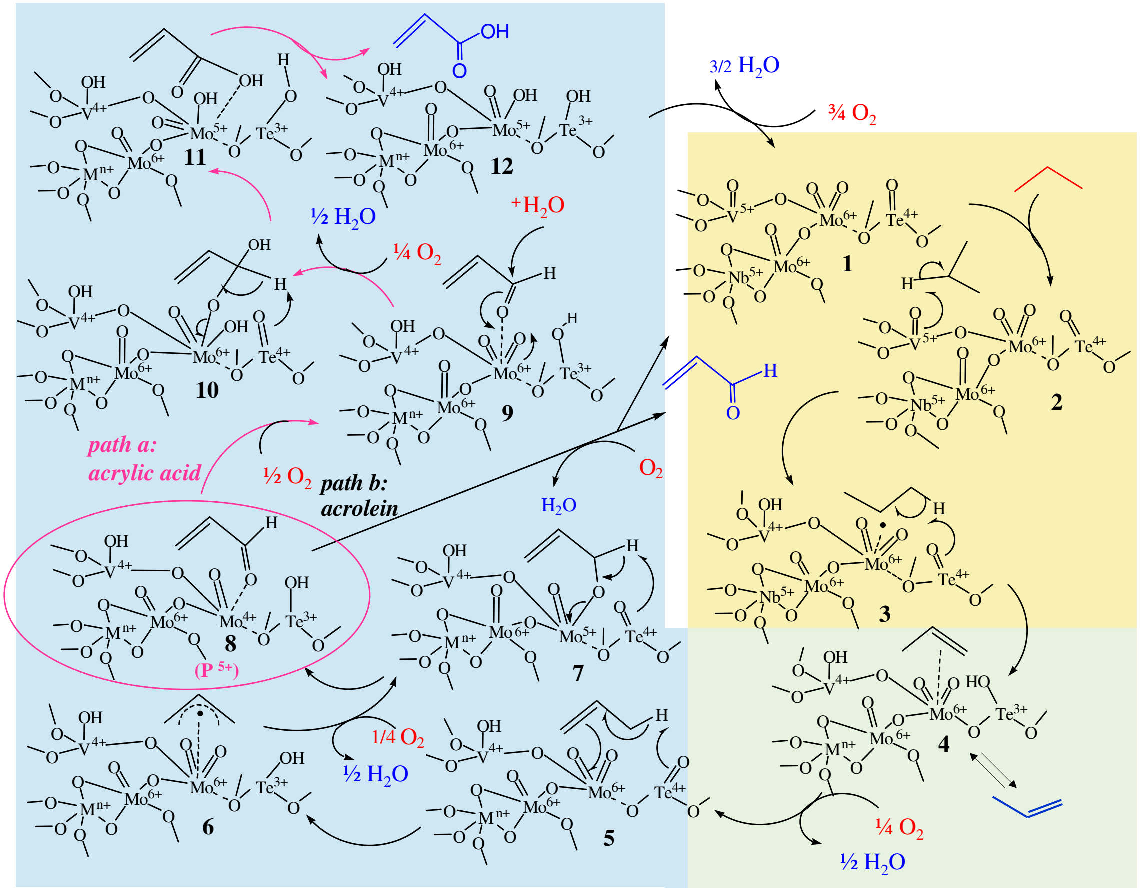

Fig. 5 Proposed propane/propylene oxidation mechanism over MoV(Nb)TeO catalysts. (M1 domains: no. 1–4 and no. 4–12; M2 domain: no. 4–12)

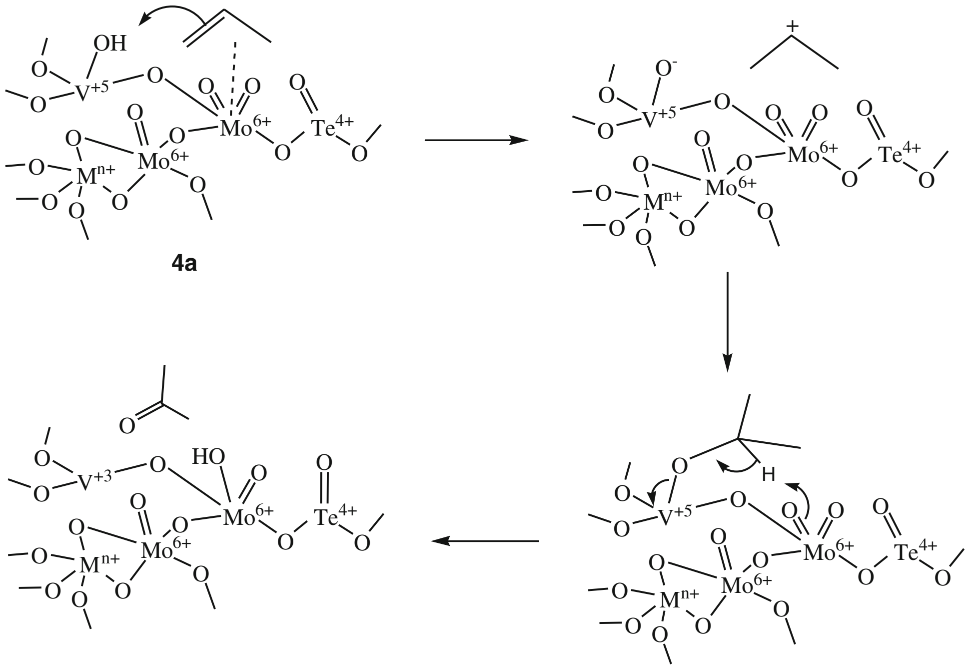

Fig. 6 Proposed mechanism for the formation of acetone over MoV(Nb)TeO-M2 catalysts

[24, 25], which were synthesized for the ammoxidation reaction of propylene to AN, will not perform satisfactorily in the conversion of propylene to AA. This has now been clearly confirmed by experiment. M2 ($MoV_{0.54}Te_{0.59}O_x$) catalysts containing Te-overlayers that satisfactorily ammoxidize propylene to AN (~24% max. AN yield, Fig. 1), give only meager amounts of AA (~3% max. AA yield, Fig. 3) in the oxidation reaction of propylene. The oxidation either stops at acrolein at very low conversions or leads to unwanted side reactions (acetic acid and acetone) as the propylene conversion is forced higher, ultimately leading to complete combustion. Conversely, crystalline M2 ($MoV_{0.31}Nb_{0.06}Te_{0.37}O_x$) compositions containing no amorphous overlayers give excellent yields of both, AA (~34%, Figs. 3, 4) or AN (~45%, Figs. 1, 2). While it is possible that some positive catalytic contribution might also arise from trace incorporation of Nb into the $MoV_{0.31}Nb_{0.06}Te_{0.37}O_x$-M2 phase used in this study, it is currently unproven, but is under active investigation and will be reported shortly.

At this juncture it is difficult to assert that all amorphous overlayers on top of crystalline catalysts are generally undesirable in selective oxidation and ammoxidation reactions. Our study reported here definitely supports this view and is consistent with the thesis that both selective oxidation and ammoxidation of light olefins and paraffins are demanding reactions and require catalysts where specific key catalytic elements are arranged in proper order and sequence within bonding distance of reactants and products; the catalyst surface requiring a minimum short range order for the desired catalytic events to take place. Longer range order is desired for site isolation to prevail, so that high selectivity of a sought after product can be achieved even at commercially desired high conversions. Amorphous overlayers appear undesirable, since they are structureless and would therefore be unable to fulfill the demands of complex reaction sequences, even if they possessed all of the needed catalytic elements.

5 Conclusions

We have demonstrated that crystalline M2 ($MoV_{0.31}Nb_{0.06}Te_{0.37}O_x$) compositions, particularly when doped with P, give excellent yields of AA (~34%) from propylene under selective oxidation reaction conditions and excellent yields of AN (~45%) under ammoxidation conditions. Conversely, M2 ($MoV_{0.54}Te_{0.59}O_x$) compositions with amorphous overlayers of Te–molybdate on top of the crystalline base give fair yields of AN (~24%) in the ammoxidation reaction of propylene, but fail in the selective oxidation reaction of propylene to AA (~3%); the reaction stops either at acrolein or continues to the undesirable byproducts acetic acid and acetone as conversion is forced to higher levels.

Therefore, it is conjectured that amorphous surface overlayers, if they are not innocuous catalytic bystanders, become “troublemakers” in certain catalytic processes. Crystalline catalysts having well defined surface compositions, well defined arrangements of key catalytic elements, and no unwanted amorphous overlayers become therefore the catalysts of choice in selective oxidation and ammoxidation catalysis.

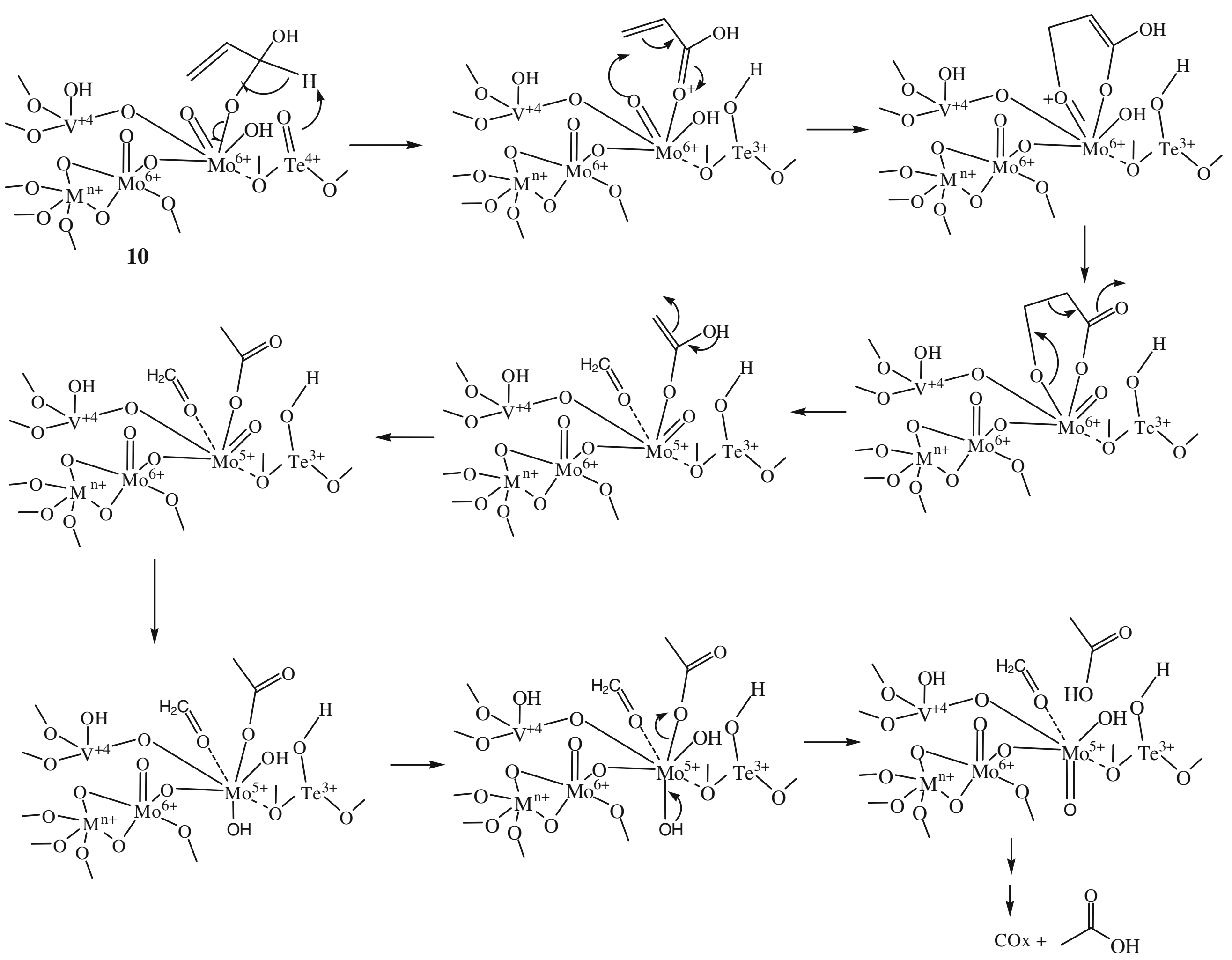

Fig. 7 Proposed mechanism for the formation of acetic acid over MoV(Nb)TeO-M2 catalysts

Doping of the crystalline M2 phase with P leads to significant AA yield improvements over the base and should be seriously considered in future attempts to improve the M1/M2 propane/propylene catalyst system.

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