

Rationalization of the Catalytic Behavior of Lanthanide Oxides and Praseodymium Molybdates in Total and Selective Oxidation of Isobutene

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The purpose of this work is to examine critically the correlations between ionization potential or absolute hardness and the catalytic behavior of binary and ternary oxides containing lanthanides (Ln) in alkene oxidation. Five lanthanide oxides (La_2O_3 , Sm_2O_3 , Pr_6O_{11} , Tb_4O_7 , and CeO_2) and three praseodymium molybdates ($\text{Pr}_2\text{Mo}_3\text{O}_{12}$, $\text{Pr}_6\text{MoO}_{12}$, and Pr_2MoO_6), were used as pure phases or in mixtures with MoO_3 in the partial and total oxidation of isobutene. The catalytic performances of their mixtures with MoO_3 are described in the context of the “remote control mechanism”, according to which the lanthanide-based oxides are identified as donors of spillover oxygen. Their donor ability is evaluated through the synergetic effects on methacrolein selectivity and correlated with the physical properties mentioned above. In the case of ternary oxides such as praseodymium molybdates, the concepts of average ionization energy and average absolute hardness are proposed to take into account the fact that the electron density and therefore the reactivity of mobile surface oxygen species are influenced by the presence of both metals in the lattice. The results obtained with the pure Ln-based oxides are in line with the literature concepts of ionization energy and absolute hardness. As far as the mechanical mixtures are concerned, it is shown that the above correlations, when combined with the “remote control” concepts, provide a comprehensive view of the influence of ionization energy or absolute hardness for both single phase and biphasic catalysts exhibiting phase cooperation.

Introduction

Although the catalytic potential of lanthanides in oxidation catalysis has been mainly described in total oxidation processes, experimental results show that they also play an essential role in controlling selective oxidation. In particular, ternary $\text{Pr}-\text{Mo}-\text{O}^1$ and quaternary $\text{Bi}-\text{Pr}-\text{Mo}-\text{O}^{2-4}$ phases were described as catalysts for the partial oxidation of propene and isobutene. The results indicated a strong dependence of the activity and selectivity in acrolein or methacrolein on the Bi/Mo and the Pr/Mo composition and were analyzed in terms of differences in surface acidities. The interest of $\text{Bi}-\text{Ce}$ molybdate solid solutions in ammoxidation of propene to acrylonitrile was also mentioned.⁵ High catalytic activities were observed in single-phase regions whose composition corresponds to the maximum mutual solid solubility, i.e., in regions where the maximum atomic dispersion of Bi and Ce was achieved in the molybdate lattice. It was suggested that the $\text{Ce(IV)}/\text{Ce(III)}$ redox couple was responsible for optimizing the catalytic efficiency of the bifunctional Bi/Mo -based catalytic site by facilitating the electron transfers and increasing the mobility of oxygen ions and anion vacancies. However, there is so far no global view on the actual role played by lanthanides in multiphase oxidation catalysts. The present paper, resting on results we published previously and other literature data, will focus on the way to rationalize the catalytic behavior of lanthanide-based binary (Ln_xO_y) or ternary ($\text{Ln}-\text{M}-\text{O}$) oxides in alkene oxidation by

referring to fundamental physical and chemical properties. Another important objective of this paper is to proceed a step forward in the analysis of phase cooperation in catalytic oxidation. More precisely, we shall attempt to show that the “remote control” concepts invoked to explain phase cooperation, on one hand, and the correlations with ionization energy and absolute hardness of catalytic cations, on the other hand, can be unified within a single conceptual picture.

We previously reported experiments dealing with the catalytic behavior of lanthanide-based oxides in total and selective oxidation of isobutene.⁶⁻⁷ Five lanthanide oxides (La_2O_3 , Sm_2O_3 , Pr_6O_{11} , Tb_4O_7 , and CeO_2) and three praseodymium molybdates displaying different stoichiometries ($\text{Pr}_2\text{Mo}_3\text{O}_{12}$, $\text{Pr}_6\text{MoO}_{12}$ and Pr_2MoO_6) were investigated for their properties in isobutene oxidation to methacrolein and CO_2 at 400 °C, either as pure phases or when associated with oxides such as MoO_3 or Sb_2O_4 . After detailed discussion of the various possible interpretations, it was concluded that the catalytic results collected with the multiphase catalysts could be interpreted within the framework of the “remote control” theory, which is based on the migration of active oxygen species (“spillover” oxygen) from a donor to an acceptor phase.⁸ The keypoint of this mechanism is that cooperation occurs between two separate oxide phases, in the absence of any mutual contamination. One of these phases, the acceptor, is the catalytically active phase for the oxidation reaction. The other one, the donor, shows absolutely no catalytic activity with respect to alkene oxidation but generates spillover oxygen and governs in this way the efficiency of the first one by creating and/or regenerating selective active sites on its surface. This mechanistic model has

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been successful in accounting for the synergetic effects observed on the yield and selectivity of a wide range of multiphasic oxidation catalysts.^{9,10}

The objective of this paper is to explain the catalytic behavior of the above-mentioned lanthanide oxides and molybdates, as pure phases and mixtures, in total and selective oxidation of isobutene by taking into account some selected physicochemical properties. It is therefore necessary to begin with a discussion of the catalytic behavior of the pure Ln_xO_y and $\text{Pr}_x\text{Mo}_y\text{O}_z$ phases in isobutene oxidation on the basis of literature data. This introductory section will summarize the attempts made with other catalytic materials to correlate activity in oxidation with electronic properties of catalytically active cations in oxides. At the beginning of the discussion, a special section will describe the formal concepts on which our analysis will be based.

In their investigations on the total oxidation of butane, Hattori et al. correlated the catalytic properties of a wide series of lanthanide oxides to thermodynamic properties; they observed that the most active oxides, i.e., the nonstoichiometric ones, were those exhibiting the lowest standard formation enthalpies.¹¹ Nevertheless, this correlation could not explain the differences in catalytic behavior among the various lanthanide sesquioxides or between the different nonstoichiometric oxides. On the other hand, these authors found a perfect correlation between the catalytic properties of the lanthanide oxides and the 4th ionization energy of the metals involved: the lower the 4th ionization energy, the more active the oxide was in total oxidation.

In a first approach, the validity of Hattori's correlation was therefore checked with respect to the catalytic behavior of the lanthanides oxides and praseodymium molybdates mentioned above in isobutene oxidation. In addition, relationships with the fundamental acid–base properties were looked for. In particular, the catalytic performances will be analyzed with respect to the absolute hardness, a theoretical concept which combines the ionization potential and the polarizability of the concerned ions. These correlations are in line with the fact that oxidation reactions in heterogeneous catalysis usually involve a mechanism that was developed upon formal concepts proposed by P. Mars and D. W. van Krevelen in a completely different reaction, namely, the oxidation of SO_2 into SO_3 .¹² In the case of selective catalytic oxidations, the mechanism includes activation of the substrate on a metallic cation, insertion of surface lattice oxygen, and a redox process occurring on the catalyst surface, a mechanism which is called “Mars and van Krevelen” in this field. Therefore, such reactions require both acid–base and redox properties of the catalyst. Moreover, as proposed by Haber, catalytic reactions involving oxygen can be divided into two groups: (i) electrophilic oxidations where oxygen is activated into electrophilic species (O^- , O_2^-), which are responsible for the attack of the reactive molecule on its high electronic density sites; (ii) nucleophilic oxidations in which additions of nucleophilic oxygenated species (O^{2-}) occur on previously activated molecules.¹³ In partial oxidation reactions of hydrocarbons, the first step is the nucleophilic attack of the C–H bond by the O^{2-} species. In a recent monograph by B. K. Hodnett,¹⁴ the general features of heterogeneous catalytic oxidation have been reviewed, with particular attention to the hydrocarbon activation and the various types of oxygen species involved in these processes.

The second part of this paper is devoted to our results obtained with the Ln_xO_y – MoO_3 and $\text{Pr}_x\text{Mo}_y\text{O}_z$ – MoO_3 mixtures, in line with previous attempts to generalize the behavior of multiphasic catalysts involved in allylic oxidations and oxidative dehydro-

genations, by referring to “remote control” effects. In particular, a tentative “donor scale” of oxide phases had been derived from the comparison of the catalytic synergies observed between MoO_3 , taken as the reference acceptor phase, and different donor phases, when they were used in the selective oxidation of isobutene to methacrolein. In the context of that work summarized in a review paper,⁹ the properties determining the donor strength were discussed, and the donor character was evaluated in a semiquantitative way by relating it to the magnitude of the catalytic synergy measured on methacrolein selectivity. The general conclusion was that a good donor of spillover oxygen would be an oxide where the ionization potential of the cation, as modified by its environment, would lie between given limits. In the case of so-called oxosalts, account must be taken of the “ionicity” of the oxoanion. Comparing compounds with identical oxoanions, it was suggested that the ionization potential of the cation determined this optimum.⁹ Similarly, the acceptor strength of oxide phases was evaluated from the synergy measured on the intrinsic methacrolein yield, by considering that the acceptor ability of an oxide would be characterized by its propensity to increase the number of selective catalytic sites created and/or regenerated by spillover oxygen on its surface. For this purpose, $\alpha\text{-Sb}_2\text{O}_4$, which is totally inert toward isobutene oxidation, was taken as the reference “donor” phase.

The concepts of Weng and Delmon were based on the very different “roles” of donors and acceptors. According to them, efficient donors are assumed to dissociate molecular oxygen into atomic species (O^{2-} with some partial additional charge). Their role is therefore 2-fold, namely, (i) kinetic, i.e., to accelerate the dissociation process, and (ii) thermodynamic, i.e., to give a specific increment of free enthalpy (via an excess of electrical charge) to the O^{2-} species. Both aspects depend on the polarization of some metal–metal or metal–oxygen bonds, namely, the polarization of the metal–X bond which should be reflected by the ionization energies. The acceptor must enable a concerted reaction in which its electronic shells are involved in a complicated way, according to mechanisms similar or identical to those occurring in homogeneous catalysis with organometallic complexes. In this case, the constraints are, for instance, coordination number and geometry, ligand field, and electron back-donation. The whole “remote control” concept takes into account the dynamic nature of the catalytic process and the corresponding movement of spillover oxygen.

Recently, Leboutteiller and al.¹⁵ proposed using another acid–base concept as a predictive tool for the catalytic behavior of oxides: the optical basicity (Λ), a concept originally proposed by Duffy for the characterization of glasses,^{16,17} and describing the electrodonating power (i.e. the Lewis basicity) of oxygen atoms contained in oxide networks. Initially defined for ionic solids, the concept of optical basicity was later adapted for oxides with significant covalent character, like most transition metal oxides, by using correlations between the Λ -values of simple oxides and the corresponding so-called “ionic-covalent parameter” (ICP) defined by Portier and al.¹⁸ The ICP parameter is a dimensionless number which reflects the influence of the relative extent of covalency in an oxide or oxosalt on the Lewis acidity of the metal cations. This approach allowed to calculate Λ -values for any mixed oxide by taking into account the coordination numbers and valencies of the various ions concerned. In recent successive studies,^{19–22} Bordes and Courtine described correlations between the difference of the ionization potentials of reactants and products, which is assumed to be related to selectivity, and the optical basicity of selective oxide catalysts in a wide range of oxidation reactions: mild oxidations

of alkanes, alkenes and aromatics,^{19,21} alkane oxidative dehydrogenations,^{19,21} oxidation of alcohols,²² ammoxidation, and total oxidation of hydrocarbons.²² The global approach proposed by these authors focuses on the electronic structure of oxygen, following Haber's ideas and, therefore, attempts to evaluate the thermodynamic energy of oxygen. These concepts do not explicitly permit a connection with the rate-determining aspects of oxygen adsorption and dissociation, which constitute a strong kinetic limitation in selective oxidation. Similarly, this approach does not leave room for a direct relationship with the role of coordination and detailed electronic mechanism during the reaction. It is therefore absolutely necessary to find a concept and a language which unifies these various points of view. The remote control concept postulates that surface mobile oxygen species (O_{so}) are the same on the donor (which generates them) and the acceptor (which consumes them). In recent talks,²³ Bordes also considers two-phase (or multiphase) catalysts and evaluates the corresponding parameter Λ of her theory. The correlations seem to work well, showing thereby that the assumption that a single type of surface oxygen species should be present, as speculated by the "remote control mechanism", is sensible.

Experimental Section

Catalysts preparation, analytical techniques used, and reaction conditions have been reported elsewhere, together with an extensive description of the catalytic results which were taken into consideration for the present discussion.^{6,7} Only essential information will be summarized before starting the discussion.

The catalytic results considered are the yields in methacrolein (Y_{met}) and CO_2 (Y_{CO_2}) and the selectivity in methacrolein (S_{met}). The yield in methacrolein represents the ratio of the number of moles of methacrolein formed to the number of moles of isobutene introduced. To express the yield in CO_2 in such a way that it might be directly comparable to Y_{met} , we must take into account the formation of 4 mol of CO_2 per mole of isobutene converted. If Y_{CO_2} is taken as the ratio of the number of moles of CO_2 produced to the number of moles of isobutene converted, we must therefore use $Y_{CO_2}/4$. The selectivity in methacrolein is defined as the ratio between methacrolein yield and isobutene conversion ($S_{met} = Y_{met}/X_{iso}$), X_{iso} being defined as the number of mole of isobutene converted with respect to the initial number of mole of isobutene in the feed. According to the definition of yields given above, if methacrolein and CO_2 are the only products observed, the total isobutene conversion corresponds to $X_{iso} = Y_{met} + Y_{CO_2}/4$.

Mixtures were characterized by their mass composition (expressed as x_m , which is defined as the ratio of the mass of lanthanide oxide or molybdate to the total mass of the mixture). The synergetic effects on Y_{met} and Y_{CO_2} were evaluated from the difference between the experimental values and the theoretical ones. The theoretical values $(Y_{met})_{th}$ and $(Y_{CO_2})_{th}$ were calculated for the various AB mixtures, assuming that the oxides do not interact and contribute to the reaction only proportionally to their respective amounts in the mixture, according to the following expression:

$$(Y_{AB})_{th} = Y_A x_A + Y_B x_B$$

where Y_i represents the experimental yield of compound i and x_i the weight ratio of component i in the mixture AB.

The above relationship assumes zero-order reactions as a first approximation or, more precisely, that isobutene conversions

remain sufficiently low so that the respective yields can be considered as proportional to the conversion values.

To take into account the actual differences between the specific surface areas of the concerned compounds, the synergy on the different yields in AB mixtures were actually evaluated from the difference between the experimental values normalized for a standard specific surface area of 1 m²/g ($Y_{AB}/S_{BET} = Y^*_{AB}$, called real intrinsic yield) and the theoretical intrinsic yield, $(Y^*_{AB})_{th}$, i.e., the one that would be obtained in the absence of any cooperation. Because it is impossible to measure the respective surface areas developed by each phase in the mixture, the calculation of the theoretical intrinsic yield $(Y^*_{AB})_{th}$ was based on the following expression, in which the total surface area is evaluated from the weighed sum of the respective surface areas of the two components, according to

$$(Y^*_{AB})_{th} = [Y_A x_A + Y_B x_B] / [(S_{BET})_A x_A + (S_{BET})_B x_B]$$

where $(S_{BET})_i$ is the specific surface area of the oxide i and x_i the weight ratio of component i in the mixture AB.

The synergy on yield for the AB mixture, ΔY^*_{AB} was defined as

$$\Delta Y^*_{AB} = [Y^*_{AB} - (Y^*_{AB})_{th}] / [(Y^*_{AB})_{th}]$$

in which Y^*_{AB} is the real intrinsic yield of the AB mixture, i.e., $Y^*_{AB} = [Y_{AB}] / [(S_{BET})_{AB}]$, where $(S_{BET})_{AB}$ is the experimental specific surface area of the AB mixture and Y_{AB} is the experimental yield of the AB mixture.

The synergy on methacrolein selectivity is defined by the following expressions: Theoretical $(S_{AB})_{th}$ and real (S_{AB}) methacrolein selectivities are defined, respectively, as

$$(S_{AB})_{th} = [Y_A x_A + Y_B x_B] / [X_A x_A + X_B x_B]$$

and

$$S_{AB} = [Y_{AB}] / [X_{AB}]$$

where X_{AB} is the experimental conversion of the AB mixture. The synergy on methacrolein selectivity, ΔS_{AB} , is consequently defined as

$$\Delta S_{AB} = [S_{AB} - (S_{AB})_{th}] / [(S_{AB})_{th}]$$

Summary of the Catalytic Results

Pure Oxides. The catalytic results obtained with the oxides mentioned in the Introduction (La_2O_3 , Sm_2O_3 , Pr_6O_{11} , Tb_4O_7 , and CeO_{2-x}) on one hand, and the three pure praseodymium molybdates ($Pr_2Mo_3O_{12}$, Pr_6MoO_{12} , and Pr_2MoO_6) on the other hand^{6,7} are summarized in Figures 1 and 2. As shown in Figure 1, lanthanide oxides in general favor total oxidation, and the nonstoichiometric ones are the most active (Pr_6O_{11} and CeO_{2-x}). Figure 2 indicates that $Pr_2Mo_3O_{12}$ and Pr_6MoO_{12} give exclusively partial and total oxidation, respectively, while Pr_2MoO_6 gives rise to both partial and total oxidation products.

Mixtures Ln_xO_y - MoO_3 and $Pr_xMo_yO_z$ - MoO_3 . The performances (synergies on methacrolein and CO_2 productions) of the mixtures associating MoO_3 with lanthanide oxides or molybdates are summarized in Figures 3 and 4, respectively. These figures only include mixtures with mass ratio $x_m = 0.5$. The mixtures with La_2O_3 and Sm_2O_3 exhibit small synergetic effects, those with CeO_{2-x} and Pr_6O_{11} give a positive synergy on methacrolein production and a negative synergy for total oxidation, and that with Tb_4O_7 gives positive synergies on both partial and total oxidation. As illustrated by Figure 4, the

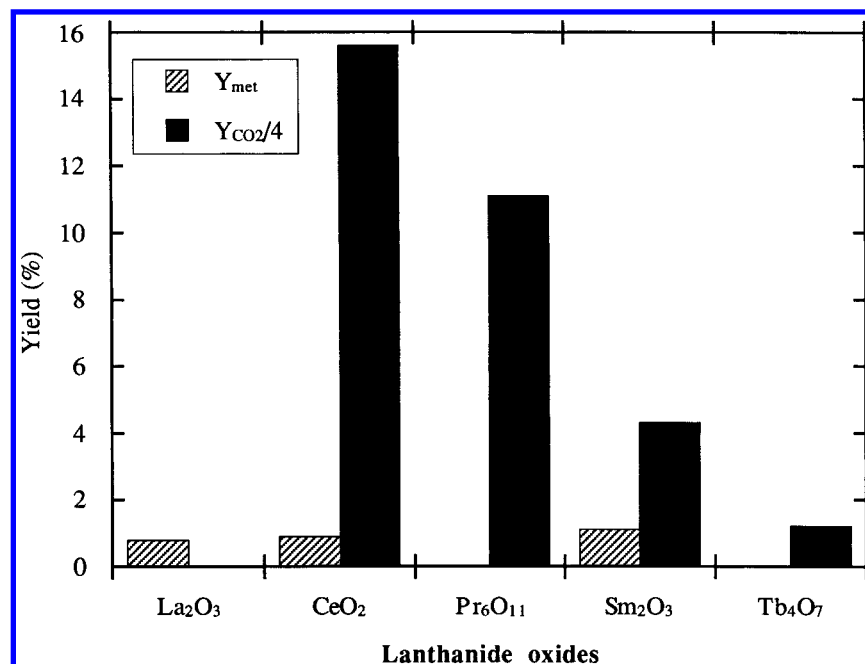


Figure 1. Yields in methacrolein (Y_{met}) and CO_2 ($Y_{\text{CO}_2/4}$) for the lanthanide oxides (Reaction conditions: 600 mg catalyst; 500–800 μm . Reactant mixture: $i\text{-C}_4\text{H}_8/\text{O}_2/\text{N}_2$, 8.3/19.3/72.4 vol %. Total flow rate: 30 mL min^{-1} ; $T = 673$ K.).

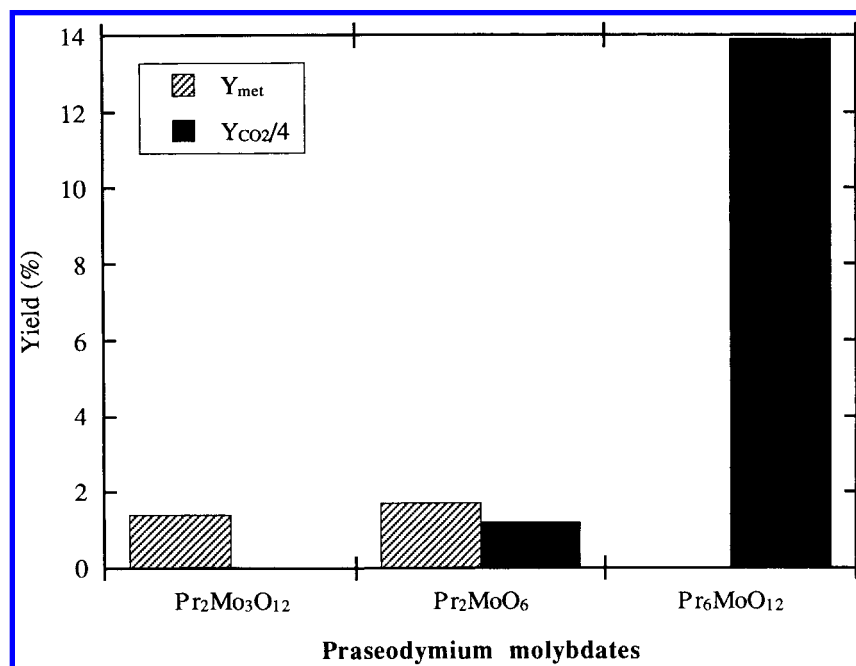


Figure 2. Yields in methacrolein (Y_{met}) and CO_2 ($Y_{\text{CO}_2/4}$) for the praseodymium molybdates (Reaction conditions: 600 mg catalyst; 500–800 μm . Reactant mixture: $i\text{-C}_4\text{H}_8/\text{O}_2/\text{N}_2$, 8.3/19.3/72.4 vol %. Total flow rate: 30 mL min^{-1} ; $T = 673$ K.).

mixtures containing $\text{Pr}_2\text{Mo}_3\text{O}_{12}$ and Pr_2MoO_6 give positive synergies on both methacrolein and CO_2 production, and the mixture based on $\text{Pr}_6\text{MoO}_{12}$ gives positive synergy on partial oxidation and negative synergy on total oxidation.

Discussion

Summary of Theoretical Concepts. *Ionization Energy.* The formation and interconversion of the surface oxygen species require electron transfers between the catalyst and gaseous oxygen. In selective oxidation catalysis, the actual oxidizing agent is a reducible metal cation. The corresponding redox processes can therefore be correlated to the ionization energy of the metal cation(s) included in the oxide catalyst. With respect to that point, it is necessary to distinguish between binary oxides,

which are constituted by a metallic cation surrounded by oxygen atoms and ternary oxides, which in our case can be considered as the association of different entities: a metallic cation and an oxoanion. In the latter case, two kinds of chemical bonds can be distinguished: bonds with mainly covalent character in the oxoanion, and mainly ionic character between oxoanions and cations.²⁴

In ternary oxides, it has been demonstrated that the electrodonating power of the cations depends both on the ionization energy of the cation itself and on the effective negative charge of the neighboring oxygens, which is in turn related to the extent of covalency within the oxoanion group. For the same oxoanion group, the electrodonating power of the cation increases when its ionization energy decreases. For a same cation, an enhance-

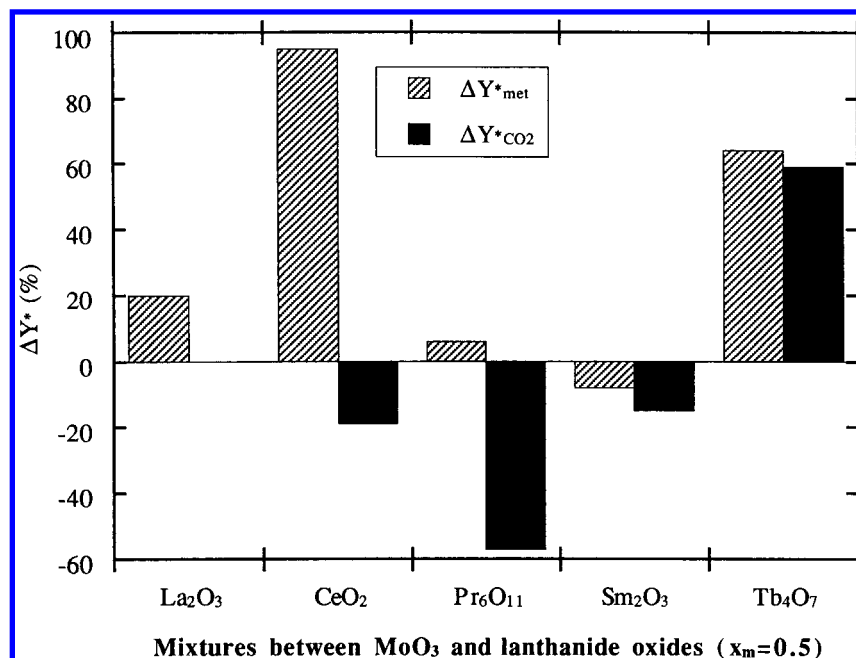


Figure 3. Synergies on the yields in methacrolein (ΔY^*_{met}) and CO₂ ($\Delta Y^*_{\text{CO}_2}$) for the MoO₃-LnO_x mixtures ($x_m = 0.5$).

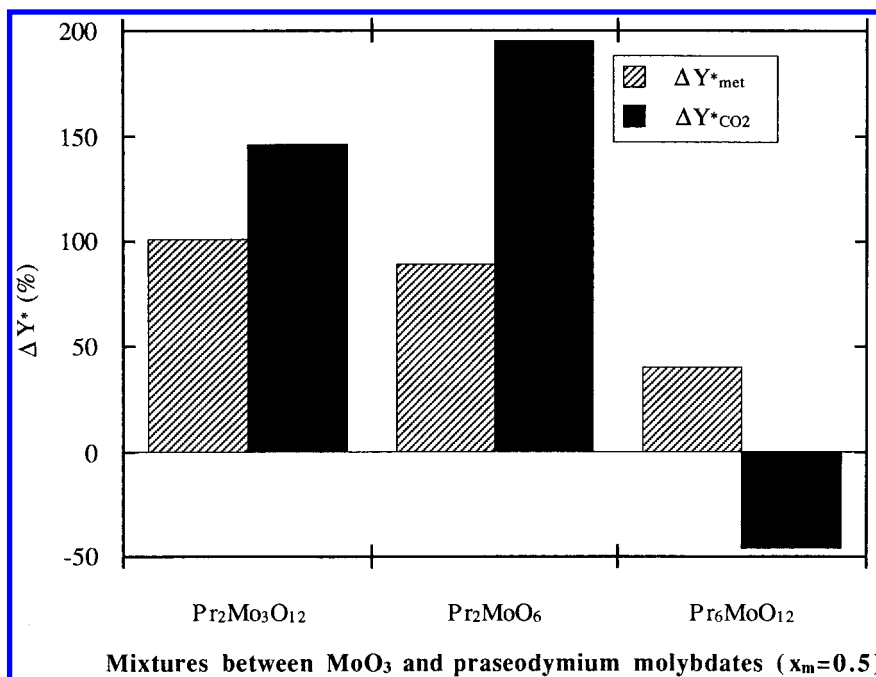


Figure 4. Synergies on the yields in methacrolein (ΔY^*_{met}) and CO₂ ($\Delta Y^*_{\text{CO}_2}$) for the MoO₃-Pr_xMo₃O_x mixtures ($x_m = 0.5$).

ment in the ionicity of the bonds within the oxoanion would increase the effective charge of the oxygen atoms and, consequently, enhance the electrodonating ability of the cation.^{24,25} The results of ref 9 supported this view.

Acido-Basicity. A strong line of interpretation in the open literature analyzes the catalytical behavior of oxides by considering their Lewis acid-base properties. Whereas coordinatively unsaturated metallic ions in a high oxidation state or anionic vacancies can be considered as acidic centers, oxygenated anions and hydroxyl groups constitute basic sites. According to the same approach, hydrocarbons such as alkanes, olefins, and aldehydes are considered as weak or very weak Lewis bases. By referring to Pearson's HSAB concepts,²⁶ Vedrine et al. suggested that the oxidation of an alkene would be more selective if the catalyst involves a hard cation (Mo⁶⁺, V⁵⁺, W⁶⁺) rather than a soft one because the interaction would be weaker

and promote partial oxidation rather than total oxidation.²⁷ Absolute hardness, noted η , is defined as:

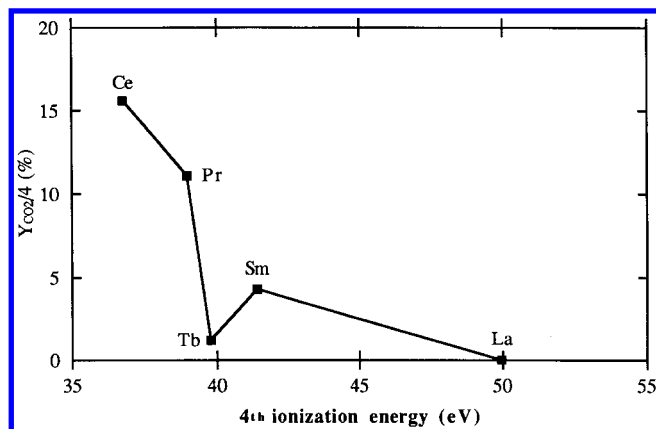
$$\eta = (I - A)/2$$

where I represents the ionization energy and A the electron affinity. According to this definition, this parameter is actually a measurement of the energy difference ΔE between the ionic HOMO and LUMO levels, in the sense that $\Delta E = 2\eta$.

Because the 4f^{*n*} electron configuration leads to low 4th ionization energy values, a peculiarity of all lanthanide Ln³⁺ ions (Ln = Ce to Lu) is to display absolute hardnesses relatively low (between 36.6 and 45.2 eV) compared to that of La³⁺ (49.95 eV), although they all behave as relatively hard acids. The electron configurations and the corresponding values of I , A , and η for the lanthanide ions relevant to this work are listed in Table 1.

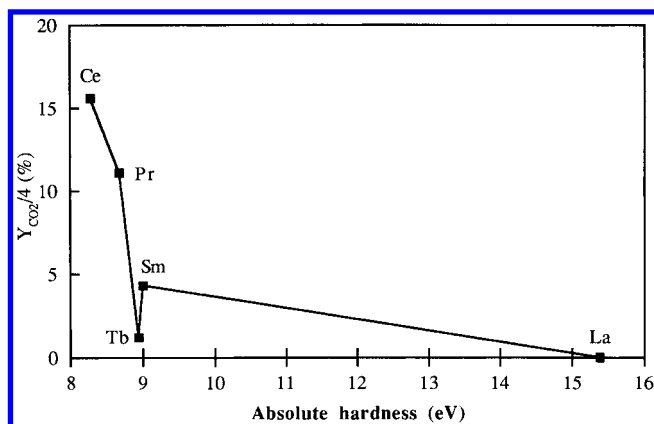
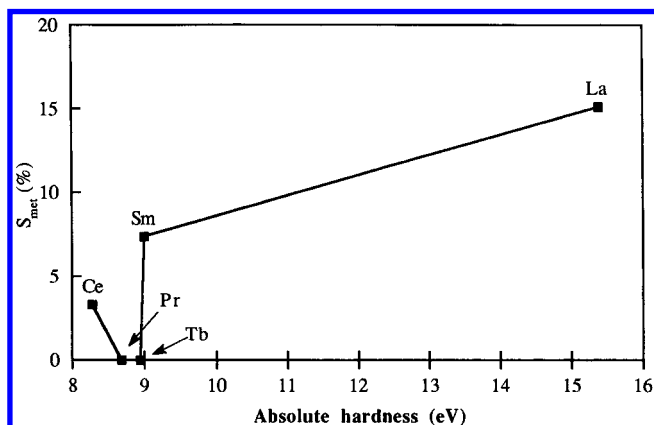
TABLE 1: Electron Configuration, Ionization Energy (*I*), Electron Affinity (*A*) and Absolute Hardness (*η*) of Different Ln³⁺ and Ln⁴⁺ Cations²⁸

cation	electron configuration	<i>I</i> (eV)	<i>A</i> (eV)	<i>η</i> (eV)
Ln ³⁺	[Xe] 4f ⁰	49.95	19.18	15.38
Ce ³⁺	[Xe] 4f ¹	36.76	20.20	8.28
Pr ³⁺	[Xe] 4f ²	38.98	21.62	8.68
Sm ³⁺	[Xe] 4f ⁵	41.40	23.40	9.00
Tb ³⁺	[Xe] 4f ⁸	39.80	21.91	8.94
Ce ⁴⁺	[Xe] 4f ⁰	65.55	36.76	14.39
Pr ⁴⁺	[Xe] 4f ¹	57.53	38.98	9.27
Tb ⁴⁺	[Xe] 4f ⁷	66.46	39.80	13.33

**Figure 5.** Evolution of the CO₂ yields obtained with pure Ln_xO_y phases with respect to the 4th ionization energy of the lanthanides.

Pure Oxides in Total and Selective Oxidation. *Binary Oxides Ln_xO_y. Ionization Energy.* In line with Hattori's work on total oxidation of butane,¹¹ a correlation between the catalytic properties of our five lanthanide oxides for total oxidation with respect to the 4th ionization energy of their respective cations has been established. Figure 5 shows the evolution of CO₂ yields (in %) with respect to the 4th ionization energy of the lanthanides. It can be observed that the most active lanthanide oxides are characterized by the lowest 4th ionization energies (CeO_{2-x} and Pr₆O₁₁). As far as cerium oxide is concerned, this statement refers to the fact that significant amounts of Ce(III) are present, in relationship with the intrinsic nonstoichiometry of this compound. In its tetravalent state, cerium displays the electron configuration 4f⁰. Any involvement of its electron shells in the redox process would therefore concern the 6s subshell, which is characterized by a significantly higher ionization energy. The same situation also holds for La³⁺, and actually, La₂O₃ was shown to produce no CO₂.

This trend corresponds to the guidelines announced in the above overview of the theoretical concepts. Catalysis is fundamentally a phenomenon modifying kinetics. The so-called "Mars and van Krevelen mechanism" describes a steady-state based on two reactions that adopt the same rate by involving oxidized and reduced parts of the catalysts in adjusted proportions. The first one is hydrocarbon oxidation by lattice oxygen, the second one replenishment in oxygen by adsorption of O₂ and adequate ionization of the oxygen species formed subsequently. There are therefore two facets in the tendencies mentioned above, and these tendencies are necessarily linked to each other in a narrow way. The first one refers to thermodynamics: in principle, the lower the ionization energy of the metal ion, the easier the formation of electrophilic oxygen species, and consequently, the higher the tendency to total oxidation.¹³ The second aspect concerns kinetics: when ionization energies are higher, the rate of electron transfer to oxygen

**Figure 6.** Evolution of the CO₂ yields obtained with pure Ln_xO_y phases with respect to the absolute hardness of the Ln³⁺ ions.**Figure 7.** Evolution of the selectivity in methacrolein obtained with pure Ln_xO_y phases with respect to the absolute hardness of the Ln³⁺ ions.

diminishes. This fact is reflected in the frequently observed diminution of overall activity when selectivity increases.

Hardness. A correlation can also be found between catalytic performances of lanthanide oxides and their acid–base properties, as obvious from Figure 6, where CO₂ yields are plotted against the absolute hardness of the respective Ln³⁺ ions. It appears clearly that oxides containing the softest cations are the most active for total oxidation. As it has been suggested that the oxidation of an alkene would be more selective if it involves a hard cation rather than a soft one, Figure 7 presents a plot of the selectivity in methacrolein of the lanthanide oxides in function of the absolute hardness of the respective Ln³⁺ ions. Globally, this plot confirms that, among oxides possessing some oxidation activity, those containing harder cations give rise to higher selectivities in partial oxidation. However, these results do not allow a quantitative analysis between the different oxides with weak absolute hardness.

Ternary Oxides Pr_xMo_yO_z. To correlate the catalytic performances of the praseodymium molybdates (Pr₂Mo₃O₁₂, Pr₆MoO₁₂, and Pr₂MoO₆) to their acid–base properties, we can neither use the previous approach, because the metals present in these three phases are the same, nor rely upon the idea that the bonds are of different nature around Pr and Mo. However, it is admitted, and very often proven experimentally, that oxygen is mobile in and on the crystalline network of oxides active in catalytic oxidation. It can thus be safely assumed that reactive oxygen ions are statistically present with similar probabilities in the vicinity of the different metals involved. We defined consequently an "average absolute hardness" by taking into account the relative proportions of their respective cations in

TABLE 2: Catalytic Properties of Praseodymium Molybdates in Correlation with the Calculated Average Absolute Hardness (η^*) and the Average Ionization Energy (I^*)

phase	average absolute hardness η^* (eV)	average ionization energy I^* (eV)	$Y_{CO_2}/4$ (%)	S_{met} (%)
Pr_6MoO_{12}	11.6	51.5	13.9	0
Pr_2MoO_6	15.5	68.2	1.2	22
$Pr_2Mo_3O_{12}$	21.0	91.6	0	100

the ternary phase. On the basis of the generic formula $Pr_xMo_yO_z$ and of the absolute hardness of Pr^{3+} (8.68 eV) and Mo^{6+} (29.18 eV), the average absolute hardness (noted η^*) has been calculated according to the following relationship:

$$\eta^*(Pr_xMo_yO_z) = ((\eta(Pr^{3+})x) + (\eta(Mo^{6+})y))/(x + y)$$

A similar argument led to the concept of “average ionization energy” (noted I^*). Table 2 summarizes these average absolute hardness and ionization energy calculated for the three praseodymium molybdates together with their catalytic properties for total and selective oxidation. In line with the earlier suggestion that the oxidation of an alkene would be more selective if it involved a hard cation rather than a soft one, the phase with the highest average absolute hardness ($Pr_2Mo_3O_{12}$) gives exclusively partial oxidation, that with the lowest average absolute hardness (Pr_6MoO_{12}) produces exclusively CO_2 , and the molybdate with intermediate hardness (Pr_2MoO_6) generates both methacrolein and CO_2 . The agreement between the catalytic activity and the so-called average ionization energy (I^*) can also be pointed out: the phases characterized by the lowest or the highest I^* value, i.e., Pr_6MoO_{12} and $Pr_2Mo_3O_{12}$, are found respectively to exhibit the highest and lowest catalytic activity for CO_2 production, with methacrolein selectivities of 0 and 100%. Although these results are obtained with only three compounds, this follows the trends already suggested in the literature. Let us notice that, if supported by more data on series of oxides containing the same two metals but in various proportions, the usefulness of the concepts of “average absolute hardness” and “average ionization energy” could be validated.

Mixtures $Ln_xO_y-MoO_3$ and $Pr_xMo_yO_z-MoO_3$. Ionization Energy. By referring to the fact that the selectivity in methacrolein could be considered as a measurement of the donor properties of spillover oxygen,⁹ we evaluated the donor ability of the five lanthanide oxides from the corresponding change in selectivity values, ΔS_{met} , and correlated them to the ionization energies of the respective cations as given by the literature.²⁸ This correlation requires to take into account the fact that Pr_6O_{11} and Tb_4O_7 are mixed valency oxides. Actually, praseodymium oxide contains both Pr^{3+} and Pr^{4+} ions and could be formally described as “ $4PrO_2 \cdot Pr_2O_3$ ”. Similarly, terbium oxide is constituted by Tb^{3+} and Tb^{4+} ions and could be formulated as “ $2TbO_2 \cdot Tb_2O_3$ ”. Therefore, the ionization energies used in the upper part of Figure 8 are calculated account taken of the relative amounts of trivalent and tetravalent ions in the mixed valency oxides and also the elemental 4th and 5th ionization energies which are associated to them. These values are called “weighed ionization energies”. For lanthanum and samarium oxides, the graph refers to the 4th ionization energy ($Ln^{3+} \rightarrow Ln^{4+}$) and, for cerium oxide, to the 5th ionization energy ($Ln^{4+} \rightarrow Ln^{5+}$). The graph of the evolution of the donor-properties (ΔS_{met}) of lanthanide oxides in mixture with MoO_3 (x_m is constant and equal to 0.5) with respect to weighed ionization energies is presented in the upper part of Figure 8 (Figure 8a).

The analysis of Figure 8a shows that the best donors are associated with intermediate ionization energies. A good donor

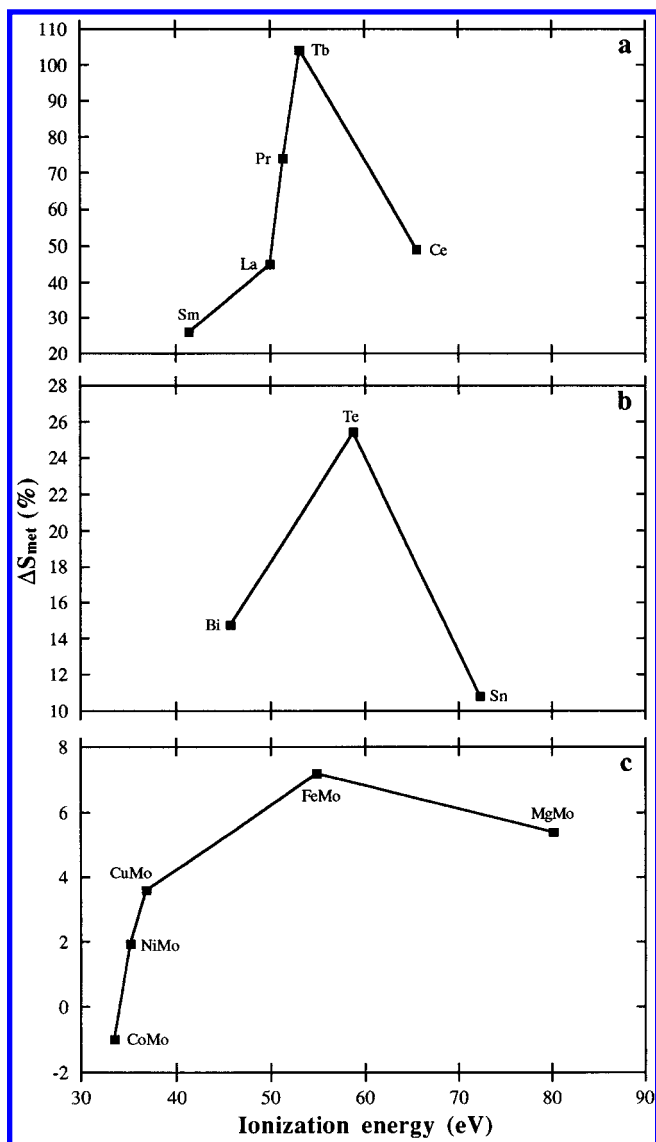


Figure 8. Evolution of the donor properties (synergy on methacrolein selectivity, ΔS_{met}) of mixtures associating MoO_3 and various oxides ($x_m = 0.5$) with respect to the ionization energies (adapted from ref 9). Values corresponding to the binary Ln_xO_y phases (Figure 8a) refer to weighed ionization energies.

would correspond to an oxide with well adjusted electrodonating properties. Oxides with pronounced donor character (weak ionization energy) probably produce electrophilic oxygenated species leading to total oxidation;¹³ oxides with weak donor character, because they are characterized by high ionization energies and are too slow to dissociate and ionize, probably do not possess sufficient activity. Actually, referring to the end of the section concerning ionization energy, the correlations correspond to a “convolution” of thermodynamic and kinetic factors, i.e., electrodonating properties and rate of oxygen activation, respectively. The “well-adjusted” and balanced surface coverage rate by reduced and oxidized parts of the catalyst changes the average ionization energy of the cations involved in the catalytic event. This is unfortunately very difficult to investigate experimentally. Perhaps very sensitive oxygen adsorption using pulse methods could detect the changes of surface properties between different steady state regimes imposed, for example, by varying the oxygen/hydrocarbon ratio in the feed. The parameters in the correlation are actually the result of the interaction of kinetic aspects (respective coverage

TABLE 3: Relationship between Synergetic Effects Observed in $\text{Pr}_x\text{Mo}_y\text{O}_z\text{--MoO}_3$ Mixtures ($x_m = 0.5$) and the Average Ionization Energies (I^*) and Absolute Hardness (η^*)

phase mixed with MoO_3 ($x_m = 0.5$)	ΔX^* (%)	ΔY^*_{met} (%)	ΔS_{met} (%)	I^* (eV)	η^* (eV)
$\text{Pr}_2\text{Mo}_3\text{O}_{12}$	133	101	-13	91.6	21.0
Pr_2MoO_6	107	89	-8	68.2	15.5
$\text{Pr}_6\text{MoO}_{12}$	-36	40	117	51.5	11.6

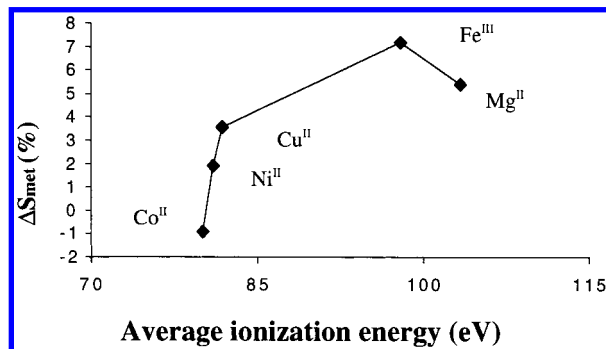


Figure 9. Evolution of the donor properties (synergy on methacrolein selectivity, ΔS_{met}) of mixtures associating MoO_3 and various metal molybdates ($x_m = 0.5$) with respect to the average ionization energies (adapted from ref 9).

ratio) and thermodynamic factors (ionization energy). The best catalysts correspond to an adequate compromise.

These results are similar to those obtained by Weng et al., who already commented on donor properties of mixtures associating MoO_3 and various oxides (TeO_2 , Bi_2O_3 , SnO_2) or molybdate phases $\text{M}_x(\text{MoO}_4)_y$ ($\text{M} = \text{Fe}^{\text{III}}$, Cu^{II} , Co^{II} , Ni^{II} , Mg^{II}).⁹ Figure 8 summarizes these literature data (panels b and c of Figure 8 for binary and ternary oxides, respectively) and those of the present work (Figure 8a, weighed values) and shows that the best donors are characterized by an intermediate ionization energy, i.e., the molybdate $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ (54.8 eV) and the oxide TeO_2 (58.7 eV). It is striking that the three maxima occur at relatively close values (53.1 eV for Tb_4O_7). The absolute numerical ΔS values characterizing the various series in Figure 8 cannot be directly compared because they refer to sets of experiments carried out in slightly different conditions with respect to catalyst preparation and catalytic reactions.

When the catalytic performances of the $\text{Pr}_x\text{Mo}_y\text{O}_z\text{--MoO}_3$ mixtures are analyzed according to the same viewpoint (Table 3), the pronounced synergetic effect observed in the case of the $\text{Pr}_6\text{MoO}_{12}\text{--MoO}_3$ mixture ($\Delta S = 117\%$) is perfectly in line with the average ionization energy of $I^* = 51$ eV, which results in a position close to the maximum of curve 8a. The other two phases, characterized by larger I^* values give rise to slightly negative ΔS values (-8 and -13% for Pr_2MoO_6 and $\text{Pr}_2\text{Mo}_3\text{O}_{12}$, respectively), suggesting the absence of any significant synergy for partial oxidation in these two cases. In this case, as shown in Table 3, there is also a clear reverse relationship between the synergetic effects measured, on one hand, on isobutene conversion or yield in methacrolein, and on the other hand, on methacrolein selectivity. As shown in Figure 9, the validity of this approach can be strengthened by generalizing it to the various metal molybdates cited in ref 9.

Hardness. As for the previous section, we will take into account the various valences of praseodymium and terbium atoms in the respective oxides. "Weighed" will refer to absolute hardness where the proportion of Ln^{3+} and Ln^{4+} cations is taken into account. The graph obtained for the five lanthanide oxides

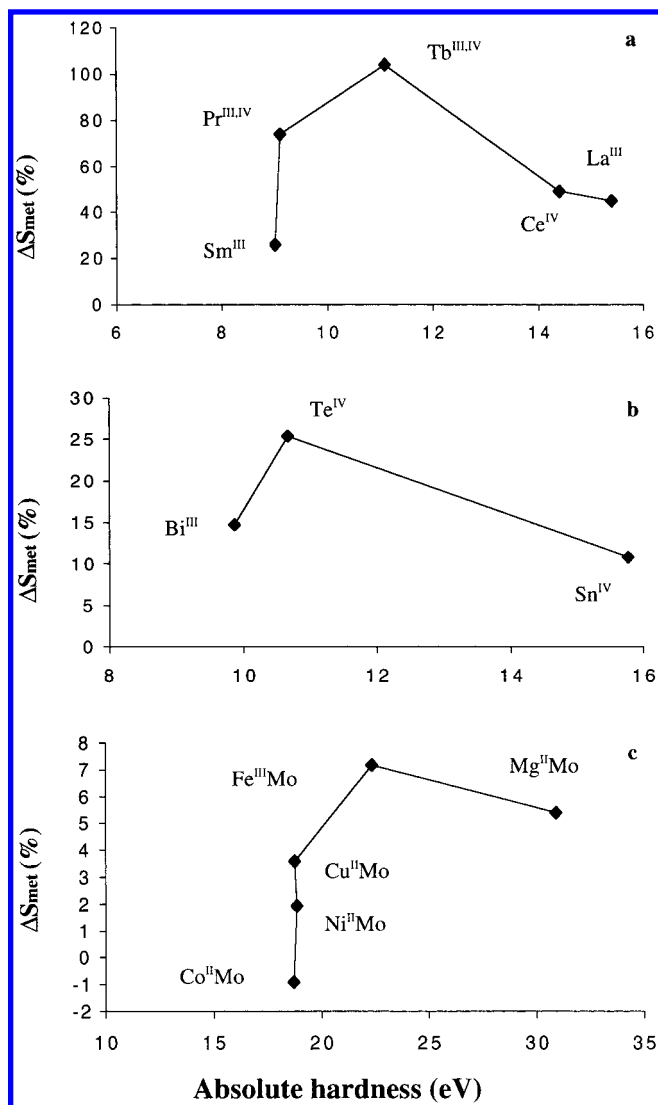


Figure 10. Evolution of the donor-properties (synergy on methacrolein selectivity, ΔS_{met}) of mixtures ($x_m = 0.5$) associating MoO_3 and (a) lanthanide oxides, (b) binary oxides (ref 9), and (c) metal molybdates (ref 9) with respect to the weighed absolute hardness.

in mixture with MoO_3 (x_m constant and equal to 0.5) according to this approach is presented in Figure 10a. The graph shows a correlation between the weighed absolute hardness of the lanthanide oxides and their donor character. The best donors are characterized by an intermediate absolute hardness. In fact, samarium, which has the weakest absolute hardness gives little synergy and lanthanum, which has the highest one, gives also little synergy in comparison with praseodymium and terbium. Panels b and c of Figure 10 illustrate how the same correlations can be proposed to describe the catalytic behavior of the mixtures between MoO_3 and other binary oxides or metal molybdates already mentioned above.⁹

In addition, the behavior of the mixtures between the various praseodymium molybdates and MoO_3 is also compatible with our analysis (Table 3). The maximum synergetic effect on methacrolein selectivity occurs for the $\text{Pr}_6\text{MoO}_{12}\text{--MoO}_3$ mixture: $\text{Pr}_6\text{MoO}_{12}$ is characterized by an average absolute hardness of 11.6 eV, a value which is very close to that of the weighed absolute hardness of Tb_4O_7 ($\eta^* = 11.14$ eV) which corresponds to the maximum of the curve ($\Delta S = 104\%$) in Figure 10.

Conclusions

Ionization energies and absolute hardnesses are shown to be useful theoretical tools which could allow to predict the catalytic behavior of oxides within the context of oxidation catalysis. This approach is demonstrated for pure binary or ternary oxides. It is also valid for mixtures between two different oxides, taking into account the framework that the "remote control theory" provides. In particular, the catalytic activity of pure lanthanide oxides for total oxidation of isobutene can be correlated with the 4th ionization energy of their respective metals: the most active oxides correspond to those containing the cations displaying the weakest ionization energies. Moreover, in mixtures associating MoO₃ and lanthanide oxides, a bell-shape relationship was obtained when relating the synergetic effect on methacrolein selectivity, i.e., a property related to the oxygen spillover donor ability of the lanthanide oxides, with the ionization energies of their respective cations. In the case of mixed valency oxides such as those of Pr or Tb, weighed values of the ionization energy were used to take into account the fact that both electronic states are assumed to be involved in the catalytic process. The results indicate that the best donors contain Lnⁿ⁺ cations which are characterized by intermediate ionization energies. This situation allows an adequate compromise between the ability to dissociate molecular oxygen at a sufficient rate and the fact that the oxygen species do not display a too electrophilic character which would lead to total oxidation. The catalytic behavior of the various praseodymium molybdates was found to fit this analysis provided an average ionization energy calculated over the lanthanide and molybdenum cations is considered.

Similar correlations were established between the catalytic activity of pure lanthanide oxides and the absolute hardnesses of the respective cations, taken as a measurement of their acid–base properties. The oxides containing the softer cations favor total oxidation while those containing the hardest cations lead to selective oxidation. When considering the concept of average absolute hardness, the catalytic behavior of the praseodymium molybdates could also be rationalized. Similar correlations also hold in mixtures between MoO₃ and lanthanide oxides or Pr molybdates, for which the oxygen spillover donor properties of the lanthanide oxide or molybdate could be related to the Lewis acid–base properties of their respective cations, represented by average or weighed values of the absolute hardness.

Globally, as far as ionization energy or absolute hardness are considered, total oxidation on lanthanide oxides seems to rest on Ln³⁺ ions favoring the production of electrophilic oxygenated species. Partial oxidation requires an appropriate balance of Ln³⁺ and Ln⁴⁺ ions which would modulate the oxidation properties. This simple approach could be improved further by taking into account not only the catalytically active phase but also the characteristics of the reactants and products that adsorb on, or desorb from, the catalyst surface, respectively.

These results concerning catalytic oxides containing lanthanides also lead to more general conclusions. The first one is the confirmation that correlations with ionization energy and/

or absolute hardness can be used when average valencies are considered for mixed valency oxides. The second one concerns phase cooperation that attracts increasing attention. The present work adds new examples where the consideration of ionization energy of one phase (the donor) explains selectivity in the frame of the "remote control" theory.

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References and Notes

- (1) Lopez Nieto, J. M.; Fierro, J. L. G.; Gonzalez Tejuca, L.; Kremenec, G. *J. Catal.* **1987**, *107*, 325.
- (2) Kremenec, G.; Lopez Nieto, J. M.; Tascon, J. M. D.; Gonzalez Tejuca, L.; Weller, S. W. *Ind. Eng. Chem. Res.* **1987**, *26*, 1419.
- (3) Kremenec, G.; Lopez Nieto, J. M.; Tascon, J. M. D.; Gonzalez Tejuca, L. *J. Less Comm. Metals* **1988**, *138*, 47.
- (4) Kremenec, G.; Lopez Nieto, J. M.; Fierro, J. L. G.; Gonzalez Tejuca, L. *J. Less Comm. Metals* **1987**, *135*, 95.
- (5) Brazdil, J. F.; Grasselli, R. K. *J. Catal.* **1983**, *79*, 104.
- (6) De Smet, F.; Ruiz, P.; Delmon, B.; Devillers, M. *Catal. Lett.* **1996**, *41*, 203.
- (7) De Smet, F.; Ruiz, P.; Delmon, B.; Devillers, M. *Appl. Catal. A: Gen.* **1998**, *172*, 333.
- (8) Delmon, B. *Heterog. Chem. Rev.* **1994**, *1*, 219.
- (9) Weng, L. T.; Delmon, B. *Appl. Catal. A: Gen.* **1992**, *81*, 141.
- (10) Weng, L. T.; Ma, S. Y.; Ruiz, P.; Delmon, B. *J. Mol. Catal.* **1990**, *61*, 99.
- (11) Hattori, T.; Inoko, J.; Murakami, Y. *J. Catal.* **1976**, *42*, 60.
- (12) Mars, P.; van Krevelen, D. W. *Chem. Eng. Sci., Spec. Suppl.* **1954**, *3*, 41.
- (13) Haber, J. *Pure Appl. Chem.* **1978**, *50*, 923. Haber, J.; Serwicka, E. M. *React. Kinet. Catal. Lett.* **1987**, *35*, 369. Bielanski, A.; Haber, J. *Catal. Rev. Sci. Eng.* **1979**, *19*, 1.
- (14) Hodnett, B. K. *Heterogeneous Catalytic Oxidation*, 1st ed.; John Wiley & Sons: New York, 2000; Chapter 3, pp 66–101.
- (15) Leboutteiller, A.; Courtine, P. *J. Solid State Chem.* **1998**, *137*, 94.
- (16) Duffy, J. A.; Ingram, M. D. *J. Non-Cryst. Solids* **1992**, *144*, 76.
- (17) Duffy, J. A. *Geochim. Cosmochim. Acta* **1993**, *57*, 3961.
- (18) Portier, J.; Campet, G.; Etourneau, J.; Shastry, M. C. R.; Tanguy, B. *J. Alloys Compounds* **1994**, *209*, 59.
- (19) Moriceau, P.; Leboutteiller, A.; Bordes, E.; Courtine, P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5735.
- (20) Moriceau, P.; Taouk, B.; Bordes, E.; Courtine, P. *Stud. Surf. Sci. Catal.* **2000**, *130B*, 1811.
- (21) Moriceau, P.; Leboutteiller, A.; Bordes, E.; Courtine, P. In *Proceedings of the DGMK-Conference "Selective Oxidations in Petrochemistry"*, Hamburg, Germany, Oct 1998; Emig, G., Kohlpaintner, C., Lücke, B., Eds.; Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V. (German Society for Petroleum and Coal Science and Technology) Hamburg, 1998; p 95.
- (22) Moriceau, P.; Taouk, B.; Bordes, E.; Courtine, P. *Catal. Today* **2000**, *61*, 197.
- (23) Bordes, E.; Courtine, P. *Abstracts of the Workshop From Theoretical Chemistry to Industry*, Krakow, Poland, May 3–7, 2000; Polska Akademia Nauk and Komitet Badan Naukowych: Warszawa, 2000.
- (24) Haber, J.; Mielczarska, E. *Russ. J. Phys. Chem. (Engl. Transl.)* **1979**, *53*, 1663.
- (25) Dziewiecki, Z.; Haber, J.; Mielczarska, E. *React. Kinet. Catal. Lett.* **1975**, *3*, 55.
- (26) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.
- (27) Vedrine, J. C.; Millet, J. M. M.; Volta, J. C. *Catal. Today* **1996**, *32*, 115.
- (28) Huheey, J. E.; Keiter, E. A.; Keiter, E. L. *Inorganic Chemistry. Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993; Chapter 2, pp 36–37.