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Volcano Relationships in Catalytic Reactions on Oxides

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It has been shown that the existing data on the oxidation of carbon monoxide, decomposition of hydrogen peroxide, and the isomerization of butene on oxide catalysts can be extended—an interpretation very similar to that involved in the Sabatier-Balandin views on heterogeneous catalysis. In each case, the plot of electroactivity against the appropriate representation of metal-oxide bond energy, for a series of oxides, yields a volcano-shaped curve.

INTRODUCTION

One of the principal interpretative guide lines in heterogeneous catalysis was introduced by Sabatier (*1*) and developed by Balandin (*2*). According to the Sabatier–Balandin (to be abbreviated as S-B in the following discussion) views, if a formation or a rupture of, e.g., a metal–oxide, M–O, bond is involved in the critical stage of a heterogeneous catalytic reaction on an oxide catalyst, the activity exhibited by a series of oxides would be related to their M–O bond energies in a volcanic manner, i.e., a maximum in energy with increasing bond energy should be observed. As a direct consequence of the volcano relationship, it follows that on one arm of the volcano, the activity increases with increasing M–O bond energy; whereas on the other arm, the activity decreases with the increasing M–O bond energy.

It has been shown previously that volcano relationships are exhibited by the available data on the catalytic decomposition on N_2O (*3*), catalytic oxidation of toluene (*4*), benzene (*5*) and ammonia (*6*) on a series of oxide catalysts. The object of the present paper is to explore whether the existing data on the oxidation of carbon monoxide, on the decomposition of H_2O_2 and on the isomerization of butene can lend themselves to interpretations in terms of the volcano relationships.

THE MAGNITUDE OF THE M–O BOND ENERGY

It should be briefly mentioned here, following previous expositions of the subject (*3–8*), that the magnitude of the M–O bond energy may be represented by the heat of formation per equivalent (exothermic), $-\Delta H_e$, values if the bond formation or fission involved is:

$$\mathrm{MO(S)} \rightarrow \mathrm{M(S)} + \mathrm{O(G)}. \tag{1}$$

Here, S and G refer to the solid and gas phase, respectively.

The enthalpy per equivalent, of reaction (1), $(\Delta H_1)_e$, is:

$$(\Delta H_1)_e = -\Delta H_e + K. \tag{2}$$

Here, K is a constant and is equal to 118/4 = 29 kcal, i.e., it is the heat of dissociation, per *equivalent*, of the oxygen molecule.

If the bond formation or rupture involved critically in the catalytic reaction is

$$\mathrm{MO(S)} \rightarrow \mathrm{M(G)} + \mathrm{O(G)}, \tag{3}$$

the M–O bond energy would be given by the heat of atomisation per equivalent, i.e., $\Delta H_{\mathrm{atom}}/\mathrm{eq}$. Although, it is more appropriate to assume that reaction (1) is the bond formation/rupture involved in the catalytic oxidation, reaction (3) is also assumed to represent the magnitude of the bond energy in some discussions (*7*). It will be shown that irrespective of the quantity (i.e., either

$-\Delta H_e$ or $\Delta H_{\text{atom}}/\text{eq}$) chosen to denote the M–O energy, volcano-shaped relations are observed for the catalytic reactions to be considered here. It should be emphasized that the discussion of Eqs. (1) to (3) and their significance is purposely presented here in a brief form only, since previous publications (*3–8*) examine these matters in somewhat more detail.

It is *important* to emphasize here that in the catalytic reactions on oxides involving the formation/rupture of M–O bonds, the fission of the bonds does not usually proceed all the way to give metal M either as solid [i.e., Eq. (1)] or as gas [i.e., Eq. (3)]. In other words the oxide involved in the catalytic reaction is usually not reduced to its metallic state as is implied by Eqs. (1) and (3). More often than not, the catalytic oxidation/reduction on an oxide merely involves a *change in its stoichiometry* by a type of reaction such as the following:

$$M_mO_n(Y) \overset{\Delta H_4}{\rightleftharpoons} M_mO_{n-1}(Z) + \tfrac{1}{2}\, O_2, \qquad (4)$$

where the higher phase oxide Y is reduced to the lower-phase oxide Z with the liberated oxygen atom being utilized in the catalytic oxidation [i.e., the forward reaction in Eq. (4)]; in the backward direction of reaction (4), the oxygen contained in the gaseous reactants oxidizes the lower-phase oxide Z to its initial state, i.e., the higher phase oxide Y. In other words a mere change in the stoichiometry of the oxide catalyst is involved. However, in principle, the reaction (4) is not much different from the corresponding reaction (1) because the enthalpy change in reaction (4) is:

$$\Delta H_4 = 2(-\Delta H_e + K). \qquad (5)$$

In other words the reaction (4) involves exactly the same bond breaking (or making) as that in reaction (1) except that the enthalpy change is twice in value; this is because the bond breaking being considered in Eq. (4) is per oxygen *atom* whereas that in reaction (1) is as per equivalent [through Eq. (2)]. If the enthalpy changes (i.e., the value of the bond formation/rupture involved), both in reactions (1) and (4) are taken in their normalized form, i.e., as per equivalent (neither per mole, nor per atom but as per atom-equivalent), the two values would become identical and will be given by Eq. (2). What one is trying to stress here is that whether the oxidation/reduction of the oxide catalyst in the catalytic reaction leads to a change of stoichiometry [i.e., Eq. (4)] or a complete decomposition (or formation) of the oxide [as in reaction (1)], the energetic quantity representing the bond energy, *when taken in its normalized form*, is the same, i.e., as that given by Eq. (2). Hence $-\Delta H_e$ values of the oxide catalysts are valid representations of the M–O bond energy for the transformations either those in reaction (1) or (4).

Similarly for the case in which the M–O rupture/formation follows the path described in Eq. (3), it becomes immaterial (as far as the normalized (per equivalent) values of the appropriate bond energy terms are concerned) whether the oxidation–reduction in the catalytic reaction leads to a change in stoichiometry of the oxide or its complete dissociation into M and O.

With the foregoing comments in mind, one may now explore whether the various reactions being considered here exhibit volcano-shaped relationships or not, when the measure of M–O bond is denoted either by $-\Delta H_e$ or by $\Delta H_{\text{atom}}/\text{eq}$. This examination is carried out in the next sections.

THE OXIDATION OF CARBON MONOXIDE

The relative order of activity exhibited by various oxides towards the oxidation of CO as reported by Dowden, Mackenzie and Trapwell (*9*) is presented in Table 1 together with the $-\Delta H_e$ and $\Delta H_{\text{atom}}/\text{eq}$ values for the oxides (*10*). The previous interpretation (*9*) of this activity was in terms of semiconductivity of the oxides, i.e., the three types (*n*-type, *p*-type, insulating) of oxides showing three distinct orders of activity. An alternative interpretation in terms of the volcano plots may be put forward, however. In Fig. 1, the order of activity has been plotted against the $-\Delta H_e$ values of the corresponding oxides. A volcano relationship is clearly obeyed if one ignores the point for HgO. On the ascending (i.e., left) arm of the volcano, decreasing activity is

TABLE 1
Catalytic Activity of Oxides for the CO Oxidation[a]

Oxide	Activity order[b]	$-\Delta H_e$ (kcal)	ΔH_{atom}/eq (kcal)
CoO	15	28.6	108.9
Cu_2O	14	20	130.8
NiO	13	29.2	109
MnO_2	12	31.0	77.3
CuO	11	18.8	88.9
Fe_2O_3	10	32.1	95.6
ZnO	9	41.6	86.8
CeO_2	8	75 (CeO)	132 (Ce_2O_3)
TiO_2	7	56.4	114.1
Cr_2O_3	6	45	106.6
ThO_2	5	73	122
ZrO_2	4	65.4	131.4
V_2O_5	3	37.3	91.5
HgO	2	10.8	47.8
Al_2O_3	1	65.3	122.1

[a] For sources of these data, see text.
[b] Decreasing activity.

associated with increasing M-O bond energy (i.e., higher $-\Delta H_e$ values); this would indicate that the rate determining-step (r.d.s.) in the CO oxidation on these oxides is probably the fission of the M-O bond in Eq. 1 (*4*, *5*). On the right arm (i.e., the descending branch) of the volcano, increasing activity with increasing $-\Delta H_e$ values is observed so that the r.d.s. on Al_2O_3, ZrO_2, ThO_2 and CeO is, most likely, the formation of the M-O bond as in Eq. 1 (*4*, *5*) (see below, however). These bond formation/rupture processes may, alternatively, lead to the change in the stoichiometry of the oxide catalyst as pointed out in the discussion of Eq. (4) above.

It should be noted that in the S-B volcano plots, a *maximum* in activity is predicted with increasing bond energy, whereas the reverse situation obtains in Fig. 1. Conceptually, however, the S-B plots and the volcano in Fig. 1 are quite similar since in both cases, activity increases with increasing M-O bond energy on one arm of the volcano whereas the opposite trend obtains on the other arm. It should be mentioned here that volcano plots exactly similar to the one in Fig. 1, i.e., opposite in shape to the S-B plots, have also been observed for the catalytic decomposition of N_2O on oxides (*3*).

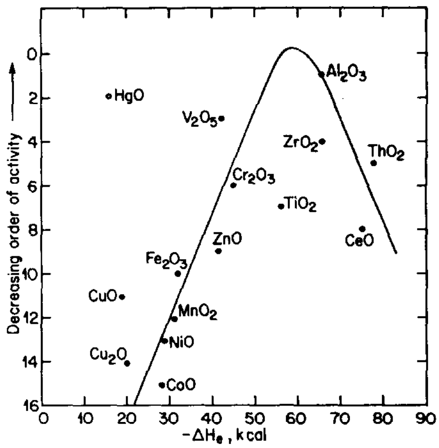

Fig. 1. A plot of the activity order for the oxidation of CO on the shown oxides against their heat of formation per equivalent (exothermic), $-\Delta H_e$ values. The data and the source references given in Table 1 and the significance of this volcano relation discussed in the text.

Even if one chooses to represent the M-O bond energy by ΔH_{atom}/eq, a rough volcano plot is observed (Fig. 2). The basic feature of this plot is the same as that of Fig. 1, i.e., increasing activity with increasing bond energy on one arm of the volcano and decreasing activity with increasing bond energy on the other. HgO again, does not obey the volcano, in addition to a noticeable departure from the shown trend exhibited

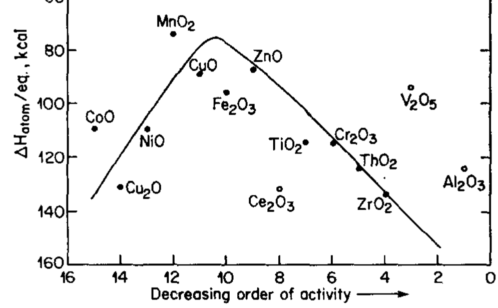

Fig. 2. A plot of the activity order for the oxidation of CO on the shown oxides against their heats of atomisation per equivalent, ΔH_{atom}/eq, values. See Table 1 and the text for details.

by Ce_2O_3, Al_2O_3 and V_2O_5. The important point to note in Figs. 1 and 2 (as well as the subsequent ones) is that an overwhelming majority of the points, in each case, can be fitted to a rough volcano curve, notwithstanding some scatter and departures from the general trend.

It is necessary to emphasize that the trends depicted in Figs. 1 and 2 should be treated merely as general rough tendencies rather than rigorous interpretations of data. This is because the scatter in Figs. 1 and 2 is large so that one may, if one chooses to stretch the point, draw the "best" straight lines rather than the volcano curves through these data. However, at least in the opinion of the present author, the points in Figs. 1 and 2 not only appear to follow volcano relationships somewhat better than the straight line graphs but are also more consistent with some general catalytic theory (*1*, *2*), and some previous interpretations of a large variety of data on heterogeneous catalytic reactions (*3-6*). This may perhaps be interpreted as a somewhat subjective interpretation of the present data; on the other hand, the present viewpoint is no less plausible and objective than the previous interpretations of these data (*9*).

It should be noted that the "relative order of activity" used in Figs. 1 and 2 is a very qualitative, although quite valid, criterion of the relative activities of the catalysts towards CO oxidation. It is possible, although not very likely, that if the relative order of activity were replaced by rates per unit area at a given temperature, in Figs. 1 and 2, somewhat different trends might arise. However, as regards the factors determining, in a rough way, the relative activities of oxides towards the CO oxidation, data of Dowden, Mackenzie and Trapwell (*9*), as plotted in Figs. 1 and 2 appear quite adequate. It should be emphasized here that when one obtains an activity series from an eminent source such as Dowden, Mackenzie and Trapwell (*9*), it is understood that these authors (*9*) put forward the activity series after making appropriate corrections for the surface area, etc., in order to make the relative comparisons valid.

A minor point that merits attention in Table 1 is the fact that the catalytic activity refers to CeO_2 whereas the $-\Delta H_e$ and ΔH_{atom}/eq values used for this material are, respectively, for CeO and Ce_2O_3. This is because the relevant data could not be found in the literature for CeO_2. In any case, if one uses these values in their normalized form (i.e., as per equivalent), the $-\Delta H_e$ values, e.g., for CeO, CeO_2, Ce_2O_3 should be roughly close to each other. This may be illustrated by taking the case of some other oxides. For iron oxides, the $-\Delta H_e$ values for FeO, Fe_2O_3 and Fe_3O_4 are, respectively, 31.9, 32.1 and 33.4 kcal. Similarly, for the case of cobalt oxides, the $-\Delta H_e$ values for CoO and Co_3O_4 are 28.6 and 26.3 kcal, respectively (10). It is clear, therefore, that the $-\Delta H_e$ values for various stoichiometric oxides are not too different. It should be added, however, that the differences in the ΔH_{atom}/eq values of oxides of various stoichiometries of a given metal would be somewhat more appreciable than the differences in the $-\Delta H_e$ values.

In the interpretation of Fig. 1 given above, it was stated that on the left arm of the volcano, the probable r.d.s. step is a rupture of a M–O bond [e.g., Eq. (3)] whereas on the right arm, formation of a M–O bond [e.g., reverse of Eq. (3)] is indicated as the r.d.s. It appears more valid to suggest that although the above possibilities are not excluded, the most likely bond formation/rupture to be involved in the r.d.s. is such as that represented by Eq. (4), i.e., in which a bond making or breaking leads only to a change in the stoichiometry of the oxide. In the light of discussion given above in the section on "The Magnitude of the M–O Bond Energy," it is clear that the mechanistic conclusions stay the same whether Eq. (3) or (4) is involved in the catalytic reaction.

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

The data on the activity order for the decomposition of H_2O_2 *vapor* on various oxides (Table 2) have been taken from Thomas and Thomas (*11*), whereas the $-\Delta H_e$ and ΔH_{atom}/eq values are from San-

TABLE 2

CATALYTIC DECOMPOSITION OF H_2O_2 BY OXIDES[a]

Oxide	Activity order[b]	$-\Delta H_e$ (kcal)	ΔH_{atom}/eq (kcal)
Mn_2O_3	9	39	89.9
PbO	8	26.1	78.8
Ag_2O	7	3.7	101.6
CoO	6	28.1	108.9
CuO	5	18.8	88.9
Fe_2O_3	4	32.0	95.6
CdO	3	30.4	73.5
ZnO	2	41.6	86.8
MgO	2	72.0	119.3
Al_2O_3	1	65.3	122.1

[a] For sources of these data, see text.

[b] Decreasing activity.

derson (*10*). The relation between catalytic activity and either $-\Delta H_e$ values (Fig. 3) or ΔH_{atom}/eq values (Fig. 4) is again volcanic. Although the detailed nature of these volcano plots (Figs. 3, 4) is different from the S-B plots or the correlations in Figs. 1 and 2, the basic conceptual similarity is obvious: activity increases with increasing bond energy on one arm of the volcano whereas the opposite is true for the other arm. It appears that surface areas and particle size were taken into account (*11*) in determining the activity series given in Table 2. It is not possible to suggest a detailed mechanism for the decomposition of H_2O_2 on the basis of these correlations (Figs. 3 and 4) or data (Table 2) except that on the arm of the volcano on which the activity increases with increasing M-O bond energy, a r.d.s. involving formation of a M-O bond is indicated; on the other arm, a r.d.s. involving the rupture of the M-O bond appears likely. An examination of Figs. 3 and 4 points out another difficulty, namely, that depending on whether one represents the M-O bond energy by $-\Delta H_e$ or ΔH_{atom}/eq, the different catalysts lie on different arms of the volcano although some of the oxides (ZnO, CdO and CuO) occupy the same arm of the volcano in both Figs. 3 and 4. A further detailed examination of this case is needed before one is in a position to put forward reliable mechanistic suggestions consistent with the rough trends exhibited by Figs. 3 and 4.

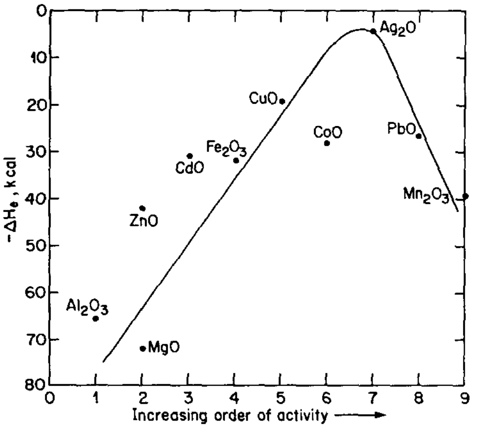

FIG. 3. A plot of the activity order for the decomposition of H_2O_2 on the shown oxides against their $-\Delta H_e$ values. See Table 2 and the text for details.

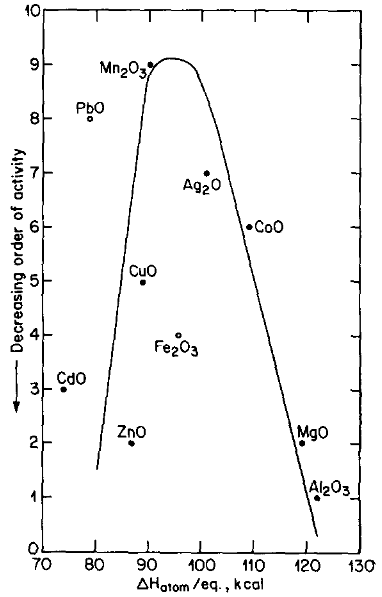

FIG. 4. A plot of the activity order for the decomposition of H_2O_2 on the shown oxides against their ΔH_{atom}/eq values. See Table 2 and the text for details.

THE ISOMERIZATION OF BUTENE

Shannon, Kemball and Leach (*12*) have recently reported some results on the isomerization of butene on oxide catalysts. It appears that the activity of the oxides for the butene isomerization (Table 3) can be

TABLE 3

ACTIVITY PATTERN OF OXIDES FOR BUTENE ISOMERIZATION

Oxide	T (°C)[a]	$-\Delta H_e$ (kcal)[b]	ΔH_{atom}/eq (kcal)
TiO_2	110–150	56.4	114.1
V_2O_5	42	37.3	91.5
Cr_2O_3	10–20	45	106.6
MnO	285	46	108.9
Fe_2O_3	75	32	95.6
Co_3O_4	−15	26.3	93
NiO	25	29.2	109
CuO	>300	18.8	88.9
ZnO	0–60	41.6	86.8

[a] The temperature, T, is the approximate average value for various samples of a particular oxide and refers to the reaction temperature at which the rate constant $k = 2 \times 10^{-5}$ s^{-1} m^{-2}; the data have been read off Fig. 2 in Ref. (*12*).

[b] The heats of formation per equivalent, $-\Delta H_e$, and ΔH_{atom}/eq values are from Ref. (*10*).

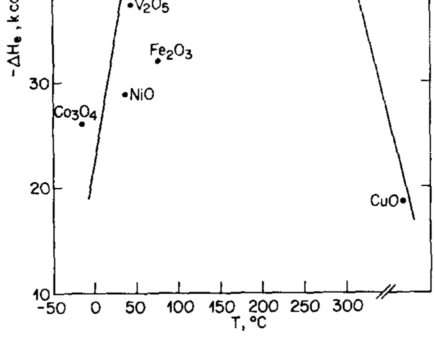

FIG. 5. A plot of the activity order for the isomerization of butene on the shown oxides against their $-\Delta H_e$ values. See Table 3 and the text for details.

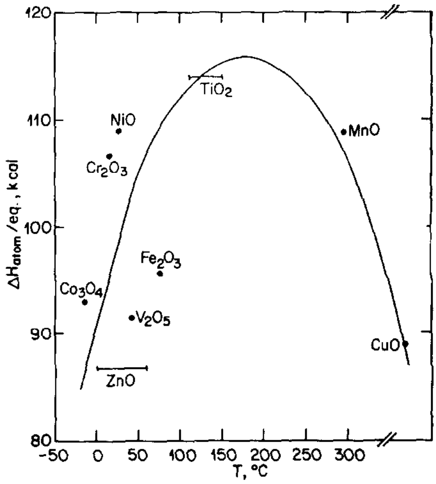

FIG. 6. A plot of the activity order for the isomerization of butene on the shown oxides against ΔH_{atom}/eq values. See Table 3 and the text for details.

correlated with either $-\Delta H_e$ or ΔH_{atom}/eq values of the oxides in a volcanic manner (Figs. 5 and 6, respectively). The significance of these correlations is, of course, similar to that pointed out for the case of CO (Figs. 1 and 2) and H_2O_2 (Figs. 3 and 4); i.e., for the oxides on the left arms of the volcanos in Figs. 5 and 6 (e.g., Co_3O_4, NiO, Fe_2O_3, V_2O_5, ZnO and Cr_2O_3), activity *decreases* (T°C increases) with increasing M–O bond energy so that a r.d.s. involving *rupture* of a M–O bond [e.g., backward step in Eq. (4)] is suggested; the opposite would, of course be true for the oxides on the right arms of the volcanos in Figs. 5 and 6 (i.e.. CuO and MnO). It is obvious, of course, that for a reaction as complex as the isomerization of butene, *several* bond formation/rupture events [i.e., repetitions of Eq. (4)] may be involved for one complete act of the isomerization of butene. The present considerations do not allow more detailed interpretations of the data in Figs. 5 and 6 except that for the oxides on the left arms of the volcanos isomerization of butene leads to the reduction of the oxide to its lower stoichiometric state, i.e., the forward reaction in Eq. (4); for the oxides on the right arms of the volcanos (CuO and MnO) the isomerization of butene is very fast with the result that the reconversion of the lower stoichiometric oxide to the higher [i.e., backward reaction in Eq. (4)] one becomes the r.d.s.

GENERAL COMMENTS OF THESE VOLCANO PLOTS

As stated in a previous section above, the volcano plots observed here are different from the conventional S-B volcano plots in that a *maximum* in activity is not observed with increasing M–O bond energy. However, in one *fundamental* aspect, all these correlations (Figs. 1–6) are conceptually related to the S-B volcano plots in that the catalytic activity, in every case, increases with increasing M–O bond energy on one arm of the volcano whereas on the other arm an opposite trend is obtained. A further analysis of these plots (Figs. 1–6), that goes beyond this basic conceptual similarity with the S-B volcano relations, would have to wait until a deeper significance of these correlations suggests itself to the present author or some other investigators. For the present, it is believed that these correlations (Figs. 1–6) and their general interpretation as outlined in the foregoing sections offer sufficient interest to merit their presentation in the literature.

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