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Surface Structures Formed on Cobalt Oxide During Catalytic Oxidation: An Infrared Study

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Reaction intermediates formed on cobalt oxide (Co_3O_4) during catalytic oxidation have been studied using infrared spectroscopy. The adsorption of CO, CO_2, ethylene, cyclohexane, cyclohexene, oxygen, H_2O, D_2O, H_2O^{18}, and various mixtures of these gases was investigated. The adsorption of CO or CO_2 at room temperature was found to give rise to a bidentate carbonate surface complex which, for the most part, converts to a monodentate species when water is introduced to the sample. No hydrocarbon entities were found to exist on cobalt oxide from infrared analysis, indicating that only minor amounts of these compounds are adsorbed, if at all, on the surface at any specific time. Carbonate reaction intermediates were observed (plus water formed by the oxidation reaction) only when cobalt oxide samples were heated to approximately 325°C in the presence of a hydrocarbon. The amount of carbonate intermediate found when hydrocarbon–oxygen mixtures were introduced to freshly degassed cobalt oxide samples was quite small at room temperature, increased substantially when the sample was heated to about 200°C, and showed further increases in adsorbed material when the samples were heated to 325°C in the hydrocarbon–oxygen mixtures.

INTRODUCTION

Recent interest in the development of an oxidation catalyst for the conversion of CO and hydrocarbons to carbon dioxide and water has led to several investigations (*1–5*) involving cobalt oxide in various forms. Knowledge of reaction intermediates is always desirable since such information may enable one to understand what characteristics of the catalytic surface are important for catalytic activity. It was, therefore, of interest to determine the surface species present during the oxidation reaction using various cobalt oxides as the catalyst. Since infrared spectroscopy has proved to be an invaluable tool for such studies, it was the method used to elucidate the surface structures in this study.

Adsorption studies of carbon monoxide, carbon dioxide, and selected hydrocarbons by various metal oxides have been reported (*6–15*), and no general conclusions regarding surface structures can be drawn from these. Since Eischens and Pliskin (*13*), using silica supported nickel oxide, suggested the structure $\mathrm{Ni}\cdots\mathrm{O}\overline{\cdots}\mathrm{C}\overset{=}{\cdots}\mathrm{O}$ as a surface intermediate formed during the oxidation of carbon monoxide, as determined by infrared spectroscopy, a number of other oxide catalysts have been subjected to the same general type of study. Further investigations on nickel oxide (*7–9*) show some disagreement as to the exact surface species, but do point to the need of having access to the entire infrared spectral range in making more meaningful assignments of the observed bands, as do the infrared studies on the oxides of zinc (*11–15*), titanium (*12*), and chromium (*14*).

The results obtained in the present study for cobalt oxide provide additional information which may be useful for predicting reaction intermediates in similar systems in the future. The technique employed allows the use of the entire infrared spectrum from 4000 to 700 cm^{-1}. We have determined the chemisorption of CO_2, CO, ethylene, cyclohexane, cyclohexene, H_2O, D_2O, H_2O^{18}, and O_2 on the surface of cobalt oxide at room temperature and also at temperatures to 325°C. Not only were the pure gases chemisorbed, but various mixtures of the gases were also allowed to react. Samples were exposed to the higher temperatures both with the reacting gases present and after the reacting gas had been introduced and subsequently removed by evacuation, leaving only the adsorbed material, in an attempt to determine the origin of the oxygen consumed in the oxidation process.

EXPERIMENTAL

Cobalt oxide (Co_2O_3, 60 m^2/g) was prepared by the procedure of Merrill and Scalione (*16*), and the powder was formed into wafer-thin, self-supporting discs, each weighing approximately 50 mg, in a steel die at a pressure of 20–30 tons/inch^2. A sample disc was tied with thin platinum wire to a quartz carriage and then placed within the body of a quartz cell similar to that described by Low *et al.* (*17*). This method enables the sample to be positioned within the furnace zone of the cell. A calibration procedure permitted the temperature at the sample position to be estimated by means of an external thermocouple.

A freshly prepared disc of the cobalt oxide was used for each chemisorption experiment. The samples were degassed at about 550°C for 8–10 hr using conventional high-vacuum equipment capable of 10^{-6} Torr which converted the Co_2O_3 to material designated as Co_3O_4. The N_2 BET surface area of the Co_3O_4 after this treatment was 25–30 m^2/g. Carbon dioxide was obtained in the solid form and further purified by distilling several times from liquid-nitrogen-cooled traps, discarding the first and last portion of each distillation by pumping on the system. Carbon monoxide (Matheson Company) was passed through a series of cold traps cooled with liquid nitrogen. Oxygen gas (National Cylinder Gas, Div. of Chemetron Corp.) was further purified by passing through a charcoal trap cooled with a dry ice-acetone mixture. Research-grade ethylene (Matheson Company) was distilled several times from liquid-nitrogen-cooled traps. All gases were stored in 2-liter bulbs equipped with high-vacuum stopcocks until used.

Cyclohexane (Matheson, Coleman, and Bell), cyclohexene (Eastman Organic Chemicals), and water were each distilled three times under vacuum and stored in evacuated "fingers" attached to high-vacuum stopcocks. All dissolved gases which might have been present in the liquids were removed by repeated freeze–thaw cycles with pumping.

The infrared spectra were recorded on a Perkin–Elmer Model 521 spectrometer. The instrument was operated with a slit setting of twice the normal setting, with all other settings being those used in the normal mode of operation as suggested by the manufacturer. Background spectra were taken immediately after the samples were degassed. Subsequent spectra were then recorded after the reacting gas had been introduced to the samples, and again after the samples had been reevacuated at room temperature. Spectra were also recorded before and after each special treatment of the samples, such as heating or exposure to additional gases.

RESULTS AND DISCUSSION

Chemical analysis of the cobalt oxide samples indicated that a mixed cobalt oxide system resulted from the degassing treatment used to remove all adsorbed gases from the freshly prepared Co_2O_3. Before being exposed to the higher temperature necessary to condition the samples for the infrared work, the composition of the cobalt oxide was predominantly Co_2O_3 (less than 3% of the cobalt was found in the 2+ oxidation state). The samples after the heat treatment were determined to contain a much higher portion of Co(II). The exact Co(III)/Co(II) ratio was not determinable with sufficient accuracy because of the small amount of material in each sample. However, this mixed oxide system, formed by the loss of oxygen from the

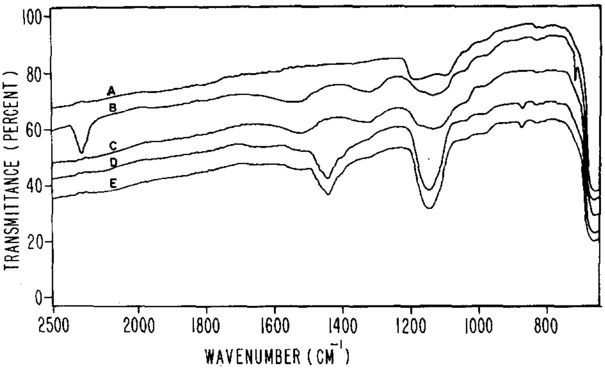


Fig. 1. (A) Background spectrum after degassing (see text), (B) 40 Torr of CO_2 added, (C) cell evacuated 10 min at 25°C, (D) 15 Torr of H_2O added to cell, (E) cell evacuated 15 min. The ordinates have been displaced to prevent overlap.

cobalt oxide lattice at temperatures where Co_2O_3 is no longer thermally stable, was found to contain 72.5% total cobalt. This is in good agreement of the calculated value of 73.5% for the structure Co_3O_4 which is the material assumed to be the adsorbate throughout this report.

Introducing 40 Torr of carbon dioxide into a cell containing a freshly degassed Co_3O_4 pellet causes the appearance of a number of bands in the infrared spectrum. This is seen in Fig. 1 and listed in Table 1. The ordinates of all traces reproduced in the figures have been displaced to prevent overlap, and, therefore, the percent transmittance in each case is relative. The bands observed at about 2350 and 720 cm^{-1} correspond to bands generally assigned to gaseous CO_2; and since these bands disappeared completely after only two minutes of evacuation of the cell, they were presumed to arise from carbon dioxide not associated with the Co_3O_4 surface. On the other hand, evacuation of the cell at room temperature for extended periods of time (up to 24 hr) had no observable effect on the infrared bands observed at 1545, 1324, and 1134 cm^{-1}. Consequently, the material responsible for the appearance of these bands is attributed to strongly chemisorbed surface complexes.

Addition of 40 Torr of carbon monoxide to a cell containing a freshly degassed Co_3O_4 pellet produces a spectrum as shown in Fig. 2 with specific bands centered at frequencies as listed in Table 1. The bands

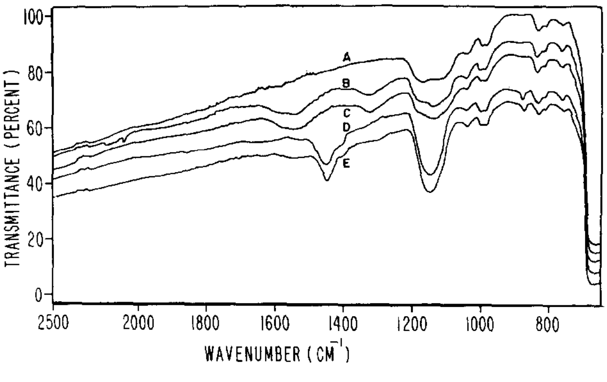


Fig. 2. (A) Background spectrum of degassed Co_3O_4, (B) 30 Torr of CO added, (C) cell evacuated 30 min at 25°C, (D) 15 Torr of H_2O added to cell, (E) cell evacuated 15 min. The ordinates have been displaced to prevent overlap.

TABLE 1
INFRARED ABSORPTION BANDS

Adsorbent	Sample history	Adsorption bands (cm^{-1})										
CO_2	40 Torr of CO_2		2350		1545			1324		1134		
	Cell evac. 10 min				1545			1324		1134		720
	15 Torr of H_2O	3430		1650	1545	1444	1408	1324	1145	1134		
	Cell evac. 30 min	3430(d)		1650(d)[a]	1545	1444	1408	1324	1145	1134	876	
CO	40 Torr of CO	2170	2130	2070	1545			1324		1134		
	Cell evac. 10 min			2070(d)[a]	1545			1324		1134		
	Cell evac. 30 min				1545			1324		1134		
	15 Torr of H_2O	3430		1650	1545	1444	1408	1324	1145	1134		
	Cell evac. 30 min	3430(d)		1650(d)[a]	1545	1444	1408	1324	1145	1134	876	
C_2H_4 (results same for cyclohexane and cyclohexene)	100 Torr of C_2H_4				No bands observed							
	100 Torr C_2H_4: Δ 325°C				1545	1444	1408	1324	1145	1134	876	
	Cell evac. 10 min				1545	1444	1408	1324	1145	1134	876	
$C_2H_4 + O_2$ (results same for cyclohexane + O_2 and cyclohexene + O_2)	100 Torr O_2: 100 Torr C_2H_4: Cell evac. 10 min				1545(w)[b]			1324(w)[b]		1134(w)[b]		
	100 Torr O_2: 100 Torr C_2H_4: Δ1.5 hr at 200°C: Cell evac. 10 min	3400(w)[b]		1630(w)[b]	1545(i)[c]			1324(i)[c]	1140	1134(i)[c]		
	100 Torr O_2: 100 Torr C_2H_4: Δ1.5 hr at 325°C	3430	2350	1650	1545	1444	1408	1324	1145	1134	876	720
	Cell evac. 10 min	3430(d)[a]		1650(d)[a]	1545	1444	1408	1324	1145	1134	876	
H_2O	15 Torr of H_2O	3430		1650					1155	1112		
	Cell evac. 30 min	3430(d)		1650(d)[a]					1155	1112		
D_2O	15 Torr of D_2O		2530				1240		1155	1112		
	Cell evac. 10 min		2530(d)[a]				1240(d)[a]		1155	1112		
H_2O^{18}	15 Torr of H_2O^{18}	~3430	~1650						1155	1112		
	Cell evac. 30 min	~3430(d)	~1650(d)[a]						1155	1112		

[a] (d) Absorption band decreased in intensity.

[b] (w) Weak.

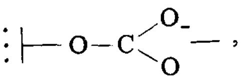
[c] (i) Absorption band increased in intensity.

at 2170 and 2130 cm^{-1} are attributed to gaseous CO and can be immediately removed by evacuation of the cell. A band observed at 2070 cm^{-1} was more persistent to evacuation; approximately 20 min pumping was required for the complete removal of the species giving rise to this band. This 2070 cm^{-1} band is not shifted markedly from the region where gaseous CO bands occur and is, therefore, assigned to a weakly chemisorbed CO molecule on the cobalt oxide surface. As in the case of the adsorption of CO_2, long periods of evacuation of the cell at room temperature produced no observable changes in the 1545, 1324, and 1134 cm^{-1} bands.

Several authors attribute the persistent bands in the 800–1550 cm^{-1} region to surface carbonates arising from the strong interaction of CO and CO_2 with metals and metal oxides. For instance, Blyholder (*9*) assigned bands at 1560, 1330, 1040, and 830 cm^{-1} to a bidentate attachment of a carbonate species to an iron surface. Yates (*12*) has reported the adsorption of carbon dioxide on titania surfaces and tentatively classified the absorbed species as a CO_2^- group formed by an electron-transfer reaction with the surface. He based his analysis on two bands at 1580 and 1320 cm^{-1}, there being no band in the 1000 cm^{-1} region of the spectrum to suggest a carbonate species. Stuart and Whateley (*18*) ascribe bands at 1640 and 1220 cm^{-1} to a bidentate carbonate species without the observance of any bands at lower frequencies; however, their BeO samples cut off all infrared radiation below about 1150 cm^{-1}. Iron and copper oxides produce several surface species when CO_2 gas is introduced (*6*), as evidenced by a large number of absorption bands with surface species such as surface carbonate ions, carboxylate ions, and carbonate-like complexes being predicted. Infrared studies of the adsorption of CO and CO_2 on zinc oxide (*11, 15*) and nickel oxide (*7, 9*) also predict surface carbonate-type structures, predominantly of the bidentate carbonate form.

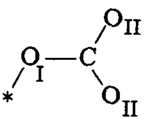
A direct adsorption of carbon dioxide onto a metal ion by the transfer of an electron from adsorbent to adsorbate, as predicted by Yates for the complex on titania, does not seem likely in our case. Carboxylate ions of this type should not give rise to a band observed at 1134 cm^{-1} but should only show bands arising from the symmetric and asymmetric C–O stretching vibrations, which are typically found in the 1350–1400 and 1560–1580 cm^{-1} regions. Also, the O–C–O torsional vibration is usually observed at about 650 cm^{-1} for carboxylate ions. The band at 1134 cm^{-1} is believed to arise from the same species that produces the 1545 and 1324 cm^{-1} bands, since all three bands appear simultaneously when a small increment of CO_2 is adsorbed; and all three bands increase proportionately in intensity when additional increments of CO_2 are added.

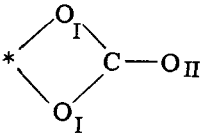
A carbonate-type species similar to the free ion, CO_3^{2-}, is also an unlikely candidate in the present case, for an ion of this type should give rise to infrared absorption bands at 1430–1410 cm^{-1}, 880–860 cm^{-1}, and at about 680 cm^{-1} (*22*). No bands were observed in these regions that could be assigned to such a structure. One additional structure, that of the bicarbonate-like species



requires some consideration. A structure of this type has been proposed by previous workers (*6, 14, 23*) on the basis of bands which they observed in the 1630–1650 and 1330–1390 cm^{-1} regions of the spectrum. Since we did not observe a band above about 1550 cm^{-1}, a structure similar to a and 1134 cm^{-1} can be assigned to a surface bicarbonate ion is unlikely.

From consideration of the above and from the analysis of infrared spectra of several Co(III) carbonate complexes (*19*), it appears that the bands at 1545, 1324, carbonate formed by the interaction of both CO_2 and CO with the cobalt oxide surfaces. Unidentate carbonate complexes with cobalt (*19*) and most other metals (*20, 21*) show two C–O_{II} stretching bands in the 1470–1450 cm^{-1} and 1380–1350 cm^{-1} regions and

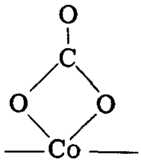




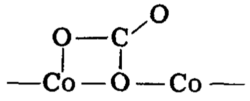
one C–O_I stretching band in the 1070–1050 cm^{-1} region. For bidentate carbonate complexes of similar metals, one C–O_{II} stretching band appears in the 1640–1590 cm^{-1} region, and two C–O_I stretching bands are observed in the 1290–1260 cm^{-1} and 1040–1020 cm^{-1} regions. The observed bands do not coincide exactly with the reported bands for any specific carbonate complex; but by the appearance of the band shapes and positions, some predictions can be made regarding the nature of the surface structures and will be discussed below. No band was observed in the 820–840 cm^{-1} region which could be attributed to the out-of-plane bend of a bidentate (or monodentate) carbonate. However, there are several medium-intensity background bands in this region which could obscure such a band if it were broad and weak.

The symmetry is the same for both the unidentate and bidentate carbonate ligands, and therefore it is not possible to make a distinction by means of selection rules alone between these two modes of coordination to the surface. However, upon coordination, the ν_1 vibration of a simple XY_3 (~1080 cm^{-1} for CO_3) becomes infrared-active, and the ν_3 asymmetric vibration (~1440 cm^{-1} for CO_3) splits into its two components, the splitting being much more pronounced for the bidentate than for the monodentate complex (*19*, *24*). The difference between ν C–O_I and ν C–O_{II} is only about 100 cm^{-1} for the monodentate complexes, but is approximately 300 cm^{-1} for the bidentate complexes. The two bands observed at 1545 and 1324 cm^{-1} and proposed as arising from the degenerate ν_3 vibration are approximately 250 cm^{-1} apart, suggesting a bidentate attachment to the surface. The bands observed here are not in exact agreement with the bidentate carbonate cobalt complexes reported by Fujita *et al.;* however, the cobalt in their compounds was all in the 3+ oxidation state, whereas the oxidation state of the cobalt in the present work is mixed, as previously mentioned.

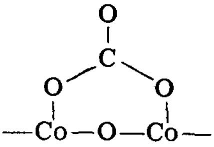
A structure similar to I or II below may exist on the Co_3O_4 surface, rather than the form shown as Structure III, since one



(I)



(II)



(III)

might expect the two metal atoms in Form III to exert a greater influence on the splitting of the degenerate vibrations than the single metal atom postulated in I. Organic carbonates exhibit a much greater (~600 cm^{-1}) splitting of the ν_3 vibration than even the bidentate carbonates of metal complexes. The two bands at 1545 and 1324 cm^{-1} lie slightly outside the range predicted for bidentate carbonate ligands.

Although a very stable surface carbonate was found to exist on the cobalt catalyst at room temperature as outlined above, infrared spectra indicate that a desorption of the complex occurs upon evacuating the samples at elevated temperatures. This desorption process is slow up to about 200°C, becoming somewhat more perceptible at temperatures between 200–300°C, and only becomes appreciable at temperatures above 300°C. A spectrum identical to the original background spectrum could be obtained only after degassing the carbonate-covered Co_3O_4 sample for about 5 hr at 300°C. Degassing an identically treated sample at 400°C for about 1 hr produced the same effect. Carbon dioxide or carbon monoxide could again be adsorbed on these samples after degassing to produce the carbonate species already identified in the original adsorption step.

Introducing 18 Torr of H_2O to Co_3O_4 samples, after the carbonate complex had been formed and all gaseous material removed, produced immediate changes in the surface composition as noted by the infrared spectra. Several new bands appeared as seen in Traces E and F of Figs. 1 and 2, respectively. New bands appeared at 3430, 1650, 1444, 1408, 1145, and 876 cm^{-1}, with a simultaneous decrease in the 1545 and 1324 cm^{-1} bands. The 1134 cm^{-1} band was somewhat masked by the new, intense, 1145 cm^{-1} band.

The broad, weak bands at 3430 and 1650 cm^{-1} can be attributed to H_2O molecules adsorbed on the Co_3O_4 surface. No evidence was found for dissociation of the water molecule into OH groups, as no band was observed for surface O–H stretching in the 3600 cm^{-1} region. A decrease in the 3430 and 1650 cm^{-1} bands upon prolonged evacuation of the cell indicated that the water was not strongly chemically bonded to the surface, although after 2 days of pumping a small portion of the 3430 and 1650 cm^{-1} bands remained.

Evacuation of the cell up to 48 hr caused no apparent changes in the remaining bands below about 1600 cm^{-1}. The appearance of bands at 1444, 1408, and 876 cm^{-1} with the accompanying decrease in intensity of bands at 1545 and 1324 cm^{-1} suggests that much of the "bidentate" carbonate species converts to a "monodentate" type upon the introduction of H_2O, with the lesser amount remaining as the "bidentate" form. The "monodentate" surface carbonate is proposed on the basis of what has already been said concerning the splitting of the ν_3 vibration and also by comparison to infrared spectra of the monodentate cobalt carbonate complexes. The band previously observed at 1134 cm^{-1} and attributed to the ν_1 vibration of the "bidentate" surface carbonate, and which is also expected for the "monodentate" species, is difficult to consider because of very intense broad bands caused by the adsorption of H_2O. However, an increase in absorption in the region 1120–1140 cm^{-1} can be seen when a comparison is made of Traces E and F of Figs. 1 and 2, respectively, and Trace C of Fig. 3. (Trace C of Fig. 3 is the spectrum resulting from the adsorption of H_2O on a freshly degassed Co_3O_4 sample.) This increase in adsorption is thought to be due to the ν_1 band of the newly formed "monodentate" species and to the residual 1134 cm^{-1} band of the "bidentate" species.

The bands at 1155 and 1112 cm^{-1} of Fig. 3 appear to be an effect of the addition of H_2O and not directly due to the adsorbed water molecule. Addition of D_2O produces the same two bands; if these bands were due to an adsorbed water molecule, the exchange of deuterium for hydrogen should show a noticeable shift of the bands. The bands observed at 3430 cm^{-1} and 1650 cm^{-1}

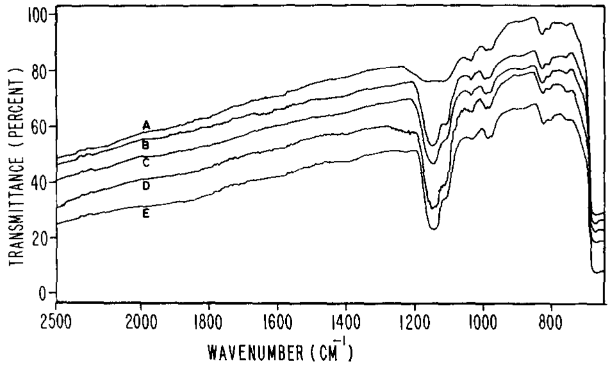


FIG. 3. (A) Background spectrum of degassed Co_3O_4, (B) 15 Torr of H_2O added, (C) cell evacuated 30 min at 25°C, (D) 15 Torr of D_2O added to freshly degassed Co_3O_4 sample, (E) Cell evacuated 30 min at 25°C. The ordinates have been displaced to prevent overlap.

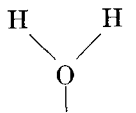
are shifted to 2530 and 1240 cm^{-1}, respectively, for the weakly held H_2O and D_2O. Further, the addition of H_2O^{18} to freshly degassed Co_3O_4 produced results identical to those observed for H_2O in the 1200–1100 cm^{-1} region. The instrument's scale expansion features were used in an attempt to detect small band shifts which are believed to be noticeable, should they occur, since the 1155 and 1112 cm^{-1} bands are sharp and relatively well defined. The other two bands observed for adsorbed H_2O (at 3430 and 1650) are both weak and broad, and, therefore, little can be said about small shifts in these bands.

Stuart and Whateley (*18*), in an investigation of beryllium oxide, reported a band at 1580 cm^{-1} in the infrared background spectrum that was affected greatly by the chemisorption of H_2O and D_2O, the band becoming much more intense because of the chemisorption. It was proposed that this was due to some defect property of the BeO surface which must be involved in the chemisorption process. Little and Amberg (*14*) proposed that a band at 1370 cm^{-1} on chromia–alumina catalysts resulted from intensification of an already existing band at 1370 cm^{-1} in the spectrum of the surface. Basila (*25*) attributed a band at 1394 cm^{-1} found on silica–alumina surfaces to an Al–O stretch which was enhanced or depressed by the adsorption of gaseous materials.

A somewhat similar mechanism may exist in this case for the 1150 and 1115 cm^{-1} bands, which apparently arise from interaction of H_2O with adsorption sites, since when H_2O covers the surface neither CO nor CO_2 will adsorb. However, if the gaseous (and a portion of the weakly held) H_2O is removed from the sample, and CO subsequently added, weak adsorption bands attributable to a "bidentate" carbonate species are formed. Heating the cell at 110°C for several hours in the presence of 40 Torr of CO produced a noticeable increase in the intensity of the surface carbonate bands; and further heating at 225°C produced an even larger increase in these bands. Accompanied by this carbonate formation is a steady decrease in the intensity of the 1155 and 1112 cm^{-1} bands. Also, a small amount of the adsorbed water decomposes into surface hydroxide groups at the higher temperature, as indicated by the appearance of a band at 3555 cm^{-1}; in the case of D_2O a band is observed at 2705 cm^{-1}.

The above evidence suggests that active sites for the formation of surface carbonates are also active for the adsorption of H_2O and that at lower temperatures H_2O is preferentially adsorbed. At elevated temperatures, the H_2O can be desorbed, leaving certain sites vacant for further reaction. This is in line with the previous statement that H_2O was only moderately adsorbed on the surface, since some of it could be removed by prolonged evacuation of the sample, whereas once the carbonate is formed it is very stable at temperatures below about 200°C. It also appears that by evacuation of the H_2O-treated samples and by heating these samples in the presence of CO, one can produce the type of adsorption sites necessary for the formation of only the "bidentate" carbonate, because no evidence was found for the formation of a "monodentate" species. However, subsequent addition of H_2O again caused the formation of the "monodentate" carbonate structure.

The adsorption of H_2O or D_2O is clearly the influencing factor for the 1155 and 1112 cm^{-1} bands. These bands may arise from enhancement of already existing bands found at 1176 and 1122 cm^{-1} in the cobalt oxide spectrum, similar to the chromia–alumina system described by Basila (*25*). An alternative explanation could be a possible surface defect site produced by the formation of Co_3O_4 from Co_2O_3 upon the loss of lattice oxygen at temperatures above about 300°C. Adsorbed water could then interact with these defect sites, producing a



species which ultimately affects the electronic properties of the Co–O lattice and thus indirectly causes the observed bands.

Since the main product of the oxidation reaction of CO and hydrocarbons is the same (i.e., CO_2), it was suspected that similar surface intermediates may exist for these two cases. The present study was, therefore, extended to include the adsorbed states of hydrocarbons on cobalt oxide (Co_3O_4) before any oxidation had occurred (room temperature adsorption) and also for cases of partial oxidation. No adsorbed material was observable by infrared analysis when a Co_3O_4 sample was exposed to 100 Torr of ethylene at room temperature, nor were any bands observed after the Co_3O_4 sample was heated for 1.5 hr at 200°C in the presence of 100 Torr of ethylene. Increasing the temperature of the Co_3O_4 pellet to 325°C in the presence of 100 Torr of ethylene produced the spectrum shown as Trace C of Fig. 4 after evacuation of the cell for 10 min at room temperature.

The amount of ethylene that is adsorbed on degassed Co_3O_4 is not sufficient to give observable infrared bands if adsorption takes place at room temperature. Heating the Co_3O_4 samples to 325°C in the presence of ethylene, cooling the sample, and then evacuating the cell gave no indication that ethylene was adsorbed as a hydrocarbon entity. Heating the samples in the presence of 100 Torr of ethylene at the higher temperature produced a series of bands that indicate the formation of both "monodentate" and "bidentate" carbonate surface species, along with adsorbed water. These assignments were made by comparison of the spectra of this adsorbed material to the spectra obtained after adsorption of CO_2 and CO discussed above and reproduced as Figs. 1 and 2. Trace C of Fig. 4 is identical to Trace E of Fig. 1 and to Trace E of Fig. 2. No infrared evidence of gas-phase CO_2 was found after heating the sample at 325°C in an ethylene atmosphere.

Exposing a Co_3O_4 sample, prepared and degassed in the general manner already described, to 100 Torr of oxygen plus 100 Torr of ethylene at room temperature resulted in the appearance of very weak bands at 1545, 1324, and 1134 cm^{-1} in addition to bands attributable to gas-phase ethylene. Trace B of Fig. 5 shows the resulting spectrum after the cell had been evacuated for 10 min. The results of heating the sample in the presence of a mixture of 100 Torr O_2 and 100 Torr ethylene at 200°C for 3 hr and then evacuating the cell at room temperature are shown in Trace C of Fig. 5. The observable changes in the spectrum are increases in intensity of the 1545, 1324, and 1134 cm^{-1} bands plus weak, broad absorptions in the 3400, 1630, and 1140 cm^{-1} regions. Heating the sample for an additional 1.5 hr in the presence of oxygen and ethylene at 325°C and after evacuation of the cell for 30 min produced a spectrum as shown as Trace D of Fig. 5. New bands have appeared at about 2350, 1445, and 878 cm^{-1}, accompanied by increased absorption in the 3430 and 1650 cm^{-1} regions. Also, a significant increase in the intensity of the 1140 cm^{-1} band can be

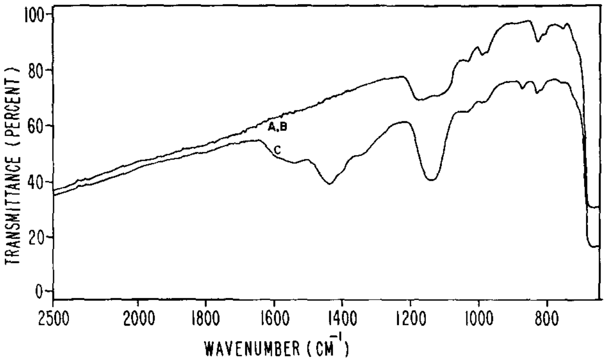


FIG. 4. (A) Background spectrum of degassed Co_3O_4, (B) sample was heated at 200°C for 1.5 hr in the presence of 100 Torr of ethylene; cell evacuated 10 min, (C) sample was heated at 325°C for 1.5 hr in the presence of 100 Torr of ethylene; cell evacuated 10 min. The ordinates have been displaced to prevent overlap.

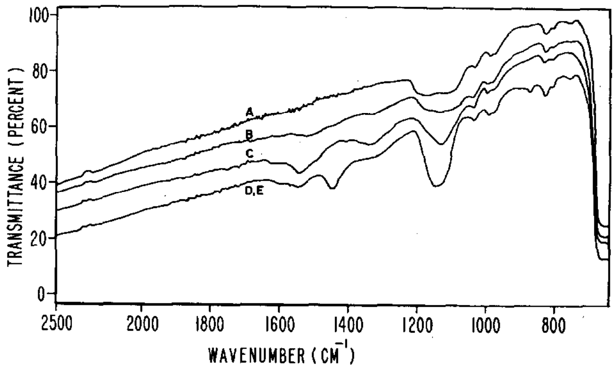


FIG. 5. (A) Background spectrum of degassed Co_3O_4, (B) 100 Torr of C_2H_4 + 100 Torr of O_2 added to cell and cell evacuated 10 min, (C) sample was heated at 200°C for 1.5 hr in the presence of 100 Torr of C_2H_4 + 100 Torr of O_2; cell evacuated 10 min, (D) sample was heated at 325°C for 1.5 hr in the presence of 100 Torr of C_2H_4 + 100 Torr of O_2; cell evacuated 10 min, (E) 15 Torr of H_2O added; cell evacuated 30 min. The ordinates have been displaced to prevent overlap.

noted. Exposing this sample of 18 Torr of H_2O caused no observable change in the infrared spectrum.

A bidentate-like carbonate complex is the only surface structure identified when Co_3O_4 is exposed to a mixed atmosphere of 100 Torr oxygen and 100 Torr ethylene at room temperature. The band positions recorded for the adsorbed material after such treatment were identical to those observed after exposing Co_3O_4 to CO_2 or CO. However, the amount of reaction was quite small, as indicated by the very weak absorption. Heating the sample in the oxygen–ethylene atmosphere at 200°C for 1.5 hr only increased the absorption band intensities that presumably arise from the "bidentate" carbonate. A small increase in absorption at about 3400 cm^{-1} and at 1630 cm^{-1} was also noted when the sample was heated at 200°C. This increase is probably due to H_2O of the oxidation reaction. This H_2O is evidently not of the same variety as the adsorbed H_2O already discussed, since the bands for adsorbed H_2O were found at 3430 and 1650 cm^{-1} and no conversion of the "bidentate" to "monodentate" complex was seen; we remember that adsorbed H_2O has been shown to promote this effect. The amount of adsorbed carbonate and the amount of H_2O present is, however, small; and it is quite possible that there is an abundance of suitable surface sites which can accommodate both adsorbed water and "bidentate" carbonate at such low surface coverages.

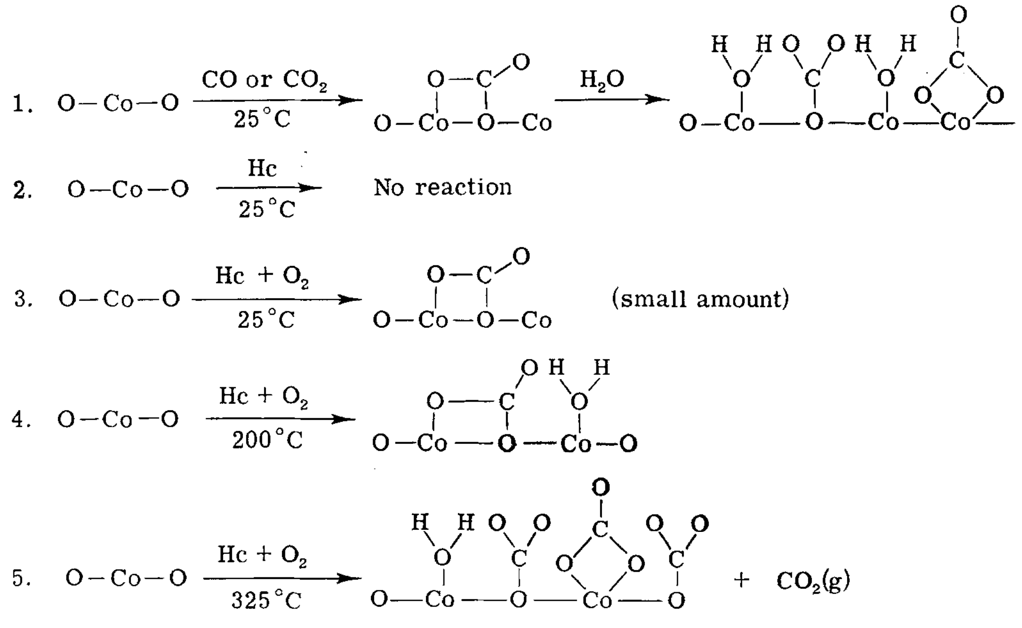
Three surface structures ("monodentate" carbonate, "bidentate" carbonate, and adsorbed water) were again observed when the Co_3O_4 sample was heated at 325°C for 1.5 hr in the presence of oxygen and ethylene. All absorption bands increased significantly, and new bands which could be removed by evacuation of the cell for 1 min were observed at about 2450 and 720 cm^{-1}. These two bands correspond to the bands for gaseous CO_2 and are therefore assigned to a species which results from the oxidation of ethylene over the cobalt oxide in the presence of oxygen.

Identical results as those reported above for ethylene were obtained for the cyclohexane and cyclohexene systems; i.e., no absorption bands were noted that would indicate a hydrocarbon fragment on the Co_3O_4 surface. Adding a mixture of either cyclohexane or cyclohexene with oxygen at room temperature produced only very weak bands, attributable to a "bidentate" carbonate species; heating Co_3O_4 in the presence of either cyclohexane or cyclohexene at 200°C gave no indication of reaction, whereas heating the same samples at 325°C produced absorption bands indicative of adsorbed H_2O, "bidentate" carbonate, and "monodentate" carbonate;

heating the Co_3O_4 in the presence of cyclohexane and oxygen or cyclohexene and oxygen at 200°C produced bands similar to a "bidentate" carbonate surface species with a small amount of H_2O being evident; and heating the same samples at 325°C in oxygen–hydrocarbon atmospheres resulted in infrared spectra which indicated both forms of surface carbonates previously described along with the adsorbed water produced from the oxidation reaction.

The evidence indicates that both "monodentate" and "bidentate" carbonate structures exist as surface intermediates on Co_3O_4 during the hydrocarbon oxidation reaction. Similar structures also exist in the case of CO oxidation when water is present to promote the conversion of some of the "bidentate" material to "monodentate." It is also apparent that at temperatures below about 325°C very little oxygen of the cobalt oxide lattice is available for the promotion of the oxidation process.

The observed spectra indicate that the following set of reactions may be occurring under the specific conditions stated:



Hc = hydrocarbon
O—Co—O = hypothetical Co_3O_4 surface

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