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Concepts in Selective Oxidation of Small Alkane Molecules*Robert Schlögl*

1.1

Introduction

The subject of heterogeneously catalyzed selective oxidation has been reviewed many times. Under the keyword combination “selective catalytic oxidation” the ISI database reports about 5400 papers. Over 100 reviews on the topic have been published. In the present discussion, the subjects of methane activation and model studies of unselective CO oxidation, which represent large fields, are excluded. Homogeneously or biologically catalyzed selective oxidation, a combined field that is about 10-fold larger in scientific coverage, is also excluded from this chapter.

Instead, the present chapter deals mainly with the activation of C₂, C₃ and C₄ hydrocarbons focussing on oxidative dehydrogenation and oxo-functionalization as target reactions. This seemingly limited field of research encompasses a central entry port to commodity molecules used in chemical industry. The issues of selectivity and energy conversion are of enormous practical relevance as the potential is great for making the chemical industry more sustainable is in this small area of catalytic chemistry. However, the still limited success in performing these reactions effectively sheds light on the level of our scientific understanding of these reactions. The science is based upon a set of phenomenological concepts referred as “principles” in the literature, enabling the discovery and optimization of the present catalytic materials.

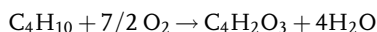
By far the most influential principle is that of “lattice oxygen” [1–3]. It states at its core that atomic oxygen that can selectively oxidize a hydrocarbon has to come from a lattice position of the catalyst. The reduction of the metal centers is thought to arise from oxygen anion transport from deeper layers of the catalyst to its surface. Gas-phase oxygen, being detrimental as reagent with organics, re-oxidizes the catalytic material in a spatio-temporal separation between the hydrocarbon redox chemistry and the catalyst redox chemistry. This separation is widely referred to as the “Mars–van Krevelen type (MvK)” reaction “mechanism” [4, 5]. The original derivation by the authors Mars and van Krevelen [6] did, however, not contain any interpretation of their finding in SO₂ oxidation over vanadium oxides. In their

kinetic work a second term had to be added to the conventional Langmuir equation to explain the experimental finding. Only much later was it realized that this term should describe the “slow re-oxidation of the catalyst,” for which there is little experimental evidence [7]. The postulated general validity of the principle is questioned by the operation of monolayer oxide catalysts [8], which have little ability to deliver lattice oxygen, and by numerous findings in homogeneous catalytic oxidation where molecular oxides such as RuO_4 afford excellent [9] selective oxidation.

Another strongly prevailing principle is that of “phase cooperation” [10–13]. This states that high-performance oxidation catalysts must be of the multi-phase type, as the different functions required in performing the selective oxidation of a hydrocarbon are only adequately optimized when independent functionally optimized phases cooperate in the catalytic cycle. This intuitively appealing concept renders it almost impossible applying the tools of functional analysis to selective oxidation as the chemical and structural complexity arising from a multi-element-multi-phase oxide (MMO) overwhelms all analytical possibilities of today’s experimentation and theory. Recent developments in catalyst synthesis have shown on the model level [14–16], as well as with high-performance systems [17–21], that substantial catalytic action can be obtained from proven single-phase systems.

At present, the field is still without an unchallenged scientific base despite the enormous effort invested into the issue and the many papers written. This situation is unsatisfactory with respect to the enormous relevance of selectivity in large-scale industrial processes. In the opinion of the author this is not due to a lack of excellent ideas – almost all possible ideas about the function of these catalysts have been proposed. It is a rational experimental approach beyond the principles described in the literature that is needed to unify the concepts into a scientific foundation for better catalyst developments. A parallel search for such catalysts has been advocated and performed [22] with great effort but apparently no success in solving the challenges of the field. This statement is not negative against high-throughput experimentation as such but shows that this technique also requires a scientifically sound basis for its useful application [23].

The above critical remarks do not diminish the enormous success in the development of oxidation reactions that seem close to impossible within the framework of homogeneous chemistry. The most successful process is the one-step reaction of butane to maleic anhydride (MA):



The process solves the problem of activating the poorly reactive butane and then abstracting eight protons without cleaving a carbon–carbon bond. In addition, three oxygen atoms are attached without forming any carbon oxides. This is only possible as the product MA is kinetically stable against further oxidation at the remaining protons, as the locations of further attack are strongly bound to the cyclic carbon skeleton. The reaction occurs in many intermediate steps that are all stabilized against oxidative attack due to chemisorption at an active site that has to become progressively less active during the whole transformation. We assume that the active

site stores electrons from the substrate in its structure and becomes progressively reduced, which in turn reduces its ability to activate C–H bonds. With release of the product we expect concomitant release of water from stored OH groups and re-oxidation by oxygen from the feed. As there are no split oxygen molecules at hand (excluding special oxidants) the active site has to accommodate one extra oxygen atom for every two-center bond being made. The fact that per turnover 14 electrons have to be stored at the active site and that the highly suitable vanadium cation changes its oxidation states between 5 and 3 would call for an active site consisting of seven vanadium centers and a suitable combination of terminal and bridging oxygen atoms. A minimum size of an active site of vanadium species would be two centers as they can store the four electrons required to activate one molecule of oxygen. Such a cluster is hardly a “lattice.” It also can not be a section of an oxide lattice, as then the reacting site would not be isolated electronically, as through oxygen ion diffusion and electronic conductivity the oxidation state of the active site would be kept as constant as possible so as to minimize the free energy of the system. The active site is thus seen as a cluster supported on a matrix of a foreign material (supported catalyst) or of a compound from which the cluster originates by segregation (self-supported). The cluster exhibits a structure capable of adsorbing activated oxygen and of holding protons as intermediate hydroxyl groups. The adsorbed oxygen, being part of the coordination geometry of the cluster in its regenerated state, has been called “surface lattice oxygen” [8, 24, 25], a term for which the author sees no need as this oxygen is an adsorbate situated at a high energy position of the structure.

The general principle of site isolation [26] is the consequence of many observations in selective catalysis that are not confined to selective oxidation. High performing catalysts exhibit isolated sites, minimizing the influx of electrons and activated reactants (oxygen, hydrogen) during conversion of a substrate molecule. This principle of site isolation [1, 2, 26–32] is the most powerful rule for finding selective oxidation catalysts. It is, however, mostly applied in a crystallographic manner, meaning that structures are sought that exhibit strong variations in atom density in their motifs by combining locally dense building blocks with linking polyhedra, leaving substantial empty space in the unit cell “channels.” A particular, instructive example of site isolation is the idealized crystal structure of salts of heteropolyacids (HPA), a family of compounds [18, 33–35] capable of performing many selective oxidation reactions.

It is apparent that logical clashes occur when in the literature the principle of site isolation is applied in conjunction with phase cooperation and lattice oxygen dynamics. Both concepts require for their operation a close contact of the active site with its environment and suggest a continuing exchange of reactants and electrons during the conversion of a substrate molecule. Elaborate sets of assumptions are made to remedy these clashes. The purpose of this review is to suggest a reconciliation of these conflicting concepts as all of them are based on undeniable observations. Table 1.1 gives a (incomplete) list of reviews that highlight the complexity of the arguments that arose from the applications of empirical principles. The list is split into two groups: articles covering reactions and those dealing with the structure and function of catalysts. There is no ordering within the groups.

Table 1.1 Some relevant reviews for the field of selective oxidation.

Year	Topic	Reference
Reactions and processes		
2006	Kinetics of C ₂ ,C ₃ ODH reactions	[36]
2001	Propane oxidation	[37]
1997	Propane ammoxidation	[38]
1999	Ethane activation	[39]
1995	ODH reactions	[40]
1997	ODH of alkanes	[41]
2000	Epoxidation	[42]
1979	Selective oxidation reactions	[43]
2002	C ₄ activation	[44]
1985	C ₄ oxidation	[45]
2000	General review, 30 years of selective oxidation	[46]
1999	Advances in selective oxidation	[31]
Mechanism, catalysts and methods		
2002	Molecular structures of catalysts	[47]
2006	Molecular structures of monolayer oxides	[48]
2001	Heteropolyacid systems	[33]
1996	Key aspects for catalyst design	[49]
2003	<i>In situ</i> studies	[50]
2001	<i>In situ</i> studies	[51]
2003	Active oxygen species	[52]
1992	Di-oxygen as selective oxidant	[2]
1991	V monolayer catalysts	[53]
2000	Family of oxide monolayer catalysts	[54]
1991	Promoter effects in oxidation	[55]
1992	Defects in oxidation catalysts	[56]
1992	Phase cooperation in oxidation	[57]
2000	Solid state chemistry	[58]
2004	Nanostructures	[59]
2003	Lattice oxygen	[60]
1996	IR studies in selective oxidation	[61]
1991	Theory, a generalized concept	[62]
2007	Theory of propane activation	[63]

1.2

The Research Field

The field is defined here around the activation of butane, propane and ethane plus the oxidation of propene. The reason for this boundary is the similarity of the chemistry and the great need to understand the mechanism of selectivity of activated oxygen in these multi-step reactions. The processes cannot be conducted at high temperatures such as with methane activation as the target products are not stable under conditions where alkane activation is fast. The selective oxidation of

ethylbenzene to styrene and that of *o*-xylene are also not covered as the initial substrates are already activated. The reader is referred to the literature on xylene oxidation [31, 64] and ethylbenzene [65–69] dehydrogenation.

The set of reactions defines the materials largely contained within this set of scientific studies. It deals mostly with vanadium oxides and vanadium phosphates followed by complex MMO phases and HPA. Figure 1.1 shows some relevant trends from the ISI database statistics.

Figure 1.1(a) reveals that the field has been recognized (cited) for about 20 years, although the roots go back about 20 years longer [46]. By looking at the derivative of the growth of citations in Figure 1.1(b) one can state that interest is growing above the trends for more complete coverage of the literature and for the general rapid growth of scientific communication. Following the initial accumulation in the early 1990s a first evolution in activity can be observed. After a period of scientific disappointment steady growth since 2000 is seen, triggered by the advent of model catalysis, nanoscience and the families of complex oxides on the material side. Further motivation may be the pressing need to utilize alkane feedstock on the process side. Some extra trends can be seen upon sorting the total citations into subjects. There is no mega-trend in the field as no individual subject covers more than 7% of all papers. A broad distribution of topics can be found in the literature dealing mainly with phenomenological reports and to a surprising extent with the derivation and discussion of the “principles” mentioned above. Few papers discuss the mode of operation of selective oxidation based upon *in situ* observations or upon theory covering in a fragmented view only part of a catalytic cycle. The largest subset in citations is captured by vanadium oxide systems, showing also a more-than-average increase in citations and in paper output. A “trend” in citations can be stated for gold catalysts (excluding the CO oxidation literature) driven initially by epoxidation and since 2004 by oxidation of bio-feedstock. Titania as the second most frequently reported-on subject (not shown in Figure 1.1) profits both from the gold rush and the increase in vanadia research where it is used as substrate and co-catalyst. Figure 1.1(c) compares the popularity of the main reaction substrates propane and butane by their normalized citations evolving in time. There is a parallel trend for both substrates, with butane having some periods of excess popularity. These periods coincide with the increase in communication activity seen in Figure 1.1(b), allowing to conclude that butane oxidation seems to be a more attractive topic than propane oxidation as judged from citation behavior. It is stated that the number of citations for propane is more than twice as frequent as the numbers for butane in every year analyzed. The reviewer notes that the distribution of topics in the paper literature does not agree well with technical practice nor industrial needs in the future. Although neither conference contributions nor patent literature are added to the picture, the open literature deals with the subject of academic relevance in far greater intensity (citations) than with hard technical issues. This is in contrast to other areas of technology (semiconductors, materials, automation) where science and technology reflect each other much more closely in open scientific communication.

Figure 1.2 reports the regional distribution of active groups as obtained from the locations of the authors of papers. There is broad worldwide interest in the topic. Three nations contribute over 12% each to the communication production; a group of

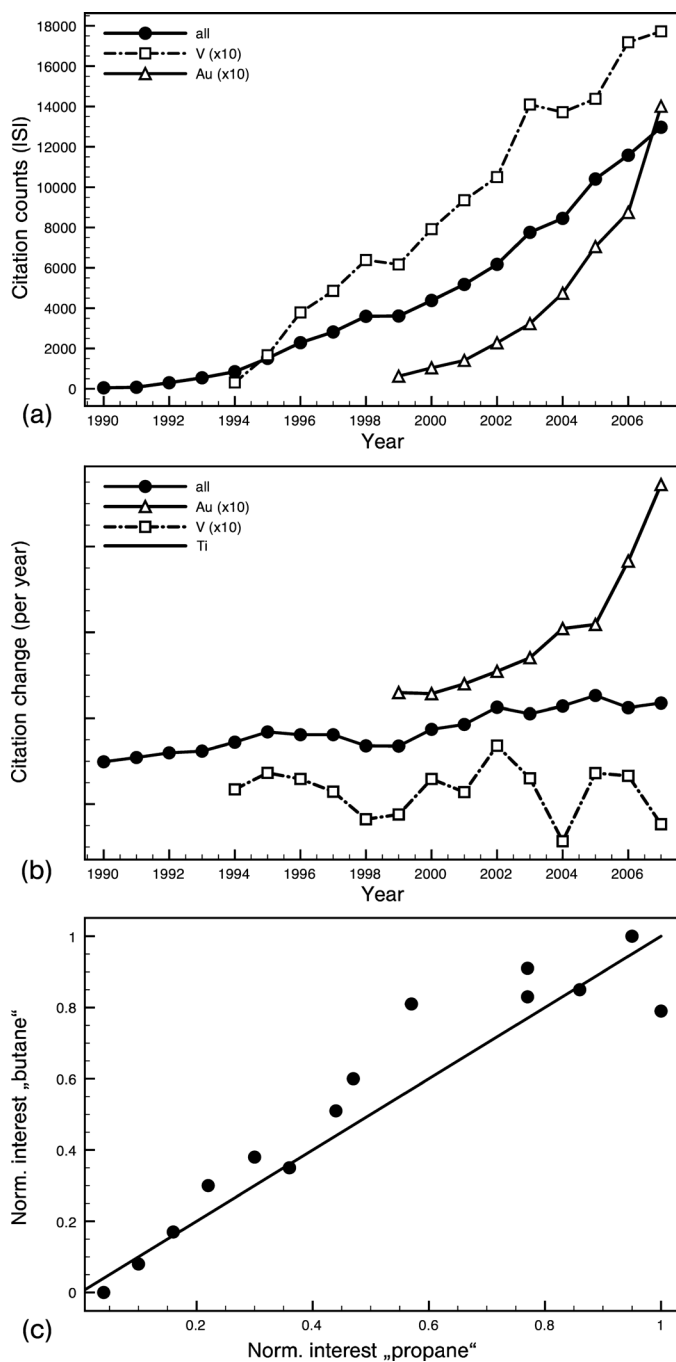


Figure 1.1 Analysis of the scientific literature for selective oxidation.
 (a) Number of citations over time; (b) derivatives of (a); (c) correlation plot for the substrates butane and propane on a normalized scale.

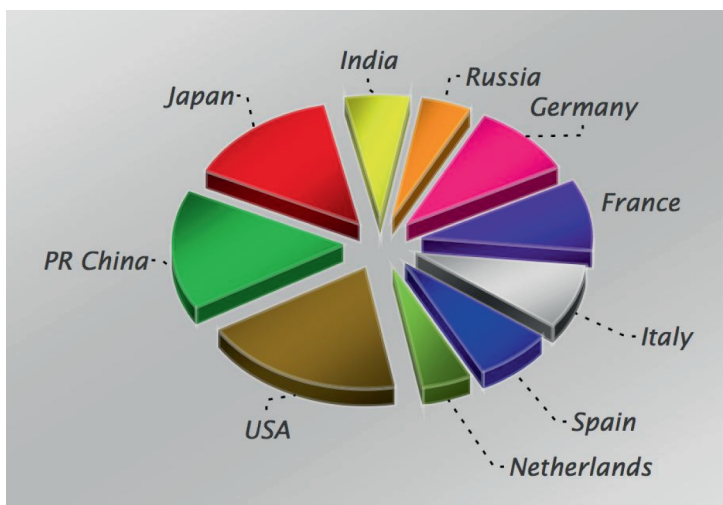


Figure 1.2 Regional distribution of 5300 papers on selective oxidation created from the author affiliations.

seven more nations contribute more than 3% each to the field. It is perhaps no surprise with respect to the technical relevance and resource allocation in the world that Asia is the region of development followed by the USA. If Europe were to cooperate in a common research effort it would outnumber all other nations, an observation that may be surprising given that neither resources nor consumption of the products of selective oxidation coincide with this trend. What would be consistent, however, is the strong support that fundamental science finds in Europe, a direction from which substantial breakthroughs are to be expected in the future.

1.3

Substrate Activation

A fundamental issue in selective oxidation is the activation of C–H bonds that is always required for ODH (oxidative dehydrogenation) and oxo-functionalization and is detrimental for epoxidation. A particular case is silver [70] as catalyst, which can achieve highly selective epoxidation of ethene as well as highly selective dehydrogenation of methanol to formaldehyde although it is notably in both cases “only” the same metallic catalyst. We will return to this case in the next section, which deals with the multiplicity of active oxygen species.

The issue of C–H activation has been addressed many times in the literature. It is common ground to state that the initial C–H activation should be the rate-determining step in the overall process of selective oxidation. This statement can be verified under conditions of proper kinetic studies when limited conversions and small concentrations of reducing products leave the catalyst in its original and active state and when no substantial re-adsorption or site-blocking of products occur.

A prototype study for this issue was performed for the conversion of ethane to acetic acid [71] and the same group highlighted in an earlier comparative study of C_3 oxidation [54] that, although initial propane activation is a difficult step, subsequent reactions associated with either excessive residence times of intermediates or with branching of reaction sequences into total oxidation may interfere with the overall selectivity to partial oxidation products.

On the basis of the general reasoning that selectivity in partial oxidation is limited by the fact that a catalyst capable of activating the first C–H bond of an alkane will also activate C–H bonds of the more reactive products and intermediates, a semi-empirical rule was established [72] linking partial bond strength to kinetic selectivity compiled from the open literature. This approach [45] defines a difference in bond energy between the bond to be activated and the strength of the successively activated C–H or C–C bond. An empirical rule often used in the literature states that promising selectivity can only be reached if this energy difference is less than 40 kJ mol^{-1} . A “universal” curve of many reported observations against the energy difference shows a surprising correlation. The correlation is so surprising as, principally, there is no immediate relation between thermodynamic quantities such as the bond energy of molecules at 0 K and kinetic observations of selectivity of partial oxidations at high temperatures, ambient pressure and not always well-specified conditions. One paper that explicitly discussed the case of propane activation stated that other kinetic factors [72] than the main reaction to the target molecule, such as branching and extended residence times of intermediates and products, can strongly affect the observed performance. The reviewer supports the view that the universal relation of bond energies and selectivity, although seemingly built upon a physical concept (bond strength variations), is merely an empirical correlation rather than a physics-based structure–function relation. However, this view does not deny the usefulness of the relation in discussing kinetic results with respect to likely boundary selectivity that can be expected for a given product.

One of the first studies that shed light on the details of the activation of propane over a single site vanadium catalyst [63] was performed without any a-priori assumptions or speculative geometries [73] of active sites. This was partly possible as the type of monolayer-grafted vanadia catalyst [8, 74] used is one of the best studied systems [54, 75] and it is clearly established – despite some problematic spectroscopic interpretations [48, 76] – that no extended ordering such as oxide crystallites is present in the catalyst’s selective form. Although the work did not model a complete catalytic cycle it clearly shows that under the assumed reaction conditions, including realistic reaction temperatures, an energetically well-conceivable pathway of activation exists that involves an early surface radical structure that converts into propene via either a second activation or an addition–elimination of a hydroxyl species. This pathway was not enforced upon the system but found from a large selection of geometrically possible options and under full consideration of the electronic open-shell character of catalyst and substrate during reaction. The reaction path is redrawn from the data of ref. [63] in Figure 1.3. The paper discusses the transferability of the results for cases of defective bulk oxide systems of vanadium and molybdenum oxides. The only conceivable uncertainty in the selection of reaction pathways

made concerns the absence of co-adsorbates and of solvation by water being present as a required or adventitious component in all oxidation reaction atmospheres.

From Figure 1.3 the first step is the abstraction of one proton, clearly by the action of a vanadyl (possibly also molybdenyl) group. The resulting radical intermediate has four possible reaction pathways that are energetically at least conceivable. The most facile route is abstraction of the second hydrogen through a fresh second group (pathway A). This has the advantage of not having to reduce the vanadium site to oxidation state $+III$ but requires the close proximity of the second site or violates the concept of site isolation. Careful kinetic control of an ODH process or a desired further oxidation would favor such a reaction scenario. Under prevailing site isolation conditions, reaction pathways B–D will also lead to propene with, however, higher energy barriers. Pathways B and C require the participation of a V–O–substrate bond in the reaction and pathway C suggests the production of isopropanol as intermediate, which would be an excellent precursor for deeper oxidation. Pathway D is the most direct route. The resulting intermediate (5) is the same as obtained from pathway B assuming stabilization by water solvation.

The resulting hydrated reduced active site is intuitively the most plausible product. In the literature it is assumed [63] that this species is rapidly re-oxidized. This view is supported by numerous experimental observations and speculative statements [77–82] on various systems but it has never been shown directly that the monomeric species is rapidly re-oxidized. In Figure 1.3 the steps connected by colored arrows deal with re-oxidation; a disproportionation reaction liberates one active site from the dual site pathway A. In any case the reduced species is re-oxidized by a di-oxygen molecule that can only react to give peroxy-species that has been verified to exist [83] on a relevant V(III) vanadia model system. Using *in situ* photoluminescence spectroscopy it was concluded that a highly electrophilic oxygen species, which here would be assigned to a decomposing peroxy group, can regenerate [84, 85] pre-reduced highly disperse vanadium. Regeneration of the active site would require thermal recombinative action of two adjacent sites or sacrificial oxidation of the product, which would limit the selectivity of the overall process to 8/9 of all propene produced if only reaction with the product is assumed to regenerate the active site. Interestingly, a mono-oxo oxidant (N_2O) that can re-oxidize a spent active site without participation of other sites or of additional redox partners gives for highly disperse systems an increased selectivity that was ascribed to an “overall lower degree of oxidation” [80] of the active surface. The structures (4 and 5 in Figure 1.3) allow explaining a direct electronic effect [54] of the support R in the process as the polarity of the support-oxygen bridge to the active V atom will affect the energy barrier for these reaction routes. The alkoxy-intermediates (2 and 3 in Figure 1.3) that react through high barriers are the intuitive starting structures for consecutive deeper oxidation to oxygenates or eventually CO_x . Their participation is frequently discussed [3, 72, 86–88] in the literature and agreement exists that this intermediate is most relevant for obtaining selective oxidation products.

There is no reason to assume that the ODH of alkanes, be it as stand-alone reaction or as initial process for deeper oxidation, will not proceed as shown schematically in Figure 1.3. The problem of re-oxidation of the active site, which has not yet been

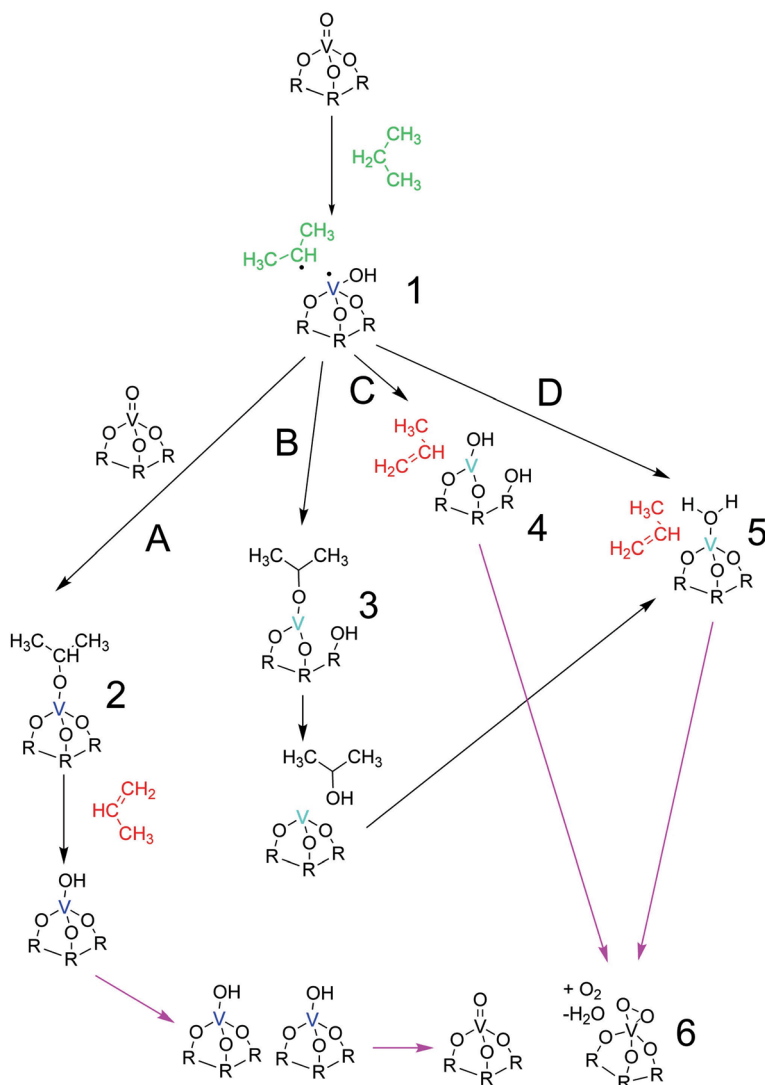


Figure 1.3 Activation of propane on a single-site vanadium oxide system. The figure is redrawn from the results of ref. [63].

treated rigorously, would not occur, however, if one assumed dimers as active sites. On bulk oxides no information about the size of isolated sites under reaction conditions is available. On the monolayer systems [76, 81, 89] some dimeric or oligomeric sites co-exist with monomeric sites. Until a rigorous theoretical study of the mode of operation of such a site has been carried out, the intuitive suggestions displayed in Figure 1.4 may serve to illustrate both the complexity of the reaction pathways and also the possibilities of achieving selective operation without chemi-

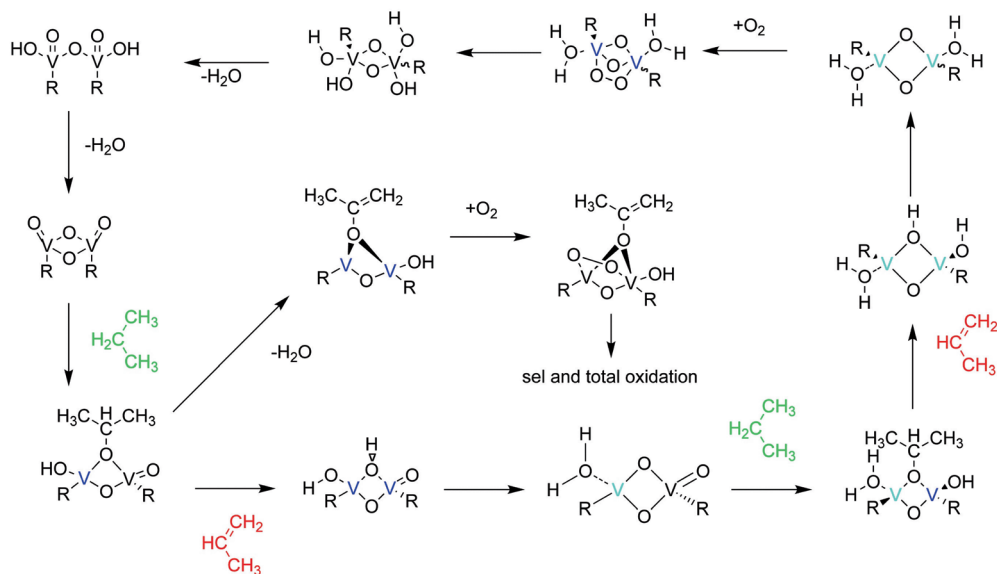


Figure 1.4 Hypothetical sequence of events of propane oxidation on a dimeric active site of vanadium oxide. The steps are extrapolated from the results shown in Figure 1.3.

cally unexpected structures. We know [90, 91] that dimeric sites will be present in an initially dehydrated state at the reaction temperature. They can perform, without mechanistically required losses in selectivity, oxidative dehydrogenation as shown in the outer cycle of Figure 1.4. The dimeric nature allows the active site to accumulate the four electrons that are required for activation of one di-oxygen molecule. Perfect site isolation is conserved in this cycle. It is of course speculative that all intermediates take the form sketched in Figure 1.4. In the presence of a suitable chemical potential of oxygen, the regeneration of the partly reduced site will begin while alkoxides are still attached to the site. This path (center of Figure 1.4) will lead to the creation of a different type of reactive oxygen, being less strongly reduced (more electrophilic) than the oxygen constituents of the active site. Such species are well-suited precursors to react with alkoxides to give oxygenates (aldehydes and carboxylic acids).

The fact that the active site is already partly reduced will diminish its ability (nucleophilicity) to activate all C–H bonds. In this way the oxygen activation on a site that is partly reduced will create a situation in which oxygen transfer can occur selectively without simultaneous activation of many reactive sites at the alkoxide. Obviously, for such a fortunate situation no external regeneration of the active site by lattice oxygen or by withdrawal of electrons to distant electron sinks (phase cooperation) must occur. The concept of site isolation finds in such an interpretation a natural cause: a catalytic site must be constructed in such a way that its electronic structure is allowed to fluctuate between a highly active initial state and moderate consecutive states as the conversion of the substrate molecule proceeds. The site is

catalytic if it is ensured that at the end of the transformation the reactivity of the site is so low that the converted product can desorb, leaving space for electronic and structural reorganization that may be associated with dehydration of the site. This property will be referred to as “adaptive.”

On monolayer oxidation catalysts it is quite possible that a distribution of monomeric and oligomeric sites can co-exist. Such catalysts can perform complex selective oxidation reactions [8, 92–94] without having to rely on multi-element systems. In bulk catalysts such a concept seems more problematic as, despite contrary statements [10, 26, 95], it is incorrect that certain elements of a structural motif are electronically isolated from other elements; active bulk redox catalysts are either metals or narrow band-gap semiconductors and exhibit electronic structures with substantial covalent bonding character distributed over all atoms in the unit cell. A boundary case may be mixed oxides where multivalent metal centers are completely surrounded by main group element oxo groups that would confine the electronic interaction to certain regions of the unit cell. In the MMO systems this is not the case, as anisotropic but extended electronic interactions operate throughout the crystal. Even if these extended interactions are small, in the highest oxidation state of the system they will inevitably increase the filling of metal d-bands during partial reduction upon catalytic action. An exception in the class of bulk catalysts are the heteropolyacid systems being used as partially salified crystalline and stable materials with an electronic structure of a molecular solid [18, 33, 96].

For such catalysts it is postulated that segregation driven by free energy minimization at the termination of the bulk will occur, thereby separating the active surface in a matrix and in isolated embedded sites [73, 97] that are by constitution not dissimilar to metal-oxo clusters present on supported systems. In such a case, one would expect two types of sites competing for reactants: those from the surface matrix without site isolation and those from the isolated active sites. Consequently, one would expect parallel pathways of reaction for selective and for unselective oxidation. The non-isolated sites remain electronically activated through exchange with the bulk and act unselectively. The isolated sites can fluctuate in their electronic structure, so allowing for partial oxidation following the above arguments of the need for adaptive sites to cope with the increasing reactivity of the substrate with progressing activation. Observations about crystal face selectivity [27, 88] need to be taken with care as, unlike in metal single crystals, the fracture of an oxide is not a method [98] for producing a uniquely bulk-terminated surface. The material basis for such a working catalyst is further discussed below.

The oxidation of propane to acrylic acid is a prominent example of where the splitting of the reaction over more than one site is discussed. A literature compilation [72] of data suggests two sites and a competition between partial and total oxidation via direct and intermediate deep oxidation. Data from the same system compiled in Figure 1.5 support this view. In Figure 1.5(a) one observes, under kinetically relevant conditions of below 10% conversion, opposing trends for total and partial oxidation where not only the sign of the trend but also the shape of the curve indicate that different sites and different limiting factors operate in this reaction. The side product acetic acid is also not a direct precursor to total combustion. From a

set of such measurements a tentative reaction network based upon kinetic parameters was constructed (Figure 1.5b). The MMO catalyst is a suitable system as it exhibits a high barrier towards direct combustion of the feed. The selective oxidation path exhibits a kinetically difficult step after propane activation leading to detectable amounts of propene, which is in agreement with the above discussion of Figure 1.3. The difficult step is the oxidation of the activated alkane for which “acrolein” stands only as proxy, as the structure of the real intermediate is unknown. The desired product occurs with the lowest apparent kinetic barriers in the whole network. This observation helps in understanding the finite yield of an activated molecule. The low numbers indicate, according to expectation, that these barriers are “apparent” activation energies and will not allow any conclusion about the rate-controlling elementary step. The overall low productivity of the system may be traced back to a low initial production of activated alkane that is shared by three parallel reaction channels. Re-adsorption and conversion of initially desorbed propene may make a substantial, but in these experiments undetectable, contribution to selective oxidation. Such a scenario is in line with perceptions that more than one active site must cooperate to first create an olefin and then to oxidize it. Also in agreement with Figure 1.3 it is conceivable that, via the intermediate iso-propanol that cannot be detected in the gas phase, further oxidation to the detectable acetic acid occurs, contributing to the CO_x formation.

The present discussion shows that more than one type of activated oxygen operates in the network of alkane activation. Besides the ubiquitous “lattice oxygen” there are alternative concepts of reactive oxygen species that will be described in the next section. A critical material property linking alkane activation and alkane oxidation is that of acidity. Selective oxidation always requires the management of protons, thus calling for carefully designed acid–base properties. This is also advocated in the literature [8, 92, 99–101] but only limited hard information can be found on this difficult issue – hampered severely by a practical definition of acid–base properties on a solid when no redox-active probe molecules [102] can be applied. The concept of initial activation by strongly acidic sites [103, 104] (super-acids) can operate in a homogeneous fluid phase. The often discussed C–H activation of alkanes over solid acids such as zeolites is a complex issue as, often, additional metal species are present [105, 106] or the reactivity is short-lived [107] with radical species involved.

A typical study in which the lattice oxygen issue and the surface acid–base have been compared deals with two model reactions probing C–C bond breaking of methyl ethyl ketone vs. dehydration of 2-butanol [108] over TiO_2 -supported monolayer catalysts. The study, employing mainly temperature-programmed techniques of probe molecule adsorption, found that the lattice-oxygen modifier antimony has simultaneously a strong moderating effect on the surface acidity, thereby highlighting that the two effects are hard to separate. The reviewer notes that the use of the term “lattice oxygen” here differs somewhat from the initial meaning of oxygen atoms diffusing through the bulk as on a monolayer catalyst at around 573 K it would be hard to activate “true” lattice oxygen. The mobile oxygen species detected should be ascribed to adsorbates located at defects of the ideal termination.

In the literature [109] on homogeneous C–H bond activation substantial evidence exists for selective radical activation using nitrogen-containing non-metallic

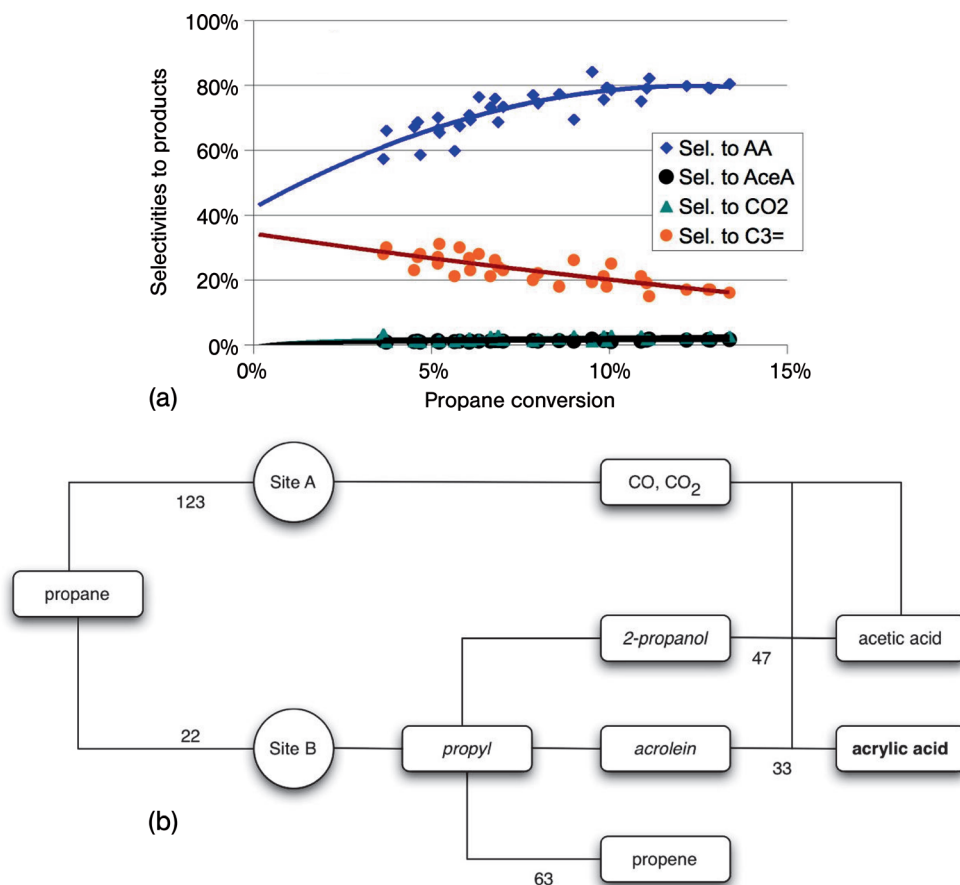


Figure 1.5 Performance (a) and experimentally derived reaction network (b) of a MoVTe catalyst (phase mixture 70% M1, 30% M2 phase, prepared by the slurry method, chemical composition as in the literature) under kinetic conditions ensuring no more

than 10% conversion. A parallel microreactor “Nanoflow” was used and the catalyst was diluted 1 : 1 with SiC. The numbers in the reaction network are apparent activation energies in kJ mol^{-1} . Data kindly provided by S.B. Abd Hamid [32].

catalysts. Such pathways, observed under mild conditions in the presence of moderating solvents, work well with activated alkanes and with strong nucleophiles such as bromine as initial activators. In gas-phase heterogeneous catalysis the participation of such pathways seems less likely, in particular when product selectivity is taken into consideration. There are, however, reports [110, 111] about heterogeneously created radicals performing catalysis in the homogeneous gas phase. This issue, extensively studied with methane activation [112], still needs further careful studies.

1.4

Active Oxygen Species

The extensive and controversial discussion about the nature of active oxygen species may benefit from a separation of two issues: (1) the number and chemical nature of active oxygen species and (2) the location of active oxygen species. The present chapter refrains from reporting again the different views on both issues as this has been done several times in the reviews mentioned in Section 1.1.

Active oxygen species occur through reductive activation of di-oxygen (generally) at catalyst surfaces having to present four free-electrons per oxygen molecule. From this, oxides in their highest oxidation states clearly cannot activate oxygen and, for such materials, defects encompassing lower-valent metal centers need to be present. Successive activation via hyperoxo, peroxy and mono-oxo species renders the activated oxygen consecutively more nucleophilic and less electrophilic with respect to its reactivity towards co-adsorbed organic substrates. For semiconducting oxides the metal sites of oxygen activation become progressively more oxidized. Consequently, the bonding interaction between oxygen and metal site becomes progressively stronger, which is another way of explaining the change in reactivity from electrophilic to nucleophilic. It is important to realize that the gradual adaptation of reactivity with extent of activation occurs only at isolated sites. This interconversion is key to understanding the multiple reactivity of “simple” [87, 113] activated oxygen, which in turn is the key to understanding selectivity in oxidation catalysis. This mode of operation requires pre-formed defects in high-valent oxides and operates at low temperatures. The peroxy intermediate has been well-characterized by surface science [83] both in structure and its reactivity, decomposing in vacuum substantially below ambient temperature. This does not mean that such a species would not be reactive at conventional oxidation temperatures and pressures; its resulting low stationary coverage asks for rapid consumption as an electrophilic species or for a low kinetic probability of the reaction channel. The critical need for defects explains also the observation that catalyst treatments that intentionally create lattice defects [114] seem to be beneficial for catalyst preparation. Studies of the VPO system [115–117] suggest this with a non-uniform picture about the origin and stability of the activation. Several reports on the action of MMO systems [99, 118–121] also clearly find that lattice defects are beneficial for catalytic action [32] and may even be a prerequisite [56] for activity.

The undisputed relevance of lattice defects for catalytic function is, however, often associated with the possibility that reducing gas-phase molecules create active oxygen in an oxide catalyst through defect formation. Active oxygen may stem from the lattice and diffuse to the surface where it undergoes, by recombinative desorption, gradually the same interconversions from initially very nucleophilic (O^{2-}) oxo-anion to the more electrophilic charged di-oxygen species. This process has been observed to exist on oxidation catalysts numerous times with multiple techniques, as reported in the reviews mentioned in Table 1.1. The often quoted [3, 13, 46, 122] unambiguous relevance of lattice oxygen as reactant for selective oxidation in general is, however, to be considered with some reservations. Many studies were carried out

under gas phase conditions with a low chemical potential of oxygen; thermodynamics thus predict a tendency of oxides to release oxygen according to the potential gradient from bulk to surface. Experiments in which pulses of organic feed only or in which reduced pressures (high vacuum) are applied will thus always show the involvement of lattice oxygen [123] and also support isotopic scrambling experiments [4, 33, 71, 124–127] between gas pulses and bulk oxygen. The process of sequential reduction of a catalyst by organic feed followed by a re-oxidation in a separate reactor (riser concept [123]) is a macroscopic proof of this action of lattice oxygen.

The quantification of diffusion processes was a major application of the analytical technique TAP (temporal analysis of product) [80, 87]. An example [128] of the use of TAP experiments at various pressure levels and by studying qualitatively the response function of a complex MMO catalyst can be found in a study of the mechanism of propane oxidation to acrylic acid. The paper relies on temporal evolution curves and draws far-reaching conclusions from the observation of hysteresis loops that can have many different origins other than lattice oxygen participation. The temperature at which such oxygen diffusion sets in will depend on the type of oxide and on the defect status. Densely packed oxides exhibit oxygen diffusion [129, 130] typically above 773 K, whereas typical MMO systems characterized by complex structural motifs with substantial void fractions in their unit cell, and hence anisotropic pathways for oxygen diffusion associated with a non-dalton composition in oxygen [4, 125], do show the onset of oxygen diffusion at about 650 K, a typical temperature for selective oxidation reactions.

If a catalytic cycle should be maintained, oxygen diffusion out to the surface must be complemented by an inward diffusion of surface-activated oxygen resulting from accumulation of reduced metal centers required to activate gas-phase oxygen. Not all studies mentioned here ensured in their experiments that the conditions of “lattice oxygen” catalysis were such as to fulfill the conditions of cyclic reversibility [34, 51, 82, 131, 132] as opposed to stoichiometric and irreversible reduction [133] caused by a structural phase transition. As long as complex MMO oxides are being used and the extent of reduction is kept to levels where no bulk transformation can be detected this condition can be verified [20, 99, 118, 121, 134, 135]. The kinetics of re-oxidation of partly reduced oxide catalysts was found to be rapid [77, 78, 80, 82] and always faster than its reduction.

Nanostructuring [32, 59, 94, 136] and arrays of defects [137] (sheer defects) create a partition into nanodomains of larger crystals, resulting from the typical high-temperature calcination reactions required [19, 121] to form defined phases of MMO. The resulting grain boundaries and sheer planes create pathways [99] for enhanced oxygen transport [56] and thus will support [118] lattice oxygen participation. A suitable structure for lattice oxygen participation is salts of heteropolyacids, where the loose packing of the individual molecules given by the intrinsic size of the Keggin units provides stabilization [138] for defective molecules (lacunary species) and for transport of oxygen to the outer surface. This structural property may be one reason for the enormous and versatile [33] catalytic activity of HPA catalysts in selective oxidation. In contrast, if no long-range structure is present then amorphous [115, 118, 134, 139, 140] oxides may become too strong as donors,

giving rise to excess active oxygen. This will lead to over-oxidation with the resulting energy release triggering re-crystallization of the amorphous oxide and hence causing deactivation; hence there is a clear optimum of defects in a catalyst that seems to be much closer to nano-sized well-ordered entities rather than to highly disordered or amorphous solids.

The enormous body of experimental observations [16, 25, 54, 80, 87, 113, 118, 141–143] on oxygen ion diffusion in conjunction with selective oxidation does not, however, allow us to conclude directly that this oxygen is relevant for catalytic selective oxidation under conditions of an oxygen chemical potential that is equal to or larger than the decomposition potential of the catalyst; such conditions always apply when gas-phase oxygen is co-fed with the organic substrate, and usually in stoichiometric excess over the desired extent of oxidation. The almost general extrapolation in mechanistic discussions of the role of lattice oxygen determined under conditions of under-potential oxygen abundance [123] to situations with oxygen over-potential [141] with respect to catalyst decomposition seems, despite its frequent occurrence, not to be justified. The next section presents a hypothesis that explains the participation of oxygen mobility [141, 144–146] in the generation of active sites rather than in the conversion of the substrate that can equally well explain the experimental observations without having to assume unjustified extrapolations. The reviewer states that lattice oxygen can and does perform selective oxidation and that all preparative steps enhancing oxygen diffusivity can be useful for enhancing catalytic action up to the point where excess lattice oxygen becomes detrimental. All this does not mean, however, that the role of the diffusing oxygen [147] is the same in the two fundamentally different regime of reacting atmosphere with oxygen deficit and oxygen surplus.

Irrespective of how oxygen becomes “activated” there is broad agreement [1, 31, 33, 40, 46, 54, 142, 148–153] that several species of oxygen must co-exist to explain selective oxidation and substrate activation. There is also broad agreement that species may be categorized into nucleophilic and electrophilic with respect to substrates. Theory has ascribed this differentiation to the strength and polarity of the metal-to-oxygen bond. Semi-empirical [143] and quantum chemical approaches [16, 88, 154–156] at different levels have been used to assure the variability of the metal–oxygen interaction as a function of local chemical composition and structural coordination. We can be certain that a substantial differentiation of the metal–oxygen bonding exists on a structurally diverse [1, 5, 131, 142] oxide surface. It is reassuring that today we can state a substantial unification between the concept of heterogeneous sites at oxides and its counterpart on metals [98, 152, 157, 158] as being the relevant locations for catalytic reactivity. Tacitly, the assumption that every site at a surface capable of adsorbing a species can also induce its reaction has been replaced by the idea that many sites adsorb species but few of them react [159–161] the substrates to give products.

Figure 1.6 depicts the fundamental reactivity of nucleophilic and electrophilic oxygen. On oxides we can assign nucleophilic oxygen to strongly bound oxygen with a metal–oxygen bond polarized towards the oxygen atom. Electrophilic oxygen is usually more weakly bound (it has to be if it is to be transferred to a substrate) with

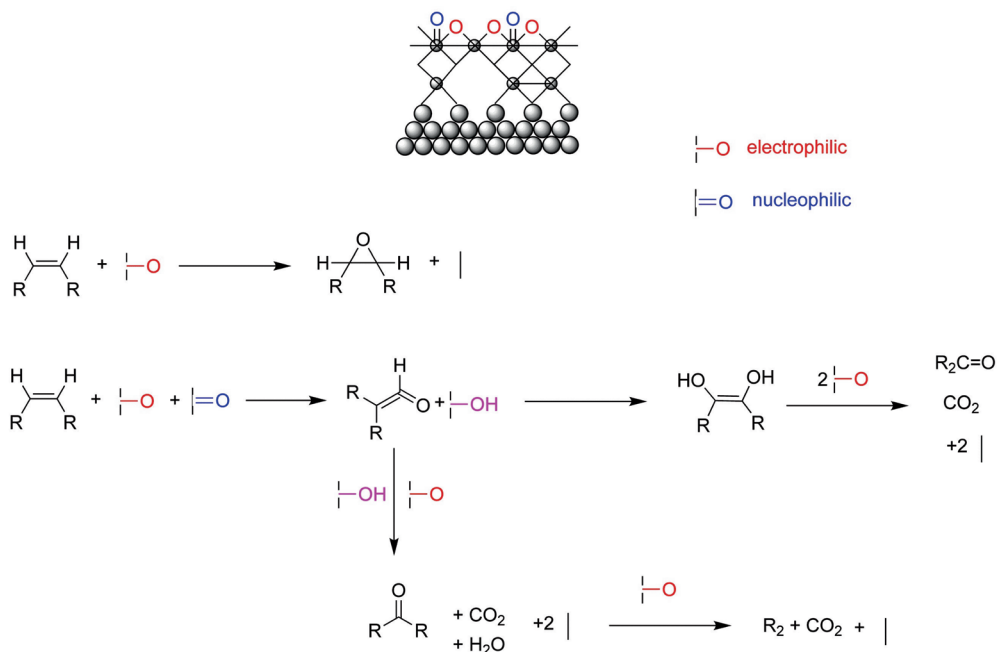


Figure 1.6 Schematic representation of location and reactivity of nucleophilic and electrophilic oxygen. Vertical lines denote active surface sites.

a bond polarization leaving a positive partial charge on the oxygen. The top scheme in Figure 1.6 gives one possible location on a defective oxide surface. The scheme also illustrates that the designation of “lattice oxygen” is not correct as we consider only reactive oxygen that must be site-isolated from the bulk lattice. Semantically a “surface lattice” describes the situation correctly but there is no need to discriminate this location from a chemisorption of oxygen on a defect site (where the bridging oxygen atoms are exposed to the surface) with different charge states of the metal sites. The oxygen species must specifically not be localized as drawn in Figure 1.6 for a situation with low chemical potential of oxygen. In compounds with multiple cation types (MMO) it was suggested that the electronegativity of M in M=O groups would create the bond polarization [77, 162, 163]. Adsorbates with formal O^- electron configurations can be particularly electrophilic [1, 2, 27, 142]. It is not excluded that all three situations co-exist on a complex oxide, thus allowing not for only two idealized oxygen species but for a distribution of reactivity of the prototype “nucleophilic” and “electrophilic”. This serves as the basis for assuming that multiple reaction pathways act in parallel on the same substrate.

The electrophilic reaction pathway leads, with an olefin, to the epoxide and a free site as symbolized in Figure 1.6. A purely nucleophilic site would catalyze oxidative dehydrogenation as discussed above. The frequent case of co-existence of nucleophilicity and electrophilicity leads to selective or total oxidation as seen in

the lower part of Figure 1.6. It is also seen that, in qualitative agreement with the assumed detrimental nature of gas-phase oxygen leading to weakly bound O^- , it is the kinetic availability of electrophilic oxygen that determines the selectivity to partial or total oxidation. The central quantity in designing selective oxidation catalysts is thus the control of the kinetic availability (local chemical potential) of weakly bound oxygen during a catalytic cycle.

This has been frequently recognized and the challenge arises of determining the chemical reactivity and surface abundance of activated oxygen. The usual solution of this problem is the application of an isotopic exchange reaction and kinetic analysis, as TPR/TPO cycling does not discriminate between labile reactive and labile non-reactive (sub-surface) oxygen species in a polycrystalline sample. Several studies on monolayer oxide catalysts [144, 164, 165] and on bulk phases [126, 166, 167] have revealed [147] that, depending on the redox potential over a sample, molecular (electrophilic) or atomic (nucleophilic) isotope exchange can occur. In the literature it was not made sufficiently clear that it is not the type of catalysts, as assumed, but the quantity of the oxygen chemical potential (temperature, redox state, defect state, partial pressure in gas phase) that controls the type of isotopic exchange. As the chemical potential is hard to determine with catalytic processes, one observes material discriminations [147] that are only “snapshots” of a common reactivity pattern detected under not-comparable potential conditions (usually only the gas-phase pressure is considered).

In this situation it is desirable to have other means of identification examining the nature of active oxygen. The standard surface-science tool [168] for this would be temperature-programmed desorption (TPD) or temperature-programmed reaction [169, 170] with probe molecules (CO for electrophilic oxygen, methanol for nucleophilic oxygen). A recent case study with RuO_2 as model catalyst showed that X-ray photoelectron spectroscopy (XPS) at high resolution [171, 172] can directly resolve the two types of functional oxygen even when located on an oxide bulk. These studies rest in their interpretation on a large body of data [52, 70, 166, 173, 174] that discriminate on metallic silver the reactivity of activated oxygen for either ethylene epoxidation (electrophilic) or methanol dehydrogenation (nucleophilic), both reactions of technical relevance.

Photoemission and TPD are excellent tools for analyzing activated oxygen as they can give information on the reactivity and on the quantification of the atomic oxygen species. On oxide surfaces it is, however, difficult to discriminate the active species from the lattice oxygen. It is to be expected that only a fraction of the surface holds the reactive oxygen, translating into a sensitivity problem as only a small percentage of the whole signal can be expected to carry the relevant information. By profile analysis alone it is almost impossible on a high-performance catalyst to find the reactive oxygen. Figure 1.7 shows how by applying *in situ* techniques one can prepare the catalyst surface such as to allow for the identification of reactive oxygen. Figure 1.7(a) shows the high-resolution synchrotron difference XPS spectra of a VPO catalyst [175–177] in two states of productivity. The *in situ* oxidation of butane was performed at 473 and at 673 K, marking the onset and maximum, respectively, of stable catalytic production of maleic anhydride. The difference spectrum between

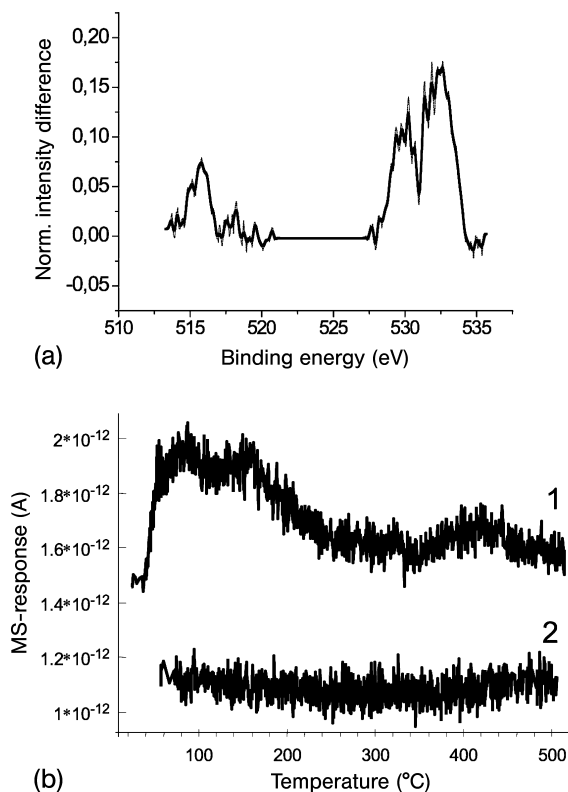


Figure 1.7 Active oxygen on a working VPO [175] catalyst. (a) XPS *in situ* difference spectra between phases of low and high performance. (b) Oxygen TPD spectrum after preparing the surface of polycrystalline VPO by *in situ* butane oxidation.

the two states reveals the species that are more prominent at the surface when high productivity is observed. In the region of vanadium 2p 3/2 we see a signature for vanadium + III with an abundance of less than 3% of that of the main vanadium content. In the oxygen 1s region we observe two features consistent with electrophilic oxygen (530 eV) and with water or phosphoric acid (533 eV). As we also see, constantly, a small excess of phosphate over its bulk stoichiometric value we would state that reduced vanadium, electrophilic oxygen and segregated phosphate are the signs of a working VPO catalyst. This is consistent with the observations from *in situ* TPD shown in Figure 1.7(b). Only after equilibrating and performing the butane oxidation *in situ* was it possible to study the presence of the relevant reactive oxygen; in cases where unreacted samples or pre-evacuated samples were used, much larger signals were found that relate to bulk-diffusion of oxygen as they will not disappear upon repetitive TDS heating cycles. Reaction-prepared VPO shows two signals at low and high temperature (trace 1 in Figure 1.7b), both of which are only present as surface species as repeated heating (trace 2) removes the signal. The

assignment to electrophilic (labile) and nucleophilic (stable) oxygen is tentative but the fact that desorption of the nucleophilic species coincides with the reaction temperature and the knowledge that both species can be found by spectroscopy [155, 175] lend some support to this interpretation.

The recent enormous progress in preparing and studying surface science qualities of relevant systems [178–180] such as vanadium oxides plus their defects has given further clear evidence that electrophilic weakly bound oxygen [83] as well as more stable defect-related oxygen [48, 181–183] do exist and exhibit a reactivity much in parallel to high-performance catalysts of the monolayer type [184, 185].

One of the most significant results from the advent of these surface science studies on oxides relevant for the present catalytic applications is the fact that oxides can be multiply terminated and that they are not terminated [154, 180, 186–190] in cuts through the bulk structure. This is not unexpected in general [98, 156, 179] but it is of great value to know this in attempts to understand the mechanisms that activate oxides for catalysis. These rigorous studies must be differentiated from more empirical studies carried out on termination issue with qualitative methods and without predictive power but with the still invaluable advantage that they can be applied [97, 191–193] to complex MMO catalyst systems. Such studies can be used to probe the surface reactivity, to address the issue of segregation of, for example, vanadium out of an MMO system and to compare different qualities of the nominally same material with speculative assumptions about the influence of defects.

As a function of the chemical potential of oxygen (partial pressure, reductive adsorbates, water, sticking coefficient, surface defects) “simple” oxides such as the transition metal sesquioxides (M_2O_3) can adopt different [194] and eventually co-existing terminations. At high potential, prevailing under conditions such as the air calcination used in synthesis under practical pressures of oxygen, such oxides are always terminated by a metal–oxygen double bond (“-yl group”) irrespective of their bulk formal oxidation state. This seems to hold also in cases when such compounds do not exist as three-dimensional bulk structures. As the oxygen chemical potential decreases, defects in the -yl termination occur, allowing rearrangement of the local coordination and binding of hydroxyl species. At even lower potential a metal-terminated surface is most stable, allowing the binding of molecular oxygen [83] and other electrophilic species. These surfaces are quite different from the expected geometry of a bulk-cut and can produce complex and also metastable surface structures.

For the present discussion it is obvious that extended surfaces of oxides in contact with practical pressures of oxygen will be inert for catalytic reactions as the surface exposes essentially oxygen electronic states and gives no access to metal d-states carrying electrons for chemisorption and activation of adsorbates. Structural defects such as steps and kinks (“roughness”), chemical effects such as pre-reduced sites or “designed” weak spots in a complex structure such as main group element atoms [26, 195, 196] in a transition metal ion matrix are pre-requisites to initiate catalytic [197] reaction. Only then can the organic substrate redox chemistry discussed above generate the stationary concentration of reduced (defective) sites [1, 114, 131, 162, 178] required for steady state operation. The kinetic barrier at which

such a steady state defect formation will occur depends substantially on the state of long-range ordering: a nanocluster of oxide with almost no translational ordering of its “surface” will adjust much more quickly in its termination according to the gas-phase potential than a semi-infinite (micron) sized well-ordered crystal face [16, 182, 190, 198] often seen in VPO or MMO catalysts.

1.5

Catalyst Material Science

Selective oxidation materials fall into two broad categories: supported systems and bulk systems. The latter are of more practical relevance although one intermediary system, namely vanadia on titania [92, 199–201], is of substantial technical relevance. This system is intermediary as titania may not be considered an inert support but rather as a co-catalysts [202] capable of, for example, delivering lattice oxygen to the surface. The bulk systems [100, 121, 135, 203] all consist of structurally complex oxides such as vanadyl phosphates, molybdates with main group components (BiMo), molybdo-vanadates, molybdo-ferrates and heteropolyacids based on Mo and W (sometimes with a broad variation of chemical composition). The reviews mentioned in Table 1.1 deal with many of these material classes.

The fact that most supported catalysts, in particular with refractory oxides, are not as efficient in selective oxidation as bulk systems is circumstantial evidence for the necessity of having a bulk delivering lattice oxygen to the active surface. Supported systems have only their “surface lattice” oxygen; however, as discussed [54, 71, 75], the electronic structure of the support will influence substantially the redox chemistry and thus the surface lattice oxygen availability of the active component. Studies comparing catalytic functions of such systems to be carried out with great care, as it is not clear that different supports always hold the same structure of the active oxide although this was strongly [204] suggested. The chemistry of metal oxide supports considered as large ligands is sufficiently different that it is not likely that even when the same synthesis method is applied one will obtain the same [76] active structure. The option of designing the support as oxygen delivery system [205, 206], which is possible with, for example, titania, ceria, zirconia and their mixtures, is counter-affected by the tendency of these supports to react with the active surface phase and form multinary compounds (e.g., spinels and perovskites) that are often difficult to identify due to their low average abundance.

On classical systems of vanadia [53] on silica and alumina the principle of site isolation [8, 47, 74] is easily fulfilled with adequate loadings of active component. In MMO systems this is much more difficult, as the electronic structure of these oxides is not that of a salt with separated anion and cation electronic interactions but is highly covalent with electronic states connecting all participating atoms [16, 190, 198, 207], in particular when the catalyst is slightly reduced [208, 209] such as when in contact with an organic feed (also when containing oxygen gas).

Bulk materials used as oxidation catalysts not only allow for oxygen transport but also accommodate a wide and homogeneous modification of their electronic

structure, ranging from wide-band semiconducting highly oxidized states with electronic formally d-0 states at the metal centers to a broad range of narrow-band semiconducting materials with d-*n* states at the metal sites. The result is a tunable electronic structure with the provision of chemically reactive electrons at or near the Fermi edge. Their concentration will depend on the extent of reduction that can be formulated as the effective oxygen chemical potential given by the reductive power of the organic substrate present under catalysis conditions. This tunability is designated as “adaptiveness”. No statement is made as to whether this tunable electronic structure that we can detect is accompanied by geometric structural transformations such as defect structures [34, 82] and their order varieties. As indicated above it is thus suggested that the site isolating properties of a supported system and the adaptiveness of a bulk MMO system can be combined in the concept of a self-supported catalyst.

Figure 1.8 presents an example of such adaptiveness for a simple reference system, namely V_2O_5 . A single crystal was studied by *in situ* XPS at various pressures of oxygen [175] at 673 K, a typical operation temperature of a MMO catalyst. Figure 1.8(a) reveals the quantitative analysis of core level spectra. With synchrotron XPS we can perform [210, 211] non-destructive depth profiling and study the surface and sub-surface regimes separately. The depth calibration is only semi-quantitative as the electron scattering will change with changing valence electronic structure of the sample. It can be seen that the surface stays stable in its chemical composition whereas the sub-surface regime loses some oxygen in accordance with the lattice oxygen concept. This implies that the oxide surface is structurally stable [133, 183, 212] and yet transmits oxygen from the bulk into the gas phase without significant kinetic hindrance. The high structural stability is expected from theoretical work [16, 131, 188] showing that creation of surface defects in an ordered oxide is a energetically very costly process that will not happen by thermal action except for “compensation” by a chemical reaction (such as water or CO_2 formation). An estimation of the extent of oxygen transport along the gradient perpendicular to the surface can be judged from the time evolution of the oxygen loss. The consequence of the lost oxygen must be a reduction of the oxidation state. It can be seen that the bulk approximates the expected value of 5.0 almost too accurately whereas the surface is defective, as derived from the slightly reduced value. The fact that the outer surface is enriched in oxygen with respect to the bulk value and that we do not lose this oxygen indicates a restructuring with vanadyl species as the reason for the stability. In agreement with single-crystal experiments [180] the oxidation state of the vanadium reduces to lower values without losing these vanadyl species, in disagreement with chemical intuition expecting a loss of $V=O$ (+5) through thermolysis. Within expectation, the extent of reduction of the vanadyl-stabilized surface is faster than that of the bulk which is buffered in its local electronic structure through the site-interacting chemical bonding. The result of the process studied will be a chemical heterogeneity in two dimensions, a patchy surface of vanadyl groups on a sub-surface of strongly reduced vanadium with a gradient back to a, on average, weakly reduced bulk.

In Figure 1.8(b) the spectroscopic consequences of the heating in various chemical potentials of oxygen can be seen directly. The reduction causes a donor state band to

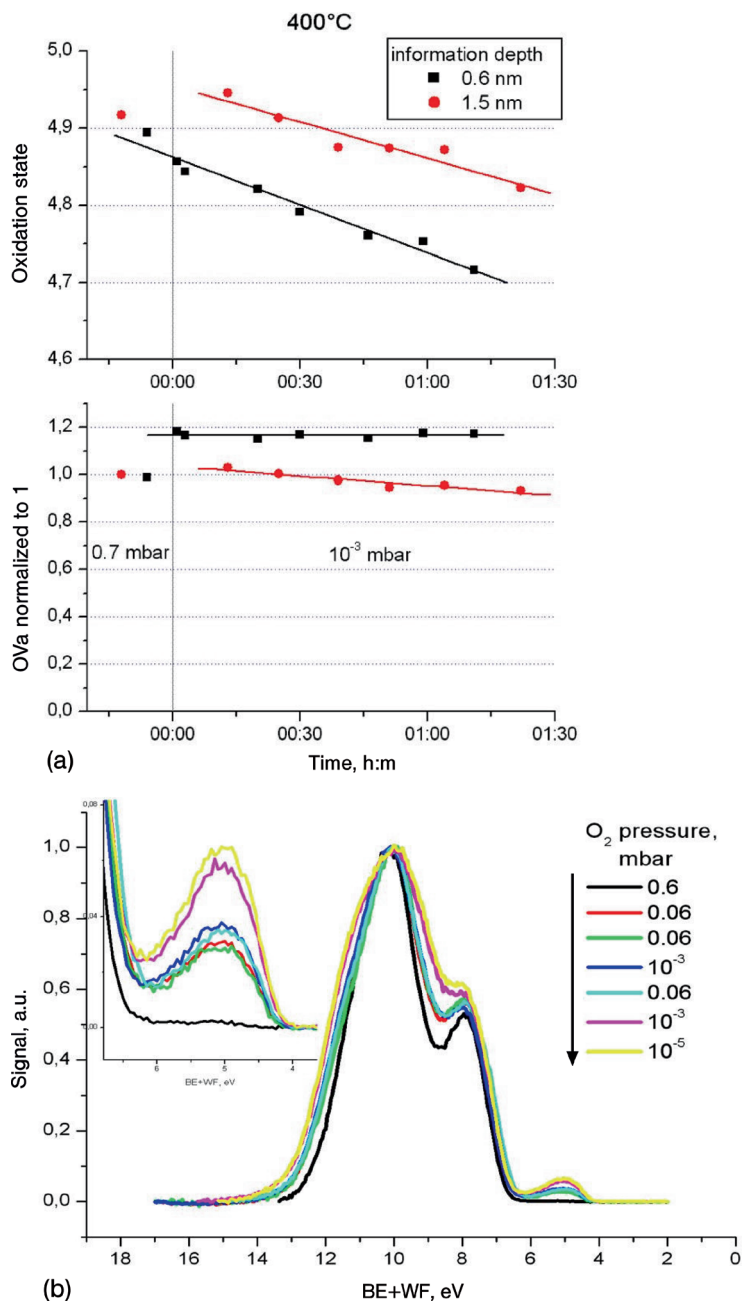


Figure 1.8 *In situ* XPS data of a single crystal of V_2O_5 (basal surface orientation) heated under different oxygen partial pressures. (a) Quantification of XPS data obtained at two levels of depth information during constant heating of the crystal at 673 K. (b) Valence band XPS data as function of oxygen partial pressure at 673 K. For experimental details see Figure 1.7 and text.

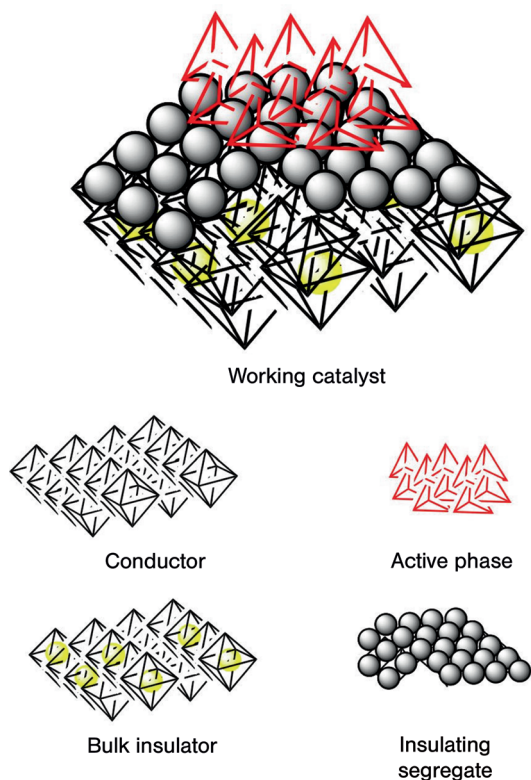


Figure 1.9 Schematic representation of the microstructure of a working oxide catalyst for selective oxidation.

fill the gap of states above the valence band of the (transparent) parent crystal. Only at high oxygen potentials is this structure stable. In agreement with the adaptiveness, the filling of the valence gap with (predominantly [182, 198]) V 3d states increases with a gradual reduction of oxygen potential (achieved in this model experiment by lowering the pressure). The gradual reduction also causes a change in the geometric structure, forming ordered or disordered sub-oxides [87, 133, 139, 183, 184], much in agreement with observations on VPO catalysts [56, 213–215] discernible by spectroscopy at the surface in the change of the shape of the main valence band transitions.

We propose as target material property for a working selective oxidation catalyst a particular microstructure as presented in Figure 1.9. The general type is always “supported,” whereby the support for bulk catalysts is the whole of the prepared material indicated in the figure as “bulk insulator.” As this phase is multi-component, at the surface we expect that segregation will occur driven by the tendency to minimize the free energy. A conducting oxide will separate from a mobile segregate. In VPO catalysts this could be a pyrophosphate with a mixture of vanadyl phosphate (as most stable phase) as bulk insulator and a V_xO_y thin layer as conducting

oxide plus some free phosphoric acid (to account for the compositional and electron balance) as mobile segregate. In other classes of MMO systems bismuth, antimony and tellurium carry the function of the mobile segregate. In Figure 1.9 it is assumed that the active component (a cluster of M_xO_y) is separated from the conductive layer by the segregate, to which the function of site isolation agent is assigned. In this picture the synthesized non-activated pre-catalyst is support and reservoir for the active phase. A microstructure of working catalysts as depicted in Figure 1.9 would explain the enormous sensitivity of the catalyst material to its activation and equilibration [95, 137, 141, 148, 150, 176, 216] conditions and the role of structural promoters [55, 213] (limiting the surface segregation against complete conversion of the pre-catalyst into several phases under harsh reaction conditions). Furthermore, the success of a supported catalyst in mimicking bulk catalyst performances would be logical [8, 74, 84, 85, 94, 154, 217–219] as both types are derived from the same fundamental building principle but represent different material realizations.

Evidently, if a pre-catalyst can undergo a material transformation as indicated in Figure 1.9, there will be a high tendency to stabilize the system through crystal growth into phase-separated stable components such as binary oxides. We have to assume that this also will be happening in proportion to the performance, as catalysis will provide the energy source driving the transformation. This simple concept can explain the experimental observation of the apparently beneficial character of several phases cooperating in a reaction: the detection of a phase mixture with the extent of mixing being proportional to the activity is an indication of the progression of the transformation of the initial single phase pre-catalyst via its active state into a deactivated multi-phase form. The concepts of phase cooperation [57, 220, 221] and of remote control [13] would find as correct experimental observations their explanation as post-mortem analysis artifact. The literature has to the knowledge of the author no report of the beneficial effect of phase cooperation witnessed by *in situ* functional analysis, which would contradict the hypothesis put forward of phase cooperation being a proxy for structural dynamics.

The fact that catalysts have a long lifetime in contrast to the estimated stability of oxo-clusters held on segregated oxides or on supports calls for a living catalyst, that is, for a concept in which this adaptive site will be regenerated during catalytic operation. This idea was formulated during *in situ* structural studies [138, 139] of HPA salt catalysts; the beneficial role of water addition [33, 162, 222, 223], despite its site-blocking function, was partly ascribed to its action [33, 96, 224] as co-catalyst for the structural regeneration at comparatively low temperatures of operation. An element of structural dynamics was also seen in the activation sequence of VPP catalysts [148, 150] and again water addition [225, 226] is an important factor here. One product of VPO activation is phases of $VOPO_4$ that exhibit a very rapid phase dynamics that are strongly, and unexpectedly, affected by the chemical potential of hydrocarbon [132] species. Other authors have advocated [162, 214, 227, 228], in attempts to describe the molecular nature of active sites at VPO systems, some elements of transformations leading to structures that differ from cuts through the bulk crystal structure.

The author suggests considering working catalysts for selective oxidation reactions as dynamic materials. By this term the ability of the pre-catalyst to transform gradually into a surface microstructure producing site-isolated active sites is controlled by the chemical potential of the reagents. The activation is thus different from a normal (surface) phase transformation [229] as it follows in its course and kinetics not only the potential and energy gradients given by the solid material. It is rather the combination of adverse influences of oxygen and water on one side and hydrocarbons on the other side that control the structural result [132] and the kinetics of the transformation process. In this way a solid state conversion is achieved, orienting its progression on the effectiveness of the catalyst in responding to the surrounding chemical potential: bad catalysts will either transform rapidly into the deactivated forms or will not start in their transformation. Good catalysts will quickly start the transformation but then progress only gradually to extend the lifetime of the active microstructure as intermediate.

This definition of catalyst dynamics, being more precise than suggestions of a “living” catalyst quoted above [148], needs to be discriminated against other perceptions of catalyst dynamics. First, in other oxidation reactions catalyst dynamics defined in the above way have been observed by forcing temporal conversion patterns with profiles of chemical potential; the action of lattice oxygen was made observable in oxides and metals [152, 206]. The structural dynamics were studied in Mo-V-W systems [126, 134] by changing the abundance of stabilizing cations and observing the effect on catalytic performance. In a review on *in situ* structural studies of high-performance catalysts [161] the relevance of structural dynamics in the above sense, with the proof of reversibility, was put forward for a metal-on-oxide support system. The still rare observations of material dynamics [82, 230–234] in chemical oscillating reactions are inspired by the work of kinetic oscillations seen in surface reactions under controlled conditions [235, 236] that are special cases of reactor oscillations [237–240] seen in studies of oxidation processes.

Catalyst transformations seen in complex selective oxidation catalysts are irreversible within the conditions of catalyst operation: they may be reversed with the addition of special agents such as high water pressures and/or oxygen but such effects have not yet been studied systematically. The operation of a riser reactor [123, 241] also requires reversible transformation of the catalyst, being discharged and re-charged with active oxygen in much the same way as a battery. The transformation affects the whole bulk of the material and occurs on forced timescales of minutes. This kind of oxygen pumping is well known [206, 242, 243] from combustion catalysts but will in most catalyst systems not be sufficiently controllable to achieve selectivity as the combined solid-state and reaction product control of the process is not operative in these systems trimmed for storage capacity.

The concept of structural dynamics is clearly demonstrated in the VPO catalyst system. The high-resolution TEM in Figure 1.10 shows an activated VPO catalyst (no promoters, made by the alcohol route) that exhibits a typical [215, 225, 244] termination with little structural order supported on a perfectly ordered crystal consistent with the pyrophosphate structure (and with other structures of the VPO family [245, 246]). The lack of long-range order is not seen due to the operation

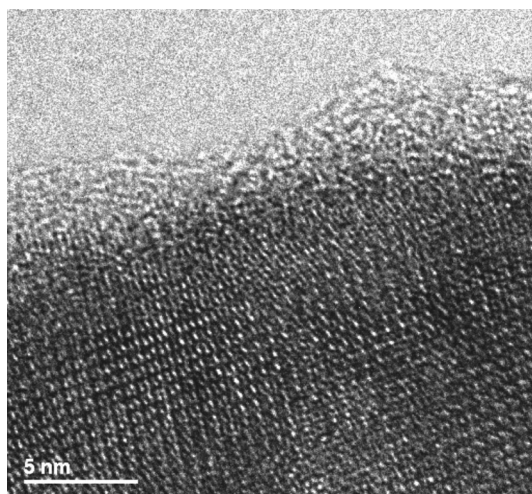


Figure 1.10 TEM image of a VPO catalyst (no promoters, prepared by the alcohol method after 100 h equilibration in feed); as 200 keV electrons at a low dose of below 10 A cm^{-2} were used the beam damage can account for only approximately half of the overlay seen above the (100) lattice image of VPO.

of an amorphous [244] active phase that is not the consequence of TEM artifacts, which tend to superimpose on this termination feature by thickening the disordered boundary layer. The poor surface ordering is the consequence of the metastability of the microstructure depicted in Figure 1.9 after cooling and transfer in uncontrolled atmospheres: the disorder is seen as the consequence of the decomposition of the active phase. Similar terminations [19, 32, 116, 133] were also seen on other MMO catalysts.

The author regrets that only limited discussion [115, 118, 137, 140, 201, 244, 247, 248] about termination issues in high-performance catalysts can be found in the literature, which may be due to difficulties in observation. There is no common conclusion about the effect of amorphous structuring as no clear distinction is made between surface disorder being not an artifact of observation (“good”) and bulk amorphousness as lack of crystallinity of the whole material (“bad”). The model catalysts community is much more advanced here and we can learn that highly ordered surfaces exist with chemically stable terminations of the -yl type; when the model systems are made reactive, massive reductions (by sputtering or electron irradiation) need to be applied [178, 235] that destroy the long-range structural ordering of the model surface. These observations are fully consistent with experiments describing the catalytic dehydrogenation of ethylbenzene to styrene over model MMO iron oxide surfaces [68] where with the onset of reaction a complete loss was documented of the long-range structural ordering.

The application of *in situ* surface analysis has given some experimental hints [155, 175–177, 244, 249] on the operation of material dynamics in working VPO

catalysts. Both XPS and XAS have been applied as detection methods for discriminating the chemical state of the reacting surface from the bulk. The whole catalyst material [132] also undergoes structural transformations [101, 102, 139, 214, 225, 250] as seen, for example, in Figure 1.9 with a less reactive sample than VPO. The TEM observation shows that the active surface without any beam damage is about 1 nm thick and thus surface analytical tools need to be used that give information about this volume as otherwise substantial differences between the active surface and the underlying bulk might not be detected. Using surface-sensitive XPS [210, 251] the evolution of the phosphate coverage was studied for the same pre-activated VPO sample [175] as employed for Figure 1.10. With heating under reaction conditions at a total pressure of about 1 mbar the phosphate became mobile and was lost with a time evolution shown in Figure 1.11(a). The presence of reducing or

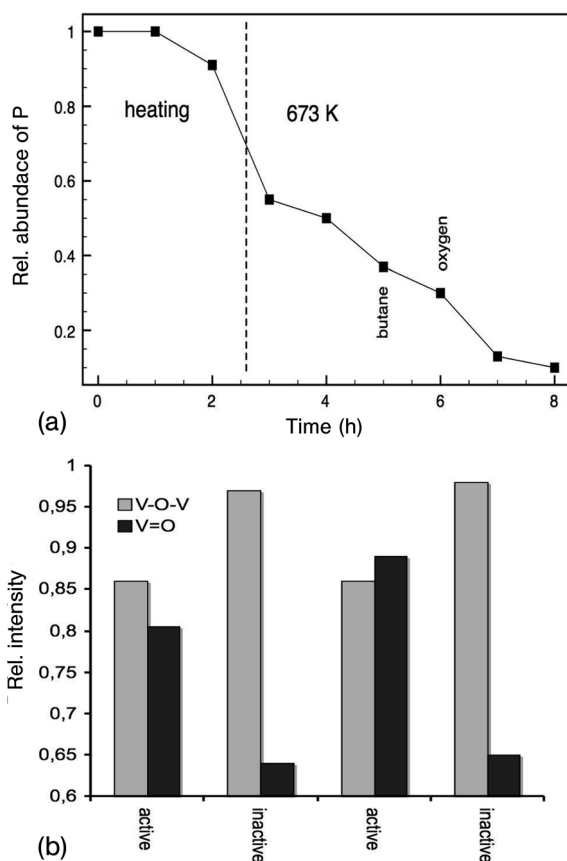


Figure 1.11 (a) Loss of phosphate from a VPO catalyst (see Figure 1.7) during heating in feed and at instances of pure oxygen or pure butane. The total pressure in the XPS chamber during *in situ* XPS was 0.22 mbar; production of MA

at steady state was ensured. (b) Evolution of integrated intensities of characteristic features for V—O—V and V=O bonds from V_{LIII} edge XAS spectrum as function of the operation and inactivity of the surface: for details see ref. [155].

oxidizing atmospheres had, under the mild conditions of the experiment, a small but not decisive effect on the evolution. We conclude that phosphate is a mobile species under reaction conditions. The substantial loss of phosphate is partly attributed to the low total pressure of the experiment and considered in its extent as an experimental artifact. The graph demonstrates, however, that within short timescales enormous re-distributions of phosphate are possible. This was held responsible [252] for the generation of either active or selective surface active layers on bulk VPO catalysts. This work uses the general approach of forcing the evolution of the structural dynamics by changes in the chemical potential of the gas phase. With the limited pressure of the *in situ* XAS experiments [155, 177] it is more practical to change the potential by the surface temperature rather than by the pressure. Figure 1.11(b) displays the result of such a forcing experiment whereby every episode was kept at steady state for 2 h. Characteristic signatures of the two bonding entities V-O-V and V=O were detected and followed in position and relative intensities with the forcing of the catalytic function. Clearly, there is a correlation of the intensity evolution with catalytic function. The convergence of relative intensities can be seen as an indication that the local electron density at V=O is reduced during operation whereas the electron density at the bridge site is enhanced. Both observations are in good qualitative agreement with the mechanistic expectations discussed with Figures 1.3 and 1.4. In the non-operating state the electron densities, as indicated by the XAS intensity changes, fit more to a fully oxidized V=O site and a more electron-rich V-O-V entity whose M-O bond distance (about 175 pm), as determined from the absolute energy position relative to that of V₂O₅, is much longer than expected [253] in the VPO structure.

Based on our experimental information and the consistent opinion of the literature that VPO is a bulk pre-catalyst that undergoes transformations at least in the surface-near volume into an active phase that is not identical with the projections of the bulk VPO structure to its terminations, we attempt to construct a diagram highlighting the elements and its interrelations that control this vital process. The complexity of the situation acknowledged in the literature is apparent from the complexity of Figure 1.12. It is thought that all known facts can be accommodated by the reaction network of Figure 1.12, which represents a “wiring diagram” of butane oxidation. It is different from all previous attempts to analyze the situation as it deliberately links the surface chemistry with its gas-phase controls to the solid state chemistry with its controls via real structure (nano-size, defects, compositional fluctuations). The linkers are the products H₂O and MA, which exert quite different and adverse effects. For simplicity, the energy flow and its enabling functions are omitted from the diagram. The obvious fact that an explanation of the catalytic operation without its controlling influences on the nature of the active sites here is impossible manifests the “gap” phenomenon [254] encountered in many metal-catalyzed reactions when surface science data (deliberately omitting the material chemistry) are used to predict catalytic performances.

The central shaded part of Figure 1.12 describes the catalytic operation of active sites. These are considered as isolated sites of a cluster of vanadium oxo species (Figures 1.3 and 1.4). They are adaptive in the sense that they need first to be activated

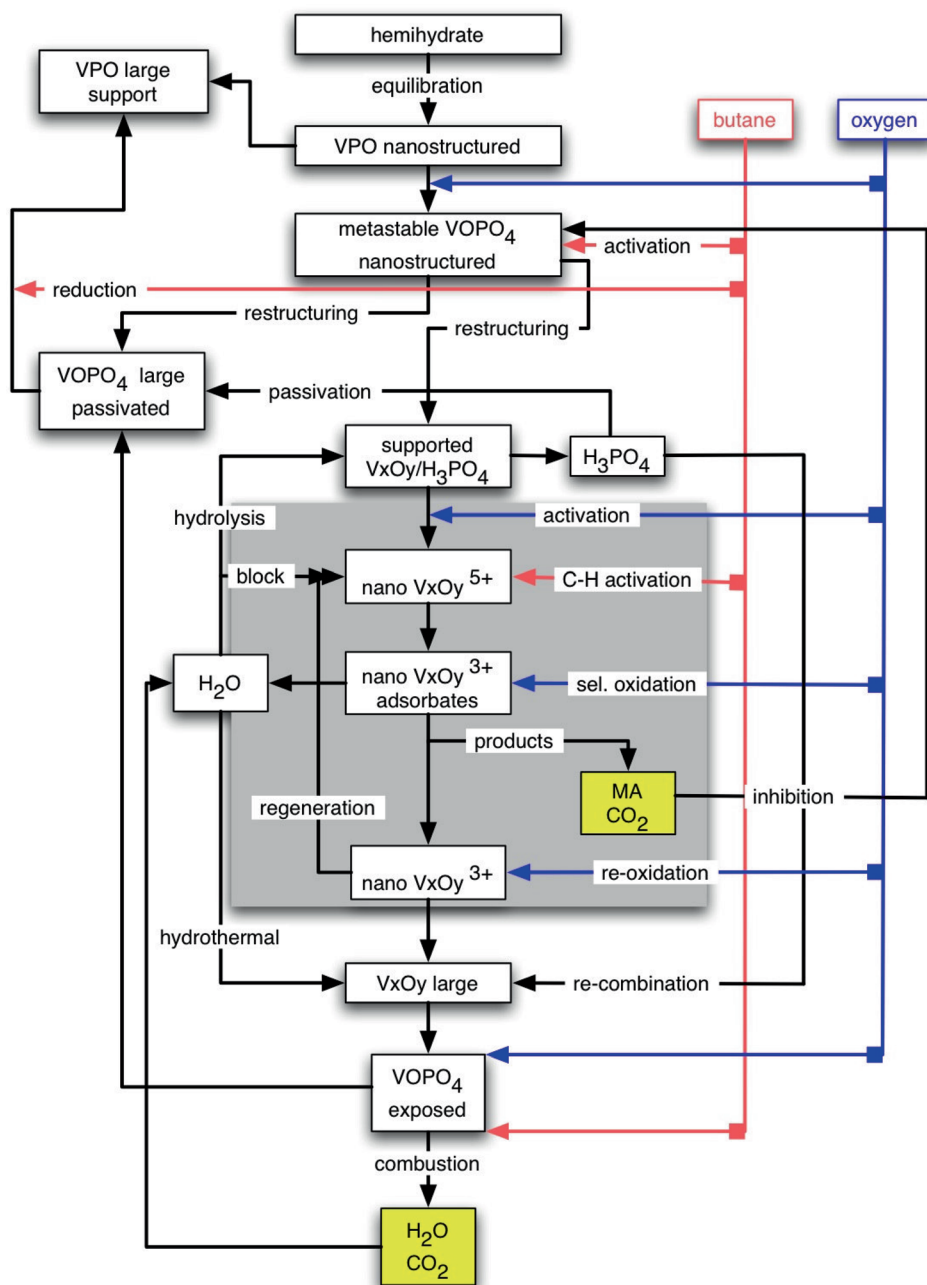


Figure 1.12 Wiring diagram of the mode of operation of the VPO system under steady state operation. The central shaded part represents the catalytic operation, the outer parts highlight the complexity of the structural dynamics creating a steady state abundance of isolated active sites.

(oxidized) to react with the alkane, producing strongly adsorbed intermediates that are successively oxidized on the same site which being, however, partly reduced and thus becomes less active in C–H activation. This adaptiveness, for which the oxidation states in Figure 1.12 are only proxies, resolves the problem of having to deal with consecutive reactions on increasingly reactive substrates and still conserving selectivity. The intensive discussion about the “right oxidation state” [255, 256] can be resolved by the fact that on the supporting tetravalent pyrophosphate small amounts of $5+$ and $3+$ species coexist; their relative kinetic stability is different from that of the support, giving, upon careful analysis, rise to the often reported slight deviation from the tetravalent state. It is conceivable from the literature reports that attempts to clean the surface for an intended accurate analysis [192] may have destroyed all active sites and thus giving rise to the conclusion that the best catalyst is purely tetravalent; the preparation has brought about the pure precursor of the system. For the central issue of selectivity in oxidation the quality of site isolation is essential and no compromise should be tolerated in coupling the electronic structure of the active site to reservoirs of electrons. This isolation reduces the overall velocity of the reaction. Total oxidation sites (or materials) can have a coupling of their sites to the electron reservoir of the bulk and thus be fast catalysts.

Oxidative regeneration of the site is in competition with its deactivation by the combined action of hydrolysis and of mobile phosphate. Both are enhanced with growing performance – an argument for operating selective oxidation catalysts with comparatively low loads. The deactivation leads to growth of the active material into three-dimensional particles in much the same way as the pre-catalyst is grown from phosphoric acid, vanadium oxide and some reducing agent. It is anticipated that first a clean surface of VOPO_4 will result that may act as combustion catalyst (no site isolation) and thus enhance the energy supply to the system and augment the chemical potential of hydrolyzing water. Both effects in conjunction with the reducing potential of the gas phase tend to decompose the vanadium phosphates and create free mobile phosphate, passivating the non-selective surface.

The whole process needs some initiation during the equilibration phase of the practical VPO system. The bulk precursor “hemihydrates” are converted into VPO, which is metastable in oxygen and temporarily converts into VOPO_4 , as frequently [192, 214, 215, 227, 245, 246, 257] found in the literature. Conflicting reports [45, 87, 258] about the role of this transformation can be resolved as follows. The initial equilibration leads to a nanostructured intergrown mixture of reactive crystallites of VPO and VOPO_4 . This material undergoes segregating structural transformations under the action of feed: a large part re-crystallizes into stable VOPO_4 that is a combustion catalyst that transforms slowly into a passivated form due to phosphate coverage as described above. Some of it is reduced to large crystals of VPO, which act as support for the main active phase.

The transformation of the initial defective VOPO_4 is thus not a side effect but the central step enabling the active phase. The defect structure controlled by addition of promoters like Co, Ga, Fe and others will affect the partitioning between large crystalline material and still nanostructured VPO that is the reactive precursor to

hydrolysis leading to $VxOy$ and mobile phosphate (presumably as phosphoric acid, as seen in Figure 1.11). This mixture is the material of the 1–2-nm thick surface layer seen in Figure 1.10 and frequently described [175, 176, 192, 214, 215, 227] in the literature. It provides the site-isolated $VxOy$ species that are well separated by phosphate from each other and from the underlying bulk. This material can be considered as the intermediate phase necessary to achieve the overall stabilization of the metastable VPO solid under the destabilizing chemical potential of the feed into the higher oxidized $VOPO_4$ – a non-topotactic solid-state redox transformation.

It is now critical that the whole process is dynamic, that is, responds in its kinetics to the reaction. Otherwise a continuous transformation would, with a linear rate law, transform all VPO into $VOPO_4$. The gas phase has a dual controlling influence on the process: The educt butane accelerates [132] at least part of the re-crystallization through the intermediate omega phase but the product MA inhibits this step and thus stabilizes the precursor; as the transformation of the $VOPO_4$ is a pre-requisite for forming the active phase that in turn leads to the chemical potential of the stabilizing MA. We see how a negative feedback loop stabilizes the catalyst for a slow transformation through a long-standing intermediate concentration of the reactive mixture $VxOy$ /mobile phosphate.

This loop is, however, affected by the availability of the reactant oxygen, which in surplus destroys the precursor VPO. Further, oxygen is positively needed to activate and re-oxidize the $VxOy$ sites but leads also to more water formation that in turn hydrothermally deactivates the active mass. Likewise, water is needed to separate, via hydrolysis, the vanadium phosphate into $VxOy$ and mobile phosphate. The multiplicity of the feedback loops is at first puzzling but explains the apparent stable steady state that can be reached with a catalyst undergoing so many chemical and microstructural transformations; the multiplicity of controls prevents one single factor becoming dominant and thus potentially destabilizing the whole process.

The idea that the equilibrating transformations should be completed before the catalyst becomes active is not right; if one drives the reaction to completion, which may, depending on the chemical potential chosen, either be well-crystalline VPO or stable $VOPO_4$, then one has taken out of the system all structural dynamics and thus prevented the system from generating new active sites. Literature statements about the stable phases thus address the deactivated forms of the catalyst that may have some activity in the final terminating layer left and so, during short episodes of *in situ* testing, still show some (misleading) productivity. A stable long-term operation of the system requires the ongoing transformation initiated in the equilibration and inhibited by the product MA. In this context the enigmatic influence of the reduction agent used to generate the precursor “hemihydrate” acquires a rational dimension, as it on one hand affects with its chemical reduction potential the kinetics of the formation of the precursor and thus its defect structure while on the other hand the molecular structure of the reducing agent will stabilize the initial solid against structural transformation. A conceivable mechanistic concept is a complexing action that prevents the relative motion of polyhedra – being the molecular nature [116, 259, 260] of this whole transformation circus.

1.6

Conclusion

The substantial and fragmented literature on selective oxidation and the *ad hoc* character of the established principles of operation of the relevant catalysts leave the general impression of a still poorly understood research field. This does not devalue the remarkable success in finding and optimizing selective oxidation catalysts but it explains the apparent difficulty in expanding the number of reactions at productivities needed for sustainable commodity production. The present chapter makes an effort to draw many facts into a consistent picture. Not all aspects of nanostructuring, ionic transport, surface acidity and local electronic structure – the physical ingredients in explaining the function of an active site – are rigorously discussed here; in most cases, complete description of the phenomena has not yet been achieved. The complex and still mostly undiscovered role of carbon deposits [251] in modifying the performance of oxidation catalysts is a subject requiring more experimental evidence before it can be integrated into a general picture. Nanostructured carbon [261] originating from side reactions on oxides was found to exhibit a quite substantial performance in oxidation catalysis.

Central is the postulation of isolated sites that consist of sufficient metal ions to accommodate the redox equivalents required for one transformation and of sufficient oxygen ions to store the protons to be converted finally into water molecules. These sites need to be isolated from the supply of electrons to realize a shortage of activated oxygen. Concomitant with this kinetic argument for selectivity is the requirement for adaptiveness; the active site must be most active for the first C–H activation and must then become moderated in this function as the activation of substrate gradually proceeds. This can be realized by a gradual reduction of the oxidation state of the active site that must not be compensated for during the transformation of the substrate. In complex transformations such as butane oxidation to MA, some redox equivalents might be used during transformation to activate gas-phase oxygen into electrophilic reagents but this action must be strictly confined to stoichiometric conditions so as not to destroy the selectivity of the reaction.

The isolated and adaptive sites are not prepared during manufacture of the catalyst but occur in a dynamic process through co-operation of the pre-catalyst reactivity with the chemical potential of the reactant gas phase. In this way a gradually interconverting pre-catalyst generates the more reactive active phase that eventually transforms the whole pre-catalyst into a deactivated stable state consisting of a mixture of well-crystallized phases. In oxide systems this transformation requires the mobility of oxygen species and thus explains the well-documented fact that lattice oxygen mobility is related to catalytic action; the phenomenon is the proxy for the structural transformation creating the active sites and is thus positively correlated with performance. This interpretation leaves unaffected the fact that active oxygen located at lattice defects (of unknown ordered termination) formally seems to complement the coordinative undersaturation of the defect site and may for this reason be considered as “surface lattice oxygen” although it is a conventional adsorbate on a high energy site.

The combination of rigorous surface science experiments on sufficiently complex structural models with the broader application of *in situ* functional analysis is essential to further substantiate this notion of oxidation catalysts as being governed by the same rules as “simpler” metal systems. The generation and deactivation of high energy “Taylor sites” in a sea of adsorbing “Langmuir sites” is the general model proposed for selective oxidation catalysts. It can be detected by the method of forcing gradients in chemical potential and analyzing the spectral response of the system.

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