JOURNAL OF CATALYSIS 31, 231-242 (1973)

Infrared Spectroscopic Study of Catalytic Oxidation Reactions Over Cobalt Oxide Under Steady-State Conditions

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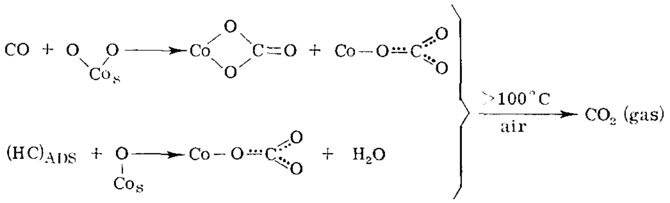
Received March 20, 1973

An infrared spectroscopic study of the catalyzed CO and hydrocarbon (HC) oxidation reactions over cobalt oxide was carried out under static conditions, and the catalyzed CO oxidation reaction under steady-state conditions. The reactions proceed principally via surface carbonate groups.



The source of the oxygen required to form the surface carbonates is the surface of the cobalt oxide. This oxygen is replenished from gas phase oxygen. Under steady-state reaction conditions changes in the surface concentrations of these groups are observed when the CO feed concentration is changed. Concurrent measurements of the background transmission were used to determine the state of oxidation of the cobalt oxide under the reaction conditions, which demonstrated that the cobalt oxide goes through an oxidation–reduction cycle when functioning as an oxidation catalyst.

INTRODUCTION

The catalytic oxidation of CO over metal oxides has been the subject of numerous studies (*1*, *2*). This reaction is generally assumed to take place between adsorbed CO and adsorbed O_2 or between adsorbed CO and surface lattice oxygen. For the latter mechanism, when CO_2 is desorbed the catalyst surface is left in a reduced state, and oxygen from the gas phase adsorbs to reoxidize the surface. A change of this type, in which the catalyst is reduced or oxidized, can be observed via electrical resistance measurements, and studies of this type have been done (*3*, *4*) when various gases are adsorbed on surfaces. Most of these resistance measurements were carried out under static conditions.

Infrared spectroscopy is a powerful tool for identifying adsorbed species, and Eischens and Pliskin (*5*) were the first to demonstrate the presence of carbonate groups on the surface of nickel oxide during the oxidation of CO in a static CO/air mixture at 25°C. Baddour, Modell, and Heusser (*6*) carried out an ir spectral study of CO oxidation on palladium metal under steady-state conditions which allowed them to observe the changes in the intermediate surface species during the actual reaction.

Infrared spectroscopy can also be used

to monitor resistance changes during chemisorption by observing changes in the background transmission of the sample. Changes of this type have been observed in ZnO when CO is adsorbed (*7*). The background transmission is related to the resistance of the sample, in the sense that the higher the resistance the greater is the background transmission. Several spectroscopic studies of CO adsorption on cobalt metal (*8–10*) have shown the presence of carbonyl type species. The adsorption of various organic compounds on cobalt metal has also been studied (*11, 12*). Adsorption of CO on partially oxidized, supported cobalt metal has been briefly reported (*10*), in which carbonyl type species were observed in addition to those observed on the metal.

The oxidation of hydrocarbons over cobalt oxide has received less attention, although recent studies have included determining the oxidation kinetics by competitively adsorbing various olefins and paraffins (*13*) and by alternately adsorbing oxygen and propylene (*14*). Levy (*15*) observed the coexistence of CoO–Co_3O_4, using X-ray diffraction, during the catalytic oxidation of butane and propylene between 250 and 500°C.

Since cobalt oxide is a good catalyst for the complete oxidation of CO and some hydrocarbons, it has received attention for possible use in controlling automotive exhausts. Due to its practical importance, as well as due to the ambiguities in the proposed mechanisms for CO oxidation over metal oxides (*2*), an infrared spectroscopic study was undertaken in which the surface of the cobalt oxide catalyst was observed under steady-state reaction conditions. Static spectroscopic and vacuum balance experiments were also carried out. Besides the identification of various adsorbed species observed under precatalytic conditions, the main importance of this study for catalytic purposes lies in: (a) the direct observation of the intermediate adsorbed species that lead to oxidation of CO while the catalytic reaction is actually taking place under steady-state conditions, and (b) a measure of the changes in the oxidation–reduction state of the catalyst under actual reaction conditions.

EXPERIMENTAL METHODS

Materials. The cobalt oxide was prepared by the calcination of cobalt carbonate. This produces a powder with a specific surface area of about 30 m^2/g. For the spectroscopic studies, about 50 mg of cobalt oxide powder was pressed at 7 tons/$in.^2$ to form a 1 in. diameter self-supporting disc.

Gravimetric. The powder was suspended in an Ainsworth vacuum balance connected to a conventional vacuum rack and equipped with a furnace. Weight changes of the sample were recorded on a strip chart recorder.

Spectroscopic. The self-supporting cobalt oxide disc was mounted in a cylindrical steel furnace fitted with water-cooled infrared transmitting end plates and mounted in a Perkin-Elmer 421 spectrometer. For the static experiments the furnace cell was connected to a conventional vacuum rack. In the static spectroscopic and gravimetric experiments, the samples were preheated *in situ* at 400°C in air for at least 15 min and then evacuated at 300°C.

After mounting in the furnace cell, the transmittances of the oxidized cobalt discs before adsorption were about 3 to 4% at 2500 cm^{-1}, and increasing towards lower frequencies. When adsorption took place, the background transmittance increased. The reference beam attenuation used is given with the spectra. Generally, screens were used for attenuation, rather than a variable attenuator, since the change in background transmittance can be used to obtain information about the behavior of the catalyst. Due to the low transmittances slow scan speeds ($\sim$ 75 cm^{-1}/min) and twice normal slit openings were used (spectral slit width 2.3 cm^{-1} at 1600 cm^{-1}).

For the steady-state reaction experiments a similar furnace cell was used, except that steel inlet and outlet tubes were mounted at the side of the furnace so that the gas mixtures passed over the cobalt oxide disc. The sample was initially exposed to a CO/air mixture at the temperature of the experiment and then allowed to stand for at least 20 min using a flow of pure air. This was done so that the changes in surface species at a given temperature were due only to those contributing to the catalytic reaction. Then, with a fixed flow of air, various flows of CO were admixed and spectra of the catalyst disc were taken. The specific flow rates and temperatures used are given with the results.

RESULTS AND DISCUSSION

Desorption Products

To determine if any of the chemisorbed species desorb reversibly, or if only the final products of the reactions are desorbed, the gas phase only was observed by placing 0.3 g of cobalt oxide on the floor of the furnace. CO, propylene or hexane was added to the cell at a low temperature and then evacuated. The cell was closed and the temperature was incrementally raised. Spectra were taken to indicate which of the desorbed species was present in the gas phase.

Carbon monoxide was added to the cell at 70°C and a small quantity of CO_2 appeared. The cell was evacuated, closed, and the temperature was raised. Below 150°C no gaseous products were observed. At 150°C traces of CO_2 appeared, and at various temperatures up to 280°C increasing quantities of CO_2 were desorbed. In no case was CO observed. The addition of air produced more CO_2.

Propylene was added to the cell at 50°C. A spectrum was taken prior to evacuation. The propylene bands were observed as well as a low band extending from 3570 cm^{-1} down to at least where the strong CH stretching bands begin at 3150 cm^{-1}. This low, broad band is probably due to H_2O condensed on the cooled cell windows and produced as a product of the propylene adsorption. No CO_2 was observed. On evacuation the propylene bands and the broad water band were removed. With the cell closed, nothing was observed up to 150°C. At various temperatures up to 280°C increasing quantities of CO_2 appeared. No detectable amounts of water or organics were observed. On adding air, more CO_2 appeared.

Hexane was admitted to the cell at 20°C, evacuated and the temperature was raised. At 60°C some gaseous hexane appeared, and at 120°C a larger quantity of hexane appeared. Up to 220°C no further hexane was desorbed. Minute quantities of CO_2 were observed at temperatures above 200°C.

The cobalt oxide was allowed to stand in 1 atm of CO for 20 min at 220°C, cooled to 50°C and evacuated. These are conditions under which bulk reduction of the cobalt oxide takes place. On raising the temperature to 150°C no desorption products were observed. With increasing temperatures above 150°C increasing quantities of CO_2 appeared. No carbon monoxide was observed. On adding air to the cell at 120°C, more CO_2 was produced.

One can summarize by saying that CO_2 is the only desorption product when CO is adsorbed on cobalt oxide. Propylene adsorption on cobalt oxide yields water initially, and only CO_2 thereafter. When hexane adsorbs, a large amount desorbs reversibly.

When propylene or hexane were admitted to the cell at 100°C and air added, large quantities of both CO_2 and H_2O were observed in the gas phase.

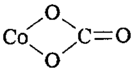
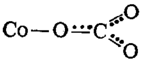
CO and Hydrocarbon Oxidation Under Static Condtions.

The cobalt oxide was exposed to carbon monoxide or one of the hydrocarbons, both in vacuum and with added air, and at various temperatures. The various absorption bands observed, together with the assignments of the species (*16*) are listed in Table 1.

Figure 1 shows spectra in which carbon monoxide was added to the cobalt oxide at 80°C. The CO bonds immediately to the

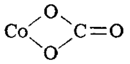
TABLE 1

OBSERVED INFRARED ABSORPTION BANDS USED TO IDENTIFY ADSORBED SPECIES

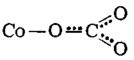
Species		ir bands [frequencies (cm^{-1})][a]			
	Bidentate carbonate	1600	1290	1040	835
	Unidentate carbonate	1545 1525	1350	1322	1040
CO_3^{2-}	Uncoordinated CO_3^{2-} ion	1420	1110		835
$Co\cdots O\cdots C\cdots O$? $Co{-}C\equiv O^+$	Terminal carbonyl	2185			
CO	Gaseous CO	2120	2170		
CO_2	Gaseous CO_2	2350			

[a] All frequencies are ±20 cm^{-1}. Where a band is listed in more than two places, it is not possible to determine to which species it belongs. Frequency assignments were taken from Ref. (*16*).

surface oxygen atoms, producing at least two distinct species, viz:



Bidentate carbonate



Unidentate carbonate

The large increase in background transmission occurred when any gas (NO at low temperatures, propylene, hexane, CO, SO_2 or H_2) except oxygen was adsorbed on the surface. This is a very important phenomenon for understanding the behavior of the catalyst and is discussed below. On admitting air to the sample at 120°C the background transmission decreases (Fig. 1,

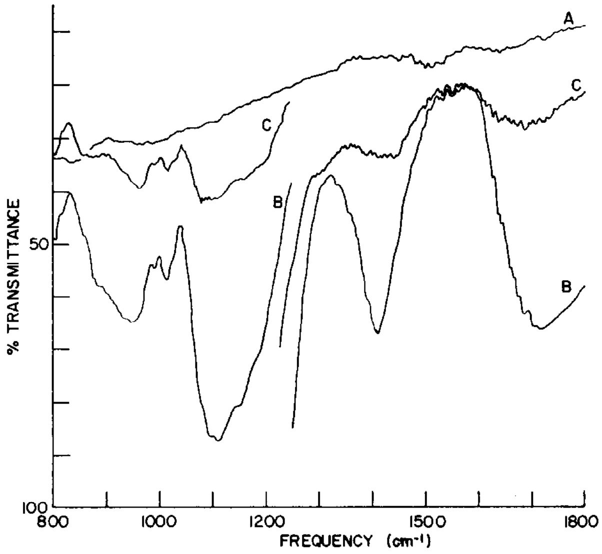


FIG. 1. Spectra of cobalt oxide (A) at 80°C after heating in air at 400°C and evacuating at 300°C; (B) at 80°C after adding 20 Torr CO and evacuating; (C) after adding air at 120°C. 95% reference beam attenuation was used, except curves B and C below 1200 cm^{-1}, where 89% reference beam attenuation was used.

curve C) but does not return to the original value at this temperature, higher temperatures being required. The same experiments were carried out at ambient temperature. The same bands appeared, but addition of air gave only a very slight decrease in the background transmission. The absorption bands observed are rather irregular in shape, indicating that the band for each carbonate actually consists of several bands differing slightly in frequency. These differences probably arise due to the nature of the oxygen atom to which the carbon atom bonds. Davydov *et al.* (*17*) demonstrated spectroscopically that dissociatively chemisorbed oxygen on MnO_2, Fe_2O_3 and Cr_2O_3 has various forms. They observed several infrared bands within the single and double metal oxygen bond absorption region which have different chemical and thermal stabilities.

On the cobalt oxide these surface carbonates are stable in air or vacuum up to near 100°C. Between 100 and 150°C in air some of the surface carbonates decompose to gaseous CO_2 as shown by the decrease in intensities of the carbonate bands (cf. Fig. 1). Above 200°C in air, only small amounts of the surface carbonates remain. In vacuum the surface carbonates are more stable and do not decompose significantly until one exceeds about 190° This is in reasonable agreement with the desorption experiments.

A careful search was made for the presence of a terminal carbonyl group, Co—C≡O, since groups of this type are often observed with transition metal oxides (*16*). On a copper chromite catalyst this carbonyl group can be observed (*18*) and has been shown to be the principal surface intermediate in the low temperature oxidation of CO. No bands were observed between 2000–2500 cm^{-1} after heating the cobalt oxide in an atmosphere of CO for several minutes at various temperatures between 40 and 150°C. When the cobalt oxide was heated at 220°C in 500 Torr CO for 20 min, conditions under which cobalt oxide undergoes bulk reduction, the background transmission increased for about 15 min. On cooling to 40°C and evacuating, bands due to the carbonates were observed (Fig. 2) as well as a strong band at 2185 cm^{-1}. The position of this band is the same as one of the three bands due to terminal carbonyl groups on cobalt metal observed by Gardner and Petrucci (*8*). They assigned this band to a linearly adsorbed CO which has 9 valence electrons.

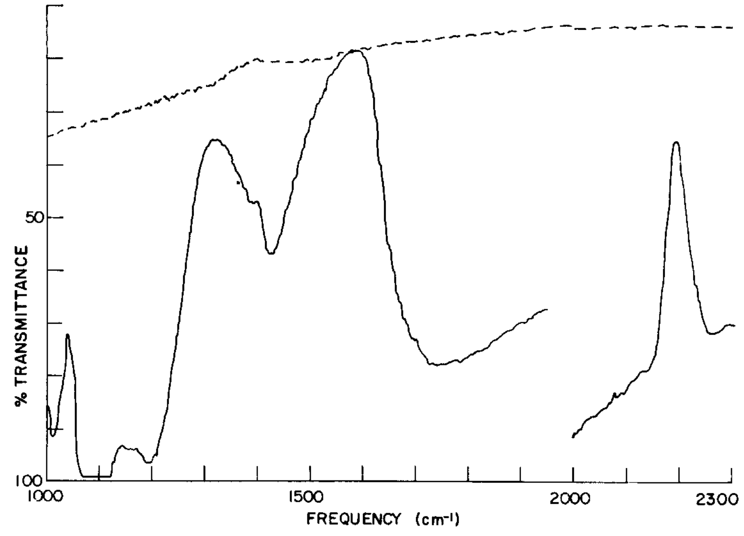


FIG. 2. Spectra of cobalt oxide (- -) at 40°C after heating in air at 400° and evacuating at 300°C, (—) evacuated at 40°C after heating at 220°C for 20 min with 500 Torr CO. Reference beam attenuations used were: (- -) 95%; (—) above 2000 cm^{-1}, 89%; and below 2000 cm^{-1}, 81%.

Ferreira and Leisegang (*10*) observed bands at 2130 and 2180 cm^{-1} on a partially oxidized cobalt metal sample, which they ascribed to CO ligands attached to lattice cobalt ion and oxygen ion sites, respectively. Their spectra do not cover the region below 1800 cm^{-1} where the carbonate bands would appear. A complete discussion of the structures of these carbonyls has been given by Gardner and Petrucci (*8*) and by Little (*16*).

Up to 150°C in vacuum there was little change in the carbonyl band intensity, indicating strong adsorption. After heating for 1 hr in vacuum at 220°C, and then lowering the temperature to 40°C, about one-quarter of the original intensity of this band remained. Addition of air at 40°C had no effect, but at 150°C after 3 min in air, the carbonyl and carbonate band intensities were much reduced.

To follow the formation of this surface species, the cobalt oxide was heated at 180°C in 100 Torr CO for 3 min intervals. Spectra were taken after each interval and the terminal carbonyl band was observed to slowly increase with time. Thus, although this carbonyl band is slowly removed in the presence of air at 150°C the rate of adsorption is very slow and must be an activated process.

Since the rate of adsorption is very slow in comparison to the rate at which the carbonates form, it does not seem probable that this can be an important intermediate for CO oxidation in this lower temperature range. Being an activated process, it could of course become sufficiently fast to be of importance at higher temperatures.

When propylene is admitted to the cobalt oxide sample at 50°C (Fig. 3) there is again an immediate large increase in the background transmission of the sample and absorption bands appear. The bands are similar to those which appear when CO is adsorbed, although the intensities in general are less. The band assigned to the bidentate carbonate, which appears with CO, is absent with propylene, and there is at least one band near 1430 cm^{-1} which does not appear when CO adsorbs under similar conditions. Although CO_3^{2-} ions have a band here, the possibility that some formate groups have formed cannot be excluded. Surface formate groups on alumina have a CH vibration at 1390 and C–O vibrations at 1378 and 1587 cm^{-1} (*19*).

At about 180°C in vacuum, a few of the bidentate carbonates are observed to form, as shown by an increase in the absorption

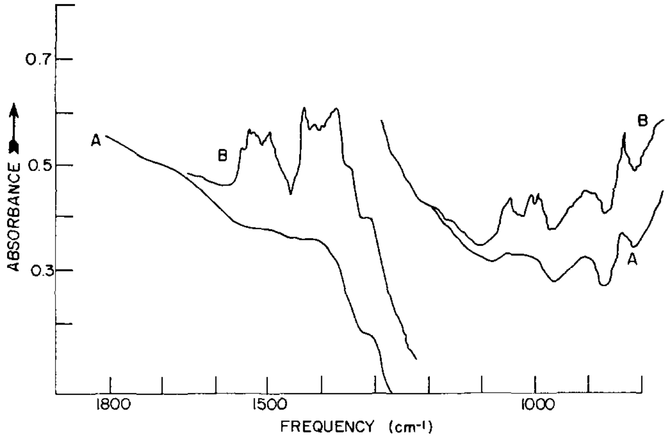


FIG. 3. Spectra of cobalt oxide at 50°C (A) after heating in air at 400°C and evacuating at 300°C (B) evacuated after adding 100 Torr propylene. Curve A has been slightly moved, using 95% reference beam attenuation, so as to better show the absorption bands on curve B. Reference beam attenuations of curve B are: 89% above 1200 cm^{-1} and 77% below 1300 cm^{-1}.

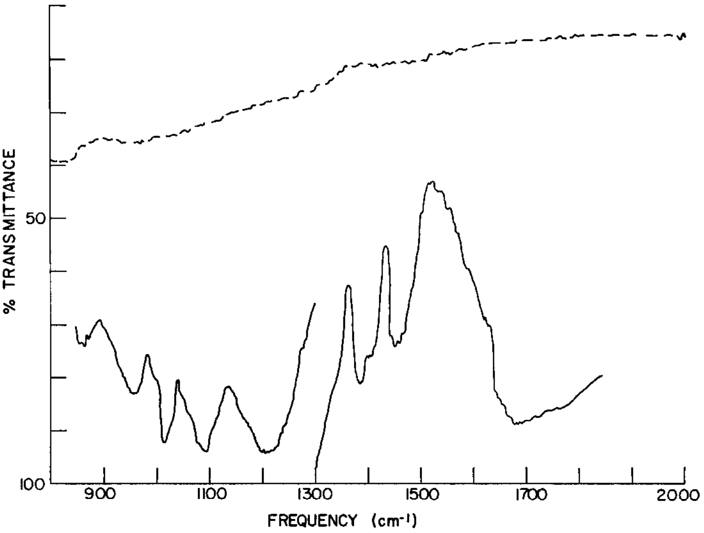


FIG. 4. Spectra of cobalt oxide at 40°C (- -) after heating in air at 400° and evacuating at 300°C and (—) evacuated at 40°C after heating in 500 Torr propylene for 15 min at 220°C. Reference beam attenuations used were: (- -), 95%; (—) above 1300 cm^{-1}, 89%; and below 1300 cm^{-1}, 83%.

at 1600 cm^{-1}, similar to that shown in Fig. 4 (cf. Figs. 3 and 4). This is an interesting reaction, indicating that one of the oxygen atoms of the unidentate carbonate has returned to the surface of the catalyst without breaking the C–O bond.

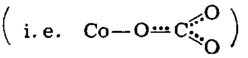
When 500 Torr propylene was added to the cobalt oxide at 220°C, conditions under which bulk reduction takes place, there was again a very large increase in the background transmission. On lowering the temperature to 40°C and the pressure to several Torr, low broad bands between 2850 and 3150 cm^{-1} were observed, but with evacuation these bands disappeared completely. With these strongly reduced samples it is possible to observe the CH stretching band region. The spectrum of this sample, after complete evacuation, is given in Fig. 4. Under the conditions of oxidation catalysis, which is of principal interest here, the CH stretching band region of the spectrum is not observable due to the low transmittance. The differences between this spectrum and that of the propylene adsorbed at 50°C (cf. Figs. 3 and 4) consist mainly in the presence of the band near 1600 cm^{-1} due to the bidentate carbonate and the lower intensity of the band near 1400 cm^{-1} due either to carbonate ions or formate groups.

Hexane behaves similarly to propylene, except that at 75°C some weak bands are also observed at 1145, 1175, 1375 and 1400 cm^{-1} which are probably due to some adsorbed hexane which has not been cracked and transformed to the carbonates. The desorption experiments showed that adsorbed hexane is present on the surface up to about 120°C.

From this point, the reactions proceed the same as when CO is adsorbed, i.e., at temperatures above 100°C in air the surface carbonates start decomposing to give gaseous CO_2. Above 200°C in air, only traces of the carbonates remain.

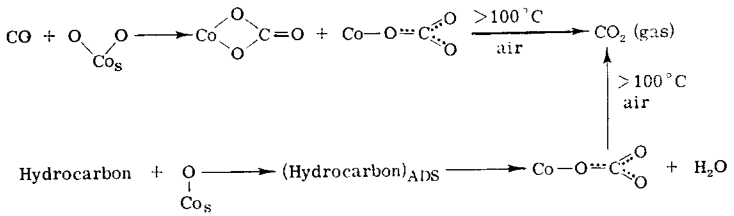
When methane is admitted to the sample, there are no changes in the background transmission, showing that the methane does not interact with the cobalt oxide at these temperatures (100°C) and behaves essentially like an inert gas.

It is important to note that the source of the oxygen required to form the surface carbonates is the catalyst itself, since these carbonates form in the absence of any gas phase oxygen. Thus, the adsorbing CO bonds to one of the surface oxygen atoms and also picks up an adjacent oxygen atom to form the carbonate



Davydov *et al.* (*20*) proposed that CO oxidation over MnO_2 proceeded via the formation of carbonate species involving the oxygen of MnO_2 and gaseous CO and that desorption of CO_2 resulted in anionic vacancies on the surface which are filled immediately with gaseous oxygen.

An important property of cobalt oxide as a catalyst for hydrocarbon oxidation is that it is a good cracking catalyst also, at least insofar as these surface reactions are concerned. When the hydrocarbons adsorb on the cobalt oxide, they are cracked and transformed to the surface carbonates at low temperature. The behavior of these surface species can be summarized in the following simplified diagrams:



Gravimetric Study

When CO was added to the cobalt oxide in the vacuum balance at various temperatures up to 190°C, only an initial weight gain was observed, without any subsequent weight losses. This initial weight gain is due to the formation of the surface carbonate and carbonyl groups. Thus, in the absence of oxygen, some of the carbonates and carbonyls are stable up to 190°C. At temperatures above 200°C, addition of CO gives an initial weight gain and then a continuous weight loss which is far in excess of the amount of oxygen which could be present on the surface. This is due to the decomposition of the surface groups to give CO_2. Since the atmosphere is pure CO, when one surface group desorbs, a CO molecule adsorbs to form a new surface group, which in turn desorbs as CO_2. The source of the oxygen required is from the bulk of the catalyst. This, of course, is not a catalytic reaction, but the reduction of a metal oxide with CO. The importance of this result is that at temperatures below 190°C, any oxidation–reduction changes of the catalyst are limited to the surface of the catalyst.

By adsorbing a given gas and then evacuating one can calculate the number of strongly adsorbed molecules. At 30°C there are 4 (± 2) molecules CO/100 $Å^2$ adsorbed.

Carbon Monoxide Oxidation Under Steady-State Conditions

The optical transmittance of any substance, aside from specific absorption bands, is a function of its dielectric constant or electrical conductivity. An extreme case would be a metal, where the charge carriers are electrons. Being a nearly perfect conductor, the optical transmission is zero. When a metal is oxidized the electrons are no longer available as charge carriers. In the case of *p*-type oxide conductors the charge carriers are either cations or anion vacancies, and addition of oxygen reduces the number of charge carriers and hence the conductivity. Thus, changes in the optical transmission should be a measure of the electrical conductivity of the sample, in the sense that the greater the background transmission, the lower the conductivity.

When any of the reacting gases, except oxygen, adsorbs on the cobalt oxide surface, there is a large increase in the background transmission. Upon admitting oxygen to the sample the background transmission drops, and on completely desorbing the bonded species in the presence of oxygen, the transmission returns to its original (low) value. These changes are consistent with a model in which the cobalt oxide behaves as a *p*-type conductor, in that under strong reducing conditions (pure CO atmosphere) the electrical conductivity drops, whereas under oxidizing conditions the electrical conductivity rises. The important point, however, in this catalytic study, is the experimental observation that reduction of the catalyst surface increases the background transmission and oxidation of the catalyst surface decreases that background transmission.

Experiments were carried out between 40 and 260°C using a constant air flow of 200 cm^3/min and admixed CO using flows from 0 to 90 cm^3/min, which is approximately stoichiometric. At 100°C and lower, the changes observed were very small. In Figs. 5 and 6 are given typical sets of spectra. The upper spectra were taken with a fixed reference beam attenuator. The spectra clearly show: (a) the greater the amount of CO in the gas flow, the greater is the background transmittance, and (b) the changes in the transmittance are completely reversible and the base line returns to its original position in the absence of CO. The lower spectra are the same as those recorded at the top of the figure, except that the base lines have been superimposed to show more clearly the changes in intensities of the specific absorption bands. These spectra show: (a) the greater the amount of CO in the gas flow, the greater is the amount of CO_2 produced, and (b) for low concentrations of CO, the bands at 1600, 1530, 1410, 1300, and 1170 cm^{-1} increase with increasing CO and decrease with decreasing amounts of

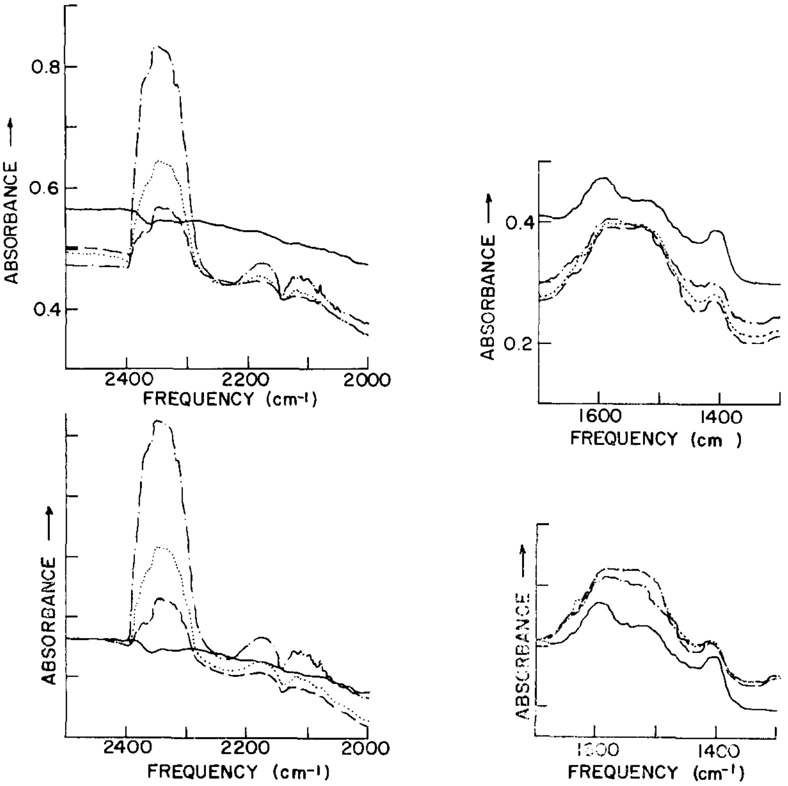


FIG. 5 (upper). Spectra at 180°C of cobalt oxide taken with fixed reference beam attenuator using various CO concentrations. (lower) The same spectra with the base lines superimposed. A constant air flow = 200 cm^3/min was used. (—) CO = 0; (– –) CO = 6 cm^3/min; (· · ·) CO = 11 cm^3/min; (— ·) CO = 30 cm^3/min. (—) CO = 0.

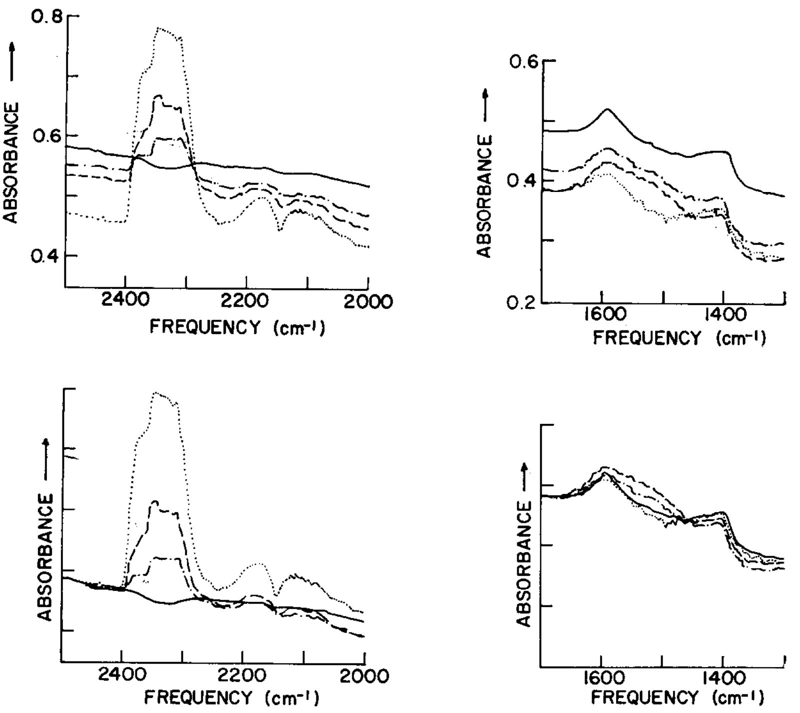


Fig. 6 (upper). Spectra at 220°C of cobalt oxide taken with fixed reference beam attenuator using various CO concentrations. (lower) The same spectra with the base lines superimposed. A constant air flow = 200 cm^3/min was used. (—) CO = 0; (- -) CO = 11 cm^3/min; (· · ·) CO = 44 cm^3/min; (— ·) CO = 6 cm^3/min. (—) CO = 0.

CO. These are the bands due to the carbonate groups (cf. Table 1). This clearly shows that these are intermediates in catalytic oxidation, since the desorption experiments showed that the carbonate groups give only CO_2 as a product. The changes are completely reversible. At any of these temperatures, a certain number of the carbonate groups do not decompose. These groups can be largely decomposed (i.e., desorbed) by heating to higher temperatures. This indicates a spectrum of bonding energies with the surface, with the weakest contributing to CO oxidation in this temperature range. The spectra taken under these conditions are admittedly poor, principally due to the low steady-state concentrations of the intermediates on the surface, but also due to the broadening of the bands at these higher temperatures.

Although the carbonyl band, if present, would be obscured by the gas phase CO bands, it is not probable that this is an important intermediate up to 180°C, since at that temperature the rate of adsorption of CO to form the carbonyl group is very slow. Also, the state of catalyst reduction during the oxidation reaction is not very great, so that not many metal atoms can be available. The possibility that the carbonyl group is an important intermediate at higher temperatures, particularly with rich CO/O_2 mixtures, cannot be excluded.

In Fig. 7 are given plots of (change in transmission) vs (amount of CO in air) taken at various temperatures. Although the points are rather scattered, it is seen that the general trend is for greater proportions of CO to give greater transmissions, or greater degrees of catalyst reduction, and that the degree of reduction goes through a maximum at about 180°C, for low amounts of CO. For high proportions of CO, the total flow rate becomes significantly higher, so that the results are not strictly comparable. At 150°C the very

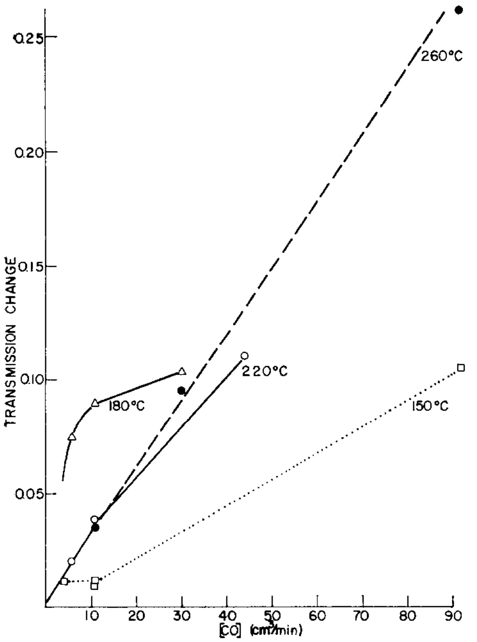


FIG. 7. Plots of change in transmission (absorbance units) against CO concentration, at various temperatures. A constant air flow = 200 cm^3/min was used. (□ · ·) 150°C; (△ —) 180°C; (○ —) 220°C; (● - -) 260°C.

slightly reduced state of the catalyst indicates that the rate determining step (RDS) of the oxidation process is the decomposition of the carbonate group, while at 180°C the large state of catalyst reduction indicates that the RDS is reoxidation of the catalyst surface by gaseous oxygen. At 220°C and above, using low proportions of CO, an intermediate catalyst reduction state is observed, suggesting that the RDS might be the rate of CO adsorption. That the state of catalyst reduction during the reaction goes through a maximum at about 180° indicates that either rate determining step has changed or that another mechanism is contributing to the overall reaction. Since these changes in transmission (or resistance or oxidation state of the catalyst) are completely reversible, they clearly demonstrate that the catalyst goes through an oxidation–reduction step during the course of the catalytic reactions on the surface.

At the highest temperature (260°C) used here, no bands over the background were observed with varying CO indicating that the steady-state concentrations of the carbonates are very small. The presence of the catalytic reaction is readily detected, however, by the variation in gaseous CO_2 produced and in background transmission with varying CO.

Quantitatively, the greatest transmission changes occur when a fully oxidized bare surface adsorbs one of these gases (CO, propylene, H_2), (Figs. 1–4). Although the term *fully oxidized* is somewhat nebulous, it refers here to the surface that has been heated to 400°C in air and on which no specific absorption bands due to adsorbed species are observed.

When very high concentrations of CO were used (air 200 cm^3/min, CO > 20 cm^3/min), the intensities of the carbonate absorption bands were somewhat less than when lower CO concentrations were used, although the amount of CO_2 produced was large with large CO concentrations. This could indicate that a carbonyl intermediate contributes to the catalytic oxidation with rich CO mixtures, or that due to the large amount of reaction when using high CO concentrations the exothermicity of the oxidation reaction raises the catalyst surface temperature resulting in a lower steady-state surface carbonate concentration.

ACKNOWLEDGMENT

The author gratefully acknowledges the suggestion of Professor S. W. Weller that electrical resistance measurements can be used to determine the oxidation state of a metal oxide.

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