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Surface State Additives in the Catalytic Oxidation of Carbon Monoxide*

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A catalyst system with zinc oxide as a support and redox couples deposited as additives on the surface was examined as a catalyst for CO oxidation. The Fermi energy of the system was controlled by these "surface state" additives, as determined by a study of the electrical properties of the ZnO. Evidence is presented that the rate of CO oxidation depends on such control of electron availability. Manganese and chromium additives, with a low "surface state energy," cause an active catalyst, while additions of iron cyanide, with a high "surface state energy," lead to an inactive catalyst. Evidence is presented that the low temperature form of adsorbed oxygen, probably O_2^-, is the active form for CO oxidation. A low Fermi energy increases the ratio of the low temperature to high temperature form and thus increases the catalytic activity. The experiments illustrate a new experimental technique, where the electrical properties of a supported catalyst are monitored by using a suitably chosen support.

INTRODUCTION

In those cases in which electron transfer at the catalyst/reactant interface plays a dominant role in the course of a catalytic reaction, control of the electron availability (electrochemical potential of electrons) at the surface will affect the catalytic process. In earlier reports we have discussed the use of electronically active surface additives to control both the electron availability (*1*) (the surface Fermi energy) and the concentration of reactant ions at the surface, and discussed from a theoretical point of view how such surface additives could act as promoters for a catalytic reaction (*2*).

In more recent work (*3*), we have studied various redox couples on ZnO, and determined the electronic energy levels contributed by such additives, by considering the additives as surface states at the ZnO surface. From such experiment and theory it was concluded that these energy levels do control the electron availability and surface Fermi energy. In the research to be described here we have attempted to utilize these concepts in a study of the rate of a redox reaction, the oxidation of CO by oxygen.

The oxidation of CO was chosen as the test reaction because there is substantial evidence in the literature that the reaction involves electron transfer, at least on ZnO, and that the density of charged oxygen ions is a dominant parameter. Chon and Prater (*4*) find that O^- is the form of oxygen on ZnO at the reaction temperature, and thus conclude it is probably the active species. Doerffler and Hauffe (*5*) suggest both O^- and O_2^- are active forms of oxygen. Sancier (*6*) interpreted spin resonance measurements in terms of the reaction at room temperature of CO with two forms of sorbed oxygen, identified as O^- and O_2^-, and concluded the rates were very different for the two forms. On the other hand, Amigues and Teichner (*7*) suggest the form

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of reactive oxygen is neutral atoms because, under their conditions, the rate of oxidation varies with oxygen pressure. However, by conductance changes they observe an interaction between CO and some negative oxygen ion.

The influence of electronically active surface additives on such an electron transfer reaction can arise in three ways:

a. It can control the total reservoir of electrons available at the surface. For example if O_2^- is a critical intermediate in a reaction, a deposit of a reducing agent R as the surface additive can result in the reaction

$$\mathrm{R} + \mathrm{O}_2 \rightleftarrows \mathrm{Ox} + \mathrm{O}_2^-, \qquad (1)$$

where Ox is the oxidized form of the species R. In this sense the surface state is acting as a reservoir of electrons, permitting more adsorbed species O_2^- than would be possible on the semiconductor with no additive. For each available R molecule, one molecule of O_2^- can be formed. The molecule may be adsorbed either on a crystallite of the additive or on the substrate.

b. The electrochemical potential for electrons can be controlled. Depending on whether the species R is a strong reducing agent or not (in other words, depending on its electronic energy level, or "surface state energy") a given reactant species can or cannot be reduced. For example, if the surface state energy of R is low, the Fermi energy will be low, and only reactants which are very strong oxidizing agents will become reduced. At equilibrium the Fermi energy is the same both in the substrate and in the additive crystallites, so the Fermi energy, as measured in the substrate, describes the whole system. Thus we can use electrical measurements and surface state theory to monitor this behavior.

c. The additive can act as an active center for adsorption of a reactant, forming some active complex with reactant gases. This is the dominant effect assumed for a surface additive such as platinum on silica. In the present experiments we have chosen additives on the basis of their electron activity rather than on the basis of their ability to form complexes. However, it is impossible to rule out the possibility of such complexes. Therefore, the experimental results must be examined for indications that catalytic activity due to surface additives arises from (a), (b), (c), or to combinations of these effects.

The theory of one-equivalent surface states (*1*) predicts that the electrochemical potential for electrons, the Fermi energy E_F, for a catalyst system of equilibrium will be given by

$$E_F = E_t + kT \ln[\mathrm{R}]/[\mathrm{Ox}], \qquad (2)$$

upon deposition of a reducing agent R and the corresponding oxidizing agent Ox to the surface in the concentration ratio [R]/[Ox]. Here E_t is a measurable energy parameter associated with the additive redox couple. For convenience in this paper we will define E_t as described by Eq. (2) as the "surface state energy" of the additive redox couple, ignoring in these qualitative discussions the complications of surface state band formation and of Franck-Condon effects (*2*).

In principle, from (2) we can shift the Fermi energy about ±0.2 eV from the value E_t by changing the concentration ratio [R]/[Ox] of the additive. To obtain greater variation in E_F, we use different redox couples with different values of E_t. On ZnO we have studied several redox couples (*8*) and found the values of E_t (relative to E_c, the energy of the ZnO conduction band) as given in Table 1.

The objective of the present study was to vary the equilibrium Fermi energy of the catalyst system by using various redox couples as indicated by Table 1, and to explore the possibility of an optimum Fermi energy E_F for the CO oxidation reaction.

EXPERIMENTAL METHODS

To prepare a catalyst pellet, 2 g of SP-500 ZnO (New Jersey zinc) powder were suspended in 10 ml of aqueous solution containing the surface additive and subsequently filtered through a Buchner funnel. Pellets were also made with 2 g of α-Al_2O_3 (1 m^2/g) and 10 g of a low specific area quartz powder. The solution, 0.1 *M* in

TABLE 1

ENERGY LEVELS[a] OF SURFACE ADDITIVES ON ZnO, $E_c - E_t$(eV)

Experimental method	$Fe(CN)_6^{4-}$ $Fe(CN)_6^{3-}$	MnO_2^{2-} MnO_4^-	O_2^- O_2	Cr^{2+} Cr^{3+}
Surface potential	−0.1	−0.85	−0.9	−1.1
Resistivity	−0.05	−0.45	No value[b]	−0.6

[a] Probable error estimated as ±0.15 eV.

[b] Measurement not useful for volatile species.

KOH, contained various concentrations of the additives listed in Table 1 in the form of potassium or nitrate salts. The chromium nitrate, the iron cyanides and the potassium permanganate were reagent grade materials, the potassium manganate was prepared by heating potassium permanganate in air to 200°C to permit the reaction

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2\uparrow. \quad (3)$$

The total additive retained by the catalyst was evaluated by measuring the water retention and assuming no specific adsorption. For example, approximately 0.6 ml of solution was retained by 1 g of ZnO after filtering. In the case of ZnO the concentrations are reported in terms of molecules deposited/cm^2 where we assumed a catalyst area of 2 to 3 m^2/g. The deposition of chromium differed in that: (a) For high concentrations it was deposited (on any of the oxides) from an alcohol solution, since $Cr(NO_3)_3$ is only soluble below about $5 \times 10^{-3}\,M$ in an 0.1 M KOH aqueous solution. For low concentration, an aqueous solution was used. The solvent did not appear important. (b) During deposition on ZnO (but not on SiO_2 or Al_2O_3) essentially all available chromium becomes adsorbed; the remaining alcohol becomes colorless. Thus the surface coverage with chromium on ZnO was estimated assuming complete adsorption, for all concentrations used.

Mixed additives of ferrocyanide and chromium were of interest because there is no apparent reaction between the ions in aqueous solution (a solution phase reaction occurs between manganate and ferrocyanide with very low ferrocyanide concentrations so a mixed ferrocyanide/manganate additive is not possible at high concentration). Samples with mixed chromium and iron cyanide additives were prepared by first depositing the chromic ion, flushing out the excess alcohol with water and then after about 10 min, depositing the ferrocyanide from aqueous solution in the usual way.

The sample was dried in air for at least 16 hr at a temperature of about 140°C, then the resulting cake was gently broken using a mortar and pestle, and the powder was pressed into a pellet. This pellet was heated for 1 hr in the reaction chamber under vacuum (approx. 10^{-5} Torr) at a temperature of 150°C to dry the sample further. Then the temperature was increased to the reaction temperature (250°C) and when the outgassing was completed, the reactants were admitted, normally first CO followed by O_2 a few seconds later. For the "blank" measurements a sample of ZnO was pretreated in a similar way except that the surface additive was absent from the aqueous solution.

A circulating reactor was used, with a total volume of about 1 liter. The CO_2 pressure was monitored by passing sample aliquots over a silica GLC column. The limit of detection was about 0.02 Torr CO_2.

All results to be described were obtained with a catalyst temperature of 250°C. It was found in a few tests that the CO_2 pressure in the range observed did not affect the rate, so no attempt was made to remove the small amounts of CO_2 produced.

MEASUREMENTS OF CATALYTIC ACTIVITY

In the absence of additives the rate of CO oxidation with the blank ZnO catalyst was found to be 0.1 Torr/min. With 2 ×

10^{15} molecules/cm^2 of ferrocyanide deposited on the catalyst surface (from a solution 0.1 *M* in ferrocyanide) about the same oxidation rate was observed. For the other additives listed in Table 1 the rate of CO-oxidation was increased, as shown in Fig. 1, up to 100-fold at high concentration of manganese or chromium. The results of Fig. 1 show the rate of CO_2 formation as a function of additive concentration relative to the rate found for the blank (0.1 Torr/min). The oxygen and CO pressure are each 380 Torr in these measurements.

The initial rate of CO_2 production differed from the steady state rate, depending on the order of reactant admission, and depending on the time the sample was in the one reactant before the other was admitted. A very extreme example of this is shown in Fig. 2, curve b. Here the pressure of CO_2 as a function of time is shown for a sample prepared with a combined chromium and ferrocyanide additive. When CO is admitted first (solid triangles) the rate of CO_2 formation reaches a steady state value rapidly. Because of this observation, CO was admitted first in the rest of the reported experiments. With chromium as the sole additive (curve a of Fig. 2) the oxidation rate is insensitive to whether CO or O_2 is admitted first.

Figure 3 shows the CO_2 formation rate with the chromium additive and with a mixed chromium/ferrocyanide additive. The CO pressure is shown on the abscissa; the oxygen pressure is sufficient to bring the total pressure to 1 atm. No significant oxygen pressure dependence was found. It is notable: (a) the rate is proportional to CO pressure over a significant range, then becomes independent of the pressure of the reactants; and (b) the rate is decreased by a factor of 7 when about 10% ferrocyanide

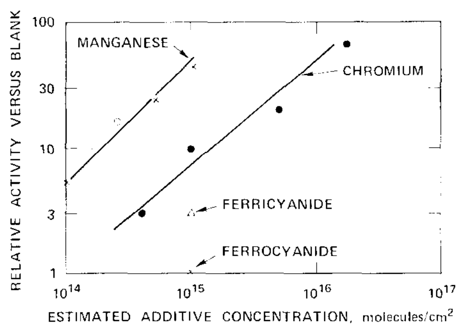

FIG. 1. Rate of CO_2 generation as a function of additive and additive concentration: (○) with K_2MnO_4; (×) $KMnO_4$; (●) $Cr(NO_3)_3$; and the iron cyanides are in the form of potassium salts. The CO and O_2 pressure are each 380 Torr.

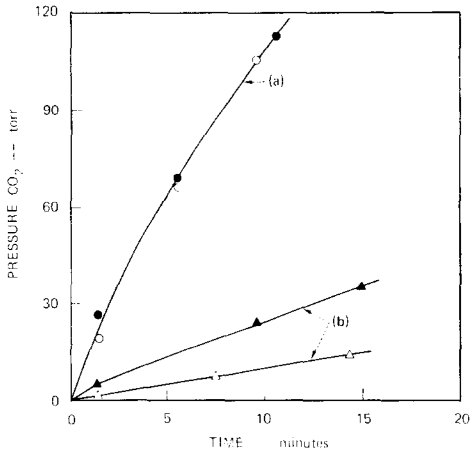

FIG. 2. CO_2 pressure vs time, $p_{CO} = 560$; $P_{O_2} = 200$ Torr: (●▲) pre-anneal for 10 min in 200 Torr CO; (○△) pre-anneal for 10 min in 25 Torr O_2; (a) additive 1.6×10^{16} Cr^{3+} molecules/cm^2; (b) additive 1.6×10^{16} Cr^{3+}/cm^2 + 1.6×10^{15} Fe^{2+}/cm^2.

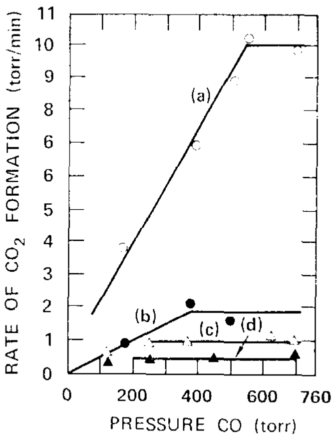

FIG. 3. Rate of CO_2 formation with varying oxygen/CO mixtures: Additives: (a) Cr, 10^{16} molecules/cm^2; (b) Cr + Fe ($10^{16}/10^{15}$); (c) Cr, 10^{15} molecules/cm^2; (d) Cr + Fe ($10^{15}/10^{15}$).

is deposited on the active chromium promoted sample.

A few measurements with alumina and with silica as the support have also been made. In these studies it was found that with both permanganate and chromic nitrate, the oxidation rate is approximately the same for a given total additive concentration and independent of the support, Al_2O_3, SiO_2, or ZnO.

OXIDATION STATE OF ADDITIVE

The measurement of the surface state energy for the adsorbed species should to some extent make it unnecessary to know the chemical form of the additives. However, such measurements only serve in lieu of a measure of the electrochemical potential for electrons. They do not indicate the reservoir of electrons available. To determine the availability of electrons (or of empty levels capable of oxidizing reactants), we need to know the concentration of the reduced form of the additive.

The oxidation state of the additive is unfortunately not known in these measurements. We can assume that independent of whether manganate or permanganate is added from solution, the additive is dominantly manganate and MnO_2 in accordance with Eq. (3) by the time we reach reaction temperature of 250°C. We make this assumption in our analysis of the density of manganate in Fig. 1.

There is some evidence that the chromic nitrate disproportionates to Cr^{2+} and Cr^{6+} when adsorbed. It is found that if ferrocyanide is added to the zinc oxide immediately after chromic nitrate is adsorbed, the ferrocyanide becomes yellow, consistent with oxidation to ferricyanide by the chromic ion. However, if the chromic nitrate is adsorbed for about 5 min before the ferrocyanide is added, the ferrocyanide is no longer oxidized. During the 5 min the ZnO turns from blue to pink, indicating a chemical change in the chromium, possibly disproportionation.

There is no reason to believe any large fraction of the ferrocyanide or ferricyanide changes in oxidation state during deposition.

ELECTRICAL MEASUREMENTS OF THE CO/O_2 REACTION: MECHANISM OF CO OXIDATION

In order to analyze the influence of surface state additives on the CO oxidation it was necessary to explore the mechanism of the CO oxidation reaction. Thus, the reaction of CO with oxygen was examined qualitatively by its influence on resistivity. Since our catalytic reaction chamber was not equipped with electrical contacts, the resistivity measurements had to be made separately in a different system as described earlier (*3*), using pressed, indium-doped ZnO pellets.

According to Chon and Pajares (*8*) there are two forms of oxygen, O_2^- and O^- on the zinc oxide surface. The dominant form depends on the temperature. If the temperature is over 225°C, the oxygen is adsorbed in the high temperature form, identified by Chon and Pajares as O^-. If the temperature is 175°C or less, the oxygen is adsorbed in the low temperature form, identified by Chon and Pajares as O_2^-.

We identified the low temperature form of oxygen as the apparent active form for the CO oxidation as follows. A low temperature form of oxygen was adsorbed on a ZnO pellet with a Cr + Fe surface additive by: (i) admitting CO at about 200°C to remove previously adsorbed oxygen; (ii) outgassing the CO at 10^{-6} Torr at 250°; (iii) cooling to 175°; and (iv) admitting 25 Torr oxygen. The resistance of the pressed pellet after step (iii) was a few ohms [see also Ref. (3)], but rapidly increased to the order of $10^6\ \Omega$ due to oxygen adsorption. Then (v) the system was evacuated to 10^{-6} Torr, and 50 Torr of CO were admitted. The resulting variation of resistance with time after CO admission is shown in the curve marked O_2 in Fig. 4. A high temperature form of oxygen was prepared using steps (i) and (ii) above, but admitting the oxygen at 250°C after step (ii). After annealing in oxygen for 10 min, the system was evacuated for 10 min, then cooled to 175°C in vacuum. This evacuation procedure did not remove the oxygen, for the resistance remained high. Again at 175°C, CO was admitted, and the curve

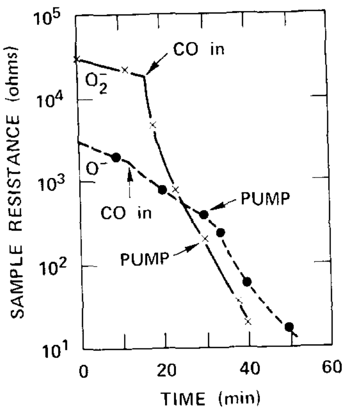

FIG. 4. Decrease of resistance of pressed pellet due to CO, with different oxygen species adsorbed: The treatment to provide the oxygen species indicated is discussed in the text. The sample has chromium ($10^{15}/\text{cm}^2$) plus ferrocyanide ($10^{14}/\text{cm}^2$) as a surface additive. The CO pressure used is 50 Torr, the temperature, 165°C.

marked O^- in Fig. 4 shows the reaction of CO with the high temperature form of oxygen. The observation of the different reaction rate with CO is supporting evidence that there are two different forms of oxygen. Apparently the low temperature form is more active. This particular mixture of chromium and ferrocyanide is illustrated because a substantial difference was observed. With only chromium in the additive the return to the base resistivity is always rapid for either method of adsorbing oxygen; with only ferrocyanide the return is always slow. With no additive on the ZnO, results similar to those in Fig. 4 are obtained, but the temperatures used must be from 25 to 50°C lower, to avoid outgassing the O^- upon evacuation at high temperature, and to lower the rate of the CO reaction at the low temperature to a convenient value.

It is clear from Fig. 4 that the reaction of CO with the high temperature form of oxygen is much slower than the reaction with the low temperature form. If we assume with Chon and Pajares (*8*) that O_2^- is the low temperature form this implies the most rapid reaction scheme is

$$O_2 + e \rightleftarrows O_2^-, \qquad (6)$$

$$O_2^- + e \rightleftarrows 2O^-, \qquad (7)$$

$$2CO + O_2^- \rightarrow 2CO_2 + e, \qquad (8)$$

where Eq. (8) is not broken down into more detailed steps as we have no information. In these reactions we do not know the chemical form of the oxygen (complexes with CO or CO_2 may occur, for example) and we concern ourselves only with the probable oxidation state of oxygen.

Another important measurement for this discussion has been reported elsewhere. That is the observation (*3*) of the activation energy for electron injection from the species O_2^- and O^-. It was found that electron injection from O_2^- showed an activation energy of 0.9 eV, that from O^- an activation energy of 0.4 eV. These should represent the activation energies of Eqs. (6) and (7), where the electron goes to the conduction band at the surface.

DISCUSSION

The evidence as provided by the electrical measurements support qualitatively the conclusions of Doerffler and Hauffe (*5*) and of Sancier (*6*) that we are concerned with two forms of ionized oxygen, and the conclusion of the latter that one form reacts much more rapidly. There is some question regarding which is the active form—our results indicate the low temperature form is reactive, and Chon and Pajares (*8*) have identified this as the O_2^- form. Sancier, on the other hand, suggests the O_2^- form, as identified by an ESR triplet, is less reactive than another form, which he suggests may be O^-. But the evidence seems strong that at least two forms of ionized oxygen exist, of which the low temperature form is reactive. (A possibility exists that the high and low temperature forms of oxygen are O^{2-} and O^- rather than O^- and O_2^-.)

It is clear that the addition of chromium ions (or manganate ions) results in increased activity. This increase, evident in Fig. 1, may be associated with increased electron availability and Fermi energy control, or it may be associated with complex or coordination effects.

There are two factors that point to electron availability as being the key factor. The first indication is the consistent pattern of the results when viewed in terms of the electrochemical potential for electrons (Fermi energy). With a low equilibrium Fermi energy, the activity is high. Both the chromium and manganese additives, with very low Fermi energies, show strong catalytic action. Iron cyanide, with its high energy level, provides low activity. With ferricyanide on the surface we expect the Fermi energy to be lower than with ferrocyanide, and indeed the activity is higher.

The second indication is the strong influence of ferrocyanide in destroying the catalytic action of chromium (Fig. 3). If chromium acts as an active center due to a local chemical bonding mechanism, one might expect only about 10% of the centers would be removed when 10% ferrocyanide is added. But the activity decreases by a factor of 7. This is more consistent with the electronic picture: A chromium-treated sample has a low Fermi energy at 250°C, as observed in resistivity measurements. The resistance ρ of a pressed pellet in CO or vacuum at 250°C is high ($\rho = 10^4\ \Omega$). With 10% ferrocyanide added, the Fermi energy at 250°C in CO or vacuum becomes very high ($p \cong 5\ \Omega$).

We make the assumption that the dominant variable we are controlling with the additives is the Fermi energy and discuss the results in terms of this assumption. The role of the additive by this assumption is to provide electrons for oxygen ion formation, and to adjust the Fermi energy to select the form of oxygen ion. The difference between the chromium and the ferrocyanide additive then lies in the difference in Fermi energy, as in Eq. (2).

A difference in Fermi energy is expected to lead to a difference in the form of oxygen because a low Fermi energy does not permit O^- formation. As discussed above, the reverse direction of Eq. (7), with the electron transferring to the conduction band, proceeds with an activation energy of 0.4 eV. When Eq. (7) approaches equilibrium, however, the electron moves not to the conduction band, but to a much lower energy, the Fermi energy. Thus if the Fermi energy is more than 0.4 eV below the conduction band at the surface, Eq. (7) shifted to the left, favoring the O_2^- form of adsorbed oxygen. If the Fermi energy is much more than 0.9 eV below the conduction band, Eq. (6) is shifted to the left, and oxygen is not adsorbed at all. Therefore, to favor the O_2^- form of oxygen, the Fermi energy should be between about 0.5 and 0.9 eV below the conduction band.

Now from Eq. (1), neglecting the oxygen surface states, the Fermi energy is close to the energy level of the dominant surface state. As discussed in Ref. (*3*), the energy level parameter as determined by the powder resistivity measurement is probably the more appropriate value to use. Ferrocyanide, with its surface state close to 0.1 eV from the conduction band, should favor the formation of O^- (the high temperature form) formation, while chromium and manganese should favor formation of the low temperature form, O_2^-. Hence chromium and manganese should be catalytically active.

During the actual catalytic reaction, we cannot neglect the oxygen surface states, and the system is not at equilibrium. Thus the use of the Fermi energy concept is inaccurate, and the electron exchange should be discussed in terms of energy levels. When the electron source is chromium, with its low energy level, clearly O_2 can be reduced but the reduction of O_2^- to form O^- is probably endothermic, so the rate of O^- formation may be low. On the other hand, when the source of electrons is Fe^{2+}, the reduction of O_2^- is exothermic so it will tend to be converted to O^-. Thus qualitatively the concepts of energy levels can be used in nonequilibrium catalysis, but we know too little, as yet, about the rate constants to analyze the reaction in detail.

In the above discussions there has been no mention of the role of the semiconductor catalyst. The Fermi energy, from Eq. (1) does not apparently depend on the catalyst, and the source of electrons has now been switched from catalyst to the additives.

We suggest two possible roles for the semiconductor support in such a system. The first role is that of providing electron exchange levels. If direct electronic transitions between the additives and the reactants are slow, the bands of the semiconductor can act as a reservoir of energy levels to accelerate the redox processes. The second role is that of determining the surface state energy level, either for reactants or for additives. An example of a reactant–semiconductor interaction may be methanol, which after reacting with the ZnO surface is oxidized easily (1.3 eV activation energy for electron removal).

It would appear from the high catalytic activity on Al_2O_3 and SiO_2 systems that the manganate and chromium additive systems studied here provide a Fermi energy close to the optimum value independent of substrate, and a large density of energy levels (surface states is a convenient name for them) which anchor the Fermi energy at the optimum value. Zinc oxide itself may also, under some conditions, provide a Fermi energy close to the optimum value, but if there are no surface states in the region, zinc oxide will not anchor the Fermi energy so the Fermi energy is controlled by the reactants (in this case oxygen) (*10*).

CONCLUSIONS

We have assumed that electron exchange reactions dominate the CO oxidation reaction, and explored the action of nonvolatile additive redox couples.

The models of semiconductor catalysis have insisted that the energy levels of electrons, and the Fermi energy, dominate the analysis. We have assumed this also, and interpreted the effect of surface additives in terms of their influence on the Fermi energy.

We can equally well look upon the model from a strictly chemical point of view, where the influence of the redox couple additive is expressed in terms of a redox potential or an electrochemical potential for electrons, and the reaction proceeds because the electrochemical potential for electrons is just right, high enough to reduce oxygen to O_2^-, but low enough that: (a) it cannot further reduce O_2^- to O^-; and (b) the product, CO_3^-, can be oxidized.

Both viewpoints are valuable, of course. The redox couple viewpoint is useful because it provides a simple picture on which to base intuitive reasoning. The semiconductor surface state viewpoint is useful because it permits semiquantitative interpretation of the catalytic steps in terms of electronic transitions and in terms of measurable parameters, the surface state energies. And when so little is known about the interaction of nonvolatile redox couples at a solid surface, we have no other way at present except through surface state measurement to determine whether a strong reducing agent will still be a strong reducing agent when adsorbed on the surface.

The analysis presented has not emphasized the quantitative aspects because the reaction steps assumed may not be valid in detail. For example, there is no direct information in these data regarding the presence of complexes between negatively charged oxygen and CO, as suggested by Amigues and Teichner (*7*). Mathematical analysis including the variation of activity with temperature, reactant pressure, and additive concentration will be attempted in later reports when the detailed reaction methanism is better understood.

Perhaps one of the most intriguing new developments from this study is the new experimental concept, the use of electrical measurements on a semiconductor support to monitor the behavior of known catalysts. In the present case we have used electrical measurements on the ZnO to determine the Fermi energy of the catalysts manganese and chromium. It is clear from the results that these are the catalysts and the ZnO is being used as: (a) a support; and (b) a probe with which to measure the properties of the catalysts. It is planned to make measurements of this type on other, more effective, oxidation catalysts such as Bi_2O_3/MoO_3 mixtures, again using the support ZnO so that the Fermi energy of the catalyst can be monitored.

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