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Application of concepts in heterogeneous oxidation of hydrocarbons: Mo, V-based oxide catalysts for oxidation of ethane and of *n*- and *i*-butanes

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Declaration of interest : none

Abstract

The V and Mo-containing oxides are versatile catalysts used in a large number of reactions aiming at producing organic chemicals and intermediates like acids, anhydrides, nitriles, etc. The solid oxide catalyst is viewed as a catalytic reagent which is regenerated at each redox cycle, this principle being explicitly used in redox decoupling reactors like circulating fluid bed and catalytic membrane reactors. The selectivity to the product depends on the surface crystal field exerted by the exposed faces onto the organic molecule to be transformed. It is directly related to the structural chemistry of the solid, from its preparation up to its ageing through its use in reactors. In this paper the author, whose scientific life was dedicated to demonstrate its usefulness, wishes to illustrate the main concepts which are now agreed by the scientific community. Among them are the “seven pillars of catalysis” as put forward by R.K. Grasselli, and few others which are complementary. The differences in V-O and Mo-O systems are first evoked, before telling the story of the selective oxidations of *n*-butane to maleic anhydride, ethane to acetic acid, and isobutane to methacrylic acid on V-P-O, Mo-V-O systems and heteropolyvanadomolybdates, respectively.

Keywords: Selective oxidation of hydrocarbons; concepts; structural chemistry; redox decoupling; Mo,V oxide catalysts

1. Introduction

Several processes of selective oxidation of hydrocarbons using vanadium oxides were technically available (oxidations of SO₂ to SO₃, naphthalene to phthalic anhydride, benzene to maleic anhydride) more than eighty years ago, but for proprietary concerns the underlying concepts – when the search for catalysts was not empirical – were not discarded. In the academic literature, papers dealing with

selective oxidation using transition metal oxides were still scarce in that period. Carbon monoxide was often chosen as a molecule to oxidize, the results of which could not illustrate the selectivity concept. At that time, metal oxides were not frequently used because they were said to be less stable and less active than metals, which unfortunately were not selective at all. The basis of selective oxidation is the *redox mechanism* proposed in 1954 by Mars and van Krevelen [1]. They deliberately chose a reducible oxide, V_2O_5 , and studied how the catalyst evolved during the oxidation of naphthalene. They showed that lattice oxygens participate to the reaction and are responsible for selectivity to phthalic anhydride, and provided kinetic equations while taking into account the crystal structure of the catalyst. In 1961 J.L. Callahan and R.K. Grasselli [2] published a paper in which they proposed to use copper oxide to make acrolein from propylene. They set forth the redox principle, evoked the role of metal-oxygen bonds and underlined the importance of the crystal structure. In the academic world few groups believed in the importance of the latter, among who J. Haber (Poland), G.C.A. Schuit in the Netherlands, F. Trifirò in Italy, J.E. Germain and P. Courtine in France. Attempts to use vanadium oxide to make maleic anhydride from benzene or phthalic anhydride from o-xylene were successful [3] and the oxidation of methanol to formaldehyde using iron molybdate was beginning [4]. Considerable developments followed in patents. In his paper about the “seven pillars” of selective heterogeneous oxidation catalysis, Grasselli [5] underlined that innovative concepts could not be discarded in patents – which unfortunately is still true. Bismuth and other molybdates were soon discovered [6] but Grasselli’s group had already found in 1955 that $Bi_9PMo_{12}O_{52}/SiO_2$ was active and selective in the oxidation of propene to acrolein. Papers about multicomponent molybdates for the (amm)oxidation of propene were published later [7], after work for a while on uranium-antimony oxides [8], among other systems. Very soon it appeared that V and Mo oxides and derivatives were versatile enough to oxidize many organic molecules, from C_2 to C_8 unsaturated hydrocarbons to small oxygenated molecules (methanol, acrolein, methacrolein, isobutyric acid).

In the 1960’ appeared the willing of substituting the harmful and costly benzene by but-1-ene to make maleic anhydride. Patented studies showed that by adding a phosphate ligand to vanadium oxide instead of doping it by molybdenum (as for benzene oxidation) the obtained V-P-O catalyst showed promising performance. but-1-ene was quickly replaced by *n*-butane and, thanks to a new preparation method, the success was met, which promoted intensive research for substituting C_2 - C_4 unsaturated hydrocarbons by the homologous alkanes. Nowadays propane is oxidized to acrylic acid or acrylonitrile, isobutane to methacrylic acid, and acetic acid could be obtained from ethane, while when starting with ethylene only acetaldehyde was produced.

The scientific community soon agreed that the oxide catalyst should be regarded as a *catalytic reagent*, which is regenerated at each cycle. The demanding selective oxidation reactions are more or less *structure-sensitive* depending on the number of electrons involved in the reaction. Even the remediation catalysis is structure-sensitive because a limited number of oxides (perovskites or spinels)

is actually selective to CO₂. For a deeper insight, the solid catalyst may be viewed as exerting a *surface crystal field* which chemically polarizes the reactant molecule so as to yield the target product [9,10]. Volta et al. [11] demonstrated that the catalytic reactivity of crystal faces of MoO₃ in the presence of, e.g., propene, was different, as owed to the distribution of the surface metal-oxygen bonds. {010} faces promoted the total oxidation of propene while {100} faces yielded selectively acrolein. The poor performance of MoO₃ particles exhibiting usually {010} faces was therefore accounted for. In other words a *crystal face sensitivity* (also called catalytic anisotropy) is also to be considered. This concept should be the 8th pillar of oxidation catalysis. Among others like ‘host structure’, and multifunctionality of active sites, the notions of *site isolation* and of *phase cooperation* proposed by Grasselli to account for the selectivity of bismuth molybdates in propene oxidation to acrolein [7,12,13] were emphasized. As a beginning of a very long and fruitful collaboration (40 years), the french company CdF-Chimie came to us and answered why and how, by using such a complicated formula M^{II}_{11-x}Fe_xBiMo₁₂O_z/SiO₂, the acrolein yields could be so much enhanced, as compared to simple bismuth molybdates. Courtine et al. were working on the structural relationships between TiO₂-anatase and V₂O₅, and their consequences on reduction of V₂O₅ and rutilization of TiO₂-anatase [14]. So, noticing the strong structural relationships between the constituting molybdates, Courtine answered that the only explanation could be found in the existence of *coherent interfaces* (a pre-requisite for *phase cooperation*) between them. The written paper came far later [9] and meanwhile Sleight et al. [15] suggested the same idea.

The purpose of this paper is to illustrate the main concepts put forward when we studied several catalytic reactions of mild oxidation in the past in our laboratories. Most catalysts we studied were based on vanadium and/or molybdenum oxides to selectively oxidize C₂-C₄ olefins, alkanes and small oxygenated molecules. Our main thematics dealt with the influence of structural properties of catalysts all along their life, from preparation to use in catalytic reactors and ageing [16]. More particularly, care was taken to describe the catalytic solid (crystal structure, crystalline morphology), the influence of preparation on the crystalline morphology, the catalyst dynamics (redox system, oxide ion conductivity, evolution under redox conditions) and its stabilization (supports with or without *coherent interfaces*, a pre-requisite for *phase cooperation*). Moreover, attempts to decouple the steps (reduction by reactant and reoxidation by oxygen) of the redox mechanism were made using new reactor configurations (riser reactor, catalytic membrane reactors, and the like). From these studies stemmed the notion of *oxocapacity*. The V-P-O system, which had been a favorite subject of the author, is concentrating all characteristics of an efficient catalyst so that it deserves a dedicated paragraph. Analogies and differences between V- and Mo-based catalysts will be also pointed out by considering catalysts for ethane oxidation to acetic acid and isobutane to methacrylic acid. Some parts of our research will not be evoked (or only briefly). For example, the use of catalytic wall reactors that were studied to promote the catalytic interactions without favoring the combustion process in the oxidative

dehydrogenation of propane [17]. In a parallel way, attempts to find “rules” were made to account for the fact that, in selective oxidation, each reaction (R reactant to P product) requires a dedicated catalyst. Scales of the variation of the ionization energy when R becomes P vs. the ‘optical basicity’ (related to the oxidative power) of the ‘selective’ catalyst were set up for the main types of molecules transformed by mild oxidation (alcohols, alkanes, unsaturated hydrocarbons) depending on the deepness of oxidation [18,19]. Such scales of selectivity were aimed at choosing catalysts for unknown reactions, but using only optical basicity to characterize the mean basicity of V- and Mo-based oxides will be briefly evoked.

2. Main characteristics of V and/or Mo-based solid oxides exhibiting catalytic properties

Oxides of vanadium and molybdenum in their higher oxidation states exhibit particular and versatile electronic and structural properties [9,10]. To summarize, (i), the electronic structure of V^{5+} , Mo^{6+} (formal valences) is d^0 (empty d orbital), making these ions quite acidic, reducible and prone to adsorption, (ii) its ion size being very small, the ion “rattles” in its oxygen environment, and thus it adopts several configurations from tetrahedral MO_4 to octahedral MO_6 , and (iii), being closer from one (or more) oxygen(s) it forms short $M=O$ bond(s) with $\sigma-\pi$ bond character (covalent) and generally opposed to a long $M...O$ bond. The consequences are plural: (i), the circulation of electrons is ensured inside the distorted polyhedra and through the whole crystal, and owing to the extended defects the semi-conductivity is n (by electrons), e.g. V_2O_5 , and less often p (by holes), like for $(VO)_2P_2O_7$, catalyst for *n*-butane oxidation. These electrons are used for the adsorption of reactants on the surface and their transformation. (ii), the anisotropic distribution of M-O bonds favors the formation of layered crystal structures. Consequently, platelets are often characteristic of the crystal morphology of these oxides. (iii) the reduction of such phases, e.g. V_2O_5 and MoO_3 , proceeds by crystallographic shear planes [20] formed by the elimination of oxygen vacancies (related to O^{2-} oxide ion conductivity) giving rise to structurally related suboxides. Series like V_nO_{2n+1} ($n = 3, 4$), Mo_8O_{26} and $Mo_{17}O_{47}$ are built on distorted octahedra, but other mixed (V^{5+} , V^{4+} or Mo^{6+} , Mo^{5+} respectively) suboxides are built on tetrahedral, octahedral (e.g. in $Mo_{17}O_{47}$), and/or pentahedral (e.g. in Mo_5O_{14}), environments. The so-called θ -phase, Mo_5O_{14} , is stable only when dopants (V, Nb, W) are added. It is typically a *host structure*, from which derives the structure of M1 phase [21], and it provides catalysts for oxidation of ethane to acetic acid [22], propane to acrylic acid or acrylonitrile [23-25], and other reactions [26]. Another mechanism of surface reduction has recently been proposed by Gai et al. [27]. They showed that for MoO_3 , V_2O_5 and also $(VO)_2P_2O_7$ (among other oxides), the O^{2-} anion point defects created by the reduction aggregate into a variety of extended planar defects to accommodate the non-stoichiometry. Their surface (and bulk) can stand as well small amounts of the oxidized (or reduced) cations, like V^{5+} on the surface of VO_2 [28] or of $(VO)_2P_2O_7$ [29].

3. Comparison of V and Mo-based catalysts

3.1 General

Selectivity depends at first on the type (ionic to covalent) and nature (acidic to basic) of the metal M in the metal-oxygen M–O bond of the catalyst. Certain crystal faces may exhibit mostly ionic bonds which generally promote the formation of electrophilic oxygen species (O_2^- , O^-) leading usually to total oxidation of hydrocarbons, but also to dissociation of water. Exceptions are oxidation and coupling of methane and formation of epoxides. In modern theories of reactivity the oxidizing power, acidity, basicity, and reducing power, are steps along a same continuum, instead of distinct phenomena [30]. So, concerning the *multifunctionality* of active sites, we may consider that both acidity (basicity) and oxidizing (reducing) power are the same expression required to explain the catalytic action, Brønsted acidity being only a special case when hydrogen participates. The M^{n+} cation is characterized by a given oxidizing power (strong to low). Facing the solid surface is a reactant R which is a strong (e.g. methane) to low (e.g. butene) reducing agent (and also a more or less strong base), that must be transformed to an oxidized product P, which is more acidic. To be efficient in transforming R to P, the surface of an oxide catalyst must endeavor reduction (by R) and reoxidation (by co-fed oxygen and/or by means of diffusion of O^{2-} oxide ion), according to the redox mechanism. The reaction will be as fast as the principle of the least change is obeyed, that is the best catalyst is that one made up of a stable core onto which few layers are actually working during the reaction.

Vanadium oxide and its suboxides V_4O_9 , V_6O_{13} , VO_2 are stable without addition of dopants, at variance with molybdenum oxides (except MoO_2), as seen with the example of Mo_5O_{14} . Conversely, molybdates are more easily formed (and are better catalysts) than the corresponding vanadates, and many molybdates with Bi, Fe, Co, etc., cations are known. Also, both $V^{5+}=O$ and $V^{4+}=O$ bonds in distorted octahedra are stable, and can be stabilized in this configuration by anionic ligands like sulfate or phosphates. At variance, the only example of a molybdenyl phosphate analogous to vanadyl is $MoOPO_4$, which is isostructural with α - $VOPO_4$ and $VOMoO_4$ [31,32]. Considering heteropolyoxometalates, polyvanadates are rarely used in catalysis contrary to polymolybdates. Owing to their molecular structure, these compounds cannot be considered in the same way than the infinite rows of atoms in the above ReO_3 -related oxides. Twelve MoO_6 octahedra are arranged in the well-known Keggin primary structure, which is the main component of catalysts for the reactions we examine here. $[Mo_{12}O_{40}]^{3-}$ polyanions are held together by protons and/or alkaline cations, and water molecules. In most catalytic formulas, Mo may be partially substituted by V, W, etc., and alkaline cations by metallic cations (Cu^{2+} , Fe^{3+} , etc.), which allow to tune their redox and acidic properties. As in the case of Mo, V oxides, their catalytic behavior does obey to the Mars and van Krevelen redox

mechanism, as it will be recalled. It is necessary to use specific carriers exerting a structural effect because their thermal and chemical stability are poor.

3.2 Redox system

The redox chemistry of V or Mo catalysts is different, which bears influence in catalysis. After reduction (by the reactant R), the rate of (re)oxidation, r_{ox} , of molybdenum-based oxides or Mo oxysalts is typically very high, and at the steady state the oxidation state of Mo is very close to (VI). Though the (re)oxidation of vanadium-based oxides is always faster than their reduction, the latter rate is generally lower than in Mo-based oxides, so that mixed V^{5+} , V^{4+} valences compounds (or mixed oxides) are often present at the steady state (or in spent catalysts). Finally, when both V and Mo are present in a mixed oxide, vanadium reduces first and prevents the (over-)reduction of molybdenum [9,10,33].

It is worthwhile to use the numerical scale of acidity/basicity based on the ‘optical basicity’ (OB). First proposed by Duffy for solid ionic oxides [34], it was extended to ionic-covalent oxides by Courtine et al. [18,19,35-37]. The optical basicity Λ (OB, called “optical” because of the UV spectroscopic method used by Duffy) is the electron donor power of O^{2-} oxygen linked to M^{n+} in a simple MO_y oxide. After extension of the concept, Λ is a parameter drawn from semi-empirical correlations and it can be calculated for a mixed oxide as a linear combination of the stoichiometric composition, the valence and the individual OB of cations (which depends on their coordination). The scale of OB of cations extends from 0.33 (P^{5+} , coordination 4) to 1.71 (Cs^+ , coordination 8), the OB of Ca^{2+} in CaO being taken as 1.0 [34,35]. Using literature data, it has been shown that Λ of catalysts could be correlated successfully with their Mössbauer or XPS parameters. Optical basicity is a means to discriminate V and Mo (Table 1). For a same d^0 M^{n+} cation, Λ increases with decreasing coordination (the acidity decreases). The value of OB is the same for the cation M^{n+} than for the simple oxide $MO_{n/2}$, and the acidity decreases in the $WO_3 < MoO_3 < CrO_3 < Nb_2O_5 < V_2O_5$ series. The variation of acidity, estimated by $\Delta\Lambda$, of Mo^{6+} upon changing from octahedra to tetrahedra is smaller than for V^{5+} . For reduced species with the same VI-th coordination, the acidity decreases with decreasing valence. It is important to note that Mo^{5+} is far less acidic than Mo^{6+} , the variation $\Delta\Lambda_{redox}$ being huge, contrary to the case of vanadium. Therefore, each time a small amount of Mo^{5+} is formed (e.g. during catalytic reaction) the molybdenum oxide catalyst becomes far less acidic, whereas the variation is not that much for vanadium oxide. Optical basicity provides also a measure of the influence of a dopant (depending on its amount). Nb^{5+} ($\Lambda = 0.608$) or W^{6+} ($\Lambda = 0.511$) bring more acidity (less oxidizing power) to V or Mo-oxides, but basic Te^{6+} ($\Lambda = 1.173$) and Bi^{3+} ($\Lambda = 1.185$) (d^{10} and $d^{10}s^2$ configurations, respectively) are in the same range of OB than Mo^{5+} (all VI-coordinated for the example). Catalytic formulas could be ranked in a theoretical acidity scale by using linear combination of valence, stoichiometry and Λ of cations (taking into account their coordination and

spin if necessary). For a two components oxide or mixed oxide $A^{a+}_x B^{b+}_y O^{2-}_z$ the value of Λ is expressed by $(ax\Lambda_A + by\Lambda_B)/2z$. Linear correlations were obtained upon plotting Λ , the optical basicity of catalysts, against $\Delta I = I_R - I_P$, the difference of ionization potential between the reactant R (I_R) and the product P (I_P). Among other considerations, they allowed to understand that, e.g., a more basic catalyst is needed for the oxidative dehydrogenation of an alkane (e.g. propane to propene) than for its mild oxidation to an oxygenated compound (e.g. propane to acrylic acid), and could be used as a *predictive trend* to find catalysts in given reactions [18,19,36,37].

3.3 Equilibration and redox decoupling reactors

During catalysis, it is important that the upper reacting layers be “supported” on a stable oxide core poorly affected by over-reduction (or over-oxidation). But the redox mechanism does affect the bulk of the catalyst particle, particularly in V-based oxides which are more sensitive to the red/ox power of R/O₂ reacting mixture. Once the structure and texture have been determined by the operating conditions during synthesis and calcination/ heat treatment, the reactivity of the bulk is again involved for the whole catalyst life. Indeed, during the catalytic steps of activation, equilibration, reaction, ageing, the diffusion of vacancies to the bulk and of oxygens to the surface may continue to modify the bulk, and consequently it affects the microstructure exhibited by the surface at a nanoscale. Obviously the rate of O²⁻ diffusion process from the bulk to the surface is smaller than the rate of surface re-oxidation by molecular O₂. The diffusion of the latter may proceed faster through given faces, particularly in the case of layered crystals. Depending on the cation reducibility (oxidability) during the catalyst “equilibration”, part of the bulk becomes reduced (oxidized). It must be noticed that the reduction of O₂ to 2O²⁻ which requires 4 electrons depends on the type and value of semi-conductivity (σ_e by electrons or σ_p by holes) of the catalytic material. At the steady state there is a limited amount of O²⁻ able to participate in the reaction at each cycle, which is related to the turn-over frequency of the reaction. The question is how deep the reduction (oxidation) of the upper layers may be, without fast ageing of the whole structure. The answer depends on the operating parameters (temperature, contact time, etc.) and particularly on the reactant R to O₂ ratio when feeding this red/ox mixture in the reactor. For example, Cavani et al. [39] studied more particularly the V-P-O system for n-butane and n-pentane oxidations (*vide infra*). The *equilibration* period is a transitory state during which the solid reacts according to these conditions, up to a point when the core does not any more endeavor modifications. Today, *in situ* and *operando* methods may be coupled to catalytic studies in real conditions in order to elucidate these mechanisms, and to be able to choose the optimum operating conditions. Obviously, for any catalyst/reaction couple, the type of reactor influences the catalytic performance through heat and mass transfers (as well as hydrodynamics in special cases), but also the catalyst must be designed for its specific use [16,40]. There may be a competition for adsorption sites (leading to by-products) when reactants are co-fed, but not when separating the reduction of the

catalyst (oxidation of R reactant) from its re-oxidation. *Redox decoupling* reactors allow to tentatively optimize each step that may require different operating conditions than in a co-feeding regime [41,42]. The separation may be achieved “in time” by carrying out transient experiments (alternately feeding reactant and oxygen), as first applied to *n*-butane oxidation on VPO by Emig et al., and followed by others [43-45]. It can be achieved “spatially” by using different redox reactor designs. This was already suggested by Grasselli [2,7] and the device was studied for the oxidation of *o*-xylene to phthalic anhydride [3] using V₂O₅/TiO₂. The circulating fluidized-bed reactor (CFB) was first used by Contractor et al. [46] for the *n*-butane oxidation, and developed as a pilot, and then a commercial process for a while, by DuPont [47]. In a continuous process, the gaseous organic molecules were oxidized (the solid particles of V-P-O catalysts were reduced) in a riser reactor, and after stripping the reduced catalyst was regenerated by oxygen in a fluidized bed reactor, before entering again the riser. The amount of available O²⁻ oxygens per cycle in CFB was termed *oxocapacity*. During our collaboration, we showed that overoxidation in the fluidized bed led to the formation of δ-VOPO₄ at the best, to the very stable β-VOPO₄ at the worst (because it does not give back VPP in the operating conditions), and that too much steam or formation of too much water was responsible for the destruction of the catalyst [48] (*vide infra*). At variance with Fluid Catalytic Cracking (in which the fluidized bed is used for regeneration of the catalyst), and despite tries by few companies for other reactions, the success was not met with CFBs in oxidation catalysis. However they are now intensively studied for Chemical Looping Combustion which is based on the same principles as DuPont’s process to produce maleic anhydride (e.g.,49). Others types are catalytic membrane reactors, either a dense membrane when using an oxide ion conducting material like BIMEVOX [50], or a porous membrane [51,52], or reactors with a two-zone fluidized bed [53,54].

4. Supported and auto-supported active phases

As said above, another principle for an active and selective catalyst of oxidation is that, while surface endeavors fast redox phenomena for the turn-over to be high, its bulk structure should not change during reaction, for the ageing be very low. One well-known means is to support the active phase on a carrier that may exert only a textural effect. Sometimes it is required to exert a *structural* effect onto the active phase. In the early 1970’s it was found that the anatase form of TiO₂ used as a support for V₂O₅ catalyst was responsible for increasing its activity and selectivity in the oxidation of *o*-xylene to phthalic anhydride [3,9,14,55]. At that time, the loading was 15-30% and the thickness of V₂O₅ layers was several microns. The simple reduction of V₂O₅ (in N₂, pO₂ = 10⁻⁵ atm) was also accelerated in the presence of TiO₂ (anatase), and the obtained suboxide was V₆O₁₃ and not VO₂ [14]. The same effect was observed when supporting V₂O₅ on TiO₂(B), a polymorph whose structure is even closer to that of V₂O₅ structure, but the catalytic properties were not that enhanced [57]. Based on the observation that the structures of V₂O₅ and TiO₂ (anatase) were closely related, with very low crystallographic misfit

for certain planes, the model of *coherent interfaces* was proposed to account for this *synergetic effect* [10,41,58,59]. Coherent interfaces, already known to apply in other fields (e.g., semiconductors), and in solid state chemistry [60], are responsible for the lowering of surface energy. The consequence is that various species like electrons, but also protons, O^{2-} , as well as metallic cations with close ionic radius) are allowed to cross the interface. We showed that this model could be applied in a variety of cases like in multicomponent molybdates. Grasselli proposed to use the expression “*phase cooperation*”, which is the result of the coherence of interfaces. Further, Bond et al. [61] found that, when the thickness of V_2O_5 was limited to few monolayers, the enhancement of catalytic properties was significant. After findings in very numerous papers on the subject [e.g. 62], it turns out that it is the nature of the active sites, VO_x polyvanadates strongly linked to titanium atoms on the surface of TiO_2 , which is responsible for the performance. Cs or K dopants in industrial formulae also stabilizes vanadates and hinders their transformation to crystalline V_2O_5 . One wonders how these simple VO_x species can afford the 12 electrons to be exchanged, and the formation of 3 H_2O per reacting o-xylene, beside phthalic anhydride. Very probably they are gathered as nanosized patches on TiO_2 surface to obey the principle of *site isolation*.

However supported monolayers are not so common among mild oxidation catalysts, and most V and Mo oxides/oxyalts are used bulky (or supported on a textural carrier like silica). During equilibration on stream, not only the surface but also the deepest layers are affected by reduction/reoxidation owing to the redox mechanism as already noticed. The goal is to determine the nature and composition of the core once stable, that is once the steady state is reached, and so the experimental conditions leading to an auto-supported catalyst.

5. V-P-O catalysts: a case study

5.1 From but-1-ene to n-butane to make maleic anhydride

In the mid-1960' vanadium phosphorus catalysts were proposed in patents to oxidize but-1-ene into maleic anhydride. P. Courtine's belief being that the crystal structure of solid oxides exerts a prominent influence on catalytic properties, we began to study the synthesis, the reactivity and the structural and catalytic properties of the little known V-P-O system (P/V atomic ratio = 1.0-2.0) [63,64]. Among other phases, oxovanadium(V) phosphates α and β - $VOPO_4$ were identified for the first time, as well as vanadyl (V^{4+}) pyrophosphate $(VO)_2P_2O_7$ (hereafter called VPP) whose structural features were proposed [65]. In nitrogen ($pO_2 \approx 10^{-5}$ atm) α or β - $VOPO_4$ was reduced to VPP at ca. 750°C, this phase being observed in the selective catalyst together with $VOPO_4$. Selectivity to maleic anhydride (MA) increased with conversion of but-1-ene but it amounted to less than 45 mol% at 85 mol% conversion. Besides 2-butenes, butadiene (and carbon oxides), too many oxygenated C_2 - C_4 by-products were present [64]. Soon in patents but-1-ene was substituted by *n*-butane and the success was

quickly met, a considerable work being done by many research teams [e.g. 66-69]. The catalytic behavior was different from that observed with but-1-ene. The initial selectivity to MA was high and it decreased slightly at increasing conversion of butane, the by-products being acetic acid and CO_x with very little amounts of acrylic acid and formaldehyde. The surprise for us was that, at first sight, the same V-P-O catalyst was active and selective, $(\text{VO})_2\text{P}_2\text{O}_7$ (VPP) being detected by X-Ray diffraction (XRD) in used catalysts. It was soon recognized that when the intensity of the (200) line, formerly labelled (020), was high, the catalyst was selective to MA [32,66-70]. In first approximation it meant that the crystals were developed as platelets exhibiting mostly {100} faces. The *n*-butane oxidation was one more example of a *structure sensitive* reaction, or better said, of *crystal face sensitivity*. On the surface of {100} faces one molecule of butane can find the selective sites able to adsorb and oxidize it to get one molecule of MA and four molecules of water. As modern quantum chemical methods like DFT were still in their infancy at the end of the 1980', we used the Crystallochemical Model of Active Sites (CMAS) [71] which is based on a thermodynamic treatment of V-O and P-O bonds [72,73]. We noticed that the catalyst surface was able to transform *n*-butane into a molecule with a mirror plane symmetry (maleic anhydride) with formation of a central C=C double bond. So *n*-butane was proposed to be adsorbed and 'chelated' via the two methylene groups on vanadium sites displayed on (100) planes. This configuration was later agreed by Hodnett et al. [74] though the chosen sites were not the same. CMAS also showed how faces perpendicular to (100) could favor the formation of acetic acid and CO_x because of the display and the number of available oxygens, as well as of the symmetry of surface V sites that could provoke the scission of the C_4 molecule.

5.2 Microstructure and reactivity

According to the new method of preparation proposed by Pepera et al. [29] and in patents, V_2O_5 was refluxed in alcoholic medium with H_3PO_4 to deliver a blue precipitate of a precursor, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, which was further dehydrated to give the catalyst. We studied extensively the structure and reactivity of the precursor, VOPO_4 and VPP phases [32,75-81]. *Pseudomorphism* between $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and VPP crystals being observed by electron microscopies, we showed that $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursor decomposed *topotactically* to VPP when heated in nitrogen [75,76]. Remarkably, the pseudomorphism was also observed at the particle scale (several microns), as the rosetts constituted by several platelets were observed for both compounds [42]. It meant that the control of the shape and size of VPP particle could be obtained by the control of that of precursor [78-80]. When heated in oxidizing conditions this precursor did not deliver α or β - VOPO_4 , like when the starting hydrate was $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, but δ or γ - VOPO_4 depending on temperature [75,76]. VPP was obtained when heated in nitrogen, and it exhibited either perfect bitrapezoidal shape, or no specific ones (electron microscopies), after dehydration of the V^{4+} -hemihydrate or V^{5+} -dihydrate, respectively. We drew models of reduction of VOPO_4 to VPP by C.S. planes [32,77], or by glide planes along [021] VPP [81], and showed that interfaces between planes of VOPO_4 and VPP would be coherent (Figure

1). Though the hypothetical crystal structures of δ or γ -VOPO₄ [32,77] were later shown not to be the good ones [82], CS or glide planes apply since for in all but β forms of VOPO₄, [VO₆] pseudo-octahedra are linked to phosphate in simple ways. It was also fascinating to see how, just by modifying the crystal morphology of a precursor, different VOPO₄ structures could result by oxidation. The reactivity of VPP itself in oxidizing conditions was also shown to depend on its crystal morphology, platelets giving rise to δ -VOPO₄ and prisms to β -VOPO₄. Finally, we showed that the monocrystalline *mosaic particles* of platy VPP were built up by a great number of small crystallites, the size of which was ca. 0.4 μ m in our study [79,80]. Similar pictures were observed in literature particularly by Volta and Hutchings [69,83]. Once more, the role of the microstructure in the oxidation process was highlighted to be related to its microstructure and morphology. Complementary experiments by Temporary Analysis of Products (TAP reactor) showed that the intercrystallite boundaries were responsible for the storage of more oxygen in platy crystals, this *oxocapacity* (here defined as the oxygen storage capacity) of monocrystalline mosaic VPP particles being higher [80]. These defects could as well account for the general observation that in real catalysts the average vanadium oxidation state is significantly higher than four.

5.3. Equilibration and ageing

An equilibrated platelet catalyst should be a VPP core on the surface of which less than, say, 10 atomic layers [29] displaying the framework of {100} faces, ensure the formation of MA and water, as well as activating dioxygen and refilling of oxygen vacancies. The surface of perpendicular faces must be small, which avoids the formation of by-products, as well as overoxidation by O₂ that may lead to the transformation to VOPO₄ [77,79]. The thinner the plates the higher the catalytic performance and the lower ageing. Cavani et al. [39] studied how the equilibration period could modify both structures and catalytic properties. Again it depends on the conditions (temperature, butane or nitrogen to oxygen ratio, duration) in which the precursor is heated to give rise to VPP. When the precursor was calcined in air, 1000 h were necessary to get an equilibrated catalyst when left in a 1% n-butane/air stream. Crystalline VPP (XRD) ensured the good catalytic performance, while after 100 h only poorly crystalline VPP and VOPO₄ phases were found and the catalyst was less selective. When the procedure of dehydration of VOHPO₄·0.5H₂O was more adapted, 100 h were enough to get the equilibrated catalyst, which was stable for more than eight days [84].

The influence of P/V ratio (1.02 to 1.05) on the reactivity and stability of VPP has not yet been evoked here, though it is a very important parameter conditioning the catalytic performance and ageing through the acidic properties, redox reactivity as well as site isolation. Whatever designed for but-1-ene or n-butane oxidation, an excess of P with respect to the stoichiometric requirement is always needed to get a stable catalyst and to obtain a high selectivity to MA. Steady-state reactivity tests, transient reactivity recorded after *in situ* treatments, *in situ* Raman spectroscopy and XPS after *in-situ* pretreatment, all these experiments indicate that small differences in the P/V ratio profoundly affect

the characteristics and the reactivity of equilibrated VPP catalysts. This is because the nature of the active layer, that develops at the surface of VPP core, depends strongly on this composition parameter. In the past it has not been considered enough to justify whether or not the ultimate surface was amorphous or crystalline. To make it short [85], in the temperature range 340-400 °C, the optimal catalytic performance was observed when $P/V = 1.05$. Once pre-oxidized the resulting active layer was composed of δ -VOPO₄. A spontaneous reduction of δ -VOPO₄ to VPP occurred if the sample was treated in a stream free of oxygen (N₂ or butane). This self-reduction phenomenon experimentally observed with the pre-oxidized $P/V = 1.05$ sample did not occur with $P/V = 1.0$, the V⁵⁺ phosphate that forms by VPP oxidation being also more difficult to be reduced. The effect of steam is also depending on P/V . Stoichiometric VPP exhibited poor catalytic properties, with low selectivity to MA [48]. The reason why would be related to the main presence of α -VOPO₄ and of hydrolyzed [VO_y + (PO₄)_n] domains, both being dispersed at the surface of VPP. For $P/V = 1.05$ in the presence of steam the formation of VOPO₄·2H₂O was observed, that dehydrated to δ -VOPO₄ when steam was removed. Again, the conditions that favor the formation of the dehydrated V(V) phosphate lead to a higher selectivity to MA [84,85].

As a rule, the ageing of VPP happens by over-oxidation and hydration leading to the loss of phosphorus. Over-oxidation can be mitigated if microdomains of δ -VOPO₄ are formed because, as just seen, they can easily be reduced back to VPP, but irreversible ageing comes with the formation of β -VOPO₄ which is very stable. If water does not desorb as fast as necessary, phosphates may be lost as P₂O₅, which is one of the reasons why P/V value is kept to more than one. The formation of α -VOPO₄ and, at the worst, VOPO₄· n H₂O ($n > 2$), is also irreversible. By reduction β and α forms of VOPO₄ give rise to prismatic VPP particles. According to the equilibrium (prismatic) shape of (VO)₂P₂O₇ calculated by the Curie–Wulff method [71], the area of {100} faces would make 32% of the total external area, the remaining 68% corresponding to the perpendicular faces. Consequently in this case the catalytic performance decreases.

Therefore the particular properties of VPP are due to several features owed to its unique architecture, the pairs of edge-sharing O=V(O₄)...O pseudo-octahedra linked to phosphate groups. By the way, this is a perfect illustration of the *site isolation* concept as noticed by Agaskar and Grasselli [86]. Edge-sharing pseudo-octahedra are also displayed for {010} V₂O₅ (poorly active and not so selective to MA) but as infinite chains, whereas in VPP the active vanadium sites are separated in two spatial directions by PO₄ tetrahedra (isolated vanadium sites). The reduction of VPP is structurally controlled because phosphate groups would have to strongly reorganize in case all V⁴⁺ would be reduced to V³⁺ (the structures of V³⁺PO₄ or V₄(P₂O₇)₃ are very different). As seen above, its reoxidation to VOPO₄ is also hindered but to a less extent because of structural relationships particularly with δ -VOPO₄. As shown for the α form [32], the formation of CS planes would be possible, but why this reduction is far

more easier remains unknown. The strong binding exerted by phosphate ligands is also responsible for the stabilization of the V^{5+}/V^{4+} redox system, while, though the structure of V_2O_5 suboxides (V_nO_{2n-1}) remains close from each other, the reduction down to V^{3+} is avoided with difficulties. The V^{5+}/V^{4+} redox system is adapted to the oxidation of other molecules by addition of Mo, Pd, Mo-Nb or TiO_2 (etc.) and the catalyst becomes selective in oxidation of benzene to MA [87], ethylene to acetaldehyde [88], ethane to acetic acid [22], o-xylene to phthalic anhydride [3], respectively.

6. Mo-V-O based mixed oxides

The other versatile catalytic system is based on both Mo and V atoms. The variety of reactions is owed to the Mo/V ratio as well as the presence of heteroatoms (Figure 2). The only Mo-V-O phase with $Mo/V < 1$ was used in the 1960's in benzene oxidation to MA. The solid solution $(V_{0.7}Mo_{0.3})_2O_5$ [87] as well as $V_9Mo_6O_{40}$ [89] were proposed to be the active phase. We showed that $V_9Mo_6O_{40}$ was a mixture of V_2MoO_8 and $VOMoO_4$ [90]. The reduced phase $V_6Mo_4O_{25}$ was actually $V_2MoO_{7.5}$ ($V_4Mo_2O_{15}$), all structures (but $VOMoO_4$) being that of V_2MoO_8 which is isostructural to V_2O_5 . Other phases in the Mo-V-O system with $Mo/V > 1$ were soon used in the oxidation of (meth)acrolein to (meth)acrylic acid, like Mo_3VO_{11} [91]. More recently, several atoms among which W, Nb, Sb and Te were added to get active and selective multicomponent catalysts of (amm)oxidation of propane to acrylonitrile or acrylic acid [92-94]. This was a real challenge, and nowadays the knowledge about the structural and catalytic properties of M1 (orthorhombic) and M2 (hexagonal) phases is enormous [95-98]. Even though a *synergistic effect* between M1 and M2 could be thought responsible for the high yields of acrylonitrile (59%) [99], it is now widely accepted that the optimal catalytic properties are owed to M1. The main redox couple is V^{5+}/V^{4+} , the electric potential of which is modified by the presence of Mo^{6+}/Mo^{5+} partner, while the other atoms are responsible for the stabilization of the crystalline structures. These catalysts to which other dopants are (or not) added were also investigated in the oxidative dehydrogenation (ODH) of C_2 - C_3 alkanes by Ueda et al. [26] and others researchers. The question arises so as to understand how quite a same formula can be active and selective for all these reactions involving from 2 (ODH) to 8 (propane or isobutane to acids) electrons. The answer may be related to the behavior of the partner redox couple(s) in operating conditions, that is when the redox power of the catalytic solid faces the redox power of reactants (steam and/or oxygen, type of alkane C_2 - C_4 or other reactant).

6.1 Oxidation of ethane to acetic acid

When alkanes began to be used as reactants for mild oxidation we tackled the problem of making acetic acid from ethane. In their pioneering work, Thorsteinson et al. [100] claimed that adding Nb to Mo-V-O led to the formation of ethylene. The optimum formula was $Mo_{0.73}V_{0.18}Nb_{0.09}O_x$ but no acetic

acid was found at atmospheric pressure. The presence of an XRD line corresponding to 4.0 Å d-spacing was related to a catalyst selective to ethylene. By modifying the preparation method while keeping the same formula we succeeded in getting acetic acid at 250-300°C, though in small yields (Table 2) [22,101]. To summarize, the formation of acetic acid or ethylene was observed when Mo₅O₁₄ (θ -phase, *vide infra*) or Mo₁₈O₅₂ types, respectively, were identified by XRD. Owing to the Mo excess in catalyst composition, lines of α -MoO₃ were also seen. Soon we proposed that microdomains of [MoO₇],5MoO₆ clusters of θ -(VMoNb)₅O₁₄ could be coherently grown and ‘isolated’ in a matrix of (010) α -MoO₃ [58,59,101] (Figure 3). Some years after, Werner et al. [102] synthesized Mo₄V⁴⁺O₁₄, which is isostructural to θ -phase. Using high resolution transmission electron microscopy, the authors showed that “a continuum random network of basic structural units (distorted octahedra) was detected made up of approximately circular clusters embedded in a quadratic network”. This model fitted well our earlier proposition. We also examined the performance of other V-based catalysts supported on TiO₂-anatase (VPO doped with Pd and H₄PVMo₁₁O₄₀), but the acetic yield was again low, and in the case of vanadium oxide monolayer supported on ZrO₂ [103,104] only ethylene was produced (Table 2) So we came back to Mo-V-O system. Meanwhile other studies showed that the formation of acetic acid was correlated with the presence of the Mo₅O₁₄-type oxide and the solid state chemistry of phases based on it was thoroughly investigated [105-108]. We studied MoV_{0.4}Nb_{0.12}Pd _{ϵ} O_z ($\epsilon = 10^{-4}$) catalysts [109-111], and examined their structural and catalytic properties in the presence or not of Mo, Nb, Pd, atoms. A focus was made on their reactivity during reduction and reoxidation analyzed by thermal analysis (TGA/DSC) as well as by *in situ* analyses (HT-X-ray diffraction, X-ray photoelectron spectroscopy) to better understand the catalytic properties. The role of Nb or Pd was found to be prominent even at the stage of preparation, as revealed by the study of the dried precursors. Niobium was responsible for a textural effect consisting in a partial amorphization of the (MoVNb)O_z solids. Pd in MoV_{0.4}Pd _{ϵ} O_z or in VNb_{0.3}Pd _{ϵ} O_z favored the instability of precursors which were often volatilized under the laser beam during examination by Laser Raman Spectroscopy, except in the case of MoV_{0.4}Nb_{0.12}Pd _{ϵ} O_z [109]. After proper heat treatment (350 °C) of MoV_{0.4}Nb_{0.12}O_z and MoV_{0.4}Nb_{0.12}Pd _{ϵ} O_z catalysts, (MoVNb)₅O₁₄ (“ θ -MoVNb”, that is a solid solution of V and Nb in Mo₅O₁₄ with undefined stoichiometry) and α or h-V_{0.12}Mo_{0.88}O_{2.94} (α or h-MoV) were detected by XRD as disordered and nanosized particles. α -MoV was observed in our first paper while h-MoV was characterized when the heat treatment of precursors was improved [110]. Partial amorphization was observed each time Nb was present. The large width of the (001) line of θ -(VMoNb)₅O₁₄ nanocrystals accounted for a high degree of disorder in the stacking of (001) planes, which could be provoked by the insertion of V, Nb. The same interpretation was proposed for V in the case of stacked (010) planes of h-V_{0.12}Mo_{0.88}O_{2.94}. This phase is a solid solution of V⁵⁺ in hexagonal MoO₃ which is stable up to 410 °C for MoV_{0.4}O_z and 480 °C for MoV_{0.4}Nb_{0.12}Pd _{ϵ} O_z as shown by TGA in O₂. Its framework consists in rings of pairs of edge-sharing Mo(VI) octahedra linked by corners, which are stabilized by NH₄⁺, H⁺

and/or alkaline cations [112]. This open structure is more prone to accept foreign cations (V, Nb and may be Pd) than is the more compact structure of α - MoO_3 , and very probably it also favors – or it is a witness of – the formation of channel structures like Mo_5O_{14} . Owing to the non-stoichiometric composition, the hexagonal bronzes could act as a template for the formation of the θ -phase.

Though in very small amounts, Pd was seen to modify the reactivity of solids. The behavior of catalysts during reduction with diluted H_2 and reoxidation followed by thermogravimetric analysis was shown to be dependent on the presence of Nb, and of Pd to a less extent (Figure 4). The rates and deepness of reduction depended on the catalyst composition, reoxidation being approximately 100 times faster than reduction. Upon addition of 0.12Nb to $\text{MoV}_{0.4}$, the rate of reduction increased to a less extent than when Pd was added to $\text{MoV}_{0.4}$ and to $\text{MoV}_{0.4}\text{Nb}_{0.12}\text{O}_z$, but the deepness of reduction increased up to the formation of $(\text{VNb})_x\text{Mo}_{1-x}\text{O}_2$ suboxide. θ - MoVNb oxide was stable during reduction by ethane or propane up to 450°C (XRD), and as well as after oxidation, but very probably the reduction affected $\text{V}_{0.12}\text{Mo}_{0.88}\text{O}_{2.94}$ besides it. XPS experiments carried out after appropriate reducing and reoxidizing treatments in the pre-treatment chamber at 300°C showed that the $\text{V}^{5+}/(\text{V}_{\text{tot}})$ atomic ratio decreased along $\text{MoV}_{0.4}\text{Pd}_\epsilon\text{O}_z > \text{MoV}_{0.4}\text{Nb}_{0.12}\text{O}_z = \text{MoV}_{0.4}\text{Nb}_{0.12}\text{Pd}_\epsilon\text{O}_z > \text{MoV}_{0.4}\text{O}_z$ series during reduction, the original value being recovered by oxidation. The Mo (and Nb) oxidation state in MoVNbPd remained ca. 6+ (5+, respectively). The surface of Nb-containing solids was slightly enriched with vanadium as compared with Nb-free catalysts. In the presence of Pd, less niobium was present close to the surface, which could mean a better stabilization of the underlying stable core, being θ - MoVNb or h- MoV . These experiments showed that the reduction of all samples could be regarded as ‘reversible’ (redox system), whatever the reducing gas (hydrogen, propane or ethane).

The catalytic properties of catalysts were examined at operating temperature less than 280°C for the conversion of oxygen to be less than 100% like in former studies (Table 2). Such a low temperature favored the formation of acetic acid [22,101,109-111]. As it was not possible to compare values at the same conversion X_{C_2} of ethane due to the low activity of some formulas, the ratio of yields $R = Y_{\text{AA}}/Y_{\text{EE}}$ was used as a ‘measure’ of performance. It increased along $\text{MoV}_{0.4}\text{O}_z$ (0.31) \approx $\text{MoV}_{0.4}\text{Nb}_{0.12}\text{O}_z$ (0.33) $<$ $\text{MoV}_{0.4}\text{Pd}_\epsilon\text{O}_z$ (0.81) $<$ $\text{MoV}_{0.4}\text{Nb}_{0.12}\text{Pd}_\epsilon\text{O}_z$ (1.04) series. Upon addition of Pd in $\text{MoV}_{0.4}\text{Nb}_{0.12}\text{O}_z$ the yield of acetic acid was 2.5 times at $X = 6$ –6.5%. The highest selectivity to ethylene (70-55 mol%) was obtained with $\text{MoV}_{0.4}\text{O}_z$ and $\text{MoV}_{0.4}\text{Nb}_{0.12}\text{O}_z$, while it was very low for $\text{MoV}_{0.4}\text{Pd}_\epsilon\text{O}_z$ (range depending on conversion). Acetic acid followed the reverse trend. In the same conditions, $\text{MoV}_{0.4}\text{Nb}_{0.12}\text{Pd}_\epsilon\text{O}_z$ gave $S_{\text{AA}} = 45.5$ and $S_{\text{EE}} = 42.5$ mol%, respectively, at $X = 6.0$ mol%. The results suggest that if Pd is not stabilized as Pd^{2+} by an oxidic matrix, it may easily be reduced to Pd^0 and in such a case it acts as a catalyst of combustion of ethane and intermediates. If it is stabilized, its role in catalysis could be to promote the transformation of ethylene to acetic acid. This explanation was proposed by Baerns group [113], and it stems from a study by Montarnal et al. [87] in which Pd-

doped V_2O_5 was shown to oxidize ethylene to acetic acid. Nevertheless, the question of the location of Pd is raised. Channel structures like θ -phase and h-MoV could serve as a host structure, the hexagonal channels being (theoretically) large enough (diameter $\sim 2.15 \text{ \AA}$) to accommodate Pd^{2+} which is a large cation and accepts to be 6-coordinated ($r = 0.86 \text{ \AA}$) [38]. It is often square-coordinated (ionic radius $r = 0.64 \text{ \AA}$) and it could enter the square channels of Mo_5O_{14} (bond valence +1.86, corresponding to a slightly relaxed palladium [114]).

For layered structures like V-P-O, [22,103] or V_2O_5 [88], Pd was also shown to accelerate the rate of the V^{5+}/V^{4+} redox and to stabilize a specific suboxide, V_4O_9 , instead of VO_2 in the latter case. Pd^{2+} should be trapped in between the layers, resulting in a less strong interaction and easier reduction on-stream. It may be recalled that the catalysts here studied were not “equilibrated” as they could be in some of our studies on VPO. However at 240-260 °C, structural modifications of the catalyst bulk are hardly processing. The diffusion of lattice O^{2-} through the lattice would be also very low, which could hinder the reoxidation step. Again Pd could find its purpose as a “booster” of this reoxidation, providing it is stabilized in the structure. The question as to whether M1 (or M2) could be better catalysts was evoked in [111] but the hydrothermal preparation is very different and a higher content of vanadium is present in our (MoVNb) catalysts. Finally, adding Pd as a promotor cannot result in the same properties as adding Te (or Sb), although their optical basicity lies in the same range ($\Lambda = 1.10-1.18$). Palladium (II) is a large metallic cation with a stable oxidation state in usual conditions, while Te^{6+} , Sb^{5+} are small ($r = 0.60-0.56 \text{ \AA}$), non-metallic, versatile redox cations, exhibiting various valences and coordinations.

5.2 Heteropolymolybdates in the oxidation of isobutyric acid and isobutane to methacrylic acid

Keggin-type Mo,V heteropolycompounds have been used in very numerous reactions since the 1980's [115,116]. We began to examine their properties when ATOCHEM founded a consortium with several french research groups to study the oxidative dehydrogenation of isobutyric acid to methacrylic acid (IBA to MAA). In our group, Ernst et al. first demonstrated that the reaction obeyed to the redox mechanism, kinetic measurements showing that MAA (and acetone) were formed on bridge Mo-O-Mo of Kegging units (KU) in $H_3PMo_{12}O_{40}$, while the production of propene was due to acidic or reduced sites [117,118]. Thereafter our work was focused on $H_4PVMo_{11}O_{40}$ (H_4PVMo) and their salts. After 10 days of use of unsupported $H_4PVMo_{11}O_{40}$, IBA conversion and selectivity to MAA decreased from 90 to 88 and 69 to 68 mol%, respectively [119]. This loss of 2% yield being not faced for industrial applications, various types of solids were investigated to play the role of support. It had soon been known that heteropolymolybdic $H_3PMo_{12}O_{40}$ and heteropolyvanadomolybdic $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n = 1,2,3$) acids are unstable on-stream, and that they could not be used as catalysts unless supported on a carrier [120]. So H_4PMoV was supported by means of incipient wetness onto silica (trydimite, cristobalite), and other carriers. The stability of H_4PVMo in the operating conditions was enhanced

when a well crystallized silica like cristobalite with low surface area (5-10 m²/g) was used. For 10 days X_{IBA} increased from 93 to 92 and S_{MAA} increased from 67 to 70 mol%. The crystals frameworks of Possible *coherent interfaces* between the lattices of K-doped silica and K_xH_{4-x}PVMO were proposed by us, and the stabilization was thought to be due to the formation of the “cubic phase” observed in spent catalysts (XRD) [58,59]. We observed this famous “cubic phase” each time an alkaline (A) ion was present in the catalytic formula, whatever its amount and its location (carrier or active phase). It is thought indeed to be related with the formation of A₃PMO₁₂O₄₀ whose structure is cubic, as shown by several authors [121-123]. Thus when we observed that, upon doping the silica with potassium (2 wt%), X_{IBA} increased to 95 mol% (S_{MAA} = 70 mol%) with stability up to 10 days, we assumed that K⁺ ions made possible the formation of an interlayer of K₃PMO₁₂O₄₀ between the acid and the support. We also examined the influence of A₃PMO₁₂O₄₀ (A = K, Rb, Cs) and of silica doped by the same alkali ions on the catalytic performance and stability of H₄PVMO [124]. K-doped SiO₂ as well as H₄PVMO/K₃PMO₁₂O₄₀ were the most stable catalysts, the supported H₄PVMO layers adopting the cubic symmetry in both cases. In the absence of alkaline ion, this cubic phase is stabilized by 6 to 8 water molecules [125,126]. It explains why a given amount of steam is required in the feed in order not to observe structural collapse of the secondary structure. But adding A⁺ is an easier (and less expensive for the process) mean to stabilize the active phase even at the early stage of preparation. A possible epitaxial growth of H₄PVMO on K₃PMO₁₂O₄₀ has already been suggested, that could take place by formation of H₄PVMO₁₁O₄₀·nH₂O hydrate on the surface [121,122,127].

In the mean time, isobutane (iBu) oxidation to MAA became a challenging reaction to study in the early 1990's [128-130]. At variance when AIB was the reactant, patents often claimed the use of ammonium ions. The method developed by S. Paul and al. was therefore to take H₃PMO₁₂O₄₀ as a reference catalyst and to modify its primary and secondary structures [131,132]. Substituting one Mo by V in the primary Keggin structure would result in the modification of redox and acidic properties, while substituting part of or all protons by Cs⁺ and NH₄⁺ would modify the primary structure. They first showed that the Mars and van Krevelen model could be applied to all steps of the oxidation of isobutane. The reaction of isobutane with the oxidized sites was rate-limiting, and while MAA was stable, the transformation of MAC to MAA and possibly CO_x and by-products was 50 times faster than the isobutane reaction. The activation energies of reduction (E_r = 21.6 kcal/mol) and oxidation (E_o = 20.6 kcal/mol) were consistent with the usual data for oxidation reactions. In an attempt to enhance the catalytic performance, new catalysts based on the addition of Cs⁺ and/or NH₄⁺ to H₃PMO₁₂O₄₀ and H₄PVMO₁₂O₄₀ were examined with a methodology consisting in the coupling of the quantitative evaluation of performances and the kinetics of the reaction with the physicochemical characterization of catalysts [131]. The statistic analysis of kinetic results showed good precision obtained on k_r.Ns and k_o.Ns (Ns number of sites, k_r and k_o constant rate of reduction and reoxidation, respectively) rate

constants. The influence of the composition in Cs^+ or $(\text{NH}_4)^+$ was found to be strong as shown by values of kinetic constants that could sometimes vary from simple to double.

To summarize, part of vanadium was extracted from the Keggin primary structure during thermal treatments or in operating conditions, particularly in mixed ammonium-cesium $\text{Cs}_x(\text{NH}_4)_{3-x}\text{HPVMO}_{11}\text{O}_{40}$ ($x = 1.15, 1.75$ and 2.4) salts. A main consequence was the partial reduction of V^{5+} to V^{4+} . This reduction is commonly observed during decomposition of ammonium salts, including in the case of $(\text{NH}_4)_5\text{PMO}_{11}\text{V}^{4+}\text{O}_{40}$ studied by Hervé's group [133] in which 40% of NH_4^+ ions were released between 130 and 330 °C. Vanadium was supposed to be displayed as vanadyle (VO^{2+}) counter-cation in the secondary structure, because the composition did not change after reaction. As *i*Bu is activated on H_3PMo as well than on H_4PVMo , vanadium does not seem at first necessary for its activation, that may happen as well on Mo provided it is partly reduced. Indeed, the presence of d^1 cations (V^{4+} , Mo^{5+}) is a requirement to activate alkanes as well as to activate O_2 to O^{2-} [41,42,134]. The interest of using H_4PVMo is that the reduction of Mo is mitigated in the presence of V, the collapse of the structure is avoided, and V can activate O_2 whatever its form (oxovanadium or vanadate). During the thermal treatments, the elimination (at least partly) of NH_4^+ ions as NH_3 and water led to the partial reduction of Mo and/or V and modified the redox properties, which was highly beneficial to selectivity. Though inactive, $\text{Cs}_3\text{PMO}_{12}\text{O}_{40}$ plays a key role on the dispersion of the active phase owing to its large surface area and porous volume, and consequently on the activity and stability of catalyst. A thorough study was carried out using well defined (composition, surface area, microstructure) samples of $\text{Cs}_3\text{PMO}_{12}\text{O}_{40}$ prepared by varying the operating conditions [135-137]. It is well-known that the microporosity of alkaline salts is due to the formation of channels within the crystal lattice, owing to the anion-anion separation and anion reorientation caused by the size of the alkaline cations [138-140].

Focus was thereafter made on the improvements of these catalysts [141-144] and particularly of $(\text{NH}_4)_3\text{HPVMO}_{11}\text{O}_{40}$ (APVM) used as the active phase. To avoid, or better, to control its decomposition on stream, APVM was dispersed on different kinds of materials (SiO_2 -based supports and $\text{Cs}_3\text{PMO}_{12}\text{O}_{40}$) presenting various surface areas and pore volume in order also to increase the specific rate of reaction. Only $\text{Cs}_3\text{PMO}_{12}\text{O}_{40}$ (CsPMo) gave interesting catalytic results. The catalytic performances were significantly improved with APVM/CsPMo, $X_{i\text{Bu}}$ increasing from 2.5 to 15.3 mol% and the yield $Y_{\text{MAC+MAA}}$ from 1.4 to 15.3 mol%, respectively. The influence of APVM loading (10 to 50 wt.%) was further examined by a number of *ex* and *in situ* techniques. In air (TGA/DTA), the temperature at which bulk APVM lost its crystal water (150 °C) was significantly increased for supported catalysts (to 182 and 210 °C for 20% and 40%APMV/CPM, respectively), the formation of HPMV at 380 °C happened at and the elimination of acidic protons in the form of constitutional water (at ca. 430 °C) which resulted in the formation of inactive lacunary $\text{PMO}_{11}\text{VO}_{38}$ Keggin structure [145] did not happen till 500 °C. Under reducing atmosphere, the supported active APMV phase was

stabilized up to 560 °C. To summarize, for fresh catalysts, (i), the cell parameter of the cubic structure increased slightly for APVM/CPMo (XRD), (ii), all wavenumbers of Mo-O absorption bands were shifted to higher wavenumbers (FT-IR, Raman), (iii), the partial decomposition of APVM at the temperature of catalytic reaction (340 °C), was delayed up to 400 °C for 40% loading (TGA). For used catalysts (or catalysts pre-treated by iBu), (i), all XRD patterns were quite the same, very close to that of CsPMo, with superimposed lines of APMV (except at low loading), (ii), bands of Keggin structure remained but a band assigned to V=O appears at 1035 cm⁻¹, (iii), after reaction the V⁵⁺/V⁴⁺ and Mo⁶⁺/Mo⁵⁺ ratios generally decreased whereas Cs/Mo increased and V/Mo decreased (XPS). The catalytic experiments showed that the loading was an important parameter to adjust. While 10%APVM/CsPMo was inactive, the conversion of IBAN increased for 20-50 wt.%, ($X_{\text{IBAN}} = 14$ to 15.3 mol%), the specific surface area and pore volume decreasing upon increasing APVM loading. The selectivity to MAA was rather constant and the total yield in MAC+MAA increased with APVM loading, as a result of the decreased formation of carbon oxides and of acetic acid. Brönsted acidity plays an important role in helping to activate the C-H bond and the redox properties can be controlled by adjusting the amount of protons, and by changing the metal atoms in the primary structure. The catalytic activity was indeed directly correlated to the amount of strong and very strong acid sites according to NH₃-TPD experiments [142,143]. The highest amount of strong acidic sites on 40%APMV/CsPMo (1.54 mmol/g vs. 1.42 mmol/g for 50%APMV/CsPMo) could be related with its outstanding catalytic activity ($X_{\text{iBu}} = 15.3$ mol%), at variance with the absence of strong acidic sites on inactive 10%APMV/CsPMo. Moreover, catalysts containing high amounts of APVM were more resistant to structural and textural alterations. Only a slight deactivation was observed for 135 h ($X_{\text{IBAN}} = 12.5$ to 11.5 mol%, selectivity constant) for 40% supported-APVM which is the best catalyst.

It must be recalled that, for each molecule of isobutane oxidized to methacrylic acid, 2 H₂O must find sites to be formed, and if they do not desorb the reaction cannot proceed for long. This is frequently forgotten in considering reaction mechanisms on the surface. In the case of *n*-butane oxidation on VPP catalysts, we proposed that water is formed on vanadium and neighboring phosphate (V-OH + P-OH = V-□ + P-O + H₂O, where □ is an oxygen vacancy) [72]. In the case of heteropolyacids or salts, the stabilization of the active cubic structure depends on the presence of nH₂O in the secondary structure, the reason why (besides the mitigation of hot spots) steam is fed with reactants. *A priori* this is not a favorable situation for the formation and desorption of water molecules. If the KU is stable, P is not available as an adsorption site. The Mo-O bonds (whichever their type) in KU could provide sites of adsorption, with protons to make water, since, as shown, strong Brönsted acidic sites are required for high activity. When V is expelled from the KU it may be stabilized in the secondary structure in two configurations: As a vanadate (VO₃⁻ or VO₄³⁻) which requires charge balancing by Cs⁺ and/or H⁺, NH₄⁺, or as a penta- or tetra-hydrate of oxovanadium (VO)³⁺ or of vanadyle (VO)²⁺ (as observed by FT-IR and Raman in spent catalysts). The selectivity to MAA+MAC does not seem to depend so

strongly on the presence or not of vanadium and it is quite high when the cubic KU structure is there. Therefore, as it is often the case, high catalytic performance results from a compromise between the structural stability of the solid (related to the presence of cubic n-hydrated phase) and its surface reactivity. The ionic radius of ammonium is close to 1.4 Å with a 6-th coordination, but that of Cs⁺ is far larger (1.67 to 1.88 Å for 6-th to 12-th coordination). As observed by XRD the lines of APMV were still visible besides those of CsPM, meaning that the two phases coexisted, even in spent catalysts. Thus if part of Cs migrates up to the surface, it is certainly to compensate the presence of vanadium species out of KU. If vanadium species gather as polyvanadates they may finally end as inactive V₂O₅. The activity of such a catalyst would be low because Mo⁵⁺-O bonds are necessary to activate isobutane (and dioxygen), and such species would be formed only on stream. By supporting AVPM on Cs₃PMo₁₂O₄₀, a solid solution like (NH₄)_xH_{1-x}-yCs_yPVMO₁₁O₄₀ could be stabilized at the interface, the coherence between the two phases being possible since the same structural arrangements are found (even though the ionic radii are different). The interest of V inside KU is that, because it is more reducible than Mo (as seen in Mo-V-X-O systems, *vide supra*), it mitigates the Mo⁶⁺/Mo⁵⁺ redox couple and avoids irreversible formation of Mo⁴⁺. As a result the activity of [PVMo₁₁O₄₀] is higher than that of [PMo₁₂O₄₀]. Thus, for V⁵⁺/V⁴⁺ acting as a partner couple, the vanadium species must be in close contact to Mo via V-O-[Mo-KU] bonds. When vanadium (V or IV) is located as a counter-ion (VO)₅-6H₂O, the bonds between [KU-Mo]-O and V=O are strongly ionic. Taking into account that bonds are closer from covalency than from ionicity in selective oxidation catalysts, it is difficult to conceive that the 8 electrons necessary each time one isobutane molecule is oxidized will easily cross that barrier. So, we could imagine a core of Cs₃PMo₁₂O₄₀-supported [Cs⁺,H⁺,NH₄⁺][PMo₁₂O₄₀], with KU “capping” by surface vanadate species while Cs⁺ (and/or H⁺ and/or NH₄⁺) and water molecules maintain the electroneutrality and thus the stability.

Conclusion

In this paper was written a part of our story about catalysts of mild oxidation, exemplified by V-P-O, Mo-V-O systems and P,V,Mo heteropolyacids/salts in the oxidation of but-1-ene and n-butane to maleic anhydride, ethane to ethylene and acetic acid, and isobutane to methacrolein and methacrylic acid, respectively. Most catalytic formulas proposed in patents, and for an important purpose which is commercial success, are not stoichiometric. Not to mention dopants and carriers when they are deliberately added (for their structural or textural effects). The main difficulty was that it is not easy to determine which is the actual active and selective phase, *host structure* or not. In V-P-O system for example, why P/V = 1.6 (atomic ratio) was recommended for oxidizing but-1-ene and P/V = 1.1-1.2 for oxidation of n-butane? The excess of P is easily accommodated as polyphosphates. In both cases the main reason is to compensate the loss of P during reaction. But in the first case (P/V = 1.6), which of VOPO₄, VPP or VO(PO₃)₂ (vanadyl metaphosphate) was the active phase? Though P/V is closer

from 2, the answer is VOPO₄ because V⁵⁺ are required to activate and oxidize the olefin. The influence of the composition of the stream (also of temperature and other operating conditions) determining the red/ox power of reactants facing the red/ox power of the catalyst, VPP was formed during the reaction by reduction of VOPO₄. Though we showed how that reduction could proceed, and proposed that the active sites of the V⁵⁺/V⁴⁺ redox system could be located at the *coherent interface* between VPP and VOPO₄, I think now that the best way would have been to find a mean to stabilize VOPO₄ and avoid formation of VPP. At variance, P/V = 1.1-1.2 for *n*-butane activation and the active phase is VPP displaying both V⁴⁺ for activation and surface V⁵⁺ for oxidation of the intermediate. The *site isolation* concept is illustrated by the presence of pairs of edge-sharing octahedra linked to phosphate groups. In the case of Mo-V-O (Mo/V = 1/0.4) that we studied for activation and oxidation of ethane, two main phases were found, (Mo,V)₅O₁₄ (or Mo₄VO₁₄) and the solid solution of vanadium in hexagonal MoO₃. It reminds the case of M1 and M2 phases for (amm)oxidation of propane, M1 being thought as the active and selective phase. Since the structure of both (Mo,V)₅O₁₄ and M1 display analogous environments we believe that (Mo,V)₅O₁₄ is the active phase in which V⁴⁺ species activate ethane with the redox partners V⁵⁺/V⁴⁺ and Mo⁶⁺/Mo⁵⁺ inside the same phase. The dopants Nb for (Mo,V)₅O₁₄ or Sb, Te, etc., for M1 play the the same role, which is to stabilize the active phase, though Sb, Te, could also be involved by means of their redox couple. Finally for the case of heteropolyacids/salts the best way to stabilize the active Keggin units (again a nice example of *site isolation*) inside a cubic hydrated structure, is to support it on an adapted carrier. Whereas *coherent interfaces* are to be invoked in the case of crystallized silica (cristobalite or tridymite), this is not necessary in the case of solid solutions in which, by definition, V⁵⁺/V⁴⁺ and/or Mo⁶⁺/Mo⁵⁺ are close from each other. Through these examples stems the crucial importance of the *crystal structure* as early shown by Grasselli and other researchers, but also the *catalytic anisotropy*, which is not so much studied. The different faces of a crystalline particle exhibit a variety of M-O bonds (from strong basic M=O to double, triple bridged oxygens), as well as a *crystal field* pattern which is, or not, favorable to selectivity. For example, the {100} platelets of VPP (when prepared from decomposition of the hemi-hydrate) exhibit pairs of edge-sharing octahedra which are favorable to *n*-butane to MA, but the rods of M1 constituted by columns of polyhedra are not for propane to acrylic acid. This crystalline morphology depends on the conditions of preparation (e.g., hydrothermal, slurry, dessication, incipient wetness, etc.) which deliver (or not) a precursor whose decomposition may require specific conditions. It certainly depends also on the operating conditions during catalysis. Now that very sophisticated techniques are available, *in situ* or *operando* methods should be devoted to this question. Computational methods could also bring interesting answers about the capability of given faces vs. activation/transformation of molecules. They are as necessary as the design of catalysts for fonctionnalizing biomass molecules like glycerol, butanediol, and the like, is not that easy. However there is no reason why the concepts on which oxidation catalysis are based would not apply. Finally, this is not to forget the development of redox

decoupling reactors, as a tool to optimize the reduction/oxidation conditions, examining the ageing ways to prevent it, and, may be, to use them industrially.

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Figures (to be printed in colors when necessary)

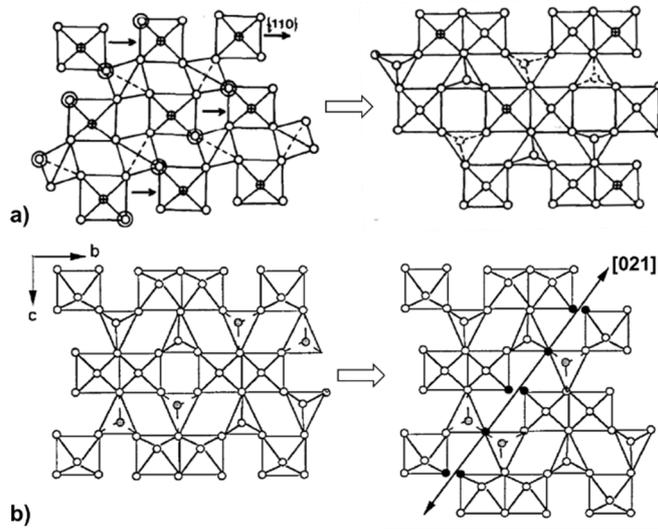


Figure 1. Extended defects in VPO ($P/V = 1$); a) Crystallographic shear planes along [110] of (001) α -VOPO₄ (left) to yield VPP (100) (right) by edge-sharing of (VO₆) pseudo-octahedra and rotation of phosphate groups (vacancies created at V-O-P bonds) (after [32]); b) Glide plane along [021] after creation of oxygen vacancies in (100) VPP (after [82]).

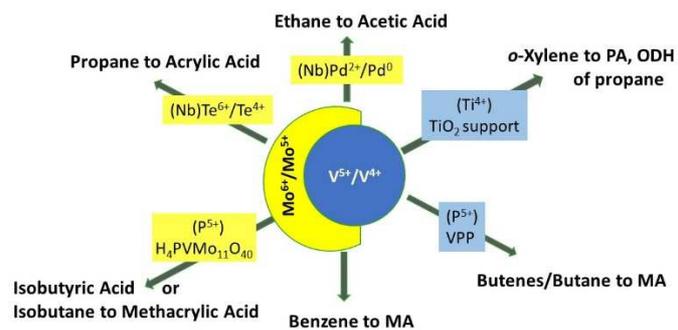


Figure 2. Heteroatoms in V-O (V^{5+}/V^{4+}) and Mo-V-O (Mo^{6+}/Mo^{5+}) systems bring selectivity in various reactions.

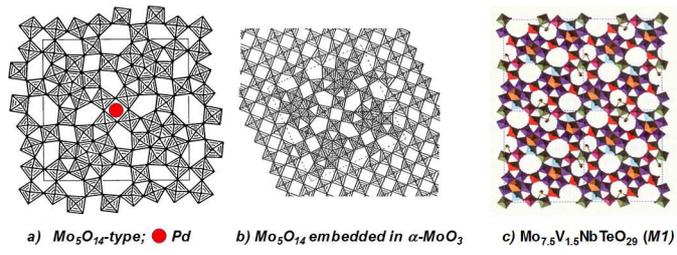


Figure 3. Structure of phases based on $\theta\text{-Mo}_5\text{O}_{14}$ framework; a) $\theta\text{-Mo}_5\text{O}_{14}$ with possible location of Pd; b) microdomain of θ in $\alpha\text{-MoO}_3$ (after [22]); c) $\text{Mo}_{7.5}\text{V}_{1.5}\text{NbTeO}_{29}$ (one of the M1 phases) (after [21]).

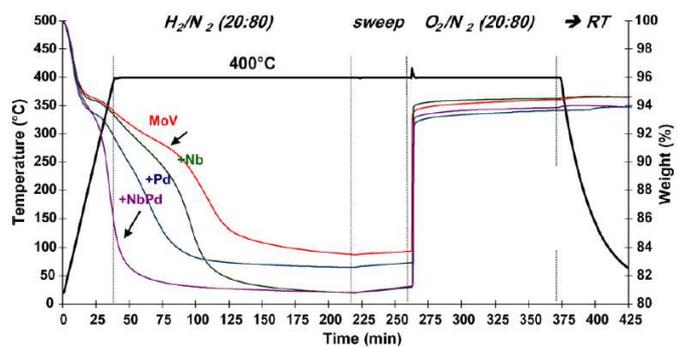


Figure 4. Influence of the composition of doped Mo,V oxide catalysts on their rate and deepness of reduction and reoxidation (TGA 400 °C) (after [112]).

Tables

Table 1. Optical basicity of vanadium and molybdenum cations

| Cation | V ⁵⁺ | V ⁵⁺ | V ⁴⁺ | Mo ⁶⁺ | Mo ⁶⁺ | Mo ⁵⁺ |
|--|---|-----------------|-----------------|--|------------------|------------------|
| Ionic radius (Å) [39] | 0.540 | 0.355 | 0.580 | 0.590 | 0.410 | 0.610 |
| Electronic configuration | d ⁰ | d ⁰ | d ¹ | d ⁰ | d ⁰ | d ¹ |
| Coordination | VI | IV | VI | VI | IV | VI |
| Λ | 0.63 | 0.69 | 0.68 | 0.52 | 0.55 | 1.17 |
| Change with coord. $\Delta\Lambda_{\text{coord}} = \Lambda_{\text{VI}} - \Lambda_{\text{IV}}$ | $\Delta\Lambda = 0.06$ (V ⁵⁺) | | | $\Delta\Lambda = 0.03$ (Mo ⁶⁺) | | |
| Change with redox $\Delta\Lambda_{\text{redox}} = \Lambda_{\text{ox}} - \Lambda_{\text{red}}$ | $\Delta\Lambda = 0.05$ (coord. VI) | | | $\Delta\Lambda = 0.65$ (coord. VI) | | |

Table 2. Catalytic performance in the oxidation of ethane to acetic acid and ethylene

| Catalyst | X _{C2} | S _{AA} | S _{C2=} | Y _{AA} | Temp | C ₂ /O ₂ /N ₂ | Contact time (s) | Ref. |
|---|-----------------|-----------------|------------------|-----------------|------|--|------------------|-------|
| VPP/TiO ₂ | 0.5 | 48 | 22 | 0.02 | 250 | 85/5/10 | 2 | |
| VO _x /TiO ₂ | 0.5 | 73 | 8 | 0.04 | 250 | 85/5/10 | 2 | |
| VPP | 0.5 | 97 | 0.5 | 0.05 | 250 | 5/2.5/92.5 | 3.8 | |
| VPP-Pd _{0.15} | 1.5 | 96 | 3 | 0.01 | 250 | 5/2.5/92.6 | 3.8 | [104] |
| | 8 | 59 | 82 | 0.05 | 250 | 5/2.5/92.7 | 3.8 | |
| Mo _{0.73} V _{0.18} Nb _{0.09} | 2 | 46 | 45 | 0.01 | 280 | 9/6/85 | 6 | |
| | 8 | 5 | 77 | 0 | 280 | 9/6/85 | 6 | |
| MoV _{0.4} | 6 | 30 | 63 | 2.3 | 260 | 40/6/54 | 1.2 | |
| MoV _{0.4} Pd _{e-4} | 2.5 | 68 | 5 | 1.7 | 260 | 40/6/54 | 1.2 | |
| MoV _{0.4} Nb _{0.12} | 6 | 26 | 70 | 1.6 | 260 | 40/6/54 | 1.2 | |
| | 12 | 29 | 65 | 3.5 | 280 | 40/6/54 | 1.2 | [112] |
| MoV _{0.4} Nb _{0.12} Pd _{e-4} | 6 | 48 | 46 | 4.8 | 260 | 40/6/54 | 1.2 | |
| VNb _{0.3} Pd _{e-4} | 2.5 | 60 | 2 | 1.5 | 260 | 40/6/54 | 1.2 | |

C₂: ethane; AA: Acetic acid; C₂₌: ethylene