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Molecular description of active sites in oxidation reactions: Acid–base and redox properties, and role of water

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Abstract

Oxidation reactions in heterogeneous catalysis usually involve a Mars and van Krevelen mechanism which includes activation of the substrate on a metallic cation, insertion of oxygen from lattice oxygen ions, a redox mechanism on the catalyst surface, and the transfer of several electrons. It follows that such a reaction necessitates both acid–base and redox properties of a catalyst the acid site being of Lewis type (cations) and the basic sites being the surface O^{2-} or OH^- species which could exhibit electrophilic or nucleophilic properties.

The active site should be able to fulfil the following requirements: H abstraction from the substrate, oxygen insertion, and electron transfer. It has been shown to correspond to an ensemble of atoms of limited size in an inorganic molecular complex. It could correspond to local structural defects including steps, kinks, coordinatively unsaturated cations or to clusters of atoms on the surface. Some examples are described namely:

(i) n-butane oxidation to maleic anhydride on $(VO)_2P_2O_7$ catalyst where four dimers of vanadyl cations on the (100) face were suggested to form the active site;

(ii) isobutyric acid oxidative dehydrogenation to methacrylic acid on iron hydroxy phosphates where trimers of iron oxide octahedra were shown to constitute the most efficient and selective catalytic site while water was observed to be absolutely necessary to facilitate the reaction which corresponds to hydroxylated surface sites ensuring the redox mechanism;

(iii) propane oxidative dehydrogenation to propene on VMgO samples which was shown to depend both on VO_x arrangements with respect to MgO and on the basicity of the material induced by MgO while vanadium cations induced acidic features.

Keywords: Heterogeneous catalysis; Acid–base properties; Redox properties; Alkane oxidation

1. Introduction

Since pioneered ideas by Taylor [1] considering a single atom as active site in catalysis, several concepts have emerged considering in particular structure sensitivity reactions as proposed by Boudart [2]. In such a case a given face of a metal or an ensemble of surface atoms of a given size were shown to determine the catalytic properties of a material. This was shown clearly for metals including single crystal faces, small metallic particles of a given size, alloying with another metal thus limiting the number of surface nearby metallic atoms of the same nature by the aleatory presence of a second metal [3]. For metallic oxides since pioneered work by J.C. Volta et al. [4,5] in 1979 on MoO_3 single crystals many other examples of structure sensitivity have been mentioned on

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metallic oxides. For instance in the case of MoO_3 single crystals the (100) side face was found very selective for propene oxidation to acrolein while the (010) basal face lead to total oxidation. It follows that it was proposed that propene is activated on the (100) face while oxygen atom supply for insertion resulting in acrolein comes from the (010) plane. This results in (1k0) face to be the most active and selective face [6]. At variance for 1-butene oxidation, butadiene was formed on all basal (010), side (100) and apical (101, $\bar{1}01$) faces while CO_x was obtained only on the basal plane [7]. For isobutene oxidation methacrolein was obtained mainly on the side face (100) as CO_x while acetone was formed on basal (010) and apical (101, $\bar{1}01$) planes [7]. Another example can be found with $Cu_2Mo_3O_{10}$ and $Cu_6Mo_4O_{15}$ compounds for butene 1 oxidation [8]. The former compound is active for isomerisation and oxidative dehydrogenation while the latter one inserts oxygen into the organic molecule resulting in crotonaldehyde. Cuprous oxide was also shown to exhibit different properties depending on the exposed faces for propene oxidation [9].

More recently a molecular description of the active sites for oxidation reactions has shown up. The main simple and even naive idea is that the stereochemistry of such molecular surface site should fit that of the reactant molecule(s) [10].

Oxidation reactions usually necessitate H atom(s) abstraction, and O atom(s) insertion from the surface into the hydrocarbon molecule and several electrons transfer. This corresponds to a redox mechanism, usually of Mars and van Krevelen type, involving cations which oxidation states vary during the catalytic cycle. The reaction mechanism involves intermediate organic species which may desorb and readsorb on the surface in a rattle-type process. Depending on the rate determining step (usually the first step of activation of the hydrocarbon molecule), the desorption of the intermediate species may be negligible which means that the whole reaction occurs at the same active site. Such site should then be able to provide the whole chemical characteristics for the reactant molecules: H abstraction, O insertion, and electron transfer. One then easily understands that its size should be large enough not only to accommodate the adsorbed reactant molecule of a given size but also to provide the above chemical characteristics. For instance for n-butane oxidation to maleic anhydride the active site should necessitate 7 lattice oxygens abstractions from the substrate, 3 oxygen atoms insertions, and 14 electrons transfers.

2. Catalysts characteristics for an oxidation reaction

In order to fulfil the requirement of an oxidation reaction the catalyst should present peculiar characteristics which are described below.

2.1. Surface defects

This parameter is very important but rather difficult to characterize. It is clear that a more defectuous surface is usually more active and/or more selective than a well defined surface. This could correspond to the existence of kinks, steps, corners as for metallic single crystals. It could also correspond to cations with unsaturated coordinations (coordinatively unsaturated sites: cus) which may then be considered as Lewis acid sites and as preferential adsorption sites. For instance for n-butane oxidation to maleic anhydride (vide infra) on $(VO)_2P_2O_7$ catalyst, the better catalyst is not the best crystallized phase obtained for instance by calcining the hemihydrate precursor above 750°C but rather the poorly crystallized $(VO)_2P_2O_7$ phase obtained from the precursor by calcination at 400 to 500°C. As a matter of fact it was shown by in situ Raman spectroscopy that starting from the VOH PO_4, 0.5 H_2O precursor and calcining it at increasing temperature under the n-butane/air flow maleic anhydride was formed when the $(VO)_2P_2O_7$ phase crystallized simultaneously with $VOPO_4$ structures [11]. Moreover, the material was at optimum MA yield if calcination was performed below 750°C while such yield decreased for samples calcined above 750°C while crystallinity was improved [12].

A high resolution electron microscopy study has shown that vanadyl pyrophosphate catalyst shows evidence of surface structure modification in n-butane environment [13].

2.2. Surface oxygen species

The nature of the surface oxygen species is obviously of prime importance since it may favour electrophilic or nucleophilic attack. It corresponds to O^-, O_2^-, super oxo $(M{-}O{-}O^{\circ})$, peroxo $(O{-}O)$ (electrophilic), or oxo ($M=O$ nucleophilic) species related to the metal oxygen bond nature and to the heat of metal oxygen formation. Such surface oxygen species including hydroxyls are usually negatively charged, i.e., should exhibit basic character. In the well accepted Mars and van Krevelen mechanism, lattice oxygen anions are assumed to be inserted in the substrate molecule or to facilitate its dehydrogenation by forming H_2O while the metallic cations ensures the redox mechanism to occur by changing their oxidation state. Depending on the nature, on the oxidation state of the cation and on its environment, the metal oxygen bonds may be more or less polarised and then the oxygen will exhibit electrophilic or nucleophilic properties.

$\overset{\delta^+}{M}=\overset{\delta^-}{O}$	$\overset{\delta^-}{M}=\overset{\delta^+}{O}$	$M=O$
nucleophilic	electrophilic	

The first case will favour deprotonation according to $M=O+H^+ \rightarrow M^+{-}OH$.

The second case (weak polarisation) will favour homolytic concerted reactions as allylic dehydrogenation of olefins.

The third case with electrophilic character will favour direct attack of a double bond or of an aromatic ring, i.e., acetone from propene (and even acetaldehyde and formaldehyde), anhydride from an aromatic ring.

2.3. General features

Catalytic properties for oxidation reaction on transition metal oxides can be considered in light of their surface acid–base features. High valent, incompletely coordinated metal ions or anionic vacancies can be regarded as acidic sites and oxygen or hydroxyl anions as basic sites.

T. Seiyama et al. [14] have investigated the conversion of propylene to acrolein or benzene over a series of oxides. They have observed that the selectivity to acrolein increases with the electronegativity values while that to benzene increases in the presence of weakly basic or weakly acidic sites. One can consider d^1 cations as strong or hard acids and d^0 or d^{10} cations empty or full d orbitals as weak or soft acids and following Pearson's approach (HSBA theory) one considers soft acid–soft-base or hard acid–hard base interaction as being favoured with respect to hard acid–soft base or soft acid–hard base interactions. Since hydrocarbons such as alkanes and olefins can be considered as weak bases one may expect catalysts with strong acid cations, e.g., most acidic cations as V^{5+}, Mo^{6+}, W^{6+} to be more selective for propene partial oxidation than weak acid since the former cations results in weaker interaction with propene than the latter ions.

The following order was then proposed [14]:

d°: $V^{5+} > Mo^{6+}, W^{6+} > Nb^{5+} > Ti^{4+} > Zr^{4+}$
d^{10}: $Sb^{5+} > Sn^{4+}$.

High selectivity can be explained by considering the adsorption/desorption steps. Acidic sites favour the adsorption of basic reactants and enhance the desorption of acidic products, thereby protecting their further oxidation to carbon oxides and water.

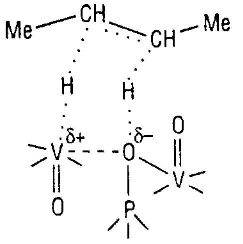
Summarizing the present state of knowledge of the role of acidity–basicity in oxidation reaction the following aspects have to be taken into account:

adsorption and activation of the hydrocarbon molecule are related to acid–base interactions;

the adsorption and desorption rates of reactants and products are also related to acid–base properties.

3. Vanadyl pyrophosphate for butane oxidation to maleic anhydride [15]

This is an interesting example widely studied all over the world since it constitutes the first example of an industrial process of activation of an alkane into an oxygenate at reasonable yield. It has been proposed that the activation of the butane molecule occurs on a vanadyl dimer site on the (100) plane exhibiting an accessible V^{4+} cation (vanadyl pointing down) and a vanadyl V = O bond (vanadyl pointing up) as shown in the following scheme (from Fig. 9 in Ref. [16]).



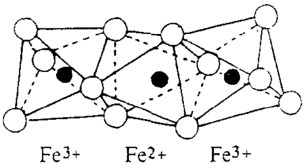
From the large amount of works (see a special issue of Catal. Today [15]) devoted to such a system, a concerted mechanism was proposed involving alkoxy intermediates [16]. A kinetics study has shown [17] that the reaction occurs according to a rattle-type mechanism but with a very small desorption of the intermediates. This implies that the very demanding reaction which involves 8 hydrogen atoms abstraction, 3 oxygen atoms insertion and 14 electrons transfer occurs in a site of limited size. Such a site should necessitate at least 4 vanadium atoms. R.K. Grasselli et al. [18] suggested that the active sites are composed of 4 vanadyl dimers separated one from the other by an excess of phosphate ions on the surface. Such a model is consistent with the model proposed by Ziolkowski [19] and Bordes [20]. During the reaction, a dynamic process occurs at the surface modifying reversibly the active site structure as shown by different techniques as Raman, X-ray photoelectron spectroscopies, thermogravimetry and micro pulse reaction [21]. Note also that in situ Raman spectroscopy showed unambiguously that maleic anhydride was only formed when the precursor (vanadyl hydrogenophosphate hemihydrate) was transformed into vanadyl pyrophosphate at the same moment when $VOPO_4$ structures were nucleated (V^{4+} and V^{5+} species simultaneously present) [11].

The nature of the acid sites on $(VO)_2P_2O_7$ catalyst has been studied by FTIR spectroscopy using pyridine adsorption at 25°C. Typical Lewis ($\bar{\upsilon}$ = 1450 and 1610 cm^{-1}) and Brönsted (υ= 1545 cm^{-1}) acid sites were observed [22]. The pyridine bands were observed even upon thermal treatment up to 300°C indicating that the acid sites are rather strong, the Brönsted sites being the strongest ones.

A study of CO_2 and SO_2 adsorption at 80°C [22] to probe basic properties of the samples showed that basicity of such materials is rather weak, indicating that the first step of butane activation is very probably more due to acid sites Lewis sites as V cation or Brönsted sites rather than to basic sites. However the concerted mechanism (vide supra) involves basic sites as weakly negatively charged lattice oxygen anions ($O^{\delta-}$) allowing dehydrogenation of butane into butene with formation of water.

4. Iron phosphates and hydroxyphosphates for isobutyric oxidehydrogenation to methacrylic acid [23–28]

Such catalysts appeared to be potentially important for the oxidative dehydrogenation of isobutyric acid (IBA) into methacrylic acid (MAA). It has been observed that the reaction proceeds via a Mars and van Krevelen mechanism and that active phases had to contained both Fe^{2+} and Fe^{3+} cations in order to be able to ensure the redox mechanism necessary for the reaction to take place. It appears that the best catalysts are containing the phase $Fe_2^{3+}Fe^{2+}(P_2O_7)_2$ which is composed, as schematised below, of face shearing FeO_6 octahedra trimers.



Such arrangement certainly facilitates the intervalency between Fe^{3+} and Fe^{2+} cations during catalytic reactions and thus a limited electron hopping between Fe^{2+} cations.

It was observed that the catalytic activity was maintained with time on stream only if a large excess of water vapour was present in the feed. An optimal value of 10 to 12 water molecules per IBA molecule was established. In the mean time it was observed that the $Fe_2^{3+}Fe^{2+}(P_2O_7)_2$ phase, where only trimers are present, was formed by dehydroxylation of the hydroxyphosphate $Fe_2^{3+}Fe^{2+}(PO_3OH)_4$ at 420°C. This transformation was shown to be reversible. Such a hydroxyphosphate was also observed to be oxidable by oxygen. The whole system could then be represented as below:

$$Fe_2^{3+}Fe^{2+}(P_2O_7)_2 \underset{420°C}{\overset{H_2O}{\rightleftarrows}} Fe_2^{3+}Fe^{2+}(PO_3OH)_4 \overset{O_2}{\rightleftarrows} Fe_{2+x}^{3+}Fe_{1-x}^{2+}(PO_3OH)_{4-x}(PO_4)_x.$$

It could then be suggested that the active phase is in fact the hydroxyphosphate and that the active sites are composed of trimers of iron hydroxyphosphate. Such trimeric species are able to undergo the redox process, while the presence of excess water ensures the existence of the hydroxyphosphate phases under catalytic reaction which occurred near 380°C.

Taking such a concept into consideration several hydroxyphosphates belonging to the $FeO–Fe_2O_3–P_2O_5–H_2O$ system have been studied such as barbosalite $Fe_2^{3+}Fe^{2+}(PO_4)_2(OH)_2$ which contains the same trimeric species, $Fe_4^{3+}(PO_4)_3(OH)_3$ which contains dimers or $Fe^{3+}Fe^{2+}(PO_4)O$ which contains infinite chains of face sharing octahedra. Under the conditions of catalysis all the tested phases were transformed into phases belonging to a solid solution of the type $Fe_{4-x}^{3+}Fe_{3x}^{2+}(PO_4)_3(OH)_{3-3x}O_{3x}$ with $0 \leq x \leq 1$. Depending upon their composition, these phases contained clusters of face sharing iron octahedra of different sizes. The more efficient catalysts contained clusters of small size (preferably trimeric FeO_6 octahedra with face sharing). The results obtained supported out above statements [26,27]. These catalysts have the same redox couple but different basic sites since O^{2-} have been substituted for $(PO_4)^{3-}$ as schematized below for the active phase of the industrial catalyst (1) and barbosalite (2):

$$Fe_3(PO_4)_x(PO_3OH)_{4-x} + yIBA \rightarrow Fe_3(PO_4)_{x-2y}(PO_3OH)_{4-x+2y} + yMAA, \quad (1)$$

$$Fe_4(PO_4)_3(OH)_{2.4}O_{0.6} + yIBA \rightarrow Fe_4(PO_4)_3(OH)_{2.4+2y}O_{0.6-2y} + yMAA. \quad (2)$$

In the hydroxyphosphates the $(PO_4)^{3-}$ ions have, thus, a minor role compared to that in the active phase previously studied. It could thus be imagined that such polymeric iron oxide polyhedra may exist in other systems and could behave similarly. As a matter of fact silicate or pyrosilicate anions may well be envisaged as counter anion in place of phosphate anions. One may then expect a different sensitivity to water and different acidic strength, presumably acid of lower strength. As a matter of fact Ilvaite, $CaFe^{3+}Fe_2^{2+}Si_2O_7O(OH)$, a natural iron hydroxysilicate sample has been shown to be active and rather selective for the considered reaction [28].

The structure was however not exactly the same as that of the phosphates since it presents a framework of edge sharing double chains of FeO_5OH octahedra connected by $(Si_2O_7)^{6-}$ groups. Sensitivity to water was much less stringent than for hydroxyphosphates but the catalytic performances remained inferior. Nevertheless this result shows that the concept of active sites above developed can be considered as valid for such a reaction.

5. VMgO catalysts [29–36]

Such a system was interesting to consider since it is basically composed of an acidic (V_2O_5) and a basic (MgO) oxides. One may then expect either to have well defined phases of given catalytic properties or to have such phases deposited on a basic support (MgO). Three phases are well known namely the orthovanadate $Mg_3V_2O_8$, the pyrovanadate $Mg_2V_2O_7$ and the metavanadate MgV_2O_6. The first phase exhibits isolated VO_4 tetrahedra (separated by MgO_6 octahedra), the second one has corner sharing VO_4 tetrahedra and the third one has an octahedral structure. The pyrovanadate phase was found by one of us [31] to be the more selective phase at equal conversion with respect to the other two phases for oxidative dehydrogenation of propane at 500°C. At variance the $Mg_3V_2O_8$ phase (exhibiting isolated VO_4 entities separated by octahedral MgO_6 entities) was found by H. Kung et al. [30] to be more efficient for propene formation in propane oxidative dehydrogenation than the other two phases. A. Pantazidis and C. Mirodatos [32] recently found for the same reaction that propene selectivity was about the same (65 to 75%) within a large range in V_2O_5 content (10 to 80 V_2O_5 wt%) and at similar conversion levels. A. Corma et al. [33] concluded that tetrahedral isolated VO_4 species are more selective for oxidative dehydrogenation of C_3 and nC_4 alkanes. It then appears that contradictory results have been obtained resulting obviously in contradictory interpretations concerning the role of atom arrangements.

The discrepancies between authors may arise from differences between samples, supposedly similar, and from different catalytic reaction conditions particularly the alkane to oxygen ratio values.

Taking the samples prepared in our group we have tried to go deeper in the characterization of the catalysts.

Reducibly and electrical conductivity measurements [34] have shown that the $Mg_2V_2O_7$ phase was more easily reduced than the other

Table 1

Catalytic data for isopropanol conversion under nitrogen (A) or air (B) in the flow at 230°C after activation of the sample at 230°C for 1h30 under N_2 flow, values taken from Ref. [35]

Samples	V_2O_5	S	A			B		
	(wt%)	($m^2\ g^{-1}$)	Conversion (%)	Propene (%)	Acetone (%)	Conversion (%)	Propene (%)	Acetone (%)
MgV_2O_6	82.1	0.1	7.5	90	10	8	90	10
$Mg_2V_2O_7$	70.1	1.7	1.5	43	57	1.7	40	60
$Mg_3V_2O_8$	60.8	0.9	2.2	69	31	2.8	74	26
MgO	0	142	0.2	0	100	0.2	0	100
40VMgO [a]	38	43	1.2	14	86	1.7	17	80
60VMgO [a]	58.5	19	3.6	24	76	4.3	24	76
V_2O_5	100	2.1	64	94	6	4.8	75	25

$m = 100$ mg; flow rate 18.6 $cm^3\ min^{-1}$.

$P_i = 2.0 \times 10^3$ Pa.

[a] mixture of MgO, $Mg_3V_2O_8$, calcined at 550°C.

$\alpha Mg_2V_2O_7$ as determined by XRD analysis.

Table 2
Catalytic data for oxidative dehydrogenation of propane (A) n-butane (B) and isobutane (C) at 540°C from ref [36]

Samples	A			B		C	
	Conversion (%)	Propene [a] (%)	COx [a] (%)	Conversion (%)	Dehydr. products [b]	Conversion (%)	Isobutene [c]
MgV_2O_6	7.4	15	53	10	33	14	19
$Mg_2V_2O_7$	6.9	53	28	11	40	9	40
$Mg_3V_2O_8$	8.3	6	94	15	13	10	20
40VMgO [d]	8	65	35	15 [c]	20	6	70
60VMgO [d]	8	65	35	42 [c]	9	17	58

Flow rate = 50 cm^3 min^{-1}, $P(C_3^=) = 2 \times 10^3$ Pa, C_3 or C_4:air = 2:98.

[a] Balance to 100% corresponds to oxygenates as ethanal, acrolein, propanal and acetic acid.

[b] Dehydrogenates correspond to butenes (major) (but 1ene and but 2 ene) and butadiene (minor).

[c] Taken at 450°C instead of 540°C because of its high conversion level due to its high surface area.

[d] Mixture of MgO, $Mg_2V_2O_7$ calcined at 550°C.

two while anionic vacancies were created according to:

$$C_3H_8 + O^{2-}_{surf} \rightarrow C_3H_6(g) + H_2O + V_O^{2-} + e^-.$$

Moreover, basicity of surface oxygen ions acts on the ability to create anionic vacancies and thus on the catalytic activity. Moreover if the sample contains more MgO that the above stoichiometries for pure phases one may imagine that its basicity may also play an additional role. The acid–base features of the catalysts were studied by the reaction of isopropanol conversion to propene (acidic feature) and acetone (basic feature) under N_2 in the feed and the redox features by the reaction under air in the feed. It was observed at 230°C (Table 1 from Ref. [35]) that the pyrovanadate sample was much more basic than the other two pure phases and that excess MgO with respect to crystallized phase stoichiometry induced even more basic character (Table 1).

As the olefins and to a lesser extent the alkanes are basic one may expect the propene desorption to be favoured by surface basic sites. In other words oxidative dehydrogenation of alkanes is expected to be easier on surfaces exhibiting more basic properties. As a matter of fact the results given in Table 2 from Ref. [36] show that $Mg_2V_2O_7$ which is more basic as shown in Table 1 is more selective for olefins in propane and to a lesser extent n-butane and isobutane oxidation reactions than the other two phases. Such a feature is even more pronounced for the samples with excess MgO at least for propane oxidation, samples which were also shown to present higher basicity (Table 1).

It follows that one may conclude that basic properties as well as atomic arrangements at molecular level play an important role in alkane oxidative dehydrogenation reactions.

6. General conclusions

In the different examples chosen in this paper we have tried to show some important characteristics of metallic oxide catalysts used for oxidation reactions. Such reactions usually proceed via Mars and van Krevelen mechanism, i.e., necessitate metallic cations as V, Mo, Cr, Fe... able to change their oxidation state in the course of the reaction and lattice oxygen anions able to be inserted into the substrate, i.e., to present a sufficient anionic mobility within the solid catalyst. Acid–base and redox properties are known to be closely related the metallic cations considered as acidic in the sense of Lewis and lattice oxygen anions as basic sites. However, the acid–basic strength influence on catalytic properties appears to be more related to Pearson's approach (HSAB) than to the usual approach features. Moreover, the influence of the basic character remains not well defined but to be of importance for oxidative dehydrogenation of light alkanes.

One of the main features is that the active sites in many reactions appear to be very efficient when they are of limited size a little like if the stereochemistry of the reactant molecule(s) and that of the surface active site have to fit at a molecular level. This could explain why a given reaction works optimally only on a given catalyst.

Another aspect shown in this presentation is a peculiar role of water which is to maintain the catalyst surface at a state hydrated enough to allow the redox mechanism to occur easily.

At last in all these oxide systems, particularly the supported oxide catalysts, the wetting of an oxide over the other (being the support or not) plays an important role which has not be presented in this paper but which exists. It results in a rather long time of activation under reactants and catalytic conditions necessary to get steady state of the reaction. An example of a multicomponent catalyst (bismuth molybdate on a Co(Fe)MoO_4 support is given in Refs. [37,38]. This phenomenon occurs rather usually and is beneficial for catalytic reaction, presumably by allowing good fitting between the surface active site at molecular level and the reactant molecules. Unfortunately such a dynamical process [37–39] makes such catalysts difficult to characterize unless in situ techniques can be used.

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