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The Appropriate Quantity Denoting the Metal-Oxygen Bond Energy of Oxide Catalysts

In a recent letter (*1*), Criado has presented a critique of our paper (*2*) in which the significance of the quantity to be used as the bond energy in oxidation reactions on oxide catalysts was discussed. As shown below, this critique (*1*) arises from an erroneous interpretation of our previous viewpoint.

It is best to develop the present analysis by stating first the points of agreement between our viewpoint (*2*) and that of Criado (*1*) or Klier (*3*). For simple oxides containing one oxygen atom (such as ZnO, NiO, CoO and MnO, etc.), the bond rupture/formation of interest in the present context is

$$\mathrm{MO(S)} \rightleftharpoons \mathrm{M(S)} + \mathrm{O(G)}, \qquad (1)$$

where S and G denote solid and gas, respectively. The bond energy of reaction (1), b_1, may be represented as (*1,2*):

$$b_1 = -\Delta H_e + K, \qquad (2)$$

where ΔH_e is the heat of formation per equivalent of the oxide MO; K is a constant whose value is equal to the heat of dissociation per *equivalent* of an oxygen molecule, i.e., $118/4 = 29$ kcal. Hence the relative b_1 values for various oxides of ZnO, NiO, etc., type may be denoted by their $-\Delta H_e$ values. For oxides containing several oxygen atoms and capable of undergoing a change in stoichiometry by bond rupture/formation during catalysis, the reaction of interest, after Klier (*3*), is

$$\mathrm{M}_m\mathrm{O}_n(\mathrm{Y}) \rightarrow \mathrm{M}_m\mathrm{O}_{n-1}(\mathrm{Z}) + \tfrac{1}{2}\mathrm{O}_2. \qquad (3)$$

To make the following arguments more easily comprehensible, one may write Eq. (3) for the particular case of a typical oxide catalyst, e.g., involving iron oxides, as

$$3\ \mathrm{Fe_2O_3} \rightleftharpoons 2\ \mathrm{Fe_3O_4} + \tfrac{1}{2}\mathrm{O_2}. \qquad (4)$$

The bond breaking involved in the forward direction of reaction (4) involves a bond energy equal to the heat of formation (exothermic) per equivalent of Fe_2O_3 (32.1 kcal); the bond breaking involved in the reverse direction of reaction (4) is the bond energy which is equal to the heat of formation (exothermic) per equivalent of Fe_3O_4 (33.4 kcal). If the oxide catalyst involved were FeO [i.e., bond formation/rupture in Eq. (1)], the bond energy value would be equal to the heat of formation (exothermic) per equivalent of FeO (31.9 kcal). Since the $-\Delta H_e$ values (i.e., the bond energy values) of FeO, Fe_2O_3 and Fe_3O_4 are *approximately* equal (ignoring the constant value of the heat of dissociation per *equivalent* of O_2), i.e., ranging from 31.9 kcal to 33.4 kcal, it is clear that the magnitude of bond energy involved in all three oxides is nearly the same. This was the reason for the viewpoint in our previous paper (*2*) that when one takes heats of formation as per *equivalent,* the bond energy values for various stoichiometric oxides are approximately of equal magnitude. On the basis of this it was stated that whether the bond involved is the one in reaction (1) or reaction (3) (forward or reverse direction), the $-\Delta H_e$ of the oxide (FeO, or Fe_2O_3, or Fe_3O_4) is an adequate representation of the bond energy. It should be added that the value of constant K of Eq. (2) would also be same for reaction (3) when the dissociation energy of the oxygen molecule involved in reaction (3) is taken as per *equivalent;* i.e., this value is 29 kcal.

The above argument is also valid for several other oxides. For example, $-\Delta H_e$

values for CuO and Cu_2O are 18.8 and 19.9 kcal, respectively; for Co_3O_4 and CoO, 26.3 and 28.6 kcal, respectively; for Mn_2O_3 and Mn_3O_4, 38.7 and 41.4 kcal, respectively; for TiO_2 and Ti_2O_3, 56.4 and 60 kcal, respectively. In short, if the $-\Delta H_e$ values for various stoichiometric oxides of a given metal are nearly the same, as indeed they are for several oxides of importance in heterogeneous catalysis, the representation of bond energy by $-\Delta H_e$ value of any of the stoichiometric oxides is acceptable with the accompanying implication that the magnitude of the quantity involved in the bond formation/rupture during heterogeneous catalysis is the same whether the catalysis proceeds through reaction (1) or (3). For cases where there is a significant difference in the $-\Delta H_e$ values of various stoichiometric oxides, e.g., V_2O_5 (37.3 kcal) and V_2O_4 (43 kcal), it will be necessary to use the precise $-\Delta H_e$ value for the oxide involved; i.e., in the reaction,

$$V_2O_5 \rightleftharpoons V_2O_4 + \tfrac{1}{2}O_2, \qquad (5)$$

one must use 37.3 kcal for the forward reaction and 43 kcal for the reverse reaction. In this particular respect, our previous viewpoint (*2*) stands slightly modified for the cases of some oxides, and some oxides only.

The erroneous nature of data in Criado's Table 1 [see Ref. (*1*)] for several cases now becomes apparent. To take again the example of iron oxide catalysts, the enthalpy change involved as per *equivalent,* in the reaction,

$$Fe_2O_3 \rightleftharpoons Fe_3O_4, \qquad (6)$$

is 1.3 kcal on the basis of the above-quoted data; our data on heats of formation are from Refs. (*4*) and (*5*) and are comparable to those quoted by Criado (*1*) for the same compounds. However, for reaction (6), Criado quotes a value of 28.2 kcal.

Criado criticizes our statement (*2*), namely, " . . . whether the oxidation/reduction of the oxide catalyst in the catalytic reaction leads to a change of stoichiometry [i.e., Eq. (3) *here*] or a complete decomposition (or formation) of the oxide [i.e., Eq. (1) *here*], the energetic quantity representing the bond energy, *when taken in its normalized form,* is the same. . . ". Let us examine this statement for the case of iron oxide. If the bond rupture/formation involved is such as in Eq. (1), the $-\Delta H_e$ is 31.9 kcal; if the forward of reaction (6) [i.e., reaction (3) as applied to iron oxide] is considered, the $-\Delta H_e$ is 32.1 kcal; when the backward of reaction (6) is involved, the $-\Delta H_e$ is 33.4 kcal; these three quantities are approximately equal, thus confirming the validity of our statement.

It is believed that the source of confusion in Criado's paper arises from the fact that he fails to distinguish between the net enthalpy change in reaction (3) here, and, the magnitude of the energy involved in the bond formation/rupture occurring in this reaction, which is reaction (6) for iron oxide. If the $Fe_2O_3 \rightleftharpoons Fe_3O_4$ process is considered, the net enthalpy change (ignoring the constant K representing the heat of dissociation per *equivalent* of the oxygen molecule (29 kcal) which is the same constant value for all oxides) per *equivalent* is 1.3 kcal as mentioned above; however, the magnitude of bond breaking/formation involved (in the forward or backward of reaction (6), respectively) is around 32–33 kcal. The discrepancies between the values cited here and those contained in Criado's Table 1 arise not only because of the foregoing confusion in this paper but also because:

i. Criado seems to be counting in his calculations the value of the constant [K appropriate for reaction (3) here [i.e., his reaction (2)];

ii. he is confusing, in an indeterminate manner, the significance of the magnitudes of various quantities in an equation such as

(3) here, when taken as per equivalent, per mole, per oxygen atom or per oxygen *atoms* etc.; one must always take all quantities in their normalized form, i.e., as per *equivalent* as discussed previously (*2*).

It would suffice to indicate the erroneous nature of data in Criado's Table 1 by citing one more example, namely, the reaction

$$Co_3O_4 \rightleftharpoons CoO. \tag{7}$$

The enthalpy change involved, per *equivalent,* in reaction (7) is 2.3 kcal, against 21.1 kcal cited by Criado; however, the magnitude of bond energy (i.e., $-\Delta H_e$ of Co_3O_4 for the forward process of reaction (7) and $-\Delta H_e$ of CoO for the backward process of reaction (7)] is around 26–28 kcal, as mentioned above.

In summary, the main point of our previous paper (*2*) is quite valid for a substantial number of oxide catalysts, although some slight modifications are called for in the assumption of identical $-\Delta H_e$ values for reactions (1) and (3) for some cases (e.g., $V_2O_5 \rightarrow V_2O_4$), as indicated above.

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