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LETTERS TO THE EDITORS

On the Correlation between Magnetic, Adsorption, and Catalytic Properties of Some Oxide Catalysts

In some recent publications (*1*) it was shown that the kinetic parameters of the reaction $CO + \frac{1}{2}O_2 = CO_2$ change sharply when changing the magnetic state of the oxide catalysts (NiO, Cr_2O_3, CuO). In the antiferromagnetic state, the frequency factor and the energy of activation have lower values than in the paramagnetic state, while the specific activity displays only a negligible change. Winter (*2*) has studied the adsorption of oxygen on NiO around Neel's temperature (T_N) and is of the opinion that below this temperature oxygen is adsorbed mainly as O_2^-, and above it, as O^-. For that reason, the mechanism of CO oxidation changes, which explains the difference between the kinetic parameters in the two magnetic states. The purpose of the present communication is to show that this difference could be explained in another way, e.g., as due to the influence of phase transformations in the solid upon the parameters characterizing the oxygen or CO chemisorption, the reaction mechanism remaining unchanged. For the sake of simplicity, only the case of oxygen adsorption on NiO has been studied, the general thermodynamic treatment being applicable to the other two oxides as well.

Assume that the oxygen atom forms a strong acceptor bond with the surface of NiO. When the catalyst is antiferromagnetic, rupture of bonds in the system of antiparallel spins occurs. For that reason, after adsorption, the antiferromagnetic catalyst will show higher values of entropy and enthalpy than the paramagnetic one (Fig. 1), all the other conditions being equal. The energy of ordered spins in a grammol of NiO is equal to RT_N (to a pair of spins corresponds $\frac{1}{3}kT_N$, $T_N = 523°K$).

If the adsorption of one oxygen atom leads to the rupture of five bonds in the spin system, the heat of adsorption of a gramatom of oxygen on antiferromagnetic nickel oxide will be lower than that on paramagnetic NiO by $\delta H = (5NkT_N)/3 = 2{,}3$ kcal/mole.

Assume that within a temperature range including Neel's temperature, the catalytic reaction proceeds by the Rideal mechanism ($O_{ads} + CO_{gas} = CO_{2\,gas}$) (*3*). According to the theory of rate chemical processes (*4*), the frequency factor is proportional to exp $(\Delta S^*/R)$, and the apparent activation energy, to ΔH^*, where ΔS^* denotes the change in entropy with the formation of an activated complex of the initial substances, and ΔH^*, the corresponding change in enthalpy. Consider the thermodynamic characteristics of the activated complex as being equal with antiferromagnetic and paramagnetic catalysts. Since the values of enthalpy and entropy of oxygen chemisorbed on an antiferromagnetic catalyst exceed those corresponding to the system O_{ads}-paramagnetic catalyst by δH and δS, the changes in ΔH^* and ΔS^* will differ by the same quantities. Hence, in the antiferromagnetic state, the values of the frequency factor and the energy of activation are lower than their values in the paramagnetic state (Fig. 1). The presence of a compensation effect (Fig. 2) indicates that the difference between the free energies of activation ($\delta F = \delta H - T\delta S$) is a small quantity, i.e., δH and $T\delta S$ have close values and $\delta F \ll \delta H$, $T\delta S$. The estimation of δH coincides in order of magni-

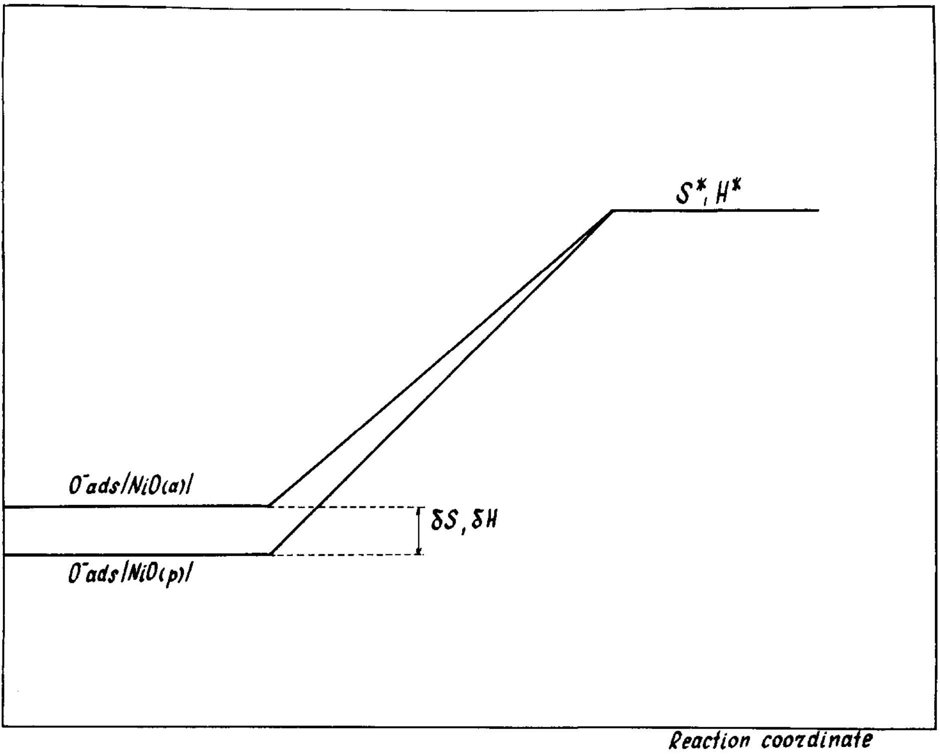

FIG. 1. Scheme of the changes in entropy (*S*) and enthalpy (*H*) during the formation of the activated complex in the reaction between CO_{gas} and O_{ads}. The change of *S* and *H* for CO_{gas} is independent of the magnetic state of the adsorbent. $O^{-}_{ads}/NiO_{(a)}$, oxygen adsorbed on antiferromagnetic nickel oxide. $O^{-}_{ads}/NiO_{(p)}$, oxygen adsorbed on paramagnetic nickel oxide.

tude with the experimental value of the difference between the activation energies (8,5 kcal/mole). The frequency factor changes correspondingly by 3,5 orders of magnitude.

The change in the parameters characterizing the strong oxygen chemisorption at Neel's temperature can also be explained by the effect of the magnetic ordering upon the structure of the energy spectrum of the electrons in NiO. The studies of some authors (*5*) show that the current carriers (polarons with small radii) move in a narrow band whose structure depends on the presence of magnetic ordering. Below Neel's temperature, the electron and hole bands are narrower than above it, i.e., in the point of the order-disorder phase transition, the forbidden gap becomes narrower by $\Delta u \simeq$ 6 kcal/mole.

For the heat of oxygen adsorption one can write:

$$Q = A - \varphi + W_{K-A},$$

where *A* is the electron affinity of the oxygen atom, φ, the work function of NiO, W_{K-A}, the energy of interaction of the O^{-} ion with the surface.

When changing the width of the forbidden gap by Δu, the thermoelectron work function changes by Δu/2, and the photoelectron work function, by Δu. With the transition from the antiferromagnetic into the paramagnetic state, the heat of adsorption changes as much as the work function. For the Rideal mechanism, the apparent activation energy of the oxidation reaction calculated according to Hinshelwood's formula (*6*) is as follows:

$$E_a = E_{ac} + \tfrac{1}{2}Q,$$

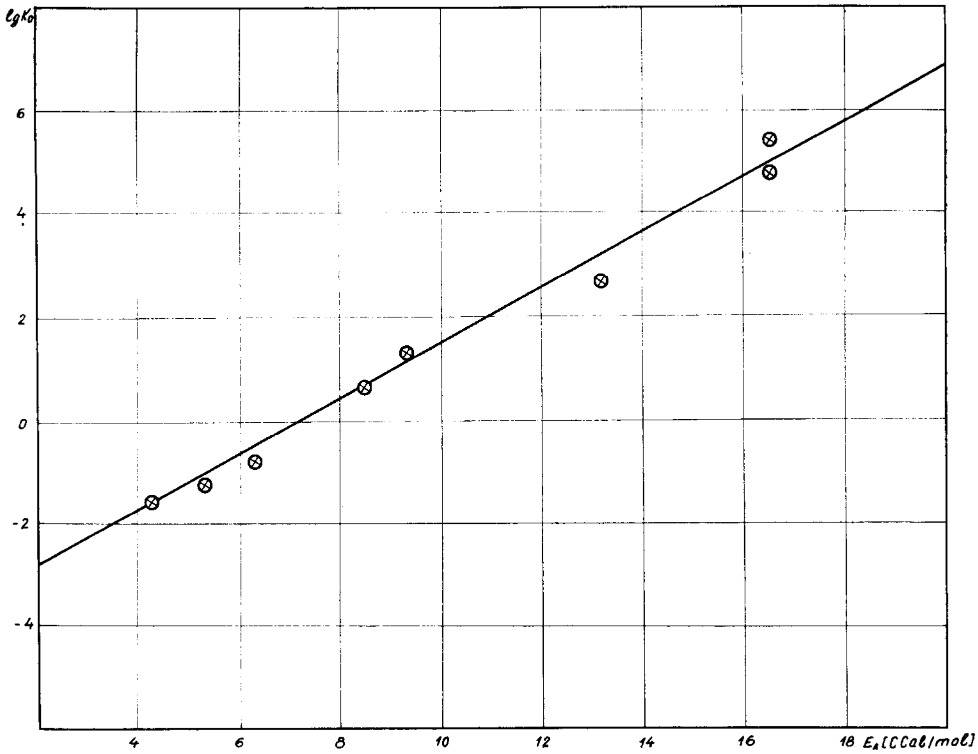

FIG. 2. Relationship between l_gK_0 and E_a for reaction $CO + 1/2O_2 = CO_2$ taking place on a NiO catalyst. The data obtained in (*1*) have been used.

where E_{ac} is the actual activation energy and Q, the heat of oxygen adsorption. Evidently, to a higher value of the heat of adsorption will correspond a higher energy of activation. The appearance of a compensation effect accompanied by a decrease in both the width of the forbidden gap and the work function is in agreement with the correlations between the catalytic activity and these semiconducting characteristics given in (*6*).

On the basis of the above considerations, the dependence of the kinetic parameters of reaction $CO + \frac{1}{2}O_2 = CO_2$ on the magnetic state of the NiO, Cr_2O_3, and CuO catalysts (the magnetocatalytic effect) can be explained. This effect is due to the difference between the quantities characterizing the strong chemisorption of the reacting gases in the antiferromagnetic and paramagnetic states. The combined study of the catalytic, adsorption, magnetic and electric properties of nickel oxide shows that the four types of properties depend on the pecularities of a collective of 3*d*-electrons.

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Reply to Bliznakov, Angelov, Mehandjiev, and Dyakova

Professor Bliznakov assumes that the mechanism of the CO-oxidation reaction and the nature of the adsorbed oxygen species remain unchanged when passing through the Néel temperature:

$$O_{(ads)} + CO_{(gas)} \rightarrow CO_{2(gas)}$$

and attempts to correlate his changes in E_a with the changes to be expected in the heat of adsorption of oxygen due to the destruction of ordered spins below T_N. So far as I am aware Bliznakov *et al.* have made no detailed study of the mechanism, their observations and conclusion being based (*1*) on measurements of the time of half-change of the stoichiometric mixture of CO and O_2 at low pressures in a static system, the CO_2 produced being continuously condensed into a trap cooled in liquid N_2. However it is first of all necessary to determine the reason for the discrepancy between for example the results of Mehandjiev and Bliznakov (*1*) (E_a increasing with addition of Li to NiO) at $3.0\text{–}8.0 \times 10^{-1}$ mm and those of Schwab and Block (*2*) and Dry and Stone (*3*) (E_a decreasing with addition of Li) at higher pressures. The answer may well lie in the different pressures used, which will almost certainly produce quite different surface coverages, and so cause alterations in the mechanism with a change in the rate-determining step and thus in the dependence of E_a upon concentration of dopent. Thus Bielanski *et al.* (*4*) have shown that in the region below 250°C the observed activation energy depends on the partial pressure of CO in the system. The observations of Bliznakov *et al.* add a further set of conflicting results to an already confused situation, and I do not think that their assumption of one mechanism over the whole temperature range can be justified. Thus there is no doubt (*5*) that at room temperatures CO_2 acts as a poison, and the desorption of this gas is therefore a rate-limiting step. On NiO prepared from the carbonate this is true up to at least 150°C (*6*): This is also the case for the oxide prepared from the nitrate (*7*). Much more work is needed over the whole temperature range before we can decide which apparent regularities are purely coincidental and which are fundamental. The kinetics of this reaction were discussed in some detail in 1959 (*8*) and again in 1962 (*9*) and the position has not been materially altered since then, except for the work of Teichner and his colleagues (*10*) upon their specially-prepared NiO of high surface area, which shows a number of points of difference from other preparations. The kinetics of the reaction and the heats of adsorption of the three gases depend critically on the method of preparation and pretreatment of the adsorbent.

My paper presents evidence to show that upon my preparations the chemisorption of O_2 is kinetically and energetically different