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Enhancement of acrylic acid yields in propane and propylene oxidation by selective P Doping of MoV(Nb)TeO-based M1 and M2 catalysts

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1. Introduction

MoV(Nb,Ta)(Te,Sb)O is one of the best known catalytic systems for the selective oxidation of propane to acrylic acid (AA) and ammoxidation to acrylonitrile (AN) [1,2]. Since its discovery [3–7] it has been studied extensively [8–24]. It is comprised of two phases: M1 (orthorhombic) $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ and M2 (pseudo-hexagonal) $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ [9,10,13]. The M1 phase performs all of the catalytic functions needed to convert propane to acrylic acid or acrylonitrile, since all key catalytic functions are located at its active center within bonding distance of each other to perform these complex transformations [9]. At high throughputs (high wwh) the M2 phase, if commingled with the M1 phase, becomes 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) [9,16].

It is postulated that if the catalytic efficiency of either or both phases could be improved, then the yields of the desired products of the combined M1/M2 system should be improved [20]. Various attempts to influence the catalytic properties of these phases through substitution of select elements are reported in the literature, with varying degrees of success [25–30].

Our current study concentrates on the selective doping of M1and M2 phases for the selective oxidation of propane and propylene to acrylic acid. It centers on the doping of these structures with low levels of phosphorous (P); well known to possess substantial acidic properties [31,32].

2. Experimental

A series of catalytic materials for the oxidation of propane were prepared with the general precursor composition $Mo_1V_{0.31}Te_{0.37}Nb_xP_yO_n$ using published methods [33–35]. 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 phosphoric acid (0.1 M) 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 N2. The nominal compositions of the catalysts were $Mo_1V_{0.31}Te_{0.37}Nb_xP_yO_n$ where $x = 0$, 0.02 and 0.09 and $y = 0$, 0.001 and 0.005. The BET surface areas of the samples with Nb0 and Nb0.02 (M2's) both with and without P doping were about 4 m^2/g. The BET surface areas of the samples with Nb0.09 (primarily M1) with and without P doping were about 7 m^2/g.

The catalysts for propylene oxidation were prepared in a similar manner as described above and as described earlier [20,31] and evaluated by high throughput experimental techniques [36]. The nominal catalyst compositions were: $Mo_1V_{0.31}Nb_{0.06}Te_{0.37}$ (M2-1), $Mo_1V_{0.31}Nb_{0.06}Te_{0.37}P_{0.0005}$ (M2-2), $Mo_1V_{0.31}Nb_{0.06}Te_{0.37}P_{0.001}$ (M2-3), and $Mo_1V_{0.31}Nb_{0.06}Te_{0.37}P_{0.005}$ (M2-4). A specific weight of catalyst (200 mg) was diluted with SiC (about 3 × volume of catalyst) to establish a consistent bed height and tested for catalytic activity in a tertiary screening six-channel reactor module. The reaction conditions were: atmospheric pressure, 290 to 370 °C, WHSV = 0.07 to 0.2 h^{-1}, and feed ratio $C_3H_8/O_2/He/H_2O = 1/2/10/1.4$ for propane oxidation and $C_3H_6/O_2/He/H_2O = 1/2/8.4/2.9$ for propylene oxidation. Each catalyst was tested at four different space

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velocities, starting with the highest, at several reaction temperatures starting at the lowest temperature.

3. Results and discussion

The main aim of the current study was to enhance the performance of M1 and M2 phases for the selective oxidation of propane and propylene to acrylic acid. Our thesis was that addition of the acidic element, P, to these phases would enhance their ability to convert intermediately formed, chemisorbed or desorbed, acrolein more efficiently to the desired acrylic acid end product. This postulate was essentially confirmed, since measured additions of P to M1 and M2 lead, as will be seen below, to improved AA yields. Conversely, the addition of basic elements such as Cs has the opposite effect, decreasing the AA yield, because acidic sites needed for AA catalysis are neutralised [31]. Somewhat unexpected was, however the significant activity enhancement of M1 with P doping, which might find an explanation in how P effects the $V^{5+}=O \longleftrightarrow \bullet V^{4+}-O\bullet$ activating site of the catalyst's active center.

3.1. Oxidation of propane over M1 and M2 catalysts

We prepared three sets of catalysts (Table 1) with varying amounts of Nb (0, 0.02, 0.09), while the Mo, V, and Te contents were kept constant (Mo 1, V 0.31, Te 0.37). These base catalysts were then also doped with 0.001 and 0.005 P. The powder XRD's (Fig. 1) reveal that the Nb0 and Nb0.02 containing systems crystallize as the M2 phase; while the Nb0.09 sample gives predominantly M1 phase. The P doped systems do not show any obvious structural deviations from the respective base systems (XRD's in Fig. 1).

These catalysts were tested for the oxidation of propane (Fig. 2) to assess their respective abilities to give acrylic acid (AA). It is well known from the literature [9,16,19–21] that MoV(Nb)-TeO compositions containing only the M2 structure are essentially inactive for the conversion of propane to AA. Nonetheless, we wanted to see if doping with P might prod the M2 structure at least partly into the desired reaction path. Not so; the two P doped M2 structures are still very inactive towards propane activation; they still lack the $V^{5+}=O$ paraffin activating moieties. Yet, interestingly (Fig. 2) they convert more effectively whatever little propylene is formed to acrolein and AA than the unpromoted base composition. Thus in M2 compositions the P doping appears to intercede in the later stages of the consecutive reaction path; i.e., at the adsorbed propylene stage leading finally to acrolein and AA. This will be discussed more fully in the Mechanistic section below.

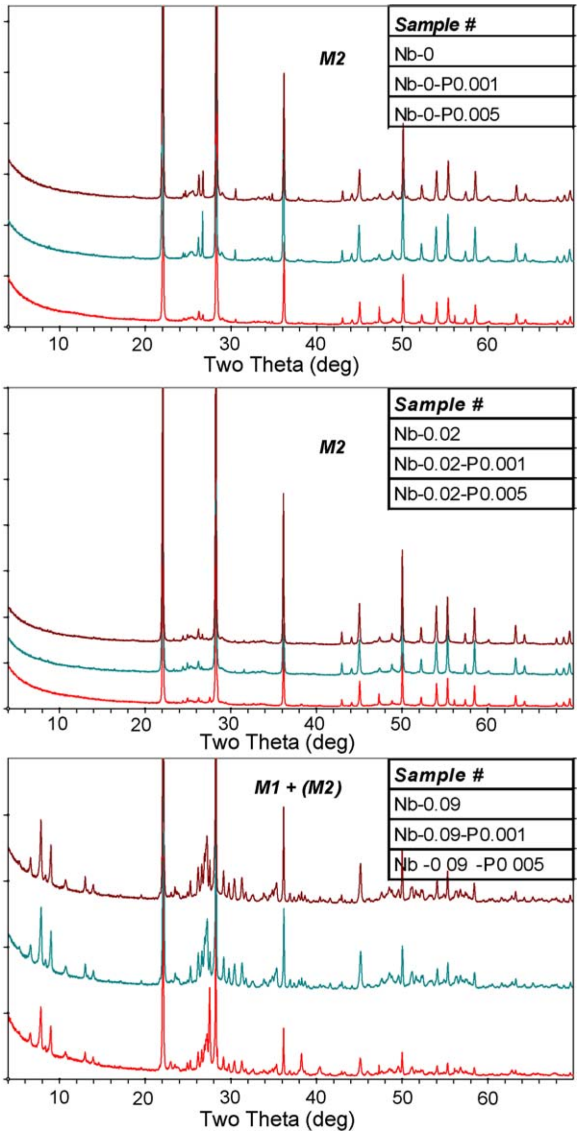

Fig. 1. Powder X-ray diffraction patterns of the P doped M2 and M1 + (M2) catalysts and their respective undoped base systems.

Table 1
M2 and M1+ (M2) Catalysts with P added to the synthesis mixture.

Sample #	Mo	V	Te	Nb	P
Nb-0	1	0.31	0.37	0	0
Nb-0-P 0.001	1	0.31	0.37	0	0.001
Nb-0-P 0.005	1	0.31	0.37	0	0.005
Nb-0.02	1	0.31	0.37	0.02	0
Nb-0.02-P 0.001	1	0.31	0.37	0.02	0.001
Nb-0.02-P 0.005	1	0.31	0.37	0.02	0.005
Nb-0.09	1	0.31	0.37	0.09	0
Nb-0.09-P 0.001	1	0.31	0.37	0.09	0.001
Nb-0.09-P 0.005	1	0.31	0.37	0.09	0.005

It is an entirely different matter with P doped M1 catalysts (Fig. 2). Again, it is well known (same as above) that MoV(Nb)TeO compositions having the M1 structure are effective for the conversion of propane to AA. We confirm this here also. But what is new is that the P doped M1 compositions are much more active for propane oxidation than the base. Here, the doping effect appears to be most pronounced in the earliest, the activating stage of the catalytic process. This too will be discussed more thoroughly in the Mechanistic section below.

The selectivities to AA at maximum conversion of propane are shown in Fig. 3 for the three sets of catalysts. The selectivity to AA of the M2 Nb0 base composition is practically nil and is markedly increased to 15% with P 0.001 and to 17% with P 0.005 doping. The AA selectivity of the M2 Nb0.02 base is also practically nil and rises steeply to 27% at P 0.001 and 34% at P 0.005 doping. Conversely, as expected, the AA selectivity of the M1 Nb0.09 base lies already at a respectable 43%, but is further improved by P doping to 60% at P 0.001, falling off slightly to 58% at P 0.005. One has to use the P doping with caution; the useful range is low and very narrow!

The remarkable effect of the P doping can be illustrated even more dramatically by comparing the maximum AA yields of these three sets of catalysts (Fig. 4). The yields of AA are minute using M2 phase catalysts, unpromoted or P promoted. Although the selectivity to AA is greatly increased with P doping over the base (Fig. 3), minimal yields of AA are obtained with all M2's, since an almost zero activity multiplied by a reasonably large selectivity

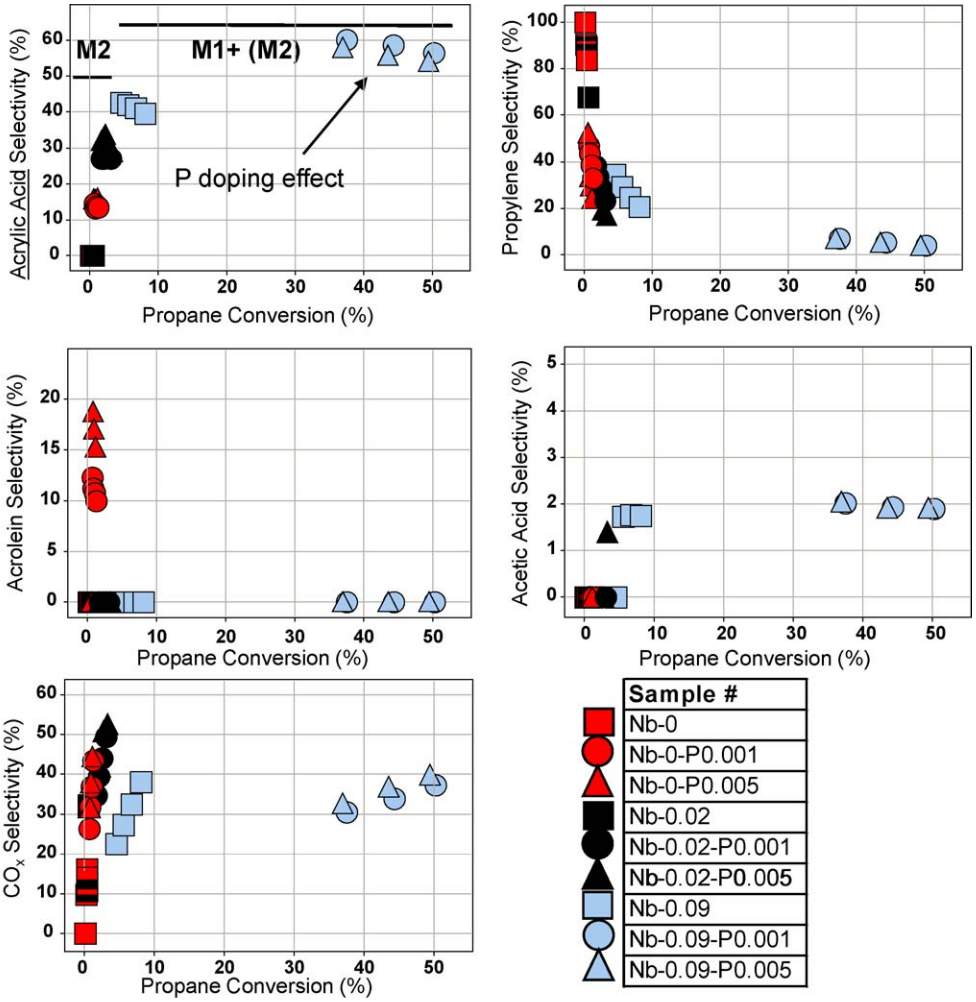

Fig. 2. Propane oxidation over P doped M2 and M1 + (M2) catalysts. Reaction temperature 390 °C; feed composition $C_3H_8/O_2/He/H_2O$ = 1/2/8.4/2.9; WHSV = 0.08 to 0.15 h^{-1}

still amounts to very little. Thus the maximum AA yields of M2 Nb0 P 0.001 and P 0.005 are in the 0.1% range and the M2 Nb0.02 P 0.001 and P 0.005 are in the less than 1% range.

In contrast to M2, the M1 catalysts give respectable AA yields from propane (Fig. 4). The unpromoted M1 base gives a maximum AA yield of about 3%. Although this is a low value for an M1 catalyst, the value is low because the M1 composition was not optimized in these experiments (i.e., we worked with an Nb0.09 rather than the optimum Nb0.12 composition) and, because of the high propane throughput (WWH) used in these experiments. The idea was to simulate real commercial conditions. However, the P promoted catalysts show exceptional potential. The M1 Nb0.09 P 0.001 catalyst gives 27% AA yield and the M1 Nb0.09 P 0.005 catalyst a 26% AA yield. Thus the improvement over the M1 base is about a factor of 9, which is remarkable. There might be an effect of

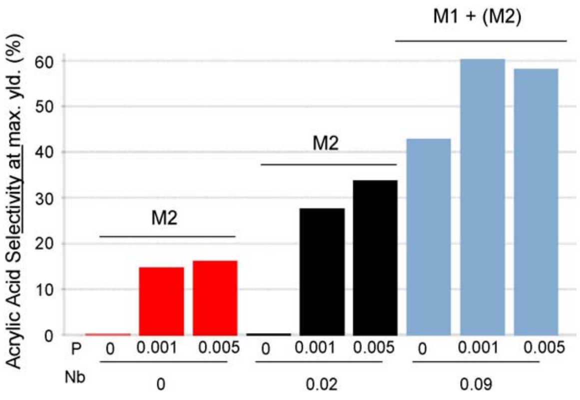

Fig. 3. Propane oxidation over P doped M2 and M1 + (M2) catalysts. Acrylic acid selectivities at maximum observed yields vs catalyst composition ($Mo_1V_{0.31}Te_{0.37}Nb_xP_y$).

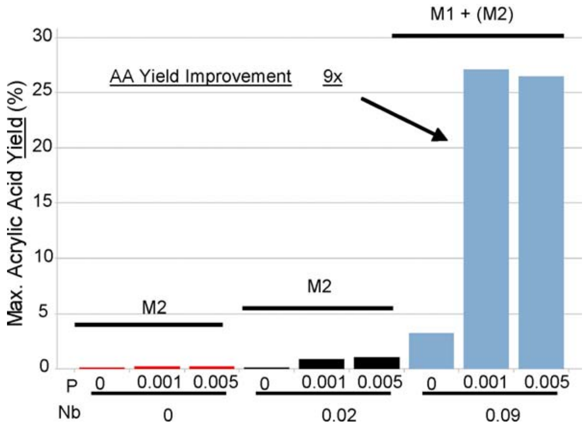

Fig. 4. Propane oxidation over P doped M2 and M1 + (M2) catalysts. Maximum observed acrylic acid yields vs catalyst composition $Mo_1V_{0.31}Te_{0.37}Nb_xP_y$.

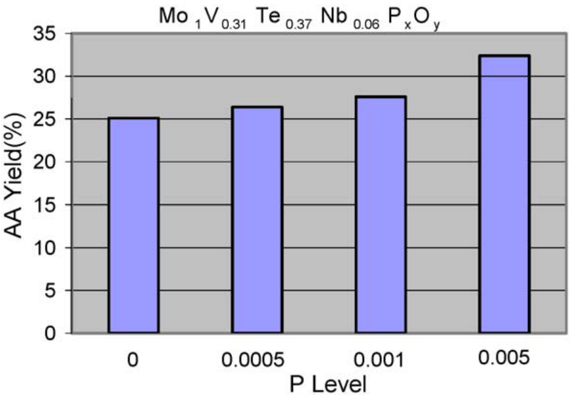

Fig. 5. Propylene oxidation over P doped M2 catalysts. Maximum observed acrylic acid yields vs catalyst composition $Mo_1V_{0.31}Te_{0.37}Nb_xP_y$.

P on the favorable formation of M1 during catalyst preparation even at levels below the optimum Nb0.12 range. But this is not obvious from the XRD's (Fig. 1).

Of course if a more active M1 base were to be made (e.g. an Nb0.12-based M1), the P doping improvement cannot be expected to be as large as the one observed here. Additional experiments are necessary to more exactly define the exact range and limits of P doping (and Nb level). Nevertheless, our experimental results are catalytically very encouraging.

3.2. Oxidation of propylene over M2 catalysts

Our thesis is that symbiosis or phase cooperation exists between M1 and M2 phases under commercially demanding conditions of high WWH and that if either of the two phases were improved, the overall AA yields of an M1/M2 mixture should also be improved. We have shown above that P doping of the M1 phase significantly enhances the AA yields in the oxidation of propane. Drawing on our earlier observations [31,37], we can state that substantial improvements in the oxidation of propylene to AA can also be obtained by doping the M2 structure with P. As illustrative examples it is shown in Fig. 5 that under comparable conditions (47% propylene conversion) the net AA yield of the unpromoted M2 base is improved from 24% to 26% at P 0.0005, 27% at P 0.001 and 32% at P 0.005. The latter is a respectable 33% AA yield enhancement over the base.

3.3. Symbiosis between M1 and M2 phases in propane oxidation to AA

While we have now shown significantly improved AA yields in propane oxidation over P doped M1 phase and substantially improved AA yields in propylene oxidation over P doped M2 phase, the P doped improvement of M1/M2 mixtures in propane

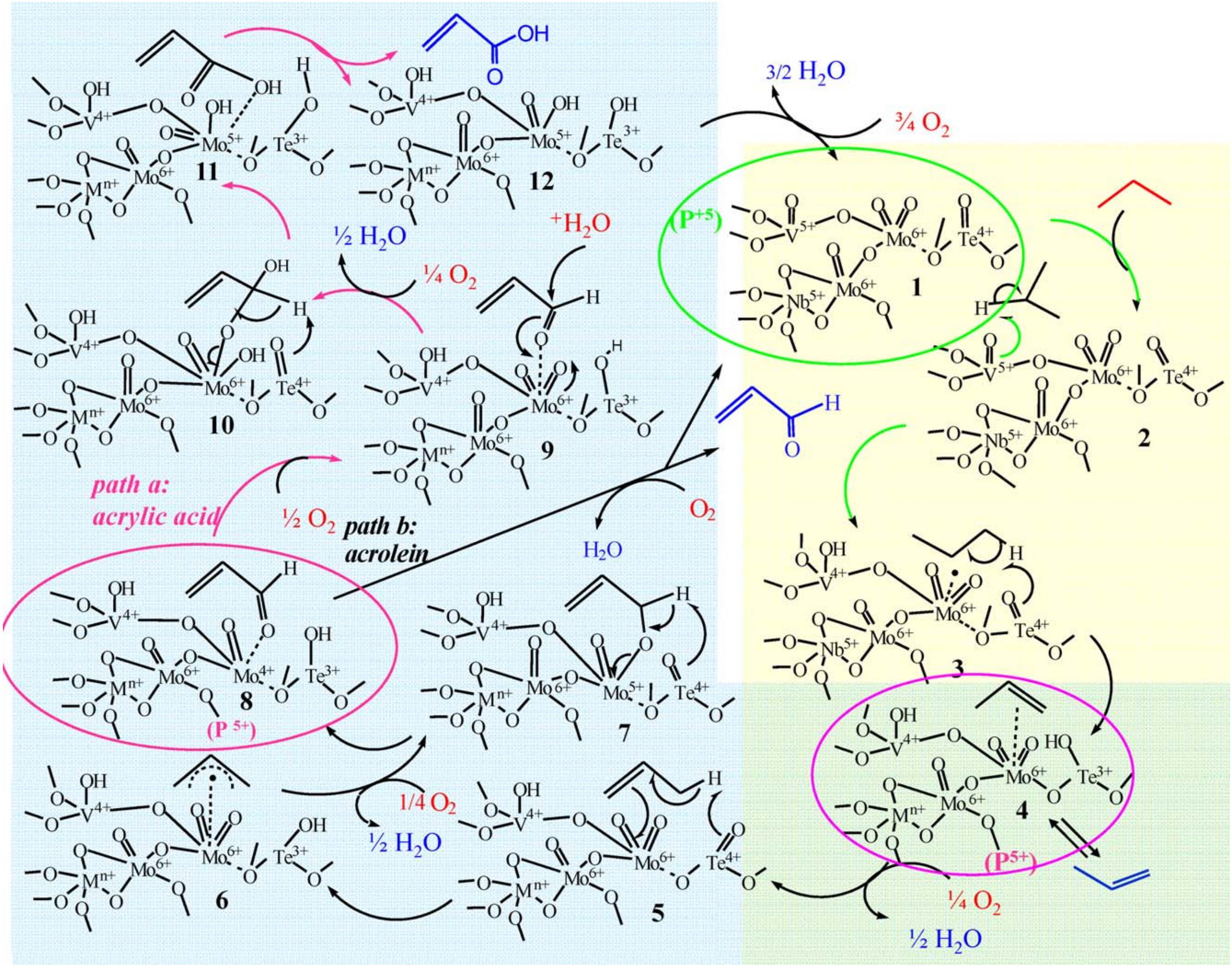

Fig. 6. Proposed propane/propylene oxidation mechanism over MoV(Nb)TeO catalysts (M1 domains: #1–#4 and #4–#12; M2 domain: #4–#12). Adapted from reference [35].

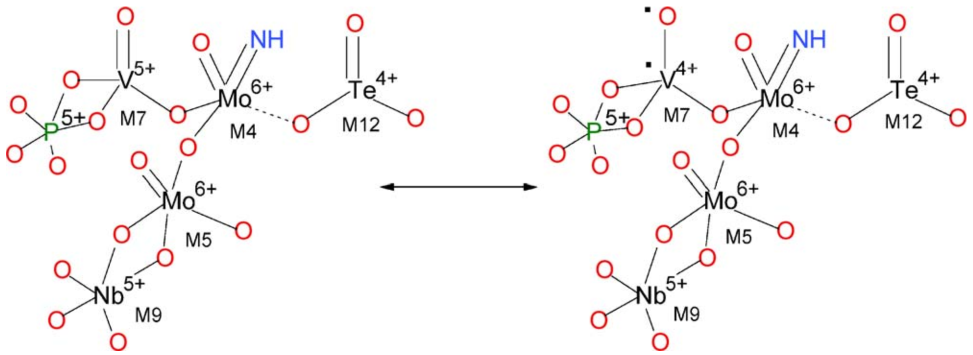

Fig. 7. Symyx draw illustration of the catalytically active center of $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ *(M1)*. Adapted from reference [9].

oxidation, while on the agenda, still needs to be demonstrated. Since both phases benefit by P doping, it should follow that optimal mixtures of M1/M2 phases, if synergy exists between the phases in oxidation of propane as it exists in ammoxidation of propane [9,15,16,20], should show the desired doping effect, and thus a higher AA overall yield. Verification is still outstanding.

3.4. Mechanistic consequences of P doping

The observed improvement in AA selectivity and yield with P doping of M1 and M2 phases, respectively can be explained on the basis of our proposed reaction mechanism shown in Fig. 6.

We are of the opinion that there are two effects, which P doping brings about in these compositions. In the M1 phase, the P doping exhibits itself in both an improved selectivity to AA but primarily in a much higher activity of propane conversion. This leads us to believe that P must be located on the M1 surface in the vicinity of $V^{5+} = O \longleftrightarrow \bullet V^{4+} - O\bullet$ activating sites of the active site ensemble as shown in Fig. 7.

Under the premise of such P/V adjacency, the P will tend to electronically push the $V^{5+} = O$ moiety to its complimentary, paraffin activating $\bullet V^{4+} - O\bullet$ resonance structure, thereby increasing the time averaged number of the activating sites. This of course would automatically lead to enhanced activity. In the mechanism (Fig. 6) steps #1 to #2, #2 to #3, and #3 to #4 are accelerated.

The second type of enhancement towards AA formation due to P doping comes in the later stages of the mechanism, with phosphorous now placed next to the spectator Mo^{6+} [38] of the Mo^{6+}-O-Mo^{4+} site as depicted in complex #4 and #8 of the mechanistic illustration. The acidic nature of the P (acting as a pseudo surface heteropoly acid) in complex #4 enhances the chemisorption of the propylene moiety, preventing its desorption and favouring its path towards the allylic intermediate (complex #6) and on to the chemisorbed acrolein intermediate (complex #8). At this juncture, the P induces and facilitates the charge transfer from the spectator Mo^{6+} to the adjacent, reacting Mo^{4+} moiety and stabilises it as Mo^{6+} in complex #9. This charge transfer facilitates the transition from complex #8 to #9 and activates complex #9 towards hydrolysis again by stabilising Mo^{6+}, thereby enhancing the transition from complex #9 to #10. The higher acidity of the P doped Mo centers enhances not only the chemisorption of propylene (complex #4) but also the surface acrolein intermediate (complex #8), inhibiting it's desorption and facilitates further surface transformations toward AA as shown in Fig. 6. Hence, path a prevails over path b in the mechanism. Path b leading to acrolein is undesirable, since under the reaction conditions it would lead to waste products CO and CO_2. The beneficial effect of P doping in the later stages of the reaction mechanism (steps #4 through #12) can occur on either M1 or M2.

A word about the very low level of P doping which is greatly effective in enhancing AA yields: it is remarkable that such low levels of P have such a large effect on both the activity and selectivity of AA production. With an M1 composition containing Nb0.09P 0.005 only 20% of the "active sites" contain a P; meaning that only every fifth site has a P. This assumes that the P is distributed throughout the whole bulk and surface uniformly. If we assume that only the active and selective sites attract P, then the P population increases to about every second useful site possessing a P (see reference [39] for the distribution of active/selective, waste, and inactive sites at the surface of M1 basal plane [ab direction]). Actually, these P site concentrations are not all that out of line to expect a doping influence on the catalytic behavior. Since we see a beneficial doping effect even at P 0.001 levels, one might, but not necessarily has, to reason that there could be a surface enhancement of P, which is possible; perhaps akin to VPO catalysts. Conversely, too much P is undesirable, actually also logical, since at the higher concentrations the dopant changes drastically and deleteriously the nature of the catalyst. From our study we have learned that the window of P doping is very narrow and still needs to be further optimized for best catalytic results.

As to the life of the P doped catalysts, no extensive life tests were conducted, but we did not observe any decline in performance over limited time on stream. Actually, there is ample precedent [1,2] that P containing Bi-molybdates exhibit excellent life properties over years of commercial operation. By analogy, we do not expect P containing M1 and M2 compositions tending towards life problems.

4. Conclusions

Doping of crystalline M1 and M2 phases with P in selective oxidation of propane or propylene to AA enhances significantly the desired AA yields at commercially relevant high hydrocarbon conversions. It comprises a promising approach to improve AA yields and is worth further study with the possibility of commercial implementation (Table 2).

Table 2
M2 catalysts with P added to synthesis mixture.

Sample #	Mo	V	Te	Nb	P
M2–1	1	0.31	0.37	0.06	0
M2–2	1	0.31	0.37	0.06	0.0005
M2–3	1	0.31	0.37	0.06	0.001
M2–4	1	0.31	0.37	0.06	0.005

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