JOURNAL OF CATALYSIS 69, 371–383 (1981)

Photocatalytic Properties of Perovskites for H_2 and CO Oxidation—Influence of Ferroelectric Properties

HENRI VAN DAMME[1] AND W. KEITH HALL[2]

Department of Chemistry, Laboratory for Surface Studies, University of Wisconsin,
Milwaukee, Wisconsin 53201

Received April 21, 1980; revised November 11, 1980

The oxidation of H_2 and CO was studied over $LaCoO_3$, $SrTiO_3$, $BaTiO_3$, and related materials such as $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$, ZnO, and TiO_2 in the dark and while being irradiated with band-gap light. No effect of light on the rate of H_2 oxidation was found with any of these materials, but a strong photocatalytic effect was observed for CO oxidation over TiO_2, ZnO, $SrTiO_3$, and $BaTiO_3$. In addition, a very similar behavior related to the ferroelectric properties of the catalyst was observed for CO oxidation, and less clearly for H_2 oxidation, over $BaTiO_3$ in the dark. The effect of light is discussed in terms of band-to-band transitions followed by hole capture, whereas the influence of ferroelectricity is thought to arise from the effect of polarized surface layers on the shape of the energy bands.

INTRODUCTION

The photocatalytic properties of transition metal oxides at the gas–solid interface are of current interest not only for potential applications but also for a better fundamental understanding of the relationship between catalytic activity and solid-state properties. To date, photocatalysis has been largely restricted to the study of ZnO and TiO_2 and a few perovskites. These wide band-gap semiconductors exhibit a quite remarkable photoactivity in several reactions such as the oxidation of CO, hydrocarbons, or alcohols, and the decomposition of N_2O (*1–6*). Yet, the study of the light sensitivity of other catalysts for these and for other reactions is essential to advance the understanding of charge transfer processes in catalysis.

Along the same lines, correlation of catalytic activity with dielectric properties could also prove to be useful. The study of ferroelectric catalysts is in this respect particularly interesting since the large spontaneous polarization of ferroelectric solids is likely to affect both the kinetics of charge transfer at the catalyst–adsorbate interface and the free energy of polar-adsorbed species.

As pointed out by Voorhoeve (*7*), perovskite-related oxides are well suited for these studies. This isostructural class of ABO_3 compounds includes a large variety of transition metal oxides among which are insulators, metallic conductors, and Mott insulators as well as semiconductors (*7–9*). The electronic properties of perovskites are dominated by the oxygen and B-ion levels. The oxygen $2p$ orbitals form the valence π band, whereas the B-ion s and p orbitals form widely separated antibonding bands. The B-cation d orbitals occupy the intermediate energy region; they are split by the crystal field into a group of σ^* orbitals and a group of π^* orbitals which are formed from the usual e_g and t_{2g} atomic orbitals, respectively.

In the present work, a limited but representative choice of perovskites, ($LaCoO_3$, $SrTiO_3$, and $BaTiO_3$) has been investigated. In $LaCoO_3$, the d electrons are thought to be localized. It is a "hopping" semiconductor with a small energy barrier (~0.1 eV) for conduction. In $SrTiO_3$ and $BaTiO_3$, the d electrons are delocalized and energy band

---

[1] On leave from the CNRS Centre de Recherche sur les Solides à Organisation Cristalline Imparfaite, Orléans, France.

[2] To whom all correspondence should be addressed.

0021-9517/81/060371-13$02.00/0

formation occurs. These materials are insulators when pure but can be made semiconducting (n type) by reduction. Their band gaps (~3.2 eV) essentially represent the energy difference between the valence π band of the anions and the primarily antibonding B-cationic π^* band. The major difference between $SrTiO_3$ and $BaTiO_3$ is that the latter exhibits ferroelectric distortion at low temperatures.

In the present work, the effect of light on the activity in H_2 and CO oxidation has been analyzed. The comparison between the titanates and $LaCoO_3$ is in this respect particularly interesting in view of their widely different electronic properties. Also, the influence of the ferroelectric properties of the catalyst was determined by comparing the dark reaction rates over $BaTiO_3$ and $SrTiO_3$. The electronic properties of these two catalysts are very similar, but their dielectric properties differ considerably. $SrTiO_3$ remains paraelectric, i.e., nonpolarized from 2000 K down to a few degrees Kelvin, whereas $BaTiO_3$ becomes ferroelectric with a very large internal polarization ($P = 0.26\ \mathrm{C\ m^{-2}}$) below 120°C (*10*). It should be kept in mind, however, that these polarization characteristics, which are valid for the bulk of the material, could become significantly different at the surface and as the specific surface area increases. Moreover, a tetragonal surface layer may exist to temperatures higher than that of the ferroelectric phase transition [cubic to tetragonal at 120°C] (*19*). This distortion is due to electrostatic forces which give a relaxed surface layer with an outward shift of O^{2-} and an inward shift to Ti^{4+} (*7*).

Ferroelectric properties have been related to several anomalies in catalytic reaction rates. Over $NaNbO_3$, $KNbO_3$, and $LaFeO_3$, higher than expected rates of CO oxidation were detected (*11*) near the para-ferroelectric transition temperature (Curie temperature, T_c). This was explained in terms of relaxation effects and was taken as evidence that an electronic mechanism was rate determining. Over $BaTiO_3$ a large and discontinuous decrease in activation energy was observed for CO oxidation and N_2O reduction by CO when crossing T_c from above (*12*). The fact that no such effect was found for H_2–D_2 exchange led to an interpretation in terms of dipole–dipole interactions between polar intermediates (carbonate species) and the polarized solid.

As suggested above, the influence of the large polarization of a ferroelectric catalyst on the rate of charge transfer processes at the catalyst–adsorbate interface cannot be neglected. Indeed a similarity may exist between anomalies connected to ferroelectricity on one hand and photocatalytic effects on the other; the optical excitation effective in producing photocatalytic effects with oxides is associated with O^{2-} to metal-ion charge transfer and consequently with an important change in the polarization of the metal–oxygen bond. Thus, it might be possible to provide a common framework to describe photocatalysis and what could be called "ferrocatalysis." The present paper contains some experimental evidence in support of this view.

EXPERIMENTAL

Materials. TiO_2 (anatase) with a nitrogen BET surface area of 11.2 m^2/g was furnished by the New Jersey Zinc Company. The ZnO (Kadox-25) was obtained from the same source. The other materials were prepared in glass and porcelain vessels in order to avoid contamination with metals. $BaTiO_3$ and $SrTiO_3$ were prepared by dissolving the alkaline earth nitrates and $TiCl_4$ in cold water. The hydroxides were then precipitated with tetramethylammonium hydroxide. After washing, the precipitates were dried at 100°C and calcined at 650°C ($BaTiO_3$) and 550°C ($SrTiO_3$), yielding materials with surface areas of 18 and 64 m^2/g, respectively. A modified $BaTiO_3$ with hexagonal structure, $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$, which has significantly different electronic properties and does not exist in the ferroelectric state, was also studied for comparison. It was prepared following the procedure of Dickson *et al.* (*13*), by calcining a mixture of $BaCO_3$, Fe_2O_3, and TiO_2 in a porcelain crucible in air at 1100°C for 15 hr. The surface area was 0.67 m^2/g. $LaCoO_3$ was prepared in a similar way by decomposing the appropriate mixture of the nitrates at 950°C in oxygen for 15 hr. This method yielded a material with a surface area of 7.5 m^2/g. All catalysts were characterized by X-ray diffraction using Cu$K\alpha$ radiation with a Ni filter (*14*).

The gases, H_2, O_2, and CO, were purified by passing through large traps filled with glass beads and with a 5A molecular sieve, at 77 K for H_2 or at 193 K for CO and O_2. These were periodically degassed at 350 to 400°C.

Apparatus. All experiments were performed in a glass recirculation system. The recirculation loop included a bellows pump, a trap, a manometer, and a quartz reaction cell with a 2.5-cm-diameter–2-mm-thick window fused to the bottom. The catalyst (200 mg) was spread on the window and illuminated from below with a 1000-W xenon lamp. With materials with a well-characterized band gap (TiO_2, ZnO, $BaTiO_3$, and $SrTiO_3$) only near-uv light (300–400 nm) was used. This was obtained using appropriate filters. The other catalysts ($LaCoO_3$, $Ba[Fe_{0.33}Ti_{0.67}O_{2.67}]$) were irradiated with "white light" from the source. The reaction cell was heated in an open-ended furnace with a 2-mm-thick quartz filter at the bottom; the latter restricted the convection of hot air from the light source to the cell. Under these conditions, the temperature fluctuations of the reaction cell from the beginning to the end of a 5-hr run did not exceed 3°C. For runs performed at room temperature and below, the cell was immersed in a quartz Dewar having a bottom made of two 3-mm-thick windows. The Dewar was filled with a cold liquid, generally a melting ice-water–ethanol mixture, which was partially renewed from time to time in order to maintain the temperature within ±3°C.

Procedure. Three types of pretreatment were used. The oxidizing pretreatment consisted of circulating dry O_2 over the sample at 520°C for at least 3 hr. This has been shown to lead to a fairly completely dehydroxylated oxygen-saturated surface (*14*). The reducing pretreatment consisted of circulating dry hydrogen over the sample for 1 hr at 700°C. This treatment, which was applied only to the titanates, produced also a dehydroxylated surface, but with a significant concentration of surface oxygen vacancies (*14*). The dehydration pretreatment consisted of evacuation of the sample at the temperature of the next reaction run for 15 hr. This is thought to provide a surface with a higher anion vacancy concentration than the oxidizing pretreatment.

After one of these pretreatments, the system was evacuated for the time necessary for the sample to reach the temperature of the reaction. The cell was then isolated and the reactants were introduced into the loop where they were mixed. The trap was filled with liquid nitrogen and then the reaction cell was connected. All experiments were conducted with a starting total pressure of 120 Torr of stoichiometric (2/1) CO/O_2 or H_2/O_2 mixtures.

The initial reaction rates were determined either by following the drop in pressure with time in the circulation loop (230 ml) or by measuring volumetrically the CO_2 or the H_2O produced and trapped after a given reaction time. The first procedure was more convenient when the rates exceeded 10^{-4} mole g^{-1} hr^{-1}, but was no longer accurate enough for rates below this value, at least for reaction times of a few hours. The second procedure was then used. Actually, the validity of the second procedure for determining initial reaction rates relies on the assumption that, during the time used to trap a sufficient amount of products, the reaction remained zero order with respect to total pressure and with respect to time. This was always true, except for CO oxidation over $BaTiO_3$ where, in two runs, a slightly faster initial rate was observed before reaching the zero-order stage. Both methods were found to be equally reliable. They agreed within a few percent at temperatures higher than about 200°C. As the temperature decreased, however, the rate calculated from the pressure drop was always larger than the rate calculated from the amount of trapped product because some CO_2 or H_2O remained on the catalyst, regardless of whether the reaction was performed in the dark or under illumination. The adsorbed product was recovered either by evacuating the sample at higher temperature through the trap, or more efficiently, by circulating pure O_2 in the loop. Taking into account the additional amount of product recovered in this way, the agreement between the two methods was a good as that at higher temperatures.

RESULTS

The Reaction of CO with O_2

The effect of light on the reaction rate over $SrTiO_3$ is shown in Fig. 1. A characteristic photocatalytic (PC) enhancement is evident; at temperatures below about 300°C the activation energy for the reaction during irradiation was lower than that for the reaction in the dark. At high temperatures, the results obtained in the light cannot be separated from those obtained in the dark, because the higher activation energy process prevailed. As the temperature was lowered, however, irradiation with band-gap light produced a significant rate enhancement. The Arrhenius plot for the dark reaction remained linear, whereas that for the reaction in the light leveled in the characteristic fashion. As the temperature was further lowered, the dark reaction became too slow to be measured by our methods, whereas the PC reaction remained easily measurable and, remarkably, became almost temperature independent.

The apparent activation energy, E_a, is plotted as a function of temperature in Fig. 2. In the high-temperature region the activation energy was constant at about 20 kcal mole^{-1}. In the intermediate region E_a decreased linearly with temperature and within experimental error obeyed

$$E_a = b(T - T_0), \qquad (1)$$

where b is a constant and T_0 is about 420 K. In the low-temperature region E_a again became a constant less than 2 kcal mole^{-1}. Such a behavior, with a very small activation energy at low temperature has already been observed with other photocatalysts (*6*).

The *dark* reaction rate for CO oxidation was measured over a fresh $BaTiO_3$ catalyst with significantly different results. The behavior resembled that for $SrTiO_3$ under irradiation (compare Figs. 1 and 3). The Arrhenius plot exhibited the same charac-

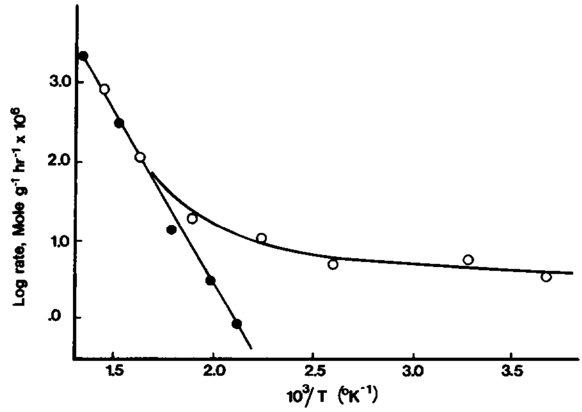

FIG. 1. Carbon monoxide oxidation over oxygen-pretreated $SrTiO_3$, in the dark (●), and under irradiation (○).

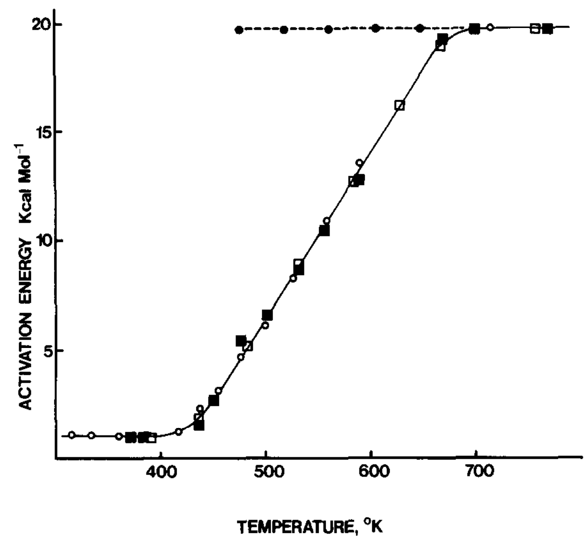

FIG. 2. Temperature dependence of the apparent activation energy for carbon monoxide oxidation over $SrTiO_3$ under irradiation (○) and in the dark (●) and over $BaTiO_3$ in the dark prior to irradiation (■) and under irradiation (□). Both catalysts were pretreated in oxygen.

teristic bending as that for a PC effect with a low-temperature region where the rates are almost temperature independent and, in addition, there was a slight discontinuity in the vicinity of T_c, the ferroelectric Curie temperature (~120°C). Although these observations are likely to be related to the ferroelectric properties of $BaTiO_3$, care was taken to check that they were not simply an artifact due to the experimental procedure. First, it was checked that the bending of the Arrhenius plot was reproducible and not related to the aging of the catalyst. Two different samples were used. For the first, the experimental points were obtained starting from the high-temperature end of the plot, whereas for the second they were obtained starting from the low-temperature end. As shown in Fig. 3 the points are indistinguishable; moreover, points then taken during irradiation fell on the same curve.

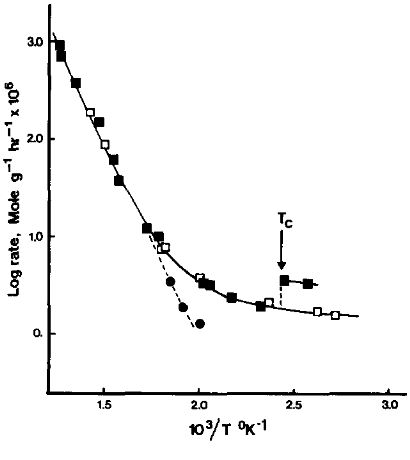

FIG. 3. Carbon monoxide oxidation over oxygen-pretreated $BaTiO_3$, in the dark prior to irradiation (■), under irradiation (□), and in the dark after irradiation (●).

The following observation suggests that a close physical relationship exists between this "ferrocatalytic" (FC) effect and the more classical PC effect. As shown in Fig. 3, the FC effect was observed below ~370°C as long as the catalyst had not been irradiated with band-gap light. After a few hours of irradiation, however, the reaction rates measured in subsequent runs in the dark were significantly lower than those that had been measured before the irradiation. Indeed these data (●, Fig. 3) fell as expected for an extrapolation of the high-temperature data. The Arrhenius plot was not nearly linear over the temperature range where measurements were possible. Remarkably, the rates measured *under illumination* (□) were still identical with those obtained previously in the dark. In other words, the FC properties of the catalyst were destroyed, but the PC properties were now displayed. The variation of the activation energy with temperature was identical with that for $SrTiO_3$ (see Fig. 2).

In contrast to this rather complicated behavior, $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$ and $LaCoO_3$ had much simpler properties: no PC nor FC effects were detected for CO oxidation (Fig. 4). The absence of the FC effect for $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$ was not unexpected since, as pointed out above, this material has no ferroelectric phase in the temperature domain investigated.

The Reaction of H_2 *with* O_2

No PC effect was found for this reaction over any of the catalysts studied, not even with the titanates (compare Figs. 1 and 5). Evidently the rate-limiting step is not the same for the two reactions and that for H_2 is not affected by light. An attempt was made to ascertain whether the rate-limiting steps might involve the dissociation of H_2 or of O_2. A $BaTiO_3$ sample containing 1% by weight of Pt was prepared and tested. No PC effect was observed on this sample (Fig. 5), but the experiment was not conclusive since, due to the extremely high activity of Pt itself, it would have been very difficult to detect a small rate increase due to a PC effect at the $BaTiO_3$–Pt interface.

Concerning the FC effect for H_2 oxidation over $BaTiO_3$, the results (Fig. 6) were less clear than those for CO oxidation. Nevertheless, there was an ill-defined break in the Arrhenius plot in the vicinity of the Curie temperature (120°C). At the low-temperature end the activation energy appeared to be quite low (~2 kcal $mole^{-1}$), suggesting the existence of a FC effect. This has however to be considered with caution in view of the unusually large scatter of the experimental points of Fig. 6. The likely origin of this is the way these measurements were made. They were the first ones made and the runs performed under illumination and those performed in the dark were randomly alternated. Although this is ordinarily a safe procedure for detecting a PC effect, it is about the worst one when the FC effect is superimposed. The

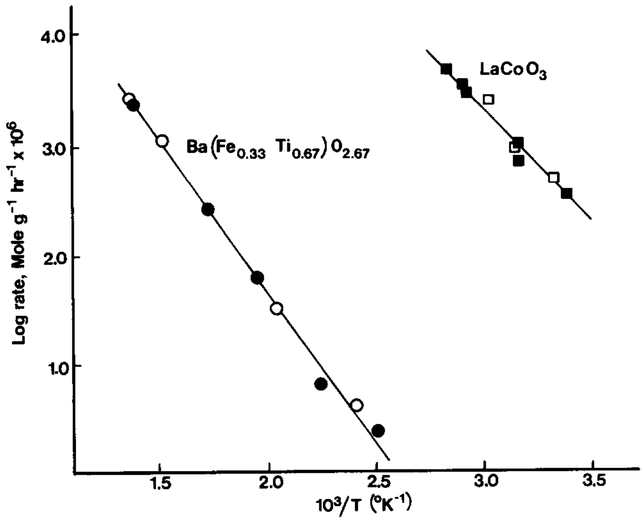

FIG. 4. Carbon monoxide oxidation over oxygen-pretreated $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$ and $LaCoO_3$ in the dark (● and ■, respectively) and under irradiation (○ and ○, respectively).

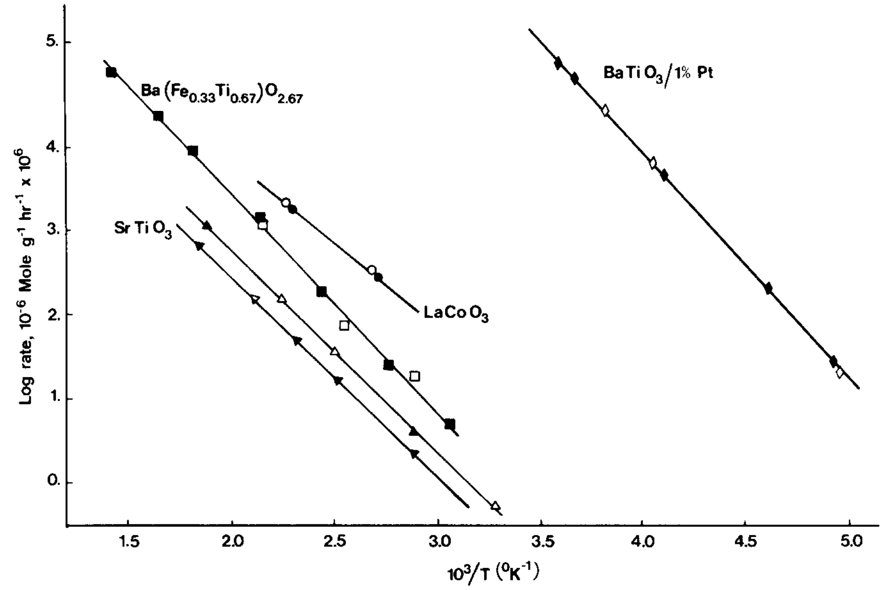

FIG. 5. Hydrogen oxidation over oxygen-pretreated $LaCoO_3$ (●, ○), oxygen pretreated $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$ (■, □), $SrTiO_3$ pretreated either in oxygen (▲, △) or under vacuum (▼, ▽), and $BaTiO_3$+ 1% Pt pretreated in hydrogen (◆, ◇). The open symbols refer to reactions performed under irradiation, whereas the solid symbols refer to reactions performed in the dark.

effect of light on the FC properties reported above would make a large scatter in the experimental data unavoidable.

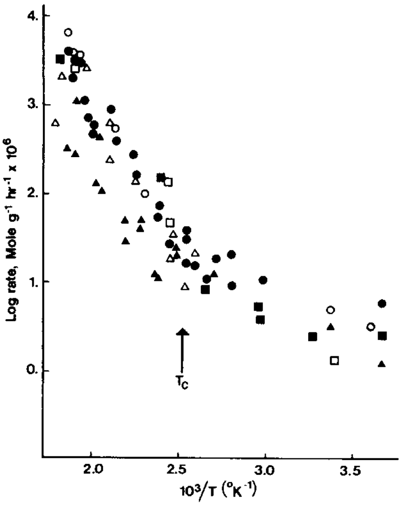

FIG. 6. Hydrogen oxidation over $BaTiO_3$ pretreated in oxygen (●, ○), in hydrogen (■, □), or under vacuum (▲, △). Open symbols refer to reactions performed under irradiation and solid symbols refer to reactions performed in the dark.

Relative Activities of Catalysts

Tables 1 and 2 list the data for the oxidations of H_2 and CO, respectively. For the former, the rates of the light and dark reactions were always the same; thermal activation energies varied from 9 to 15 kcal/mole. Per unit area, $SrTiO_3$ and $BaTiO_3$ were less active than $LaCoO_3$ and $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$ by about two orders of magnitude. Varying the pretreatment did not strongly affect the activity of $SrTiO_3$ and $BaTiO_3$. A surface partially covered by OH groups seemed to be somewhat less active than a completely dehydroxylated surface, but the activity of a reduced (i.e., oxygen-deficient) catalyst was very similar to that of an oxidized (oxygen-saturated) one.

The titanates (and TiO_2) were also the least active catalysts for carbon monoxide oxidation. These materials responded to light however, whereas the other materials (which were more active in the dark) did not.

TABLE 1

Reaction Rates for H_2 Oxidation

Catalyst	Surface area (m^2/g)	Pretreatment[a]	E_{app} for the dark reaction (kcal mole^{-1})	Dark rate at room temp.[b] (molecule g^{-1} s^{-1})	Rate under irradiation at room temp.[b] (molecule g^{-1} s^{-1})
$LaCoO_3$	7.5	OX	9.05	1.7×10^{15}	1.7×10^{15}
$BaTiO_3$	18.	OX			
		V	15.5 ± 2.5	5×10^{14}	5×10^{14}
		RD			
$SrTiO_3$	64.	OX	10.95	9×10^{13}	9×10^{13}
		V	10.95	7.5×10^{13}	7.5×10^{13}
$Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$	0.67	OX	11.95	$\sim 10^{14}$	$\sim 10^{14}$
$BaTiO_3$+ 1% Pt		RD	9.65	1.7×10^{19}	1.7×10^{19}

[a] OX = in oxygen; V = under vacuum; RD = reduction in hydrogen. See Experimental section.

[b] In case no measurements were performed at room temperature, the values given have been extrapolated from results obtained at higher or at lower temperature.

DISCUSSION

Qualitatively, the results reported here for the dark reaction rates over $LaCoO_3$, $SrTiO_3$, and $BaTiO_3$ are in good agreement with the ease and extent to which these materials can be reduced. The oxidation of H_2 or CO is much faster over $LaCoO_3$ than over the titanates and this was also found for the rate of reduction of the catalyst by H_2 or CO in the absence of O_2 (*14*). At 400°C, $LaCoO_3$ was reduced in 1 hr by about 1*e*/mole, whereas $SrTiO_3$ and $BaTiO_3$ were reduced only to 0.02*e*/mole after several hours at 700°C. Other studies of CO oxidation over $LaCoO_3$ (*15, 16*) and $BaTiO_3$ (*12, 17*) have already noted this large difference. The activity of $LaCoO_3$ for CO oxidation measured in this work is a little larger than values previously reported. This may have resulted from a small contamination with Co_3O_4 which is known to be extremely active (*16*).

The most significant points of our work are related to the PC and FC effects, viz., no PC effect was observed for H_2 oxidation on any of the materials studied (including ZnO and TiO_2); a strong PC effect with light

TABLE 2

Reaction Rates for CO Oxidation

Catalyst	Surface area (m^2/g)	Pretreatment[a]	E_{app} for the dark reaction (kcal mole^{-1})	Dark rate at room temp.[b] (molecule g^{-1} s^{-1})	Rate under irradiation at room temp.[b] (molecule g^{-1} s^{-1})
$LaCoO_3$	7.5	OX	9.75	4.2×10^{16}	4.2×10^{16}
$BaTiO_3$	18.	OX	19.5	1.7×10^{8}	2.2×10^{14}
$SrTiO_3$	64.	OX	19.6	$\sim 10^{10}$	8.3×10^{14}
$Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$	0.67	OX	12.8	1.7×10^{12}	1.7×10^{12}
TiO_2 (anatase)	11.2	OX	10.2	1.7×10^{12}	5.3×10^{15}

[a] OX: in oxygen, see Experimental section.

[b] In case no measurements were performed at room temperature, the values given have been extrapolated from results obtained at higher or at lower temperature.

of band-gap energy was observed for CO oxidation over the *d*-band catalysts ($SrTiO_3$ and $BaTiO_3$) but no effect was found over the other catalysts ($LaCoO_3$ and $Ba(Fe_{0.33}Ti_{0.67})O_{2.67}$). Parallel to this, a FC effect was observed for CO oxidation over $BaTiO_3$ which was quenched by irradiation with band-gap light; these effects were present but less clear for H_2 oxidation. Remarkably, they were characterized by almost temperature independent reaction rates at low temperature.

In considering first the temperature domain in which a FC effect is observed for the oxidation of CO over $BaTiO_3$ in the dark, it is significant that the region where the rates are almost temperature independent does not terminate abruptly at T_c, as suggested by Kawai *et al.* (*12*), but rather decreases gradually over a temperature range above T_c. This may seem surprising since the spontaneous polarization of the solid is expected to drop to zero above T_c and so the FC effect should be lost. This apparent inconsistency can be resolved when one considers the peculiar surface properties of ferroelectrics and of $BaTiO_3$ in particular. In this material the para-ferroelectric transition is associated with a first-order transition, the structure going from cubic above T_c to tetragonal below T_c. The polarization of the cubic phase is zero, whereas the spontaneous polarization of the tetragonal phase is about 0.26 C m^{-2} at 23°C. Actually, this simple behavior applies only to the bulk phase. $BaTiO_3$ is known to have several types of surface layers which could behave quite differently from the bulk (*18*). Aberdam and Gaubert (*19*) have suggested the existence of a surface layer which remains tetragonal up to about 430°C, whereas Anliker *et al.* (*20*) proposed a tetragonal surface layer up to 500°C. These observations are in agreement with theoretical calculations (*21*) which show that surface relaxation of the titanium and oxygen ions can induce tetragonal distortions in the surface layers with a fourfold tetragonal axis normal to the surface.

The electric properties of these surface layers have been extensively studied. The evidence points to the presence of intense space-charge fields which, for $BaTiO_3$, have been estimated to be of the order of 10^6–10^8 V cm^{-1}, i.e., sufficient to cause spontaneous field emission and electroluminescence (*22*). The same observations were made for $KNbO_3$ which is isomorphous with $BaTiO_3$ (*23*). Thus, the FC effect which we observed above T_c is probably associated with ferroelectric surface layers and the discrepancy between our results and those of Kawai *et al.* (*12*) may be due to the likely sensitivity of these systems to thermal history (catalyst preparation and pretreatment) and to particle size. It appears, from our experimental procedure, that the surface layers we are dealing with are stable at least up to the catalyst pretreatment temperature, i.e., to 520°C.

A second interesting point is that the FC effect is quenched by irradiation with band-gap light, suggesting that the polarized surface layers are destroyed or compensated by the electron–hole pairs generated by the optical excitation. This agrees with the fact that a relatively small number of electrons in the π^* band of perovskites can quench ferroelectric distortion (*7*) and with the observation of Bhide *et al.* (*24*) that the electroluminescent properties of $BaTiO_3$ can be quenched entirely by irradiating the crystal. A simple calculation shows that the magnitudes of the polarization effects associated with ferroelectricity are well within the range of those associated with band-gap light excitation. Indeed, the dipole moment of a unit cell of $BaTiO_3$ is about 1.7×10^{-29} C m (*10*). On the other hand, the light-induced transfer of an electron from O^{2-} to Ti^{4+} (a process which could equivalently be described in terms of band-to-band transition followed by charge trapping) would lead to a dipole moment of $\rho \simeq (1.6 \times 10^{-19}$ C) $(2 \times 10^{-10}$ m) $\simeq 3.2 \times 10^{-29}$ C m. This shows that the polarization due to small ferroelectric displacements (~0.1 Å) of the positive ions Ba^{2+} and Ti^{4+} with respect to the O^{2-} ions could be compensated by the light-induced polarization associated with the O^{2-} to Ti^{4+} charge transfer.

Turning now to the mechanism by which highly polarized surface layers could affect the catalytic reaction rate, a first possible explanation would be, as considered by Copeland *(25)* for reactions on metal surfaces, that the high surface fields produce an important reduction in the rotational freedom of adsorbed polar molecules, thereby decreasing their entropy. Due to the rotational contribution to the partition function of the activated complex in transition-state theory, this could lead to an increased concentration of activated complex and thus finally to a large increase in rate constant. Although there is little doubt that the highly polarized surface layers of $BaTiO_3$ could modify the orientational freedom of polar adsorbed species, it seems more questionable that this could lead to a temperature-independent rate process since it does not modify the enthalpy component of the activation energy.

Another possible explanation for the FC effect would be that polarization of the catalyst modifies the rate of the limiting step by altering the stability of some important species on the surface. This is the explanation proposed by Kawai *et al.* to account for the change in activation energy that they observed in the vicinity of T_c *(12)*. From the fact that some CO_2 is strongly adsorbed on the catalyst as carbonate species, they suggested that CO_2 desorption (carbonate decomposition) is the rate-limiting step of the overall reaction and that the change in activation energy is related to the change in binding energy between the adsorbed CO_2 and the surface. Although this explanation, in terms of a modification of the equilibrium properties of the catalyst–adsorbate system, is a plausible one, it does not seem to be entirely satisfactory to us for the following reasons: (i) it leads to the surprising conclusion that the heat of adsorption of a highly polar carbonate species would be lower on a polarized solid than on a nonpolarized solid; (ii) as well as we could estimate, the amount of strongly adsorbed CO_2 (defined as the amount of CO_2 which remained adsorbed on the catalyst at the temperature of our experiment), was a function of temperature only, whether the reaction was studied in the dark, under illumination, or above or below T_c.

It seems to us that a third possibility, based upon the effect of ferroelectric layers and optical excitations on the rate of charge transfer at the catalyst–adsorbate interface, leads to a more satisfying explanation of the FC effect and to a unified picture of both the FC and PC effects. The basic assumption is that charge transfer is part of the rate-limiting step for CO oxidation, at least in the FC and PC branches. This assumption seems to be reasonable since ionic forms of oxygen on oxide surfaces are well known. A priori, charge transfer could be associated either with the generation of active species (O_2^-, O^-, O_3^-, CO^+, . . .) or with the desorption of the reaction products (CO_2^-, CO_3^-, CO_3^{2-}). The main features to take into account when describing charge transfer at the surface of n-type semiconductors like $BaTiO_3$ or $SrTiO_3$ in the presence of an electron-attracting species like oxygen, is the "upward" curvature of the energy bands (Fig. 7A) *(26–28)*. Due to the electronegative character of oxygen, electrons are transferred from the solid to the adsorbed oxygen species ("surface state") and a double layer is developed as adsorption proceeds. An electrostatic repulsion potential results which decreases the density of electrons near the surface in the solid and also the rate and extent of further adsorption. Provided the surface barrier is not so high that further adsorption is stopped for kinetic reasons, equilibrium will be reached when the energy levels of the surface states approach the chemical potential of the electrons in the solid. Thus, another important characteristic is the pinning of the Fermi level at the energy of the majority surface states, which in the present case probably corresponds to the

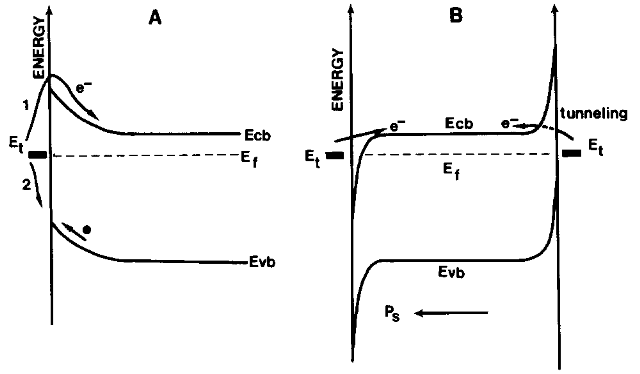

FIG. 7. Model for electron transfer at the surface of an n-type semiconductor in the presence of electron-attracting species, A, showing the conduction and valence bands (CB and VB), the Fermi level (E_f), and the energy of the surface states (E_t) and B, after taking into account the effect of the ferroelectric surface layers. P_s is the spontaneous polarization.

O_2/O_2^- redox level or, at higher temperature, to the O/O^- level.

The first point which is apparent from Fig. 7A is that in the dark, i.e., when the concentration of positive holes in the valence band (VB) is negligible, charge transfer between the adsorbed species and the surface layers of the solid can only occur by electron injection into the conduction band (CB) or by transfer of an electron from the CB to the surface states. Under usual conditions the double layer is too wide to allow quantum mechanical tunneling and this is clearly an activated process (Path 1) since the electron has to overcome the electrostatic potential barrier resulting from the formation of the double layer. Such a mechanism could be operative for the oxidation of CO in the dark over $SrTiO_3$, ZnO, or TiO_2 for instance, and also perhaps over $BaTiO_3$ at high temperature, when the FC effect is no longer effective. This is supported by the fact that the activation energies measured for these dark reactions are very similar to each other and close to what may be expected for the double-layer barrier arising from adsorption of oxygen on a wide band-gap semiconductor (*29*).

In the dark, the concentration of positive holes in the VB is negligible, but upon illumination with light of band-gap energy, they are produced in appreciable concentration as electrons are excited from the VB into the CB. These positive holes drift toward the surface where they can recombine with electrons from adsorbed species. This provides an explanation for the PC effect in terms of hole capture. In the absence of a detailed kinetic analysis in the PC branch, the hole capture reactions which are involved can obviously not be identified. As suggested by Murphy *et al.* (*6*) for ZnO, hole trapping could be involved in the reactions of CO_3^{2-}, CO_3^-, O^{2-}, O^-, or CO, for instance. As indicated by Fig. 7A, the main difference between electron injection (Path 1) and hole capture (Path 2) on an n-type semiconductor is that the former is basically an activated process whereas the latter is not. This could explain why the activation energy in the PC branches at low temperature is close to zero (Figs. 1 and 3).

On a ferroelectric catalyst in the dark the concentration of positive holes is still negligible but as shown by Lines and Glass (*18*), the band bending is dramatically modified by the strong polarization. Along the polarization direction, the upward curvature of the energy bands near the surface may be entirely compensated, or even overcompensated, by a downward bending due to the internal polarizaton (Fig. 7B). As a consequence, electron injection could become almost a nonactivated process *along* the polarization direction. Alternatively, in the *opposite* direction, the upward bending of the energy bands could be increased to such an extent that, due to the concomitant narrowing of the space charge layer, electron tunneling might become feasible. Either effect could account for the temperature independence of the reaction rates in the low-temperature FC branches below T_c and would provide a qualitative explanation for the apparent similarity of the FC and PC effects, both being basically nonactivated charge transfer processes from surface states to the CB or to the VB, respectively. The assumption that electron tunneling could become important in $BaTiO_3$ is in agreement with the fact that spontaneous field emission, i.e., spontaneous ejection of electrons into vacuum, has been observed from this solid (*22*).

Besides these various aspects of CO oxidation, another interesting point is the absence of PC effect for H_2 oxidation over all the catalysts studied and, as far as we can estimate from the very large scatter of the experimental data (Fig. 6), the likely presence of a FC effect over $BaTiO_3$ for this reaction. Possibly electron transfer is no longer rate limiting with this reaction. Parallel chemical factors could be responsible for the FC response. Also, probably the rate-limiting step for hydrogen oxidation is no longer electron injection as for carbon monoxide oxidation, but possibly the reverse, i.e., electron transfer from the solid to the adsorbed phase for generating the active oxygen species. The generation of positive holes would be of no help for this process, but the modification of the bending of the energy bands would still be effective.

In conclusion, it appears that the PC and FC effects reported herein may be accounted for as processes dominated by charge transfer in the boundary layers of the catalyst. It must be pointed out, however, that this is not inconsistent with a more chemical description of the catalytic process as an oxidation–reduction cycle where catalyst oxygen is given up to the reactant to be oxidized in one step and recovered in the next, as suggested by correlation of the catalytic activity with the rate of reduction of the catalyst (*30, 31*). Indeed, reduction of the catalyst clearly implies that the electrons from the surface oxide ions must be recovered by the solid as the reactant is oxidized. Thus, both the catalytic oxidation reaction and the catalyst reduction may involve similar charge transfer steps. Significantly, no PC effect was present with the most easily reducible oxides, e.g., $LaCoO_3$. As noted by Morrison (*29*) it is paradoxical that it is the materials with wide band gaps and which depend on electron transfer in the rate-limiting step which are generally the poorest catalysts.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the support of this research by the National Science Foundation (Grant OIP75-21230). In addition, one of us (HVD) is grateful to the Centre National de la Recherche Scientifique for a leave of absence in order to carry out this research.

REFERENCES

1. Thevenet, A., Juillet, F., and Teichner, S. J., *Jap. J. Appl. Phys.*, Suppl. 2, Pt. 2, 529 (1974).
2. Djeghri, N., Formenti, M., Juillet, F., and Teichner, S. J., *Discuss. Faraday Soc.*, **58**, 185 (1974).
3. Cunningham, J., Finn, E., and Samman, N., *Discuss. Faraday Soc.* **58**, 160 (1974).
4. Cunningham, J., Kelly, J. J., and Penny, A. L., *J. Phys. Chem.* **74**, 1992 (1970); **75**, 617 (1971).
5. Tanaka, L., and Blyholder, G., *J. Phys. Chem.* **75**, 1037 (1971); **76**, 1807 (1972).
6. Murphy, W. R., Veerkamp, T. F., and Leland, T. W., *J. Catal.* **43**, 304 (1976).
7. Voorhoeve, R. G. H., *in* "Advanced Materials in Catalysis" (J. J. Burton and R. L. Garten, Eds.). Materials Science and Technology Series, Chap. 5, p. 129ff, Academic Press, New York, 1977.
8. Goodenough, J. B., and Longo, J. M., "Landolt-Bornstein Tabellen, New Series III/4a, pp. 126–314. Springer-Verlag, Berlin, 1970.
9. Goodenough, J. B., *in* "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 5, pp. 145–399. Pergamon, Oxford, 1971; *in* "Solid State Chemistry" (C. N. R. Rao, Ed.), pp. 215–364. Dekker, New York, 1974.
10. Kittel, C., "Introduction to Solid State Physics," 5th ed.. Wiley, New York, 1976.

11. Parravano, G., *J. Chem. Phys.* **20,** 342 (1952).
12. Kawai, T., Kunimori, K., Kondow, T., Onishi, T., and Tamaru, K., *Z. Phys. Chem. Frankfurt* **86,** 268 (1973).
13. Dickson, J. G., Katz, L., and Ward, R., *J. Amer. Chem. Soc.* **83,** 3026 (1961).
14. Crespin, M., and Hall, W. K., *J. Catal.* **69,** 359 (1981).
15. Voorhoeve, R. J. H., Remeika, J. P., and Trimble, L. E., *Ann. N.Y. Acad. Sci.* **272,** 3 (1976).
16. Yao, Y. F., *J. Catal.* **36,** 266 (1975).
17. Mikhailova, I. L., Sazonova, I. S., Keier, N. P., and Belosludtseva, T. V., *Kinet. Katal.* **9,** 565 (1968).
18. Lines, M. E., and Glass, A. M., "The Principles and Applications of Ferroelectrics and Related Materials," pp. 117–126. Oxford Univ. Press (Clarendon), London/New York, 1977.
19. Aberdam, D., and Gaubert, C., *Surface Sci.* **27,** 571 (1971).
20. Anliker, M., Brugger, H. R., and Kanzig, W., *Helv. Phys. Acta* **27,** 99 (1954).
21. Ai Ahmad, L. *Surface Sci.* **12,** 437 (1968).
22. Drougard, M. E., and Landauer, R., *J. Appl. Phys.* **30,** 1663 (1959).
23. Katpatal, A. G., and Deshmukh, K. G., *J. Phys. D* **5,** 1937 (1972).
24. Bhide, V. G., Gondhalekar, R. T., and Shringi, S. N., *J. Appl. Phys.* **36,** 3825 (1965).
25. Copeland, R. F., *J. Phys. Chem.* **75,** 2967 (1971).
26. Stone, F. S., *in* "Advances in Catalysis and Related Subjects," Vol. 13, p. 1. Academic Press, New York/London, 1962.
27. Many, A., Goldstein, Y., and Grover, N. B., "Semiconductor Surfaces." Interscience, New York, 1965.
28. Frankl, D. R., "Electrical Properties of Semiconductor Surfaces." Pergamon, London, 1967.
29. Morrison, S. R., "The Chemical Physics of Surfaces." Plenum, New York, 1977.
30. Popovskii, V. V., Mamedov, E. A., and Boreskov, G. K., *Kinet. Katal.* **13,** 145 (1972).
31. Onishi, Y., and Hamamura, T., *Bull. Chem. Soc. Jap.* **43,** 996 (1970).