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Properties of Bismuth Oxide Catalysts for Oxidative Dehydrogenation Dimerization of Propylene

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The electronic properties of bismuth oxide shed light on the mechanism of its catalytic activity for the oxidative dehydrogenation dimerization of propylene. Variations in the electrical conductivity and thermoelectric power, as the gas phase contacting a pellet of this *p*-type semiconductor was changed, provided information about the nature of species adsorbed at reaction temperature.

SCOPE

The complete investigation of any heterogeneous catalytic system includes characterization of the bulk solid, determination of the nature of the surface active sites, and identification of the type(s) of adsorbed species that are formed on the surface. When the solid has sensitive electrical properties, it may be possible to use changes that occur in these properties to gain insight into some of these characteristics. Bismuth oxide is such a material (it is a *p*-type semiconductor), and it is a catalyst for several reactions among them being the dimerization of propylene to form 1,5-hexadiene (and ultimately benzene through cyclization) in the presence of oxygen at high temperature (OXDD).

The purpose of these experiments was to study the interaction of the reactants oxygen and propylene with Bi_2O_3. To a pellet of the material were attached electrical leads and thermocouples which allowed one to measure simultaneously the temperature, electrical conductivity, and thermoelectric power as the partial pressures of the adsorbates were changed. The observations were analyzed according to an electrical conductivity model which assumes that the individual catalyst particles in the compressed solid pellet are each composed of an interior core and an external shell.

Whereas earlier studies of the electronic properties were conducted in closed systems, a flow reactor was used in this investigation so as to reproduce the reaction conditions at which the kinetic data were collected. It is desirable to make the maximum number of observations of the catalytic system at reaction conditions in order to deduce with less ambiguity some of the details of the reaction mechanism; these experiments were designed to extend the amount of information available for the bismuth oxide catalyst.

CONCLUSIONS AND SIGNIFICANCE

The electronic properties studied in this work, the conductivity and thermoelectric power (Seebeck Effect), indicate that both of the reactants for the OXDD reaction, propylene and oxygen, were adsorbed on the surface of the oxide. Based on the data of this work and data from similar catalytic systems, a model is advanced to explain the adsorption-desorption phenomena. From this model it was concluded that the oxygen is adsorbed as a negative species (perhaps O^{-2}) and that there is more than one type of charge carrier (positive cation vacancy "holes" due to rapid electron exchange between Bi^{+3} and Bi^{+5}, plus some other type) responsible for the pellet conductivity. The oxygen adsorption sites are probably these bismuth cation centers. The electrical effects observed with oxygen are reversible as the partial pressure is cyclically changed.

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The other reactant, propylene, behaves in a much more complex manner. In addition to being adsorbed, it will completely reduce the oxide if exposed to the catalyst in the absence of O_2 at 550°C. However, small pulses of propylene (each equivalent to removal of less than a monolayer of oxygen from the catalyst) will first remove *adsorbed* oxygen, followed by removal of *lattice* oxygen. This latter removal does not significantly affect the conductivity or thermoelectric power.

These experiments have shown that there is a very important interplay between the surface and bulk parts of this catalyst. They have contributed to a better understanding of the relative importance of the various phenomena involved in the OXDD reaction through identifying one of the surface species. It is hoped that once a complete understanding is achieved, an even more effective catalyst can be developed for this potentially significant reaction.

Changes in electronic properties of semiconducting solids that occur during interaction with gases frequently provide considerable information about the mechanism of catalytic reactions over these materials (Hauffe, 1955; Parravano and Boudart, 1955). In addition to physical mass transport factors, the three chemical steps that are involved in heterogeneous reactions may be conveniently separated into:

1. Chemisorption of reactants
2. Reaction of adsorbed surface species to form products
3. Desorption of products into the gas phase

The chemisorption step is often accompanied by direct electron interaction between the chemisorbed gas and the catalyst surface (Hauffe, 1955). In many cases there is a charge transfer between the chemisorbed gas and the surface either by donation of electrons to the surface or withdrawal of electrons from the surface. The direction of the charge transfer is determined by the characteristics of the adsorbent and adsorbate and can be influenced by particularly favorable energy levels of the disordered electrons (in the solid) and by their mobility (Hauffe, 1955). For some cases (depletive chemisorption) the amount of chemisorption, when compared with the total surface area, is small; thus the amount of active surface area is small. The concept of "active centers" (Taylor, 1950) is one explanation for the apparently small amount of catalytically active surface. In light of today's technology, the "active centers" may be regions where there exist energetically favorable conditions for the exchange of electrons between adsorbate and adsorbent.

Bismuth oxide is a p-type semiconductor. It is also an effective catalyst for the formation of 1,5-hexadiene from propylene at high temperatures via the oxidative dehydrogenation dimerization (OXDD) reaction:

$$2C_3H_6 + (1/2)O_2 \rightarrow C_6H_{10} + H_2O \qquad (1)$$

(Swift et al., 1971; Massoth and Scarpiello, 1971; D'Alesandro and Mitchell, 1974). The purpose of this research has been to shed light on the mechanism of this reaction through an investigation of the electronic changes that the catalyst undergoes when the various gaseous reactants and products are chemisorbed.

THEORETICAL BACKGROUND

There are two types of semiconductors, n-type and p-type. The n-type semiconductor is one in which there exist quasifree electrons in the solid. These "liberated" electrons are usually the result of either an excess of metal ions residing in the interstitial lattice positions or of anion vacancies. Zinc oxide is an n-type semiconductor by virture of an excess of metal atoms in the crystal lattice (Hayward and Trapnell, 1964). Some p-type semiconductors are characterized by cation vacancies in the lattice. For the condition of electrical neutrality to be maintained, each cation vacancy must be balanced by the neighboring cation(s) having a higher oxidation state. Nickel oxide is such a p-type semiconductor whereby for every Ni^{+2} vacancy, there exist two neighboring nickel ions in the trivalent state (+3) to maintain electrical neutrality (Hayward and Trapnell, 1964). Electrical conductivity in a p-type material is presumed to occur by the interchange of oxidation states between neighboring cations. Certainly, the conductivity would be related to the number of such defects and by the ease with which the interchange of oxidation states between ions is accomplished, i.e., the mobility of defects.

The attack of oxygen on an oxide surface at high temperatures is accompanied by the high mobility of lattice metal ions which may diffuse to the surface, react with the chemisorbed oxygen, and then reside in the surface region. The number of ions and electron defects in a semiconductor changes with increasing oxygen partial pressure; the nature of the change in defect density with oxygen partial pressure is dependent upon the disorder nature of the oxide. For a p-type oxide, such as nickel oxide, the following relation will describe the attack of the oxygen molecules upon the nickel (+2) lattice ions.

$$Ni^{++} + (1/2)O_2\ (g) \rightleftharpoons NiO + Ni\,\square + 2\,\oplus \qquad (2)$$

Thus, the concentration of nickel vacancies, $\square$, and holes, $\oplus$, will increase with increasing oxygen partial pressure. The presence of the oxygen has caused a nickel ion to leave its lattice site, thus creating a nickel vacancy ($Ni\square$).

The two electrical properties of interest in this study are the conductivity and thermoelectric power. Both of these electrical characteristics are dependent upon the bulk and surface conditions of the catalyst. For the OXDD reaction of propylene and oxygen over bismuth oxide, the kinetic data indicate that both propylene and oxygen are adsorbed on the surface of the catalyst (White, 1977). With measurements of the aforementioned electrical properties, it is possible to confirm the adsorption of oxygen and propylene at reaction conditions. A bulk property important to the electrical conductivity of the catalyst is the oxidation state of the bismuth cation, which may be influenced by the composition of the gas phase. This oxide can be easily reduced by removing oxygen with a reducing agent such as propylene. Pulses of propylene can be passed over the catalyst in an inert carrier gas stream and the electrical properties measured after each pulse. Correlations between the electronic properties and the state of reduction can be established through measurements of this type.

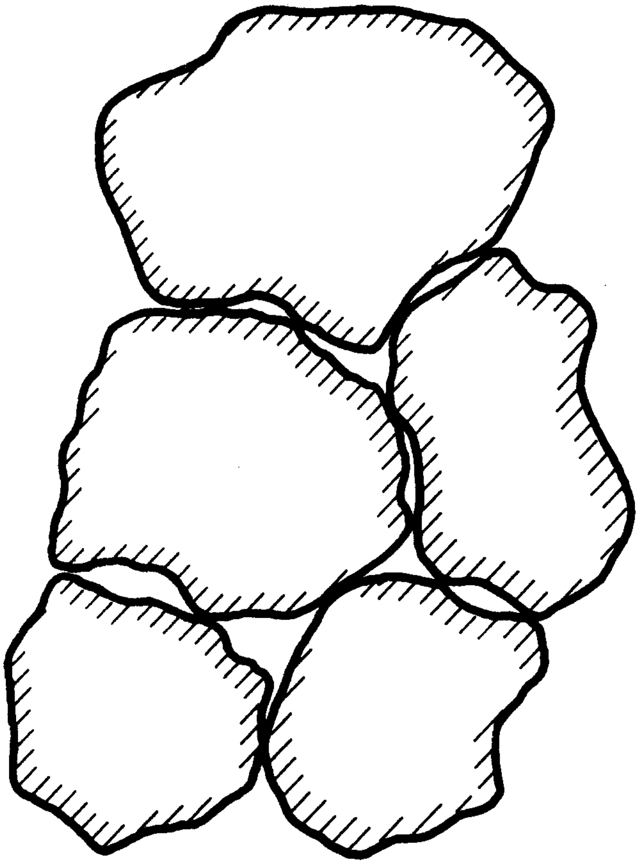

Figure 1. Two region model for compressed granular powders.

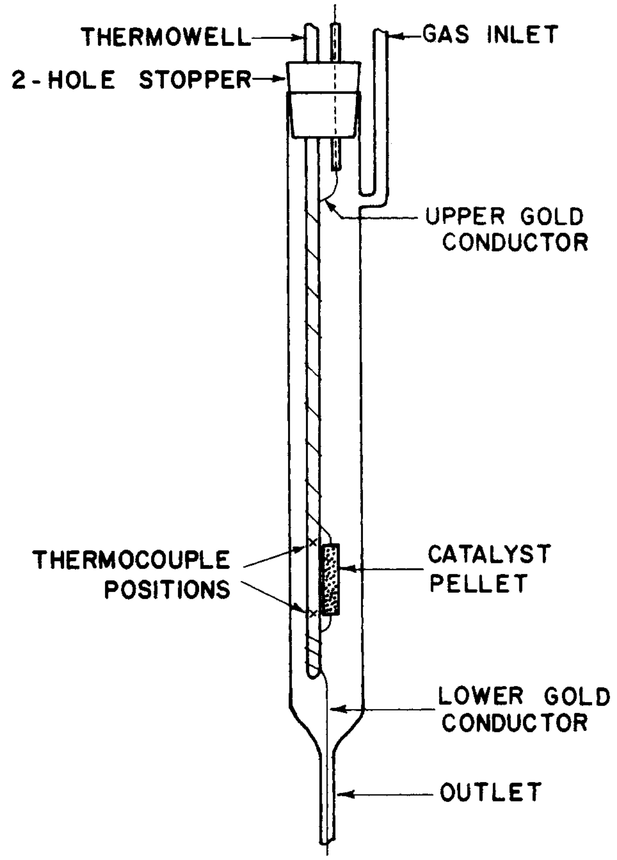

Figure 2. Flow reactor for electrical properties experiment.

A mathematical model that describes the electronic properties of granular solids during chemisorption assumes that the granules have different surface and bulk properties, e.g., the charge carrier concentration and band structure of the surface region are different from the corresponding properties of the interior (Leland). Through the measurement of at least two independent electrical properties, it is possible to approximate this inhomogeneity of the granules.

The charge transfer process between a chemisorbed gas and a granular solid may be modeled with the concerted measurements of the overall thermoelectric power, Q_o, and the overall electrical conductivity, σ_o, of the solid. The thermoelectric power (mV/°K) is simply the slope of a curve obtained when the voltage generated across the pellet (Seebeck EMF) is plotted versus an externally induced temperature gradient. The model parameter which characterizes the inhomogeneity of the solid induced by the chemisorption process is the heterogeneity factor, f, which is defined from the thermoelectric power and electrical conductivity data as

$$f = -\left\{\frac{mk_b}{e} + 1\right\} \tag{3}$$

The electrical conductivity and thermoelectric power are measured for a compressed pellet of semiconducting oxide in equilibrium with a chemisorbing gas at various partial pressures and temperatures. From these data a plot of $\ln \sigma_o$ vs. Q_o may be constructed.

Depending on the sign of the slope m, f can have either positive or negative values. A zero value of f implies that the material is "homogeneous," i.e., the electronic properties of the interior are the same as those at the surface. Values of $f > 0$ indicate surface-interior inhomogeneity with a single dominant type of charge carrier, whereas $f < 0$ requires the action of at least *two* different types of charge carriers (or an irreversible chemical reaction with the surface) in an inhomogeneous setting. Changes in f as a function of chemisorption will provide information about the nature of the surface-gas interaction.

Values of overall conductivity and overall thermoelectric power indicate the anionic or cationic nature of the adsorbate and the direction of charge transfer. The sign of the overall thermoelectric power may be used to distinguish between n-type and p-type semiconductors. Further, the trend of the overall electrical conductivity with amount of gas adsorbed will indicate the charge of the chemisorbing species. For p-type semiconductors, the overall conductivity will increase for adsorption of negative-charged species; it will decrease for adsorption of positively charged species. This argument holds for the case when only one type of charge carrier dominates. Should the system of interest involve secondary charge carriers, the analysis must be somewhat more sophisticated to model the events.

Leland has proposed that a pellet of polycrystalline material is actually composed of small granules of the solid which are in point contact with each other (Figure 1). In the most general case the surface region of the granules is presumed to have different electronic properties than the interior. Further, electrical conduction is assumed to occur through the surface regions in a parallel path to conduction through the interior region. While the actual conduction paths may be tortuous, it is assumed that the real path may be approximated by an equivalent set of parallel conducting paths each consisting of a series of alternating interior and surface region material with a common average cross sectional area and the same average overall length. Inherent to the model is the flow of current in only one direction as a result of the applied gradients. According to this idealized model, materials in the surface and interior regions along the conduction paths may be replaced by two homogeneous

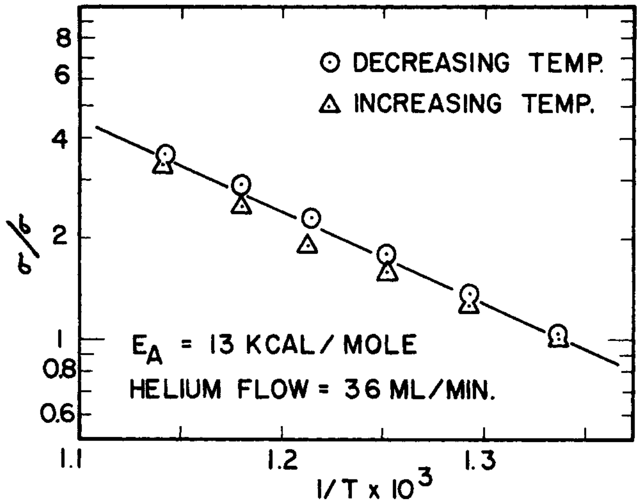

Figure 3. Arrhenius plot for temperature dependence of electrical conductivity of Bi_2O_3 in a flowing stream of helium.

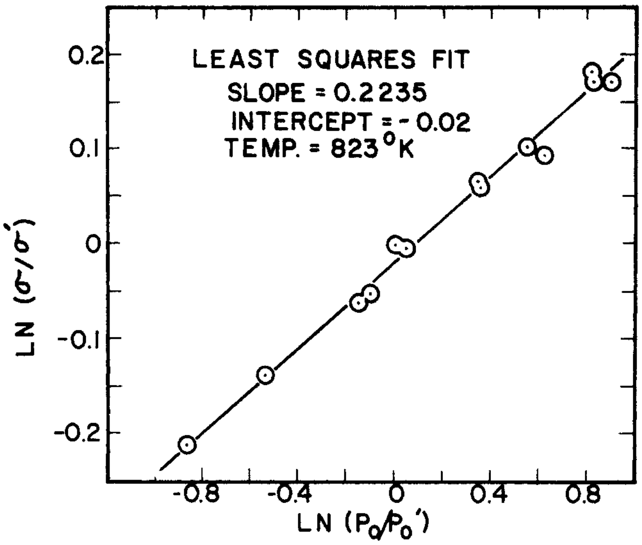

Figure 4. Electrical conductivity versus oxygen partial pressure.

semiconductors which make the same contributions as the actual regions to the overall measured conductivity and thermoelectric coefficient for the heterogeneous powder. These two homogeneous equivalents are then combined to describe the measured behavior of the heterogeneous sample. Since the details of this development will be shown elsewhere (Leland), only the results are presented here. For the case where only one type of charge carrier is dominant, then

$$ln\ \sigma_o = -\left[\frac{e}{k_b} + \left(\frac{e}{k_b}\right)^2\left(\frac{1 - x_s}{x_s}\right)\frac{(|Q_o| - |Q_l|)^2}{|Q_o|}\right]|Q_o| + K_o \tag{4}$$

This equation describes the variation of the overall electrical conductivity with the overall thermoelectric power assuming the two region model to represent adequately the electronic properties of the powder. For certain ranges of partial pressure of the chemisorbing gas at isothermal conditions, the plot of $ln\ \sigma_o$ vs. Q_o is linear. A nonzero heterogeneity factor describes the situation when the experimental slope of $ln\ \sigma_o$ vs. Q_o does not equal $-e/k_b$. Mathematically, the heterogeneity factor may be related to other electronic quantities by the following equations.

$$f = -\{mk_b/e + 1\} = (e/k_b)\frac{(1 - x_s)}{2x_s}(Q_o - Q_{vac}) \tag{5}$$

This development is valid for the system in which there is only one type of charge carrier, i.e., f is greater than zero. Solving for x_s, one obtains

$$x_s = \frac{(e/k_b)(Q_o - Q_{vac})}{(e/k_b)(Q_o - Q_{vac}) + 2f} \tag{6}$$

For more than one type of charge carrier, the model becomes very complicated.

EXPERIMENTAL

All the electrical properties tests were conducted in a flow reactor (Figure 2). The catalyst (surface area = 0.7 m^2/g), in the form of a pellet, was subjected to various reaction conditions.

To test for oxygen adsorption at reaction temperatures, a stream of oxygen and helium was passed at 1.55 atm (157 kPa) over the catalyst pellet in the flow reactor. The gases were premixed in a glass vessel containing molecular sieves, type 4A, and the oxygen partial pressure was monitored by a Perkin Elmer 3920 gas chromatograph.

In the propylene tests, pulses of propylene were introduced via a 10 mL doser into a helium stream that flowed through the reactor at 1.55 atm (157 kPa) pressure. This procedure allowed us to introduce a known amount of propylene, 2.4 mL-STP, into the reactor as a pulse.

The temperature of the reactor was controlled to within ±1.0°K of the set point by a Leeds and Northrup controller, Electromax #6261. The catalyst pellet temperature was measured by two iron-constantan thermocouples. A temperature gradient was applied across the pellet by means of an auxiliary heater surrounding the flow reactor. An air bath furnace supplied the majority of the heat to maintain the reactor at the desired temperature.

A cylindrical pellet 20 mm in diameter and about 2 mm thick was made from 5.0 g of partially reduced bismuth oxide (200-325 mesh powder) since it was difficult to form the pure oxide into a mechanically strong pellet. Two gold conductors were pressed into the pellet as it was formed by inserting the wires into the powder prior to applying a pressure of 83 MPa for 2 h. After the pellet was formed, it was reoxidized inside the reactor with molecular oxygen.

The reactor was basically a flow system with a thermowell inserted axially through most of its length. The pellet was suspended from the gold conductors which were wrapped around the thermowell. Reactants plus helium were introduced at the top of the reactor and flowed down past the pellet and out of the reactor.

A Wayne-Kerr Conductance-Capacitance Bridge (range 99 millimhos to 0.0001 micromhos) was used to measure the conductivity of the catalyst pellet.

RESULTS

Temperature Dependence of Bi_2O_3 Conductivity

Others (Rao et al., 1969) have shown that bismuth oxide is a semiconductor at temperatures for which the OXDD reaction will occur (673-873°K). In their work the electrical properties of Bi_2O_3 were investigated for various oxygen atmospheres. In this work the conductivity of bismuth oxide was measured as a function of temperature in an atmosphere of flowing helium. As shown in Figure 3, the conductivity increased with increasing temperature as it should for an intrinsic semiconductor. Although there appears to be a small increasing/decreasing temperature hysteresis in the conductivity-temperature curve (as was observed also by Rao et al., 1969), the data may be correlated with an exponential relationship as follows:

$$ln\ \sigma/\sigma_o = ln\ C_o + (-E_A/RT) \tag{7}$$

where E_A = 13.1 kcal/gmol, or 0.57 eV (electron volt). The band gap energy for crystalline bismuth oxide is 2.2 eV. Rao et al. reported a value for the band gap of 1.4 eV on their samples.

The temperature effect reported in this work clearly reflects many different processes of which the promotion of an electron across the band gap is but one. In making comparisons of the temperature effects, the atmosphere above the semiconductor is a significant factor. Only in this work and in the study of Rao et al. are the atmospheres specified. Even small impurities in the gases will drastically alter the electrical conductivity data while having only a minor effect on the thermoelectric power.

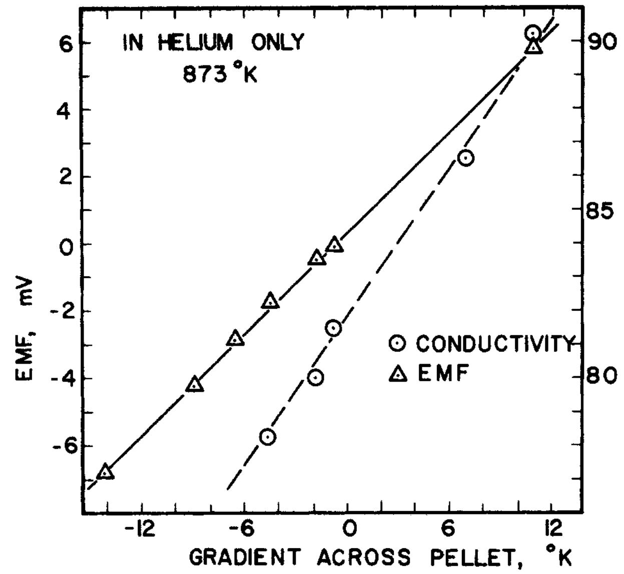

Figure 5. Electrical properties of Bi_2O_3.

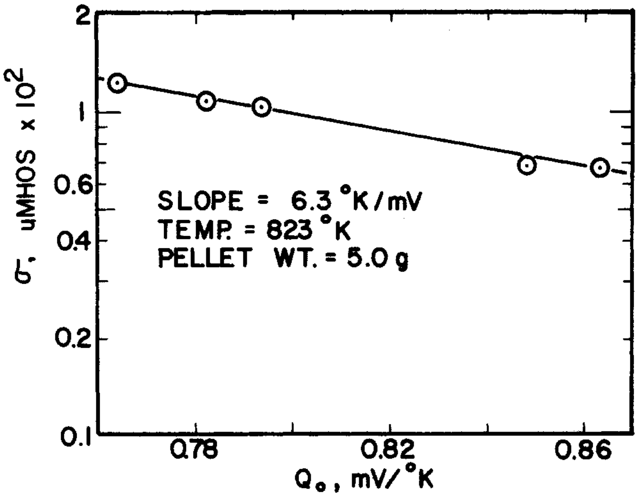

Figure 6. Electrical conductivity versus thermoelectric power—Oxygen partial pressure tests.

Oxygen Adsorption Tests

Tests were made to determine if oxygen is adsorbed in measurable amounts on bismuth oxide at OXDD reaction temperatures near 823°K. Since at most only a small amount of oxygen adsorption is expected under these conditions, bulk effects and all other surface effects must be minimized so as to make the test for adsorption valid.

The oxidation state of the catalyst was stabilized by pretreating the virgin Bi_2O_3 in an oxygen-helium stream at 823°K for 1 h prior to the tests. Equilibrium calculations indicate that the reaction

$$Bi_2O_3 \rightleftharpoons 2Bi + 3/2\ O_2 \tag{8}$$

at 823°K has an equilibrium constant of $K = 10^{-36}$, which means that the bismuth oxide does not decompose or recombine to any measurable extent at reaction temperatures as long as there is a finite partial pressure of oxygen. The bulk oxidation state of the bismuth cations is not affected by the partial pressure of oxygen during these tests.

Initially, only the electrical conductivity was measured as a function of the partial pressure of oxygen. The procedure was to vary the ratio of oxygen to helium flow-rates at a constant reactor temperature. The data are presented in Figure 4 in normalized form since only ratios of oxygen partial pressures and ratios of conductivities are required in the equations. The slope of the curve, $m = 0.223 \pm 0.001$, agrees well with a literature value of $m = 0.222$ (Rao et al., 1969) for the equation

$$\sigma_o/\sigma_o' = e^{-0.02}(P_o/P_o')^m \tag{9}$$

Subsequent testing of the catalyst involved measuring both the conductivity and the thermoelectric power as a function of oxygen partial pressure. This experiment is a powerful test for the adsorption of oxygen.

For each oxygen partial pressure, sufficient data were collected to determine the thermoelectric power. Typical EMF vs. induced temperature gradient curves for determination of Q_o are shown in Figure 5.

The conductivity vs. thermoelectric power data are presented on a semilog plot, Figure 6, for the oxygen partial pressure tests at 823°K. From theory, the slope of the curve of conductivity, σ_o, vs. thermoelectric power, Q_o, can be related to the nature of the adsorbing species. A curve with slope $\{d(ln\ \sigma_o)/dQ_o\}$ that is equal to the ratio of the charge of an electron divided by the Boltzmann constant $(-e/k_b)$, indicates that no charge is transferred between the adsorbate and the adsorbent, hence no ionosorption occurs. The slope of the curve in Figure 6 (−6.3°C/mV) does not equal $-e/k_b$ (−11.6°C/mV) and indicates that oxygen forms a strong electron withdrawing species adsorbed at reaction temperatures.

The electrical property data for the oxygen partial pressure tests may be summarized as follows.

1. Bismuth oxide is a p-type semiconductor, since Q_o is positive.

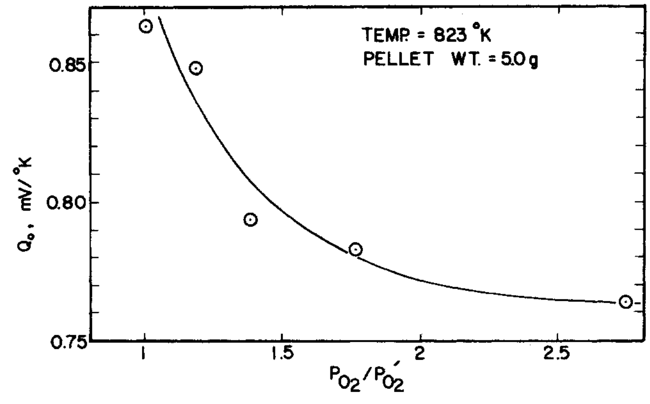

Figure 7. Thermoelectric Power versus oxygen partial pressure.

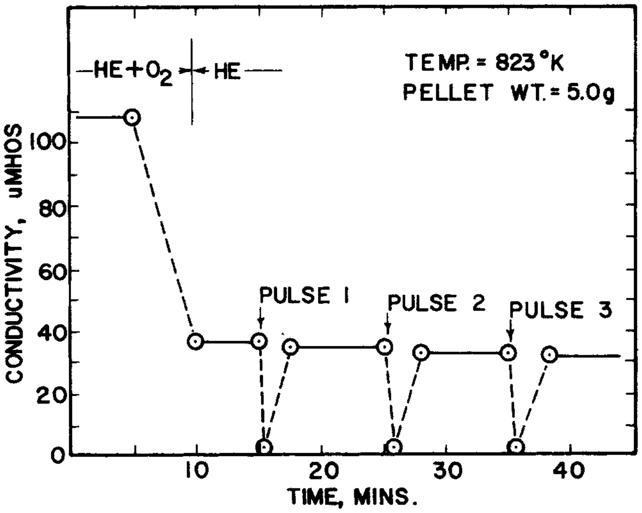

Figure 8. Schematic of conductivity versus time for propylene pulse test.

TABLE 1. ELECTRICAL PROPERTIES DATA FROM PROPYLENE PULSE EXPERIMENTS

Propylene Pulse No.	Conductivity μMhos	Thermoelectric Power mV/°C
(O_2 + He)	108.0	0.476
(He only)	37.0	0.520
1	34.0	0.536
2	32.6	0.548
3	32.2	0.521
4	33.0	0.520
5	32.3	0.519
6	32.9	0.526
7	30.8	0.463

These entries are the steady-state values of the property *after* the pulse of propylene (designated by pulse number) had passed over the pellet.

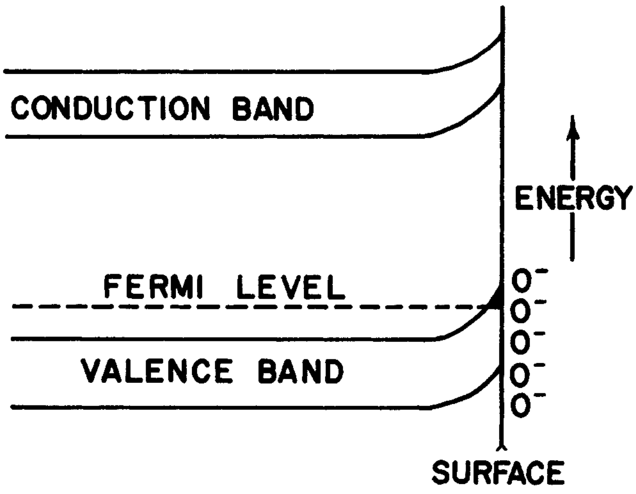

Figure 9. Electron band energy diagram.

2. Its conductivity increases as the oxygen partial pressure is increased.

3. The thermoelectric power decreases as the oxygen partial pressure is increased (Figure 7).

4. The f value is negative (-0.46), which according to the model implies that oxygen is adsorbed and that there are at least two types of charge carriers.

Propylene Adsorption Tests

Results to be published later indicate that the OXDD reaction can be adequately described by Langmuir-Hinshelwood kinetics with both O_2 and propylene being adsorbed on one type of site. The adsorption of O_2 was confirmed in the preceding section, and the purpose of this section is to demonstrate adsorption of propylene. It was not possible to repeat the procedure of the oxygen partial pressure tests using propylene as the "adsorbate" since the oxide is easily reduced by propylene.

The test for propylene chemisorption was to pass pulses of propylene in a helium carrier gas over the oxide pellet and to observe transients in its electrical conductivity. Since each pulse of propylene caused only a small amount of the oxide to be reduced (about 10% of the surface atoms removed), the transients in electrical conductivity are indicative of adsorption-desorption effects only if fluctuations in the catalyst temperature may be ruled out as a cause for the transients in the oxide electrical conductivity. The OXDD reaction and the deep oxidation total combustion reaction are both exothermic, which will cause the temperature to increase as the pulse of propylene passes over the catalyst. Conversely, reduction of the oxide to Bi metal is an endothermic process which will tend to cool the catalyst as the propylene pulse passes over it.

The same reactor and catalyst pellet described previously were used for these experiments. With He as a carrier gas, pulses of propylene (2.4 mL-STP) were introduced; electrical properties were measured during and after each pulse.

Typical transient results are shown schematically in Figure 8 for pulses of propylene passed over the bismuth oxide pellet at 823°K. The conductivity decreased rapidly after each pulse was introduced, but it then rapidly returned to nearly (but not quite) the original value. Simple heat effects alone could not have been responsible for these results. For the conductivity to have decreased an order of magnitude (from about 30 about 3 μMhos) due to heat effects alone would have required a temperature decrease of about 200°K based on the activation energy found in Figure 3. The heat capacity of the pellet simply precludes this as a viable explanation.

A second objective of these propylene pulse experiments was to examine the manner in which the bismuth oxide is reduced by propylene. In Table I are recorded the "equilibrium" conductivity and thermoelectric power values that were observed following each pulse after the conductivity had returned to near the original value. Before the first pulse, the conductivity and thermoelectric power were 108.0 μMhos and 0.4762 mV/°K, respectively. When the oxygen-helium gas mixture was replaced by the helium carrier gas (O_2 concentration = 1 ppm), the observed conductivity and thermoelectric power were 37 μMhos and 0.519 mV/°K, respectively. The seven pulses of propylene were sufficient to remove almost one layer of oxygen, oxidic and/or adsorbed, from the surface of the bismuth oxide. While both σ_o and Q_o changed significantly with the decrease in gas phase oxygen concentration, neither changed very much with the subsequent pulses of propylene.

DISCUSSION

The data from the oxygen chemisorption tests may be explained by the following model. Bismuth oxide is a p-type semiconductor by virtue of cation vacancies. To preserve electrical neutrality, for every two cation vacancies present in the solid there must exist three (neighboring) bismuth cations in the pentavalent state, the only other stable oxidation state of bismuth. Electrical conductivity occurs through these positive cation vacancy "holes," i.e., electrons are exchanged between neighboring trivalent and pentavalent cations.

Even when oxygen in the crystal lattice is present in excess, a p-type semiconductor may also result. Conduction in such a material is a consequence of the presence of energetically favorable acceptor states. For the case of bismuth oxide, the pentavalent bismuth cation may act as an electron acceptor according to the following equation

$$Bi^{+5} + 2e^- \rightleftharpoons Bi^{+3} \qquad (10)$$

where electrons are abstracted from the valence band, giving rise to the conditions for conductivity.

When oxygen is adsorbed on the surface of a p-type solid, such as bismuth oxide, there is an abundance of electrons to form oxide ions by the following reaction:

$$\tfrac{1}{2}\, O_2 + 2e^- \rightleftharpoons O^{2-} \qquad (11)$$

the electrons being supplied by the valence band, which is almost full. As oxygen becomes adsorbed and is converted to the negatively charged ions, there are sufficient electrons in the valence band of the bismuth atoms near the surface to form a monolayer of chemisorbed oxygen. As adsorption increases, the conductivity should increase proportionally, as was observed in the oxygen partial pressure tests, Figure 4.

The data of the thermoelectric power versus oxygen partial pressure (Figure 7) and the negative value of the heterogeneity factor ($f = -0.46$) for oxygen tests at 823°K may be explained by the presence of secondary charge carriers. Consider the electron band energy diagram, Figure 9. The valence band is bent upward by the effect of the chemisorbed oxygen atoms reacting with electrons of the valence band. For the region near the surface (cross-hatched area, Figure 9) the top of the valence band is higher than the Fermi level, which allows electrons in the conduction band to participate as secondary carriers in the electrical conductivity. This can account for the negative value of f. A similar observation was made for the adsorption of oxygen on nickel oxide, NiO (Leland). When the valence band bends upward across the Fermi level, electrons rather than holes become more stable in the surface region. In spite of this, the entire surface region retains its overall p-type character since this level involves only one of the carrier species and the $2p$ holes in the valence band are still predominant. A consequence of such bending is to lower the thermoelectric power (as was observed) due to a decreased overall p-typeness. The increase in conductivity may be attributed to either an increase in concentration or mobility of the new carriers over those which were replaced. Although this model was developed by Leland to explain the electronic properties of NiO, it appears to fit the Bi_2O_3 results as well.

A change in sign of the thermoelectric power from positive to negative corresponds to a change from p-type to n-type conductivity. As oxygen is adsorbed onto the surface of Bi_2O_3, the value of the thermoelectric power, Figure 7, decreases while the electrical conductivity increases, Figure 4. These observations could be explained by the formation of n-type carriers, the presence of which serves to lower the value of the thermoelectric power while at the same time increasing the electrical conductivity.

There can be little doubt that oxygen is chemisorbed into the surface of the catalyst at reaction temperatures and that this oxygen increases the electrical conductivity and decreases the thermoelectric power. These observations suggest the following conclusions:

1. Chemisorbed oxygen is residing on the surface as negative charged ions, probably O^{-2}.

2. The oxygen atoms are chemisorbed on the bismuth cation centers.

3. The region near the surface has a number of pentavalent bismuth cations as a result of reaction with oxygen to form chemisorbed oxide ions.

Because propylene can cause bulk reduction of Bi_2O_3 at high temperatures, the propylene pulse experiments are more difficult to interpret. The decrease in conductivity from 108 to 37 μMhos when oxygen was removed was caused by a decrease in the amount of chemisorbed oxygen ions. The first pulse of propylene in Table I probably removed the last vestiges of adsorbed oxygen, as indicated by the further decrease of σ_o to 34.0 μMhos. Essentially no *permanent* changes were observed in either the electrical conductivity or thermoelectric power as almost a layer of lattice oxygen was removed.

However, with each pulse there was a large *transient* decrease in the electrical conductivity. There are at least two possible explanations for this behavior. First, the lattice oxygen in the surface layer which was removed by the propylene may be rapidly replaced with oxygen diffusing from the interior of the solid. At these high temperatures the mobility of oxygen ions in the lattice is quite fast. Such migration to the surface restores the original surface properties after the transient perturbation; this assumes the surface is predominately responsible for the electrical conductivity of the entire solid.

A second exaplanation for this observation involves the adsorption/desorption of propylene. Since propylene may be considered a source of electrons due to its *pi*-electron system, it has a tendency to form positive species (cations) by electron transfer to the solid. These positive species would have just the opposite effect from oxygen on the electrical conductivity, namely, they should cause a decrease. The decrease/increase in conductivity observed in Figure 8 may correspond to the adsorption/desorption of propylene as the pulse passes over the catalyst.

Which of these two possibilities predominates, or whether both are responsible for the phenomena, is not clear. Perhaps similar tests made in a very sensitive rapid response microbalance may help to resolve the issue. There can be no question about propylene being adsorbed under conditions of the OXDD reaction; it can even reduce the entire oxide! However, these experiments do not give an indication about exactly how much propylene is adsorbed.

In order to achieve coupling, we speculate that a propylene molecule loses an allylic H atom from the C_3 position to a surface O^{-2} and itself becomes attached to a surface B ion. A second propylene molecule may react from either the gas phase or from the surface by losing a hydrogen atom from the C_3 position to the OH group to form water, *the radical attaching in a linear fashion* to the first surface C_3H_5 species. Isotopic tracer studies to be discussed elsewhere have involved use of D-labeled molecules to support this mechanism.

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NOTATION

e = electronic charge
f = heterogeneity factor
k_b = Boltzmann constant
K_o = constant related to mobility coefficient and effective mass of the charge carrier
m = slope of isothermal $ln\ \sigma_o$ vs. Q_o plot
Q_o = overall thermoelectric power
Q_I = thermoelectric power, interior region
Q_{vac} = thermoelectric power, vacuum conditions
x_s = fraction of semiconductor with properties of the "surface"
P_o = partial pressure of gas contacting pellet
P_o' = reference partial pressure of gas
σ_o = overall electrical conductivity
σ_o' = overall electrical conductivity at reference pressure P_o'
$\text{Ni}\square$ = nickel lattice vacancies in crystal
$\oplus$ = positive holes
σ = electrical conductivity at temperature T (Eq. 7)

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