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Effect of oxygen electronic polarisability on catalytic reactions over oxides

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This work examines two partial oxidation reactions over oxides (alcohols dehydrogenation to aldehydes and aldehydes esterification to esters) to determine how reaction rates can be quantitatively correlated with physical properties of the bulk catalysts. We show that while electronegativity difference, $\Delta\chi$, metal–oxygen bond strength, $E_{\mathrm{M-O}}$, fail utterly, oxygen partial charge, q_{O}, and oxygen Madelung potential, $V_{\mathrm{Mad}}(\mathrm{O})$, do provide limited correlations for the set of roughly twelve oxides examined. However, oxygen electronic polarisability, α_{O}, does a much better job. We rationalise this finding in terms of the concept of chemical hardness in what appears to be the first successful application of this idea to oxide reactivity.

Keywords: oxygen polarisability, ethanol dehydrogenation oxides, Tishchenko reaction oxides, Madelung potential oxides, electronegativity difference

1. Introduction

Oxides are important materials for several catalytic processes, such as dehydrogenation [1,2], oxidation [2–4], and ammoxidation reactions [5–7]. Although catalysis is a surface phenomenon, bulk properties of oxides require considerable attention if one needs to understand the relevant surface–bulk dynamics. Bulk properties govern several important aspects of surface reactions, including the nature and distribution of defects and the stabilization of surface structures. Several bulk properties have been commonly discussed in connection with catalytic reactions, including electronegativity of metal cations [8], Madelung potential [9], optical basicity [10], metal–oxygen bond strength [11], basicity [12], band gap [13], and ionicity [14,15].

The objective of this work is to find the most important characteristic(s) that can track (or influence) a particular catalytic reaction. We analyze literature data for two simple reactions. (1) The dehydrogenation of ethanol to acetaldehyde over TiO_2, Fe_2O_3, Fe_3O_4, CaO and SiO_2 [16], CuO [17], and CeO_2 [18]. (2) The esterification of benzaldehyde to benzylbenzoate (also called the Tishchenko reaction) over MgO, CaO, SrO, and BaO [12].

Clearly these oxides diverge greatly in their properties. The oxides of the alkaline earth series MgO to BaO represent typical examples of ionic materials having a rock salt structure where the bulk anions and cations are six-fold coordinated. SiO_2 is the opposite: a prototypical covalent oxide. TiO_2 (anatase) is amphoteric, containing both acid (covalent) and base (ionic) sites. Fe_3O_4 is a mixed oxide composed of Fe^{2+} and Fe^{3+} cations in an inverse spinel structure, while Fe_2O_3 (hematite) is largely ionic. CeO_2 has the fluorite structure in which the cations are eight-fold coordinated, and the anions are tetrahedrally coordinated. The structure accommodates both surface and bulk defects of point and cluster varieties. CuO is the classic catalyst for alcohol dehydrogenation [19] and easily undergoes oxidation–reduction cycles Cu^0/Cu^{2+} [20].

In this work we attempt to discern more direct links to catalytic rate constants. We examine the rates of the dehydrogenation and esterification reactions given above with respect to several of the bulk characteristics we have named. In addition, we add the oxide polarisability α to the list of pertinent bulk properties.

2. Overview of correlations for adsorption and reaction

Correlating rates with electronegativity or M–O bond strength is not a new idea. Henrich and Cox [21] have outlined two general classes of reactions on oxides: acid–base reactions (usually involving H transfer) and oxidation–reduction reactions (electron transfer). These workers state that acid/base reactions should scale with Lewis acid/base strength, which in turn is affected by electronegativity [21]. Kyrlov, in an attempt to find correlations between non-metallic catalytic materials and simple reactions, has pointed out the absence of dependence between the logarithm of catalytic activity for dehydrogenation of isopropyl alcohol to acetone and the spacing separating the metal and non-metal ions [13]. However, he has indicated a very weak correlation between the electronegativity difference of non-metals and the same catalytic reaction [13]. In effect, scattering of the data is so high[1] that any reason-

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[1] A change of four orders of magnitudes is observed for materials having similar Δx, see [13], p. 127.

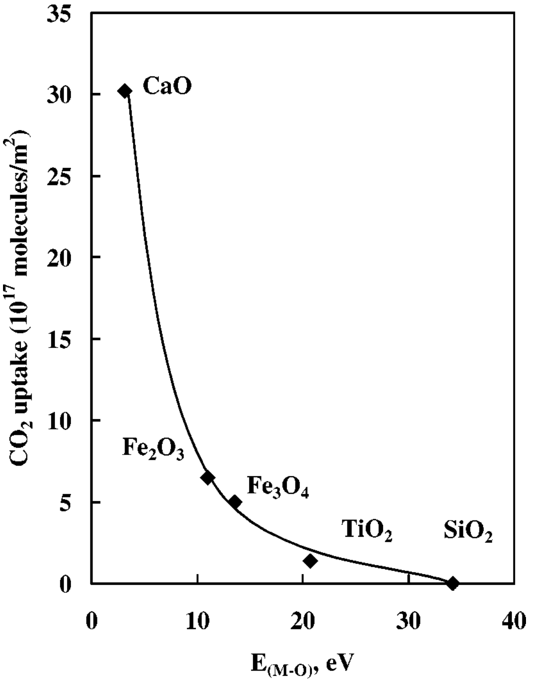

Figure 1. Plot of CO_2 uptake [16] as a function of $E_{\mathrm{M–O}}$ for several oxides; $E_{\mathrm{M–O}}$ is calculated from equation (3).

able extrapolation would be misleading. This indicates that considering materials with high electronegativity difference as more acidic is largely unfounded. Other workers have also observed a relation between the electronegativity of the metal cations and the rate of CO and CO_2 hydrogenation [8]. On the other hand, most redox reactions are limited by a step in which oxygen is removed from the lattice to leave a vacancy (although several counter examples can be identified [22–24]). In such cases, the reaction rate should correlate with M–O bond strength. Indeed, a decrease in the rate of CO oxidation to CO_2 has been well-correlated with an increase in M–O bond strength for this very reason[2] [11]. We have also found that the rate of reaction for the partial oxidation of ethanol could be successfully normalised on a series of oxides by the basic site density as titrated by CO_2 adsorption [16]. Figure 1 shows the CO_2 uptake as a function of $E_{\mathrm{M–O}}$. Although the trend is clear, materials adsorbing large amounts of CO_2 have weak M cation to O anion bond strength, the overall picture is quite more complex as indicated below.

3. Calculational details

Several bulk properties for the oxides considered here could not be drawn directly from the literature but required calculation.

Electronegativity, χ, describes the force exerted by the nuclear charge on the electrons at the periphery of an atom. Thus, an atom's electronegativity refers to the tendency to become charged rather than the state of being charged.

For oxides the electronegativity difference $\Delta\chi$ represents the difference in the atomic electronegativities χ_{O} of the neutral oxygen atom and χ_{M} of the neutral metal in their actual lattice positions: $\Delta\chi = \chi_{\mathrm{O}} - \chi_{\mathrm{M}}$. The difference was calculated using the heat of formation Q for the oxide of the formula MO_x according to [26]

$$\Delta\chi = \left[(Q + 1.13x)/2x\right]^{1/2}, \tag{1}$$

where Q is in eV. The term 1.13 appears in the equation to account for double bonding in the O_2 molecule.

The partial charge q_{O} on the oxygen in the lattice was computed using a simple relationship derived from solid-phase wave mechanic calculations (see [26] for more details):

$$q_{\mathrm{O}} = \chi_{\mathrm{O}} - 4.1. \tag{2}$$

Of course, equation (2) does not use the gas-phase value of the electronegativity for oxygen because then χ_{O} and, therefore, q_{O} would be the same for all oxide species. Instead, equation (2) implicitly uses a value for χ_{O} that is characteristic of a given oxide. To calculate χ_{O} we employed the relation $\chi_{\mathrm{O}} = \chi_{\mathrm{M}} + \Delta\chi$ together with $\Delta\chi$ computed above and conventional literature values for χ_{M} on a Pauling scale. The use of literature values for χ_{M} represents an approximation that may not reflect the actual value of χ_{M} in an oxide lattice.

We estimated the metal–oxygen bond strength $E_{\mathrm{M–O}}$ relative to the heat of formation of an ion gas beginning with the following equation [11]:

$$\begin{aligned} &y\Delta H_{\mathrm{M–O}}(\mathrm{ionic}) \\ &\quad = -\Delta H_{\mathrm{f}}(\mathrm{M}_x\mathrm{O}_y) + \Delta H_{\mathrm{sub}}(\mathrm{M}) + (y/2)\Delta H_{\mathrm{dis}}(\mathrm{O}_2) \\ &\qquad - y\sum \mathrm{EA(O)} + x\sum \mathrm{IE(M)}, \end{aligned} \tag{3}$$

where $\Delta H_{\mathrm{f}}(\mathrm{M}_x\mathrm{O}_y)$ denotes the heat of formation of the oxide [27], $\Delta H_{\mathrm{sub}}(\mathrm{M})$ the heat of sublimation of the metal [28], $\Delta H_{\mathrm{dis}}(\mathrm{O}_2)$ the dissociation energy of diatomic oxygen [27], $\sum$EA(O) the sum of the first and second electron affinities for atomic oxygen [27], and $\sum$IE(M) the sum of the first through $2y/x$ ionisation energies for the metal [27]. $E_{\mathrm{M–O}}$ was then estimated by dividing $y\Delta H_{\mathrm{M–O}}$ by the coordination number C_{O} of oxygen in the oxide. For example, C_{O} equaled 3, 4, 3, and 2 for Fe_2O_3, CaO, TiO_2, and SiO_2, respectively.

In an oxide, the O^{2-} ions have electron donor power that is governed by the various cations that polarise it. As Duffy pointed out [26], it is thus expected that the magnitude of the electron donor power of O^{2-} ions will depend on their polarisations. In fact, one may regard the unpolarised O^{2-} ions as having "floppy" electrons giving a scope for their tightening to the cations. The oxygen electronic polarisability α_{O} of a binary oxide $\mathrm{M}_x\mathrm{O}_y$ was calculated

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[2] The validity of using $E_{\mathrm{M–O}}$ to correlate reaction rates on oxides has been disputed by R.I. Masel. See [13], p. 779.

Table 1

Cation polarisability, α_M, refractive index, n, oxide polarisability, α, oxygen polarisability, α_O, and bond strength, $E_{M–O}$, for several oxides.

Oxide	α_M	n	α	α_O	$E_{M–O}$ (eV)
SiO_2	0.00165	1.544	2.83	1.41	34.2
Al_2O_3	0.052	1.696	4.48	1.46	13.5
MgO	0.094	1.737	1.81	1.71	6.6
CaO	0.47	1.837	2.96	2.49	3.6
SrO	0.86	1.870	3.93	3.07	3.3
BaO	1.55	1.980	5.25	3.7	3.0
CuO	(0.4)	2.75	3.42	3.0	7.1
CeO_2	(0.5)	2.40	5.46	2.7	9.9
Fe_2O_3	(0.3)	3.01	8.81	2.7	16.6
TiO_2	(0.3)	2.33	4.46	2.1	20.7

from the oxide polarisability α and the solid-phase cation polarisability α_{My+} using the following formulae:

$$\begin{aligned}\alpha &= (3V_m/4\pi N_a)(\kappa - 1)/(\kappa + 2)\\ &= (3V_m/4\pi N_a)(n^2 - 1)/(n^2 + 2) \qquad (4)\end{aligned}$$

and

$$\alpha_O = (1/y)(\alpha - x\alpha_{My+}). \qquad (5)$$

Equation (4) is the Lorentz–Lorenz relationship between α and the real part of the dielectric constant κ; V_m denotes the molar volume, N_a Avogadro's number, and n the refractive index. The refractive index in the visible region of the spectrum is used because the characteristic frequencies are such that only electrons respond, not ion cores. It is the electronic response that controls bonding. Values for α_{My+} and n were all taken from [26] in order to assure self-consistency in the calculation. Table 1 shows the values of α_O, α, and α_M of some oxides.

4. Correlation results using $\Delta\chi$, $E_{M–O}$, and q_O

In this section we analyse the rate of reaction with respect to several electronic properties. Figure 2 shows $\log k$ at 473 K as a function of $\Delta\chi$ for the oxidative dehydrogenation of ethanol to acetaldehyde over several unrelated oxides. The rate data were taken from three different reports [16–18]. Clearly no relation appears whatsoever; the data points scatter virtually randomly. Figure 3 presents the same rate data as function of $E_{M–O}$. If CeO_2 was ignored, there would be some trend for oxides with small $E_{M–O}$ to show higher activity; one could very roughly fit the data with a line sloping from upper left to lower right. However, there is no good reason to ignore CeO_2, and the remaining points can be fitted with a curve that gets within little better than about an order of magnitude of k in several cases. We are thus left with the conclusion that $E_{M–O}$ is also an inadequate correlation parameter. Figure 4 shows the same rate data function of q_O. There is indeed a good linear relationship for six of the eight oxides. However, CaO and SiO_2 fall far of the line, exhibiting activities that are nearly two orders of magnitude lower than the line predicts. In short, q_O yields decidedly mixed results as correlation parameters.

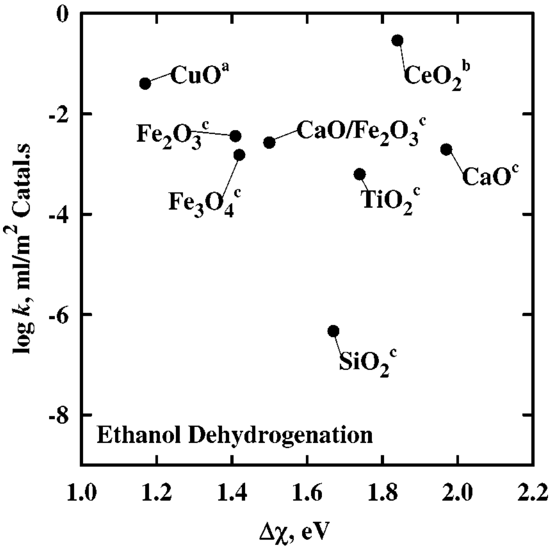


Figure 2. Plot of $\log k$ [16–18], at 473 K, vs. $\Delta\chi$ for the oxidative dehydrogenation reaction of ethanol to acetaldehyde over a series of oxides. There is no correlation.

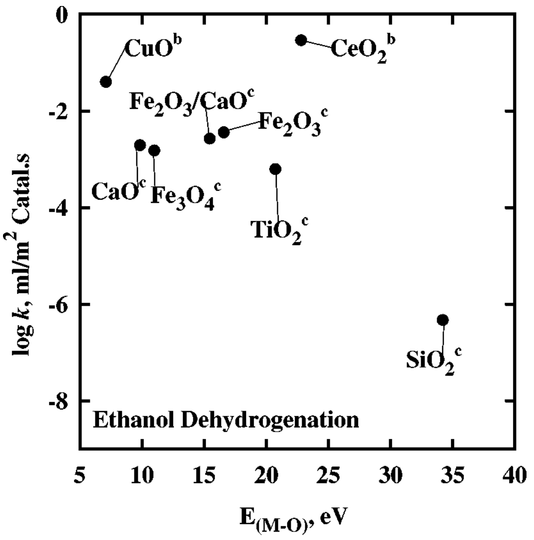


Figure 3. Plot of $\log k$ [16–18], at 473 K, vs. $E_{M–O}$ for the oxidative dehydrogenation reaction of ethanol to acetaldehyde over a series of oxides. There is no correlation.

5. Oxygen electronic polarisability

5.1. Qualitative background

We are not aware of any published work which explicitly focuses on relating oxygen polarisability to catalytic reaction rates on oxides. We pointed out earlier that the rates of acid/base reactions on oxides scale with Lewis acid/base character of the surface and, therefore (possibly) with its electronegativity. The failure of $\Delta\chi$ by itself to successfully correlate reaction rates suggests that another factor

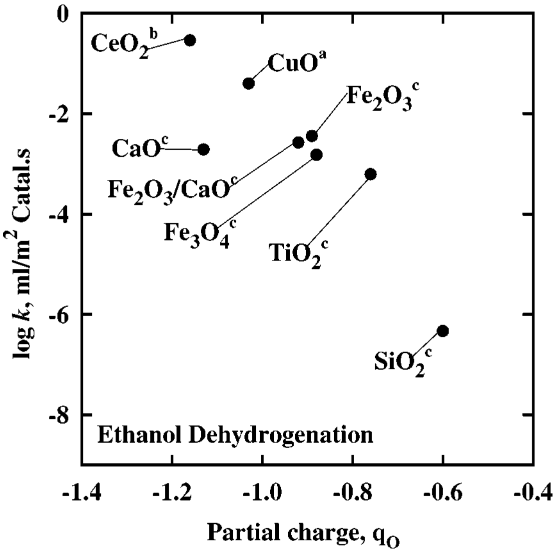


Figure 4. Plot of $\log k$ [16–18], at 473 K, vs. q_O for the oxidative dehydrogenation reaction of ethanol to acetaldehyde over a series of oxides. There is only a very crude correlation.

must be involved. Indeed, surface acid/base character is also heavily influenced by a little known chemical quantity called hardness [29]. The hardness of a surface reflects its ability to share electrons, and depends upon the positions of donor or acceptor orbitals and upon polarisability. In general, a hard surface has no low-lying unoccupied orbitals or high-lying occupied orbitals for the transfer of electrons. Thus, hard acidic surfaces like SiO_2 or Al_2O_3 can donate charge but only with difficulty. Hard basic surfaces like MgO can accept charge but only with difficulty. Conversely, a soft surface has orbitals positioned for ready transfer of electrons, and a high polarisability. A soft surface tends to form bonds having predominantly covalent character. Most metal surfaces are soft bases. In general, hard acids prefer to react with hard bases, and similarly for soft acids and bases.

The component of hardness that is easiest to measure experimentally is polarisability. The electronic polarisability α of a material describes the tendency of the bonding electrons to remain near their ion cores in the presence of an electric field. Since most of the valence electrons in an oxide are associated with the anion, the net material polarisability is dominated by the polarisability α_O of the oxygen. Materials scientists have found several interesting relationships between α (as well as a related quantity: the change in the Auger parameter [30]) and the bulk properties of binary and ternary oxide materials [31–33].

5.2. Correlations with experimental reaction rates

We begin with the oxidative dehydrogenation reaction of ethanol to acetaldehyde. For dehydrogenation of an alkoxide intermediate $CH_3CH_2O–M^{z+}$ to occur, one H from the $–CH_2–$ group must be transferred to the surface. In the discussion given below, we will argue that this H must be in the form of a hydride. The hydride transfer weakens the M–O bond and favors its dissociation via a redox reaction involving water elimination. The following steps may describe the dehydrogenation reaction of ethanol on a metal oxide. First, one **M**–**O** bond is broken and one **M**–OCH_2CH_3 and one **O**–H are formed:

$$\begin{aligned} &CH_3CH_2OH + \mathbf{M}^{z+}\text{–}\mathbf{O}^{2-} \\ &\quad \to CH_3CH_2O\text{–}\mathbf{M}^{z+} + \mathbf{O}H^-(s) \end{aligned} \tag{6}$$

Next, a hydride is transferred from the ethoxy group to the metal cation and a subsequent breaking of the **M**–**O** bond occurs:

$$CH_3CH_2O\text{–}\mathbf{M}^{z+} \to CH_3CHO(g) + \mathbf{M}^{z+}H \tag{7}$$

Both steps result in acetaldehyde formation. Next, the reactive metal hydride reacts with surface hydroxyls (formed in equation (6)) giving water and reducing the metal cation:

$$\mathbf{O}H(s) + \mathbf{M}^{z+}H \to \mathbf{M}^{z+-x} + H_2\mathbf{O} + V_O \tag{8}$$

The value of x depends on the nature of the metal cation as well as the stability of its reduced states. Finally, in the presence of gas-phase oxygen, oxygen vacancies V_O are then regenerated.

$$\mathbf{M}^{z+-x} + V_O + \tfrac{1}{2}\mathbf{O_2} \to \mathbf{M}^{z+} + \mathbf{O}^{2-} \tag{9}$$

Combining equations (6)–(9) yields the oxidative dehydrogenation reaction of ethanol over a metal oxide.

$$CH_3CH_2OH + \tfrac{1}{2}\mathbf{O_2} \to CH_3CHO(g) + H_2\mathbf{O} \tag{10}$$

At high temperatures, H_2 sometimes becomes the elimination product [34,35].

Figure 4 plots the relationship between α_O and the rate constant k. The data group fairly closely about a line:

$$\log k\ (\mathrm{ml\,g_{catal}^{-1}\,s^{-1}}) = 3.27\alpha_O - 10.84. \tag{11}$$

While some points (particularly CeO_2) do deviate a bit from the line, comparison of figure 5 with figures 2–4 shows that polarisability provides a far better fit than the other parameters we have considered. The deviations in figure 5 might arise from several sources. There may be significant errors in the values we used for the metal cation polarisabilities. We have not accounted for potential variations in α_O originating in structure-sensitivity effects. Finally, we have not accounted for bonding factors that depend on the positions of molecular orbitals.

We have also plotted Kyrlov's isopropanol dehydrogenation to acetone data [13] for the same series of oxides and found that indeed the oxygen electronic polarisability fits also accurately the trend (figure 6).

We next consider the Tishchenko reaction involving the conversion of benzaldehyde to benzyl benzoate. Tanabe and Saito [12] have studied the effects of the basic properties of alkaline-earth oxides (BeO, MgO, CaO, SrO, and BaO) on this reaction.

The Tishchenko reaction requires H transfer from one adsorbed aldehyde, which is oxidised, to another adsorbed aldehyde, which is reduced to alkoxide. This process may

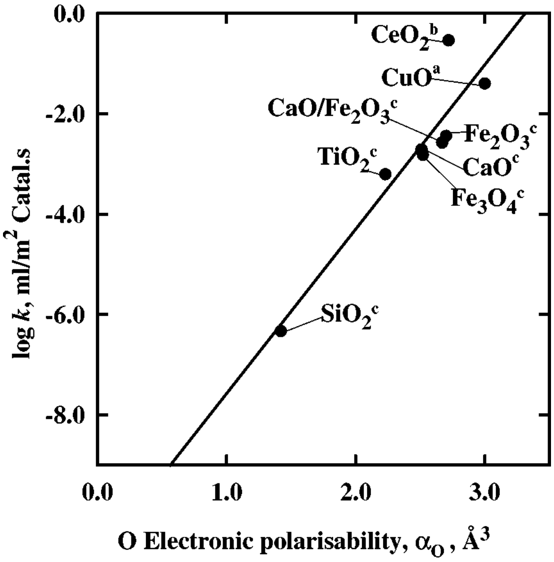


Figure 5. Plot of $\log k$ [16–18], at 473 K, vs. α_O for the oxidative dehydrogenation reaction of ethanol to acetaldehyde over a series of oxides. The correlation is fairly good.

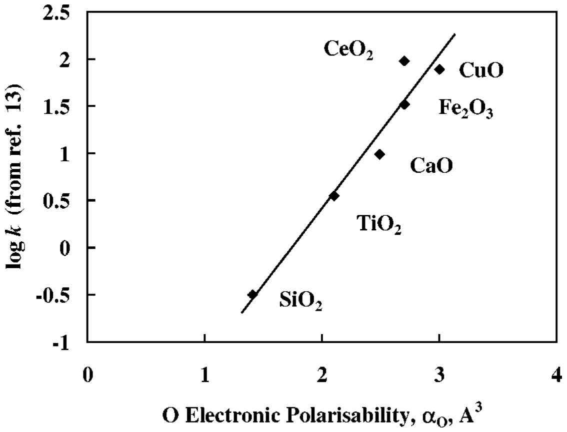
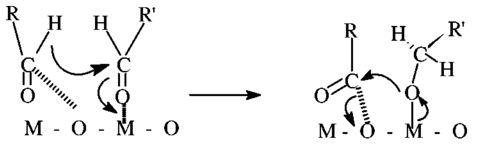


Figure 6. Plot of $\log k$ [13] vs. α_O for the oxidative dehydrogenation reaction of isopropanol to acetone over a series of oxides.

form a complex in a transition state that requires participation of the surface oxygen:



$$\rightarrow \mathrm{RC(O)OCH_2R'} \tag{12}$$

where an adsorbed aldehyde molecule with the participation of a surface oxygen anion transfers a hydride to another adsorbed aldehyde molecule. This process results in a carboxylate species close to an alkoxide species. The proximity helps drive the reaction.

Figure 7 shows a plot of $\log k$ [5] versus α_O. Indeed, if BeO is excluded there is a good parabolic relationship:

$$\log k\ (\mathrm{m^2_{catal}\,s^{-1}}) = 3.66\alpha_O^2 - 11.35\alpha_O - 4.44. \tag{13}$$

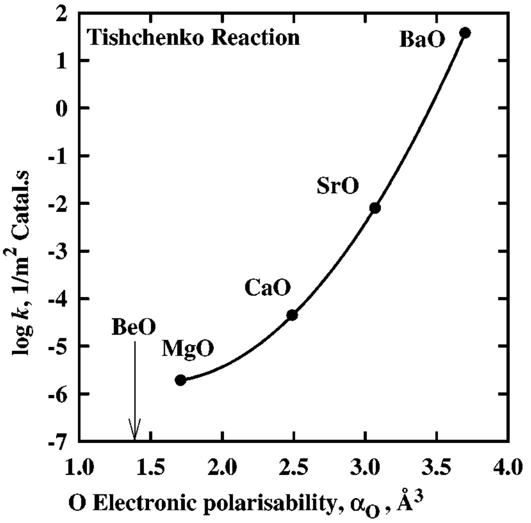


Figure 7. Plot of $\log k$ [12], at 453 K, vs. α_O for the Tishchenko reaction of benzaldehyde to benzyl benzoate over the series Be to Ba oxides. The correlation is fairly good.

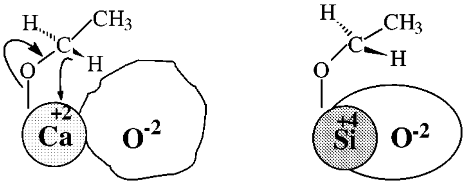


Figure 8. A schematic representation of the effect of the oxide polarisability on the dehydrogenation of alkoxides.

We are uncertain about how much significance should be attached to the precise functional form. Figure 7 treats a family of alkaline earth oxides that is far more homogeneous in character than the diverse oxides of figures 5 and 6. Furthermore, there is no good reason to exclude BeO entirely; its rate was simply too low in published reports to assign a specific number. However, the functional form is less important than the fact that figure 7 shows a clear trend of increasing rate with increasing α_O.

5.3. Discussion of correlations

Let us consider how the rate data discussed above can be rationalized in terms of Lewis acidity, hardness, and polarisability. We will first examine the dehydrogenation of ethoxides. A representation of the dehydrogenation reaction is found in figure 8. The first step of the reaction involving hydrogen transfer to the surface appears to be rate limiting for the overall reaction, as it is in several related reactions [22–24].

There are two possibilities for the hydrogen transfer: as H^+ or as H^-. H^+ is a hard acid while H^- is a soft base [29]. With H^+ transfer, a hard acid would need to combine with a hard base. The O^{2-} anion provides the most obvious possibility. With H^- transfer, a soft base would need to combine with a soft acid. The metal cation provides the most obvious possibility. Thus, considerations of hardness by themselves do not indicate which kind of transfer is most likely. However, the two transfers have very different site requirements whose properties can help make the distinction. H^+ transfer would result in the formation of carbanion next to an oxygen anion, which seems unlikely to occur. H^- transfer would result in the formation of a carbocation next to an oxygen anion, which seems quite likely to occur. Thus, one may conclude that hydride transfer is the most likely reaction path.

Hydride transfer should be facilitated by increasing softness of the metal cation. The data in figures 5 and 6 confirm this notion; softer, more polarisable surfaces show higher rates.

We now consider the Tishchenko reaction. During the initial hydrogen transfer between adsorbed aldehydes, the aldehyde that loses the hydrogen acts as a Lewis acid with respect to the surface oxygen, which acts as a nucleophile toward the aldehyde's central carbon atom. Being rich in electrons from the C=O, this area of the aldehyde can be considered quite soft, and would prefer to react with a surface that is also soft. As we mentioned above, MgO represents a hard basic surface; not surprisingly, its reactivity is low. BeO is less polarisable and, therefore, even harder, and its reactivity is unmeasurably low. On the other hand, the oxides of Ca, Sr, and Ba exhibit progressively higher polarisabilities and, therefore, progressively greater softness and higher reactivity.

We note that our explanation in terms of hardness (as represented mainly by polarisability) is consistent with the explanation of Tanabe and Saito [12], who found a good correlation between the catalytic activity of the above reaction and the basicity of these oxides. Our picture agrees with this result, but nuances it considerably by distinguishing between hard and soft bases and offering an underlying reason for their hardness. Several theoretical researchers [34–36] have pointed to a correlation with the Madelung potential of oxygen anions, V_{Mad}: 23.90, 20.98, 19.57, and 18.22 for MgO, CaO, SrO, and BaO, respectively. Indeed, figure 9 also shows that a similar trend is observed if one plot $\log k$ as a function of V_{Mad}(O). However, the Madelung potential in this context serves only as a proxy for the diffuseness of the oxygen orbitals. Electrons in diffuse orbitals are more polarisable and, therefore, make the surface softer, which is exactly the property needed to accelerate the reaction of a soft compound like an aldehyde.

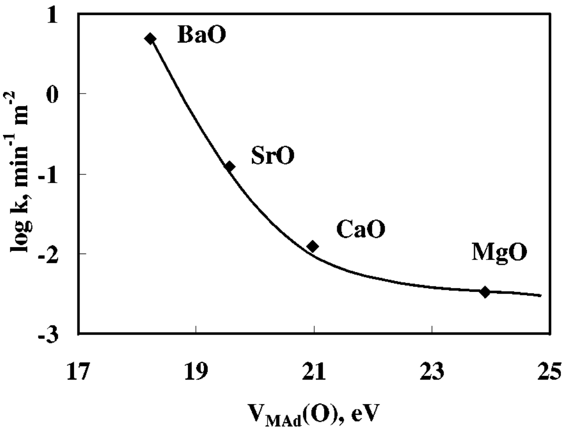


Figure 9. Plot of $\log k$ [12], at 453 K, vs. V_{Mad}(O) [36] for the Tishchenko reaction of benzaldehyde to benzyl benzoate over the series Mg to Ba oxides. The correlation is fairly good.

For both alcohol dehydrogenation and aldehyde esterification, it is easy to see why electronegativity, oxygen partial charge, and M–O bond strength could be rationally invoked as contributing to the reaction. Electronegativity does indeed play some role in determining acid–base behavior. However, for these reactions the correspondence between $\Delta\chi$ and reactivity is spotty. With respect to partial charge, surface oxygen anions carrying more negative charge tend to be more polarisable (other things being equal). Similarly, other things being equal, oxygen anions that are more weakly bonded to their metallic neighbours tend to have electrons more available for bonding with other atoms, again making the oxygens more polarisable. Nevertheless, an accurate account of surface activity for these reactions should more properly account for chemical hardness.

Finally, we note that the form of the correlations we have presented invokes an exponential dependence on polarisability. This form is expected, since a more quantitative treatment of hardness [29] shows that the polarisability enters into the interaction energy between the adsorbate and surface. Presumably, this interaction energy ultimately finds its way into a reaction activation energy, yielding the observed functional form. The data we have shown do not scale exactly linearly with polarisability on a logarithmic scale. We suspect deviations from linearity arise from our neglect of factors in the chemical hardness that depends on the positions of molecular orbitals.

6. Conclusions

In this work we show, first, that contrary to commonly accepted belief, regarding partial oxidation reactions over oxides, there is no entirely adequate correlation between reaction rates and the bulk oxide properties of electronegativity difference, metal–oxygen bond strength, or oxygen partial charge. Second, we show that the chemical hardness, as represented by the electronic polarisability of the oxygen anions, can be used to correlate catalytic activity of several oxides that have few common intrinsic characteristics. This finding appears to represent the first successful application of the concept of hardness to the reactivity of oxide surfaces. Both cases discussed here involved hydride transfer, but we expect that the concept may be generalised to much larger classes of Lewis acid–base reactions.

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