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Catalysis Today 61 (2000) 197–201

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Correlations between the optical basicity of catalysts and their selectivity in oxidation of alcohols, ammoxidation and combustion of hydrocarbons

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Abstract

The optical basicity Λ of metallic oxides is obtained by a linear combination of the optical basicity of cations and depends on their valence, coordination and spin state. Λ quantifies the electron donor/acceptor power of the solid, which may be correlated with its redox properties. During catalysis, it is expected that the electron donor/acceptor property of the selective catalyst matches the acceptor/donor property of the reactant to be selectively transformed into the product. The selectivity is accounted for by ΔI which is the difference between the ionization energies of reactant and product. Each selective catalyst/reactant–product couple is characterized by $\{\Lambda, \Delta I\}$ value. Linear relationships between the $\{\Delta I, \Lambda\}$ obtained for various catalyst/reaction couples are drawn for several types of selective oxidation reactions: mild oxidation of alkanes, of olefins and of alcohols, ammoxidation of hydrocarbons, total oxidation of alkanes and of olefins. © 2000 Published by Elsevier Science B.V.

Keywords: Optical basicity; Selective mild oxidation; Ammoxidation; Total oxidation

1. Introduction

Despite the large progress in the knowledge of catalytic phenomena occuring during the selective oxidation of hydrocarbons, predictive trends based on concepts that would allow to a priori choose a selective catalytic formula do not yet exist. Owing to the development of computing facilities, expert systems are now proposed which gather the main characteristics of reactions and catalysts [1]. Our purpose here is to propose a concept which could be added to these data. The Lewis/Brönsted acidity/basicity of catalysts has long been known as a suitable parameter to correlate to catalytic performance [2,3], including reactions of mild oxidation (MOX) [4–8]. A large amount of experimental data is available, in which the mean strength and distribution of acid/base sites is given. The trouble is that, up to now, there was no absolute scale of acidity/basicity. The 'optical basicity', Λ, has been introduced in inorganic chemistry by Duffy and represents the mean electron donor power (Lewis-type basicity) of the lattice oxygen in oxides [9]. First validated for ionic solids, this concept has been recently adapted to ionocovalent oxides by considering the 'ionocovalent parameter' (ICP) [10]. Λ can now be calculated for any oxygen-based inorganic compound, provided the optical basicity of the individual cations is known [11].

During selective oxidation catalysis of hydrocarbons, it is known that the actual oxidizing agent is the metallic cation which is reducible [12]. However, the *result* of MOX is that surface lattice oxygens (O^{2-}) are inserted in the reaction product and in water, or

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0920-5861/00/$ – see front matter © 2000 Published by Elsevier Science B.V.
PII: S0920-5861(00)00380-1

only in water in the case of oxidative dehydrogenation (ODH). Moreover, the first step of the reaction, which is the activation of the hydrocarbon, proceeds by the nucleophilic attack of a C–H bond by O^{2-}. Any parameter accounting for lattice oxygen properties like the optical basicity is therefore welcome. Since electrons are exchanged between the solid and the molecule for the reaction to proceed, there should be a relationship between the electron donor power (Λ) of the catalyst and a similar parameter accounting for the transformation of the molecule. Very recently, we have assumed that selectivity could be represented by the difference ΔI between the ionization energies of the reactant and of the product. By gathering the $\{\Lambda, \Delta I\}$ values characteristic of {selective catalyst/reactant–product} the couples, two linear relationships were obtained for MOX and ODH of hydrocarbons [13,14], one for unsaturated C_2–C_6, and the other for paraffinic C_1–C_8 reactants. These results prompted us to examine reactions of oxidation using other reactants, like alcohols, as well as total oxidation or ammoxidation of hydrocarbons.

Table 1
Values of Λ calculated for some catalysts (alphabetical order) (after [11])

Cation Charge, CN[a]	Λ[b]	Catalyst formula	Λ
Ag^{+}, II	1.25	Bi_2MoO_6	0.86
Bi^{3+}, V	1.19	$Bi_2Mo_3O_{12}$	0.71
Ce^{4+}, VI	0.65	$CuFe_2O_4$	0.81
Cu^{2+}, IV	0.56	Fe_3O_4	0.79
Cu^{+}, II	0.98	$Fe_2Mo_3O_{12}$	0.61
Fe^{3+}, VI	0.77	$FePO_4$	0.50
Li^{+}, IV	0.48	$H_4PVMo_{11}O_{40}$	0.48
La^{3+}, VIII	0.68	$Mg_2V_2O_7$	0.72
Mg^{2+}, VI	0.78	$Mg_3V_2O_8$	0.72
Mo^{6+}, VI	0.52	MnO_2	0.88
Mo^{6+}, IV	0.55	MoO_2	0.96
Mo^{5+}, VI	1.17	Mo_5O_{14}	0.75
Ni^{2+}, VI	0.91	α-$NiMoO_4$	0.62
Pd^{2+}, IV	0.85	β-$NiMoO_4$	0.64
Sb^{5+}, VI	0.98	α-Sb_2O_4	1.05
Sn^{4+}, VI	0.87	Sb_2O_4/SnO_2	0.96
Ti^{4+}, VI	0.75	USb_3O_{10}	0.97
V^{5+}, VI	0.63	$0.1V_2O_5/0.9TiO_2$	0.72
V^{5+}, IV	0.69	V_6O_{13}	0.68
W^{6+}, VI	0.51	$(VO)_2P_2O_7$	0.49

[a] Coordination.
[b] Same Λ value for cation and corresponding oxide; no correction for $\Lambda_{\mathrm{surface}}$.

2. Recall on the semi-empirical relationships between optical basicity and ionization energy [14]

Because the papers on optical basicity in catalysis are very recent, we think it is necessary to recall only the main findings. More details can be found in the paper by Moriceau et al. [14]. The optical basicity Λ of an oxygen-based compound can be calculated for any composition. For example, the optical basicity of a mixed oxide $A_x^{a+}B_y^{b+}O_n^{2-}$ or of a mixture of oxides (xAO_p+yAO_q, $p+q=n$) is obtained by Eq. (1):

$$\Lambda = \frac{1}{2}n(ax\Lambda_{\mathrm{A}} + by\Lambda_{\mathrm{B}}) \tag{1}$$

where a and b, Λ_{A} and Λ_{B} stand for the valence and optical basicity of cations A and B, respectively. The optical basicity is a function of the electronegativity and polarizing power of the cations and depends on their valence, coordination and spin state (if necessary) in the compound. Values of Λ of some cations, catalysts and supports are given in Table 1. These solids range from acidic (e.g., SiO_2, $(VO)_2P_2O_7$, WO_3, etc.) to more basic (e.g., Bi_2MoO_6, Cu_2O, Ag_2O, etc.) [11]. By using Eq. (1), the optical basicity of any formula, as complex as those claimed in patents, can be calculated even though the active/selective phase(s) is not known. However, assumptions on the valence and coordination of cations at the steady state have often to be made when these values are not given in the literature. Another problem to solve is that the optical basicity is a theoretical parameter which is a characteristic of the bulk of solids, not of their surface. Experiments performed on single crystals of NiO [16] showed that the polarizability of oxygen is higher on surface than in bulk. By using the appropriate relationships proposed by Duffy [9,15], the following Eq. (2) is obtained for NiO:

$$\Lambda_{\mathrm{surface}} = \Lambda_{\mathrm{bulk}} + 0.12 \tag{2}$$

This equation may be used as an approximation to evaluate the surface optical basicity of bulky solids which do not exhibit a layered morphology. In such cases, the surface oxygen is then more basic than bulk oxygen. Finally, various correlations between optical basicity and catalytic parameters like enthalpy of adsorption, values of selectivity, etc., have shown that Λ is a suitable parameter characterizing the solid catalyst [14].

The second part of the model concerns the use of the ionization energy of the reactant and of the product. The difference $\Delta I=(I_R-I_P)$ is assumed to account for the selective reactant-to-product reaction (the product being not CO_2). This difference being negative or positive according to whether the product is more or less stable than the reactant, the absolute value $|\Delta(I)|$ was used in order to compare various MOX and ODH. At first sight, $|\Delta(I)|$ represents only the net exchange of electrons during the considered reaction, but it really depends on the structure of the reactant and of the product molecules. For example, although the ODH of ethane to ethylene and of propane to propene are two-electrons reactions, the $\Delta(I)$s are different (+1.01 and +1.22 eV, respectively). When the number of carbons differed during the reaction (e.g., benzene to maleic anhydride), the following correction was applied:

$$\Delta I = \frac{(I_R - I_p)n_p}{n_R} \tag{3}$$

where n_R and n_P are the carbon number of reactant and product, respectively. Each catalyst/reactant–product couple is characterized by $\{|\Delta(I)|, \Lambda\}$ values. Let us recall that no experimental value of selectivity is used, the chosen catalyst being considered as selective in the reaction when its selectivity is higher than 50 mol% [14]. Examples of well known selective catalysts are $0.1V_2O_5/0.9TiO_2$ for *o*-xylene to phthalic anhydride or $(VO_2)P_2O_7$ for *n*-butane to maleic anhydride. By plotting ΔI against Λ, more than 50 catalyst/reaction couples involving C_1–C_8 saturated and unsaturated hydrocarbons and a few oxygenated reactants, were shown to be distributed among two straight lines with good reliability factors (ca. 0.95) (Fig. 1). Mild oxidation and ODH reactions cannot be distinguished by separated lines because either the points are not numerous enough, or the Λ range is too wide to propose an accurate enough relationship. Each line corresponds to the type of hydrocarbon to be oxidized: oxidation of ‘paraffinic’ bonds (OP), and oxidation of ‘olefinic’ bonds (OO). However, the type of C–H bond which is to be modified selectively determines the position of the representative point $\{\Delta I, \Lambda\}$. This is the reason why C–H bonds belonging to paraffinic hydrocarbons (e.g., *n*-butane) or alkyl radicals (e.g., *o*-xylene, toluene) lie on the same line OP (Fig. 1), the alkyl groups (methyl) only being modified during the reaction. On the OP line, ethylbenzene→styrene on $AlPO_4/Al_2O_3$ and *n*-butane→maleic anhydride on $(VO)_2P_2O_7$ require the most acidic catalysts (Fig. 1, down left, $\Lambda=0.48$ and 0.49, respectively) while methane coupling to ethylene requires a more basic catalyst (up right, Li_2O/MgO, $\Lambda=0.88$). Similarly on the OO line, but-1-ene to maleic anhydride requires a more acidic catalyst ($VOPO_4$, $\Lambda=0.48$) than epoxidation of ethylene (Ag_2O/Al_2O_3, $\Lambda=1.25$).

3. Results and discussion

During the elaboration of the above model, we had observed that, in the case of MOX of methanol to formol on $Fe_2(MoO_4)_3$–MoO_3 (Mo/Fe=2.5/1) [17], the representative point ($\Delta I=0.2$ eV; $\Lambda=0.55$) was far from fitting OP line in Fig. 1. Our explanation was that the optical basicity required for the MOX of an alcohol, which is more acidic than hydrocarbons, could be different [14]. Using the same model, we have gathered some examples of selective catalysts for the mild oxidation of alcohols from literature, and calculated the corresponding Λ and ΔI. The obtained linear relationship is presented in Fig. 1, line OA. As in the case of the MOX of paraffinic bonds, the slope of OA line for alcohols is positive. Since the oxidation of alcohols is a means to study the nature, number and strength of acid sites according to whether the catalyst orientates the transformation to the alkene or to the ketone (or aldehyde) [18], we expect to find a parallel relationship with optical basicity in a forthcoming paper.

The case of Ammoxidation of Hydrocarbons has been similarly treated, because the same type of iono-covalent oxides than in pure MOX is known to be selective [19]. Examples are not numerous enough in literature to draw one line for each type of reactant (saturated/unsaturated reactant molecule) with certainty. The linear relationship between ΔI and Λ is shown in Fig. 2, line AP. The same kind of relationship was also drawn when considering catalysts selective in combustion of hydrocarbons. Among them, perovskites are more particularly known to be selective since they are used extensively in the control of automotive exhaust catalysis [20]. Eqs. (2) and (3) were systematically used to calculate $\Lambda_{surface}$ because of the compact structure of catalysts and ΔI because of the carbon stoichiometry of the reactions,

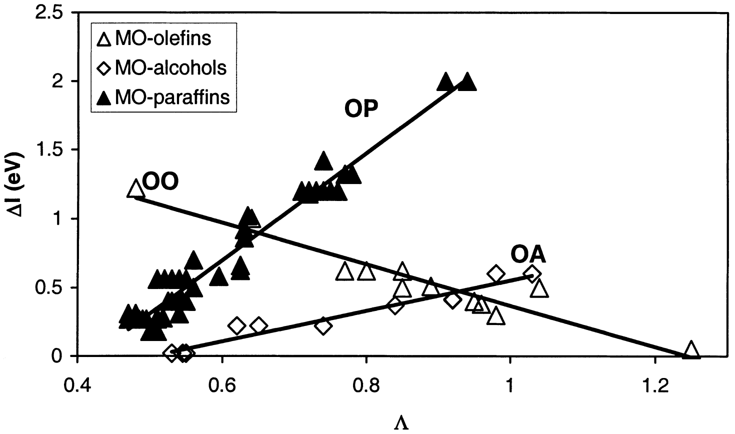

Fig. 1. Variation of ionization energy $|\Delta I|$ (eV) during reactant-to-product reaction plotted against optical basicity Λ of catalysts for MOX reactions; line OP: oxidation of paraffins; line OO: oxidation of olefins; line OA: oxidation of alcohols.

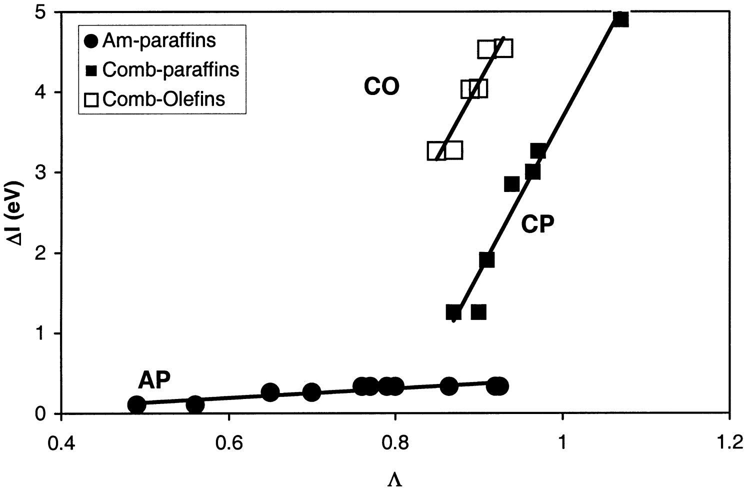

Fig. 2. Variation of ionization energy ΔI (eV) during reactant-to-product reaction plotted against optical basicity Λ of catalysts for ammoxidation and combustion on various catalysts; line AP: ammoxidation of paraffins; line CO: combustion of olefins; line CP: combustion of paraffins.

respectively. Two lines are obtained depending on the nature of the reactant, paraffin or olefin (Fig. 2, lines CP and CO, respectively). Their slope is positive and steeper than for other reactions, as due to the very high ionization energy of CO_2 compared to that of hydrocarbons and alcohols.

4. Conclusion

The various reactions which have just been considered have a common feature: all of them are performed on oxide catalysts, and the oxygens linked to reducible cations are responsible for selectivity according to the redox mechanism. According to the principle of initial and final states, we propose that *selectivity* is accounted for by the difference ΔI of the ionization energies of reactant and of product, in other words by the electron donor/acceptor power of the reaction. Facing the reaction, the catalyst must have the right electron acceptor/donor power which is represented by Λ, the *optical basicity*. The optical basicity is a theoretical parameter which is calculated by means of empirical equations and takes into account the valence and coordination of the metallic cation(s).

Six linear relationships have been drawn between $|\Delta I|$ and Λ obtained for each reaction/catalyst couple. Their slope depends on the type of reaction (MOX, ammoxidation, combustion) and on the molecular structure of the reactant as related to that of the final product. Consequently, by using these correlations it should be possible to find new potentially selective catalysts, or at least to exclude catalysts the optical basicity of which would not fit the optimum range of Λ for the wanted reaction ($|\Delta I|$). Progress is still needed in order to improve the accuracy of the model, particularly in determining the actual value of Λ on-stream. Work is also in progress to understand why relationships between $|\Delta I|$ and Λ are linear and to give a physical meaning to these various slopes.

Uncited reference

[15].

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