

Appendix I: Literature Survey and Theoretical Concepts

I.1 Major classes of catalysts for propane ODH

I.1.1 Vanadium-based catalysts

Vanadium and molybdenum oxides are the main compounds present in catalysts used for selective oxidation of alkanes. Vanadium is definitely the preferred element and is present in almost all catalysts formulations, giving the highest productivity and the highest yield at the lowest temperature. The selectivity to ODH products depends on the specific alkane feed, on the vanadium content, and on the nature of the matrix and/or support in which the vanadium atoms are incorporated. It has been proposed that the acid-base character of the catalysts determines the selectivity because of the influence that this parameter has on the adsorption/desorption processes of the olefinic intermediates and the reaction products. Table I.1 lists the most studied V-based systems and their main structural and catalytic characteristics.

Table I.1: Literature survey on the most important V-based catalysts.

Catalysts	Reaction and temperature	Structural characterization	Catalytic results	References
V-Mg-O and $\text{VO}_x/\text{Al}_2\text{O}_3$	Butane ODH, 733-823 K	Isolated VO_4 in $\text{Mg}_3\text{V}_2\text{O}_8$, polym. tetrahedral V^{5+} in $\text{VO}_x/\text{Al}_2\text{O}_3$.	$\text{XC}_4^\circ = 40\%$, $\text{S}_{\text{butadiene}} = 27\%$ (VMgO) $\text{S}_{\text{butadiene}} = 3\%$ ($\text{VO}_x/\text{Al}_2\text{O}_3$)	(116)
V-Mg-O	Propane ODH, 773-813 K	MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, $\text{Mg}_3\text{V}_2\text{O}_8$, Mg, MgO	Improvement of the catalytic results because of phase synergy	(117)
V-Mg-O	Butane ODH, (use of iodine) 773-853 K	$\text{Mg}_3(\text{VO}_4)_2$, small amounts of $\text{Mg}_2\text{V}_2\text{O}_7$ and V_2O_5	$\text{XC}_4^\circ = 56\%$, $\text{S}_{\text{butadiene}} = 67\%$	(118)
V-Al-O-N	Propane Ammoxidation, 723-823 K	Amorphous, high S_{BET}	$\text{ACN prod.} = 812 \text{ l kg}^{-1} \text{ h}^{-1}$	(119,119)
VO_x/ZrO_2	Propane ODH, 606 K	V_2O_5 , ZrV_2O_7	$\text{XO}_2 = 30\%$, $\text{SC}_3^\circ = 55\%$ (VO_x/ZrO_2)	(120-123)
VO_x/Supp (Supp. = ZrO_2 , TiO_2 , HfO_2 , SiO_2 , Al_2O_3)	Propane ODH, 606 K	VO_x structures depends on the identity of the support and V content	$\text{XO}_2 = 25\%$, $\text{SC}_3^\circ = 55\%$ (VO_x/HfO_2)	(124)
V-Sb-O	Propane Ammoxidation, 753 K	Sb_2O_3 , $\text{VSbO}_{4.5}$	$\text{Y}(\text{ACN}) = 11\%$, $\text{XC}_3^\circ = 30\text{-}40\%$	(125-129)

I.1.1.1 V-Mg-O and $\text{VO}_x/\text{Al}_2\text{O}_3$ catalysts

Nieto and coworkers (116) investigated some V-Mg-O and $\text{VO}_x/\text{Al}_2\text{O}_3$ catalysts, showing that the tetrahedral V^{5+} species are the main vanadium species. By observing

the TPR patterns, it was pointed out that the reducibility of V-species in the V-Mg-O catalysts was lower than in the $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst. V^{4+} and V^{3+} species are formed after reduction of the V-Mg-O and the $\text{VO}_x/\text{Al}_2\text{O}_3$ catalysts, respectively.

The reducibility of the atoms can influence the selectivity to ODH products and this could be explained by its effect on the rate of the selective redox processes involving species on the catalyst surface. For example in the case of n-butane, a higher reaction temperature accelerates redox exchange on the catalyst, which results in a higher selectivity especially on V-Mg-O, whose reducibility is lower than that of $\text{VO}_x/\text{Al}_2\text{O}_3$ (116).

I.1.1.2 ZrO_2 -supported VO_x catalysts

Other studies of alkane ODH reactions dealt with VO_x species supported on ZrO_2 , which is an excellent support for the synthesis of highly dispersed oxides (121-123). Zirconia can be prepared with high surface area ($>300 \text{ m}^2\text{g}^{-1}$) and it can be maintained at relatively high values even after oxidation at high temperatures. Also, in contrast with more weakly interacting supports such as SiO_2 , ZrO_2 inhibits the sintering of the supported oxide in the presence of water at high temperature. In addition, zirconia does not reduce under conditions of alkane ODH reactions. ODH rates and selectivities were measured on VO_x/ZrO_2 and on two bulk vanadium compounds: V_2O_5 and ZrV_2O_7 (124).

The structure of VO_x dispersed on ZrO_2 depends on both the surface density of VO_x and the calcination temperature. The observed increase in the rate of C_3H_8 conversion per V atom with calcination temperature suggests, therefore, that the oxygen in polyvanadate species is more active than the one in isolated vanadyl species. It was therefore concluded that high activity and propene selectivity require V-O-V species in large polyvanadate domains residing on the surface of the ZrO_2 support (124).

I.1.1.3 Other supported vanadium catalysts

Khodakov et al. (124) prepared different supported vanadium oxide catalysts, with a different vanadium loading. At given vanadium surface density, the structure of VO_x species will depend on the ability of a given support to disperse the surface VO_x species. X-ray diffraction measurements showed that VO_x species inhibit the conversion of metastable tetragonal ZrO_2 to its monoclinic form and the crystallization of amorphous HfO_2 into monoclinic and orthorhombic structures, but they do not influence

the crystallinity of the anatase TiO₂ structure. Also in this case, X-ray diffraction shows that the structure of dispersed VO_x species depends on the identity of the support and on the VO_x surface density.

Oxidative dehydrogenation rates (per V-atom) on supported vanadia depend on support composition and on VO_x surface density. Reaction rates (per V-atom) increase as VO_x surface density increases for all the supports, suggesting that polyvanadate domains are more active than monovadate species. Zirconia-supported catalysts show the highest oxidative dehydrogenation rates and SiO₂-supported catalysts the lowest activity, while the other supports give intermediate reaction rates (TiO₂>HfO₂>Al₂O₃).

I.1.2 Niobium-based catalysts

Niobium is in the same group of the periodic table as vanadium and is expected to display similar properties, with the difference that niobium is much more difficult to reduce than vanadium. Because easy reduction often causes low selectivity in selective oxidation reactions, the interest for Nb-based catalysts is fully justified. Various Nb-containing catalysts were studied for the oxidative dehydrogenation of propane. Table I.2 lists the most studied Nb-based systems and their main structural and catalytic characteristics.

Smits et al. (130) found that niobium oxide shows a very high selectivity in this reaction (72 %, at 853 K), at 20 % O₂ conversion. The activity of niobia can be improved without diminishing its selectivity by adding other suitable elements as vanadium, chromium and molybdenum (131,132).

I.1.2.1 V-Nb oxide catalysts

I.1.2.1.1 Structural characterizations

Some Nb-V prepared catalysts have already been investigated from the point of view of their physico-chemical characteristics and their catalytic behaviour in propane ODH (132). All characterization data indicate the existence of two or three different active sites at the surface of the catalysts: isolated vanadium atoms, pairs of vanadium atoms, or ensembles of three vanadium atoms. The isolated vanadium sites are less active than the vanadium clusters. It is reasonable to assume that ensembles of vanadium atoms are more active than isolated vanadium atoms, since a bridging oxygen atom between two easily reducible vanadium atoms is more active than a V-O-Nb site.

Little is known about the diffusion of vanadium ions in a niobia matrix (130), but it is known that an ion diffuses faster when it is smaller and has a lower oxidation state. It seems that V^{4+} diffuses faster due to its lower oxidation state despite its larger size (0.63 Å for V^{4+} , 0.59 Å for V^{5+}). If the ion size is less important than its charge for bulk diffusion, it will be even more for surface diffusion. The increased vanadium mobility under reducing conditions also causes an increase in the sintering rate. As a result, the surface areas observed after use were usually lower than for fresh materials. A preparation method, which causes the vanadium to be distributed homogeneously at the surface and in the bulk, is preferred over a method, which deposits vanadium only at the surface: vanadium can be reduced during use and the increased mobility caused by this reduction makes the catalyst more homogeneous. The key point to reach high catalytic performances appears to be the ability to tune the catalyst architecture, by controlling the nature and interdispersion of the oxide phases present in these catalysts. This can be possible by improving adequate preparative procedures such as the sol-gel method.

Table I.2: Literature survey on the most important Nb-based catalysts.

Catalysts	Reaction and temperature	Structural characterization	Catalytic results	References
Nb-V-O	Propane ODH, 698K	TT- and T-Nb ₂ O ₅ , β -(Nb ₂ V) ₂ O ₅ , V ₂ O ₅	SC ₃ [°] = 75-91%	(132)
Nb-V-O	---	T-Nb ₂ O ₅ , VNb ₉ O ₂₅	---	(133)
Nb ₂ O ₅ /V ₂ O ₅	Propane ODH, 658-773 K	Nb ₂ O ₅ , V ₂ O ₅	XC ₃ [°] = 17 % YC ₃ [°] = 9 %	(134)
Nb-V-O	Propane ODH, 673 K	TT-, T-Nb ₂ O ₅ , VNb ₉ O ₂₅	C ₃ [°] Consumption = 1.79 (μmol m ⁻² s ⁻¹) catal. prep. by adsorption	(130)
Nb-Si, Nb-V-O, Nb-V-Si	Propane ODH, 723-773K	V ₂ O ₅ , NbVO ₅ , VNb ₉ O ₂₅ , V ₄ Nb ₁₈ O ₅₅	XC ₃ [°] = 25 %; SC ₃ [°] = 47 % (Nb-V-Si)	(135-137)
Ta _x Nb _{1-x} VO ₅	---	Solid solution of NbVO ₅ and TaVO ₅	---	(138)
Nb-V-Mo	Ethane ODH, 573-823 K	MoO ₃ , Mo ₆ V ₉ O ₄₀ , Mo ₃ Nb ₂ O ₁₁	SC ₂ [°] = 20% → 60,80% (adding Nb to Mo-V)	(139,140,142)
Nb-Mo-O on SiO ₂	---	Nb ₂ Mo ₃ O ₁₄ on SiO ₂ (very low S _{BET})	---	(141)
Nb-Mo-V-Te	Propane oxidation to acrylic acid, 613-673 K	TeM ₃ O ₁₀ , Te ₂ M ₂₀ O ₅₇ , TeMo ₅ O ₁₆ M = Mo, Nb, V	XC ₃ [°] = 50 %, S _{acryl.acid} = 50 %	(143-148)
Nb-Sb-V	Propane Ammoxidation, 773 K	SbNbO ₄ , SbVO ₄ , (SbNb _{1-x} V _x O _n)	XC ₃ [°] = 25% S _{ACN} = 39%	(149)

I.1.2.1.2 Preparation methods

Watling et al. (134) prepared some bulk vanadia-niobia with different vanadium oxide loadings using four different preparation methods: (i) adsorption of $\text{VO}(\text{acac})_2$ onto niobia; (ii) coprecipitation from a mixed oxalic acid solution of niobium and vanadium; (iii) calcination of mixed oxalates; (iv) impregnation of niobia with NH_4VO_3 . For the coprecipitated catalysts, the surface concentration of vanadium increased in parallel with the bulk vanadium concentration. The surface concentration of vanadia for a particular bulk concentration in fresh catalysts, and the specific surface areas are also influenced by the preparation method. The coprecipitated vanadia-niobia samples had a specific surface area of $27 \text{ m}^2\text{g}^{-1}$, while catalysts prepared by adsorption and impregnation or melt catalysts exhibited values of $19 \text{ m}^2\text{g}^{-1}$ and $39 \text{ m}^2\text{g}^{-1}$, respectively (130).

Generally speaking, in Nb-V systems the active site is a vanadium ion at the surface, and the activity and selectivity of this site depends on the number of neighbouring vanadium and niobium ions. Neighbouring vanadium ions provide further activity, while neighbouring niobium ions improve the selectivity. The optimal activity and selectivity are given by a site having both vanadium and niobium as neighbours (V-O-V*-O-Nb). When the density of vanadium atoms at the surface is too low, the chance of one vanadium site having a vanadium ion as a neighbour is small, making the catalyst quite selective but not very active.

I.1.2.2 V-Nb-Mo catalysts

Catalysts based on Mo, V and Nb were also prepared, characterized and tested in the dehydrogenation of ethane (139) and propane (135,137).

I.1.2.2.1 Major crystalline phases

V-Nb-Mo catalysts were shown to contain the crystalline phases MoO_3 , $\text{Mo}_6\text{V}_9\text{O}_{40}$ and “ $\text{Mo}_3\text{Nb}_2\text{O}_{11}$ ” (actually $\text{Mo}_3\text{Nb}_2\text{O}_{14}$: in fact there is no reason, nor experimental evidence that Mo is fully reduced into Mo(IV) in this phase (137)) (139,140). The formation of these phases is highly temperature dependent. The $\text{Mo}_6\text{V}_9\text{O}_{40}$ sample consists of agglomerates of high crystalline, very loose, sponge-like particles. The crystalline $\text{Mo}_3\text{Nb}_2\text{O}_{14}$ phase is a powder with a low surface area of 2

m^2g^{-1} , consisting of rectangular shaped crystals. At higher calcination temperatures, the amount of crystalline component of the catalyst increases very quickly at the expense of the amorphous part. In addition, the size of the particles increases also, leading to a lower surface area of the catalyst. The phases $\text{Mo}_6\text{V}_9\text{O}_{40}$ and $\text{Mo}_3\text{Nb}_2\text{O}_{14}$ have to be considered for their possible contribution to the catalytic activity of the sample.

I.1.2.2.2 Catalytic activity

Addition of niobium to the most performant Mo/V oxide catalyst results in a significant increase in activity (139). At 683 K, the Nb-containing catalyst is about twice as active as the Nb-free catalyst. An additional effect of niobium in ethane ODH is to increase the selectivity to ethene from 20 up to 60-80%. One possible explanation for this effect could be that niobium combines with molybdenum or vanadium, and thus eliminates some total oxidation sites. It is known that MoO_3 is not a very selective catalyst for ethane ODH. The nature of this active catalyst is still unresolved. Thorsteinson et al. (142) correlated the activity of their catalyst with the intensity of an XRD line ($2\theta = 22^\circ$), the niobium-free catalyst having a weaker line at that position. It is suggested that the addition of niobium to a Mo/V oxide catalyst increases the activity and selectivity for ethane ODH. It is possible that the role of niobium is to form a new phase ($\text{Mo}_3\text{Nb}_2\text{O}_{14}$), which could be responsible for the enhanced activity and selectivity.

I.1.2.3 Sb-Nb-V catalysts

Mimura et al. (149) investigated Sb-Nb-V composite oxides for the ammoxidation of propane to acrylonitrile. SbNbO_4 is activated by the addition of vanadium (V^{4+}) for the ammoxidation of propane. The XRD patterns of Sb-Nb-V mixed oxides show that for a Sb/Nb ratio equal to 1, SbNbO_4 is observed. At increased concentrations of V ions in the mixed oxide, another crystalline phase is observed: SbVO_4 . It is known that SbNbO_4 is isostructural to $\alpha\text{-Sb}_2\text{O}_4$ with orthorhombic symmetry. It consists of sheets of Nb-O octahedra linked by Sb^{3+} ions. When V^{4+} ions are added to SbNbO_4 , they substitute for Nb^{5+} in $(\text{NbO}_4)^{3-}$. The catalytic activity of SbNbO_4 is very low and the selectivity for acrylonitrile is also low, but both are drastically enhanced when V^{4+} is added in SbNbO_4 : some authors proposed the creation of Sb^{5+} ions in the SbNbO_4 lattice by substitution of V^{4+} ions for Nb^{5+} ions (149).

I.2 Sol-Gel method and its potentiality in catalysis

1.2.1 General principles

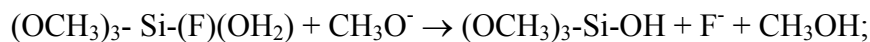
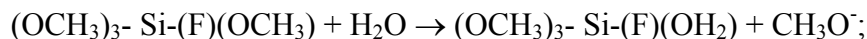
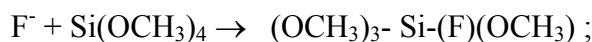
A sol is defined as a stable dispersion of colloidal particles in a liquid medium (150). For having solid particles characterized by a higher density than the liquid medium, their size must be small enough in order to ensure that the gravitational forces overcome the forces responsible for this dispersion.

A gel can be defined as a 3-D solid network interconnected in a liquid medium. If the solid network is constituted of colloidal particles, then the gel is defined as colloidal. If the solid network is constituted of macromolecules, the gel is defined as polymeric. When a sol transforms into a colloidal gel, it goes through the gelation point (151), corresponding to the total conversion of a viscous liquid into a solid (gel), in which the initial homogeneous dispersion already present in the sol, is definitely fixed and cannot be changed.

The general steps of a sol-gel process are:

- i) **Mixing:** the colloidal solution can be obtained by adding water (at pH values preventing eventually undesired precipitation) to an alcoholic solution of the metal alkoxides.
- ii) **Hydrolysis and polycondensation:** the M-OH bonds, due to hydrolysis, can react in order to give M-O-M bonds in a condensation reaction. This is a critical step in the sol-gel process, which is influenced by a large number of parameters such as temperature, solvent and nature of the alkoxide. The kinetics of the different steps of the sol-gel method are important ($K = k_h/k_c$). For example, in the case of TMOS (tetramethoxysilane), the hydrolysis rate increases with acid or base concentration. The used solvent and the temperature can influence k_h , obviously the acid nature can increase K , increasing the hydrolysis rate (k_h), whereas on the contrary, hydroxyl ions favour condensation (k_c).
- iii) **Aggregation:** this step must be controlled in order to avoid heterogeneous aggregations.
- iv) **Gelation:** the viscosity of the colloidal solution increases quickly and a solid phase appears. The gelation time depends on sample-holder shape, pH, solvent, amount of water and viscosity. For example in the case of TMOS, a

gelation agent like NH_4F can be used in order to facilitate the formation of $(\text{OCH}_3)_3\text{-Si-OH}$ by a nucleophilic activation according to the following equations:



- v) Aging: during this step, polymerization processes are always involved, resulting in an increase of intermolecular bridging bonds and gel contraction.
- vi) Drying: the liquid is removed out of the gel: during this last step the gel may break because of the small pore size.

In catalysis, one of the great promises of the sol-gel synthesis is that one might hope to make solid surfaces with an adequate homogeneity of composition and new catalytic properties by connecting different dissolved oxide precursors in wanted proportions. In some cases, one might also expect a metastable oxide structure and composition, that is quite far from that presented by stable materials; by this way, it would be possible to create surface reactive sites of desired acid-base properties, while simultaneously mastering their number. In the sol-gel process, it is assumed that the different alkoxides decompose simultaneously and can therefore react randomly with each other. If not, only alkoxide A will react with A, B with B, making a non-homogeneous solid. In the extreme case, completely random structures might be expected. To direct such a random and homogeneous assembly, one would ideally like the dissolved components and their assembling networks to remain in solution until solidifying by gelation upon forming an infinite polymeric network avoiding precipitation of the evolving intermediates. On the other hand if a certain degree of order is required, one would like at least to control phase separation and other ordering processes. The degree of molecular level randomness and homogeneity should have a profound influence on the catalytic properties of a site: it can also have a dramatic effect on aging, energetics and thermal behaviour of the gels (which, naturally, will also affect catalytic properties) (152).

The main disadvantages of the sol-gel method are (153): (i) high cost of the raw materials; (ii) large shrinkage during processing; (iii) residual fine pores; (iv) residual hydroxyl; (v) residual carbon; (vi) health hazards of organic solutions and (vii) long

processing times. The most severe limitation of the classical sol-gel method is the cost associated to the use of alkoxide precursors.

1.2.2 Application of the sol-gel method to the preparation of supported molybdate catalysts

The application of the sol-gel method in catalysis is well known: some illustrative examples of sol-gel prepared catalysts and their applications are mentioned hereafter.

In the case of the oxidative dehydrogenation of propane, for example, dispersion of NiMoO_4 in a silica matrix led to the stabilization of the β -phase (62). The authors concluded to strong interactions of the molybdate ions with silica oligomers, because their presence caused a dramatic increase of the gelation rate and changes in the colour of the sol. With a 1:1 Mo/Ni molar ratio, a significant amount of nickel oxide was formed after thermal activation: the influence of temperature on the formation of nickel molybdate is very important (high calcination temperature and long calcination treatment lead to total formation of NiMoO_4). Adding a complexation agent (like a chelating amine) strongly improves the yield in molybdates because nickel ions are *protected*. It was also claimed that the 2:1 Mo/Ni atomic ratio was the minimum required to afford the complete engagement of nickel cations in the formation of NiMoO_4 , by thermal treatment, but actually this ratio also leads to the formation of MoO_3 besides NiMoO_4 . Moreover, β - NiMoO_4 entrapped into silica appeared to be unaffected by grinding contrary to β - CoMoO_4 which is transformed into the α -phase in case of vigorous grinding.

SiMoCo catalysts were prepared by sol-gel method and tested in thiophene HDS (154). It was found that these catalysts are characterized by lower activities if compared to the ones of the catalysts prepared by wet impregnation. However, the activity of SiMoCo catalysts (XRD revealed the presence of CoMoO_4) prepared by sol-gel method could be improved by introducing nitrilotriacetic acid (NTA) during the procedure: in fact it seems that NTA is completely available for complexing the metals avoiding the embedding of these ions inside the larger pores. Another method, to improve further the catalytic activity, was to prepare the silica by sol-gel method, first and to impregnate it with aqueous solution of Co nitrate and ammonium heptamolybdate adding also NTA. It was found that a sol-gel prepared silica is characterized by a lower specific surface

area and higher fraction of small pores than the commercial one. This feature is important since the higher the fraction of the large pores, the higher the fraction of ions embedded in the silica matrix which are unavailable for catalyzing the thiophene HDS process. With a higher fraction of small pores, a higher number of ions is available for the catalytic process. The number of ions, which are not trapped in the silica matrix, could also improve by using NTA, which complexes those ions and prevents them from the encapsulation.

A sol-gel route was also applied to the preparation of bismuth molybdates dispersed into silica xerogels produced by hydrolysis/condensation reactions involving silicon alkoxides (97). The gels containing low molybdate loading were characterized by high surface area values, particularly when treated at lower temperature, but these values were smaller than those found for a pure silica sample ($852 \text{ m}^2\text{g}^{-1}$) prepared from TMOS under the same conditions. As expected, the surface area dramatically decreased for the high-loaded samples, where the massive presence of crystalline bismuth molybdate appears to hide the silica pores.

The XPS spectra showed unsatisfactory Bi/Mo atomic ratios that were lower than the expected ones. In agreement with EDX investigations, molybdenum concentration was higher in the outermost layers, associated with bismuth enrichment in the bulk. During gelation, the rapid evaporation of the inner solvent generates high salt concentrations gradients, which could effectively cause the selective migration of ions. Assuming that the major part of the pores has a diameter smaller than 2 nm, access to them would be very difficult for many of the major species which are present. This is the case of polynuclear entities like $[\text{Mo}_7\text{O}_{24}]^{4-}$, $[\text{Mo}_8\text{O}_{26}]^{4-}$, which are the more abundant Mo-containing moieties present at highly acidic pH; on the other side, smaller species like essentially those containing bismuth could reach more easily the inner region of the material, where the salt concentration is lower.

The sol-gel method was successfully applied for the preparation of praseodymium molybdates dispersed in silica matrix (155). It was found that $\text{Pr}_2\text{Mo}_3\text{O}_{12}$ was the only obtained phase even if different Pr/Mo ratios were adopted in the formulation of the catalyst. These molybdates, tested in the selective oxidation of methane, propane and isobutene, were characterized by a scarce catalytic activity. However, they displayed interesting results in methanol oxidation giving good selectivity towards DME.

I.2.3 Sol-gel preparation of mixed supports

A major interest of the sol-gel method is its ability to be used as a synthetic pathway to mixed supports combining two or more elements, in such a way that the acid-base properties of the support can be tuned and adapted for a given application.

For example, $\text{TiO}_2\text{-Al}_2\text{O}_3$ (156) prepared by sol-gel was found to be characterized by a monodisperse distribution of nanometric particles, a surface area superior to $200 \text{ m}^2\text{g}^{-1}$ and a mean porous size of about 1 nm. A sol-gel route was also applied to produce $\text{SiO}_2\text{-Al}_2\text{O}_3$ xerogels (157), leading to the creation of materials with unique structural and surface chemistry features: the analysis of acid-base properties of these xerogels revealed surface groups that are not present in commercially available materials obtained in a more traditional way. $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (158) and $\text{SiO}_2\text{-ZrO}_2$ (159) were also prepared by sol-gel methods. The sol-gel synthesis of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ mixed oxides led to the formation of solid solutions upon calcination at 823 K for 3 h. These solid solutions were heterogeneous, because zirconia itself was constituted of several crystallographic phases: 30 % monoclinic- ZrO_2 , 42 % tetragonal- ZrO_2 and 28% cubic- ZrO_2 ; moreover, the broad diffraction peaks indicated that these solids were constituted by very small, highly dispersed crystallites. In the case of $\text{SiO}_2\text{-ZrO}_2$, the use of a strongly basic gelling agent led to the preparation of amorphous mesoporous materials. Only at high silica content and after drying at low temperature, micropores were detected. The physico-chemical characteristics of $\text{SiO}_2\text{-ZrO}_2$ differ from that of the two pure oxides: SiO_2 has a high surface area and a low OH density without peculiar acidic character, while ZrO_2 exhibits a low surface area with high contents of OH and acid sites. Increasing the amount of Zr in the mixed oxides was shown to increase the density and lower the strength of the Brönsted acid sites.

I.3 Overview of the basic physico-chemical concepts used

I.3.1 Ionization energy (IE)

The key features involved in the activation of molecular oxygen on the catalyst surface are: the coordination, the electron transfer phenomena between the oxide lattice and gaseous oxygen, the dissociation and the incorporation of oxygen in the oxide lattice. Because the redox process involves a reducible metallic cation acting as the actual oxidizing agent of the catalytic event, the catalytic behaviour could be in some way related to the ionisation energy of the metallic cation.

At this stage, it is also necessary to distinguish between binary oxides, constituted by a metallic cation surrounded by oxygen atoms, and ternary oxides which can be considered as an association of a metallic cation and an oxoanion. In the latter case, there is a chemical bond with prevalent ionic character between the metal and the oxoanion and chemical bonds with prevalent covalent character within the oxoanion.

The electrodonating power of a single cation depends on the ionisation energy of the cation and on the effective charge of the neighbouring oxygens: for the same oxoanion group, the electrodonating power of the cation increases when its ionisation energy decreases; for the same cation, an enhancement of the ionicity of the bonds within the oxoanion increases the effective charge of the oxygen atoms and enhances the electrodonating ability of the cation (160).

The concept of IE has already been used at several occasions. For example, Hattori (115) found a perfect correlation between the catalytic properties of the lanthanide oxides and the 4th ionisation energy of the metals involved: the lower the 4th ionisation energy, the more active the oxide was in total oxidation. De Smet (113), in line with Hattori's considerations, found a correlation between the catalytic properties of some lanthanide oxides for total oxidation with respect to the 4th ionisation energy of their respective cations: they observed that the most active lanthanide oxides are characterized by the lowest 4th ionisation energies (CeO_{2-x} and Pr_6O_{11}). In the case of a ternary phase, taking into account that oxygen is mobile in and on the crystalline network of oxides active in oxidation, they assumed that reactive oxygen ions are statistically present with similar probabilities in the vicinity of the different metals involved. An "average parameter" was defined by taking into account the relative proportions of their respective cations in the ternary phase and it was calculated as follows:

$$I^*(\text{A}_x\text{B}_y\text{O}_z) = \frac{I(\text{A})x + I(\text{B})y}{(x + y)}.$$

I.3.2 Standard enthalpy of oxide formation

Miura et al. (161) suggested that the standard enthalpy of oxide formation could be an useful tool for the interpretation of the catalytic properties of oxides in oxidation. The availability of oxygen atoms of oxide lattice depends on their mobility and also on the reducibility of the cation. The standard formation enthalpy of oxide formation could quantify this reducibility. If we take into account negative values of the standard

enthalpy of oxide formation, the lower the absolute value, the easier the reducibility of the metallic cation.

I.3.3 Acido-basicity: the absolute hardness

A common trend in the literature is to analyse the catalytic behaviour of oxides by considering their overall acid-base properties. In terms of Lewis acidity, metal ions at a high oxidation state, or coordinatively unsaturated, as well as anionic vacancies can be considered as acidic centers; on the other side, oxygenated anions and hydroxyl groups are basic sites.

T. Seyama and coworkers (162), observed that for a series of oxides the conversion of propene to acrolein, the selectivity towards acrolein increases with the electronegativity values of the cations and in the case of conversion of propene to benzene, the selectivity increases in presence of weakly basic or weakly acidic sites.

Pearson classified metal ions characterized by small size, highly charged and low polarizability as hard Lewis acids, while those characterized by larger sizes and high polarizability are soft acids. Also Lewis bases can be classified as hard and soft; their character does not only depend from the nature of the atom directly bounded to the metal, but also from the nature on the entire molecule.

By referring to Pearson's approach (163), soft-soft and hard-hard interactions are favoured with respect to the crossed interactions.

Generally speaking, adsorption and activation of the hydrocarbon molecule are both related to acid-base interactions; the adsorption and the desorption rates of reactants and products are also related to acid-base properties.

Considering that hydrocarbons such as alkanes or olefins are thought to be weak bases, Vedrine et al. (164) suggested that the oxidation of an alkene would be more selective if the catalyst involves a hard cation (hard acidic cation) rather than a soft one (soft acid cation) because the interaction would be weaker and promote partial oxidation rather than total oxidation. High selectivity can be explained by taking into account the adsorption/desorption steps. Acidic sites favour the adsorption of basic reactants and enhance the desorption of acidic products, thereby protecting them from further oxidation to carbon oxides.

To go one step further along this approach, it is possible to refer to the absolute hardness scale (η) defined by Pearson as $\eta = (I - A)/2$, where I represents the ionisation

energy and A the electron affinity. This parameter is a measurement of the energy difference ΔE between the ionic HOMO and LUMO levels, according to $\Delta E = 2\eta$. In particular, all lanthanides except La^{3+} are characterized by a $4f^n$ electron configuration which leads to a low 4th ionisation energy and to a consequent low absolute hardness, even if they all behave as hard acids.

I.3.4 Acido-basicity: the optical basicity of catalyst oxygen

We have already said that the interaction between the catalyst and the molecule that must be oxidized is based on the electron-donating and –accepting power, which can be described in terms of Lewis acid-base properties. Is it possible to quantify these electron-accepting/donating properties exhibited by the catalysts in a certain reaction? We already pointed out that catalyst oxygens play a double role: they are responsible for the attack of the C-H bond of the hydrocarbon and they are inserted into an intermediate complex in order to give the oxygenated products and water. The first step is correlated to the activity and the second step to the selectivity. The catalytic activity has been already correlated to the oxygen binding energy, but also the basicity of the catalyst oxygen has been considered as a good parameter, even if very difficult to quantify.

To quantify the electron-donating power of lattice oxygen, Duffy (165) proposed a parameter called “optical basicity” Λ_{th} . Later, Moriceau and coworkers (166) thought to use the concept of optical basicity in mild oxidation and to correlate it to selectivity. Another problem to be solved was the fact that the optical basicity is a characteristic of the bulk of the solid, while the most critical aspect was to evaluate the “surface optical basicity”, Λ_{surf} .

For a mixed oxide $\text{A}_x^{a+} \text{B}_y^{b+} \text{O}_n^{2-}$, the optical basicity can be calculated according to the equation $\Lambda_{\text{th}} = 1/2n (ax\Lambda_A + by\Lambda_B)$, where Λ_A and Λ_B are the optical basicity of cations A and B, respectively. The scale of basicity derived from this formula is satisfactory only in the case of ionic oxides, but not in the case of transition metal oxides, because of the ionic-covalent nature of the metal-oxygen bonds. A new parameter called ICP, the “ionic covalent parameter”, was therefore defined to account for the influence of metal-oxygen bonds on the acid strength of the metallic cation. ICP could be expressed by: $\text{ICP} = \log P - 1.38X + 2.07$, where P is the polarizing power of the cation ($P = z/r^2$ with z = formal charge, r = Shannon ionic radius and $r(\text{O}^{2-}) = 1.40 \text{ \AA}$), and the electronegativity X is calculated by equation:

$X = 0.274z - 0.15 zr - 0.01r + 1 + C$, C being a correcting term, depending on each cation.

For a cation, the value of the ICP number depends on its valence and on its coordination. By combining ICP and Λ_{th} values, Leboutellier and Courtine (167) were able to set up calibration curves, and the optical basicity of most of the oxygen-containing solids was calculated.

As said before, Λ_{th} is a parameter accounting for the bulk and not for the surface: because heterogeneous catalysis is essentially a surface phenomenon, the true “surface optical basicity” should be considered.

Iguchi et al. (168) evaluated the case of NiO and found that the difference between the two optical basicity for bulk and surface was: $\Lambda_{surf} - \Lambda_{bulk} = 0.12$. The validity of this approximation can be verified by considering the XPS data: for instance Delamar et al. (169) found a correlation between the isoelectric point of solid surfaces (IEPS) and the oxygen chemical shift (since the acidic character of the oxidic surface was related to the acidity of the cation and the basic one to that of the oxygen). They plotted the IEPS of some oxides against the sum ($DO + DM$), where DO is the difference between the binding energy of O1s in the oxide and that in MgO taken as reference and DM is the difference of the binding energy of the cation and of the metal atom and they found a linear correlation (fig. VI.2). By following this example, the bulk optical basicity of some oxides was plotted against ($DO + DM$), giving also an approximately linear correlation (166).

Once everything was defined, the aim was to find a relationship between the optical basicity of a solid and a parameter accounting for the selectivity in oxidation. This parameter had to take into account the Lewis acidity/basicity of the gaseous molecules. Ai (170) suggested the use of the ionisation potential who can give indications about the acid-base character of hydrocarbons. Batiot (171) showed that formation enthalpies of the reactant and product account for the difficulty to get a high selectivity in oxidation of alkanes. The difference of the ionisation potentials (ΔI) of the organic molecules (reactant and product) can be seen as a tool to estimate selectivity.

It was then assumed that the difference $\Delta I = (I_R - I_P)$ represents the selectivity imposed by the catalyst. It must be taken into account that the ionisation energy of a hydrocarbon molecule decreases when the number of carbon increases: the higher n, the weaker is the ionisation energy and then more reactive is the molecule.

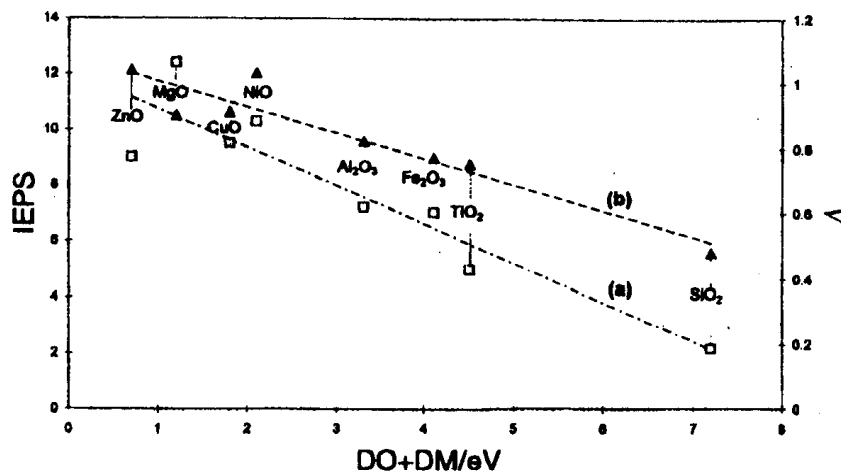


Fig.I.1: Linear relationship between: (a) IEPS and (DO+DM) of oxides; (b) optical basicity Λ_{th} and (DO+DM) (full triangles). Λ_{surf} used for MgO, NiO and Al_2O_3 .

When the number of carbons differs during the reaction, the following correction must be applied: $\Delta I = (I_R - I_P)n_P/n_R$. ΔI values are positive when the product is less stable than the reactant, so that the absolute values $|\Delta I|$ are used for comparing all reactions. A given catalyst involved in a certain reaction is therefore characterized by a couple of values $[|\Delta I|, \Lambda_{th} \text{ (or } \Lambda_{surf})]$.

When C_1 - C_4 alkanes react, a certain range of optical basicity is considered through variety of catalyst formulation, because very active and selective catalysts have not been found yet. According to that, the ODH of propane would require catalysts with Λ_{th} *ca.* 0.72 – 0.76.

Generally speaking, it is possible to calculate the optical basicity of any compound even though the phase is not known, but assumptions on valence, coordination number have to be made; moreover, when the coordination number and the valence of the cation is the same in two allotropic forms, the calculated optical basicity is the same. Another drawback of this parameter is that different preparation methods can bring a strong modification in selectivity and obviously the calculation of Λ does not allow to discriminate between two samples with the same chemical composition.

I.4 Basic concepts on the role of the acido-basicity in catalytic oxidation

In all partial oxidation processes, the total oxidation of the reactant organic compound to CO_x is the main side reaction, which must be avoided. Transition metal oxides carry surface acido-base properties and it has been always attempted to relate these properties with activity or selectivity in oxidation reactions.

Table I.3 summarizes the surface acid-base properties of some binary metal oxides correlated to the charge and the size of the corresponding metal cations. These comments refer to the bulk of the oxide. If one considers first the Brönsted acidity of the M-O-H groups, which depends on the covalency of the M-O bond and on the number of oxygen atoms on which the negative charge of the anion resulting from the O-H dissociation can be delocalized, metal oxides are generally referred to as basic or amphoteric. Because oxygen is one of the most electronegative elements, its bond with metals is very ionic and this gives rise to the basic nature of oxides and hydroxides. On the contrary the bond of oxygen with non-metals is more or less covalent and this explains the acidic properties to the oxide. Because the electronegativity of an ion increases with its oxidation state, the oxides of metals in a high oxidation state are characterized by covalent M-O bonds and behave as acidic oxides too, in contrast to the lower metal oxides that are typically basic oxides.

In addition, the oxides of metals at low oxidation state are very ionic and this leads to Lewis acidity associated with surface coordinatively unsaturated metal cations. The strength of the surface Lewis sites depends on the ionicity of the M-O bond, on the polarizing power of the cation and its coordination number. In ionic oxides, when the cation is very small, highly charged and has a small coordination number, Lewis acidity is predominant, otherwise, basicity predominates.

Generally speaking, the oxides of semi-metal elements (like silica) are covalent and no coordinative unsaturation is present on the surface, which is saturated by OH groups. They do not show Lewis acido-basicity, while the hydroxyl groups are Brönsted acidic.

The oxides of high oxidation state metals are characterized by very weak basicity. Cations can be bonded to oxygen ions, giving metal-oxygen double bond, whose coordination is very elastic: in spite of the covalency of metal-oxygen bonds, strong Lewis acidity can appear. The OH groups are covalently bonded to the metal and

the anion charge is delocalized on terminal double-bonded oxygens, resulting in medium or strong Brönsted acidity. Highly ionic metal oxides with highly reducible cations normally favor total oxidation, although some of them can show a certain degree of selectivity in oxidative dehydrogenation processes. The most used metal oxides in selective oxidation involve transition metals in a high oxidation state.

Table I.3: Acid-base properties of binary oxides from Busca et al (112).

Binary oxides	Characteristics	M-O bond nature	Acidity	Basicity
SiO ₂	Semi-metal Small-size cation	Covalent	Bronsted Medium/weak	None
MoO ₃ , V ₂ O ₅ , Nb ₂ O ₅	Semi-metal High oxidation state Medium-size cation	Largely covalent	Bronsted and Lewis Medium to strong	None
γ-Al ₂ O ₃	Metal Small-size cation	Ionic	Lewis Strong	Weak
TiO ₂	Metal Medium-size cation	Ionic	Lewis Medium	Medium/weak
SnO ₂ , ZrO ₂ , CeO ₂	Metal Large-size cation	Ionic	Lewis Medium/weak	Medium/strong
MgO, CaO, CuO	Metal Low oxidation state Large-size cation	Ionic	Lewis Medium to weak	Strong/very strong

The surface acid-base properties of the transition metal oxides are also influenced by their oxidation state. For instance, in the case of chromia and chromites, when they are covered by chromate species characterized by covalent Cr^{VI}=O bonds, they show Brönsted acidity and negligible basicity. On the contrary, the reduced surfaces of chromia and metal chromites are characterized by very ionic Cr³⁺-O bonds, without Brönsted acidity but with significant basicity and nucleophilicity. This trend is normally expected when reducing a metal oxide to lower oxides, which would have lower electronegativity and higher cation size.

The catalysts normally used in oxidation reactions are complex materials, sometimes called multicomponent. The main component is usually a mixed oxide: the crystal structures of mixed oxides are frequently not directly related to those of the component oxides and their acid-base properties are sometimes dominated by one of the two components. We have already said that the key factor for performing selective oxidation catalysis is to let the desired product desorb without further transformation and consequent overoxidation: so these complex catalysts should not react too strongly with these compounds.

As it is known in basic organic chemistry, olefins are very reactive towards electrophilic species and in particular Brönsted acids. Busca and coworkers (112) underlined the role of weak Brönsted acidity in facilitating the combustion of olefins through hydroxylation followed by oxidative dehydrogenation. According to these statements, Brönsted acid catalysts cannot be used to produce olefins with high selectivity.