The Catalytic Activity of Metal Oxides of the Fourth Period in the Hydrogen-Oxygen Reaction. A Commentary on a Paper by Popovskii and Boreskov

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In spite of many efforts¹⁾ to correlate the catalytic activity of metal oxides with such electronic properties of the corresponding oxides as the semiconductivity and the electronic configuration of the metal ion, there still remain some cases where the classical oxidation-reduction concept²⁾ sounds better than modern electronic interpretations. Undoubtedly, the catalyst activity of metal oxide is so sensitive to the mode of preparation or to the surrounding atmosphere that difficulty is often encountered in interpreting the observed activity data, the temperature threshold for a reaction in a majority of cases being a conventional measure of the catalyst activity.

Recently Popovskii and Boreskov³⁾ investigated the hydrogen-oxygen reaction on the metal oxides of the fourth period in a systematic and careful manner. Excess oxygen was used so that the catalyst activity might be compared at a certain oxidation level. The rate data were given in terms of the volume of hydrogen consumed per unit hour and per unit area of the metal oxides at temperatures of 150 and of 300°C respectively.

Their data are reproduced in Fig. 1 in relation to the atomic number of the constituent metal ion in the way they adopted.

The order of the catalyst activity was found to be:

$$Co_3O_4 > CuO > MnO_2 > NiO > Fe_2O_3 > Cr_2O_3 > V_2O_5 > ZnO > TiO_2$$

at 150°C. The activity at 300°C was nearly parallel with this. While such an activity series was consistent with the familiar relationship in respect to the type of semiconductor, i.e., *p*-type>*n*-type, Popovskii and Boreskov favored the parallel relationship with a work function series of these oxides proposed as:

$$CuO > NiO > V_2O_5 > ZnO > TiO_2$$

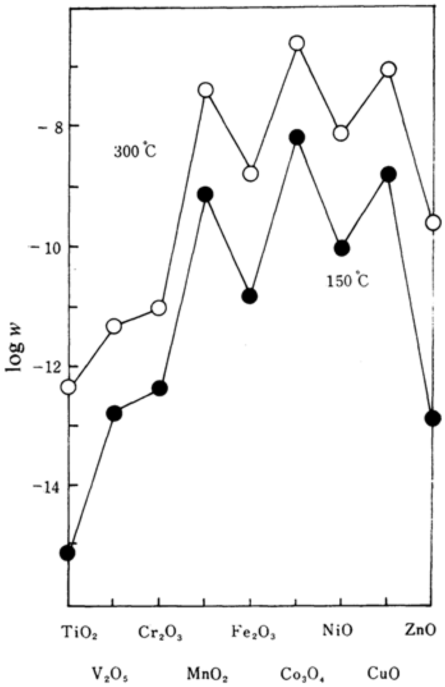

Fig. 1. The catalytic activity of metal oxides of the fourth period for the hydrogen-oxygen reaction after Popovskii and Boreskov.³⁾

suggesting that the electron transfer from the substrate to the oxide is rate-controlling.

It should be noted, however, that the work function of metal oxide is in general sensitively dependent on the pretreatment of the oxide as well as on the atmosphere. At present the value of the work function, as far as metal oxide is concerned, does not seem to be well-established. It has been reported⁴⁾ that the work function of zinc oxide is, at an oxidation level, greater by 1.0 eV. or even more than that of nickel oxide, contrary to the above order proposed by Popovskii and Boreskov.

On the other hand, it would be interesting to see if the relative catalytic activity of the

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1) See, for example, F. S. Stone, "Advances in Catalysts," Vol. 13, Academic Press, New York (1962), p. 1.

2) Sol Weller and S. E. Voltz, *Z. physik. Chem. N. F.*, **5**, 100 (1955); S. Makishima, Y. Yoneda and Y. Saito, International Congress on Catalysis, Paris, 1960.

3) V. V. Popovskii and G. K. Boreskov, *Prob. Kin. Cata. Nauk. S. S. S. R.*, **10**, 67 (1960).

4) H. H. Jacobs, *J. Appl. Phys.*, **17**, 596 (1946); F. Wilessov and A. Terenin, *Naturwiss.*, **46**, 167 (1959).

oxides quoted above accords with the relative reducibility of the corresponding oxide by hydrogen. Let us, therefore, investigate how the bond strength of oxygen with the surface may be correlated with the catalyst activity.

The chemisorption of hydrogen would be instantaneous under the experimental conditions; the H_2–D_2 exchange reaction is known to occur on the metal oxides at much lower temperatures.[5] The same may perhaps be true with the oxygen chemisorption. It is assumed that the act of depriving the chemisorbed oxygen atom to yield water is rate-controlling. Let us assume, moreover, that the heat of the formation of metal oxide per g. atom oxygen is a measure of the strength of the oxygen-surface bond. The heat of formation of metal oxide per g. atom oxygen does not depend appreciably on the valency state of the constituent metal ion, at least for the metal oxides under investigation. Current investigations[6] fortunately indicate that there is a close correspondence between the chemisorption and the formation of the bulk compounds. Thus, one may expect some kind of regular relation between the catalyst activity of the metal oxides of the fourth period and the heat of the formation of the corresponding metal oxide. Table I shows the heats of formation of metal oxides per g. atom oxygen, together with the kinetic data for the hydrogen-oxygen reaction obtained by Popovskii and Boreskov.

TABLE I. THE HEAT OF FORMATION OF METAL OXIDE PER g. ATOM OXYGEN AND THE KINETIC DATA FOR THE HYDROGEN-OXYGEN REACTION AT 150°C

Catalyst	Heat of formation $\Delta H°$, cal.	$\Delta H°$/g. atom oxygen cal.	Rate, w cc./hr. cm^2	Activation energy kcal.
TiO_2	228350	114180	6.3×10^{-16}	21
V_2O_5	381960	76390	1.8×10^{-13}	18
Cr_2O_3	274670	91560	4.1×10^{-13}	18
Fe_2O_3	202960	67650	1.4×10^{-11}	15
MnO_2	126400	63200	$\sim10^{-9}$*	14
Co_3O_4	—	63000**	6.5×10^{-9}	11
NiO	57640	57640	2.6×10^{-10}	8
CuO	37740	37740	4.9×10^{-9}	13
ZnO	84670	84670	1.3×10^{-13}	24

* Estimated from the plot of Fig. 1.

** Mean of CoO (56910) and Co_2O_3 (207300).

The thermochemical values were taken from "Handbook of Chemistry and Physics," 42nd Ed., Chemical Rubber Publishing Co. (1960).

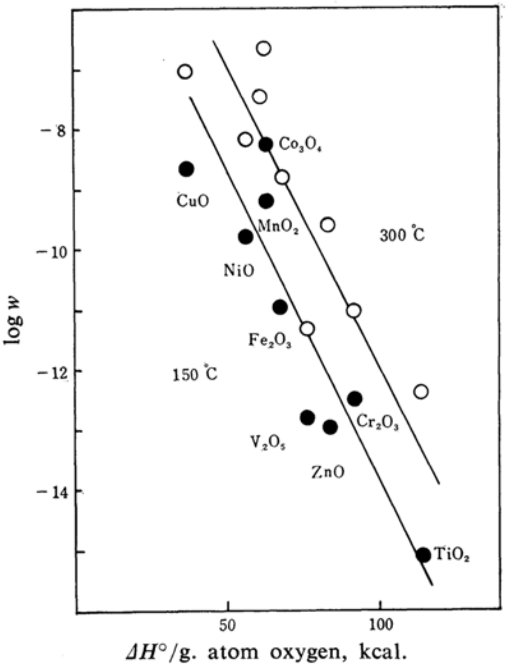

Fig. 2. The relation between the catalytic activity of metal oxides and the heat of formation of metal oxides per g. atom oxygen.

An attempt was made to plot the rate data (log w) against the heat of formation of metal oxide as given by the third column of Table I. This plot is shown in Fig. 2.

It may be seen from Fig. 2 that an approximately linear relationship exists between the catalyst activity of the metal oxides and the heat of formation of these oxides at 150 and 300°C respectively. It is shown, in other words, that the weaker the oxygen-surface bond, the faster the rate of hydrogen-oxygen reaction.

Sachtler et al.[7] described the relative catalytic activity of metals in the decomposition of formic acid by the use of the heat of formation of metal formate, arriving at a so-called volcano-shaped curve. The present approach is quite similar to this. The use of the heat of formation in any way instead of the strength of the surface bond must, of course, be only approximate. However, it does seem useful as one can readily correlate the kinetic data in terms of the thermodynamic quantities available in the "Handbook."

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[5] D. A. Dowden, N. Mackenzie and B. M. W. Trapnell, *Proc. Roy. Soc.*, **A237**, 245 (1956).

[6] M. W. Roberts, *Nature*, **188**, 1020 (1960); D. Brennan, D. O. Hayward and B. M. W. Trapnell, *Proc. Roy. Soc.*, **A256**, 81 (1960); W. M. H. Sachtler and L. L. van Reijen, *Shokubai*, **4**, 147 (1962); K. Tanaka and K. Tamaru, ibid., **4**, 328 (1962).

[7] J. Fahrenfort, L. L. van Reijen and W. M. H. Sachtler, *Z. Elektochem.*, **64**, 716 (1960); W. M. H. Sachtler, Lecture read before the Catalysis Club of Japan, July 26, 1961, Sapporo.

Indeed, there is a rough parallelism between the activation energy of the hydrogen-oxygen reaction given in the fifth column and the heat of formation of metal oxide per g. atom oxygen given by the third column of Table I. It is hoped that modern electronic theory will be successfully applied on the basis of knowledge gained from the classical viewpoint.

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Note added in proof.—An explanation compatible with this commentary was put forward very recently by Boreskov, Dzisyak and Kasatkina (*Kin. Kata.*, **4**, 388 (1963)) in the homomolecular exchange of oxygen isotope on metal oxides; these authors noted that the calalytic activity of metal oxides of the fourth period in the above-mentioned reaction or in the hydrogen-oxygen reaction may be determined by the bond energy of oxygen with the surface and not by the electronic work function of the oxides.