Optical basicity: a scale of acidity/basicity of solids and its application to oxidation catalysis.

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Optical basicity: a scale of acidity/basicity of solids and its application to oxidation catalysis

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Abstract

After recalling the concept and applications of Duffy's 'optical basicity' of a solid oxide (Duffy, J.A. Geochim. Cosmochim. Acta. **1993**, *57*, 3961-3970), a Lewis-related acidity/basicity scale of transition metal cations and of oxides, oxysalts, mixed oxides is built by using ICP, the Ionic Covalent Parameter (Portier, J. et al., J. Alloys Comp. **1994**, *209*, 59-64). This scale allows to rank catalysts as well as oxides used as supports. For example, increasing basicity is found along (hydrogen or cationic) zeolites < heteropolyacids < $(VO)_2P_2O_7$ < MoO_3 < V_2O_5 ~ $NiMoO_4$ < Bi_2MoO_6 < Cu_2O < Sb_2O_4/SnO_2 < Ag_2O < K_2O, and SiO_2 < γ-Al_2O_3 < α-Al_2O_3 < CeO_2 < ZrO_2 ~ TiO_2 < MgO < SnO_2 series of catalysts and of supports, respectively. Optical basicity Λ_{th} being a characteristic of bulk oxide, a scale of surface optical basicity, Λ_{surf} is proposed by plotting the XPS O1s binding energy against Λ_{th}, which results in a logarithmic scale, while a correcting factor may be used in the case of catalysts exhibiting a compact crystal structure. As the goal is to be able to predict the acidity/basicity that would be necessary for a selective catalyst to exhibit in a given reactant-to-product oxidation, the difference of ionization potential ΔI, which corresponds to the electron donor power during the reaction, is plotted against optical basicity Λ, which is the electron donor power of oxygen in the solid. Linear correlations between ΔI and Λ are set-up, and their usefulness is discussed in several cases, one being mild oxidation of alkanes. The slope (positive for saturated C-C, negative for unsaturated C=C reactants) and intercept depend on the relative basicity/acidity of reactants and on the extent of oxidation, respectively. Theoretical considerations are proposed to tentatively account for these linear relationships.

Keywords
Optical basicity; acidity/basicity scale of solid oxides; ionization potential of organic molecules; selectivity in oxidation; predictive relationships.

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1- INTRODUCTION

Solid oxides used in catalytic reactions belong to the whole periodic table. Their role in catalysis depends mostly on their acid-base and redox properties. Schematically, acidic (basic) oxides of the right (left) part of the periodic table are involved in cracking, isomerisation, alkylation, etc., of hydrocarbons, and/or are used as supports of metals or of other oxides. Redox catalysts are mainly found among the transition metal oxides, and are more particularly involved in mild or total oxidation of hydrocarbons or of other molecules (alcohols, etc.). If parameters describing the catalytic activity are numerous and fairly well-known, selectivity is always related to kinetics, e.g., expressed as a ratio of the rates of one process compared to another one. Finding parameters able to account for selectivity in mild oxidation has been one of our concerns in our group but till recently our attempts failed because of the lack of parameters accounting for the solid state properties of transition metal oxides. Indeed there are little answers when one tries to understand why only vanadium oxide supported on titania is able to transform selectively o-xylene into phthalic anhydride, or why Mo_3VO_{11} is selective in the oxidation of acrolein to acrylic acid. Similarly, the fact that, e.g., n-butane, is selectively oxidized into butadiene, maleic anhydride, or CO_2 if $CoMoO_4$, $(VO)_2P_2O_7$, $LaCrO_3$ are respectively used as catalysts, is not explained. This means that well-defined properties of the catalyst are required to get selectivity in a given type of reaction. In these reactions, the surface lattice oxygens (O^{2-}) of the metallic oxide are directly responsible for the selective formation of the wanted product. The commonly used two-stepped scheme proposed by Mars and van Krevelen[1] describes this participation:

$$[\text{R-C-H}] + 2\,\text{K}\boldsymbol{O} \rightarrow [\text{R-C-}\boldsymbol{O}] + \text{H}_2\boldsymbol{O} + 2\,\text{K} \quad [1]$$

$$2\,\text{K} + \text{O}_2 \rightarrow 2\,\text{K}\boldsymbol{O} \quad [2]$$

The first step consists in the transfer of surface lattice oxygen ***O*** to the molecules of product (RC***O*** and H$_2$***O***) leaving the catalyst in its reduced form K, which is regenerated as K***O*** by gaseous oxygen, generally cofed with the reactant [R-C-H] in usual reactors. Therefore, the properties of O^{2-} species linked to metallic cations determine the catalytic properties, and particularly the selectivity to products. Among them, a key parameter is the nucleophilicity as noticed by Haber[2] who showed that nucleophilic (O^{2-}) and electrophilic (O_2^-, O_2^{2-}) oxygen species were responsible for mild and total oxidation, respectively. However there was no scale of nucleophilicity/electrophilicity or more generally of basicity/acidity utilizable for transition metal oxides till recently. To account for selectivity as a general concept allowing to classify reactions, it would be necessary to have available parameters accounting for a similar type of property in the gas phase, for the organic reaction, and in the solid phase, to characterize the nucleophilicity of oxygen. Moreover, thermodynamic parameters would be more appropriate than kinetic ones which depend strongly on experimental conditions: the initial state would be the reactant facing the oxidized K***O*** form and the final state would be the wanted product facing the reduced form K of the 'selective' catalyst. Oxidation catalysis proceeding by an exchange of electrons which accompanies the exchange of ***O*** species, we have thought that the *ionization energy* of the organic molecules could be useful to account for the gas phase reaction. Finding a parameter of the same type for solid oxides was not so easy. Modern theories of reactivity propose to consider the oxidizing power, acidity, basicity, reducing power, as steps along a same continuum, instead of distinct phenomena[3]. Among bulk parameters, Zhang's scale of electronegativity[4], optical electronegativity and optical basicity[5],[6], electronic polarizability[7], Racah parameter[8], ICP[9],[10] (ionic-covalent parameter), were used recently to quantitatively describe the acid (base) or redox behavior of oxides in various applications. General correlations of catalytic *activity*, with, *e.g.*, Me-O bond strength, electronegativity, or oxygen partial charge, are numerous[11],[12],[13],[14]. Auroux and Gervasini[15],[16] used some of these parameters in order to predict heats of adsorption and acid strength. Differential heats of adsorption of probe molecules such as NH_3 or CO_2 as a function of coverage have been worked out for different simple oxides, and relationships between the charge/radius ratio or the percentage of ionic character and average heats of of CO_2 adsorption or ammonia adsorption, respectively, were obtained. Idriss and Seebauer[17] showed recently that the rates of oxidative dehydrogenation of ethanol to acetaldehyde and of benzaldehyde esterification are correlated with the oxygen electronic polarisability α_O.

Successful correlations with experimental catalytic selectivity are far less numerous. For example, Vinek et al.[18] showed on a series of oxides that the XPS binding energy of O1s is related to the electron pair donating (EPD) strength of oxygen, and hence to selective dehydrogenation (on more basic oxides, high EPD of O^{2-}) or selective dehydration (on more acidic oxides, low EPD of O^{2-}) of alcohols. This EPD/EPA approach was later used[19] in oxidation reactions and it was shown that selectivity increased with acid strength.

We have had an even more ambitious goal: to classify catalytic oxides known to be selective in different oxidation reactions, in order to further use the resulting classification as a predictive trend. Among the bulk parameters mentionned above, optical basicity Λ as well as ICP seemed the most appropriate parameters because both take into account not only the type (ionic to covalent) of Me-O bond but also the extent (through polarizability) of the negative charge borne by oxygen. Duffy et al.[20],[21],[22] started from the principle that a quantitative scale of basicity could be provided if the magnitude of the electron density of the oxygen atoms was known. The word ‘optical’ means that optical spectroscopy was the origin of the measurements performed by using suitable probes. Metal ions (Tl^{+}, Pb^{2+}, Bi^{3+}) were inserted into the oxidic material whose acidity had to be determined. The expansion of their d outer orbital (nephelauxetic effect) upon coordination to the O^{2-} Lewis base depends on the polarization state of these O^{2-} and the shift of the UV frequency is related to Λ. This method was particularly useful in the case of molten oxidic systems (metallurgical slags) and glasses, and Λ could be successfully correlated with several properties of oxidic media in the solid or liquid state: refractive index[6],[23], viscosity[24], redox equilibria[25],[26],[27] acid-base neutralization reaction between oxyanion species[28]. However, the method it is not applicable when transition metal oxides are concerned because of the presence of the own d orbitals of metals. Lebouteiller and Courtine[29] plotted optical basicity against ICP values and were able to set-up a new quantitative scale of optical basicity (or better said: optical acidity) of all types of cations related to the same O^{2-} base. This scale has been recently used by Lenglet[30],[31] who found correlations with the Racah parameter of transition metal oxides. Catalytic applications to selective oxidation of various reactants were proposed by Moriceau et al.[32],[33],[34] by plotting optical basicity of the corresponding catalysts against the potential ionization difference $\Delta I = I_R - I_P$ of the gas phase, and linear correlations were obtained. Calibrations of these lines with the most well-known oxidation reactions, and within a reasonable limit of error, were carried out. These correlations allow to classify reactions and also to a priori determine the optimum optical basicity that would be required for a catalyst to be selective in the chosen reaction.

This paper aims at summarizing most findings using optical basicity scale. First, the concepts of optical basicity and of ICP will be recalled and some examples given. Then the choice of ionisation potential as a means to account for a ‘thermodynamic’ selectivity will be justified. The linear correlations obtained when plotting ΔI against the optical basicity will be then discussed. Finally, the thermodynamic nature of optical basicity will be discussed and attempts to account for the linearity of correlations between ΔI and Λ will be proposed.

1- SCALE OF OPTICAL BASICITY OF SOLID OXIDES

4-1. After Duffy

As first proposed by Duffy et al.[5,6],[20-22], the so-called ‘optical basicity’ characterized by Λ, allows to classify oxides as a scale of acidity which is referred to the same O^{2-} base. It accounts for physical and chemical behaviour of phases and gives indications, for example, on the structural modifications in glasses, on the effective electronic charge carried by ions in an oxide, on the M-O bond lengths or on redox equilibria in melted glasses. The optical basicity is built on Lewis acidity concept and is particularly adapted to the study of non aqueous non protonated systems. This parameter first obtained from UV spectroscopic measurements is a 'measure' of the donating electron power of O^{2-} to the M^{n+} cation in MO_y oxide. Indeed the polarizing power of M^{n+} influences the capacity of O^{2-} ions to give a part of their electronic charge to other cations in the solid phase, and as such it depends on M coordination. Therefore Λ characterizes the electron acceptor power of the M^{n+} cation as well as the electron donor power of O^{2-}, and the result is that it characterizes the acidity of the whole solid vs. the same O^{2-} base. For example, Λ MgO = 0.78 (Λ $^{VI}Mg^{2+}$ = 0.78, in which valence and coordination of $^{VI}Mg^{2+}$ are VI and +2). The reference chosen by Duffy et al. is CaO for which $\Lambda = 1.0$.

Duffy's scale is satisfactory for most s-p oxides but not for transition metal oxides. Examples are WO_3, MoO_3 and V_2O_5, the optical basicity Λ of which was found greater than 1.0 which is the value of basic CaO[6,7]. The main reason is that the optical basicity of transition metal oxides cannot be directly measured because the own d orbitals of cations are involved and because their metal-oxygen bonds have an ionic-covalent character. This problem was side-stepped by Portier et al.[9,10] who succeeded in building a similar scale, but based that time on a new parameter, the Iono-Covalent Parameter ICP. ICP, which is an adimensional number, accounts for the influence of the covalence of metal-oxygen bond on the acid strength of the metallic cation, and is calculated by equation [3]:

$$ICP = \log P - 1.38\chi + 2.07 \qquad [3]$$

where P is the polarizing power of the cation ($P = z/r^2$, z = formal charge, r = Shannon ionic radius[35] with rO^{2-} = 1.40 Å). The electronegativity χ (in Pauling-type scale) is calculated by [4]:

$$\chi = 0.274\, z - 0.15\, z\, r - 0.01\, r + 1 + c \qquad [4]$$

in which *c* is a correcting term, depending on each cation. For a given cation, the value of ICP depends on its valence, its coordination and eventually its spin state (low or high) in the solid[9,10].

By plotting Λ values determined for simple oxides by Duffy et al.[5,6] against ICP of cations, Lebouteiller and Courtine[29] showed that cations are distributed among straight lines depending upon their electronic configuration. Five lines, for s-p, d^0, d^1-d^9, d^{10} and $d^{10}s^2$ configurations were obtained, the equations of which are presented Table 1. As ICP does, the theoretical optical basicity Λ_{th} obtained from these correlations depends on the valence, coordination and spin of the cation(s)[32]. When several valences and/or coordinations exist, the basicity is obtained as follows, e.g., for Fe_3O_4 which crystallizes as inverse spinel:

Λ_{th} Fe_3O_4 = 3Λ $^{IV}Fe^{3+}$ + 2Λ $^{VI}Fe^{2+}$ + 3Λ$^{VI}Fe^{3+}$ = 0.785

with Λ $^{IV}Fe^{3+}$ = 0.66; Λ $^{IV}Fe^{2+}$ = 0.76; Λ $^{VI}Fe^{3+}$ = 0.77; Λ $^{VI}Fe^{2+}$ = 1.00 (high spin configurations). In the case of two polymorphs, the value of Λ_{th} is different only if the coordination of cation(s) is different. This is the case of the α and γ forms of Al_2O_3 because the latter is a defective spinel, and Λ_{th} γ-Al_2O_3 = 0.50 while Λ_{th} α-Al_2O_3 = 0.60, while is less acidic. Similarly, the acidity of GeO_2-quartz (Λ_{th} $^{IV}Ge^{4+}$ = 0.54) is higher than that of GeO_2-rutile (Λ_{th} $^{VI}Ge^{4+}$ = 0.66). Conversely, the anatase and rutile forms of TiO_2, the band gap of which is slightly different (3.2 and 3.0 eV, respectively) cannot be distinguished by the value of Λ_{th} because of VI coordination in both oxides.

Figure 1 shows the example of d^0 and d^1-d^9 lines which gather most transition metal cations which are commonly used in catalytic oxidation. The most acidic cations lie on the left of the figure. Redox couples involve transition metal cations which may be both in d^0/d^{1-9} configuration (first group), like W^{6+}/W^{5+} or W^{6+}/W^{5+}, Mo^{6+}/Mo^{5+}, V^{5+}/V^{4+} etc., or in the same second group d^{1-9} like Fe^{3+}/Fe^{2+} or Mn^{4+}/Mn^{3+}, or in d^9/d^{10} like Cu^{2+}/Cu^{+} (third group). The acidity/basicity of a same element depends mostly on its configuration at the highest valence and on its coordination. For cations of the first group (d^0 line) with the same valence, acidity decreases with decreasing coordination (Λ_{th} $^{VI}W^{6+}$ = 0.51, Λ_{th} $^{IV}W^{6+}$ = 0.54). For the same coordination, acidity generally decreases with decreasing valence ($^{VI}V^{5+}$ > $^{VI}V^{4+}$; $^{VI}Mo^{6+}$ > $^{VI}Mo^{5+}$). However the case of group VIa M cations (M = Cr, Mo, W) is special because Λ_{th} $^{VI}M^{6+}$ < Λ_{th} $^{VI}M^{4+}$ < Λ_{th} $^{VI}M^{5+}$, that is M^{5+} is less acidic than M^{4+}. Moreover, when comparing V and Mo, the oxides of which are among the most used in selective mild oxidation, it is striking that Mo^{5+} is far more basic than Mo^{6+} (ΔΛ = Λ $^{VI}Mo^{5+}$ - Λ $^{VI}Mo^{6+}$ = 1.17-0.52 = 0.65) while ΔΛ = 0.68-0.63 = 0.05 only for V^{4+}/V^{5+} couple. For redox couples lying on the same d^1-d^9 line (group 2), cations in their higher valence state are generally less acidic than in their lower state (Λ $^{VI}Mn^{4+}$ = 0.88; Λ $^{VI}Mn^{3+}$ = 0.81; this was the case of Λ_{th} $^{VI}Mo^{4+}$ < Λ_{th} $^{VI}Mo^{5+}$ just seen), and the lowest coordination corresponds to more acidic cations (in high spin configuration, Λ_{th} $^{VI}Fe^{3+}$ = 0.88, Λ_{th} $^{IV}Fe^{3+}$ = 0.66). Therefore, the value of Λ_{th} is really meaningful as it reflects most structural characteristics.

1-2. Mixed oxides

By using the optical basicity Λ_{th} of cations in their appropriate coordination, valence and spin, it is possible to calculate the theoretical optical basicity of mixed oxides, oxysalts or of any oxygen-containing solid, if the stoichiometry is known. Given a $M_i^{z_i+}{}_{x_i}O^{2-}{}_y$ oxide (or mixture), Λ_{th} is calculated by the linear combination of stoichiometry x_i , valence z_i and Λ_i of the i cations (y = oxygen stoichiometry), according to:

$$\Lambda = \frac{1}{2n}\sum_i x_i\, z_i\, \Lambda_i \qquad [5]$$

or $\Lambda_{th} = (ax\Lambda_A + by\Lambda_B)/2n$ for $A^{a+}{}_x\, B^{b+}{}_y O^{2-}{}_y$. Using data from [ICP, Λ] correlations, the optical basicity of, e.g., $(VO)_2P_2O_7$ is ($\Lambda\ {}^{VI}V^{4+} = 0.68$, $\Lambda\ {}^{IV}P^{5+} = 0.33$):

$\Lambda_{th}\ V_2P_2O_9 = (2 \times 4 \times 0.68 + 2 \times 5 \times 0.33)/18 = 0.486$.

Such Λ_{th} values can be calculated for any oxygen-containing phase, including hydrated/anhydrous/cation exchanged zeolites (proton being considered as any cation, $\Lambda\ {}^{I}H^{+} = 0.40$), or supported oxides. In the latter case, either the support has only a textural effect consisting in the dispersion of the active phase, and then it may be neglected, or its action is also synergistic or leads to bi-functionality. In the case of, e.g., the V_2O_5/TiO_2 system in which synergistic effects are well-known[36,37], the role of TiO_2 is prominent. $0.1V_2O_5/TiO_2$ and V_2O_5/TiO_2 $\Lambda = 0.72$ and 0.68, respectively ($\Lambda\ {}^{VI}Ti^{4+} = 0.75$). Another interest of the correlation is to account for the variation of acidity (Λ) upon modification by another cation or by a promotor. For example, $H_4PMo_{11}VO_{40}$ is a strong acid as $\Lambda_{th} = 0.51$. By replacing all or some of the protons by cations the basicity of O^{2-} is modified in Λ_{th} range 0.511 ($H_3Zn_{0.5}$) to 0.532 ($HCe_{0.75}$)[32]. In the case of $0.05V_2O_5/TiO_2$ example, doping by 5% K[38] results in higher $\Lambda_{th} = 0.743$ instead of 0.737 and then in higher basicity, as expected.

The optical basicity of mixtures like the so-called multicomponent oxides claimed in patents is also calculable. However, it is necessary to make assumptions as far as the valence and coordination of cations are concerned, on which moreover the oxygen stoichiometry depends. For example, in the case of $P_{1.5}Mo_{12}V_{0.5}Bi_{0.3}As_{0.4}Cu_{0.3}Cs_{1.4}O_y$ which has been claimed selective in the oxidation of isobutane to methacrylic acid[39], the oxygen stoichiometry can be calculated by assuming that the most stable valence and usual coordination for all elements (y = 43.45), so that Λ_{th} is 0.547.

On Figures 2 and 3 is presented a decreasing (from the left to the right) acidity scale of some known catalysts and of some oxides often used as supports. As expected, zeolites are the most acidic compounds, followed by heteropolyacids and then by WO_3, MoO_3, $(VO)_2P_2O_7$, V_2O_5 , etc. More basic (e.g., Bi_2MoO_6, Cu_2O) solids are found on the right. Clays like chrysotile, $Mg_3(OH)_4Si_2O_5$ ($\Lambda_{th} = 0.562$), may be considered as basic[40] as compared to zeolites because of the contribution of Mg ($\Lambda\ {}^{VI}Mg^{2+} = 0.78$) to Si ($\Lambda\ {}^{IV}Si^{4+} = 0.48$), but are less basic than most oxides used in selective oxidation. Silica is the most acidic oxide in the support series, followed by γ-Al_2O_3, α-Al_2O_3, etc., and MgO is the most basic. The strongest bases are found in the K_2O-Cs_2O series (Λ_{th} = 1.40-1.7).

1-3. Surface evaluation of optical basicity

The former considerations on optical basicity Λ are driven for bulk but not for the surface of solids, which, obviously, is concerned when dealing with catalysis, but also with adhesion, corrosion, etc. As it is well-known, the surface compared to the bulk may have very different properties and the main problem to solve is to know to what extent. We have considered first the cases where the crystal structure of the catalyst is anisotropic so that their layered morphology is directly obtained by preparation. Mild oxidation being structure-sensitive reactions, it is known that by changing the crystal morphology the selectivity is modified, as shown on MoO_3 and V_2O_5[41,42], or $(VO)_2P_2O_7$[43,44,45,46]. Therefore we have assumed that the known selective reaction proceeds on crystals with their natural habitus, e.g., {010}V_2O_5 for o-xylene to phthalic anhydride, or {100}$(VO)_2P_2O_7$ for n-butane to maleic anhydride, or {010}Bi_2MoO_6 for propene to acrolein. In such cases we have considered in first approximation than $\Lambda_{surf} \sim \Lambda_{th}$. The same remark holds for monolayers of active phases on supports and Λ_{th} of the monolayer/support system is used directly. In the case of 'bulky' compounds like NiO or Co_3O_4, the structures of which are cubic, we propose a correction on Λ_{th} by considering the results obtained by Iguchi and Nakatsugawa on NiO[47]. These authors have found that the polarizability of oxygen αO^{2-} is increased on the surface as compared to the bulk of NiO. By using a relation driven by Duffy[16] between Λ and αO^{2-}, the mean estimation of Λ_{surf} is $\Lambda_{surf} = \Lambda_{th} + 0.12$, which is assumed to give the maximum of deviation of Λ when a cubic solid is dealt with [32].

A more accurate way is to consider XPS data which provide a means to correlate surface to bulk properties. Delamar[48] found a linear correlation between IEPS and (DO+DM), where DO is the difference between the binding energy (BE) of O1s in the oxide and that in MgO taken as reference, and DM is the difference of BE of cation and of metal atom, respectively. By plotting Λ_{th} (or Λ_{surf} when appropriate) against (DO + DM) we also found a linear correlation[32]. Another try is to use the BE O1s data[49,50]. Plotting it against Λ results in the following logarithmic equation (Figure 4):

$$\text{BE O1s} = -3.79 \ \text{Ln}\ \Lambda + 529.7 \qquad [6]$$

in which the intercept value, 529.7 eV, is the BE O1s found experimentally for CaO (taken by Duffy as reference, Λ = 1). However, the Auger parameter, which is related to refraction index[51], would be more suitable to go farther because BE O1s is known to vary, sometimes widely, with the real surface state of the examined material. Since photoelectrons emerge from a thin surface layer of approximately 20-30 Å thick, the O1s line may be distorted because of the contribution of OH, H_2O and CO_3^{2-} groups[52]. In this context, however, there is a general correlation between BE O1s and Λ of the simple oxides (which could be refined by taking into account their structure), from the most acidic (P_2O_5) to the most basic (Cs_2O) oxides. As such, it gathers metal and transtion metal oxides, including zeolites and most supports,. Because of the small range of BE O1s when considering d^0 (mean BE ~530.2 eV) and d^1-d^9 (mean BE ~529.5 eV) oxides, it is quite difficult today to use reliably the correlation when dealing only with a series of closely related oxides like V, Mo, W, Nb oxides, except by considering accurate experimental data.

As a partial conclusion, we have made available a parameter, Λ_{th}, which varies with stoichiometry and with valence, coordination, spin state of cation(s) in the oxide structure and which is calculable for any oxygen-containing solid. Scales of bulk and of surface acidity/basicity are proposed by using optical basicity as a suitable parameter, which allows to rank oxides, and which can be used for several applications and particularly in catalysis as seen further.

2- IONIZATION POTENTIAL AND SELECTIVITY

Selectivity to a given product is a kinetic parameter, generally understood as a ratio of rates, and which depends therefore on experiments. Here we are looking for a 'thermodynamic selectivity' that could be used to rank selective oxidation reactions, and further to be compared with the acidity/basicity of catalysts. Free enthalpy of formation or ionization potential are suitable thermodynamic parameters for the reactant and the wanted product to compare the oxidation reactions. Free enthalpies per mole of oxygen were used by Bordes[53] in the following manner: the Δ_rG_{MOX} of Mild OXidation (e.g., butene to butadiene, to furan, to maleic anhydride and other intermediates) reactions was compared to the Δ_rG_{TOX} of Total OXidation of the same reactant (e.g., butene to CO_2). The difference was plotted against the initial selectivity of these reactions and a linear correlation resulted.

More recently, we have chosen the ionization potential of molecules as a representative parameter to be correlated to acid-base properties in several reactions. This parameter has already been used by Ai[54] to compare reactions, as well as by Richardson[55] who has correlated the degree of ionization of aromatics determined from ESR spectroscopy data with the electron affinity of cations in cationic zeolites. The ionization potential I of a C_n (n = number of carbons) hydrocarbon depends on n and also on the type (linear or branched) of the considered isomer. The I potential decreases when n increases, because the greater n, the higher is the HOMO orbital, the weaker is the ionization energy, and then the more reactive is the molecule. This is verified with series of C_2-C_4 paraffins and olefins, respectively (Figure 5a). When oxygen is present in a molecule, I increases with the amount of O in the same series (saturated C-C or unsaturated C=C compounds). For example, I = 9.95 and 10.52 eV for propanal and propanoic acid, while I = 10.1 and 10.6 eV for acrolein and acrylic acid, respectively.

To account for selectivity, we proposed to use the difference of ionization potential between the reactant and the product which is wanted (which is not CO_2 when mild oxidation is considered). When starting from a same reactant, the deepness of oxidation is accounted for by this difference, $\Delta I = (I_{Reactant}-I_{Product})$. For example, ΔI = 0.37 and 0.87 eV for propene oxidation to acrolein and to acrylic acid, respectively. ΔI represents the difference of electron donor power when the reactant become the product (scheme 1a). The main difference with non catalytic reactions is the exchange of electrons which proceeds

$$\begin{array}{ll} R \rightarrow R^+ + e^- & I_R \\ \\ \underline{P^+ + e^- \rightarrow P} & -I_P \\ \quad R \rightarrow P & \mathbf{\Delta I = I_R - I_P} \end{array}$$

a) Non catalytic reaction

$$\begin{array}{ll} R \rightarrow R^+ + e^- & I_R \\ \left.\begin{array}{l} K_{ox} + e^- \rightarrow K_{red} \\ K_{red} \rightarrow K_{ox} + e^- \end{array}\right\} \boxed{\Lambda} & \\ \underline{P^+ + e^- \rightarrow P} & -I_P \\ \quad R \rightarrow P & \mathbf{\Delta I = I_R - I_P = f(\Lambda)} \end{array}$$

b) Catalytic reaction

Scheme 1. Comparison of ΔI for a) non catalytic and b) catalytic oxidation (one-electron redox).

through the catalyst (scheme 1b), and thus we assume that the electron donor power (Λ) of a selective catalyst must fit the difference of electron acceptor power (ΔI) of the gas (liquid) phase reaction. A simple thermodynamic cycle may be drawn because ionization energy is a state function (scheme 2). The interest of

$$\begin{tikzcd} \text{Reactant} \arrow[r, "\Delta I"] \arrow[d, swap, "I_R"] \arrow[d, "K\boldsymbol{O}"] & \text{Product} \\ {[\text{Reactant}]^+} \arrow[r, "\text{Cat.}"] & {[\text{Product}]^+} \arrow[u, "-I_P"] \arrow[u, swap, "K"] \end{tikzcd}$$

Scheme 2. Thermodynamic cycle applied to catalytic oxidation

Thermodynamic relationships has been put in evidence, e.g., by Hodnett et al.[56,57] who used enthalpies of formation of reactant and of product to account for the difficulty to get a high selectivity in mild oxidation of alkanes. However enthalpies are not state functions, contrary to ionization energies which allow to predict what type of catalyst (characterized by Λ) could fit a given reaction (characterized by ΔI). ΔI is not only the net exchange of electrons during the reaction, but it also depends on the structure of the molecules of reactant and of product. Figure 5b shows what happens when ΔI is plotted against n in the case of oxidative dehydrogenation (ODH) of C_2-C_4 alcanes, during which two electrons are exchanged per molecule. It is seen that ΔIs are different and that ΔI increases with n, including for ODH of i-butane to i-butene, but decreases for n-butane to but-1-ene (ΔI very close for but-2-enes). Considering now the (more or less) selective catalysts described in litterature[58],[59] for ODH reactions, it is striking that catalysts based on vanadium oxide (or vanadates) are rather more selective for C_2 and n-C_4 (ΔI = 1.01-0.95 eV), while catalysts based on molybdenum oxide (or molybdates) are rather more selective for C_3 and i-C_4 (ΔI = 1.24-1.27 eV) oxidations.

ΔIs have been calculated for a series of mild and total oxidation reactions involving molecules with n = 1-8. ΔIs range from 0.15 to 2.01 eV in the case of mild oxidation, and up to 5.3 eV when combustion of phenol is considered[33,34]. When the number of carbons differs during the reaction (e.g., benzene oxidation to maleic anhydride), the following correction is applied:

$$\Delta I = (I_R - I_P)\, n_P/n_R \qquad [7]$$

where n_R and n_P are the carbon number of reactant and product, respectively. In the case of ammoxidation reaction, ammoniac is considered as a reactant (the other being oxygen on which are based the correlations), and ΔI is calculated by:

$$\Delta I = [(I_R + I_{NH3})/2 - I_P]\, n_P/n_R \qquad [8]$$

Sometimes the reaction is not selective enough (or better said, the fully selective catalysts have not yet been found), so that when two products are equally obtained the following equation can be used:

$$\Delta I = [I_R - (I_{P1} + I_{P2})/2]\, n_P/n_R \qquad [9]$$

This is the case, e.g., of propene which is generally found in noticeable amounts besides acrylic acid or of acrolein in the oxidation of propane.

As a partial conclusion, by considering a ‘thermodynamic selectivity’ which is the difference between ionization energies of reactant and product, various reactions of oxidation can be ranked. ΔI represents the electron acceptor power of the gas (liquid) phase reaction and is the analogue of Λ which represents the electron donor power of the selective solid catalyst.

3- CORRELATION BETWEEN IONIZATION ENERGY AND OPTICAL BASICITY

4-1. Correlations between Λ and experimental values of selectivity

Although the aim of this paper is to show how a thermodynamic relationship between Λ and ΔI allows to predict the type of catalysts needed for a reaction, it is worth recalling that Λ can be correlated with experimental parameters related to catalysis, or values of selectivity, provided the same reaction is studied[33]. For example by using data proposed by Matsuura[60], the heat of adsorption ΔH_{ads} for a series of catalysts of oxidation of 1-butene to butadiene, or the Mössbauer quadrupole shift values for Fe^{3+}-containing catalysts of propene ammoxidation, could be related to the Λ value of the respective catalysts[33]. In a study of the ODH of isobutyric acid to methacrylic acid on polyoxometallates $H_{4-zx}M_xPMo_{11}VO_{40}$ (z = valence of M)[61,62,63], in which M was varied, selectivities from 57 to 77 mol% were obtained at isoconversion (90 mol%). These experimental values of selectivity were correlated to calculated Λ_{th} values. Indeed, by replacing all or some of the protons of $H_4PMo_{11}VO_{40}$ which is a strong acid (Λ_{th} = 0.51) by various cations, the basicity of O^{2-} is modified in a Λ_{th} range of 0.511 ($H_3Zn_{0.5}$) to 0.532 ($HCe_{0.75}$). By plotting selectivity vs. Λ, a volcano curve was obtained, the maximum of which corresponds to $H_2CuPMo_{11}VO_{40}$ (Λ_{th} = 0.519). The electron donor power of the active oxygens in this compound is assumed to be optimum to ensure both the activation of the reactant (a basic oxygen is needed to abstract H from H-(C-) in isobutyric acid) and the desorption of the product (a more basic site is needed to allow desorption of the more basic C=C of methacrylic acid)[33]. Another highly selective catalyst for the same reaction is $Fe_2P_2O_7$ which is the main active phase found at the steady state[64,65] and it is remarkable that its optical basicity Λ_{th} = 0.52 is very close to that of the other selective catalyst, $H_2CuPMo_{11}VO_{40}$.

4-2.Linear [ΔI,Λ] correlations: alkanes and alkyl-aromatics

Correlations [ΔI,Λ] were first drawn for partial oxidation of alkanes and of unsaturated hydrocarbons. As ΔI, difference of ionization energy, may be negative or positive according to whether the product is more or less stable than the reactant, the absolute value |ΔI| (further written ΔI) was used to be plotted against Λ in order to compare the various reactions starting from C_1 (methane) to C_8 (o-xylene) reactants. Both oxidative dehydrogenation (ODH) and mild oxidation (MOX) reactions were examined, the idea being that the mechanism is more or less similar, at least for the activation step. Let us recall that, to be used as a predictive trend, such correlations cannot be based on experimental values of selectivities, as it is obvious that the catalytic properties of the catalyst depend strongly not only on its preparation but also on operating parameters. Therefore, for well-known reactions performed industrially like, e.g., propene, n-butane or benzene, o-xylene oxidations to acrolein, maleic anhydride and phthalic anhydride[66,67,68,69], respectively, the optical basicity was calculated for the 'well-known' selective catalyst, that is for bismuth molybdates, vanadyl pyrophosphate or $0.7V_2O_5$-$0.3MoO_3$ and V_2O_5/TiO_2, respectively. A first calibration curve was then drawn. In the case of ODH or MOX of alkanes, highly 'selective' catalysts are not yet known and a variety of formula taken from academic or patent literature can be used. Examples were chosen so as to get a range of Λ_{th} and then a new, optimized, calibration line was obtained. An example is isobutane oxidation to methacrylic acid (ΔI = 0.42 eV, eq.[7]) for which the formula $P_{1.5}Mo_{12}V_{0.5}Bi_{0.3}As_{0.4}Cu_{0.3}Cs_{1.4}O_y$ (Λ_{th} = 0.54, vide supra) has been claimed selective[37]. In another patent[70], methacrolein is found besides methacrylic acid (ΔI = 0.565, eq.[10]) for the formula $PMo_{12}VAg_{0.1}As_{0.25}KO_y$, thus y = 41.92 and Λ_{th} = 0.53. Obviously in these cases the actual valence state and coordination of cations at the steady state is not known. This point is particularly important each time molybdenum is involved, as compared to vanadium. Indeed, for ^{VI}Mo for example there is a large difference of Λ_{th} between Mo^{6+} (0.52) and Mo^{5+} (1.17), whose Λ_{th} is higher than that of Mo^{4+} (0.96) (Figure 1).

Each reaction/catalyst couple being characterized by [ΔI,Λ_{th} (or Λ_{surf})], it has been noticed that the 52 catalysts (Λ = 0.45 to 0.95) in 26 reactions (ΔI = 0.15 to 2.01 eV) are distributed among two straight lines with reliability factors R^2 close to 0.94-0.93. Slopes are positive or negative when oxidation of paraffinic bonds or of unsaturated bonds is concerned, respectively, as explained below.

4-2.1. **MOP line**

The **M**ild **O**xidation of **P**araffins (**MOP**) line (positive slope) gathers twenty nine [ΔI,Λ_{th}] couples and is attributed to reactions involving paraffinic bonds (Figure 6)[33]. Alkyl-aromatics like toluene, ethyl-benzene or o-xylene (oxidized into benzoic acid, styrene or phthalic anhydride, respectively) also fit this **MOP** line because only the methyl (ethyl) group(s) are transformed to acid or anhydride groups, as well as some O-containing reactants (ODH of isobutyric acid, MOX of acrolein and methacrolein) for similar reasons (C-C $\rightarrow$ C=C, or –(O=)C-H $\rightarrow$ -(O=)C-OH). However this is not the case of alcohols (vide infra). Another advantage of thermodynamics which considers only the initial and final stages and not the way the transformation happens is that the points representing methane coupling (to ethylene) performed, e.g., on Li_2O/MgO, the mechanism of which is known to involve radicals (at least partly)[71,72], are situated close to **MOP** line. Similarly, the [ΔI,Λ] of MOX of methane to synthesis gas (ΔI = 2.27 eV, eq.[8]) fits also the line if NiO is considered to be the actual selective phase (Λ_{surf} = 1.03).

It is interesting to examine more closely the reaction/catalyst couples in the light of the known experimental characteristics, the more so because highly selective catalysts are not yet known in alkane oxidation (Figure 7). The exception is $(VO)_2P_2O_7$ (Λ = 0.486). Known as the selective catalyst for n-butane oxidation to maleic anhydride (MaA)[64,66,73], its acidity is close from that of catalysts like aluminum phosphate (ethyl-benzene to styrene)[74], or from heteropolyacids like $H_4PMo_{11}VO_{40}$. By adding promotors like Fe^{3+} or Co^{2+} its selectivity to MaA is known to increase[66],[75],[76]. The addition of these dopants which are less acidic (Λ = 0.77 and 0.98, respectively) than V^{4+} (0.68) brings the representative Λ values closer to the calibration line, as well as some more acidic V^{5+} (0.63) which must be present in small amounts on surface[73]. Pentane oxidation to MaA on $(VO)_2P_2O_7$ fits also the line. When considering the oxidation of C_2-C_4 alkanes, ΔIs of MOX are far lower than ΔIs of ODH, which means that the optimum optical basicity of catalysts is also fairly different. Less acidic cations are needed for ODH, from an optimal Λ_{opt} = 0.68 for ethane to ethylene to Λ_{opt} = 0.78 for i-butane to i-butene. Operating conditions like the alkane-to-oxygen ratio which is generally greater than one render the feed more reducing. This is in accordance with the fact that the acidity of d^0 cations is lower (at iso-coordination) when reduced (d^1-d^9) than when oxidized (see Fig. 1). In MOX of alkanes, the observed formation of the olefin in substantial amounts besides the acid (e.g., propane to propene and to acrolein or to acrylic acid) may be also explained by this reducing action of the reactant on the cation. Actually, it would be necessary to know the mean valence state and coordination of the cations *at the steady state* to get a more realistic value of optical basicity. A good example is given by $AgMo_3P_2O_{14}$ studied by Costentin et al[77] in ODH of propane who measured the Mo^{6+}/Mo^{5+} ratio by XPS of the most selective catalyst and found it equal to 2/1. Calculating Λ of $AgMo_3P_2O_{14}$ gives 0.514 (too acidic), but for $AgMo^{5+}{}_2Mo^{6+}P_2O_{13.5}$ the value of Λ is 0.735, which fits **MOP** line. Other examples may be found in[33].

Two zones are worthwhile to be examined (Figure 7). Beginning by ethane oxidation (zone 1), the ΔIs of both MOX and ODH lie in the same range (0.86-0.94 eV), which is not the case of C_3 or C_4 alkanes. Although it depends on experimental conditions and thus on the reducing power of the mixture, ethylene and acetic acid are often obtained together which is accounted for by the correlation (Λ_{opt} = 0.64-0.66). Today the best catalysts are based on MoVO system (V/Mo < 1) in which the reduced Mo_5O_{14} oxide is identified[78],[79],[80],[81],[82],[83]. Its calculated Λ_{th} is 0.752, but if MoO_3 (Λ_{th} = 0.52) which is always detected besides Mo_5O_{14} is taken into account, Λ_{th} = 0.65 for Mo_5O_{14}/MoO_3 = 1/1. If that type of catalysts is promoted with Pd, its Λ_{th} increases a little (Λ_{th} ${}^{VI}Pd^{2+}$ = 1.11), while it decreases upon addition of Nb^{5+} (Λ_{th} ${}^{VI}Nb^{5+}$ = 0.61). As already mentionned, the actual Λ_{th} depends on the relative amounts of cations and of their valence at the steady state. Catalysts based on V_2O_5/TiO_2 (Λ_{th} = 0.69) were also studied[84]. To account for the oxidation of o-xylene to phthalic anhydride which proceeds on the same system, it is necessary to use less vanadium as compared to TiO_2, so that Λ_{th} = 0.737 for a theoretical formula like $0.05V_2O_5/TiO_2$, value which can be increased by considering all V^{4+} (Λ_{th} = 0.68) and thus Λ_{th} = 0.743 fits better the **MOP** line. MOX of propane to acrolein (ΔI = 0.95) with $\Lambda_{opt} \approx 0.67$ lies also in this zone.

Second (zone 2), three MOX reactions involving C_3 and i-C_4 (direct oxidation of propane to acrylic acid, isobutane to methacrylic acid and methacrolein to methacrylic acid), are in the same ΔI range (0.30-0.42 eV). The optimum Λ_{th} are ca. 0.49-0.55. It is striking that patents claim for the same type of multicomponent Mo-based oxides, the Λ of which is very close from that of polyoxomolybdates, often claimed for MOX of isobutane. Recently new systems were proposed, beginning by MoVO doped with both acidic (e.g., Al, Λ_{th} $^{VI}Al^{3+}$ = 0.60) and more basic cations like Te (Λ_{th} $^{VI}Te^{6+}$ = 1.173, Λ_{th} $^{VI}Te^{4+}$ = 0.751). For example, by adding Al and Te to the raw formula $Mo^{6+}{}_6V^{4+}{}_2O_{22}$ (hypothesis), this material (Λ_{th} = 0.549) becomes less and less acidic along $Mo^{6+}{}_6V^{4+}{}_2Al^{3+}O_{22.5}$ < $Mo^{6+}{}_6V^{4+}{}_2Al^{3+}Te^{4+}{}_{0.5}O_{23.5}$ < $Mo^{6+}{}_6V^{4+}{}_2Al^{3+}Te^{6+}{}_{0.5}O_{24}$ (Λ_{th} = 0.552 < 0.578 < 0.589). Catalysts for MOX of acrolein to acrylic acid (ΔI = 0.50 eV) must be slightly less acidic (Λ_{th} = 0.57). As far as propylene is concerned as a reactant, ΔI = 0.37 eV for its oxidation to acrolein lies in the same range. However, because propene is not an alcane, the basicity of the catalysts must be higher, as discussed further (see **MOO** line, Figure 8).

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4-2.2. **MOO** line

The **M**ild **O**xidation of **O**lefins (**MOO**) line gathers MOX and ODH reactions of C_2-C_4 olefins to epoxides, aldehydes and acids or anhydrides (Figure 8). Epoxidation of ethylene proceeds on alumina supported silver which here is supposed to undergo oxidation to Ag_2O (Λ_{th} = 1.25) during the course of the reaction. Heterogeneous catalysts for epoxidation of propylene are not very selective. In the past, we tried to use thallium oxide doped with dysprosium[85] and we decided to take this point (Λ_{th} = 1.25) into account because it lies not too far from the calibrated line. Benzene and but-1-ene oxidations to maleic anhydride on $(V_{0.7}Mo_{0.3})O_5$ and $VOPO_4/(VO)_2P_2O_7$[86] respectively fit the line. According to **MOO** line, more basic catalyst should be used to oxidize propene (Λ_{opt} = 0.93) than propane (Λ_{opt} = 0.67) to acrolein. Several catalysts have been reported for MOX of propene to acrolein (Sb_2O_4/SnO_2, Cu_2O, USb_3O_{10} and bismuth molybdates)[87,88,89] whose Λ range from 0.71 ($Bi_2Mo_3O_{12}$) to 0.97 (USb_3O_{10}, Cu_2O) while Λ_{th} = 0.96 for Sb_2O_4/SnO_2. Pure bismuth molybdates seem therefore not to fit the line although they are very well-known catalysts of this reaction. Because their rate of reoxidation (by air) is far higher than their rate of reduction (by propene), the presence of Mo^{5+} is difficult to check but this cation is known to form temporarily. If it is assumed that 2/3 of Mo is Mo^{5+} at the steady state, the obtained Λ_{th} is 0.998 (Λ_{opt} = 1.0). When multicomponent molybdates are used, the role of cations like Co^{2+}, Ni^{2+}, Bi^{3+}, etc., is to bring more basicity to acidic Mo^{6+} so that a better fit may be obtained. Several experiments[66,89,90] have shown that Bi^{3+} in bismuth molybdates could be responsible for the oxidation step of propene to allene (ΔI = 0.04 eV) and Λ_{th} is roughly in accordance since Λ_{th} $^{VIII}Bi^{3+}$ = 1.18. As it is common to find also acrylic acid besides acrolein, eq.[8] gives ΔI = 0.62 eV, which is the same value than for MOX of isobutene to methacrolein. The same Mo-based multicomponent oxides are generally used for both reactions, which is accounted for by the correlation. According to the **MOO** line, the optimum Λ_{opt} of a catalyst for the direct MOX of propylene to acrylic acid (ΔI = 0.87 eV) should be 0.67. Industrially, the reaction is performed in two reactors, catalysts based on molybdate type ensuring propylene oxidation to acrolein (ΔI = 0.37, line **MOO**, Λ_{opt} = 1.0) and e.g., Mo_3VO_{11}[91] (Λ_{th} = 0.54) ensuring oxidation of acrolein to acrylic acid (ΔI = 0.50 eV, line **MOP**, Λ_{opt} = 0.54).

If the standard error is small on ΔI (± 0.02 eV), it is certainly high on Λ because the value of Λ on surface or at the steady state cannot be ascertained. Moreover, several solids are tried for ODH of alkanes, as already mentioned, with little success as far as selectivity is concerned. For sure, however, the correlations show that a catalyst for ODH must be less acidic than for MOX of alkane. It must be emphasized that these correlations are given for a 'theoretical selectivity' but do not apply to activity parameters, as far as different reactions are compared. Up to now, and to give an example, our attempts failed in correlating optical basicity of oxides with the turn-over frequency measured for various oxidation reactions by using the very thorough work presented by Wachs et al.[92].

4-3. Other mild oxidation reactions

Following the same method, [ΔI,Λ] couples were plotted for the mild oxidation of C_1 to C_6 alcohols to aldehydes or ketones (Table 2). The positive slope of the obtained **MOA** line shown Figure 8 is smaller than that found for MOX of paraffinic bonds (see Table 5). The ammoxidation of hydrocarbons was also examined but the literature is scarce and examples are not numerous enough. In the case of paraffins and alkyl-aromatics, data are available mainly for propane and toluene. A [ΔI,Λ] **AP** line was tentatively drawn to represent this type of reaction[34], where ΔI was calculated by eq.[9]. The large contribution to ΔI of ionization energy of ammoniac which is high is responsible for the small positive slope, and the reliability coefficient is poor also because of the chosen reactions which are not numerous enough. However its slope and intercept are gathered in Table 5, together with those of other lines.

4-4. Combustion of paraffins and of olefins

Tables 3 and 4 gather [ΔI,Λ] couples obtained for the total oxidation of paraffins (**TOP** line) and of toluene (C_1-C_7), and that of olefins (**TOO** line) (C_2H_4 to i-C_6H_{12}) and of phenol. The slope of **TOP** line is positive, whereas it is negative for **TOO** (Fig. 5), as it was observed for MOX of paraffins and MOX of olefins, respectively. To replace noble metals which are the most active catalysts, several perovskite-type oxides are commonly used in these reactions of combustion which become more and more important for pollution abatement (combustion, soot particulates, VOC). These solids have a versatile ABO_3 structure, well-known to accommodate nearly all types of cations A and B, the coordination of which may change according to stoichiometry.

4-4.1. Total oxidation (combustion) of paraffins (**TOP** line)

The most used catalysts are perovskite-type oxides containing B = Fe, Co and/or Mn cations, all of which exhibiting various valences, and which may form solid solutions together[93],[94]. Cation A is mainly represented by lanthanum which can be partially substituted, the most often by Sr, to increase defects and catalytic activity (here, activity may be confounded with selectivity). The optical basicity varies widely upon substitution of A (e.g. La^{3+} substituted by more basic Sr^{2+}) and slightly less upon substitution of B. Studying n-butane combustion on $La_{0.2}Sr_{0.8}Co_{1-y}Fe_{1-y}O_3$ catalyst, Yamazoe et al.[95] have shown that activity increases along y = 1< 0.6 < 0.8 < 0.4 which is nearly parallel to the calculated $\Lambda_{surf,}$ increasing as y = 1 < 0.8 < 0.6 < 0.4 (Table 3). For the same reaction, Seiyama et al.[96] found that $La_{0.8}Sr_{0.2}Co_{0.4}Fe_{0.6}O_3$ (Λ_{surf} = 1.23) is more active than $La_{0.6}Sr_{0.4}CoO_3$ (Λ_{surf} = 1.0), itself known as the most active composition in the $La_{1-x}Sr_xCoO_3$ system[97]. When the B site composition was fixed as in $La_{1-x}Sr_xCo_{0.4}Fe_{0.6}O_3$ and x was varied, the activity was found to increase as x = 1.0 < 0.8 < 0.6 < 0 < 0.4 < 0.2, again nearly parallel to Λ_{surf} increasing along x = 1.0 < 0.8 < 0.6 < 0.4 < 0.2 < 0 . Then we may conclude that activities follow roughly the same trend than optical basicity Λ_{surf}. The cation deficient perovskites such as $La_{1-x}Sr_xMnO_3$, are known to act as "suprafacial" catalysts[88,89],[98],[99] because their structure does not contain enough ion vacancies to allow lattice oxygen to be mobile enough, whereas in Co- and Fe-perovskites, considered to be "intrafacial catalysts", oxide ions are highly mobile[88,89],[100],[101],[102]. The oxide ion vacancies which are created by charge compensation are able to accommodate extra-oxygen in the lattice, which leads to the variation of the oxygen composition depending on temperature and oxygen partial pressure. This phenomenon cannot be directly accounted for by optical basicity (unless the exact stoichiometry, valence, coordination, spin state at the steady state are known), and may explain the few discrepancies observed in the above parallelism between the activities and Λ_{surf} in the 0.97 -1.32 range.

The above and other examples of combustion catalysts are shown to fit the **TOP** line (Fig. 9). Another type of perovskite-related are $YBa_2Cu_3O_{6+y}$ catalysts (known for their superconductivity). When y = 1 (Λ_{surf} = 1.027) the catalyst is highly selective in the combustion of toluene at all oxygen pressures that were investigated[90].

4-4.2. Catalytic combustion of olefins and other unsaturated compounds (**TOO** line)

Perovskites and spinels are also claimed to be active in the combustion of olefinic compounds. Examples including other oxides are given in Table 4 and Figure 10 (**TOO** line). Among numerous catalyts to eliminate Diesel engine soots, the spinel-type $Cu_{1-x}K_xFe_2O_4$ (x = 0-0.2) catalyst was proposed by Shangguan et al.[103] who found that the surface composition of potassium was quite different from the overall composition of their sample and increased with the doping amount. They showed that all K was not dissolved in the spinel lattice and segregated on surface. The figurative point for K_2O (Fig. 10) is a measure of the deviation from the point C_2 on the correlation **TOO** line representing ideally the catalytic combustion of pure olefinic bonds of the σ-π type which are the main constituent of soots. Other examples of catalysts of combustion of Volatile Organic Compounds (VOC) are also provided. Phenol and pseudocumene C_9H_{12}, often considered as VOC representative, were studied[104] using CuO/Al_2O_3 and SnO_2-V_2O_5 catalysts.

4- Theoretical aspects

The above linear correlations between Λ and ΔI have distinct slopes and intercepts (Table 5), which seem to depend on, (i), the relative electron donor power or (Lewis-related) acidity/basicity of the reactant and, (ii), on the extent of the considered oxidation reactions. Although it is not (yet) possible to explain all of these findings, we shall try to bring more light, on the one hand, by considering thermodynamics of redox systems to account for the particular nature of optical basicity which looks like an intensive parameter, and on the other hand, by using the charge transfer theory to account for the linear nature of [ΔI,Λ] correlations.

4-1. Attempts to give a thermodynamic definition of optical basicity

It is worth recalling that in selective oxidation reactions, whatever their goal (partial or total oxidation), the same type of mechanism has been proposed by Mars and van Krevelen for mild oxidation as well as by Voorhoeve[105] ('intrafacial' mechanism) for combustion. Even though the 'suprafacial' mechanism is considered in certain cases, it is obvious that the basicity of surface oxygen species bound to, e.g., a perovskite, is higher than that on vanadium oxide. Therefore, as surface lattice oxygen participates to the reaction and is inserted in the oxygenated product, it is legitimate to try to find a parameter to account for its 'quality'. Meanwhile the cation undergoes reduction, which is not taken into account in the above work because, as a catalyst, it is supposed to come back to its intial, oxdized state, by means of gaseous dioxygen.

However there are applications to electrochemistry in which optical basicity is used as a parameter useful to predict redox equilibria in particular media, like in molten silicates[21,22,26-27], and is related to standard electrode potentials E° in aqueous solution[106].

Duffy et al.[6,27,106] have studied the bulk redox equilibria of many cationic couples such as Fe^{3+}/Fe^{2+}, Sn^{4+}/Sn^{2+}, As^{5+}/As^{3+}, etc., taking place in molten alkaline silicates (at 1400°C) and containing various concentrations of Li^+, Na^+ or K^+. In the presence of oxygen, and applied to, e.g., Fe^{3+}/Fe^{2+}, the following equation represents the combination of two half-equations according to:

$$4\,Fe^{3+} + 2\,O^{2-} = 4\,Fe^{2+} + O_2 \qquad [10]$$

In alkali iron silicate glasses, $\ln([Fe^{2+}]/[Fe^{3+}])$ was found to decrease with increasing basicity along Li_2O < Na_2O < K_2O (activities confounded with concentrations). Three distinct $\ln([Fe^{2+}]/[Fe^{3+}]) = f(\Lambda_{exp})$ curves (Λ_{exp} is the experimental optical basicity) depending on the alkali oxide were drawn, and were combined in a single relationship according to equation [11] :

$$\ln [Fe^{2+}]/[Fe^{3+}] = 7.51 - 15.33\,\Lambda, \text{ or } \Lambda = 0.489 - 0.065 \ln [Fe^{2+}]/[Fe^{3+}] \qquad [11]$$

This equation looks similar to the well-known Nernst equation for one-electron redox (eq.[12]):

$$E = E° + (RT/F) \ln [Fe^{3+}]/[Fe^{2+}], \text{ where } E = -\Delta_r G_T/F \text{ and } E° = -\Delta_r G°_{298}/F \text{ (F = Faraday)} \qquad [12]$$

In other words, equation [11] is related to the free enthalpy ΔG of the redox system as if Λ would take part in a thermodynamic state function of the system.

In order to check this hypothesis, let us combine eqs.[11] and [12], in which E and E° = -0.77 V refer to the equilibrium potential of Fe^{2+}/Fe^{3+} redox (in molten silicate medium, F/RT = 6.9378 at 1673K) and at 25°C (in aqueous medium), respectively. It gives (eq.[13]):

$$\ln[Fe^{2+}]/[Fe^{3+}] = - 6.9378\,(0.77 + E) = 7.51 - 15.33\,\Lambda, \text{ and:}$$

$$\Lambda = 0.838 + 0.452\,E \qquad [13]$$

Using the experimental data provided by Duffy and choosing the value $\ln [Fe^{2+}]/[Fe^{3+}] = -1$, for instance, gives $\Lambda_{exp} \sim 0.55$ (after Figure 7b in [6]). On the other hand, the value of E can be calculated from the Nernst equation by means of the chosen value, $\ln[Fe^{2+}]/[Fe^{3+}] = -1$, and thus $E = -0.77 + 1/6.9378 = -0.625$ V. Using eq.[13], we find $\Lambda = 0.838 + [0.452(-0.625)] = 0.55$, that is, as expected, the same numerical value than Λ_{exp} in [6].

We assume therefore that Λ is a dimensionless coefficient which is tightly associated to $\Delta_r G_T$ state function. Using eq.[11] and replacing ln ($[Fe^{2+}]/[Fe^{3+}]$) by (E°-E)F/RT which is equal to $(-\Delta_r G°_T + \Delta_r G_T)/RT$ leads to the expression:

$$\mathbf{\Lambda = a.\Delta_r G_T + b} \qquad [14]$$

where a = 1/15.33RT = and b = -(1/15.33RT)($\Delta_r G°$ + 7.51RT) for Fe^{3+}/Fe^{2+} redox system. Other values of a and b may be found in[105].

Taking into account the definition of the free enthalpy state function, and more particularly its consequences on solid state properties[107], it is not surprising that Λ_{th} has been already related to one of the intensive variables, such as refractive index, viscosity, etc., as recalled in Introduction.

4-2. Attempts to account for linear relationships between ionization potential of molecules and optical basicity of catalysts.

According to Richardson[55] who has applied the charge transfer theory to catalysis on cationic zeolites, the number of cation radicals N^+ coming from the activation of N molecules is related to the ionization potential of the molecule, to the electron affinity of the cation in the oxide, and to the dissociation energy W of the excited state of the charge transfer complex (all in eV), according to:

$$N^+ = N \exp[-(I-A-W)/kT] \qquad [15]$$

(T = temperature and k = Boltzman constant). Following the thermodynamic cycle presented in scheme 2, this relationship can be applied to the [reactant molecule-KO] and [product-K] couples. The reactant molecule, R, is adsorbed on KO (oxidized form) and the product, P, desorbs from K (reduced form of the catalyst). In the following, I_R and I_P are the ionization potential of reactant R and product P, A_{KO} and A_K are the electron affinity of cation in KO and K, and W_{R-KO} and W_{P-K} are the dissociation energy of the excited state of the charge transfer complexes corresponding to R on KO and P on K, respectively[33].

The following equations hold for reactant R and product P, respectively:

$(-I_R + A_{KO} + W_{R-KO})/kT = \ln(N_R^+/N_R)$, or $I_R = (A_{KO} + W_{R-KO}) - kT \ln(N_R^+/N_R)$

and $(-I_P + A_K + W_{P-K})/kT = \ln(N_P^+/N_P)$, or $I_P = (A_K + W_{P-K}) - kT \ln(N_P^+/N_P)$

Then: $\Delta I = |I_P - I_R| = (A_K + W_{P-K}) - (A_{KO} + W_{R-KO}) + kT[\ln(N_R^+/N_R) - \ln(N_P^+/N_P)]$

$= (A_K - A_{KO}) + (W_{P-K} - W_{R-KO}) + kT[\ln(N_R^+/N_P^+) + \ln(N_P/N_R)]$

Let us consider that the N_P/N_R ratio represents the conversion of R to P. At the steady state, this ratio is constant, and $(A_K - A_{KO})$ and $(W_{P\text{-}K} - W_{R\text{-}KO})$ also are constant. Then:

$\Delta I = (A_K - A_{KO}) + (W_{P\text{-}K} - W_{R\text{-}KO}) + kT\,[\ln(N_P/N_R) + \ln(N_R^+/N_P^+)]$

or: $\Delta I = \alpha + \beta \ln(N_R^+/N_P^+)$ [16]

where $\alpha = [(A_K - A_{KO}) + (W_{P\text{-}K} - W_{R\text{-}KO})] + kT \ln(N_P/N_R)$, and $\beta = kT$.

Let us assume that, in the temperature range (350-550°C) corresponding to that generally used in mild oxidation, α and β vary little with T. If, furthermore, the molecular N_R^+/N_P^+ ratio is supposed to be close from the $[N_R^+]/[N_P^+]$ concentration ratio, then it should be proportional to the [KO]/[K] redox ratio, so that relation [16] becomes:

$\Delta I = \alpha' + \beta' \ln [KO]/[K]$ [17]

Using a generalized equation similar to eq.[11] by which Λ was related to $\ln[Fe^{2+}]/[Fe^{3+}]$ gives:

$\ln [M^{z+}]/[M^{(z+n)+}] = a'\Lambda_{th} + b'$ [18]

in which a' and b' are constant and depend on the $M^{z+}/M^{(z+n)+}$ redox. By combining eqs.[17] and [18] where [KO]/[K] replaces $M^{z+}/M^{(z+n)+}$, the following expression [19] is obtained:

$\Delta I = \alpha' - \beta' [a'.\Lambda + b']$, and then :

$\mathbf{\Delta I = m + p\,\Lambda}$ [19]

where $p = -\beta' a'$ and $m = \alpha' - \beta b'$. Therefore, eq.[19] accounts for the linear equations gathered in Table 5, if p and m are supposed to be constant in the considered range of temperature (ca. 300-550°C for MOX, 700-1000°C for combustion).

5- Conclusion

This paper aimed at finding theoretical or empirical parameters able, (i) to account for the mean acidity/basicity or electron acceptor/donor power of the solid catalyst, (ii) to account for the mean acidity/basicity or electron acceptor/donor power of the reactant-to-product selective reaction, in order to, (iii), combine them to account for the selective action of the catalyst suited for the reaction, and, later, to, (iv), forecast the optimum acidity/basicity of a (new) catalyst in a given (new) reaction. To our opinion, this ambitious goal is quite well reached by plotting the optical basicity against the variation of ionization potential during the reaction. After recalling the concept and applications of Duffy's optical basicity of a solid oxide and its extension to transition metal oxides, catalysts and supports have been classified by means of Λ_{th}, from acidic zeolites to basic oxides. As Λ_{th} depends on valence, coordination and spin state of the cation(s), this parameter really accounts for structural characteristics of the solid oxide. The way the acidity is varied by adding dopants or other oxides is easily accounted for by Λ_{th}. However, for e.g., V^{4+}-Ti^{4+}-O system, the value of Λ_{th} would be the same for the mixed oxide xVO_2-$(1-x)TiO_2$ (which does not exist), for $V_xTi_{1-x}O_2$ solid solution or xVO_2 supported on $(1-x)TiO_2$, and, by doping such a system by K^+, Λ_{th} will not tell if K^+ affects V more than Ti. In the case of multicomponent catalysts (e.g., molybdates) of known stoichiometry, an evaluation of Λ_{th} is obtained, provided the valence and coordination of cations is 'imagined'. The evaluation of the *surface* optical basicity has been tentatively addressed by proposing a standard correction for bulky solids, and by a relationship between the O1s binding energy and Λ_{th}.

A simple criterion, which has the same nature than Λ_{th} of the catalyst, was used to represent the electron donor power during reaction: the absolute value of the potential ionization difference, $\Delta I = |I_R - I_P|$, weighed by the ratio n_P/n_R of carbon in product and reactant molecules respectively. The linear correlations obtained between ΔI and Λ_{th} show that their slope is related to the electron donor power of the reactant, positive when C-C (alkanes, alkyl-aromatics) or C-H (alcohols) bonds are to be transformed, and negative when C=C bonds are concerned. The intercept depends on the extent of oxidation, and its absolute value increases from mild to total oxidation, respectively. A main difficulty is the actual state of cations at the *steady state*, but each time accurate experiments allow to determine the mean valence state, the calculated Λ_{th} fits fairly well the correlations. These lines may be used as a *predictive trend*, and allow, for example, to precise that more basic catalysts are needed for alkane ODH than for its mild oxidation to oxygenated compound. As a variety of solids has been catalytically experienced in literature, it would be worthwile to consider far more examples than what is proposed here to refine the relationships observed. Finally, theoretical considerations are proposed to tentatively account for these linear relationships. Optical basicity would be closely related to the free enthalpy, and, as an intensive thermodynamic parameter, it is normal that it could be related to several characteristic properties, including now catalytic properties.

Table 1. Ionic Covalent Parameter (ICP) plotted against optical basicity of cations. Slope a and intercept b of linear relationships ICP = aΛ + b (after[29]).

Electronic configuration	a	b	Reliability factor R^2
s-p	- 0.672	1.451	0.989
d^0	+ 2.982	- 1.322	0.999
d^1-d^9	- 0.644	1.144	0.991
d^{10}	- 0.729	1.390	0.999
$d^{10}s^2$	- 13.844	17.134	0.896

Table 2. Mild Oxidation of Alcohols (**MOA** line)

Λ_{th}	ΔI (eV)	Reactant	Product	Catalyst	Ref. **MOA**
0.55	0.02	Methanol	Formaldehyde	$2MoO_3$-$Cr_2Mo_3O_{12}$	1
0.56	0.02	id	id	$4MoO_3$-$Cr_2Mo_3O_{12}$-$Fe_2Mo_3O_{12}$	2
0.57	0.02	id	id	$0.5Fe_2(MoO_4)_3$-MoO_3	3
0.625	0.23	Ethanol	Acetaldehyde	$0.08MoO_3$-$0.25TiO_2$-$0.8Al_2O_3$	4
0.65	0.23	id	id	V_4O_9	5
0.74	0.23	id	id	Mg_5CeO_7	6
0.845	0.38	Butanol-2	Butanone-2	$9SnO_2$-MoO_3	7
0.92	0.44	Propanol-2	Acetone	Mn_3O_4	8
0.92	0.41	Allylic alcohol	Acrolein	Mn_3O_4	9
0.98	0.60	Cyclohexanol	Cyclohexanone	2CuO-ZnO-$0.4Al_2O_3$	10
1.04	0.60	id	id	CuO-CoO	11

Table 3. Total Oxidation of Paraffins (**TOP** line)

Λ_{th}	ΔI (eV)	Reactant	Catalyst	Ref. **TOP**
0.908	1.23	Methane	$La_{0.5}{}^{3+}Sr_{0.5}{}^{2+}Co^{2+}O_3$	1
0.853	1.23	Methane	$La_{0.2}{}^{3+}Sr_{0.8}{}^{2+}Co^{2+}O_3$	2
0.902	1.23	Methane	$La^{3+}{}_{0.2}Sr^{2+}{}_{0.8}Co^{2+}{}_{0.5}Co^{3+}{}_{0.5}O_3$	3
0.952	2.82	Propane	$La^{3+}{}_{0.2}Sr^{2+}{}_{0.8}Co^{3+}O_3$	4
0.957	2.82	Propane	$La^{3+}{}_{0.5}Sr^{2+}{}_{0.5}Co^{2+}{}_{0.5}Co^{3+}{}_{0.5}O_3$	5
0.995	3.24	Butane	$La^{3+}{}_{0.5}Sr_{0.5}Co^{3+}{}_{1-y}Fe^{3+}{}_{y}O_3$ $y = 0.2$	6
0.987	3.24	Butane	$y = 0.4$	7
0.979	3.24	Butane	$y = 0.6$	8
0.971	3.24	Butane	$y = 0.8$	9
0.963	3.24	Butane	$y = 1.0$	10
1.00	3.643	Hexane	γ-MnO_2	11
1.027	4.95	Toluene	$Y^{3+}Ba^{2+}{}_2Cu_3O_{6+x}$	12

Table 4. Total Oxidation of Olefins (**TOO** line)(*)

Λ_{th}	ΔI (eV)	Reactant	Catalyst	Ref. **TOO**
0.65	5.30	C_6H_5OH	$CuO(10\%)/Al_2O_3$	1
0.75	5.04	C_9H_{12}	SnO_2 - V_2O_5	2
1.038	3.27	C_2H_4	$La_{0.8}Sr_{0.2}MnO_3$	3
1.135	3.27	C_2H_4	$La_{1.2}Sr_{0.8}Co^{3+}O_3$	4
1.075	3.27	C_2H_4	$LaMnO_3$	5
1.012	4.04	C_3H_6	$La_{0.85}Ca_{0.15}Co^{3+}O_3$	6
1.042	4.04	C_3H_6	$La_{0.85}Sr_{0.15}CoO_3$	7
0.965	4.04	C_3H_6	Co_3O_4	8
0.849	4.53	i-C_4H_8	$La_{0.2}Sr_{0.8}Co^{3+}O_3$	9
0.904	4.53	i-C_4H_8	$La_{0.5}Sr_{0.5}Co^{3+}O_3$	10
0.908	4.53	i-C_4H_8	$La_{0.8}Sr_{0.2}Fe^{3+}O_3$	11
1.317	2.51	C_1 *	La_2CuO_4	12
1.50	1.52	C_2 **	La_2CuO_4 + K_2O	13

* Handbook of Physical Chemistry, 76th Ed.,C.R.C. Press (1966)

** C_2 is considered here as a main constituent of soot with σ-π bonds >C = C<.

Table 5.

Linear relationships between ΔI and Λ drawn for mild oxidation and total oxidation of various reactants

Reactions	ΔI range (eV)	Λ range	$\Delta I = p\Lambda + m$ p	m	Reliability factor R^2
Paraffinic bonds mild oxid. **MOP**	0.18-2.00	0.48-0.91	4.09	- 1.73	0.94
Olefinic bonds mild oxid. **MOO**	0.06-1.22	0.48-1.25	-1.51	+1.90	0.93
Ammoxidation of alkanes	0.11-0.34	0.49-0.93	0.58	- 0.15	0.81
Alcohol mild oxidation **MOA**	0.02-0.60	0.53-1.03	1.11	- 0.56	0.95
Paraffinic bonds, total oxid.**TOP**	1.26-4.90	0.87-1.07	23.08	-19.16	0.90
Olefinic bonds, total oxid.**TOO**	3.20-4.54	0.85-0.93	-4.585	+8.44	0.96

Figure captions

Figure 1. Linear relationships between Ionic-Covalent Parameter (ICP) and optical basicity Λ_{th} for transition metal cations. Cations M are labelled as z-CNM, where z = valence and CN = coordination. Vanadium and molybdenum are illustrated (bold labels).

Figure 2. Scale of acidity/basicity (Λ_{th}) of some well-known catalysts.

Figure 3. Scale of acidity/basicity (Λ_{th}) of some well-known oxidic supports.

Figure 4. Logarithmic relationship between the binding energy of O1s (BE O1s) and optical basicity Λ_{th} of oxides. Range of BE O1s and Λ_{th} for oxides (represented by cations) is shown by ellipses.

Figure 5. Effect of n = number of carbons in C_2-C_4 hydrocarbons. a) On their ionization potential; Cn= indicates olefin. b) In the case of ODH, on the difference of ionization potential ΔI between reactant and product; Cn indicates ODH of C_n alkane.

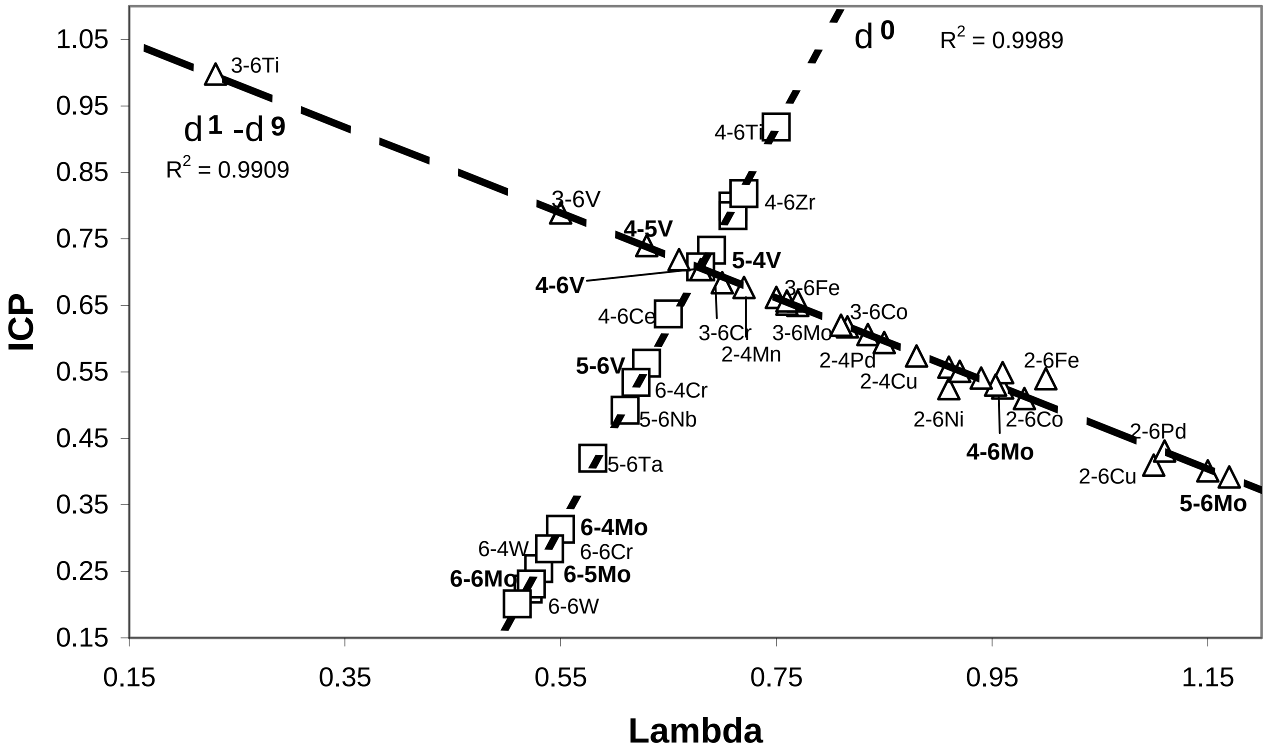
Figure 6. **MOP** line. Mild oxidation and ODH of C_1 to C_8 paraffins and alkyl-aromatics. Linear correlation between ΔI and Λ of catalysts. Several catalysts may be represented by their Λ value for the same reaction.

Figure 7. **MOP** line. Linear correlation between ΔI of C_1 to C_8 paraffins and alkyl-aromatics and Λ of catalysts. Comparison between optimal values of Λ for some examples (see text).

Figure 8. **MOO** line. Mild oxidation and ODH of C_2 to C_6 olefins and aromatics. Linear correlation between ΔI and Λ of catalysts. Several catalysts may be represented by their Λ value for the same reaction.

Figure 9. **MOA** line. Mild oxidation of C_1 to C_6 alcohols. Linear correlation between ΔI and Λ of catalysts. Several catalysts may be represented by their Λ value for the same reaction. Me= methyl; Et = ethyl, etc.

Figure 10. **TOP** and **TOO** lines. Total oxidation C_1 to C_9 hydrocarbons, VOC and carbon. Linear correlations between ΔI and Λ of catalysts for paraffinic C-C or C-OH bonds and for C=C bonds. Several catalysts may be represented by their Λ value for the same reaction. Same labels as in Fig. 5.



ICP
Lambda
d 0
R2 = 0.9989
d 1 -d 9
R2 = 0.9909
1.05
0.95
0.85
0.75
0.65
0.55
0.45
0.35
0.25
0.15
0.15
0.35
0.55
0.75
0.95
1.15
3-6Ti
4-6Ti
4-6Zr
3-6V
4-5V
5-4V
4-6V
3-6Fe
3-6Co
4-6Ce
3-6Cr
2-4Mn
3-6Mo
2-4Pd
2-4Cu
2-6Fe
5-6V
6-4Cr
5-6Nb
2-6Ni
2-6Co
4-6Mo
2-6Pd
2-6Cu
5-6Mo
5-6Ta
6-4Mo
6-4W
6-6Cr
6-6Mo
6-5Mo
6-6W

Fig. 1

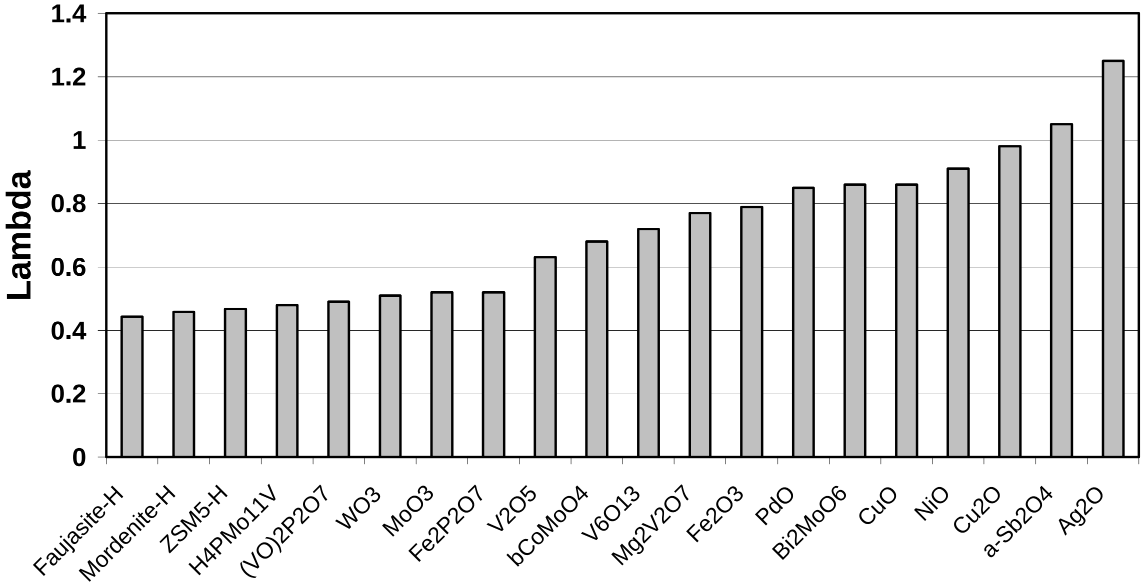

1.4
1.2
1
0.8
0.6
0.4
0.2
0
Lambda
Faujasite-H
Mordenite-H
ZSM5-H
H4PMo11V
(VO)2P2O7
WO3
MoO3
Fe2P2O7
V2O5
bCoMoO4
V6O13
Mg2V2O7
Fe2O3
PdO
Bi2MoO6
CuO
NiO
Cu2O
a-Sb2O4
Ag2O

Fig. 2.

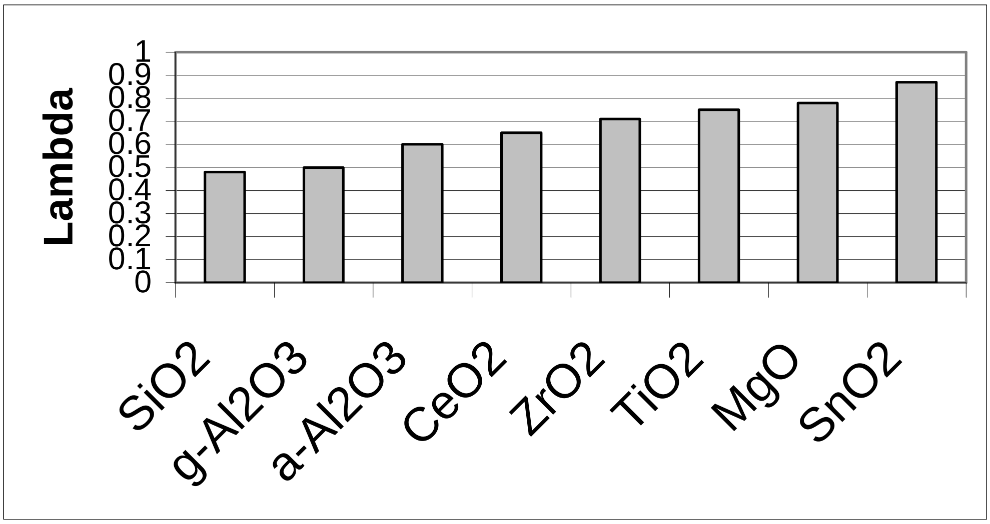
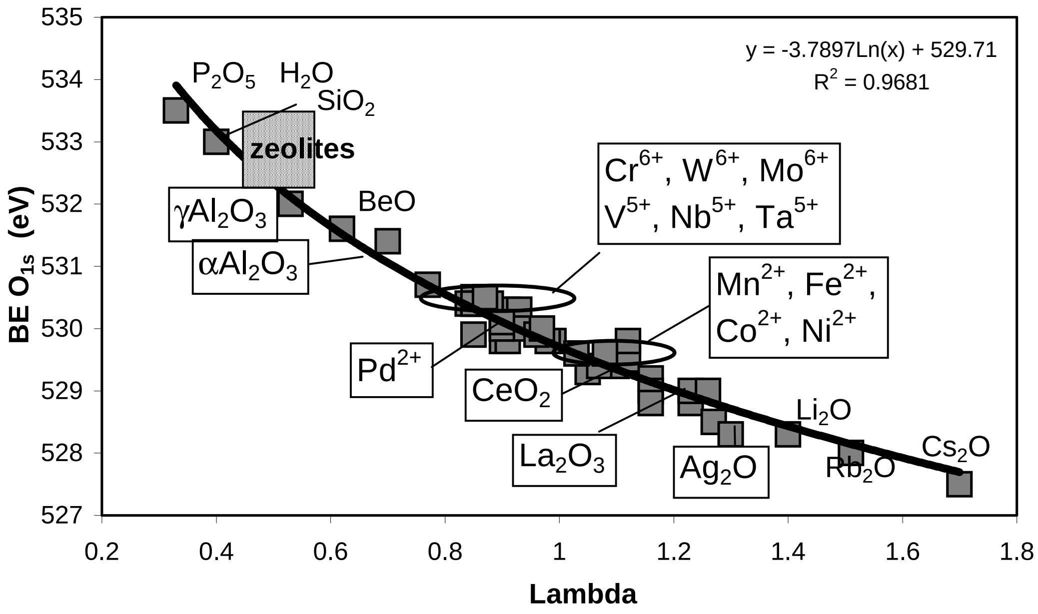

Lambda
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
SiO2
g-Al2O3
a-Al2O3
CeO2
ZrO2
TiO2
MgO
SnO2

Fig. 3.



y = -3.7897Ln(x) + 529.71
R2 = 0.9681
P2O5
H2O
SiO2
zeolites
γAl2O3
BeO
αAl2O3
Cr6+, W6+, Mo6+
V5+, Nb5+, Ta5+
Mn2+, Fe2+,
Co2+, Ni2+
Pd2+
CeO2
La2O3
Ag2O
Li2O
Rb2O
Cs2O
BE O1s (eV)
Lambda
535
534
533
532
531
530
529
528
527
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8

Fig. 4.

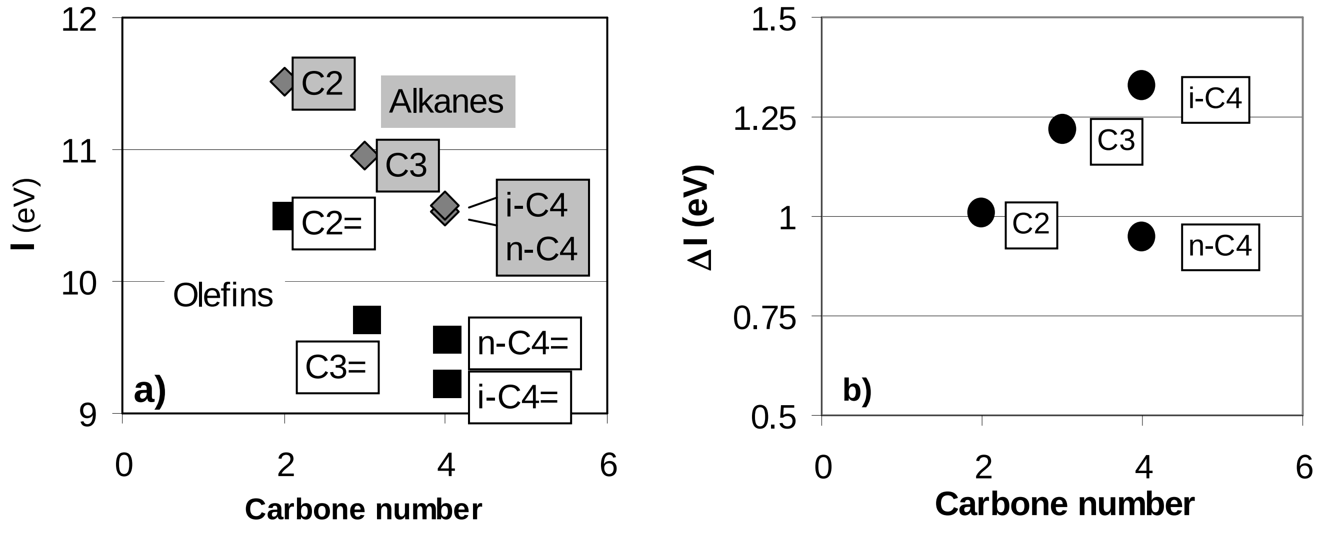

12
11
10
9
I (eV)
C2
Alkanes
C3
i-C4
n-C4
C2=
Olefins
C3=
n-C4=
i-C4=
a)
0
2
4
6
Carbone number
1.5
1.25
1
0.75
0.5
ΔI (eV)
i-C4
C3
C2
n-C4
b)
0
2
4
6
Carbone number

Fig. 5

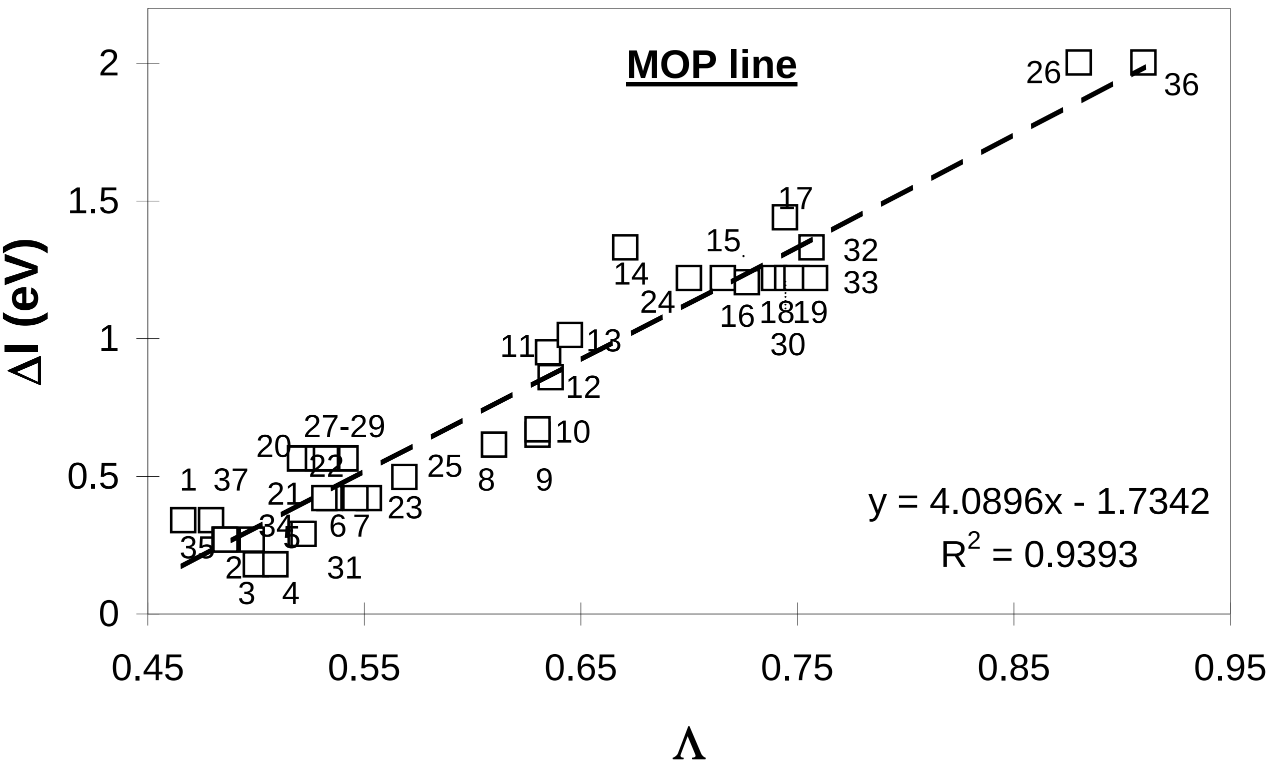

MOP line
ΔI (eV)
Λ
2
1.5
1
0.5
0
0.45
0.55
0.65
0.75
0.85
0.95
y = 4.0896x - 1.7342
R2 = 0.9393
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27-29
30
31
32
33
34
35
36
37

Fig. 6

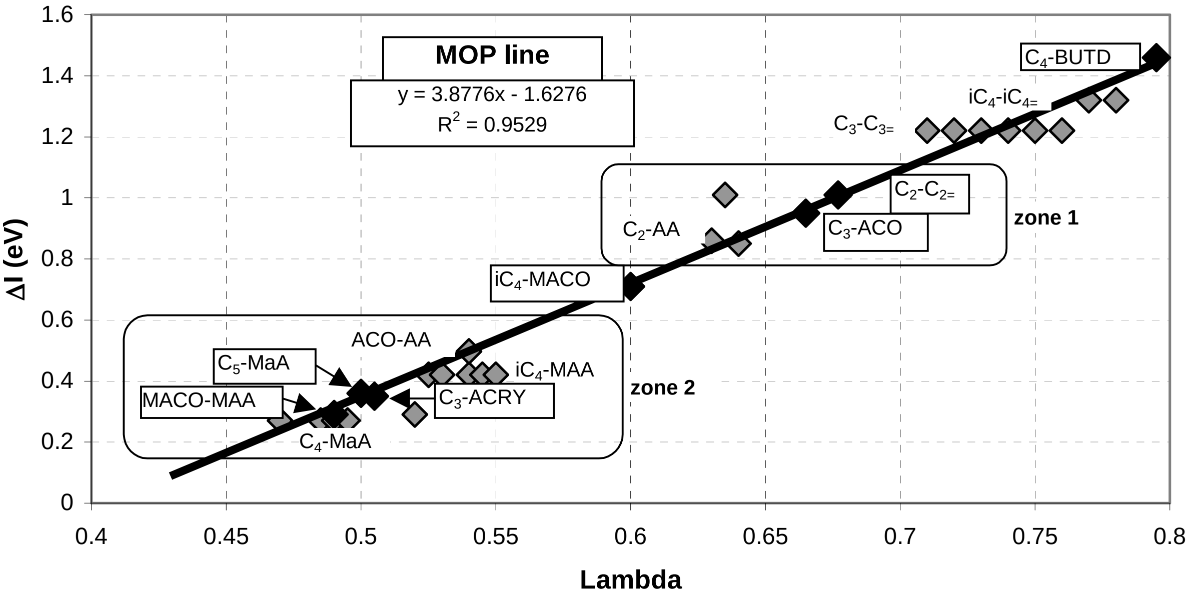
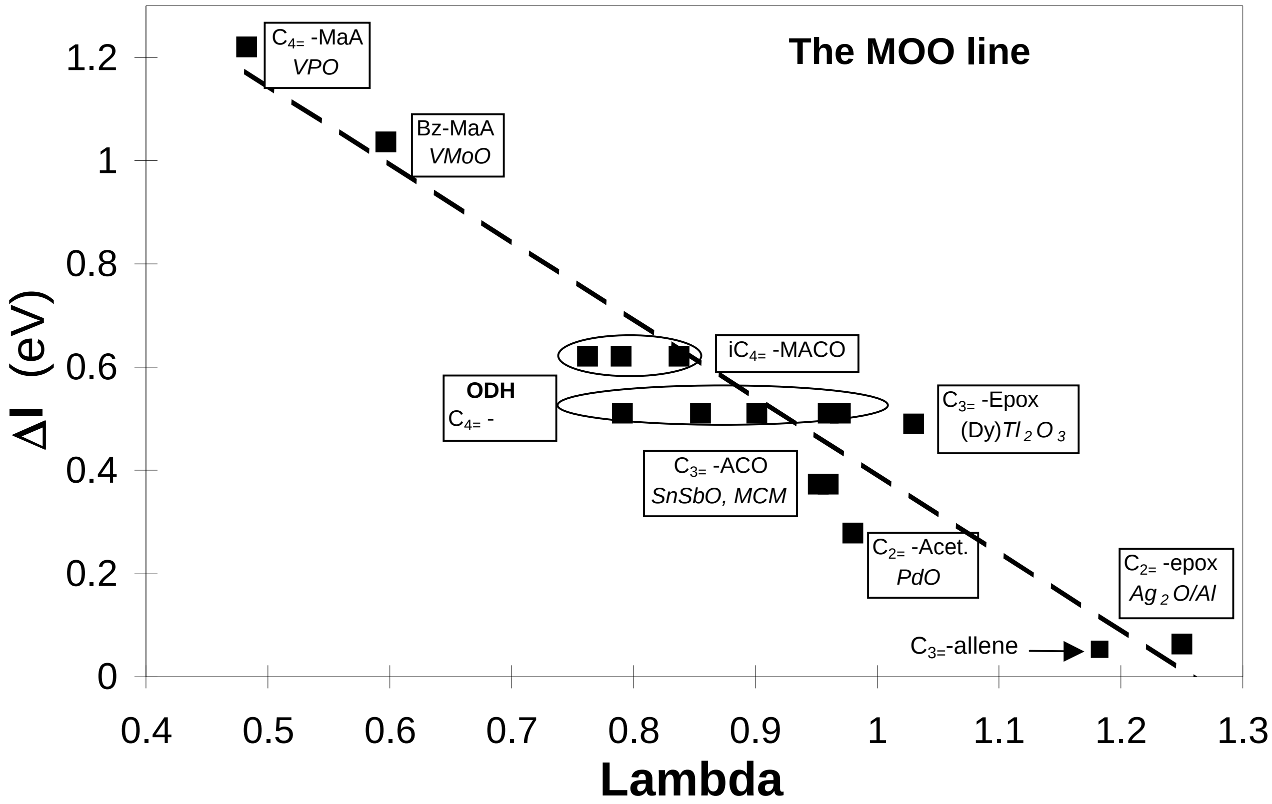

MOP line
y = 3.8776x - 1.6276
R2 = 0.9529
C4-BUTD
iC4-iC4=
C3-C3=
C2-C2=
zone 1
C2-AA
C3-ACO
iC4-MACO
ACO-AA
C5-MaA
iC4-MAA
zone 2
MACO-MAA
C3-ACRY
C4-MaA
ΔI (eV)
Lambda
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.4
0.45
0.5
0.55
0.6
0.65
0.7
0.75
0.8

Fig. 7



The MOO line
C4= -MaA
VPO
Bz-MaA
VMoO
iC4= -MACO
ODH
C4= -
C3= -Epox
(Dy)Tl 2 O 3
C3= -ACO
SnSbO, MCM
C2= -Acet.
PdO
C2= -epox
Ag 2 O/Al
C3=-allene
ΔI (eV)
Lambda
1.2
1
0.8
0.6
0.4
0.2
0
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3

Fig 8

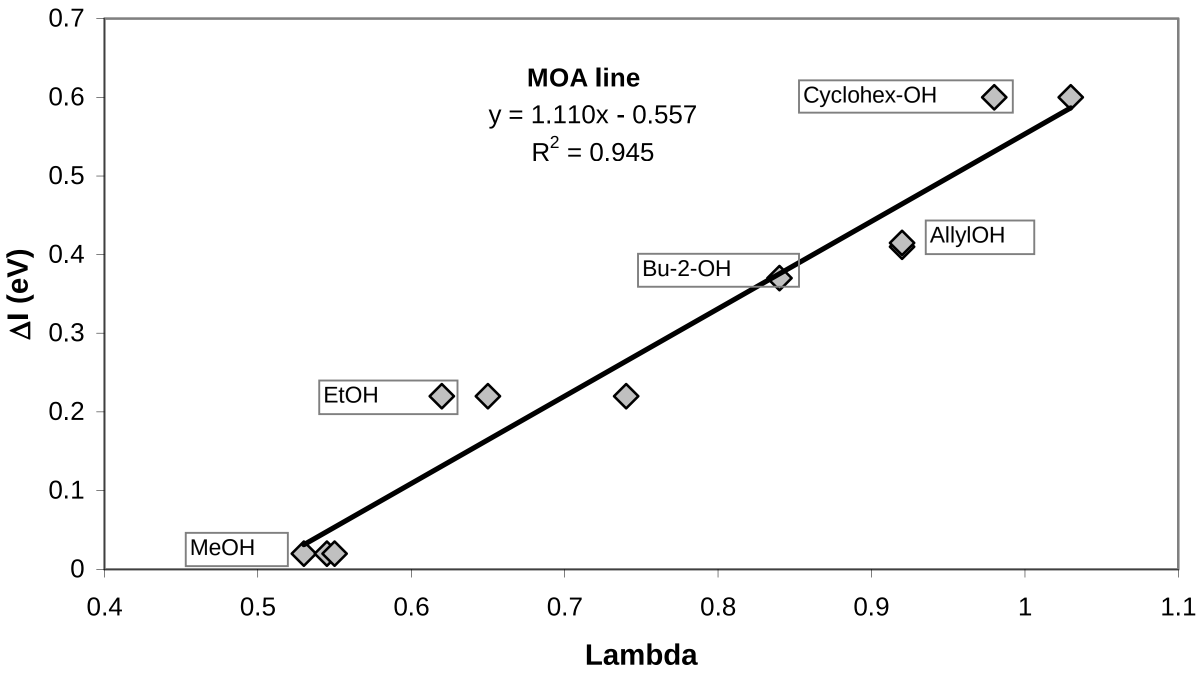

MOA line
y = 1.110x - 0.557
R2 = 0.945
Cyclohex-OH
AllylOH
Bu-2-OH
EtOH
MeOH
ΔI (eV)
Lambda
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1

Fig. 9.

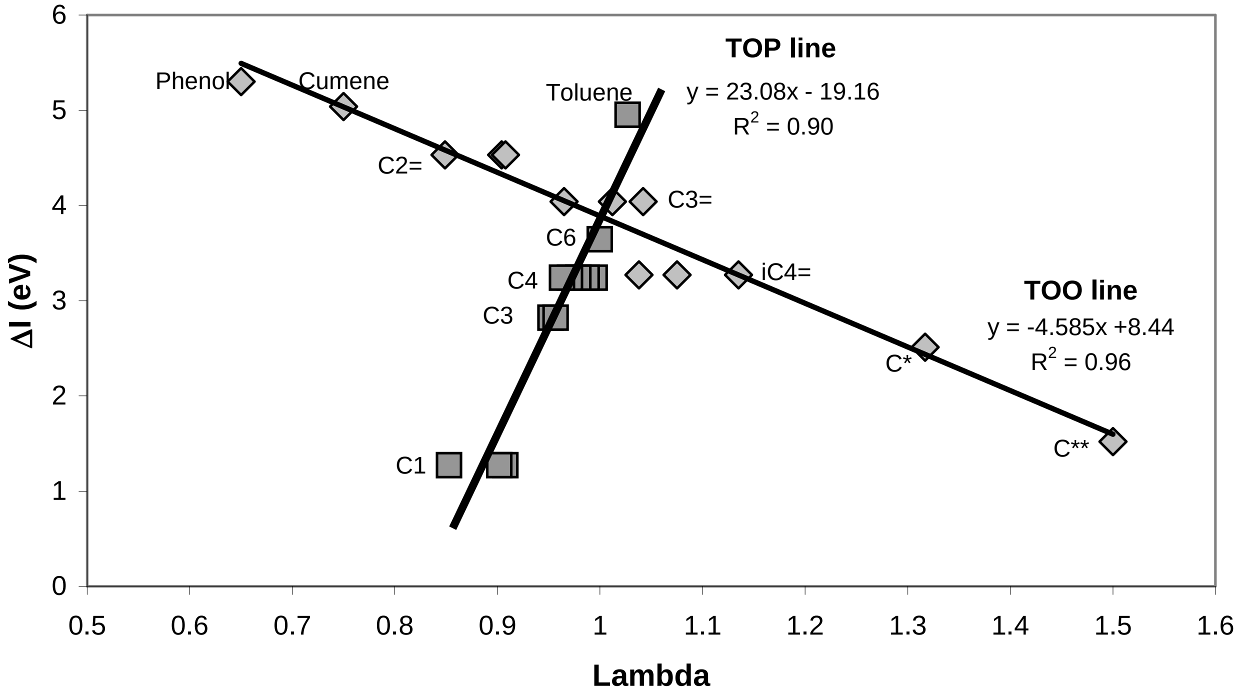

TOP line
y = 23.08x - 19.16
R2 = 0.90
TOO line
y = -4.585x +8.44
R2 = 0.96
Phenol
Cumene
Toluene
C2=
C3=
C6
C4
C3
iC4=
C*
C**
C1
ΔI (eV)
Lambda
0
1
2
3
4
5
6
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6

Fig. 10

REFERENCES

[1] Mars, J.; van Krevelen, D.W. Oxidations carried out by means of vanadium oxide catalysts. Chem. Eng. Sci, Special Suppl., **1954**, *3*, 41-

[2] Haber, J. Catalysis by transition metal oxides. In *Solid State Chemistry in Catalysis*, Eds. R.K. Grasselli and J.F. Brazdil. ACS Symposium Series, **1985**, *279*, 3-21.

[3] Noguera, C. *Physique et chimie des surfaces d'oxydes*; Eyrolles: Paris, 1995; 219 pp.

[4] Zhang, Y. Title. Inorg. Chem., **1982**, *21*, 3886.

[5] Duffy, J.A. *Bonding, energy levels and bands in inorganic solids*; Longman Scientific&Technical: New-York, 1990; 249 pp.

[6] Duffy, J.A. A review of optical basicity and its applications to oxidic systems. Geochim. Cosmochim. Acta. **1993**, *57*, 3961-3970.

[7] Dimitrov, V.; Sakka, S. Electronic oxide polarizability and optical basicity of simple oxides. I. J. Appl. Phys. **1996**, *79*(3), 1736-1740.

[8] Lenglet, M. Spectroscopic study of the chemical bond in 3d transition metal oxides. Correlation with the ionic-covalent parameter. In *Trends in Chemical Physics*, **1997**, *6*, 121-543.

[9] Portier, J.; Campet, G.; Etourneau, J.; Shastry, M.C.R.; Tanguy, B. A simple approach to materials design : role played by an ionic-covalent parameter based on polarizing power and electronegativity. J. Alloys Comp. **1994**, *209*, 59-64.

[10] Portier, J.; Campet, G.; Etourneau, J.; Tanguy, B. A simple model for the estimation of electronegativities of cations in different electronic states and coordinations. J. Alloys Comp. **1994**, *209*, 285-289

[11] Tanaka, K.-I. ; Ozaki, A. Acid-base properties and catalytic activity of solid surfaces. J. Catal., **1967**, *8*, 1-7.

[12] Klier, K. Oxidation-reduction potentials and their relation to the catalytic activity of transition metal oxides. J. Catal., **1967**, *8*, 14-21.

[13] Sokolovskii, V.D. Donor-acceptor concept of covalent interaction of substrate with catalysts. React. Kinet. Catal. Lett., **1982**, *20*(1-2),79-86.

[14] Pankratiev, Yu.D. Correlation between oxygen binding energy and catalytic activity of oxides. React. Kinet. Catal. Lett., **1982**, *20*(3-4), 255-259.

[15] Auroux, A.; Gervasini, A. Microcalorimetric study of the acidity and basicity of metal oxide surfaces. J. Phys. Chem., **1990**, *94*, 6371-6379.

[16] Auroux, A. From strong solid acids to strong solid bases: characterization of the acid/base centers of catalyst surfaces by adsorption microcalorimetry. Proc. NATAS 29th Ann. Conf. on Thermal Analysis and Applications, **2001**, 53-58.

[17] Idriss, H.; Seebauer, E.G. Effect of oxygen electronic polarisability on catalytic reactions over oxides. Catal. Lett. **2000**, *66*, 139-145.

[18] Vinek, H.; Noller, H.; Ebel, M.; Schwarz, K. X-ray photoelectron spectroscopy and heterogeneous catalysis, with elimination reactions as an example. J. Chem. Soc., Faraday Trans. I. **1977**, *73*, 734-746.

[19] Noller, H.; Vinek, H. Coordination chemical approach to catalytic oxidation reactions. J. Molec. Catal. **1989**, *51*, 285-294.

[20] Duffy, J.A. The refractivity and optical basicity of glass. J. Non-Cryst. Solids, **1986**, *86*(1-2), 149-60.

[21] Duffy, J.A.; Ingram, M.D. Establishment of an optical scale for Lewis Basicity in inorganic oxyacids, molten salts and glasses. J.A.C.S. **1971**, *93*(24), 6448-6454.

[22] Duffy, J.A. Redox equilibria and stereochemistry of metal ions in glass: a chemical bonding approach. Proc. Int. Cong. on Glass, 19[th], Edinburgh, July 1-6, **2001**, 248-257. Publ.: Soc. of Glass Technology, Sheffield, UK.

[23] Iwamoto, N.; Makino, Y.; Kasahara, S. Correlation between refraction basicity and theoretical optical basicity. Part II. Lead monoxide-silicon dioxide, calcium oxide-aluminum oxide-silicon dioxide, and potassium oxide-titanium dioxide-silicon dioxide glasses. J. Non Cryst. Solids, **1984**, *68*(2-3), 379-397.

[24] Mills, K.C. Viscosities of molten slags. Natl. Phys. Lab., Teddington/Middlesex, UK. NPL Rep. DMM(A) **1992**, 116 pp.

[25] Jeddeloh, G. The redox equilibrium in silicate melts. Phys. Chem. Glass. **1984**, *25*(6), 163-4.

[26] Baucke, F. G. K.; Duffy, J. A. Oxidation states of metal ions in glass melts. Phys. Chem. Glass. **1994**, *35*(1), 17-21.

[27] Baucke, F. G. K.; Duffy, J. A. The effect of basicity on redox equilibria in molten glasses. Phys. Chem. Glass. **1991**, *32*(5), 211-18.

[28] Dent-Glasser, L.S.; Duffy, J.A. Analysis and prediction of acid-base reactions between oxides and oxysalts using the optical basicity concept. J. Chem. Soc., Dalton.Trans. **1987**, *20*, 2323-2328.
[29] Lebouteiller, A.; Courtine, P. Improvement of a bulk optical basicity table for oxidic systems. J. Solid State Chem. **1998**, *137*, 94-103.
[30] Lenglet M. Spectroscopic study of the chemical bond in 3d transition metal oxides. Correlation with the ionic-covalent parameter. Trends Chem. Phys. **1997**, *6*, 121-142.
[31] Lenglet M. Ligand field spectroscopy and chemical bonding in Cr^{3+}-, Fe^{3+}-, Co^{2+}- and Ni^{2+}-containing oxidic solids. Mater. Res. Bull. **2000**, *35*, 531-543.
[32] Moriceau, P.;Lebouteiller, A.; Bordes, E.; Courtine, P. A new concept related to selectivity in mild oxidation catalysis of hydrocarbons : the optical basicity of catalyst oxygen. Phys. Chem. Chem. Phys. **1999**, *1*, 5735-5744.
[33] Moriceau, P.; Taouk, B.; Bordes, E.; Courtine, P. A common concept accounting for selectivity in mild and total oxidation reactions: the optical basicity of catalysts. Stud. Surf. Sci. Catal., **2000**, *130B* (International Congress on Catalysis, 2000, Pt. B), 1811-1816.
[34] Moriceau, P.; Taouk, B.; Bordes, E.; Courtine, P. Correlations between the optical basicity of catalysts and their selectivity in oxidation of alcohols, ammoxidation and combustion of hydrocarbons. Catalysis Today, **2000**, *61* (1-4), 197-201.
[35] Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallog. A, **1976**, *A32*(5), 751-67.
[36] Courtine, P.; Bordes, E. Mode of arrangement of components in mixed vanadia catalysts and its bearing for oxidation catalysis. Appl. Catal. A: Gen., **1997**, *157*, 45-65.
[37] Bordes, E.; Courtine, P. Synergistic Effects in Multicomponent Catalysts for Selective Oxidation. Stud. Surf. Sci. Catal., Grasselli, R.K.; Oyama, S.T.; Gaffney, A.M.; Lyons, J.E.; Eds, **1997**, *110*, 177-184.
[38] Grzybowska, B.; Gressel, I.; Samson, K.; Wcislo, K.; Stoch, J.; Mikolajczyk, M.; Dautzenberg, F. Effect of the potassium promoter content in V_2O_5/TiO_2 catalysts on their physicochemical and catalytic properties in oxidative dehydrogenation of propane. Polish J. Chem. **2001**, *75*(10), 1513-1519.
[39] Sumitomo Chemicals, JP 09,020,700-A, **1995**.
[40] Pillared clays. R. Burch, Ed. Catal. Today, **1988**, *2*(2-3). Elsevier, 367 pp.
[41] Volta, J. C.; Portefaix, J. L. Structure sensitivity of mild oxidation reactions on oxide catalysts. A review. Appl. Catal. **1985**, *18*(1), 1-32.
[42] Volta, J.C., Tatibouet, J.M. Structure sensitivity of oxide in mild oxidation of propylene molybdenum(VI).
J. Catal. **1985,** *93*, 467-80.
[43] Bordes, E. Crystallochemistry of V-P-O phases and application to catalysis. Catal. Today, **1987**, *1*, 499-526.
[44] Bordes, E. Reactivity and crystal chemistry of V-P-O phases related to C_4-hydrocarbon catalytic oxidation. Catal. Today, **1987**, *3*, 163-174.
[45] Higarashi, H.; Tsuji, K.; Okuhara, T.; Misono, M. Effects of consecutive oxidation on the production of maleic anhydride in butane oxidation over four kinds of well-characterized vanadyl pyrophosphates. J. Phys. Chem. **1993**, *97*(27), 7065-71.
[46] Bordes, E.; Ziolkowski, J.; Courtine, P. A dynamic model of the oxidation of n-butane and 1-butene on various crystalline faces of $(VO)_2P_2O_7$. Stud. Surf. Sci. Catal., **1990** (New Developments in Selective Oxidation, Centi, G. and Trifirò F. Eds., *55*, 625-633.
[47] Iguchi, E.; Nakatsugawa, H. Application of a polarizable point-ion shell model to a two-dimensional periodic structure: the NiO (001) surface. Phys. Rev. B: Condensed Matter. **1995**, *51*(16), 10956-64.
[48] Delamar, M. Correlation between the isoelectric point of solid surfaces of metal oxides and X-Ray Photoelectron Spectroscopy chemical shifts. J. Electron Spectrosc. Rel. Phenom., **1990**, *53*, c11-c14.
[49] http://www.lasurface.com
[50] http://www.srdata.nist.gov
[51] Dhanavantri, C. ; Karekar, R.N. An empirical generalized relationship between the change in Auger parameter and the refractive indices of optical dielectric materials. J. Electron Spectrosc. Rel. Phenom., **1993**, *61*, 357-365.
[52] Nefedov, V.I. ; Gati, D. ; Dzhurinskii, B.F.; Sergushin, N.P.; Salyn, Ya.V. An X-ray photoelectron spectroscopic study of certain oxides. Russ. J. Inorg. Chem. **1975**, *20*(9), 1279-1283.
[53] E. Bordes, Propriétés structurales des phases catalytiques à l'état stationnaire, Doctorat d'Etat, Compiègne (France), **1979**.
[54] Ai, M. Oxidation of propane to acrylic acid. Catal. Today, **1992**, *13*(4), 679-84.
[55] Richardson J.T. ESR studies of cationic oxidation sites in faujasite. J. Catal. **1967**, *9*, 172-177.

[56] Batiot C., Hodnett, B.K. The role of reactant and product bond energies in determining limitations to selective catalytic oxidations. Appl. Catal., **1996**, *137*(1), 179-91.
[57] Batiot, C.; Cassidy, F. E.; Doyle, A. M.; Hodnett, B. K. Selectivity of active sites on oxide catalysts. Stud. Surf. Sci. Catal. **1997**, 110 (3rd World Congress on Oxidation Catalysis, 1997).
[58] Kung, H.H. Transition metal oxides. Surface chemistry and catalysis. Stud.Surf.Sci.Catal. **1987**, *45*.
[59] Bettahar, M. M.; Costentin, G.; Savary, L.; Lavalley, J. C. On the partial oxidation of propane and propylene on mixed metal oxide catalysts. Appl. Catal. A: General. **1996**, *145*(1-2), 1-48.
[60] Matsuura, I. The nature of the active sites on olefin oxidation catalysts. Proc. 6th Int. Cong. Catalysis, **1976**, *B1*, 819.
[61] Desquilles, C.; Bartoli, M. J.; Bordes, E.; Hecquet, G.; Courtine, P. Oxidative dehydrogenation of isobutyric acid by heteropolycompounds. Effect of alkali-containing supports. Erdoel, Erdgas, Kohle, **1993**, *109*(3), 130-3.
[62] Bartoli, M. J.; Monceaux, L.; Bordes, E.; Hecquet, G.; Courtine, P. Stabilization of heteropoly acids by various supports. Stud. Surf. Sci. Catal. **1992**, *72* (New Dev. Sel. Oxid. Heterog. Catal.), 81-90.
[63] Desquilles, C.; Bartoli, M. J.; Bordes, E.; Courtine, P.; Hecquet, G. Oxidative dehydrogenation of isobutyric acid by heteropoly compounds - effect of alkali containing supports. Erdoel, Erdgas, Kohle, **1992**, *9204* (Proc. DGMK-Conf. Sel. Oxid. Petrochem., 1992), 69-79.
[64] Belkouch, J., Taouk, B., Monceaux, L., Bordes, E., Courtine, P., Hecquet, G. Cesium promotion of iron phosphate catalysts in the oxidative dehydrogenation of isobutyric acid to methacrylic acid Stud. Surf. Sci. Catal. **1994**, *82*, 819-28.
[65] Millet, J.M.M., Védrine, J. Role of cesium in iron phosphates used in isobutyric acid oxidative dehydrogenation. Appl. Catal. **1991**, *76*(2), 209-19.
[66] Grasselli, Robert K.; Burrington, James D. Selective oxidation and ammoxidation of propylene by heterogeneous catalysis. Adv. Catal. **1981**, *30*, 133-63.
[67] F. Cavani, F. Trifirò, P. Arpentinier, The catalytic technology of oxidation. Vol.1. Technip, Paris, **2001**. 324 pp.
[68] A. Bielański, M. Najbar, Appl. Catal. A: General, 157 (1997) 223.Bz-MAA
[69] Hodnett, B. K. Vanadium-phosphorus oxide catalysts for the selective oxidation of C4 hydrocarbons to maleic anhydride. Catal. Rev.- Sci. Eng. **1985**, *27*(3), 373-424.
[70] Asahi Chemical Industry, JP 02,042,032, **1990**.
[71] Pitchai, P.; Klier, K. Catal. Rev.-Sci. Eng. **1986**, *28*, 13
[72] Baerns, M.; Ross, J.R.H. Catalytic chemistry of methane conversion. In *Perspectives in Catalysis*, J.M. Thomas, K.I. Zamaraev, Eds., Blackwell Sci. Publ., London, 492 pp. **1993**, 315-335.
[73] Bordes, E. Nature of the active and selective sites in vanadyl pyrophosphate, catalyst of oxidation of n- butane, butene and n-pentane in maleic anhydride. Catal. Today, **1993,** *16*, 27-38.
[74] Bautista, F. M.; Campelo, J. M.; Garcia, A.; Luna, D.; Marinas, J. M.; Quiros, R. A. Gas-phase catalytic oxydehydrogenation of ethylbenzene on $AlPO_4$ catalysts. Stud. Surf. Sci. Catal. **1994**, *82* (New Developments in Selective Oxidation II), 759-68.
[75] Hodnett, B. K.; Delmon, B. Influence of cobalt on the textural, redox and catalytic properties of stoichiometric vanadium phosphate. Appl. Catal. **1983**, *6*(2), 245-59.
[76] Sananes-Schulz, M.T., Tuel, A., Hutchings, G.J., Volta, J.C. The V^{4+}/V^{5+} balance as a criterion of selection of vanadium phosphorus oxide catalysts for n-butane oxidation to maleic anhydride: a proposal to explain the role of Co and Fe dopants. J. Catal. **1997**, *166*(2), 388-392.
[77] Costentin, G.; Lavalley, J. C.; Studer, F. Mo oxidation state of Cd, Fe, and Ag catalysts under propane mild oxidation reaction conditions. J. Catal. **2001**, *200*(2), 360-369.
[78] Merzouki, M.; Bordes, E.; Taouk, B.; Monceaux, L.; Courtine, P. Catalytic properties of promoted vanadium oxide in the oxidation of ethane in acetic acid. Selective Oxidation by Heterogeneous Catalysis, Stud. Surf. Sci. Catal., **1992**, *72*, 165-179.
[79] Merzouki, M.; Bordes, E.; Taouk, B.; Monceaux, L.; Courtine, P. Correlation between catalytic and structural properties of modified molybdenum and vanadium oxides in the oxidation of ethane to acetic acid or ethylene. In *New Frontiers in Catalysis*, L. Guczi et al., eds, **1993**, 753-764.
[80] Werner, H. ; Timpe, O.; Herein, D.; Uchida, Y.; Pfänder, N.; Wild, U.; Schlögl, R. Relevance of a glassy nanocrystalline state of Mo_4VO_{14} for its action as selective oxidation catalysts. Catal. Lett. **1997**, *44*, 153-163.
[81] K. Karim, M. Al-Hazmi, A. Khan, to Sabic, US 6,060,421, **2000**.
[82] Roussel, M. ; Bouchard, M. ; Bordes-Richard, E., Karim, K. Oxidation of ethane to acetic acid and ethylene by MoVNbO catalysts. Catal. Today, *in press.*

[83] Linke, D.; Wolf, D.; Baerns, M.; Timpe, O.; Schloegl, R.; Zeyss, S.; Dingerdissen, U. Catalytic partial oxidation of ethane to acetic acid over $MoV_{0.25}Nb_{0.12}Pd_{0.0005}O_x$. J. Catal. **2002**, *205*(1), 16-31.
[84] Tessier, L.; Bordes, E.; Gubelmann-Bonneau, M. Active species on vanadium containing catalysts for the selective oxidation of ethane to acetic acid. Catal. Today, **1995**, *24*, 335-340.
[85] Askander, J. PhD, Propriétés physicochimiques et catalytiques de l'oxyde de thallium Tl_2O_3. Compiègne,**1982**.
[86] Bordes, E.; Courtine, P. Some selectivity criteria in mild oxidation catalysis: V-P-O phases in butene oxidation to maleic anhydride. J. Catal. **1979**, *57*, 237-252.
[87] Figueras, F.; Forissier, M.; Lacharme, J. P.; Portefaix, J. L. Catalytic oxidation of propene over antimony-tin-oxygen mixed oxides. Appl. Catal. **1985**, *19*(1), 21-32.
[88] Grasselli, R.K.; Suresh, D. D. Aspects of structure and activity in uranium-antimony oxide acrylonitrile catalysts. J. Catal. **1972**, *25*(2), 273-91.
[89] Grasselli, R.K. Selectivity and activity factors in bismuth-molybdate oxidation catalysts. Appl. Catal. **1985**, *15*(1), 127-39.
[90] Grzybowska, B.; Haber, J.; Janas, J. Interaction of allyl iodide with molybdate catalysts for the selective oxidation of hydrocarbons. J. Catal. **1977**, *49* (2), 150-63.
[91] Tichý, J. Oxidation of acrolein to acrylic acid over vanadium-molybdenum oxide catalysts. Appl. Catal. A: General, **1997,** *157*, 363-385.
[92] Briand, Laura E.; Hirt, Andrew M.; Wachs, Israel E. Quantitative Determination of the Number of Surface Active Sites and the Turnover Frequencies for Methanol Oxidation over Metal Oxide Catalysts: Application to Bulk Metal Molybdates and Pure Metal Oxide Catalysts. J. Catal. **2001**, *202*(2), 268-278.
[93] Tejuca, L.G.; Fierro, J.L.G.; Editors. Properties and Applications of Perovskite-Type Oxides. In: *Chem. Ind.* (Dekker), **1993**, 382 pp. **1993**, 50.
[94] Fierro, J.L.G. Composition and structure of perovskite surfaces. In: *Chem. Ind.* (Dekker), **1993**, 382 pp. **1993**, 195-214.
[95] Yamazoe, N.; Teraoka, T. Oxidation catalysis of perovskites - relationships to bulk structure and composition (valency, defect, etc.). In *Perovskites*, Misono, M.; Lombardo, E.A. Eds. Catal. Today, **1990**, *8*, 175-199.
[96] Seiyama, T.; Yamazoe, N.; Eguchi, K. Characterization and activity of some mixed metal oxide catalysts. Ind. Eng. Chem., Prod. Res. Dev. **1985**, *24*(1), 19-27.
[97] Teraoka, Y.; Farukawa, S.; Yamazoe, N.; Seiyama, T. Oxygen-sorptive and catalytic properties of defect perovskite-type $La_{1-x}Sr_xCoO_{3-\delta}$. Nippon Kagaku Kaishi, **1985**, (8),1529-1534.
[98] Zhang, H. M.; Yamazoe, N.; Teraoka, Y. Effects of B site partial substitutions of perovskite-type lanthanum strontium cobalt oxide ($La_{0.6}Sr_{0.4}CoO_3$) on oxygen desorption. J. Mater. Sci. Lett. **1989**, *8*(9), 995-6.
[99] Nitadori, T.; Kurikara, S.; Misono, M. Catalytic properties of lanthanum manganese mixed oxides ($La_{1-x}A'_xMnO_3$ (A' = Sr, Ce, Hf)). J. Catal. **1986,** *98*(1), 221-228.
[100] Teraoka, T.; Zhang, K.M.; Okamoto, K; Yamazoe, Y. Mixed ionic-electronic conductivity of lanthanum strontium cobalt iron oxide (La1-xSrxCo1-yFeyO3-δ) perovskite-type oxides. Mater. Res. Bull. **1988,** *23*(1), 51-58.
[101] Nakamura, T.; Misono, M.; Yoneda, Y. Catalytic properties of perovskite-type mixed oxides, $La_{1-x}Sr_xCoO_3$. Bull. Chem. Soc. Japan. **1982,** *55*(2), 394-399
[102] Nitadori, T.; Misono, M. Catalytic properties of $La_{1-x}A'_xFeO_3$ (A' = Sr, Ce) and lanthanum cerium cobalt oxide ($La_{1-x}Ce_xCoO_3$). J. Catal. **1985,** *93*(2), 459-466.
[103] Shangguan, W.F.; Teraoka, Y.; Kagawa, S. Promotion effect of potassium on the catalytic property of $CuFe_2O_4$ for the simultaneous removal of NO_x and diesel soot particulate. Appl. Catal. B: Environmental, **1998**, *16*(2), 149-154.
[104] Spivey, J. J. Complete catalytic oxidation of volatile organics. Ind. Eng. Chem. Res. **1987**, *26*(11), 2165-80.
[105] Voorhoeve, R. J. H. Perovskite-related oxides as oxidation-reduction catalysts. Adv. Mater. Catal. **1977**, 129-80.
[106] Baucke, F. G. K.; Duffy, J. A. Redox equilibria and corrosion in molten silicates: relationship with electrode potentials in aqueous solution.J. Phys. Chem. **1995**, *99*, 9189-9193.
[107] Courtine, P. In *Solid State Chemistry in Catalysis*. R.K. Grasselli and J.F. Brazdil, Eds. A.C.S. Symposium Series, **1985**, *279*, 37.