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Molecular design of active sites in partial oxidation reactions on metallic oxides

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Abstract

Though a variety of examples, it is shown that the catalytic oxidation reactions which operate via a Mars and van Krevelen mechanism imply ensembles of atoms containing variable valence cations and Lewis bases such as O^{2-}, OH^- or PO_4^{3-} able to act in the different elementary steps. The structure and the size of these ensembles, defined as 'inorganic oxide molecular clusters', determine their reactional specificity. The examples chosen show that the 'designs' of such ensembles are strongly dependent on the nature of the material, on their morphology (structure sensitivity as for MoO_3, vanadyl phosphates), and on their structure (vanadyl phosphates, iron phosphates). It is also possible to build such ensembles upon dispersion of an active oxide on an inert support (MoO_3/SiO_2, V_2O_5/TiO_2).

Keywords: Molecular design; Active sites; Partial oxidation; Metallic oxides

1. Introduction

Oxidation catalytic reactions are of prime importance at an industrial level and correspond to a huge market. For instance in the US in 1994, about 31% of the catalytic production of major organic chemicals corresponded to oxidation catalytic processes (18% heterogeneous, 13% homogeneous) and 18% to oxychlorination. The market corresponds to 20 billions US $ in the USA and world wide such numbers have roughly to be multiplied by a factor of 2.5.

The concepts of oxidation began with Lavoisier's disproving of the phlogiston theory in 1773. One usually defines two groups of reactions namely homolytic and heterolytic. The first type involves radicals formed by homolytic cleavage of interatomic bonds. The second type involves an active oxygen compound or a metal ion which oxidizes the starting material in a two electrons transfer reaction. The reduced oxidizing agent must be reoxidized in a second step.

Majority of the catalysts correspond to metallic oxides with V or Mo as one of the key elements but also cations of variable oxidation states as Fe^{3+}/Fe^{2+}; V^{5+}/V^{3+}, Mo^{6+}/Mo^{5+}, Cr^{6+}/Cr^{3+}, Cu^{2+}/Cu^{+}, Sb^{3+}/Sb^{5+}, etc. Some metals (mainly Ag for ethylene epoxidation), noble metals (as Pt, Pd for total oxidation, etc) zeolites (titano silicalite TS-1 from ENI for phenol oxidation) and heteropolyoxometallates (e.g. $H_4PMo_{11}VO_{40}$ for isobutene oxidation to methacrolein) may also be used.

In majority of cases catalytic properties in oxidation reactions involve a redox mechanism between reactant molecules and surface active

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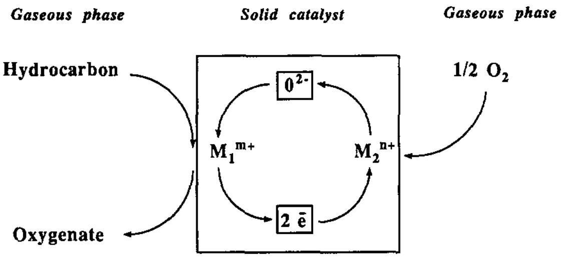


Fig. 1. Scheme of the Mars and van Krevelen mechanism.

sites as represented in Fig. 1 as suggested by Mars and van Krevelen in 1953. Such a mechanism necessitates a catalyst which contains a redox couple as for instance transition metal ions and which exhibits high electrical conductivity to favour electron transfer and at last which has a high lattice oxygen anion mobility within the material to insure the reoxidation of the reduced catalyst.

From this feature arises the idea that the active sites are not isolated ions as in the Taylor's model but rather an ensemble of ions in a kind of 'inorganic oxide cluster'. A molecular concept of the active sites has then to be defined. Several examples are chosen below to show how such a concept may be valid in oxidation reaction and how it can be determining for the choice of the metallic oxide and/or of its preparation procedure.

2. General features of oxidation catalysts and oxidation reaction

2.1. Oxidation catalysts

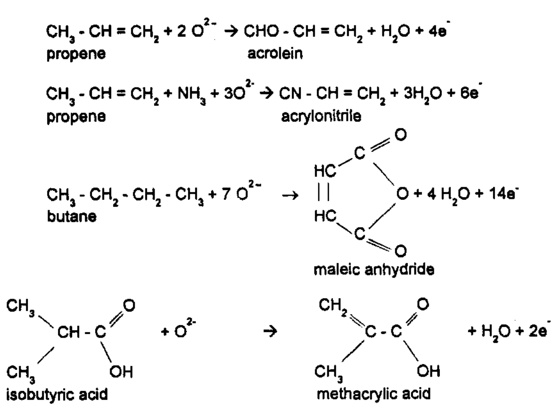
The oxidation catalysts are usually mixed oxides which operate according to the redox process suggested by Mars and van Krevelen (Fig. 1). According to this mechanism the substrate is oxidized by the solid and not directly by molecular oxygen of the gaseous phase. The rôle of dioxygen is to regenerate or maintain the oxidized state of the catalyst. The oxygen species introduced in the substrate (or giving H_2O for oxidative dehydrogenation reactions) stems from the lattice. The mechanism involves the presence of two types of distinct active sites: an active cationic site which oxidises the substrate and another site active for dioxygen reduction. An adequate structure of the material should also facilitate both electrons and oxygen species transfer.

2.2. Oxygen species

The oxygen atom incorporated into the substrate stems from the lattice and is at −2 oxidation state. Its replacement by molecular oxygen necessitates electrons according to: $O_2 + 4e^- \rightarrow 2O^{2-}$. This process has its own kinetics related to the reactivity of the sites with oxygen, their concentration, the efficiency of electron transfer, the partial pressure of oxygen, etc. Usually, it is much faster that the oxidation of the substrate, i.e. it is generally admitted that the rate determining step is the substrate activation.

Let us take some examples which will be considered in more detail later on (Scheme 1).

It clearly appears that a single and isolated metallic ion site cannot take into account all the necessary transformations involved in the reaction since several steps as replenishing of oxygen anion vacancies, H atoms extraction and electrons transfer are concerned. For instance *n*-butane oxidation reaction to maleic anhydride necessitates 7 lattice oxide ions, 8 hydrogen



Scheme 1.

atoms abstraction from the substrate, 3 oxygen atoms insertion and 14 electrons transfer!

The homolytic fragmentation of a C–H bond in the coordination sphere of the acceptor metal ion may occur via a transfer of the hydrogen to the oxygen ion at −2 oxidation state. This is a concerted action with homolytic breaking of metal–oxygen bond which transfers one electron to the metal. Without any hypothesis about the nature of the metal–oxygen bond one can write with formation of a π-alkyl complex (as usually admitted) or a δ-alkyl complex.

Depending on the nature, oxidation state of the metal ion and its environment (coordination structure), the metal–oxygen bonds may be more or less polarized and therefore the oxygen ion may exhibit electrophilic or nucleophilic properties. One may distinguish three extreme cases:

(a) $\overset{\delta^+}{M}=\overset{\delta^-}{O}$ (nucleophilic) → O^{2-}

(b) $M=O \rightarrow O^-$

(c) $\overset{\delta^-}{M}=\overset{\delta^+}{O}$ (electrophilic) → $\underline{\overline{OI}}$

Each case corresponds to specific properties.

Case (a) (nucleophilic character) will intervene in activation of a C–H bond in α of the double bond or of aromatic ring.

Case (b) (weakly polarized) will favor concerted homolytic-type reaction as for allylic dehydrogenation of olefins.

Case (c) (electrophilic character) allows one a direct attack of a double bond (oxidative breaking).

3. Structure sensitivity of oxidation reactions on oxides

Such a concept has been introduced by Boudart on metals. It has been introduced for oxides in the late seventies by Volta et al. [1], or early eighties by Tatibouet and Germain [2], Haber et al. [3], etc and it is widely accepted at present. For instance in the work by Volta et al., it was shown that single crystal type samples of MoO_3 exhibiting different relative amounts of the different faces (010) basal, (100) side and (101) and (10$\bar{1}$) apical exhibited different activity and selectivity in the oxidation of propene to acrolein and CO_x [4]. The originality of the work was to synthesize crystals of various shapes by epitaxial growth via oxyhydrolysis of $MoCl_5$ inserted between the layers of graphite. Table 1 summarizes the main results obtained for propene, but-1-ene and isobutene oxidation on MoO_3 crystals. It clearly appears that for propene oxidation the (100) face is selective for acrolein formation and the (010) for total oxidation. Such specificity depends on the hydrocarbon molecule. It may thus be proposed that the stereochemistry of the hydrocarbon molecule and that of the oxide face play a determining role.

A more precise analysis and characterization of the MoO_3 crystallites shape have shown that in fact the better plane for propene oxidation to acrolein corresponds to the (1k0) plane as shown in Fig. 2 [5]. It is then suggested that the propene activation (H abstraction) into the π-al-

Table 1
Structure sensitivity of the different faces of MoO_3 crystals in olefin oxidation at 380°C ([4])

Reactant olefin products		Relative selectivity per faces		
Reactant olefin	Products	Basal (010)	Side (100)	Apical (101), ($\bar{1}0\bar{1}$)
Propene	Acrolein	0.06	2.3	0.7
	CO, CO_2	1	0	0
But-1-ene	Butadiene	3	9.3	2
	CO, CO_2	1	0	0
Isobutene	Methacrolein	0	0.6	0.1
	Acetone	0.06	0	0.06
	CO, CO_2	0	1	0

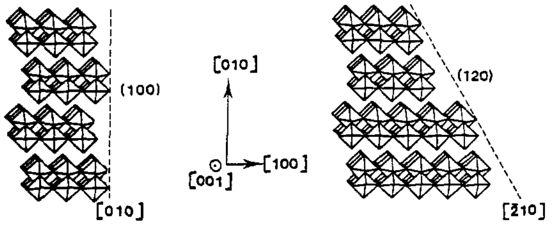


Fig. 2. Cross section view of αMoO_3 (100) and (120) planes (projection of the lattice on the (001) plane) (from [5]).

lyl intermediate occurs on the side (100) plane while the O atom insertion occurs on the (010) basal plane. Due to the layered structure of MoO_3, the lattice oxide ions are much more labile in the (0k0) plane than in the others.

Recently, such a structure sensitivity was derived for the partial oxidation of methane to formadehyde [6].

4. Vanadyl pyrophosphate [7]

Such a catalyst is well known for the oxidation of *n*-butane into maleic anhydride. The preparation necessitates the formation of $VOPO_4 \cdot 0.5H_2O$ as a precursor synthesized in an aqueous or better in an organic medium and its activation in a flow of 1 to 2% butane in air at the reaction temperature (ca. 380°C).

Here too, the preparation and the activation of the samples appeared also to be particularly crucial in order to obtain a well performing catalyst. In all cases, whatever the catalysts being good or exceptionally good, the $(VO)_2P_2O_7$ phase (V^{4+} cations) as a main constituent was detected by X-ray diffraction and by in situ laser Raman spectroscopy [8] in addition to small amounts of some $VOPO_4$ phases (V^{5+} cations) as $\alpha_{\|}$, β, γ or δ. Moreover, $VOPO_4$ pure phases were observed to be active and selective although to a lesser extent. It turned out that the presence of some V^{5+} cations on the V^{4+} catalyst surface of $(VO)_2P_2O_7$ was necessary although an excess was observed to be detrimental. Moreover the catalyst surface was observed to be richer in P than the bulk by a ratio of about 2.

The (100) face of $(VO)_2P_2O_7$ corresponding to edge sharing dimers of VO_6 octahedra bonded to the following chain by PO_4 tetrahedra was shown to be the active and selective face [9]. One has one oxygen of $V = O$ bond pointing away from the surface and the second one pointing downward in the form of a dimer as schematized in Fig. 3.

In a recent paper Grasselli et al. [10] proposed a mechanism with activated O^{2-} (peroxo) species on unsaturated V ion at the surface and have proposed that the active site is composed of an ensemble of four dimers isolated one from the other by excess of phosphate species as schematised in Fig. 3. Note that if such an assumption is true it is hard to understand how such activated oxygen species may be stable at high temperature and to understand the moving bed technology recently developed by the Du Pont researchers [11]. At variance the concept of four dimers as an active site seems reasonable and coherent with the scheme proposed by Ziolkowski [12] and Bordes [13].

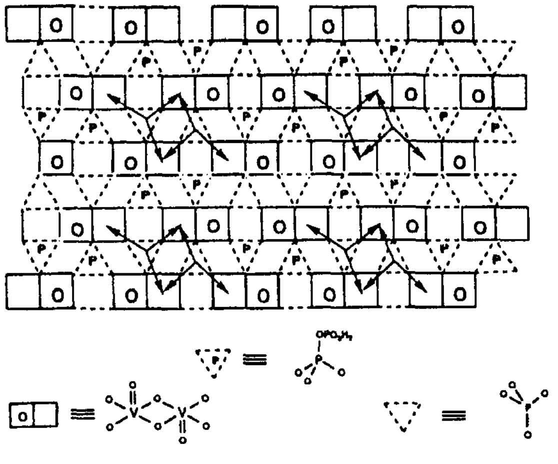


Fig. 3. Schematic representation of the surface structure of one polytype of $(VO)_2P_2O_7$. The arrows represent the possible pathways for facile exchange of surface bound oxygen, either monoatomic or diatomic, between the active sites. The 'site-isolation' due to the diffusion barrier created by the pyrophosphate groups is clearly shown by these arrows (from [10]).

5. Iron phosphates and hydroxyphosphates [14–17]

Such catalysts appeared to be potentially important catalysts for the oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA). This reaction is important as a first step to form methyl methacrylate monomer used for plexiglass or altuglass formation by polymerisation. The industrial type catalyst contains iron hydroxyphosphate of uncertain nature and Cs or NH_4 as additive and unfortunately necessitates a large amount of water in the feed (namely 10 to 12 mol H_2O per mol of IBA) to remain stable with time on steam. This makes this process difficult to be developed industrially. Taking into account the phase diagram Fe_2O_3-FeO-P_2O_5 it could be possible to select and study several phases which contain Fe^{2+}, Fe^{3+} or both cations able to insure the redox mechanism necessary for the reaction to take place as it was shown to proceed via a Mars and van Krevelen mechanism [18]. It was shown that the active phase was a phosphate with iron ion at a two oxidation states +2 and +3, $\alpha Fe_3(P_2O_7)_2$, composed of trimers of face sharing FeO_6 octahedra (as schematized in Fig. 4a) separated one from the other by PO_4 tetrahedra. The active sites were shown to correspond to a group of two trimers facing each other on their respective layers. The role of redox couple and of hydroxylation is shown below:

$$
\begin{aligned}
&Fe_2^{3+}Fe^{2+}(P_2O_7)_2\\
&\xleftrightarrow[400°C]{H_2O} Fe_2^{3+}Fe^{2+}(PO_3OH)_4\\
&\xrightarrow{O_2} Fe^{3+}_{2+x}Fe^{2+}_{1-x}(PO_3OH)_{4-x}(PO_4)_x
\end{aligned}
$$

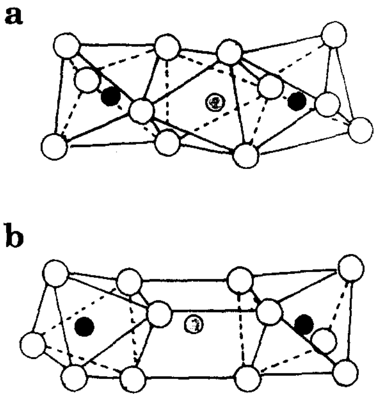


Fig. 4. Arrangements of FeO_6 octahedra in trimeric clusters isolated one from the other by P_2O_7 groups: (a) $\alpha Fe_3(P_2O_7)_2$; (b) $\beta Fe_3(P_2O_7)_2$; grey circles, Fe^{2+}; black circles, Fe^{3+}.

The way the octahedra are connected to each other may be an important parameter since it has been shown that the other polymorphic form of $Fe_3(P_2O_7)_2$ namely $\beta Fe_3(P_2O_7)_2$ was poorly active and selective. In this phase, the central iron atom is in fact occupying a FeO_6 trigonal prism (Fig. 4b).

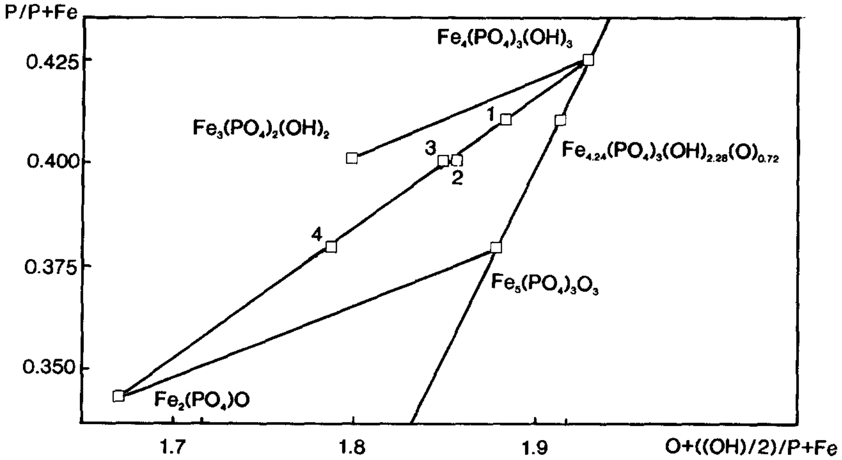


Fig. 5. Localization of the studied hydroxyphosphates in the phase diagram of the system Fe-P-O-OH. Numbers (1), (2), (3) and (4) correspond to $Fe^{3+}_{4.24}(PO_4)_3(OH)_{2.28}O_{0.72}$, $Fe_2^{3+}Fe^{2+}(PO_4)_2(OH)_2$ barbosalite, $Fe_2^{3+}Fe^{2+}(PO_4)_2(OH)_2$ lipscombite and $Fe_5^{3+}(PO_4)_2O_3$, respectively, after catalysis.

A study of iron hydroxyphosphates exhibiting clusters of face sharing FeO_6 octahedra of different sizes has been carried out. It turns out that all catalysts were belonging after catalytic testing to the same solid solution of the type $Fe^{3+}_{4-x}Fe^{2+}_{3x}(PO_4)_3(OH)_{3-3x}O_{3x}$ with $0 \leq x \leq 1$ (Fig. 5). Depending upon their composition these phases contain clusters of different sizes ranging from dimers ($Fe_4(PO_4)_3(OH)_3$ to continuous chains ($\beta Fe_2(PO_4)O$). The results showed that all samples were active and selective for the reaction even for the different sizes of the clusters but the optimum activity and selectivity were observed for the phase $Fe_3(PO_4)_2(OH)_2$ called barbosalite and containing limited size clusters, namely trimers as schematized in Fig. 4a. The added water plays a role as for the active phase of the industrial catalyst in stabilizing the hydroxylated catalysts and the redox couple is the same but implies O/OH instead of PO_4/PO_3OH couple.

In a theoretical study using extended Hückel molecular orbital calculation it has been shown that for iron octahedra assembled as dimers [19], trimers [20] or larger clusters there may occur electron exchange between Fe^{2+} and Fe^{3+} cations. This occurs in the case of trimers but neither for dimers nor for trimers in $\beta Fe_3(P_2O_7)_2$ (Fig. 6). This electron exchange between iron cations very probably favors the redox mechanism and thus the catalytic properties but should be limited to the closest neighbours to give the best performing catalysts.

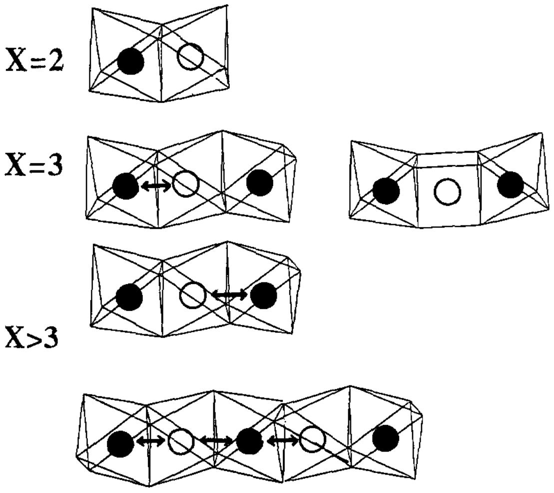


Fig. 6. Electron exchange between iron cations in $(FeO_6)_n$ octahedra clusters calculated by extended Huckel molecular orbital theory (from [19] and [20]).

Such clusters of FeO_6 octahedra also exist in other inorganic compounds. For instance they exist in ilvaite ($CaFe^{3+}Fe^{2+}_2Si_2O_7OOH$) where silicate layers replace phosphate anions and FeO_6 octahedra form ribbons. It is interesting to note that such material is active and selective for the reaction although to a lesser extent than the previous hydroxyphosphates [21]. The lower catalytic behaviour may be due to the presence of Ca^{2+} cations in the structure and/or to the silicate counter anion whose basicity in the sense of Pearson is different from that of the phosphate anion and/or the infinite size of FeO_6 octahedra clusters.

The main idea one may keep in mind from this study is that inorganic clusters of iron octahedra with iron at two oxidation states are active for the reaction studied and that one has to consider the active sites as these clusters, preferentially as ensemble of two trimers although other sizes (dimers, tetramers, pentamers...) are also active and selective but to a lesser extent. The iron oxidation state is changing during the reaction in a similar way that the V^{4+}/V^{5+} redox couple on VPO catalysts (vide supra, Section 4). This again shows that metallic oxides have to be considered with a dynamical view during the oxidation reaction.

6. Supported oxide catalysts

Supports are very often used in catalysis for several reasons, namely:

(i) Dispersion of the active phase in order to increase the surface to volume ratio since heterogeneous catalysis is occurring at the solid surface.

(ii) Heat transfer: this is a particularly important aspect in oxidation reactions because of the high exothermicity involved. This holds particularly true at industrial scale since the hot spot problem is very crucial and should be monitored with precision within a few degrees to avoid local overactivity and subsequently overheating and presumably irreversible phase transformation of the catalyst.

(iii) Attrition: this aspect is of main importance for fluidized or solid transported beds. One very usually uses silica or carborundum as a binder or as a coating to limit attrition.

(iv) Formation of new catalytic sites: this point will be emphasised below in some examples. One will see that well dispersed species of limited size could be formed and exhibit peculiar catalytic properties.

(v) Modification of the active phase properties due to its chemical interaction with the support, including epitaxial induced modifications. In some cases the chemical effect of the support will be determining for catalytic properties. For example several oxides (V_2O_5, MoO_3, Re_2O_7, CrO_3...) deposited on several oxide supports (SiO_2, TiO_2, Al_2O_3) were shown by Wachs et al. [22] to exhibit very different catalytic properties in methanol oxidation reactions as summarized in Table 2.

6.1. Molybdenum oxide supported on silica

Different procedures may be used such as impregnation of silica with a molybdate salt or grafting molybdenum chloride or molybdenum based organometallic compounds such as Mo carbonyls on to the hydroxyl groups of silica or solid–solid reaction between MoO_3 and SiO_2 at temperatures near or above 500°C.

Table 2
Turn over number values in $(s)^{-1}$ for methanol reaction at 230°C on 1 wt% metallic oxide deposited on several supports (from [22])

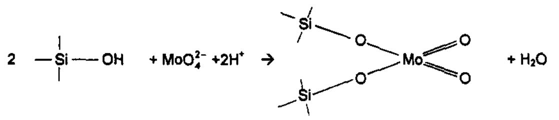
Oxide support	Supported oxide			
	V_2O_5	MoO_3	CrO_3	Re_2O_7
SiO_2	2	39	160	20
Al_2O_3	20		2	
Nb_2O_5	700	32	58	12
TiO_2	1800	310	300	1200
ZrO_2	2300	92	1300	170

An important parameter for the impregnation method is the pH of the molybdate solution. As a matter of fact the following equilibrium has been well established:

$$Mo_7O_{24}^{6-} + 4H_2O \leftrightarrow 7MoO_4^{2-} + 8H^+$$

The monomeric tetrahedral MoO_4^{2-} species is favored at higher pH and vice versa for the polymeric heptamolybdate anion. Moreover one defines the so-called isoelectric point of the support (ieps) or zero point charge (zpc) of a support by the pH value for which the surface charge turns from anionic to cationic, i.e. will allow cations or anions from the liquid phase to be adsorbed, respectively. One has values of 2 for silica, 5–6 for titania, 8 for alumina, etc. This clearly shows that the size of the adsorbed anion (monomeric or polymeric) adsorbed on a support will depend on the ieps (zpc) value, i.e. on the support itself. Above the ieps value, the surface of a particular oxide is negatively charged and vice versa below. The anion will thus be adsorbed for a pH value below the ieps value and as said above a lower pH value will favor polymolybdate anionic species.

In a study of ammonium heptamolybdate impregnated silica [23], the molybdenum loading was varied up to about 20 wt%. The hydroxyl groups of the silica were observed by infrared and/or UV-vis-NIR spectroscopies to decrease in intensity with Mo loading and to disappear at 7 wt% Mo loading while two UV bands were appearing at 245 and 340 nm. The former band may be assigned to tetrahedral monomeric species and the latter one to octahedral polymeric (polymolybdate) species. The former band was observed to increase in intensity proportionally to Mo loading at low Mo loading and to saturate at roughly 3 wt% Mo. The latter band was observed to appear near 2 wt% Mo, to increase proportionally to Mo content up to 7 wt% Mo and then to decrease slowly with Mo loading.



Scheme 2.

The formation of the former species was described by the reaction in Scheme 2.

Catalytic properties were studied for two reactions; namely isopropanol conversion and propene partial oxidation. The first reaction is a test reaction which allows the characterization of the acidic, basic or redox properties of a catalyst. One gets dehydration to propene or di-isopropylether for an acid catalyst, acetone for a basic catalyst in the absence of air and acetone and water for a redox type catalyst in the presence of air. The experimental results at 100°C clearly show that at low Mo loadings acidic features are favored while redox features are favored at higher loadings. This indicates that monomeric MoO_4^{2-} species are acidic (presumably as in silicomolybdic acid) while polymeric species exhibit redox properties (see Fig. 7).

The second reaction studied is propene oxidation at 380°C (see Fig. 8). Weak activity was observed for low Mo loading. At higher Mo loading propanal was the major product while acrolein was also observed. At very high Mo loadings and for MoO_3 one gets almost exclusively acrolein. Propanal is known to stem from propene by an electrophilic attack while acrolein corresponds rather to a nucleophilic attack. These results indicate that monomeric MoO_4^{2-} species does not oxidize propene in our conditions while polymeric (polymolybdate) species exhibit redox properties, with O^{2-} species being rather electrophilic. Molybdenum oxide exhibits redox properties with O^{2-} species being rather nucleophilic. One can thus realise how the size of the active site is important in oxidation catalysis. This is typical of structure sensitive reaction.

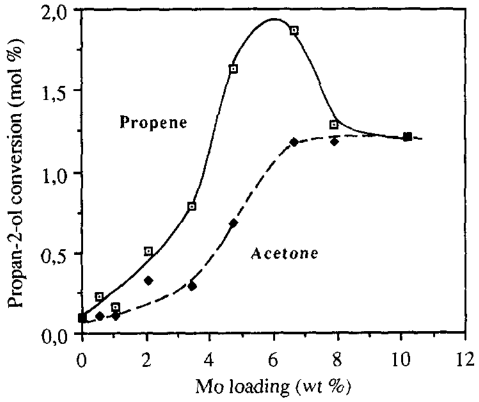


Fig. 7. Isopropanol conversion at 100°C on MoO_3/SiO_2 catalysts versus Mo loading in air (from [23]).

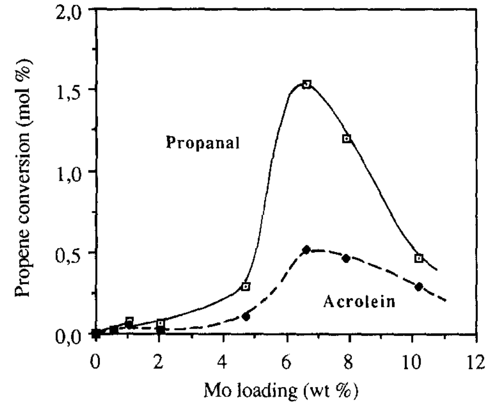


Fig. 8. Propene oxidation to acrolein (nucleophilic attack) and propanal (electrophilic attack) at 400°C on MoO_3/SiO_2 catalysts versus Mo loading (from [23]).

6.2. *Vanadium oxide on TiO_2 support*

Such a catalyst is well known for several reactions, such as *o*-xylene oxidation to phthalic anhydride and selective catalytic reduction (SCR) of NO by ammonia. The anatase form of TiO_2 appears to be better than the rutile form. Such catalysts with 1 and 8 wt% V_2O_5/anatase was prepared by Rhône-Poulenc ($S \approx 10$ m^2 g^{-1}) for an exercise of characterization by 25 different European laboratories. All results are assembled in a special issue of Catalysis Today published in May 1994, Vol. 20, no. 1. Surface vanadium species were observed to exist in three different forms: monomeric VO_4^{3-} species, polymeric vanadate species and V_2O_5 crystallites [24], the relative amount of which depended on initial at % V_2O_5/anatase and on the subsequent selective dissolution treatment.

The following conclusions could be drawn considering that a polyvanadate species occupies a ca circular zone of a diameter of 0.38 nm per V atom (i.e. 0.165 nm^2) and an isolated monovanadate species 0.66 nm per V atom (i.e. 0.43 nm^2):

(i) Monomeric VO_4^{3-} species exhibit acidic character with OH groups (Brönsted acidity) and result in propene formation for isopropanol conversion and in total oxidation for *o*-xylene oxidation. Maximum coverage equals 0.43 wt% V_2O_5.

(ii) Polyvanadate surface species exhibit redox properties, namely give rise to acetone for isopropanol conversion and phthalic anhydride for *o*-xylene oxidation.

(iii) V_2O_5 crystallites exhibit low activity for *o*-xylene conversion and high selectivity in total oxidation.

6.3. Various oxides deposited on different oxide supports

The idea is here to determine how a support may modify the catalytic properties of the different oxide species (as inorganic clusters of different size). It has been described above how the size of the deposited oxide species (monomeric, polymeric, bulk-type) results in different catalytic properties.

Vanadium oxide has been deposited on several supports as silica, alumina, titania but also zirconia, niobia, zirconium hydroxyphosphate, etc. Its reductibility was studied by reduction by hydrogen at 400°C. It was observed that V on TiO_2 and γ-Al_2O_3 was reduced rather fast and one reached a consumption such as an O/V atomic ratio near to 1 for TiO_2 and 0.65 for Al_2O_3 [25]. At variance for silica the reduction was much slower and an O/V ratio of 0.57 was obtained. Such differences were interpreted by the authors as due to different species on the surface: mainly monomeric VO_4^{3-} species for TiO_2, dimeric species $V_2O_7^{4-}$ for γ-Al_2O_3 (23) and V_2O_5 crystallites for silica [26].

The size of the polyvanadate species in solution corresponds to $V_3O_9^{3-}$, $V_4O_{12}^{4-}$ with tetrahedrally coordinated V at pH = 7 and 4.5 respectively and $V_{10}O_{28}^{6-}$ or $V_{10}O_{28}H^{5-}$ with octahedrally coordinated V at pH = 2.5. Deposition of such polyvanadates of different sizes was performed carefully on γ-Al_2O_3 support and their initial structures depicted above were shown to remain stable even after calcination in flowing air at 500°C and to be only partly modified after catalytic reaction of oxidative dehydrogenation of propane in the 350 to 450°C range. Moreover in such cases, the selectivity towards propene was observed to be the same at the same conversion level, indicating that in this size domain of polyvanadate species the catalytic selectivity was not changed, only the activity was observed to increase with vanadium loading [27].

In a study of VO^{2+} and Cr^{3+} cations exchanged or impregnated on the surface of zirconium hydrogenophosphates and compared to vanadyl pyrophosphate and chromium(III) phosphate, the best catalytic properties for ethane to ethylene oxidative dehydrogenation reaction at 500°C were observed when the material present either continuous chains of vanadyl or CrO_6 octahedra as in $(VO)_2P_2O_7$ and α $CrPO_4$ respectively or chains of limited size [28]. By comparison with bulk oxides exhibiting similar environment, it was suggested as for supported VO_x and CrO_x species on zirconium hydrogenophosphates that the catalytic performances were related to the stronger basic character of PO_4^{3-} anions with respect to O^{2-} anions.

7. Conclusions

Some general conclusions may be drawn from this general presentation:

(i) Oxidation reactions in gas-phase heterogeneous catalysis usually proceed via Mars and van Krevelen mechanism, i.e. involve lattice oxygen ions. Such ions exhibit an electrophilic or a nucleophilic character and therefore present different catalytic properties since the electrophilic oxygen interacts with a double bond or an aromatic ring while the nucleophilic oxygen interacts with a C–H bond in α of the double bond or of an aromatic ring.

(ii) Oxidation reactions are structure sensitive and therefore greatly depend on the local and surface structure of the oxide catalysts. A peculiar fitting between stereochemistry of the solid surface and of the reactant molecule(s) is to be obtained to get the best catalyst. Parameters such as reducibility and reoxidability features of the oxides are very important for catalytic reactions.

(iii) Active sites for oxidation reactions appear to be molecular 'inorganic ensembles' of metallic oxide atoms whose size greatly influences the catalytic properties. In some examples the number of atoms constituting the active sites could be established. For instance double trimers of face sharing FeO_6 octahedra are particularly active and selective for oxidative dehydrogenation of isobutyric acid to methacrylic acid on iron hydroxyphosphates; ensembles of four dimers of VO_6 octahedra are suggested to be the active sites for butane oxidation to maleic anhydride in vanadium pyrophosphate catalysts. Usually monomeric species as MoO_4^{2-} or VO_4^{3-} exhibit acidic feature and then total oxidation properties. At variance low size polymeric species exhibit better selectivity for many partial oxidation reactions than large size species or bulk-type oxide. It is thus clear that the size of these 'inorganic molecular ensembles' as active sites is important depending on the reaction considered and the support used. The characterization of such 'clusters' lying on the surface is rather difficult and the above statements for supported oxide catalysts are only qualitative. To better characterize such clusters, techniques as XANES (sensitive to local symmetry type), EXAFS (sensitive to the coordination number and nearby element distances) and radial electron distribution (RED) of X-ray diffraction peaks (sensitive to the nearby element distances) have to be used. Already data have been obtained for MoO_3 and V_2O_5 deposited on SiO_2, Al_2O_3 or TiO_2 support. This holds true only if one has one type of cluster species to analyse. The reader interested may read a chapter devoted to XANES and EXAFS techniques by Moraweck in the book by Imelik and Védrine (1988 and 1994) ([29,30]).

(iv) Oxidation catalysts have to be considered with a dynamic view under reaction conditions. This is related to the Mars and van Krevelen mechanism and also to the mobility of the oxide lattice. This latter phenomenon results from the wetting effect particularly for multicomponent and supported oxide catalysts. It follows that for many catalysts a certain time on stream is necessary before the catalyst reaches its steady state. It is frequent that in an industrial plant a steady state is reached only after one or two hundreds hours, the catalysts lasting several years before having to be replaced. For simple catalysts as doped vanadyl pyrophosphates used for butane oxidation to maleic anhydride the right size of the active sites (e.g. tetramers of vanadyl dimers) is monitored by the reactants in catalytic reaction conditions leading to the right V^{5+}/V^{4+} ratio, by the preparation procedure to change the material morphology (the (100) face of $(VO)_2P_2O_7$ being developed), and by the adequate addition of additive elements which regulate the site size and V^{5+}/V^{4+} ion ratio. The view of an oxidation catalyst as dynamical under catalytic reaction conditions is essential for our understanding of its functioning.

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