

Effect of an External Electric Field on the Oxidation of CO to CO₂ on a Nickel Oxide Catalyst

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Results are presented on the effect of an electric field on the catalytic oxidation of CO to CO₂ on nickel oxide. The catalyst was prepared by oxidation of metallic nickel. It has been found that in the conditions studied (temp 300–430°C, pressure 17–50 Torr) the reaction is of donor character.

The effect observed has been interpreted in terms of Wolkenstein's electronic theory of catalysis (1, 2). The existence of a relationship between the catalytic activity and the electronic state of the catalyst surface has been confirmed.

INTRODUCTION

The role of the electronic factor in heterogeneous catalysis on semiconductors has been considered in the electronic theory of catalysis proposed by Wolkenstein (1). According to this theory the main factor affecting the sorptive and catalytic properties of a semiconducting catalyst is the position of the Fermi level at the catalyst surface. There are several ways of changing this position. One of them, frequently employed, is a doping of a catalyst with altrivalent ions. Introduction of additions, however, brings about not only a change of the Fermi level position but also a number of uncontrolled changes in the physico-chemical properties of the catalyst. The mechanism of the incorporation of the additive, moreover, may be different at the surface and in the bulk of crystallites. This causes difficulties in the interpretation of experimental results. Thus only slight changes in the preparation method of doped catalysts may exert a profound effect on their surface and catalytic properties. The facts given above may account for the discrepancies observed in the literature concerning the correlation between the electronic factor and catalytic activity (3). An illustration of the complexity of

the problem is provided by the studies on the effect of doping of nickel oxide with chromium or lithium ions on the catalytic reaction of CO oxidation. Only by application of several methods was it possible to establish the changes of the physico-chemical and surface properties occurring on doping (4–8).

The method for changing the Fermi level position at the catalyst surface described in the present work appears to give an explanation of the role of the electronic factor in catalysis in a more simple way. The method consists in placing the catalyst under study in an external electric field of appropriate strength and then studying changes in catalytic activity occurring under the influence of this field. Already in 1958, Wolkenstein and Sandomirskii (9) and in 1966, Wolkenstein and Baru (10) published theoretical papers in which they showed the possibility of demonstration of the effect of an electric field on the chemisorption of gases on semiconductors. Since catalytic reaction involves chemisorption of the reacting gases on the catalyst surface (as one of the elementary steps), it can be expected that an electric field should also affect catalytic activity. These anticipations have been confirmed: an elec-

tric field influences both chemisorptive properties of a number of semiconductors (11–22) and some catalytic processes (23–34). Other work using the field effect (35, 36) also confirms essential conclusions of the electronic theory of catalysis on semiconductors. The studies quoted above concerning the effect of an external electric field on catalytic processes consider the problem only qualitatively. For verification of the basic assumptions of the electronic theory of catalysis it is necessary to carry out quantitative measurements: such was the aim of the work described below. The studies on the effect of an electric field were confined to a model semiconducting oxide (nickel oxide) and a model reaction (oxidation of CO to CO₂).

EXPERIMENTAL

1. Apparatus

The apparatus used has been described in detail elsewhere (37). It consisted of a conventional static set-up for catalytic studies with forced gas circulation. The main part was a reactor placed in a thermoregulated furnace which maintained the temperature constant within $\pm 0.5^\circ$. The reactor (Fig. 1) contained a cylindrical electrical condenser of capacity 32 ± 1 pF. The condenser was connected to a high-voltage source, i.e., to a stabilized supply which provided voltages up to 30 kV of positive polarization. The high voltage lead was connected to the inner plate of the condenser. Application of a voltage of 1 kV gave an intensity of $1.4 \cdot 10^5$ V/m at the position of the catalyst. The electrical network also contained an electrostatic kilovoltmeter and a microammeter to measure any leakage currents flowing through the condenser. All measurements were carried in conditions such that the leakage current was smaller than $1 \mu\text{A}$: in this way appropriate electrostatic conditions were provided. (Such conditions are indispensable for correct measurements.) This factor was also taken into account when selecting the appropriate pressure of the gases and the temperature range in which the catalytic studies were performed.

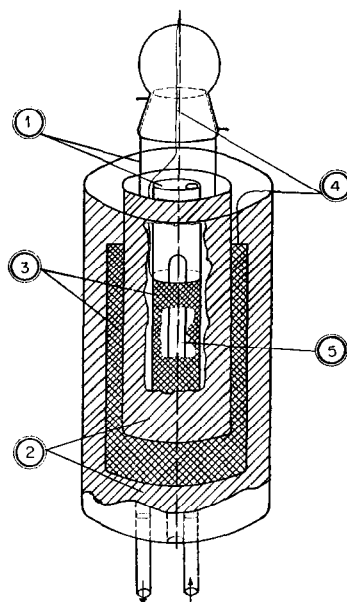


FIG. 1. Schematic diagram of reactor used in studies of the effect of an external electric field on the rate of oxidation of CO to CO₂ on nickel oxide. (1) Quartz casing; (2) cavenite shield; (3) plates of cylindrical condenser; (4) high voltage leads in PTFE insulation; (5) cavenite pocket for control thermocouples and resistor Pt 100 Ω .

2. Preparation of Catalyst and Reacting Gases

The inner plate of the condenser described above (cf. Fig. 1) was a nickel foil oxidized on the surface. Oxidation of nickel foil of purity 99.99% was carried out at 1300°C in a stream of oxygen for 4 hr. Following Mrowec (38) the oxide layer obtained under such conditions was black and its thickness was 60 μm (the thickness of the foil was 0.01 mm). It is worth mentioning that catalysts obtained under other conditions, e.g., at temperatures of 800 or 600°C, were inactive.

Oxygen and carbon monoxide were obtained, respectively, by thermal decomposition of KMnO₄ and dehydration of formic acid with sulfuric acid.

3. Pretreatment of the Catalyst and Procedure of Measurements

The catalyst (nickel oxide) prepared in the manner described above was placed in

a reactor and the system was heated to the reaction temperature. The pretreatment (standardization) of the catalyst consisted of evacuation in the reaction chamber at this temperature to a pressure of 10^{-4} Torr. The system was then washed with oxygen and again evacuated. After about 2 hr oxygen at 20 Torr pressure was introduced to the reaction chamber for 17 hr. The pressure of O_2 was then lowered to that required and CO was then admitted, thus commencing the reaction. In all experiments the gas composition was selected in such a way as to ensure an excess of oxygen with respect to the stoichiometry of the reaction: $CO + \frac{1}{2} O_2 \rightarrow CO_2$. This ensured constant composition of NiO close to the surface during the catalytic reaction. The reaction rate was followed by measuring the pressure changes with a dibutyl phthalate manometer. The reaction product (carbon dioxide) was removed by freezing at liquid nitrogen temperature. After reaching a certain value of conversion the high voltage was applied to the condenser plates and the pressure changes were again registered. The voltage applied was then changed or switched off, the pressure being measured all the time. In this way the reaction was followed both in the absence of an electric field and in the presence of a field of known intensity.

4. Results of the Measurements

Kinetic measurements carried out at 300–430°C indicate that in the pressure range under study (17–50 Torr) oxidation of CO to CO_2 (in the presence and in the absence of the electric field) is of zero order with respect to oxygen and of first order with respect to carbon monoxide. This result is in accordance with the majority of the literature data. The activation energy of this reaction derived from the Arrhenius equation is close to 60 kJ/mole without an electric field and about 40 kJ/mole with an electric field ($\sim 10^6$ V/m).

Figure 2 shows schematically the time dependence of the conversion. The arrows indicate the moments of switching on and off the high voltage. The results obtained

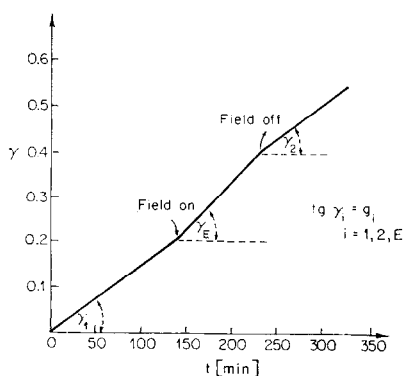


FIG. 2. Typical rate curve for CO oxidation. α , Conversion; t , time; $\operatorname{tg} \gamma_i = q_i$, reaction rate; arrows, moments of switching on and off of high voltage on the condenser plates.

in these measurements are listed in more detail in Table 1.

It has been found that in all cases the presence of the electric field (of positive polarization), inducing in the close-to-surface layer of NiO a positive space charge, causes acceleration of the catalytic process. The effect observed is larger the higher the intensity of the electric field. It is also larger the lower the reaction temperature.

INTERPRETATION OF THE RESULTS

According to the electronic theory of catalysis advanced by Wolkenstein the rate of oxidation of CO to CO_2 on nickel oxide (1, 2) may be described by the following expression:

$$g(F_s^-) = KP_{CO} \exp \left[-\frac{E_d - F_s^-}{kT} \right], \quad (1)$$

where g —reaction rate

F_s^- —position of the Fermi level at the catalyst surface with respect to the bottom of the conduction band

K —constant

P_{CO} —pressure of carbon monoxide

E_d —position of an energy level in the forbidden energy gap

k —Boltzmann constant

T —Temperature.

The high voltage of positive polarization applied to the condenser plates during the

TABLE 1
DEPENDENCE OF THE RELATIVE CHANGE IN
CATALYTIC ACTIVITY ON THE INTENSITY OF
THE ELECTRIC FIELD^a

| <i>T</i> [°K] | <i>U</i> [kV] | <i>g_E/ḡ^b</i> |
|------------------|------------------|-------------------------------------|
| 573 | 2 | 1.14 |
| | 6 | 1.41 |
| | 8 | 1.57 |
| 623 | 3 | 1.15 |
| | 4 | 1.18 |
| | 4.5 | 1.21 |
| | 5 | 1.21 |
| | 5.5 | 1.32 |
| 623 | 6 | 1.27 |
| | 8 | 1.45 |
| | 8.5 | 1.42 |
| 673 | 6 | 1.14 |
| | 9 | 1.27 |
| | 10 | 1.48 |
| 703 | 6 | 1.14 |
| | 9 | 1.27 |
| | 10 | 1.31 |

^a *T*—temperature; *U*—applied voltage on the condenser plates; \bar{g} —average rate of reaction without the electric field; g_E —rate of reaction with the electric field.

$${}^b \bar{g} = \frac{g_1 + g_2}{2} \quad g_E = tg_{\gamma E} \text{ (cf. Fig. 2).}$$

experiment gave rise to excess positive space charge in the near-to-surface layer of the catalyst. Energy bands (at the surface) are then additionally curved. The Fermi level position is then given by the equation

$$F_s^-(E) = F_s^- + V_s(E), \quad (2)$$

where $F_s^-(E)$ —position of the Fermi level as a function of the electric field intensity

E—intensity of the electric field

F_s^- —position of the Fermi level in the absence of electric field

$V_s(E)$ —bending of the energy bands due to the electric field

(index "s" indicates that these parameters pertain to the catalyst surface).

The rate of the reaction under study in

the presence of the electric field $g(E)$ can be given by the following equation:

$$g(E) = KP_{CO} \exp \left\{ -\frac{E_d - [F_s^- + V_s(E)]}{kT} \right\} \quad (3)$$

It follows from Eq. (3) that the reaction rate increases when the catalyst is placed in an external electric field of positive polarization ($V_s(E) > 0$). This is in agreement with the results obtained (Table 1). This character of the changes of the reaction rate indicates in the terms of the electronic theory a donor character for the process.

The results obtained allow a quantitative interpretation of the field effect. If we assume that the rate of the catalytic reaction is a measure of the catalyst activity then the relative change in activity due to the electric field may be described as:

$$a(E) = \frac{g(E) - g(0)}{g(0)}, \quad (4)$$

where $a(E)$ —is the relative change in catalyst activity due to electric field

$g(E)$ —reaction rate in the presence of the electric field given by Eq. (3)

$g(0)$ —reaction rate in the absence of the electric field determined by Eq. (1) or Eq. (3) at $E = 0$.

Substituting Eqs. (1) and (3) into Eq. (4) we obtain

$$a(E) = \exp \left[\frac{V_s(E)}{kT} \right] - 1. \quad (5)$$

Equation (5) is true when K and E_d are independent of the values of the electric field which seems fully justified on the basis of data given in (1). The same Eq. (5) was obtained by Wolkenstein (cf. (2) p. 309).

The bending of the energy bands $V_s(E)$, which affects the catalyst activity, is a relatively complex function of the intensity of the electric field and the electronic properties of a given semiconductor. To a first approximation this dependence may be described by the following formula:

$$V_s(E) = ELq, \quad (6)$$

where L —is the Debye screening length
 q —elementary charge.

On the basis of formulas (5) and (6) it was possible to derive theoretically the dependence of the relative change in catalytic activity (a) as a function of the intensity of the electric field (E). To determine the screening length, the concentration of current carriers, and the density of states the following simple formulas were used (39, 40):

$$L = \left[\frac{\epsilon\epsilon_0 kT}{q^2 p} \right]^{1/2} \quad (7)$$

$$p = N \left[\frac{m^{(N)}}{m} \right]^{3/2} \exp \left[-\frac{F^-}{kT} \right] \quad (8)$$

$$N = 2[2\pi m kT/h^2]^{3/2}, \quad (9)$$

where ϵ, ϵ_0 —dielectric constant of the sample
 and of vacuum, respectively

p —concentration of current carriers

N —density of states function

h —Planck's constant

$m^{(N)}$ —effective mass of density of states
 which after (40) was taken as
 equal to m , i.e., to the rest mass
 of an electron

F^- —position of the Fermi level with
 respect to the bottom of the conduction
 band.

We use Eqs. (7), (8), (9) for this calculation because the Debye screening length in NiO (about 300 Å) is three orders smaller than the thickness of the layer of NiO investigated (60 μm). After substituting (6), (7), (8) into (5) we obtain the final formula in the following form:

$$a(E) = \exp \left\{ \frac{(\epsilon\epsilon_0)^{1/2} h^{3/2} E \exp \left[\frac{F^-}{2kT} \right]}{2(2\pi m^{(N)})^{3/4} (kT)^{1/4}} \right\} - 1. \quad (10)$$

The results of the calculations are given as curves 1–4 in Fig. 3. The value of the dielectric constant of nickel oxide was taken after (41) as equal to 12. The value of the Fermi level position in NiO was adjusted to the experimental data obtained. The following values for the Fermi

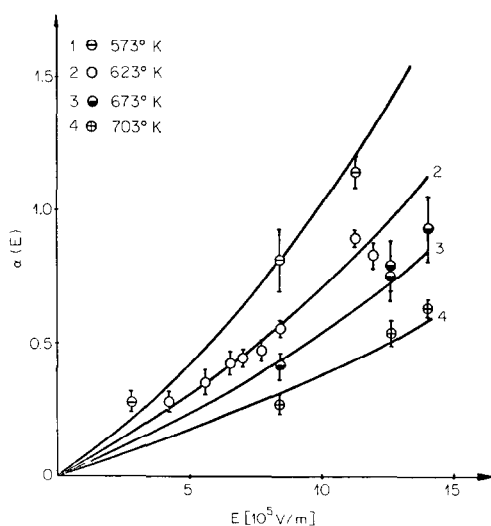


Fig. 3. Dependence of the relative change of catalyst activity on the intensity of the electric field. $a(E)$, relative change of activity; E , intensity of electric field; (1–4), theoretical curves of the observed effect for the temperatures marked on the plot.

level position were employed in calculations: 0.376, 0.402, 0.421, 0.425 eV for the temperatures of 573, 623, 673, 703°K, respectively. They are in agreement with the results quoted by other authors. Mitoff (42) gives the value of 0.42 eV at 673°K and Ziólkowski (43) the same value for 673°K and 0.35 eV for 573°K.

In calculations of the changes of the activity of nickel oxide caused by the electric field from the experimental data obtained, formula (9) was used, its numerator being multiplied by 2. By doing this we have taken into account the fact that only half the catalyst surface available for the reaction was inside the condenser. The other half of the NiO surface covered the inner surface of the plate of the nickel condenser (Fig. 1), and thus was screened by nickel.

As follows from a comparison of the curves given in Fig. 3 with the experimental points, the anticipations of the electronic theory are correct. The suggested dependences are fulfilled not only qualitatively but also with a good approximation quantitatively.

In the case of the investigations de-

scribed a high-voltage generator of positive polarization was applied. In the case of negative polarization a decrease of the rate of the reaction can be expected. The change of the activity of the catalyst in this case will also be described by Eq. (5) (2, 44).

It should be added that the curves in Fig. 3 do not imply an unlimited increase of the activity due to an electric field. The limiting value of the bending of the energy bands depends on the electronic properties of a given semiconductor. After an initial increase saturation is reached and further increase in the intensity of the electric field does not cause an increase in the reaction rate. This fact was not considered in the calculations because the construction of the apparatus used in the present study did not allow us to obtain sufficiently high electric fields to observe saturation.

The effects observed cannot be related to processes of ionization of molecules in gas phase since:

1. application of a high voltage to inactive catalyst does not produce a change of pressure in the reaction system

2. no drop of oxygen pressure due to, for instance, formation of ozone has been observed

3. if the observed effect of the influence of an electric field on activity was due to processes of ionization of gases it should then increase with temperature: in fact the inverse behavior was observed in the experiments.

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