JOURNAL OF CATALYSIS 37, 563-564 (1975)

The Magnitude of the Metal–Oxygen Bond Energy of Oxide Catalysts

Many authors (*1*) (*2*) have tried to establish correlations between the metal–oxygen bond energy of different oxides and their catalytic activity.

Among the quantities more widely used for representing the M–O bond energy are the formation enthalpy per oxygen gram-atom of the oxide and the enthalpy for the reaction:

$$MO(S) \rightarrow M(S) + O(G), \quad (1)$$

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

Klier (*1*) has considered that the oxygen exchange on oxide surfaces implies a change of the metal oxidation number rather than the formation of free metal demanded by reaction (*1*). Accordingly, this author has suggested that a more proper parameter for representing the M–O bond energy is the enthalpy for reaction (*2*):

$$M_mO_n(Y) \rightarrow M_mO_{n-1}(Z) + \tfrac{1}{2}\,O_2, \quad (2)$$

where Y and Z refer to the oxide phases.

However, Vijh has considered in a recent paper (*3*) that the enthalpies for reactions (1) and (2), if they are taken in their normalized forms (i.e., per equivalent of oxygen), are the same.

Thus, this author has concluded that: ". . . whether the oxidation/reduction of the oxide catalyst in the catalytic reaction leads to a change of stoichiometry [i.e., Eq. (4)[1]] 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 . . .".

On the other hand, provided that the normalized enthalpy for reaction (1), $(\Delta H_1)_e$, and for the oxide formation, ΔH_e, are related through the dissociation enthalpy per equivalent of the molecule of oxygen, K, by the expression:

$$(\Delta H_1)_e = -\Delta H_e + K, \quad (3)$$

this author has concluded that: ". . . $-\Delta H_e$ values of the oxide catalysts are valid representations of the M–O bond energy for the transformations either those in reaction (1) or (4)[1]".

The aim of the present letter is to point out the meaninglessness of Vijh's conclusions about the equality of both normalized enthalpies for reactions (1) and (2).

The analysis of the Born–Haber cycle of reaction (2) immediately shows that $(\Delta H_2)_e$ is a function of the formation enthalpies of both the Y and Z phases and not only of the formation enthalpy of Y [as it seems is assumed in Ref. (*3*)]. Only when the reduced phase of the oxide catalyst is the free metal are the normalized enthalpies for oxide formation and for reaction (2) the same and $-\Delta H_e$ is a proper magnitude for representing the normalized enthalpy of reaction (2).

Table 1 includes values of $-\Delta H_e$ and $(\Delta H_2)_e$ for several oxides calculated from formation heats included in Ref. (*4*). The plot of $-\Delta H_e$ against $(\Delta H_2)_e$ in Fig. 1 shows that these quantities are not even linearly correlated.

These arguments make it evident that different correlations between M–O bond energies and catalytic activity data may be

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[1] Equation (4) of Vijh's paper is Eq. (2) of the present letter.

TABLE 1

ENTHALPIES PER OXYGEN EQUIVALENT OF THE FORMATION OF OXIDES, ΔH_e, AND CHANGES IN THEIR STOICHIOMETRIES, $(\Delta H_2)_e$

Oxide	$-\Delta H_e$ (kcal/eq)	Stoichiometry change	$(\Delta H_2)_e$ (kcal/eq)
TiO_2	56.4	$TiO_2 \rightarrow Ti_2O_3$	44.0
V_2O_5	37.1	$V_2O_5 \rightarrow V_2O_4$	14.5
Fe_2O_3	32.8	$Fe_2O_3 \rightarrow Fe_3O_4$	28.2
Co_3O_4	26.6	$Co_3O_4 \rightarrow CoO$	21.1
MnO_2	31.0	$MnO_2 \rightarrow Mn_3O_4$	10.3
CuO	18.8	$CuO \rightarrow Cu_2O$	17.4
CeO_2	65.0	$CeO_2 \rightarrow Ce_2O_3$	45.5
Mn_2O_3	38.2	$Mn_2O_3 \rightarrow MnO$	22.5
ZnO	41.6	$ZnO \rightarrow Zn$	41.6
NiO	28.6	$NiO \rightarrow Ni$	28.6
MnO	46.0	$MnO \rightarrow Mn$	46.0

obtained when $(\Delta H_2)_e$ or $-\Delta H_e$ are chosen as a measure of M–O bond energy, in contradiction with Vijh's conclusions (*3*).

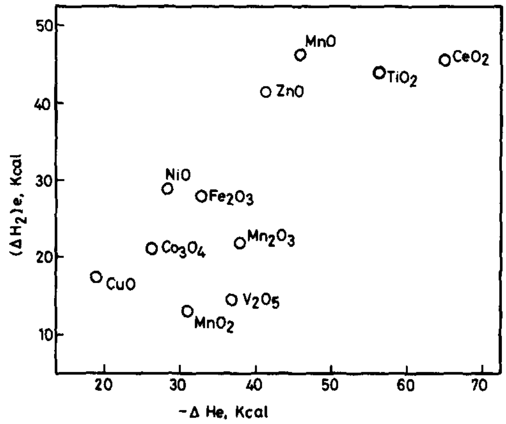

FIG. 1. Plot of $(\Delta H_2)_e$ versus $-\Delta H_e$ values.

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Received September 16, 1974