

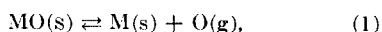
NOTE

A Possible Rough Connection Between Aspects of the Balandin and the Volkenshtein Concepts in Heterogeneous Catalysis

Two major guidelines for interpreting and predicting the behavior of catalysts are based on the ideas put forward by Balandin (1) and Volkenshtein (2). The purpose of the present note is to point out a possible way of roughly connecting some parameters of the two conceptual approaches by considering the example of catalytic oxidations on oxide catalysts.

In the Volkenshtein's approach to catalysis (2), one invokes Fermi statistics and computes the fraction of the total number of adsorbed species held weakly or strongly (the latter being either through acceptor or donor bonds) in terms of the *distances* from the Fermi level to the bottom of the conduction band and to the top of the valence band. The crucial quantity is this theory, in terms of Fig. 1 (also see discussion below), is ΔE_F .

The basic idea behind Balandin's approach (1) is that the reactants get adsorbed on the catalyst to form a surface compound and the energy of the bond between the catalyst and the reactant is related to the catalytic activity in a volcanic manner; i.e., there is a maximum in activity with increasing bond energy. In the example (oxidation) chosen here, it is generally agreed (3-5) that the bond making or breaking of interest is the enthalpy change in the reaction:



where MO is the metal oxide; *s* and *g* denote solid and gas, respectively; M and O are metal and oxygen; the forward reaction

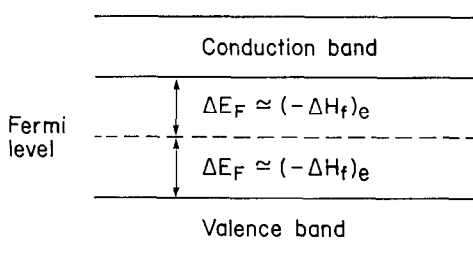


FIG. 1. A schematic representation of *rough* equivalence (see text) of ΔE_F and $(-\Delta H_f)_e$ for a catalyst. ΔE_F is the energy gap between the Fermi level and the bottom of the conduction band (or top of the valence band) assuming the semiconducting catalyst to be intrinsic; $(-\Delta H_f)_e$ is the negative of the heat of formation per *equivalent* (standard state) of the catalyst and has the significance of the energy needed to break the bond involved in the catalytic oxidation. The bond energy $(-\Delta H_f)_e$ is the basic parameter in Balandin's volcano plots whereas the Fermi level E_F is the central quantity in Volkenshtein theory of catalysis; this figure, therefore, provides a rough connection between the fundamental parameters of the two theories.

represents the bond rupture whereas the backward reaction denotes the bond formation. The enthalpy change per *mole* in reaction (1), is given by:

$$\Delta H_1 = -\Delta H_f + n(\frac{1}{2}\Delta H_D), \quad (2)$$

where ΔH_f is the heat of formation per mole of the oxide and ΔH_D is the heat of dissociation of 1 mole of the oxygen gas to give oxygen atoms; *n* is the number of oxygen atoms in one molecule of the oxide. When one is considering the formation or rupture of *one* bond (instead of 1 mole) one

must write the enthalpy change in reaction (1) as per bond, i.e., as per *equivalent*. To illustrate by example, the $\Delta H_f/\text{equiv}$ of Al_2O_3 , ZrO_2 and NiO is $1/6$, $1/4$ and $1/2$, respectively, of the corresponding $\Delta H_f/\text{mole}$ values. By making this change in Eq. (2) and by denoting equivalent by the subscript, e , one obtains:

$$(\Delta H_1)_e = -(\Delta H_f)_e + (\Delta H_D)_e. \quad (3)$$

Since $(\Delta H_D)_e$ has a constant value ($= 118/4 = 29.5$ kcal) for all oxides, the enthalpy change per bond in Eq. (1), i.e., the bond energy appropriate for the present discussion (to be denoted by $b(\text{M}-\text{O})$) and equal to $(\Delta H_1)_e$ may be written as:

$$b(\text{M}-\text{O}) = -(\Delta H_f)_e + K. \quad (4)$$

In other words the variations in $b(\text{M}-\text{O})$ values (to be used, e.g., in the Balandin's volcano plots for a given oxidation over a number of oxides) for various oxide catalysts are represented by the variations in the $-(\Delta H_f)_e$ values. It is the purpose in the following discussion to show that $-(\Delta H_f)_e$ values for oxides (or for any catalyst for that matter) are related to their Fermi level, the latter quantity being, of course, the central parameter in the Volkenshtein's theory of catalysis (2).

It has been shown previously (6, 7) that for a very large number of inorganic compounds, the following *rough* correlation is obeyed:

$$Eg = 2(-\Delta H_f)_e \quad (5)$$

where Eg is the band gap of the catalyst, oxide in the present discussion. For intrinsic semiconductors, the Fermi level may be assumed to lie at the centre of the band gap so that (8):

$$Eg = 2\Delta E_F, \quad (6)$$

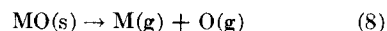
where ΔE_F is the distance (i.e., the gap) between the Fermi level and the bottom of the conduction band (or the top of the valence band) as depicted in Fig. 1. By combining Eqs. (5) and (6), we note that:

$$\Delta E_F = (-\Delta H_f)_e. \quad (7)$$

It follows, therefore, that the heat of

formation per equivalent $(-\Delta H_f)_e$ not only signifies the relative magnitude of the metal oxide bond energy for the various oxide catalysts, it is also related to the position of the Fermi level within the oxide. One thus obtains a connection between the basic parameter of Balandin's theory (i.e., the bond energy) and the central quantity in the Volkenshtein's theory of catalysis (i.e., the Fermi level). This arises, of course, because there exists a conceptual correlation between the solid state cohesion [represented here by the bond energy $b(\text{M}-\text{O})$ or $-(\Delta H_f)_e$] and semiconductivity (i.e., the band gap) of materials (6, 7).

In order to avoid any possible confusion, it is necessary to further comment here on the definition of bond energy. As used in the present context, it refers to the enthalpy change in Eq. (1), in agreement with the previous usage in the literature on heterogeneous catalysis (3-5); i.e., it is the heat of formation (standard state) of the oxide plus the heat of dissociation of oxygen, both normalized, of course, appropriately as per equivalent. In the general chemical literature (9), however, the bond energy is the average strength of a bond in an oxide corresponding to the bond rupture,



A comparison of Eqs. (1) and (8) shows that in the former case, the metal M stays solid after the MO bond rupture (as indeed is appropriate for a catalytic reaction proceeding on an oxide) whereas in the latter case the metal M finds itself in the gas phase after the fission of the bond. The bond energy as given by Eq. (8), then, is the heat of *atomization* per equivalent and is represented by the enthalpy change (per equivalent) in Eq. (8) ΔH_s , which is given by:

$$\Delta H_s = (-\Delta H_f)_e + (1/4)\Delta H_D + \Delta H_{\text{sub}}/n. \quad (9)$$

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.

In conclusion, it may be stated that the

bond energy referring to Eq. (1) may be related to the Fermi level of oxides (Fig. 1).

ACKNOWLEDGMENT

Grateful acknowledgment is made to Dr. P. Lenfant for his interest in this work.

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Received May 30, 1972