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Sabatier–Balandin Interpretation of the Catalytic Decomposition of Nitrous Oxide on Metal-Oxide Semiconductors

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It has been shown that the existing data on the catalytic decomposition of nitrous oxide on semiconducting oxides can be fit to an interpretation very similar to that involved in the Sabatier–Balandin concepts. The data exhibit volcano-shaped correlations in: (1) the plot of temperature (at which the reaction first becomes appreciable) vs heat of formation per equivalent of the oxide; (2) the plot of heat of atomization per equivalent of the oxide catalyst vs the temperature at which the reaction first becomes appreciable. The significance of the foregoing relationship is discussed in relation to the previous interpretations of these data and in the general context of Sabatier–Balandin and other ideas (e.g., Fermi level, semiconductivity, etc.) of heterogeneous catalysis.

INTRODUCTION

There are several studies (*1–3*) and discussions (*4, 5*) in the literature that deal with the catalytic decomposition of nitrous oxide on oxide semiconductors. The generally discussed (*4, 5*) results are on Cu_2O, CoO, NiO, CuO, MgO, CaO, CeO_2, Al_2O_3, ZnO, CdO, TiO_2, Cr_2O_3, Fe_2O_3, and Ga_2O_3. It is generally believed that the mechanism involves the following steps (*5*):

$$N_2O + S + e_s \rightleftharpoons N_2 + S\text{–}O^- \quad (1)$$

followed by

$$2S\text{–}O^- \rightarrow O_2 + 2e_S \quad (2)$$

or by

$$S\text{–}O^- + N_2O \rightarrow N_2 + O_2 + e_S. \quad (3)$$

Here S refers to the substrate, i.e., the oxide catalyst; e_S is the electron either drawn from the substrate [as in step (1) above] or donated to the substrate [as in step (2) above]; $S\text{–}O^-$ is the substrate–oxygen bond formed at the surface, as an adsorbed intermediate in the overall reaction, and presumably ionic since the oxygen atom is depicted to carry a negative charge in the above equations.

The previous interpretations (*4, 5*) tend to classify the catalytic activity of the oxides towards N_2O decomposition on the basis whether the catalyst is a *p*-type or *n*-type semiconductor or an insulator.

If one assumes, however, that the adsorbed intermediate formed in the reaction is a covalent one, i.e., S–O, one can interpret the available data in terms of the Sabatier–Balandin (*6, 7*) views on heterogeneous catalysis, as shown below. It should be added that for the majority of oxides, it is not at all unreasonable to assume that the surface complex S–O involves a predominantly covalent bond. This is in fact the accepted viewpoint in several studies (*8–11*) on the catalytic reactions on oxides. By making this assumption of a covalent bond in the surface complex, S–O, it will be shown that the energy of the S–O bond is related to the catalytic activity in a volcanic manner, as postulated in the Sabatier–Balandin (*6, 7*) views on heterogeneous catalysis.

SABATIER–BALANDIN INTERPRETATION OF THE CATALYTIC ACTIVITY

The fundamental idea in Sabatier–Balandin approach (*6, 7*) is that the adsorbed reactants form a surface compound on the catalyst surface and the energy of the bond between the reactant and the catalyst is related to the catalytic activity in a volcanic manner, i.e., a maximum in activity with increasing bond energy. The surface compound in the present case is S–O; assuming that the surface oxygen atom is attached to a metal site, M, of the oxide catalyst, one may equate the S–O bond with the metal–oxygen bond, M–O. The energy of this bond may be denoted as $b(\text{M–O})$. The reaction to which this $b(\text{M–O})$ refers can be taken (*8*, *9*), as:

$$\text{MO}(S) \rightleftharpoons \text{M}(S) + \text{O}(G), \tag{4}$$

where MO is the metal oxide; S and G denote solid and gas, respectively; M and O are metal and oxygen; the forward reaction represents the bond fission and the backward reaction is the bond formation. One obtains the enthalpy change in reaction (4), ΔH_4, as:

$$\Delta H_4 = -\Delta H_f + (n/2)\Delta H_D, \tag{5}$$

where ΔH_f is the heat of formation (standard state) per mole of the MO and ΔH_D is the heat of dissociation, per mole, of O_2 to give oxygen atoms; n is the number of oxygen atoms in one molecule of the oxide. For comparison of the ΔH_4 values for various oxides, one takes them in their normalized form, i.e., as per equivalent (*12*) (i.e., neither as per mole, nor per atom but as per atom equivalent), so that Eq. (5) may be written as:

$$(\Delta H_4)_e = -(\Delta H_e) + (\Delta H_D)_e \tag{6}$$

Here, the subscript, e, denotes per equivalent. The quantity $(\Delta H_D)_e$ is constant with a value equal to $118/4 = 29.5$ kcal; ΔH_e is the heat of formation per equivalent of the oxide catalyst. The $(\Delta H_4)_e$ is the enthalpy change per bond, in the bond making or breaking involved in Eq. (4), and may hence be called the bond energy, $b(\text{M–O})$. This enables one to write Eq. (6) as:

$$b(\text{M–O}) = -(\Delta H_e) + K, \tag{7}$$

where K is constant with the value $= 29.5$ kcal. One thus notes that, for various oxides, the variations in bond energies [representing the bond formation or fission in Eq. (4)] are nothing but variations in $-(\Delta H_e)$ values. In the Sabatier–Balandin volcano plots, the bond energy axis may thus be denoted by $-(\Delta H_e)$ values. When one plots the activity (defined as the temperature at which the reaction first becomes appreciable) of various oxides for the N_2O decomposition against the corresponding $-(\Delta H_e)$ values (Fig. 1), one obtains a volcano plot. The data on which this correlation (Fig. 1) is based have been presented in Table 1.

The volcano relationship also permits some mechanistic conclusions to be made. In the ascending (i.e., left arm) branch of the volcano, the activity decreases with increasing $b(\text{M–O})$, i.e., with increasing $-(\Delta H_e)$ values; this would indicate that the rate-determining step (r.d.s.) in the N_2O decomposition on these oxides probably involves rupture of a M–O bond. On the other hand, in the descending branch (i.e., right arm) of the volcano, the activity increases with increasing $-(\Delta H_e)$; this would indicate a r.d.s. involving the formation of a M–O bond.

It should be added that the $-(\Delta H_e)$ values not only signify the $b(\text{M–O})$ values but are also roughly equal to half the band gap (*13–15*) for a given oxide. In this sense, the activity would also seem to be related, volcanically, to the band gaps of the catalysts, on the basis of Fig. 1 and previous work (*13–15*). This would then tend to emphasize the importance of semiconduc-

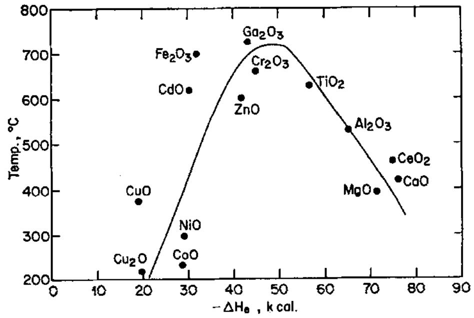

FIG. 1. A plot of heat of formation per equivalent, $-(\Delta H_e)$ against the catalytic activity (defined as the temperature, in °C, at which the reaction first becomes appreciable) of the shown oxides for the decomposition of N_2O. The data and source references are given in Table 1.

TABLE 1

CATALYTIC DECOMPOSITION OF N_2O BY OXIDES[a]

Oxide	Temp., °C	$-\Delta H_e$, kcal	ΔH_{atom}/ equiv., kcal
Cu_2O	214	19.92	131
CoO	230	28.6	109
NiO	300	29.2	109
CuO	375	18.8	89
MgO	395	71.9	119
CaO	420	75.9	127
CeO_2	455	75 (CeO)	132 (CeO_3)
Al_2O_3	530	65.3	122
ZnO	600	41.6	87
CdO	618	30.4	73
TiO_2	630	56.4	114
Cr_2O_3	660	45	107
Fe_2O_3	700	32.1	96
Ga_2O_3	725	43.0	94

[a] Notes: (1) The temperature in °C refers to the temperature at which the reaction first becomes appreciable. The data have been taken from Thomas and Thomas (*5*) and are somewhat approximate since they were read off from a figure in that book. (2) The $-\Delta H_e$ values are from Sanderson (*12*) and have been used in constructing Fig. 1. (3) The ΔH_{atom}/equiv. values are also from Sanderson (*12*) and have been used in constructing Fig. 2.

tivity (*16*), as previously suggested for the present case (*4*, *5*).

It appears appropriate to further comment here on the definition of bond energy. As used in the present context, it refers to the enthalpy change in Eq. (4) as represented by $-(\Delta H_e)$ through Eq. (7), in agreement with some previous usage in the literature on heterogeneous catalysis (*8*, *9*). In the chemical literature (*9*), however, the bond energy is the average strength of a bond in an oxide corresponding to the bond rupture,

$$MO(S) \rightarrow M(G) + O(G). \qquad (8)$$

A comparison of Eqs. (4) and (8) shows that in the former case, the metal M stays solid after the M–O bond rupture whereas in the latter case the metal M is in the gas phase after the fission of the bond. The bond energy corresponding to the transformation in Eq. (8), then, is the heat of atomization per equivalent and is given by the enthalpy change (per equivalent) in Eq. 8, ΔH_8, which is:

$$\Delta H_8 = [-\Delta H_f + (n/4)\Delta H_D + \Delta H_{\text{Sub}}]/n \qquad (9)$$

Here, ΔH_{Sub} is the heat of sublimation per mole of the metal atoms. Since metals generally evaporate to give atoms, ΔH_{Sub} per mole is the same thing as ΔH_{Sub} per atom; other terms have been defined above. The bond energy given by Eq. (9) would then be the heat of atomization by equivalent, to be denoted as ΔH_{atom}/equiv. It turns out that even when one chooses to represent M–O bond energy by ΔH_{atom}/ equiv. (Table 1), a rough volcanic correlation against the activity is again obtained (Fig. 2) although considerable spread in the points and departure of Cu_2O from the shown trend is quite noticeable. In any case activity of oxides towards N_2O decomposition shows a general volcanic trend when plotted against either of the two representations of M–O bond energy (Figs. 1 and 2). In the light of preceding discussion and some previous work (*8*, *9*, *16*), it would appear preferable to denote b(M–O), in the context of heterogeneous catalysis, by $-(\Delta H_e)$, although some cases (*17*) of catalysis by oxides are amenable to interpretation on the basis of representation of b(M–O) by ΔH_{atom}/equiv.

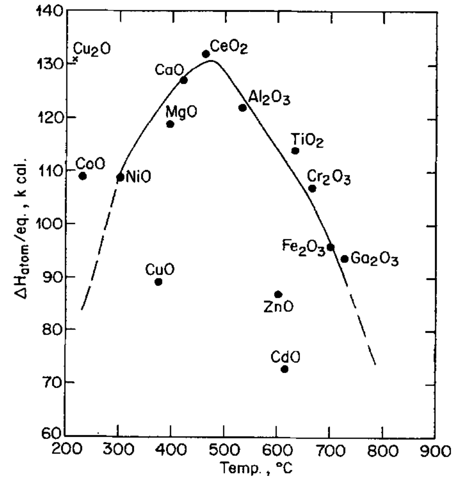

FIG. 2. A plot of heat of atomization per equivalent, ΔH_{atom}/equiv. against the activity (see Table 1) of the shown oxides for the catalytic decomposition of N_2O.

It appears pertinent to emphasize here that formally the volcano-shaped plots in Figs. 1 and 2 here are somewhat different from the ones predicted in Sabatier–Balandin theories (*7*). One generally expects a volcano correlation, e.g., in a plot of an inverted temperature scale (or an inverted energy of activation) vs the heat of formation so that the material producing the highest activity at the lowest temperature (or corresponding to the lowest energy of activation) occupies the peak of the volcano (*7*). In this sense, Fig. 1 would then be an inverted volcano plot. However, the conceptual similarity in the two types of volcanos lies in the fact that on one arm of the volcano the rate increases with increasing bond energy whereas the reverse is true for the other arm of the volcano. In this sense Fig. 1 would be consistent with the conventional Sabatier-Balandin volcano plots. Similar comments also apply to Fig. 2 in which one arm corresponds to increasing activity and the other to decreasing activity, when plotted against the heat of atomization per equivalent. One thus concludes that the volcanos in Figs. 1 and 2 are different in form but identical in content with the convention Sabatier–Balandin interpretations.

One should perhaps add here a few words of general caution regarding the type of comparisons of catalytic activities done here in Figs. 1 and 2. The rate values used can differ by several orders of magnitude unless the oxides involved have the same surface areas per gram. Further, the temperature at which the reaction becomes appreciable is a somewhat ill-defined quantity in that it depends on the sensitivity of detection. However, for illustrating the rough correlative trends shown in Figs. 1 and 2, the foregoing limitations are perhaps not too serious especially since the data have been taken from a critical and reliable source (*5*).

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