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Electron Exchange Processes in Olefin Oxidation*

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A new experimental technique is described for measurement of the relative Fermi energy of various catalysts used for partial oxidation of olefins and alcohols. The technique is based on a measurement of the conductance of a semiconducting support (TiO_2). For a number of catalyst compositions of industrial importance (in terms of selectivity and activity) the bulk Fermi energy is found to have a common value. This recurring value is near the electrochemical potential of electrons on adsorbed oxygen. Catalyst systems studied were the bismuth/molybdenum, copper oxide, vanadium oxide and iron/molybdenum systems. An attempt is made to separate the macroscopic requirements (where the Fermi energy is considered a macroscopic parameter) from the microscopic ones (where local bonding orbitals and acid centers may be considered microscopic parameters). We conclude that for reactions for which the rate-limiting step depends on electron transfer to the catalyst that the Fermi energy should be near or just above the electron exchange level for oxygen. Also the bulk Fermi energy should be stable against small variations in reactant gas compositions. Impurity band pinning of the Fermi energy may account for the excellent stability of bismuth molybdate.

INTRODUCTION

For a catalyst to be active and selective in the partial oxidation of olefins, it must perform several functions: (a) The catalyst must provide appropriate sites for olefin adsorption such that it is deformed into an active intermediate. (b) The catalyst must act as a source and sink of oxygen; it must provide active oxygen as a reactant and adsorb or absorb gaseous oxygen. If the oxygen exchange involves lattice oxygen, as appears common, then a corollary to this requirement is often a high mobility for vacancies, so the latter can move to adsorbed oxygen and thus speed up the oxygen absorption step. (c) The catalyst must act as a source and sink of electrons —it must supply electrons to reduce gaseous oxygen, and must absorb electrons at some stage before the hydrocarbon/oxygen complex can desorb as a neutral molecule.

In the present paper, the results reported bear primarily on the third function and the properties that are needed to facilitate electron transfer back and forth to the surface. The research stems from an earlier paper (*1*) in which we pointed out that a new technique provided an excellent method to measure, under catalytic conditions, one of the key electrical properties of a catalyst —the Fermi energy—and enabled comparison of the bulk Fermi energy of one catalyst (relative to a reference) with others. The free energy of electrons in a solid is the Fermi energy (the electrochemical potential for electrons), so electrons moving out of or into a solid appear to originate or return to the Fermi energy. Thus it is probable that the Fermi energy may be a key parameter. Purely on thermodynamic grounds the Fermi energy should be high enough that electron transfer to

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oxygen is exothermic, but low enough that electron transfer back to the solid is also favorable.

It is shown that there is apparently a common most favored bulk Fermi energy for a majority of the catalyst systems studied; the energy of which is related to oxygen energy levels. In order to understand the origin of such a Fermi energy requirement, the effects of the surface double layer, which shifts the surface levels relative to the Fermi energy, must be considered. The development of the model and its implications are a second objective of this contribution.

The technique developed to compare the bulk Fermi energy of various catalysts is particularly useful because the catalyst is dispersed on a support for this measurement, permitting concurrent kinetic measurements. For the present purpose, however, there is a restriction on the support: it must be a semiconductor. As discussed in the following paragraphs, we have used TiO_2 as the semiconductor support because it is a reasonably well understood semiconductor, because it is not itself a good oxidation catalyst, and because it is relatively unreactive with the catalysts it is supporting.

The bulk Fermi energy is compared for various catalysts known for their high activity and selectivity for partial oxidation of olefins. Further information can be obtained by exploring compositional variations on these catalysts that are known to lower the activity and selectivity. Measurements are also made to estimate the energy levels of adsorbed oxygen, to relate the apparent optimum in bulk Fermi energy to the energy levels of oxygen.

METHOD OF FERMI ENERGY MEASUREMENT

If a supported catalyst can exchange electrons with adsorbing species at the gas/catalyst interface, then it will also exchange electrons with the support at the catalyst/support interface, if the kinetics are sufficiently rapid. If the support is a semiconductor, such electron exchange can dominate the electrical properties of the semiconductor surface in the same way that surface states can do.

At equilibrium, the Fermi energy of the semiconductor support equalizes to the Fermi energy of the catalyst deposited on its surface. If this occurs by transfer of electrons from an *n*-type semiconductor to the catalyst (as is the case for TiO_2 and the catalysts studied here), a surface barrier develops and controls the electrical properties of the support. Measurement of these electrical properties then permits calculation of the Fermi energy of the catalyst. In the rest of the discussion we specify TiO_2 as the semiconductor support.

Figure 1 illustrates the behavior and measurement of the catalyst Fermi energy. For simplicity without loss of generality the catalyst levels are assumed to be dominated by an impurity band, such as may be expected, for example, with oxygen ion vacancies in a bismuth molybdate catalyst. The impurity band model of a catalyst is chosen for illustration to distinguish clearly between the oxide catalyst and the semiconductor support. Figure 1 shows the band model when the catalyst and semiconductor support are in electrical contact and thermodynamic equilibrium is established. Figure 1 shows that if initially the Fermi energy of electrons was high in the semiconductor support, the surface barrier in the support equalizes the Fermi levels, in this case giving rise to an insulating depletion layer (*2*). The double layer is considered to be primarily in the support on the assumption that the density of states near the Fermi energy is much higher in the catalyst than in the support.

The resulting insulating layer near the surface dominates the electrical properties of the TiO_2 surface. If the bulk TiO_2 is a reasonably good electrical conductor and the electrical conductance of a pressed powder pellet is measured, such insulating layers at the surface of each grain will cause a high intergranular resistance, and the conductance measured will be controlled by the surface insulating layer (*3*). Thus, the Fermi energy of the catalyst dominates the surface insulating layer, and the surface layer dominates the conduct-

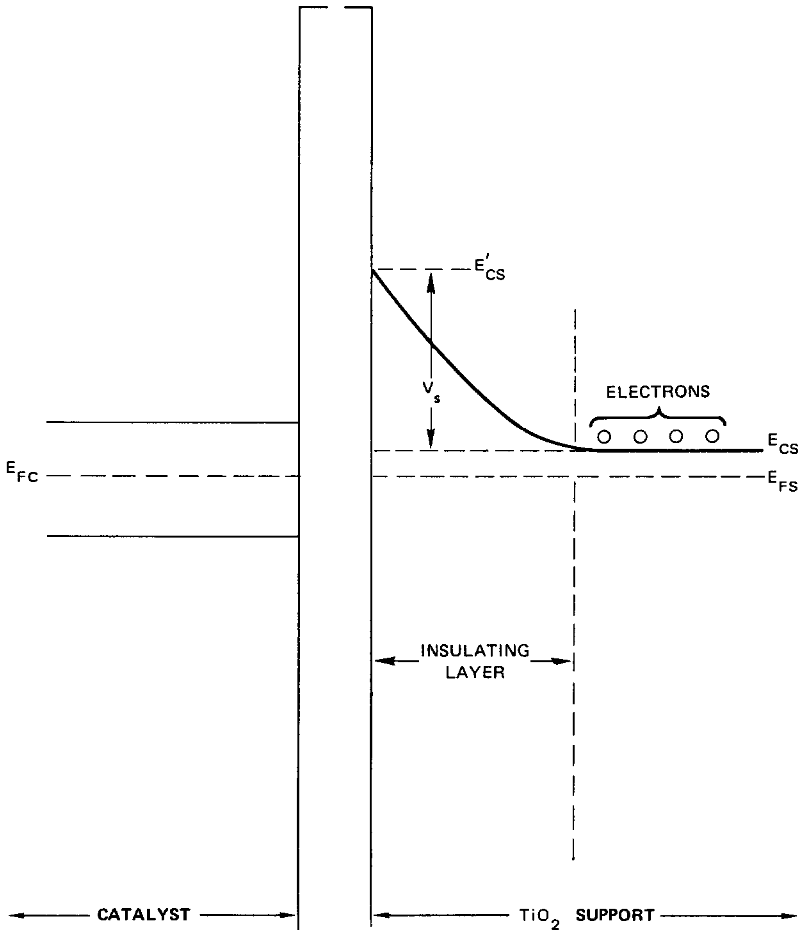

FIG. 1. Band model at catalyst/TiO_2 interface, when electronic equilibrium is established, showing appearance of the insulating layer on TiO_2.

ance. Therefore, measurements of the electrical conductance of a pressed TiO_2 pellet can be interpreted to give information about the Fermi energy of the catalyst.

A sketch of three TiO_2 grains, shown in Fig. 2, illustrates how the electrons must cross the insulating surface layer to conduct the current. The catalyst particles are indicated as small crystallites on the surface of a TiO_2 grain, covering a small fraction of the surface. However, their electrical influence, the insulating surface layer, is shown over the complete surface of the grain. The reason for this is that electrical effects extend over a wide region on a semiconductor (*2*), about a Debye screening area, L^2, $= \epsilon\epsilon_0 kT/e^2N_D$ (where L is the Debye length, ϵ_0 is the permittivity of free space, N_D is the donor density, and the other symbols are standard), which is computed to be on the order of 2×10^{-10} cm^2 for TiO_2 with a donor density, N_D, of about 10^{18} cm^{-3}, and a dielectric constant ϵ of about 100. We use TiO_2 of a grain diameter of about 0.25 μm and an area of about 6×10^{-10} cm^2/grain. Therefore a few particles of catalyst per grain of TiO_2 are sufficient to control the surface barrier over the whole surface.

Analysis of the conductance of a pressed pellet with "surface states" (here catalyst particles) defining the surface Fermi energy has been given (*3*) but will be reviewed briefly for completeness. The conductance,

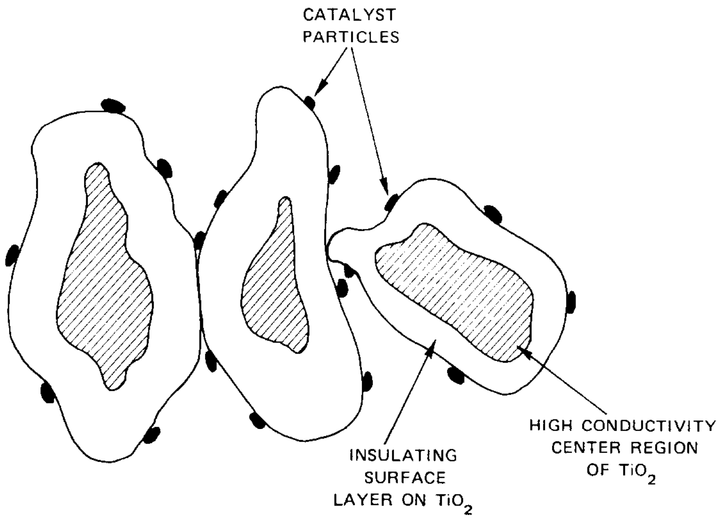

FIG. 2. Origin of contact resistance in TiO_2 pressed pellet showing three grains, the insulating layers, and the supported catalyst causing the insulating layers.

G, is assumed proportional to the density of electrons with enough energy E_{cs} or greater, as determined by the Boltzmann factor.

Thus, with E_{FS} the Fermi energy in the TiO_2, we have

$$G = \mu f(A)g(d)eN_c \exp\{-(E_{cs} - E_{FS})/kT\}, \tag{1}$$

where N_c is the effective density of states in the conduction band, μ is the electron mobility, and $f(A)$ and $g(d)$ are geometric factors determined by the grain diameter, d, and the mean contact area, A, between grains. We assume that the geometric factors are temperature insensitive, and, with E_{FC} the Fermi energy of the catalyst, Fig. 1 shows:

$$E_{cs} - E_{FS} = E_{cs} - E_{FC} \tag{2}$$

$$\text{or} \quad G = G_0 \exp\{-(E_{cs} - E_{FC})/kT\}, \tag{3}$$

it is concluded that an Arrhenius plot of G vs inverse temperature yields as activation energy the Fermi energy of the catalyst relative to the bottom of the TiO_2 conduction band as a reference.

To apply this model, two conditions should be satisfied: (a) the TiO_2 should be doped such that the donor density is high, so the conducting center of the grains is defined, and (b) the catalyst additive concentration should be sufficient to dominate the surface properties of the TiO_2 but not sufficient to provide an alternate path of electrical conductance. We deposit 5 atom% catalyst. It is clear that in many cases unacceptable complications may arise in attempts to apply this approach to a known catalyst. For example, in the present study it was not considered fruitful to apply the method to the uranium–antimony oxidation catalyst because the activation procedure for the catalyst requires a high temperature calcining which could lead to a solid state reaction between the titania and the catalyst.

EXPERIMENTAL

The TiO_2 is of the rutile structure doped with a 0.4 atom% Al_2O_3 and up to 1 atom% Sb_2O_3. The alumina dopant is present in the original TiO_2 (supplied by Glidden-Durkee) and the Sb_2O_3 is added by impregnation from solution. After impregnation, the sample was dried at 140°C and then fired at 950°C in air to promote Sb diffusion. The powder was ground and screened in 100-mesh screen, then the catalyst was added as described below.

Several metal–oxide catalyst systems

supported on the TiO_2 have been studied and compared: (a) bismuth/molybdenum oxides, (b) copper oxides at varying stoichiometry, (c) iron/molybdenum oxides, and (d) vanadium pentoxide.

Bismuth/molybdenum oxide in the ratio Bi/Mo $\cong 0.8$ was prepared by adding 1 cc solution of 0.176 N HNO_3 containing 0.145 g $Bi(NO_3)_3$ to a slurry of 1 g TiO_2 in 1 cc aqueous solution containing 0.071 g $(NH_4)_6Mo_7O_{24}$ and 0.0309 g NH_4OH. The slurry was dried in air at 140°C, pressed into a pellet and calcined for 2 hr at 510°C in air. The other samples (pure Bi_2O_3 catalyst and pure MoO_3 catalysts) were prepared by appropriate deletions of the bismuth or molybdenum salts.

The copper oxide additive was prepared by adding 0.17 g solution of reagent grade Cu_2O in 1 cc of 10% NH_4OH to 2 g TiO_2 in an oxygen-free environment. The slurry was dried under vacuum at room temperature, then dried further in air at 130°C and pressed into a pellet before outgassing under vacuum.

The iron oxide/molybdenum oxide samples (0.4 mole ratio of iron/molybdenum) were prepared by adding a solution containing 0.88 g of $(NH_4)_6Mo_7O_{24}$ in 11 cc 0.5 M NH_4OH to a slurry containing 8 g TiO_2 and 2.85 g $FeCl \cdot 6H_2O$ in 50 cc HNO_3 (pH 1). The molybdenum solution was added until the pH increased to about 2.5. The excess water was then removed by centrifuge. Iron oxide catalysts were made in the same manner omitting the molybdenum salt. In both cases, the samples were dried in air at 130°C, pressed into a pellet, and activated by baking at 450°C in air for about 1 hr.

The vanadium pentoxide was prepared by mixing 0.09 g solution of V_2O_5 in 2 cc of 48% HF with 2 g TiO_2 and drying in air at 110°C. The sample was then pressed into a pellet and mounted for further outgassing under vacuum.

Each of these pellets was further processed as follows. Aquadag (carbon) contacts were painted on, and tungsten pressure contacts were made to the Aquadag. The samples were then mounted in a vacuum system, evacuated using a trapped oil diffusion pump, and heated to 150°C under vacuum for at least 1 hr. The temperature was further slowly increased to the reaction temperature or above (maximum about 350°C for the Bi/Mo system, 350°C for the Cu_2O; 400°C for V_2O_5 and 250°C for the Fe/Mo system) allowing time for outgassing. The sample with supported vanadium was given a further treatment of 400°C in air to convert any residual fluoride to oxide.

MEASUREMENTS OF BULK FERMI LEVEL

Bi/Mo Catalyst System

Figure 3 shows the variation of conductance with inverse temperature for TiO_2 impregnated with Bi/Mo in the three compositions studied. The Fermi energy with Bi_2O_3 present is about 0.65 eV below the TiO_2 conduction band, the bismuth molybdate mixed oxide leads to an intermediate value at about 0.5 eV and that with the MoO_3 catalyst present is the same as the blank—about 0.4 eV below the reference level (TiO_2 conduction band).

A test of the stability of these Bi/Mo catalysts against oxidation and reduction was made as follows. The MoO_3 was exposed to oxygen to determine if the Fermi energy moves down due to more complete oxidation. The oxygen that adsorbs on the TiO_2 support must be desorbed before the Fermi energy of the catalyst can be measured. Separate tests indicated that about 5 min was required to outgas the TiO_2 at low temperature. Thus after exposing the supported MoO_3 for 10 min to oxygen at 150°C, the sample was outgassed 5 min and the Fermi energy was measured. The Fermi energy was unchanged. Unfortunately it was not possible to distinguish whether the Fermi energy of the MoO_3 was stable throughout the oxygen treatment, or whether it was changed but was restored during the 5 min outgassing. Similarly, there was no change in the Fermi energy of bismuth molybdate after oxygen treatment at 200°C or after reduction by propylene for 5 min at 25 Torr and 325°C. In the case of exposure to propylene con-

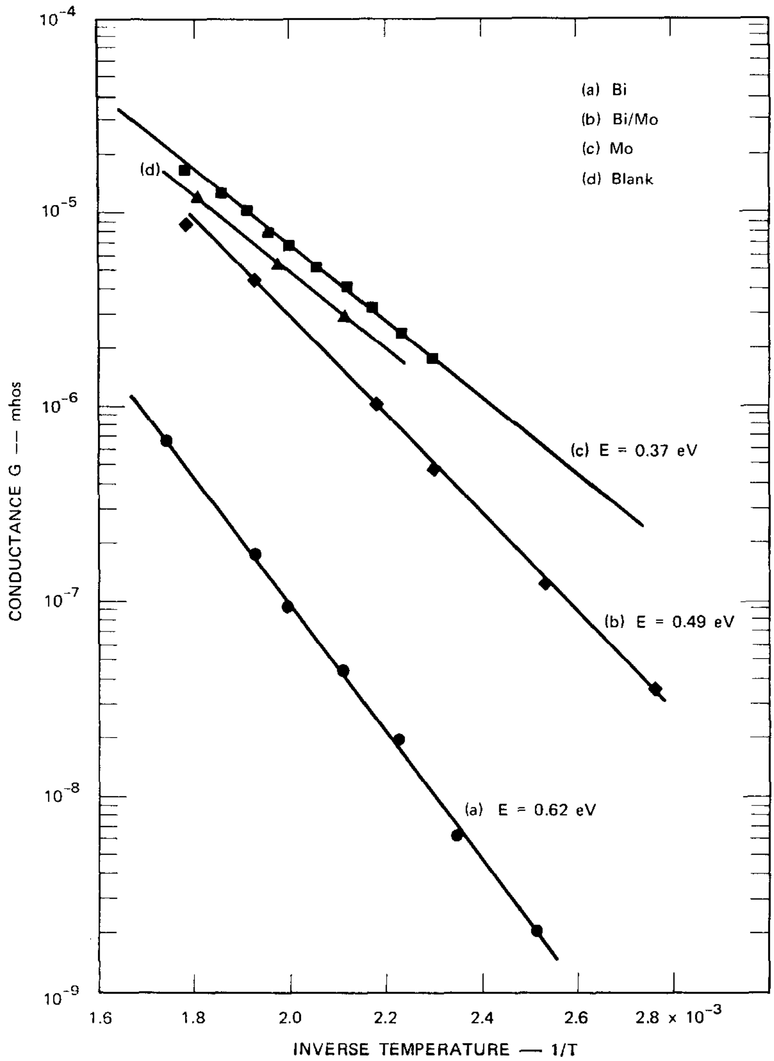

FIG. 3. Conductance/temperature relation of TiO_2 with mixed bismuth/molybdenum oxides deposited; (a) Bi_2O_3 deposited, (b) Bi/Mo = 0.8 deposited, (c) MoO_3 deposited, and (d) a blank. The activation energies shown are from an Arrhenius analysis.

ductance, measurements were the same both with propylene present and with the sample outgassed. Thus it appears that the Fermi energy of bismuth molybdate, in spite of the known rapid reduction, is stable, apparently controlled by the cation ratio, and may be insensitive to the oxygen content of the lattice. The Bi_2O_3 Fermi energy is similarly unaffected by propylene exposure at 325°C (10 min at 10 Torr).

The first three columns of Table 1 summarize the Bi/Mo results.

Cuprous Oxide Catalysts

Copper oxide was studied in the reduced form (outgassed at 350°C under vacuum), and with aliquots of oxygen added. The oxygen added was essentially totally adsorbed by the copper oxide as measured by pressure change (blank meaurements on TiO_2 alone showed no measurable oxygen absorption), and permitted investigation of the Fermi energy dependence on the copper/oxygen ratio.

TABLE 1

ELECTRON EXCHANGE LEVEL[a] (FERMI ENERGY) OF CATALYSTS

Treatment	Catalyst							
	Mo	Bi/Mo = 0.8	Bi	Cu_2O	Fe/Mo	Fe	V_2O_5	O_2^-
Outgassed (325°C)	0.37	0.49	0.62	0.36	0.59	0.80	0.24	
Oxidized (O_2)		0.50		Up to 0.60		0.80	0.28	0.63
Reduced: (a) C_3H_6; (b) C_8H_{10}; (c) MeOH		0.49	0.61(a)		0.54(c)	0.80(c)	0.11(b)	
$CH_3Br + O_2$				0.53				

[a] Probable error estimated at ±0.02 eV.

Figure 4 shows the conductance/inverse temperature plot (a) with the system outgassed, yielding $E_{cs} - E_F = 0.36$ eV, (b) with 2×10^{19} oxygen atoms absorbed in Cu_2O containing 4×10^{20} Cu ions, yielding $E_{cs} - E_F$ of 0.54 eV, (c) with 10^{20} oxygen atoms absorbed, (so that if the "reduced" sample was Cu_2O, this sample would correspond to $Cu_2O_{1.5}$) yielding $E_{cs} - E_F$ of 0.60 eV, and curve (d) with the promoter methyl bromide present, yielding again the intermediate Fermi energy with $E_{cs} - E_F = 0.53$ eV.

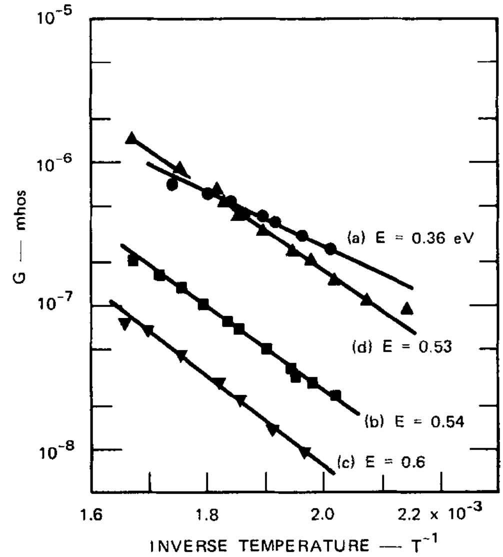

FIG. 4. Conductance/temperature relation for TiO_2 with copper oxide deposited: (a) measurements on outgassed copper oxide, (b) measurements after 0.05 oxygen atoms, (c) measurements after 0.25 oxygen atoms/copper atom added and (d) with promoter CH_3Br present during oxygen exposure.

Wood, Wise and Yolles (*4*) have found that the selectivity (acrolein/CO_2 ratio) in the propylene oxidation reaction passes through a maximum as the catalyst is oxidized. The activity shows a monotonic increase as the catalyst is oxidized. Wood (*5*) has concluded that under helium at 350°C, Cu_2O has a resistivity corresponding to oxygen-deficient cuprous oxide, (Cu_2O_{1-x}). Thus, in the present case the vacuum outgassed catalyst (Table 1) can be expected to be on the "oxygen-deficient" side of the maximum in catalytic selectivity. As the Cu_2O becomes more oxidized it passes through the optimum Fermi energy and, as described by Wood, Wise and Yolles (*4*) if the Cu_2O becomes more oxidized, it passes through a maximum in selectivity. The reason for the methyl bromide addition was to test the influence of this promoter, which has been shown (*6*) to maintain the optimum electrical characteristics and high selectivity even at high oxygen pressure.

Fe_2O_3/MoO_3 Catalyst System

With the discovery that the Fermi energy of a good partial oxidation catalyst is about the same for Bi/Mo and Cu_2O, the generality of the observation was tested by examining the Fermi energy of the Fe_2O_3/MoO_3 mixtures used for methanol oxidation to formaldehyde. The results are shown by the curves in Fig. 5; curve (a) shows Fe_2O_3 supported on the TiO_2 (both the slope and

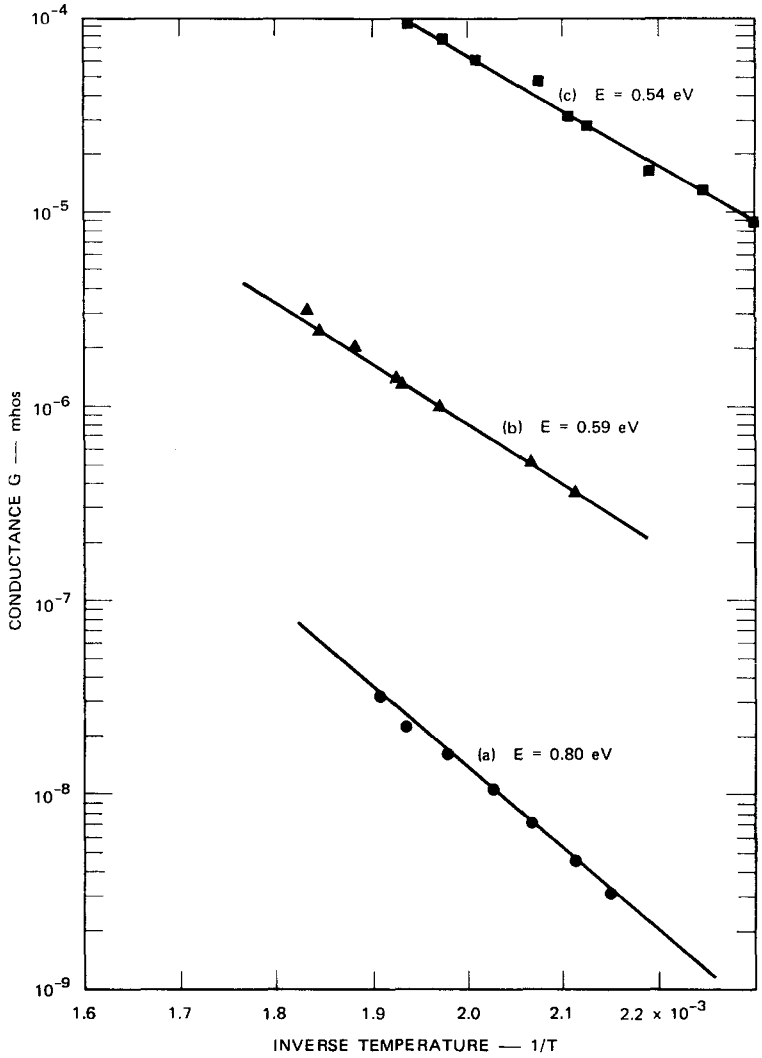

FIG. 5. Conductance/temperature relation of TiO_2 with mixed iron/molybdenum oxides deposited; (a) Fe_2O_3 only, (b) Fe/Mo = 0.4, (c) Fe/Mo = 0.4 after methanol pretreatment.

conductance were independent of pretreatment in oxygen or methanol at 250°C), curve (b) shows a catalyst having a ratio of Fe/Mo = 0.4 after outgassing, and curve (c) shows the same catalyst after a 1-min methanol treatment at 250°C, pressure 12 Torr. After exposure to reaction conditions (750 Torr air, 12 Torr MeOH 250°C) and 5 min outgassing, the conductance of the sample was between curves (b) and (c), but changed too rapidly with time to permit a conductance/temperature test.

V_2O_5 *Catalysts*

The vanadium pentoxide catalyst used for oxidation of *o*-xylene to phthalic anhydride was also examined. Literature results (7) indicate that a catalyst which is slightly reduced in xylene has the highest selectivity.

Figure 6 shows the results; curve (a) taken after the sample was exposed to 1 atm O_2 at 400°C, yielding $E_{cs} - E_F = 0.28$, and curve (b) taken after a subsequent exposure to xylene (about 1 Torr), where

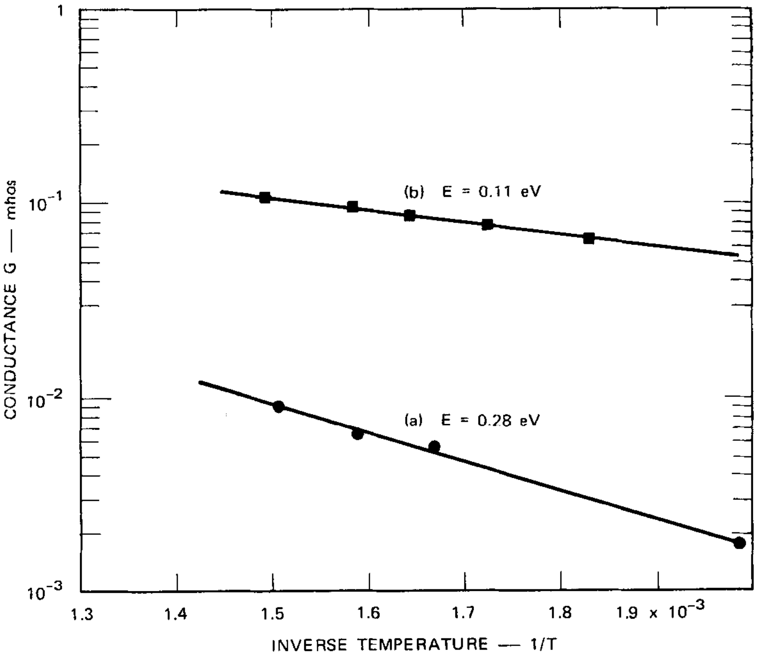

FIG. 6. Conductance/temperature relation of TiO_2 with V_2O_5 deposited; (a) after 400°C oxidation; (b) after 400°C reduction in xylene.

reduction raised the Fermi energy of the catalyst, yielding $E_{cs} - E_F = 0.11$.

The Electron Exchange Level of Oxygen

In the following discussion, the observation of an optimum value for the Fermi energy E_F is related to the ability of the catalyst to exchange electrons with oxygen. Thus it is of interest to relate the results to the energy of electrons on adsorbed oxygen. Essentially similar measurements are made on a TiO_2 pellet with no catalyst deposited—the surface barrier on the TiO_2 (Fig. 1) is produced by adsorbed oxygen.

Unfortunately accurate values for the energy of electrons on adsorbed oxygen cannot be obtained by the same technique. Two difficulties arise. First the analysis of Eq. (3) can only be accurately applied when the occupancy of the surface states is at equilibrium and the density of surface states is constant. Both these requirements cannot be simultaneously satisfied when dealing with a volatile species. In practice we forego the equilibrium requirement. Oxygen adsorption is permitted, then the temperature is lowered to the region of irreversible adsorption, and the conductance/temperature measurements made. The slope in this case should be the surface barrier height, which only approximates the parameter of interest. The second difficulty in obtaining accurate values for the average energy of electrons on oxygen is the multiplicity of oxidation states and the inevitable chemical transformations (such as dissociation of the molecule). Thus in the present study we have attempted only to measure the energy of the electron on the O_2^- species.

There will be at least two "surface states" due to oxygen, one associated with O_2^- and the reaction,

$$O_2 + e = O_2^-, \qquad (4)$$

which is expected to dominate at low temperature and high pressure (being first order in oxygen pressure at equilibrium). Another is associated with O^- and the reaction,

$$\tfrac{1}{2}O_2 + e = O^-, \qquad (5)$$

and is expected to dominate at high temperature and low oxygen pressure.

Experiments show that one form of oxygen adsorption occurs at oxygen pressures greater than about 1 Torr and temperature less than about 250°C. This species can be outgassed at 250°C or above. Similar observations were made by Tanaka and Blyholder (*8*). This form of adsorption is characterized at low temperature by a conductance/temperature relation with an Arrhenius slope of 0.63 ± 0.03 eV. If this value is interpreted as the electrochemical potential of electrons on oxygen (presumably O_2^-) relative to the TiO_2 conduction band the electrochemical potential for electrons on oxygen is a little lower than the Fermi energy for the "optimum" catalysts (bismuth molybdate, partially oxidized copper oxide, and slightly reduced iron molybdate) as indicated on Table 1.

A second form of oxygen is observed to form in the temperature interval between 250° and 400°C. This form can only be outgassed at about 400°C. The behavior in this temperature range which may be the range in which O^- dominates (at low pressure) is very complicated and needs further investigation. The behavior suggests a slow conversion of O_2^- to O^- at low pressure and high temperature. No simple electrochemical potential for electrons on O^- can be obtained from these results without much more analysis, since values of the slope between 0.25 and 0.5 eV have been observed.

Although the details of the oxygen behavior, especially of the O^-, are not understood, the results suggest that oxygen at high pressure is associated with electrochemical potentials for electrons close to, and probably just below, the Fermi energies (electrochemical potentials for electrons) of the best Bi/Mo, Cu_2O and Fe/Mo catalysts.

MECHANISM

General

In the experimental studies we have varied the stoichiometry or composition of the catalysts, causing a variation of Fermi energy, because we are interested in the corresponding variation of catalytic properties. From comparing the results of these experiments with known catalytic properties (as the catalyst composition is varied), we suggest that there is an intermediate Fermi energy, such that $E_{cs} - E_{FS} = 0.5$ to 0.55 when both the activity and selectivity are optimized. As shown in Table 1, for the three catalyst systems, Bi/Mo, Cu, and Fe/Mo, the bulk Fermi energy of the catalyst is in this range at compositions corresponding to the optimum in selectivity for partial oxidation. The single exception is the vanadia catalyst.

We suggest that this optima intermediate Fermi energy is related to the fact that the observed electrochemical potential for electrons on oxygen is close to the observed range of values. Such a connection may be justified by the following qualitative model. By the definition of the Fermi energy, electrons transferring from or to a solid can be considered to originate at or return to the energy of the Fermi level. A high activity catalyst must have a Fermi energy (at the surface) high enough that electrons from the catalyst can reduce oxygen exothermically, but low enough that electrons can be exothermically returned to the catalyst from negatively charged intermediates or products. These limits define a range within which the Fermi energy must be located. If the rate-limiting step involves reduction of gaseous oxygen, the optimum surface Fermi energy will be as high as possible within this range to accelerate oxygen reduction. On the other hand, if the rate-limiting step involves transfer of electrons from surface species to the semiconductor bands, the optimum surface Fermi energy will be as low as possible within this range, limited by the requirement that oxygen reduction must still occur. Thus, in the latter case the optimum surface Fermi energy will be near the oxygen levels. If the surface Fermi energy were the same as the bulk Fermi energy, the observations would be reconciled by these considerations. For example, there is evidence, discussed in a later section, that the V_2O_5 catalyst operates with oxygen reduction being rate limiting, hence this catalyst shows a high

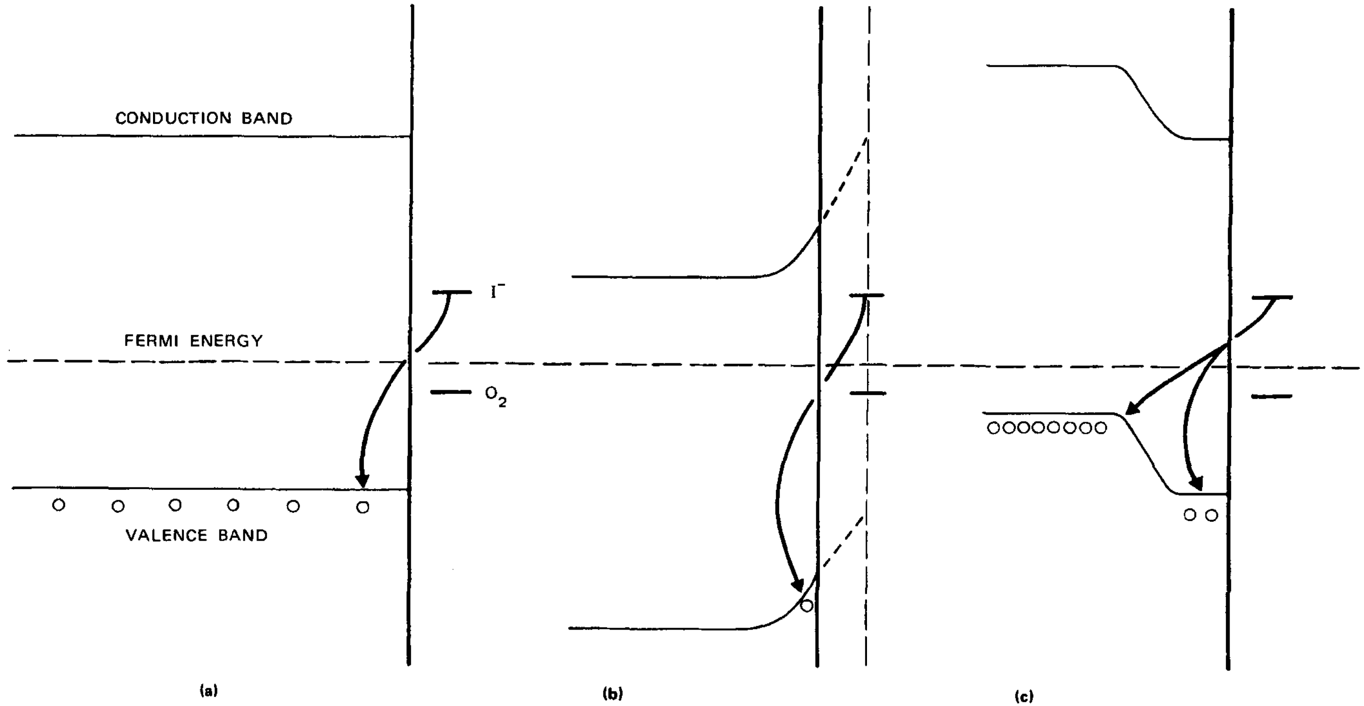

FIG. 7. Formation of the surface double layer during catalysis: (a) bulk Fermi energy optimum, (b) bulk Fermi energy too high, (c) bulk Fermi energy too low.

Fermi energy when the activity is high. On the other hand, there is evidence that the others have rate-limiting steps involving an electron transfer back to the semiconductor, hence these catalysts all have a common bulk Fermi energy near the oxygen levels.

There is, however, one important variable that must be included. That is the surface double layer. The double layer is important because it fills a compensating function. If the bulk Fermi energy is too high or too low, the formation of the double layer at the surfaces moves the surface Fermi energy into the proper range. For example, if the bulk Fermi energy is too high, the reduction of gaseous oxygen will be accelerated and the resulting negative surface charge will lower the surface Fermi energy into the necessary range.

In the diagrams of Fig. 7, a simplified two-step mechanism is used for illustration, where electrons are considered to move from the bulk to a single energy level, called O_2, and the reverse transition is from a single intermediate, called I^-, back to the bulk semiconductor. In Fig. 7, the electron returns to the valence band, corresponding to hole capture, but the concepts do not depend on whether holes or electrons are transferred. In each of these diagrams, the surface Fermi energy is ideally located, according to the present model, to provide the most active catalyst for the case where electron transfer from I^- to the semiconductor

$$p + I^- \rightarrow I \qquad (6)$$

(where p represents a hole in the valence band) is involved in the rate-limiting step. That is, the Fermi energy is low to encourage removal of electrons from I^- but still maintain O_2 reduction exothermic. In Fig. 7a the bulk Fermi energy is at a value such that the optimum is reached with no double layer, in Fig. 7b the bulk Fermi energy is too high, and in Fig. 7c the bulk Fermi energy is too low. In both 7b and 7c a double layer must form to bring the surface Fermi energy to the optimum position.

When the bulk Fermi energy is too high, as in Fig. 7b, the double layer forms as excess oxygen is adsorbed leading to a negative surface charge which moves the interior bands (and the Fermi energy) down relative to the surface energy levels. However, the valence band is clearly farther from the Fermi energy in case (b) than in case (a) so the reaction (6) is slower in case (b) because the hole concentration, p, is lower. Thus it is clear that for electron transfer to a level below the Fermi energy (from I^- to holes in the valence band in this example) the kinetics will be slower, the higher the bulk Fermi energy. Even in the case where the rate is proportional to the product between the hole density and a negatively charged surface state (such as rate α $[p] \cdot [I^-]$) the product will be smaller the larger the double layer under otherwise constant conditions. Thus the higher the bulk Fermi energy, and the greater the resulting double layer, the lower the reaction rate.

The behavior of a system when the bulk Fermi energy is initially too low, is more complex. When the catalyst is first exposed to reactants there will be no oxygen reduction. Olefin adsorption and reaction will however be highly favored. With most active oxidation catalysts the olefin will remove oxygen ions from the lattice, forming oxygen vacancies as donors, or remove cation vacancies as acceptors. Two cases emerge, one where the Fermi level changes, one where it is pinned. If the change in stoichiometry results in a higher Fermi energy, either an internal double layer will form, as illustrated in Fig. 7c, or if there is rapid vacancy diffusion, the Fermi energy throughout the catalyst will rise. The latter is apparently the case for copper oxide, for example, where the bulk conductance is highly sensitive (*4*) to the olefin/oxygen pressure ratio. The Fermi energy in such cases must rise to a level near the oxygen levels until the rate of reduction of gaseous oxygen equals the rate of oxygen removal by the olefin. If the pressure of gaseous oxygen is too high, the steady-state position of the Fermi energy can be too low. In the copper oxide system, which depends on hole capture for removal of electrons from the olefin–lattice oxygen complexes, if the steady-state Fermi energy becomes too low, holes apparently become too plentiful and multiple hole capture processes can occur leading to CO_2. For the case then when the Fermi energy is highly sensitive to the oxygen/olefin ratio, the selectivity as a partial oxidation catalyst may be poor at high oxygen pressure.

A second case is that where the Fermi energy that is too low is pinned in that position by the donor levels of the oxygen vacancies themselves, and no double layer can form. In this case oxygen reduction will either not occur or will occur slowly, and after the surface is saturated with olefin, little reaction will occur. An example of this case may be bismuth molybdate of high Bi/Mo ratio. An even more striking case may be iron oxide/molybdenum oxide with too high an Fe/Me ratio (*9*).

The above discussion is concerned only with macroscopic properties. The thesis is not dependent, except in detail, on the form of the complexes (whether O_2^-, O^-, or O^{2-} is the active surface species that forms a complex with the hydrogen from the olefin or with the olefin radical, or whether the olefin adsorbs on a cation or an anion site). These microscopic details will be important factors in determining the overall rate and the form of the product, but the present measurement provides no information regarding how they differ from catalyst to catalyst. Such a definition of the various necessary functions of a catalyst, with measurement techniques suitable for each, may be very helpful in analyzing the overall catalyst performance. An initial separation into macroscopic functions, such as oxygen transfer (including vacancy diffusion) and electron transfer (discussed here) and microscopic functions related to properties of special adsorption sites, may be convenient.

With the above model of electron transfer requirements, we can discuss the known properties of the various catalysts studied and with the new evidence speculate as to the reaction mechanism.

Bi_2O_3/MoO_3 *Catalyst System*

The bismuth molybdate catalyst system is one of the most successful oxidation catalysts for propylene oxidation to acrolein and ammoxidation to acrylonitrile.

From the results here and the results of others (*10–16*), a self-consistent picture emerges. From the results of Table 1, in bismuth molybdate the Fermi level appears to be pinned at a value determined by the Bi/Mo ratio, and in particular, at a Bi/Mo ratio near 1 or 2 where the activity is highest (*10*), the Fermi energy is optimized relative to the oxygen levels. In this range the crystal structure is such (*10*) that diffusion of oxygen ion vacancies is extremely rapid. Experiments with ^{18}O leave little doubt that under catalytic conditions, the reducing agent reacts primarily with lattice oxygen (*13–14*).

Since the Fermi level appears pinned over a reasonably wide range of oxygen pressure, the level is probably pinned by oxygen ion vacancies. The rate-limiting step (*17*) appears to involve propylene adsorption, rather than oxygen reduction. The adsorbed species is apparently an allyllic radical (*18*), formed by hydrogen removal during adsorption. Since the Fermi energy is low in the optimum catalyst, it appears that electron transfer into the catalyst is most likely involved in the rate-limiting process. Thus, we suggest the following mechanism for the rate-limiting step of propylene adsorption, where O_L^{2-} is a lattice oxygen ion:

$$O_L^{2-} \rightleftarrows O^- + e, \qquad (7)$$

$$C_3H_6 + O^- \rightarrow \text{active intermediate}, \qquad (8)$$

where the latter is the rate-limiting step, and the O^- species is required to extract a hydrogen atom from the propylene (forming an OH^- group) or to provide a site for the allyl radical adsorption.

The source and sink of electrons in this catalyst, enabling the reduction of gaseous oxygen and the removal of the negative charges from the organic/lattice oxygen intermediate complexes [Eq. (7), for example] is of great interest. The transfer of electrons to the catalyst could be to a hole in the valence band, to an empty state in an impurity band, or to the conduction band. Since bismuth molybdate appears to be an *n*-type (*11*, *12*) catalyst under reaction conditions, a valence band mechanism is unlikely. Because *n*-type catalysts are usually poor oxidation catalysts, we tend to discount a conduction band mechanism in such an excellent catalyst. If we accept an impurity band mechanism, many experimental observations can be reconciled, and the surprisingly high activity and stability can be explained.

The obvious impurity band is, of course, the band associated with the oxygen ion vacancies formed during the initial reduction of the bismuth molybdate, in the sites of the koechlinite structure (*6*) where vacancy diffusion is so favorable. Such anion vacancies form a donor band capable of donating electrons to adsorbed oxygen molecules as well as to a conduction band. This band would then control the Fermi energy. According to the present observations, the energy of the band must be on the order of 0.5 eV below our present reference energy (the conduction band of TiO_2).

Evidence for such a donor band is as follows. First, it is clear that there must be a band—removal of large quantities of oxygen must form anion vacancies or interstitial cations (yielding a donor band) or remove cation vacancies (removing an acceptor band, as discussed below with Cu_2O). The observations (*13*, *14*) of rapid diffusion of ^{18}O strongly suggest anion vacancies as the dominant imperfection introduced by reduction. Studies at SRI have shown (*11*) that about $5 \times 10^{-2}\%$ of the oxygen ions are removed during steady-state catalysis, which represents a substantial density of mobile donor levels. The observations (*11*) indicate that the rate of increase in the density of electrons in the conduction band decreases after an initial rapid rise as the material is reduced suggesting that the Fermi energy becomes pinned to the donor band when it is formed. In the present work, of course, it has been concluded that the Fermi energy is pinned at the optimum level, 0.5 eV below the TiO_2 conduction band.

Fe_2O_3/MoO_3 *Catalyst System*

According to our measurements, this catalyst system is similar to the Bi/Mo system, with iron oxide replacing the bismuth. The primary practical use of this catalyst system is the oxidation of methanol to formaldehyde. The activity of the catalyst as a function of Fe/Mo ratio has been studied by Kolovertnov and his co-workers (*9*) who found a peak of specific activity at about 65 atom% Mo. The activity dropped sharply as the Mo concentration dropped below 60%. The present model and the results in Table 1 suggest this limit corresponds to the composition at which the Fermi energy moves from the optimum value to excessively low values ($E_c - E_F$ becomes too high).

Pernicone and co-workers (*19*) have shown that lattice oxygen is available for the reaction and is not diffusion limited; they have shown that the rate of reaction in a pulse reactor is the same, with and without gaseous oxygen. These workers have demonstrated that the crystal structure of iron molybdate has an open and probably highly defective structure, consistent with rapid oxygen ion migration. They suggest product desorption as the rate-limiting step.

The available data are thus consistent with the present model relating composition to activity and specificity in partial oxidation. It remains for microscopic models (*20*, *21*) to explain why this catalyst mixture is exceptionally rapid in the partial oxidation of methanol, where other catalysts are superior for, say, the partial oxidation of propylene.

Copper Oxide

Since only one cation is present in this catalyst, the stoichiometry (copper/oxygen ratio) is the key composition variable. There is ample evidence that oxygen exchange rapidly occurs (*22*) for a thin surface region even at room temperature (*23*), and over a correspondingly thicker region at reaction temperatures.

According to Bloem (*24*), oxygen absorption or removal of lattice oxygen leads to copper ion vacancies according to

$$O_2 = 4V'_{Cu} + 4p + 2\,Cu_2O, \qquad (8)$$

where V'_{Cu} is a negatively charged copper ion vacancy, and p represents a hole. At equilibrium the hole density [p] defines the position of the Fermi energy E_F according to

$$[\mathrm{p}] = N_V \exp\{-(E_F - E_V)/kT\}, \quad (9)$$

where N_V is the effective density of states in the valence band and E_V is the energy of the valence band edge. Thus, clearly in oxygen, the oxygen pressure at steady state or the oxygen pretreatment of the catalyst (under conditions when steady state is not reached) determines the stoichiometry of the Cu_2O and hence the Fermi energy. In the catalytic case, the stoichiometry of the Cu_2O and hence the Fermi energy is determined not only by reaction (8) but also by a reaction representing oxygen removal by the olefin. The higher the oxygen/olefin ratio, the more oxidized the catalyst and the lower the Fermi energy.

With this background and the present experimental observations, the case of Cu_2O appears to be relatively straightforward, where the Fermi energy is not pinned (except when methyl bromide is present). Depending on the olefin/oxygen ratio, the Fermi energy can be too high, leading to low activity; optimum; or too low, leading to high activity but poor selectivity.

The reason that methyl bromide promotes peak activity of the catalyst for acrolein formation and promotes the optimum Fermi energy has been explained by Holbrook and Wise (*6*) in terms of a surface state which anchors (pins) the Fermi energy at the surface. This interpretation cannot be amplified with the present data.

V_2O_5 *Catalysts*

The vanadium pentoxide catalyst has been utilized in the oxidation of xylene to phthalic anhydride. The oxide must be somewhat reduced (*7*) for optimum activity. Fully oxidized catalysts lead to normal conversion but a higher CO_2 production than normal. Overreduced catalysts lead to a low rate of oxidation. The most active stoichiometry appears to be between V_2O_5 and $V_2O_{4.34}$ (two structures identifiable by X-ray). The concentration of xylene in the gas phase must be controlled carefully to provide the correct stoichiometry.

The results of Simard *et al.* (*7*) suggest lattice oxygen is extracted from the vanadia during the oxidation reaction, and the replenishment of lattice oxygen is an independent reaction. Clark and Berets (*25*) also conclude xylene removes lattice oxygen. Both these groups (particularly Simard *et al.*, who support the suggestion with X-ray data) conclude that an open lattice is present due to a phase change associated with the V_2O_5 to $V_2O_{4.34}$ transition, perhaps permitting rapid diffusion of oxygen vacancies.

Vanadia is an *n*-type semiconductor with an exceptionally low energy conduction band, such that it is energetically favorable for many substances to inject electrons. For example, Gomes (*26*) has shown that ferroine can inject electrons into V_2O_5, even at room temperature. The measurement is electrochemical, with the ferroine injecting from solution and the electron transfer observed as an anodic current. Iodide ions and ferrocyanide are also spontaneously oxidized at room temperature by electron injection. This is consistent with the observations of Clark and Berets (*25*) who observed an increase in conductance with xylene at a temperature far too low for reduction of V_2O_5 and concluded that xylene forms a positive ion, injecting electrons. On the other hand, reoxidation of the catalyst is very slow (*7*).

From this discussion it appears that vanadia is in a different class of catalysts from the others studied here—a class where the organic molecule becomes easily ionized and the slow step in oxidation catalysis is the replacement of lattice oxygen ions (*25, 27*). This conclusion is consistent with the experimental observation that the optimum Fermi energy is high, for a high Fermi energy will encourage the formation of lattice oxygen. The overall behavior will be a reduction of the catalyst, raising the Fermi energy, until the rate of oxygen reduction and lattice oxygen formation is increased to match the rate of lattice oxygen removal.

CONCLUSION

From these examples—particularly from the well-defined bismuth molybdate catalyst—we can suggest many of the qualities needed for a good partial oxidation catalyst. Such a listing provides a partial basis for reconciling many apparently conflicting requirements. We will specify requirements where oxygen is the dominant ionized species at the surface, but the requirements with a positive surface charge are similar.

An optimum partial oxidation catalyst needs the following characteristics:

1. The Fermi energy should be pinned at the optimum value by a band of levels of very high density, so that substantial changes in the stoichiometry of the crystal can occur without changing the electrochemical potential of electrons (Fermi energy). The catalyst then becomes less sensitive to the exact gas mixture and temperature.
2. A reservoir of easily accessible lattice oxygen ions should be available, a reservoir where removal can be very fast without changing the chemical potential of oxygen ions (rapid diffusion of the anion vacancies to and from the surface).
3. The Fermi energy should be at the correct value to permit reduction of oxygen at a rapid rate, and to encourage partial but not complete oxidation of product molecules.
4. The band of levels should be a donor band. Then, with rapid diffusion of vacancies and a properly placed Fermi energy, the catalyst can adsorb large quantities of weakly bound oxygen.
5. Other considerations involving local chemical complexes (organic/catalyst coordination complexes, acid centers) will certainly affect the rate and the dominant product formed in the partial oxidation. The present work provides no information about this aspect. However, there is no question that a good catalyst must present favorable adsorption sites for the organic molecule.

It is hoped that this study will be a help in distinguishing the macroscopic requirements (the electronic redox character) of a catalyst from the microscopic requirements (configuration of adsorption sites). However, the study itself pertains primarily to macroscopic requirements.

The requirements of an optimum catalyst seem to be present in bismuth molybdate. Copper oxide, and, to a greater or lesser extent, the other catalysts, lack the feature of a high density band of levels pinning the Fermi level at the optimum position Thus, for these catalysts the Fermi level is a function of the oxidation/reduction of the solid by the reactants, and the reactant composition is critical. Copper oxide seems to have a second failing in that the impurity band is an acceptor band (copper ion vacancies) so that the electrons for reducing the gaseous oxygen must come from the valence band. However, the Cu^+/Cu^{2+} band may serve as a donor band. The promoter methyl bromide apparently serves as a surface state of high density for pinning the Fermi energy. Despite the failings of copper oxide, it has two of the desirable characteristics of the above list: mobile vacancies so the oxide can act as a reservoir of available oxygen, and a Fermi energy that is reasonably insensitive to stoichiometry (Fig. 4) and adjustable to the right energy region. Thus although bismuth molybdate and copper oxide seem to have little in common (the one an *n*-type transition metal oxide, the other a *p*-type oxide of a group IB metal) they have characteristics in common needed for a good catalyst.

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REFERENCES

1. MORRISON, S. R., AND BONNELLE, J.-P., *J. Catal.* **25**, 416 (1972).
2. MANY, A., GOLDSTEIN, T., AND GROVER, N. B., "Semiconductor Surfaces." Wiley, (Interscience), New York, 1965.
3. MORRISON, S. R., *Surface Sci.* **27**, 586 (1971).
4. WOOD, B. J., WISE, H., AND YOLLES, R. S., *J. Catal.* **15**, 355 (1969).
5. WOOD, B. J., private communication.

6. Holbrook, L. L., and Wise, H., *J. Catal.* **27,** 322 (1972).

7. Simard, G. L., Steger, J. F., Arnott, R. J., and Siegel, L. A., *Ind. Eng. Chem.* **47,** 1424 (1955).

8. Tanaka, K., and Blyholder, G., *J. Phys. Chem.* **76,** 3184 (1972).

9. Kolovertnov, G. D., Boreskov, G. K., Dzis'ko, V. A., Popov, B. I., Tarasova, D. V., and Belugina, G. G., *Kinet. Katal.* **6,** 950 (1965).

10. Batist, Ph. A., Der Kinderen, A. H. W. M., Leeuwenburgh, Y., Metz, F. A. M. G., and Schuit, G. C. A., *J. Catal.* **12,** 45 (1968).

11. Sancier, K. M., Aoshima, A., and Wise, H., *J. Catal.* **34,** 257 (1974).

12. Pluta, J., *Z. Anorg. Allg. Chem.* **356,** 105 (1967).

13. Keulks, G. W., *J. Catal.* **19,** 232 (1970).

14. Wragg, R. D., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **22,** 49 (1971).

15. Sancier, K. M., Dozono, T., and Wise, H., *J. Catal.* **23,** 270 (1971).

16. Peacock, J. M., Parker, A. J., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **15,** 387 (1969).

17. Adams, C. R., and Jennings, T. J., *J. Catal.* **3,** 549 (1964).

18. Voge, H. H., Wagner, C. D., and Stevenson, D. P., *J. Catal.* **2,** 58 (1963).

19. Pernicone, N., Lazzerin, F., Liberti, G., and Lanzavecchia, G., *J. Catal.* **14,** 293 (1969).

20. Pernicone, N., Liberti, G., and Ersini, L., *Proc. Int. Congr. Catal., 4th,* Moscow, *1968.*

21. Trifero, F., Notarbartolo, S., and Pasquon, I., *J. Catal.* **22,** 324 (1971).

22. O'Keefe, M., and Stone, F. S., *Proc. Roy. Soc., Ser. A* **267,** 501 (1962).

23. O'Keefe, M., Ebisuzaki, Y., and Moore, W. J., *J. Phys. Soc.* **18,** *Suppl. 2,* 131 (1963).

24. Bloem, J., *Philips Res. Rep.* **13,** 167 (1958).

25. Clark, H., and Berets, D. J., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky and P. B. Weisz, Eds.), Vol. 9, p. 204. Academic Press, New York, 1957.

26. Gomes, W. P., *Surface Sci.* **19,** 172 (1970).

27. Dixon, J. K., and Longfield, J. E., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 7, p. 217. Reinhold, New York, 1960.