# Physical Chemistry

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## Abstract

## Full Text

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# On the Origin of the Presorption Effect and Some Other Anomalies of the Catalytic Oxidation of CO on Oxide Semiconductors

The oxidation of CO on oxide semiconductors (s.c.) is one of the most extensively studied catalytic reactions. However, its kinetics and the character of the influence of various factors on the catalytic activity of these s.c. have peculiar features which, despite the introduction of special hypotheses and models, have not made it possible to construct a stage scheme free of contradictions. As is shown below, some of these contradictions disappear when the concepts and regularities of the electronic kinetics of semiconductor catalysis are applied to CO oxidation.

**Presorption effect.** On $MnO_2$ ($^1$), NiO ($^2$), and a number of other oxides ($^3$), the appearance of the ability to catalyze CO oxidation is most closely connected with its activated adsorption, which is often accompanied by chemical reduction of the surface of the s.c. Not only do the temperature regions of catalysis and chemisorption coincide, but also the values of the activation energies $E_{\text{cat}}$ and $E_{\text{chem}}$ of both processes ($^{1,2}$). However, for chemisorption carried out in the absence of oxygen on active samples, even the initial rates $w_0$ are considerably lower than the rate of the catalytic reaction ($^{1,2,4}$). This did not permit completed chemisorption to be regarded as the rate-controlling stage of catalysis.

Chemisorbing, CO lowers the work function $\varphi$ from $n$- and $p$-semiconductors, while $O_2$ raises $\varphi$ ($^5$). In the presence of mixtures $CO + O_2$, intermediate values of $\varphi$ are obtained, indicating a partial mutual compensation of charge. Thus, in one experiment the introduction of $O_2$ increased $\varphi$ of nickel oxide by 0.35 eV, the introduction of CO decreased $\varphi$ by 0.20 eV, while the introduction of a mixture of the two gases increased $\varphi$ by 0.24 eV. According to the band model this means that oxygen decreases the band bending caused by self-charging of the surface during CO chemisorption, lowering the surface Fermi level. This should reduce the free energy of formation of positively charged surface transition complexes ($|k|$), including $CO^+_{\text{chem}}$ ($^6$), by

$$\Delta F = |e\Delta V_\Sigma| \simeq |\gamma e \Delta\varphi|. \qquad (1)$$

In equation (1), $e$ is the electron charge; $\Delta V_\Sigma$ is the change in the total diffusion

Figure 1 diagram

Figure 1: Figure 1 diagram

potential of the surface; $\gamma$ is a numerical coefficient close to 1, taking into account the contribution to $\Delta\varphi$ of the molecular dipole component and the influence of $O_2$ on the position of the Fermi level in the bulk of the s.c. $(\mu_-)$.

As experiment shows, with such positive acceleration caused by a decrease in charging, the observed change in $E$, $\Delta E_{\text{chem}} \simeq |\gamma e \Delta\varphi|$ ($^7$). The increase thereby caused in the rate constant $k$ and $w$, owing to kinetic compensation, reaches only $\exp\{[(1-\alpha RT)\Delta E_{\text{chem}}/RT]\}$, where $0 < \alpha < 1$ is the coefficient from the equation

$$\ln k_0 = \text{const} - \alpha E. \tag{2}$$

The best catalysts for the low-temperature oxidation of CO are hole-type semiconductors; therefore, chemisorption of $O_2$ enriches them with current carriers, and, upon removal of the $CO_2$ formed during catalysis, in the middle range of $O_2$ coverages,

$$\Delta\varphi_{O2} \simeq a \ln \theta/\theta_0 = a \ln \theta^*, \tag{3a}$$

$$\Delta E \simeq b \ln \theta^*, \tag{3 }$$

$$w \simeq w_0 \theta^{*\beta}, \tag{3 }$$

where $\theta$ are the current, and $\theta_0$ the initial, specific coverages with respect to $O_2$; $\theta^* > 1$ is their ratio; $\beta = -b/RT$. In irreversible adsorption, $O_2$ increases $k_0$,

**Fig. 1.** Influence of adsorption of the same amount of acceptor molecules on surface zones:
*a*—without initial bending, —with initial upward bending, —with initial downward bending; $\Delta\varphi > \Delta\varphi_a > \varphi$

whereas in reversible adsorption, owing to the dependence $\theta = f(p)$, it leads to the appearance of a concentration factor $f_1(p_{O2}) > 1$. The form of $f_1$ is determined by the charging isotherm $\Delta\varphi = f_2(p_{O2})$ in the given range of $p_{O2}$. When

$$\Delta\varphi \simeq cRT \ln p/p_0, \tag{4a}$$

$$\Delta E \simeq \delta RT \ln p^*, \tag{4 }$$

$$w \simeq w_0 p^{*\delta}, \tag{4 }$$

where $p^* = p_{O2}/p_{0O2}$. In both cases (3 ) and (4 ), the observed chemisorption $E$ of CO does not change upon addition of $O_2$. Under this interpretation, the observed "preadsorption effect" is due to the positive modifying action of adsorbed oxygen. The influence of an acceptor gas on the bending of the zones increases in the presence of an initial downward bending (Fig. 1) and decreases in the presence of an upward bending of them ([8]). Therefore the modifying action of $O_2$ should be enhanced by introducing additives that lower the work function, and should be reduced by introducing additives that raise it. Apparently, this is the origin of the observed disproportionately strong decrease in the rate of CO chemisorption on ZnO preparations containing $Li^+$ in the lattice ([9]). If this is correct, then the introduction of $SO_4^{2-}$, as well as oxides of trivalent metals that increase $\varphi$ ([7]), should bring the rates of CO chemisorption and catalysis closer together, which also, apparently, is true.

Let us note that, with such an interpretation, in principle, at a sufficiently low total pressure of the reacting mixture and at sufficiently high temperatures the preadsorption effect should disappear completely. The same result should be obtained by comparing the rates of chemisorption and catalysis under an artificially created equality of zone bending or upon compensating it with an electric field. The experimentally observed values of $E_{\text{cat}}$ should coincide with the initial values of $E_{\text{chem., obs.}}$, since during chemisorption self-charging continuously increases, shifting the distribution, and at the same time, because of biographical inhomogeneity, the controlling chemisorption band ([10]) shifts along the distribution (see Fig. 2), and usually at least partial restoration of the surface takes place. These effects are absent during the stationary course of catalysis in a flow, when a constant chemical composition is maintained with a sufficient excess of $O_2$.

In this case $\Delta V_\Sigma$ and $\Delta\varphi$, which, besides $O_2$, are also affected by $CO_2$ and the Garner $CO_3^-$ complexes ([11]), are constant, the controlling band is immobile, and reduction of the catalyst is eliminated.

**The poisoning action of water.** Catalytic oxidation of CO is characterized by a strong inhibiting action of water vapor ([12]), whose isobars correspond to surfaces with changing activation energies ([10]). Attempts have been made to explain this by adsorption blocking, by the formation of surface and bulk hydroxyl forms, etc. According to the measurements of V. I. Lyashenko ([13]) and others, adsorption of $H_2O$ charges the surface of oxide semiconductors positively, i.e., $\Delta V_\Sigma^{H_2O}$ has the same sign as $\Delta V_\Sigma^{CO}$. This should cause inhibition with increasing $F$ and $E$ by $\gamma e \Delta V_\Sigma^{H_2O}$ (Fig. 2) and a decrease in the rate by a factor of $\exp[-(1-\alpha' RT)\Delta E/RT]$. The large magnitude of the effect may be a simple consequence of the strong adsorbability of water. Similar effects should also be exerted by other well-adsorbed electron-donor molecules—for example, liquid olefins, benzene, and acetone. Under ordinary conditions the action of $CO_2$ is

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

weaker (14) because of its lower adsorbability; in addition, it may be complicated by an increase in the surface concentration of the negatively charged Garner carbonate ion-radical.

**Fig. 2.** Change in the distribution and displacement of the controlling band upon charging on a broadly inhomogeneous surface. c. b. 1—the controlling band for chemisorption and catalysis without charging; c. b. 2—for catalysis and the onset of chemisorption upon charging with $H_2O$; c. b. 2 chem.—for advanced chemisorption of CO.

**Modifying additives.** Small additions of oxides of metals of another valence may exert a strong effect on the catalytic activity of oxides. As catalysts for the oxidation of CO, mainly NiO and ZnO with additions of oxides $Me^{I}$, $Me^{III}$, and partly also $Me^{II}$, have been studied. These systems are commonly regarded as solid solutions, although the formation of the latter has been proved only for $Li_2O$, MgO, and ZnO in NiO (14). In the simple band model, changes in the activation energy of electrical conductivity indicate the direction and magnitude of the displacement of the bulk Fermi level, which, at unchanged band bending, should be accompanied by an equal in magnitude and opposite in sign change in the work function. Taking CO chemisorption in the form $CO^+$ as the controlling step, we may expect an increase in $E_{\text{chem}}$ and $E_{\text{cat}}$ when $\mu_-$ is shifted upward, and a decrease in both $E$ values when $\mu_-$ is shifted downward. For $p$-semiconductors this corresponds to a symbatic relation, and for $n$-semiconductors to an antibatic relation of the change in $E_{\text{chem}}$ with $E_\sigma$.

**Fig. 3.** Dependence of the activation energy of the catalytic reaction $E_{\text{cat}}$ for CO oxidation on the change in the activation energy of electrical conductivity $E_\sigma$ and the change in work function $\Delta\varphi$, caused by introducing additives into oxides of zinc and nickel.

The experimental dependences are quite different and very complex, as is seen from Fig. 3. In particular, Li in NiO and ZnO causes an increase in $E_{\text{chem}}$, although in both cases it lowers the position of $\mu_-$.

To explain the data of Schwab and Block (15), Hauffe (16) had to assume a change in the controlling stage and introduce the additional hypothesis of the participation in the process of special surface electron traps. However, our results do not fit within the framework of this theory and other accepted models. These difficulties are fully removed by measur—

measurements of the work function (17), which showed that the changes $\Delta\varphi$, not only in magnitude but also in sign, do not coincide with those expected from measurements of $E_\sigma$. At the same time, an almost complete correlation is observed between the changes in $\varphi$ and $E_{\text{cat}}$ (see Fig. 3), and in all cases a decrease in $\varphi$ is accompanied by an increase in $E$, and an increase in $\varphi$ by a decrease in $E$, as should be the case when the stage with a positively charged transition complex is controlling.

**Kinetics.** An analysis of the kinetic anomalies lies beyond the scope of the present article. The most difficult of them—the stable half-orders with respect to the initial [CO]—can perhaps be explained by the appearance, under certain conditions in the adsorption equilibria on the surface, of square roots of the concentrations of the adsorbing nondissociating gas. However, in order to preserve, under such an approach, a single controlling stage for all systems at first and half orders, it is additionally necessary to allow for the possibility of inversion of the sign of the carriers in the near-surface layer and for participation in the process of the chemisorption of physically adsorbed CO molecules, i.e. a two-stage chemisorption of $CO \rightarrow CO_{\text{phys}} \rightarrow CO_{\text{chem}}$. The branching of chemisorption and catalysis adopted in the presorption mechanism disappears, but the branching of the catalytic utilization of $CO_{\text{chem}}$ and its chemical reaction with the catalyst, leading to reduction of the surface, is retained. The meaning of the lower limit of catalytic oxidation (18) also changes. However, the available data are insufficient to exclude the occurrence of controlling chemisorption of CO upon impact with the surface. In both cases the weak dependence of $w$ on the content of $O_2$ in the mixture above the "lower limit" is apparently associated with saturation of the active part of the surface with oxygen already at small $pO_2$.

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