

The Surface State Representation of Catalytic Reactants and Promoters*

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To analyze charge transfer reactions on a semiconductor, the reactions are separated into steps involving chemical transformations and steps involving electron transfer (redox steps). With such a separation, the band model representation can be utilized in the description of the redox steps, with the reactants described in terms of their electronic energy levels or surface states. The identification of the appropriate surface states is discussed, and it is pointed out that for most redox couples two or more surface states must be considered in the analysis. A few illustrative examples are analyzed to show how one can utilize band theory concepts in the analysis of catalytic reactions. It is shown that the situation becomes much simpler to analyze if intentionally added redox couples are used as promoters. Moreover, in many cases where the electronic factor is important, such surface state promoters, if properly chosen, should enhance catalytic activity by orders of magnitude.

INTRODUCTION

There have been many cases of adsorption and catalysis where a catalytic rate has been assumed to be dependent on the transfer of electrons between an adsorbate and a semiconductor adsorbent. In one case at least it has been shown (1, 2) that the rate of such electron transfer follows a simple first-order law—the rate of reduction of oxidizing agents on ZnO is first order in n_s , the electron density at the surface, and first order in the density of oxidizing agent. To maximize the rate of such a reduction step, it is necessary to maximize n_s and the adsorption of the oxidizing agent. We are interested, therefore, in the control of n_s , and look to the band model to determine the controlling parameters.

When one describes adsorption in terms of the band model, wherein one deals with electronic energy levels not chemical potentials, one should utilize the concept of surface states, localized electronic energy

levels at the surface. Extensive studies are available from surface physics describing the rate of electron capture and release from surface states. When describing catalytic behavior, however, the chemical origin of such energy levels, largely ignored in the developments of surface physics, must be considered.

Hauffe and his coworkers (3) in early theories and more recently Lee and Mason (4) used thermodynamic arguments rather than surface states for analyzing electron transfer between energy bands and adsorbed species. They were able to give a complete description which, however, lacked the detail that surface state models should provide. Attempts to utilize the more descriptive surface state models have, however, suffered because it has usually been assumed (4-7) that reactants follow the idealized behavior, as explored by surface physicists, of stable surface states in constant density at a semiconductor-semiconductor oxide interface, which is quite different from the behavior of the volatile, chemically active sorbates of interest in

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catalysis. Also, it has often been assumed (5, 6) that reactant surface states have an unimportant role in the control of the electronic properties of the solid (thus ignoring their function as surface states and overemphasizing the importance of bulk doping of the semiconductor). In particular, the effect of the surface state density and charge in determining and varying the electrostatic double layer at the surface has often been neglected, despite the early proof by Weisz (8) that such a double layer must have a large effect in semiconductor adsorption and catalysis.

The objectives of the present paper are therefore twofold. The first is to formulate a surface state representation of adsorbates in a way such that chemical changes in the adsorbate can be handled separately from electron transfer steps, and to discuss when such a surface state representation (emphasizing the so-called "electronic factor") is the most appropriate model. It will be shown that when analysis in terms of surface states is appropriate, then surface states so dominate the behavior that uncontrolled surface states arising from impurities or from the host lattice, perhaps during catalyst pretreatment, will generally overwhelm any attempt to influence the catalyst by techniques such as doping. With this in mind, the second objective is to discuss the intentional addition of surface states and to suggest how these can be utilized to control the electronic properties of the catalyst and thus provide promoters or inhibitors for a catalytic reaction.

In the development of equations, we will use the energy levels of the surface states as the dominant independent variables. These are constants that can, in principle, be estimated (2) or measured (9). This is a departure from the approach of Volkenstein (6), and leads to very different formulations. Volkenstein used the surface Fermi energy as his dominant independent variable and expressed surface coverage, catalytic activity, etc., in terms of this parameter. Although the work of Volkenstein has been of great importance, we

believe his choice of the Fermi energy as the dominant variable was unfortunate, because the surface Fermi energy is neither a constant of the system (it depends upon most parameters: temperature, concentration and pressure of reactant gases, doping, etc.), nor is it an easily measurable parameter. The choice not only made experimental prediction difficult, but had the further unfortunate result that it led to underrating the electrostatic problems, which had been pointed out very early by Weisz.

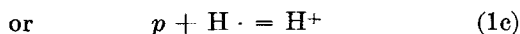
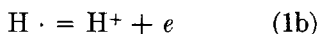
SURFACE STATES DUE TO ADSORBED SPECIES

The first step in analyzing catalysis in terms of electronic energy levels is to identify the important energy levels. In an earlier contribution (2), many of the problems in designating an energy level for a chemically active species were discussed. The importance of the Franck-Condon principle in identifying which energy level should be calculated was illustrated. These arguments are applicable in the present case also. In that work, however, the problems associated with direct bonding between the surface species and the solid were avoided, based on the assumption that the phenomena then of interest were associated with species not specifically adsorbed. In the present discussion this assumption is not valid, and local bonding of the sorbate must be considered.

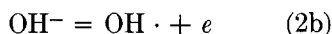
The Relation of the Surface State to the "Chemical" Bonding of an Adsorbed Species

Consider a strong reducing agent (i.e., an electron donor) approaching a semiconductor surface. It can become sorbed on the surface at various sites. One possibility is that there is negligible local interaction between the solid and either the neutral or ionized sorbate. That is, we assume the electron on the adsorbed molecule has essentially the same electron wave function as on the free molecule. If the electron leaves the molecule, it becomes a non-localized valence or conduction band elec-

tron, and the oxidized adsorbate still forms no localized chemical bond. Green and Lee (10) have termed this a charge transfer complex; we will refer to this form of adsorbate as an unbonded species. Thus, for example, using the subscript *g* to represent a gaseous species, the steps of hydrogen atom adsorption might be



where we use *e* to represent a nonlocalized electron in the conduction band, and *p* to represent a nonlocalized hole in the valence band. For specificity, we shall generally consider only *n*-type material and electron transfer, but other cases are analogous. Second, either the oxidized or reduced forms of the sorbate can chemically react with sites on the surface.



In this example, the adsorption site for $\text{H} \cdot$ is an O_L^- species at the solid surface. The site with which an adsorbate becomes bonded may be a particular lattice ion or group, or a surface defect or impurity.

In a band diagram, the two example cases will have energy levels as shown in Fig. 1. We show here the energy level of the electron just preceding the electron transfer (after reaction 1a or 2a), and designate the energy level by the redox couple referred to in the electron transfer Eq. (1b) or (2b). Thus if the level is unoccupied by an electron, the chemical species is the oxidizing agent of the couple; if the level is occupied, the chemical species is the reducing agent. (By the terms reducing agent or oxidizing agent we refer to the oxidation state of a species. Thus H^+ in this terminology is the oxidizing agent. We will use the terms strong oxidizing agent or weak oxidizing agent if we wish to describe the electron affinity.)

In adsorption involving one-equivalent electron transfer, we must deal with at least two oxidation states for each ad-

sorbate molecule. Ideally, the two oxidation states are represented by the same energy level, as is the case if only one bonding site is involved.* In the above example, if Eq. (2) were the only adsorption reaction occurring, the level $\text{OH} \cdot / \text{OH}^-$ (Fig. 1) would represent the energy of the surface state.

However, the dominant forms of the two oxidation states will often become bonded to different surface sites, and thus there may be a large difference in energy level for the two oxidation states. For example, in the reactions of Fig. 1 the dominant form of the oxidizing agent (that form most numerous and having the highest electron reactivity) may be H^+ , and the dominant form of the reducing agent may be OH^-

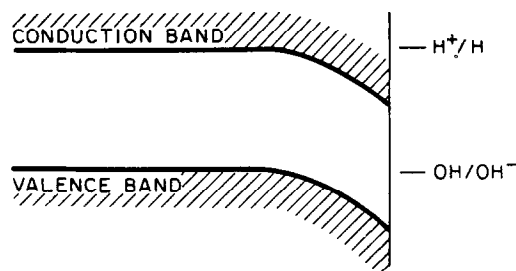


FIG. 1. Surface states due to atomic hydrogen on a semiconductor.

rather than $\text{H} \cdot$. Then the levels H^+ / H and OH / OH^- both would have to be shown on the band diagram. In general, for most cases where there are preferred bonding sites, at least two energy levels must be reflected on the band diagram.

Dependence of the Surface Fermi Level on Surface States

In this section we develop expressions for the Fermi level as a function of surface state energy levels and free energy change

* To a reasonable approximation, Franck-Condon effects (2), primarily associated with coulomb interaction (10) between the ionized adsorbate and the lattice, will always cause an energy level difference between the oxidized and reduced form of the sorbate. As in the earlier communication (2), we will consider this of negligible interest compared to the large changes associated with chemical interaction.

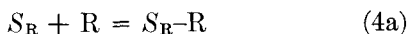
during bonding. We assume low surface coverage. The expressions obtained will then be utilized in the following sections for the analysis of the rate of a catalytic reaction, at which time the electrostatic effects are included. At that stage the Fermi energy is eliminated as a variable and the catalytic rates are expressed in terms of surface state energy levels.

We are particularly interested in one-equivalent surface states (11), where transfer of one electron or hole to the surface species leads to a stable complex. This type of surface state is of interest, first because of the relative simplicity of the associated surface state theory, and second, because there is a possibility (11, 13) of utilizing one-equivalent couples for the control of the electronic properties of the solid.

Let Ox be the oxidizing agent and R the reducing agent of the one-equivalent redox couple. We will use the symbols R and Ox to represent also the unbonded adsorbed species. Let the preferred bonding site for the oxidizing agent be S_0 and the preferred bonding site for the reducing agent S_R . Then from thermodynamics, assuming no limitation on sites:



$$[S_0\text{-Ox}]/[\text{Ox}] = \exp(-\Delta G_{\text{Ox}}/kT) \quad (3b)$$



$$[S_R\text{-R}]/[\text{R}] = \exp(-\Delta G_{\text{R}}/kT) \quad (4b)$$

where Eqs. (3a) and (4a) represent the bonding reactions, (3b) and (4b) the statistics. Here ΔG_{Ox} and ΔG_{R} are the free energy change during the bonding, almost always negative. These reactions cannot be represented on the band diagram.

We also have for the unbonded adsorbate species at equilibrium:

$$\text{R} = \text{Ox} + e \quad (5a)$$

$$[\text{R}]/[\text{Ox}] = \exp\{-(E_0 - E_F)/kT\} \quad (5b)$$

where Eq. (5a) represents the redox process, Eq. (5b) the Fermi distribution. Here E_0 is the surface state associated with the unbonded adsorbed species, and E_F is the Fermi level energy at the surface.

From Eqs. (3b), (4b), and (5b) we obtain the following equivalent expressions for E_F :

$$E_F = E_0 - \Delta G_{\text{Ox}} - \log[S_0\text{-Ox}]/[\text{R}] \quad (6)$$

$$= E_0 + \Delta G_{\text{R}} + kT \log[S_R\text{-R}]/[\text{Ox}] \quad (7)$$

$$= E_0 - (\Delta G_{\text{Ox}} - \Delta G_{\text{R}}) - kT \log[S_0\text{-Ox}]/[S_R\text{-R}] \quad (8)$$

Thus the Fermi level is affected by the surface state, the free energies of bonding, and the concentration of the adsorbate in the two oxidation states.

Here Eq. (6) is most convenient if R is the neutral adsorbate so that [R] can be estimated from a physical adsorption isotherm, Eq. (7) if Ox is the neutral adsorbate for the same reason, and Eq. (8) if both $[S_0\text{-Ox}]$ and $[S_R\text{-R}]$ are known (for example, in cases where they are deposited as nonvolatile additives on the surface). Thus if, for example, the redox system O_2/O_2^- is of interest, Eq. (7) could be used, with [Ox] the surface density of the oxygen molecule, and ΔG_{R} the estimated bonding energy of the ion O_2^- .

In principle, the energy level E_0 of the unbonded species can be estimated after appropriate measurements on the semiconductor by an activity parameter such as the redox potential, as discussed in Ref. (2). In order to estimate the ΔG 's, the energies of the bonding of the species with the surface, obviously a bonding site must be postulated, and even then the estimation can be difficult. Chemical processes, such as dissociation of a diatomic molecule, would normally be introduced during the estimation of the adsorption isotherm of the unbonded neutral species.

It should be emphasized that these expressions giving the Fermi level vs the ionized sorbate concentration, in terms of easily visualized parameters, apply only in equilibrium. For rate expressions, we would be interested in the surface state energies E_{R} and E_{Ox} of the species $S_R\text{-R}$ and $S_0\text{-Ox}$, respectively. Using combined thermodynamic and Fermi equilibrium expressions as illustrated in Eqs. (3), (4), and (5), we can easily show that

$$E_{Ox} = E_0 - \Delta G_{Ox} + \Delta G_{R,Ox} \quad (9)$$

and

$$E_R = E_0 + \Delta G_R - \Delta G_{Ox,R}, \quad (10)$$

where $\Delta G_{R,Ox}$ is the free energy change during bonding of the reducing agent on a site normally occupied by the oxidizing agent (formation of $S_{Ox}-R$ from R), and $\Delta G_{Ox,R}$ is the free energy release during bonding of the oxidizing agent on a reducing agent site. Normally these energies will be small compared to ΔG_{Ox} and ΔG_R (in the example of Eq. (2a), the bonding of $H\cdot$ on O^- to form OH^- , releasing the energy ΔG_R , is expected to be more favorable than the bonding of H^+ to O^- to form OH , releasing the energy $\Delta G_{Ox,R}$). Thus E_{Ox} will be above E_0 on the band diagram, and E_R below E_0 .

We do not plan to discuss kinetics in detail in the present contribution, but it is clear that such a system of energy levels has some interesting implications when electron transfer is rate-limiting.

With two-equivalent species, where the reactant changes in oxidation state by two electrons (the intermediate valence being unstable), the analysis, although in principle similar, can become extremely complex. As three oxidation states must be considered, we deal with a multiplicity of energy levels. Also the chemical transformations can become extremely complex, involving dissociation of molecules, strong bonding of intermediates, etc. In the later discussion we will use qualitative reasoning, when dealing with two-equivalent species, keeping in mind the method of analysis for one-equivalent species. In many cases we do not need to find n_s because of the dominance of the surface barrier, which will be discussed below. Simplification is also possible, as we will show, when one-equivalent additive is used to control E_F and n_s .

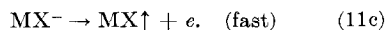
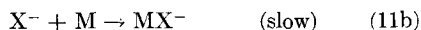
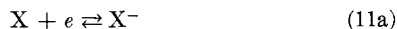
DESCRIPTION OF CATALYTIC REACTIONS USING THE SURFACE STATE MODEL

We will consider two simple cases in catalysis, one where we wish to use the

solid state concepts to increase the density of a particular reactive form (ion) on the surface, the other where we wish to control the density of free carriers at the surface of the semiconductor. The first illustrates cases of equilibrium in electron transfer steps; the second illustrates cases where electron transfer is rate-limiting. Naturally in the present paper we are analyzing only systems where the electronic factor controls the overall rate. These two simplified examples should provide a basis for qualitative treatment of more complex reactions, where interdependent chemical and electronic steps must be analyzed.

The Electrostatic Limitation on the Adsorption Isotherm

First we will discuss a typical reaction where electronic equilibrium is reached. Consider a reaction between an oxidizing agent X and a reducing agent M , where the rate-limiting step does not involve electron transfer:



Here we are interested in increasing the equilibrium amount $[X^-]$ adsorbed on the surface, for by (11b) this amount determines the catalytic rate. In this example the role of the catalyst is to present one of the reactants in an ionized and therefore reactive form.

Now from Eq. (11a) $[X^-]$ is simply proportional to the product $[X] \cdot n_s$, where n_s is the surface electron density. However, as $[X^-]$ increases, an electrostatic double layer forms repelling electrons from the surface and decreasing n_s . The influence of such double layers on the surface electron density n_s has been thoroughly analyzed in terms of the band model (12), and if we express the relationship between n_s and $[X^-]$ in band model concepts, these analyses can be immediately transferred. In the present contribution, however, only limiting approximations will be discussed for illustration.

Consider the case of an n -type semicon-

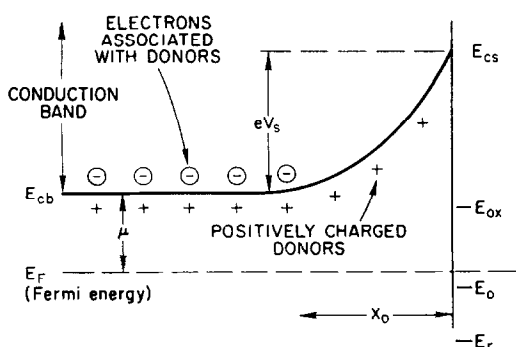


FIG. 2. Band diagram for an *n*-type semiconductor with a net negative charge on the adsorbed species.

ductor with a negative surface charge (depletion layer) and no minority carrier effects, as illustrated in Fig. 2. If eQ is the total surface charge, N_D the donor density, ϵ the dielectric constant, ϵ_0 the permittivity of free space, and x_0 the thickness of the depletion region (the region exhausted of electrons during adsorption), we can solve Poisson's equation in the depletion region and obtain the Schottky relation

$$eV_s = E_{cs} - E_F - \mu = eQ^2/2N_D\epsilon\epsilon_0, \quad (12)$$

where the energy differences eV_s and μ are shown in Fig. 2, and are positive as drawn. E_{cs} is the energy of the conduction band edge at the surface. Now if the only charged species on the surface is X^- , we can combine the analysis of the double layer, Eq. (12), with the Fermi analysis of the surface state, Eq. (8), eliminate E_F , and obtain

$$kT/\log [X_s^-]/[X_s] = -(e[X_s^-]^2/2\epsilon\epsilon_0N_D) + E_{cs} - (\mu + E_0) + (\Delta G_{Ox} - \Delta G_R), \quad (13)$$

where, for simplicity of formalism, we have substituted X_s^- for S_R-X^- and X_s for S_0-X , and have assumed most of the negative charge Q is in the form X_s^- . Eq. (13) represents a linear dependence of $[X_s^-]$ on $[X_s]$ for very low coverage. However, for large $[X_s^-]$, the relationship becomes logarithmic, and effectively $[X_s^-]$ becomes independent of $[X_s]$, i.e., $[X_s^-]$ saturates. As the left side of Eq. (13) is at most a few tenths of a volt, approximately

$$[X_s^-]^2 \rightarrow (2\epsilon\epsilon_0N_D/e)E_m, \quad (14)$$

where

$$E_m = E_{cs} - (\mu + E_0) + (\Delta G_{Ox} - \Delta G_R) \quad (15)$$

represents a surface saturated in X_s^- . With typical semiconductor values ($\epsilon\epsilon_0 = 10^{-10}$ F/m, $N_D = 10^{23}\text{m}^{-3}$, $E_m \lesssim 1$ eV), we find the critical value of $[X_s^-]$ is the order of $10^{12}/\text{cm}^2$, a very low coverage. It is to be noted that this saturated adsorption varies as the square root of the donor density N_D , and therefore is somewhat insensitive to the value of N_D chosen. Such a limitation on the density of adsorbed species for a depletion layer has been discussed by Weisz (8), Hauffe (3), and Lee and Mason (4).

Thus the rate of the catalytic reaction (11) as determined by the concentration of $[X_s^-]$, is approximately zero order in $[X_s]$ when $[X_s^-]$ is saturated.

Equation (13) is in a form such that chemical transformations including non-linear adsorption of X or splitting of an X_2 molecule can be introduced with reasonable modifications, often simply by using the appropriate free energy of transformation.

Equation (13) is also in a form such that alternate approximations for the relationship between the charge on the surface state and the surface Fermi level can be introduced. For example, if instead of a depletion region, leading to Eq. (12), an accumulation layer is present (a positive surface charge on an *n*-type semiconductor leading to excess electrons at the surface), a better approximation (though still not accurate (12)) would be

$$E_{cs} - E_F - \mu = -eQ/C \quad (16)$$

rather than Eq. (14). Here C is the capacity between the surface states and the excess electrons at the surface: its value would be similar to a Helmholtz capacity at a metal/electrolyte interface, or about $5 \mu\text{F}/\text{cm}^2$. Such a surface layer leads to a much less restrictive limitation on the quantity adsorbed. Insertion of Eq. (16) in Eq. (8) leads to an electrostatic limitation as found with Eqs. (13) and (14), but the limiting coverage of positive ions is the

order of $10^{14}/\text{cm}^2$, using the above value for C .

The form of an expression for two-equivalent reactants at equilibrium analogous to Eq. (13) depends on whether there are one or two important forms of charged species. For example, consider the calculation of the proton concentration due to hydrogen adsorption. If there is appreciable H_2^+ present, then the electrostatic equation involves two charged species, H^+ and H_2^+ , and analysis is complicated. If by some argument one concludes there is only appreciable H^+ present, then the present analysis can be used, where the concentration $[\text{H}_s]$ can in principle be calculated from the free energy of the bond assumed, and the free energy of splitting the H_2 molecule. With two-equivalent species which change oxidation state by two, the process and the analysis in terms of surface states is always complex, as discussed above.

*Control of the Catalytic Rate by
Surface State Additives (Surface
State Promoters)*

Consider again the rate of the reaction of Eq. (11), limited by the concentration of an intermediate X^- . As shown in Eq. (13), the amount of X^- that can be absorbed on the surface is very limited due to electrostatic effects. An increase in donor density will not appreciably change the limitation, as the maximum quantity is a slow function of N_D . This section shows how the electrostatic limitation can be overcome, using surface states.

If we have an additive A , a species present on the surface but not involved in the catalytic reaction, then Eq. (13) must be supplemented by Eq. (18):

$$A_s^- = A_s + e. \quad (18)$$

If K_1 is the equilibrium constant for Eq. (18) and K_2 that for Eq. (11a), we find

$$[\text{X}_s^-] = [\text{X}_s]K_1K_2[A_s^-]/[A_s] \quad (19)$$

and so $[\text{X}_s^-]$, the concentration of reactive species (and hence the catalytic rate of Eq. (11)) can be increased if $[A_s^-]$ can be

increased. From the discussion above, it is clear that the limitation on a negative ion is electrostatic in origin. To avoid this limitation an inert counter-ion is used. Thus, for example, Ag^+ would be added by use of a nonvolatile ionic salt such as AgCl . Species could also be added in a volatile form; for example, Br^- can be added in the form CH_3Br , assuming some dissociative adsorption.

The nonvolatile form has the advantage that both A and A^- (the complete redox system) can be added by use of an appropriate combination of salts, so that $[\text{X}_s^-]$ for a given $[\text{X}_s]$ can be controlled through Eq. (19) (which is equivalent to controlling E_F , the surface Fermi energy (11)). The Fermi energy should be high enough so that Eq. (11b) is not rate-limiting, but not so high that an oxidation step becomes rate-limiting. Thus there may be an optimum value for E_F .

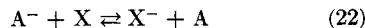
From these simple arguments it appears that the additive A_s^-/A_s should act as a promoter in Eq. (11) between X and M . Here again analysis in terms of surface state theory will provide further understanding of the limitations. If we let

$$E'_X = E_0(X) - \Delta G_{\text{ox}}(X) - \Delta G_{\text{R}}(X) \quad (20)$$

and E'_A be the corresponding quantity for the surface state A , we can apply Eq. (8) to each of these levels, eliminate E_F , and express the equilibrium constant in terms of surface states:

$$[\text{X}_s^-] = [\text{X}_s] \cdot \{[\text{A}_s^-]/[\text{A}_s]\} \exp\{-(E'_X - E'_A)/kT\}. \quad (21)$$

Physically this is an expected result by any model. It states that if the additive A^- is a "stronger reducing agent" (has a higher energy parameter E') than the reactant X ; viz. $E'_A > E'_X$, the reaction



will be driven to the right and most of the sorbed X will become ionized (without changing the surface charge). Thus in order to make $[\text{X}_s^-]/[\text{X}_s]$ as large as possible, for maximum promoter action, we want $E'_A \gg E'_X$, and we want $[\text{A}_s^-]/[\text{A}_s]$ maxi-

mized. Obviously $[X_s^-]$ cannot appreciably exceed the original amount of $[A_s^-]$ added.

This example illustrates the simplification possible with intentionally added non-volatile surface states. The electrostatic effects are controlled, the variations in n_s are controlled, and much simpler models apply.

Bulk doping should be much less effective than surface state additives in determining the rate of a catalytic reaction (with the electronic transitions at equilibrium). From Eq. (14) we see that with bulk doping we can enhance the formation of the ionized intermediate only to the extent of about 10^{13} ions/cm². With surface state additives, on the other hand, there is a one-to-one increase up to a monolayer, by Eq. (22), relatively a huge effect. The discrepancy is so great that one expects that a few "accidental" surface states, from nonstoichiometry, surface impurities, etc., arising during pretreatment or reaction conditions, will dominate over any effect due to bulk doping of the solid.

Catalysis Limited by the Rate of Electron Transfer

In this section we examine catalytic reactions where an electron transfer step itself is rate-limiting, and suggest, with the help of the band model, how much systems may be optimized. Obviously when electronic equilibrium cannot be assumed, quantitative analysis is more complex.

Consider the reaction



We assume the rate of this reaction is

$$r = k_1 n_s [X], \quad (24)$$

and the value of $[X]$ is given by the non-electronic adsorption step. We wish to examine the parameters controlling n_s , the electron density at the semiconductor surface.

The surface charge produced by the reactants is essentially zero, as we assume

rapid removal of both X^- and MX^- by Eqs. (23b) and (23c). Thus there are no electrostatic effects associated with the reactants, and the reactants have no effect on n_s .

In order to influence n_s and improve the activity, we compare bulk doping and surface additives. Bulk doping is expected to be ineffectual because again it is expected to be overwhelmed by "accidental" surface states. The electron concentration is given by

$$n_s = N_c \exp \{ -(E_{cs} - E_F)/kT \} \quad (25)$$

and substituting from Eq. (12)

$$n_s = N_c \exp \{ -(\mu + eQ^2/2N_D\epsilon\epsilon_0)/kT \}. \quad (26)$$

Thus with any "accidental" surface states, such as oxygen or sulfur, which can form negative ions on the surface and thus contribute to the surface charge Q , it is clear that n_s is decreased rapidly. In practice, of course, in this example a suitable pretreatment would be found so that the accidental surface states would contribute rather than remove electrons. However, in that case the donor density is not an important variable compared to pretreatment.

The present suggestion, therefore, is that use of surface additives is the most accurate way to control the value of n_s . With enough surface additive to dominate over accidental surface states, E_F becomes controlled by the expression

$$E_F = E'_A + kT \ln [A_s^-]/[A_s] \quad (27)$$

and Eqs. (27) and (25) then determine n_s .

Properties Required for a Surface State Promoter

The arguments of the preceding pages indicate that a surface state promoter should have certain properties. First, it should be a nonvolatile, stable, one-equivalent redox couple. If it is nonvolatile in both oxidation states, they can both be added as a neutral ionic salt mixture to the catalyst. The species must be stable, and be neither easily oxidized nor reduced to a third oxidation state with an energy level removed from the region of interest.

The couple should be one-equivalent, because a two-equivalent species is not expected to provide stable electronic properties (11). With such a one-equivalent redox couple, we can predetermine the ratio of oxidized to reduced form, and thus predetermine the Fermi energy (surface electron density) as desired.

Second, the energy parameter $\{E_0 - (\Delta G_{\text{ox}} - \Delta G_{\text{R}})\}$ of the species should be near the desired position of the Fermi energy. Small mismatch can be corrected for by varying the ratio $[\text{Ox}]/[\text{R}]$ in Eq. (8), but this correction in practice is limited to about 0.1 V up or down. Also the energy levels must be located relative to the bands of the semiconductor such that rapid electronic equilibrium can be attained. This probably means the furthest surface state (E_{R} on an *n*-type semiconductor, E_{ox} on a *p*-type) must lie within about 0.4 eV of the band edge, and preferably closer.

Third, for simplicity of interpretation no direct interaction should occur between the promoter surface state and the reactant gases. Such a direct interaction would not necessarily affect the practical benefits of the surface state promoter, but would require the use of an additional surface state energy level in the analysis.

In experimental studies of ZnO, we have reported a technique to measure the energy of surface states (9), and have used such surface states (the ferrocyanide-ferricyanide couple) to inhibit a photolytic surface reaction (13). The former research provides necessary background for the application of the surface state promoter concept. The second illustrates the use of such surface states to stabilize the surface properties, in this case preventing undesirable chemical surface reactions (the vacuum photolysis of zinc oxide).

TWO-EQUIVALENT REACTANTS

Any attempt to generalize quantitatively the behavior of two-equivalent reactants using the band model is unrewarding because both the chemical and electronic (11) steps are so variable from example to

example. However, as most reactants are two-equivalent, clearly some qualitative considerations must be examined.

There are two features that can be helpful in qualitative analysis. One is the saturation of surface charge, the other is the use of one-equivalent additives.

The saturation of surface charge, as discussed in the preceding section states approximately that electrons will be transferred to the surface until the exponential in the Fermi distribution function becomes dominated by the electrostatic effect. It can be shown, with arguments similar to those used for one-equivalent surface states, that, if there are only two charged species possible (say, O^- and $\text{O}^=$) and there are no complications due to strong binding of any of the surface species (so there are only two surface states to consider), the Fermi level will end up approximately midway between the levels (11).

As in the case of one-equivalent reactants, the addition of a nonvolatile one-equivalent additive permits a much higher surface concentration of the reactants and thus can influence the catalytic activity. In the region where the Fermi energy is controlled by the additive ratio $[\text{A}^-]/[\text{A}]$, the ratio of the two oxidation states $[\text{O}^-]/[\text{O}^=]$ is also controlled. Thus if in a reaction one oxidation state (say O^-) reacts to form one product and the other oxidation state ($\text{O}^=$) reacts to form another product, then the selectivity as well as the activity of the catalyst can be influenced.

COMBINED ELECTRON AND MOLECULE EXCHANGE BETWEEN CATALYST AND REACTANTS

We have discussed the case when electrons (or holes) only are exchanged between the catalyst and the reactants. There are obviously cases, particularly *p*-type oxidation catalysts such as Cu_2O and $\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$, where one must also consider exchange of ions or molecules, in these cases, lattice oxygen ions. If in such cases the temperature is too low to permit diffusion of ions through the lattice, then the electrostatic effects we have discussed will

dominate and the lattice oxide ion at the surface can be treated as a volatile surface state, most likely two-equivalent.

If, in addition, there is substantial diffusion of ions to and from the bulk, the situation becomes more complex. The bulk Fermi energy μ becomes determined by the reaction, providing another variable. A further complication is the influence of such diffusion to nullify the electrostatic charge at the surface.

The band model appears to be necessary to describe some of these complex reaction steps. However, even qualitative discussion must await a better knowledge of the various chemical solid state, and electronic reaction steps.

CONCLUSIONS

The band model-surface state representation of a catalytic process is excellent to describe electron transfer catalysis when few and unimportant chemical (nonredox) steps are present. Reactions that show such simple behavior can in principle be quantitatively analyzed using the approach presented, where minor chemical transformations are treated as a perturbation. From the analysis in terms of surface states, we can suggest the properties of promoter redox couples to improve the activity and perhaps selectivity of semiconductor catalysts.

As the chemical steps become more complex and more dominating, however, the

band model must be supplemented more and more by chemical models, where one views the process in terms of molecules, rather than in terms of electrons and electron energy levels only.

A need exists for a synthesis of the two models, a new basic model where electronic steps and molecular bonding steps can be visualized on the same diagram.

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