

Infrared Studies of CO, O₂, and CO₂ Gases and Their Interaction Products, Chemically Adsorbed on Nickel Oxide

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The infrared adsorption spectra of pure gases chemisorbed on nickel oxide surface were recorded. These spectra are modified in certain cases when interaction of two gases occurs on the surface of the catalyst. Structures of the adsorbed surface complexes are proposed.

INTRODUCTION

Infrared spectroscopy is at present very widely used in the study of the structure of molecules physically and chemically adsorbed on solid surfaces and, in particular, on solid catalysts (1). Very often, by analogy with the spectra of three-dimensional substances, the chemical structure of adsorbed complexes may be deduced by this technique and information on the surface state of the catalyst given (2, 3).

The oxidation of carbon monoxide at room temperature on a nickel oxide catalyst was studied by one of the present authors using various techniques, and the scheme of the reaction was proposed (4-6). The methods of gravimetry, electrical conductivity, physical adsorption of argon, and, more recently, microcalorimetry (6) have led to assumption of the existence of an intermediate adsorbed complex in the ionic form, CO₃⁻. The same conclusion has been expressed by Dell and Stone (7).

In the present work we set out to obtain confirmation of this result by employing the technique of infrared spectroscopy and to gather some further information concerning the species adsorbed by the catalyst during reaction.

EXPERIMENTAL TECHNIQUES

The infrared analysis cell, in which a high vacuum can be produced and the

sample submitted to thermal treatment, is made out of Pyrex. Two calcium fluoride windows are sealed by means of W.E. wax No. 6 (Edwards) (8). The sample, compressed into a thin pellet, is placed in a vertical position in the cell, in the center of an electric microfurnace (Fig. 1). Owing to the use of a water-cooled ground joint, the cell may be completely dismantled and the sample easily changed. A stopcock connects the cell to a vacuum line or to a gas supply.

The nickel is prepared *in situ* by decomposing, at 200°C for 24 hr at reduced pressure (10⁻⁶ mm Hg), a very pure nickel hydroxide, prepared by a method described by one of the authors (9). The nickel hydroxide, mixed in a proportion of 12.4% with finely divided silica (Cabosil) is compressed in a die in order to give it the shape of a pellet, a few tenths of a millimeter thick, which is disposed vertically in the infrared analysis cell. The pellet is then submitted to heat and high vacuum treatment. A second cell whose transparency is practically equal to that of the first one contains a second pellet of the silica-nickel hydroxide mixture which is submitted to the same thermal treatment. This reference cell is continuously maintained under vacuum, whereas the gases that are to be absorbed by the nickel oxide are introduced into the first cell only. Both

these cells are then placed in the trajectory of each of the beams of the infrared Perkin-Elmer double-beam spectrometer, model 21. A differential spectrum of the gas is thus recorded. The displacements of the recorder pencil are multiplied five times by using a scale enlarger. Under such conditions, the limits of this displacement correspond to a variation of trans-

A. Chemisorption of Pure O_2 , CO , CO_2

It has previously been shown (4-6) that at room temperature, oxygen, carbon monoxide, and carbon dioxide are adsorbed on nickel oxide in a reversible and irreversible manner. However, degassing the catalyst under vacuum at $200^\circ C$ produces a complete desorption of these gases and of their interaction products.

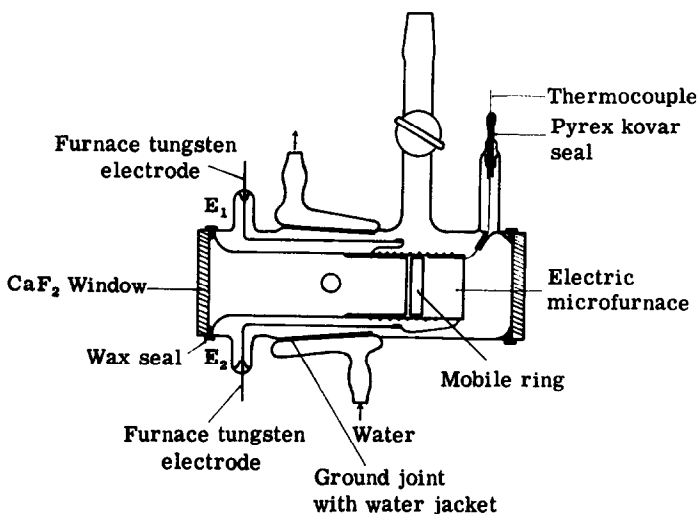


FIG. 1. Apparatus.

mission of 20% and not of 100%. All the spectra presented in the present work have ordinates graduated to 1% transmission variation. The gases employed for chemisorption are very pure (5) and are introduced very slowly at room temperature into the cell containing nickel oxide by using a Fugassi valve (4).

RESULTS AND DISCUSSION

The chemisorption of pure O_2 , CO , and CO_2 by nickel oxide and their interaction on the surface of the catalyst were studied by Teichner *et al.* (4,5). With a view to an easier comparison of previous results with those of the present work, the same plan of study was followed. Thus the authors first considered chemisorption of reagents CO , O_2 and reaction product CO_2 , then interaction of these chemisorbed gases, and, finally, the catalytic oxidation of carbon monoxide.

1. Adsorption of Oxygen

The pellet of nickel oxide becomes black rapidly after introduction into the cell of oxygen at a pressure of 10 mm Hg, necessary to saturate the surface of the solid. The formation of O^- ions on the surface of the nickel oxide (4-6) does not, however, modify the infrared spectrum in the range of $2500-1000\text{ cm}^{-1}$, except for a decrease of transmission through the sample from $1900-2000\text{ cm}^{-1}$ to higher frequencies.

2. Adsorption of Carbon Monoxide

The adsorption of carbon monoxide was effected at a pressure of 40 mm Hg maintained during a time varying up to 24 hr, a condition necessary to obtain a complete chemisorption. The spectra obtained may be divided into two regions. The first includes the range $2500-1900\text{ cm}^{-1}$ where the absorption bands always appear and dis-

appear under the same conditions. The second includes frequencies below 1700 cm⁻¹ where the absorption bands change

and 2175 cm⁻¹. They correspond to the P and R branches of the spectrum of gaseous carbon monoxide. If the nickel-oxide pellet

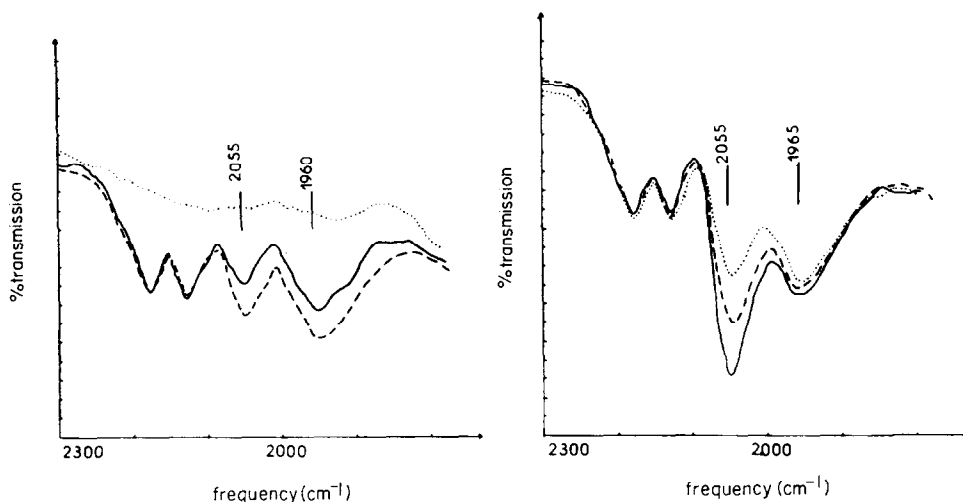


FIG. 2. Adsorption of CO for different times of contact. (a) Dotted line—background spectrum; solid line—40 min; broken line—1 hr 30 min. (b) Dotted line—3 hrs; broken line—10 hrs; solid line—19 hrs.

in frequency from one experiment to the other or during the same experiment. The spectra of these two regions may reasonably be examined separately.

is present in the cell, two new absorption bands appear, in addition to the preceding bands, one fairly wide at 1960–1970 cm⁻¹, the second narrower at 2060 cm⁻¹ (Fig. 2).

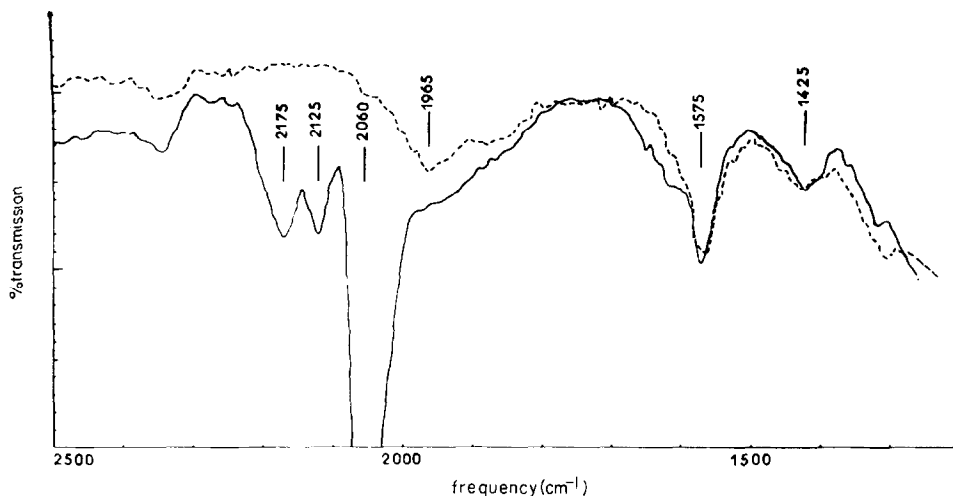


FIG. 3. Adsorption of CO and evacuation. First type of spectrum. Solid line—40 mm CO pressure; broken line—CO adsorbed after evacuation.

a. Range 2500–1900 cm⁻¹. When the cell contains only carbon monoxide or carbon monoxide and a silica pellet, the only absorption bands to appear are those of 2125

The intensity of the first band hardly varies with time while the intensity of the second band increases so far as to cover partly the first band which appears then in

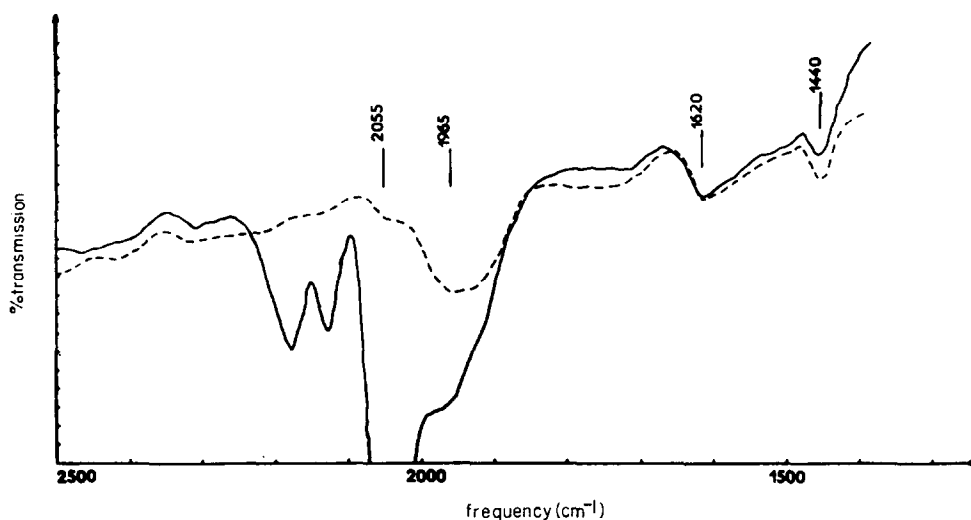


FIG. 4. Adsorption of CO and evacuation. Second type of spectrum. Solid line—40 mm CO pressure; broken line—CO adsorbed after evacuation.

the shape of a shoulder at 1960–1970 cm^{-1} . The evacuation of the cell obviously produces the disappearance of the two 2125 and 2175 cm^{-1} bands of gaseous carbon

monoxide and of the 2060 cm^{-1} band of reversibly adsorbed CO (Figs. 3, 4, 5). Only the band at 1960–1970 cm^{-1} remains and shows up clearly. The two new bands men-

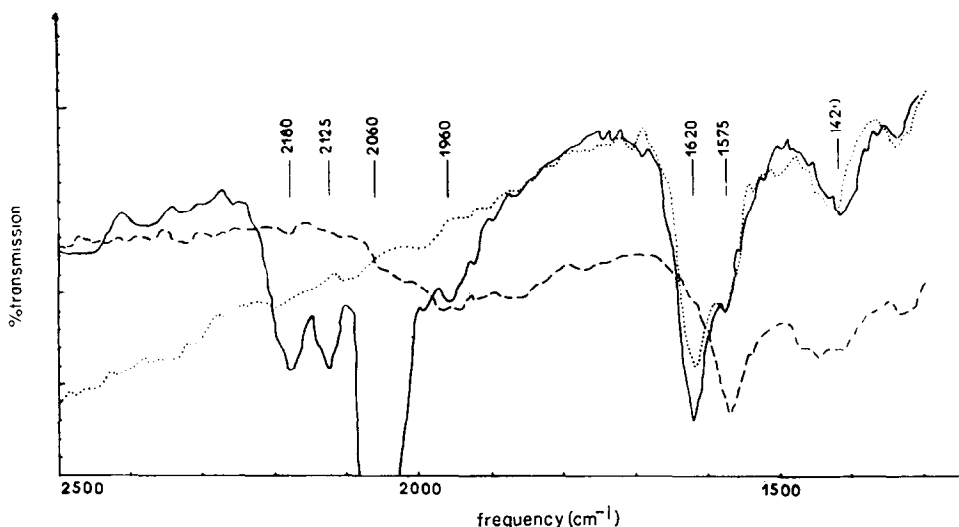
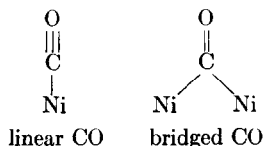


FIG. 5. Adsorption of CO and evacuation. Third type of spectrum. Solid line—40 mm CO pressure; broken line—CO adsorbed after evacuation; dotted line—CO adsorbed + 10 mm O_2 pressure.

tioned correspond to those found by many authors (2, 3, 10, 11) in the spectrum of CO chemisorbed by metals. Eischens was the first to interpret these two bands ac-

ording to two types of structure. The peak at 2060 cm^{-1} is attributed to a "linear CO" i.e., to a carbon monoxide molecule linked through carbon to a single atom of

the surface; the band at 1960–1970 cm⁻¹ is attributed to a "bridged CO," i.e., to a CO fixed on two adjacent surface atoms.



This interpretation is based on analogy with the spectra of carbonyl metals of known structure belonging to the two preceding types. Carbonyl metals, such as Ni, Fe, Co, Mn, and Rh, in which the CO group is linked to one metal atom, present absorption bands in the range 1975–2080 cm⁻¹. Nonacarbonyl iron, tetracarbonyl iron, and octocarbonyl dicobalt, whose CO groups are linked to two metal atoms, present bands between 1830 and 1860 cm⁻¹.

It seems that, in the present case, the chemisorbed CO is linked to the Ni⁺⁺ ions, as it has been shown that metallic nickel is not generated in the experimental conditions employed here (4). The CO in linear form is reversibly chemisorbed whereas the bridged CO is irreversibly adsorbed. The latter is characterized by a band at 1960–1970 cm⁻¹ which appears at the beginning of adsorption and does not disappear after evacuation. It probably corresponds to the strongest bond with the surface. The formation of nickel carbonyl is not a justifiable hypothesis as none of the other absorption bands of this compound appears in the recorded spectra.

It should be noticed that in nickel oxide the distance between the two closest Ni⁺⁺ ions is 2.97Å; since the distance Ni—CO in nickel carbonyl is 1.82Å, the angle between the two bonds of carbon in bridged CO would be about 107°.

A more elaborate analysis of the two bands produced by linear CO and bridged CO was made with a Perkin-Elmer grating spectrograph, type 112-G, in order to discover whether there was the fine structure because of possible rotation of the adsorbed CO molecule. The spectrum which was obtained (Fig. 6) clearly shows that the band, located exactly at 2058.31 cm⁻¹, does

not present any rotation line except the lines which belong to the spectrum of gaseous carbon monoxide present in the cell. The values of frequencies found on Fig. 6 do, in fact, coincide with the theoretical frequencies of gaseous CO (12). It was not possible, with the grating spectrograph, to detect the band at 1965 cm⁻¹, concerning bridged CO.

b. Region 1700–1300 cm⁻¹. It is necessary to distinguish three cases occurring in the present work:

1. A rather intense and fine band appears at 1575 cm⁻¹ (Fig. 3) and stays unchanged after evacuation of the cell.

2. A weak intensity band is formed at 1620 cm⁻¹ (Fig. 4) and, as before, does not vary in intensity or in frequency after evacuation.

3. At a pressure of 40 mm of CO, the band at 1620 cm⁻¹ has a strong intensity and reveals a shoulder at 1575 cm⁻¹ (Fig. 5). This band completely disappears after evacuation, unmasking a narrow and intense band at the frequency of the previous shoulder.

For these three cases a weak band is always observed at 1420–1440 cm⁻¹. It remains unaltered after the evacuation of nickel oxide.

It is important to mention that a catalyst freshly prepared by decomposition of nickel hydroxide presents, according to circumstances, either the band at 1575 cm⁻¹ (Fig. 3) or the band at 1620 cm⁻¹ (Fig. 4) or the two bands simultaneously (Fig. 5). When, after chemisorption, the catalyst is regenerated at 200°C in vacuum, its behavior is the same as that of a fresh catalyst. Only the bands initially recorded appear in a regenerated solid.

It was checked that this behavior, which differs from sample to sample, is not due to the rate of addition of gaseous CO to the fresh oxide which can produce a heating of the nickel oxide particles, the heat of chemisorption of CO on NiO being 29 ± 2 kcal/mole (6).

A second verification incriminating the temperature of the decomposition in vacuum of nickel hydroxide was attempted.

The nickel oxide was prepared at a temperature, given by the thermocouple of the cell (8), of 190°C . The infrared spectrum after chemisorption of CO revealed the presence of a band at 1575 cm^{-1} identical

to that observed in the spectrum of Fig. 3. Next a new sample of nickel hydroxide was decomposed at 230°C . The chemisorption of CO on this pellet led to a weak intensity absorption band at 1620 cm^{-1} similar to that of Fig. 4. For still higher decomposition temperatures of nickel hydroxide, the adsorption of CO does not lead to the appearance of a band in the region $1575\text{--}1620\text{ cm}^{-1}$ but produces a very intense and large absorption band at $2060\text{--}1960\text{ cm}^{-1}$. It would seem then that the tem-

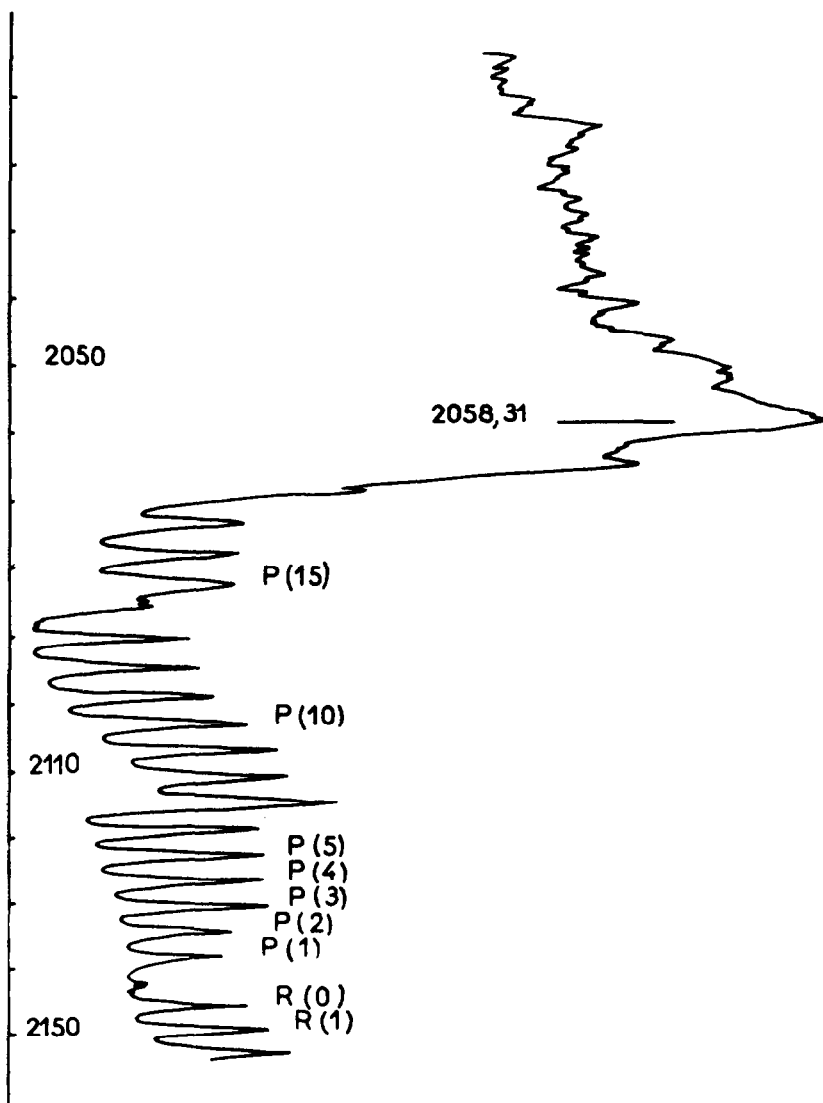


Fig. 6. Fine structure. Pressure, 40 mm CO. Ordinate, frequency (cm^{-1}).

perature of preparation of nickel oxide plays a role in the position of observed bands. The explanation of this phenomenon must be sought in the force of the bonding of CO with the nickel oxide surface. From the variation of frequencies of these bands, it is possible to compare the relative

intensity of these bands. The explanation of this phenomenon must be sought in the force of the bonding of CO with the nickel oxide surface. From the variation of frequencies of these bands, it is possible to compare the relative

strength of the two types of bonding of CO with the surface. The vibration frequency is given by the expression

$$\nu = (1/2\pi) \sqrt{k/\mu}$$

where μ is the reduced mass of the vibrating system and k is a strength of vibration constant (force constant). A displacement of ν toward higher frequencies corresponds to an increase of the strength constant as the reduced mass of a given system is fixed. The strength constant k , relative to CO bonding, can increase only if the forces of interaction between the surface and the CO group become weaker and, vice versa, it can decrease only if the CO bond with the surface becomes stronger. Thus the band at 1575 cm⁻¹ corresponds to a smaller value of the strength constant than the value relative to the band at 1620 cm⁻¹, hence to CO molecules more intensively linked to the surface.

Finally, the third case (Fig. 5) previously mentioned, where the two bands

tion, therefore, which produces the complete disappearance of the band at 1620 cm⁻¹, causes the departure of carbon monoxide fixed on the less energetic sites. It must be assumed, however, that this desorption is easier in the presence of the second type of bond, characterized by the band at 1575 cm⁻¹, in order to explain in this case the disappearance of the band at 1620 cm⁻¹ (Fig. 5). Indeed, the latter remains unchanged after evacuation of the sample if it appears alone in the spectrum (case 2; Fig. 4).

It must be pointed out here that Eischens did not observe an infrared absorption spectrum of carbon monoxide adsorbed on NiO (2).

3. Adsorption of Carbon Dioxide

The chemisorption of CO₂ on nickel oxide was effected at a pressure of 60 mm Hg, guaranteeing the saturation of the surface.

The infrared spectrum shows two ab-

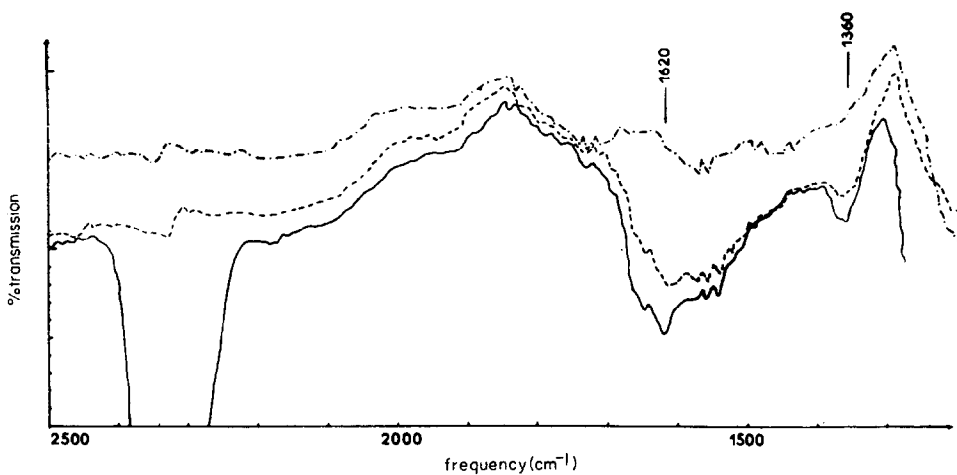


FIG. 7. Adsorption of CO₂ and evacuation. Dashed and dotted line—background spectrum; solid line—60 mm CO₂ pressure; dashed line—CO adsorbed after evacuation.

at 1620 and 1575 cm⁻¹ are observed simultaneously, can be explained by the presence of two types of interactions with the surface. It may be supposed that this coexistence results from some intermediate conditions of heating during the decomposition of nickel hydroxide. The evacua-

sorption bands at 1620 and 1360 cm⁻¹ in addition to that at 2345 cm⁻¹ due to gaseous CO₂ (Fig. 7). Only this last band is observed when the cell contains a pure silica pellet and carbon dioxide. By evacuating the cell, a small decrease of the intensity of the two peaks is observed with-

out any variation in their frequency. Eischens has likewise found the first two bands by adsorption of CO_2 on nickel oxide which was made by oxidation of metallic nickel (2). By analogy with the infrared bands of many solid bulk bicarbonates (13), he interprets these bands by supposing the formation of a bicarbonate ion, CO_3^- . However, previous studies by one of the authors (4-6) do not agree with this interpretation, at least as far as nickel oxide prepared by decomposition of nickel hydroxide is concerned. The effect of poisoning by CO_2 of chemisorptions of other gases and of the poisoning of the catalytic reaction cannot be explained if the formation of a CO_3^- ion is admitted. The results given by different techniques (*loc. cit.*) show evidence of adsorption of carbon dioxide on the cationic sites of nickel oxide. The same sites also adsorb oxygen and carbon monoxide. A surface complex which corresponds to the formula CO_3^- has been found only after interaction of gases such as CO and O_2 or O_2 and CO_2 (4-6) but never has it been found after adsorption of pure carbon dioxide.

This disagreement can be also explained by the fact that direct comparison of infrared spectra of three-dimensional bulk compounds with the spectrum of a two-dimensional structure, which does not involve interaction forces between many well-defined chemical bonds but only the influence of one solid adsorbate bond on the frequency of vibration of a function group, does not seem to allow a comparison in every case of a three-dimensional bulk structure with a two-dimensional one.

It is, however, already possible to affirm that the form of chemisorbed carbon dioxide, which presents a band at 1360 cm^{-1} quite distinct from the band at 1420 cm^{-1} characteristic of adsorbed CO, is, by this fact, different from the form given by chemisorbed carbon monoxide, though still keeping some resemblance to the monoxide because of a common band at 1620 cm^{-1} .

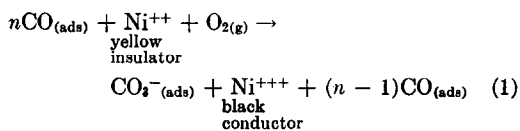
B. Interaction of Gases

The different gases are adsorbed following the sequences given below. However,

every adsorption of a gas is preceded by an evacuation of the sample at room temperature which produces desorption of the fraction of gas reversibly adsorbed (4,5).

Step 1: Adsorbed CO + Gaseous O_2

The adsorption of oxygen on a surface containing previously adsorbed carbon monoxide is possible. All former results (4-6) have led the authors to assume in this step the formation of an interaction product under ionic form, of formula $\text{CO}_3^-_{(\text{ads})}$, and the presence of an excess of CO in adsorbed phase, according to the equation,



Infrared analysis of this step shows that oxygen reacts with irreversibly adsorbed, bridged, carbon monoxide, because, in the three cases previously observed of adsorption of pure CO by itself, the band at $1965\text{--}1970\text{ cm}^{-1}$ disappears after adsorption of oxygen. But infrared spectroscopy did not give any evidence of the formation of an intermediate adsorbed complex of the type CO_3^- . Neither, in agreement with Eq. (1), was the presence of a reaction product such as adsorbed or gaseous CO_2 detected.

Indeed, no new band appears in the spectrum, whereas those already present at 1575 cm^{-1} (Fig. 8) or at 1620 cm^{-1} (Fig. 9) as well as at 1420 cm^{-1} , remain unchanged. Two hypotheses would then be possible: either oxygen reacts very little or in a different manner when the carbon monoxide is adsorbed on nickel oxide compressed into pellet form; or the formation of the $\text{CO}_3^-_{(\text{ads})}$ complex is not revealed by the infrared technique because its structure is very close if not identical to the structure of irreversibly adsorbed carbon monoxide.

The first hypothesis was discarded after studying, with the McBain balance (4, 5), the step $\text{CO}_{(\text{ads})} + \text{O}_{2(\text{g})}$ on several silica-nickel oxide pellets. These experiments confirmed that the adsorption of CO

and then of O₂ proceeds in appreciably the same manner as on noncompressed nickel oxide.

The second hypothesis leads to the sup-

assuming an interaction between oxygen ions of the lattice and the molecule of CO, adsorbed in absence of oxygen. Indeed, because of the strong compression exerted on

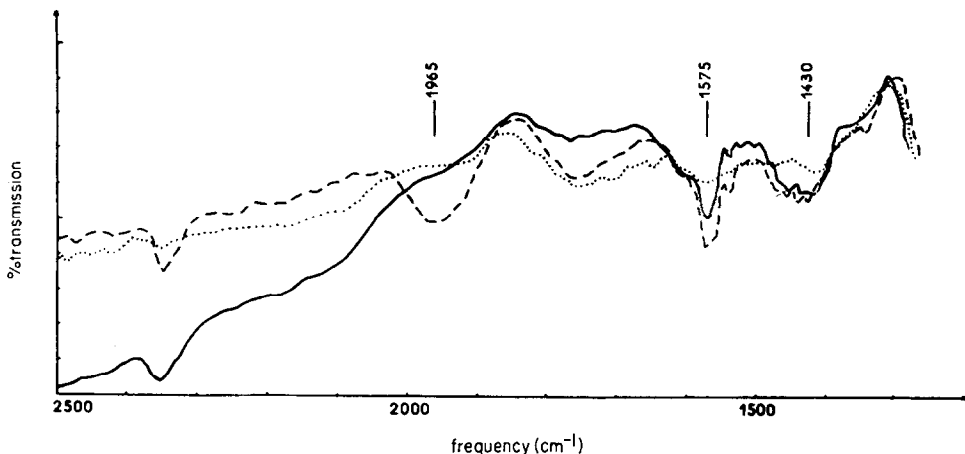


FIG. 8. Interaction of adsorbed CO with gaseous O₂. First type of spectrum. Dotted line—background spectrum; dashed line—CO adsorbed after evacuation; solid line—CO adsorbed + 10 mm O₂ pressure.

position that the CO₃⁻_(ads) complex, shown by other methods to be formed in this step, cannot be distinguished by infrared spectroscopy from CO adsorbed on nickel oxide

the Ni(OH)₂-SiO₂ pellets and because of heating at 200°C in vacuum, the lattice oxygen ions might be made more mobile (14) and would react with adsorbed CO to

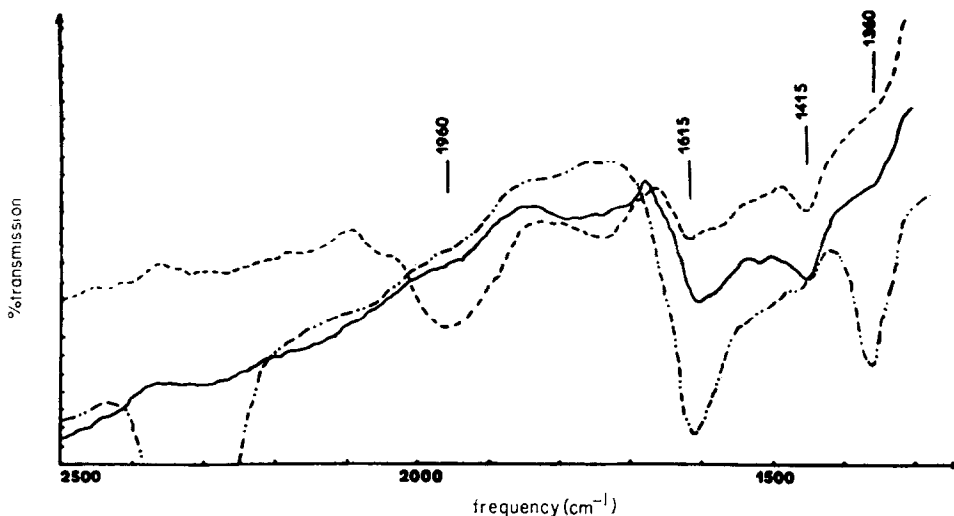


FIG. 9. Interaction of adsorbed CO with gaseous O₂. Second type of spectrum. Dashed line—CO adsorbed after evacuation; solid line—CO adsorbed + 10 mm O₂ pressure; dotted and dashed line—60 mm CO₂ pressure.

because the latter would also be adsorbed, at least partially, under the form of CO₃⁻, by reduction of nickel oxide. First we attempted to explain this phenomenon by

form a CO₃⁻ complex. In order to verify this hypothesis, a few silica-nickel hydroxide pellets were prepared at low pressure (190 kg/cm² instead of 2t/cm²). The

infrared spectra obtained gave no evidence of variation of position or intensity of the bands. Thus the hypothesis, according to which oxygen ions are made more mobile by compression and heating in vacuum and react with adsorbed CO, does not seem justified. The behavior of nickel oxide, compressed or not compressed, with regard to the adsorption of CO is thus essentially the same. It has, moreover, been shown that carbon monoxide adsorbed at room temperature cannot reduce nickel oxide (4, 5).

the form of O^- ion, it is fixed on free Ni^{++} ions [Fig. 10(b)]. Under these conditions the molecule of $CO_{(ads)}$ would come into resonance with O^- ions adsorbed in the vicinity and form a chemisorbed complex which can be represented by a formula CO_2^- or CO_3^- if carbon monoxide has a tendency to link with two neighboring oxygen ions.

These two structures are practically identical and the difference of the distances between CO and oxygen atoms of the lattice, on the one hand, and adsorbed oxygen,

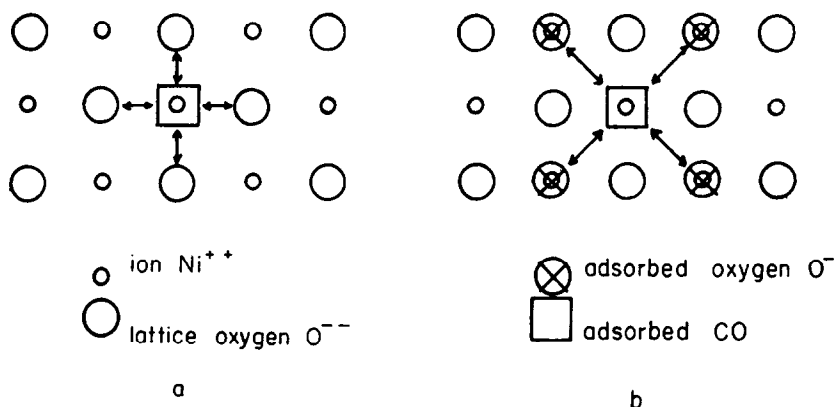


Fig. 10. Resonance structure of adsorbed CO.

The second attempt to explain the similarity of spectra before and after admission of oxygen on a catalyst containing previously adsorbed CO takes into account the crystalline structure of the solid. Nickel oxide is crystallized in a face-centered cubic system. Three planes (100), (110), and (111) are equally liable to develop on the surface of the powder. As the concentration in oxygen in the (110) plane is low and nonexistent in the (111) plane, it seems logical that bridged and linear CO are adsorbed there in preference to the other plane. On the other hand, when a molecule of CO is adsorbed on a Ni^{++} ion in the (100) plane, it can undergo interactions from O^{--} ions in the vicinity of Ni^{++} and come into resonance with these ions [Fig. 10(a)] without formation of a definite species. The frequency of vibration of the CO group should then be disturbed. If now, on the surface containing adsorbed CO, oxygen is adsorbed in

on the other, may be balanced by the difference in interaction forces exerted on adsorbed CO by these two types of oxygen. It would then seem logical that these two structures cannot be distinguished by infrared spectroscopy.

Finally a third type of spectrum of adsorbed CO, which is characterized by the simultaneous presence of the bands at 1620 and 1575 cm^{-1} exhibits a quite different behavior after admission of oxygen (Fig. 5). Indeed, when oxygen is admitted to the catalyst containing previously adsorbed irreversible CO, the band at 1620 cm^{-1} , which had disappeared after evacuation preceding the admission of oxygen, reappears while the band at 1960 cm^{-1} of bridged CO disappears, as is normal. This result can be explained only by supposing that the bridged carbon monoxide reacts with the oxygen adsorbed on neighboring Ni^{++} ions. The compound thus generated, probably the CO_3^- complex (4, 5), would

then take the resonance structure represented in Fig. 10(b).

The evacuation of nickel oxide, following the adsorption of oxygen, again produces the disappearance of the band at 1620 cm⁻¹, giving evidence that the responsible sites adsorb the carbon monoxide only weakly. However, as the band of CO_{2(ads)} at 1360 cm⁻¹ is not observed at all, it is concluded, in agreement [Eq. (1)] with previous results (4-6), that this compound cannot be formed by interaction between CO_(ads) and O_{2(g)}.

Step 2: Adsorbed CO₂ + Gaseous O₂ and Adsorbed CO₂ + Gaseous CO

The infrared spectrum of carbon dioxide irreversibly adsorbed is not modified after admission of oxygen at 10 mm Hg pressure or of carbon monoxide at 40 mm Hg pressure. This result tends to confirm that neither oxygen nor carbon monoxide can be adsorbed on nickel oxide containing CO₂, in agreement with the quantitative study of chemisorption (4) which has shown the poisoning effect of CO₂ against the adsorption of other gases.

Step 3: Adsorbed O₂ + Gaseous CO₂

The carbon dioxide is adsorbed reversibly and irreversibly on black nickel oxide containing previously adsorbed oxygen

(4). Infrared spectroscopy reveals the presence of two bands identical to those obtained after adsorption of CO₂ alone, at 1620 and 1360 cm⁻¹ (Fig. 11). Their intensity is definitely stronger, thus showing that the amount of adsorbed carbon dioxide is larger in this step than in the case where the catalyst does not contain preadsorbed oxygen. After evacuation of the sample, the intensity of the peaks from the irreversibly adsorbed carbon dioxide also remains stronger than on a catalyst not containing preadsorbed oxygen. All these results are in agreement with those given by the quantitative study of adsorbed volumes of gases in these different conditions (4).

It appears, then, that carbon dioxide is always adsorbed on nickel oxide in the same manner, whether oxygen has been preadsorbed or not. Now, previous studies (4-6) have shown, on the one hand, that the adsorption of CO₂ on an oxygenated surface leads to the formation of the CO_{3(ads)} complex and, on the other hand, that the sites on which CO₂ is fixed cannot be other than those active in the adsorption of oxygen and carbon monoxide, probably nickel ions. It is, therefore, necessary to suppose here a resonance structure, identical to the structure imagined for CO, between adsorbed carbon dioxide and either

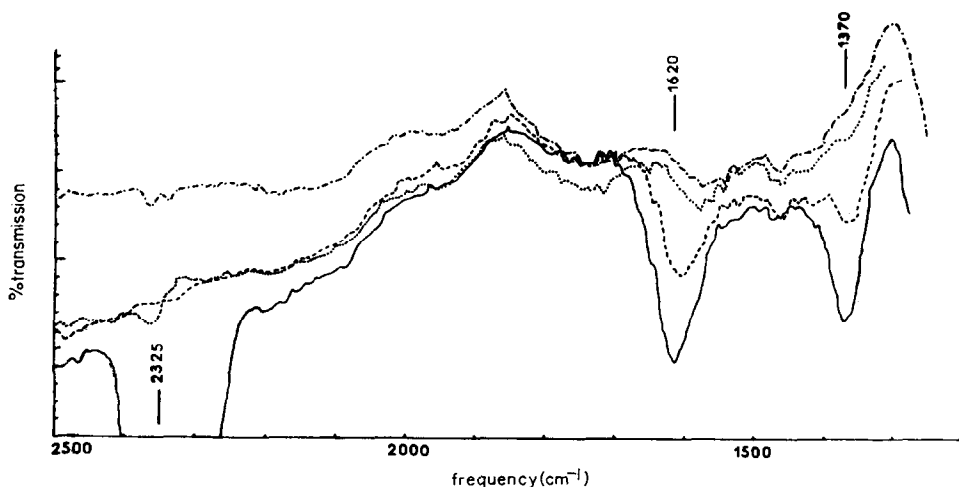


FIG. 11. Interaction of adsorbed O₂ with gaseous CO₂. Dashed and dotted line—background spectrum; dotted line—10 mm O₂ pressure; solid line—O₂ adsorbed + 60 mm CO₂ pressure; dashed line—O₂ adsorbed + CO₂ adsorbed after evacuation.

lattice oxygen ions or adsorbed oxygen ions. Figure 12(a) represents CO_2 adsorbed on pure nickel oxide and Fig. 12(b) shows the adsorption of carbon dioxide on a surface containing adsorbed oxygen. Although

original yellow color when CO is admitted (4). The infrared spectrum exhibits, in addition to gaseous CO bands, two bands at 1620 and 1360 cm^{-1} which are characteristic of adsorbed CO_2 (Fig. 13). A slight

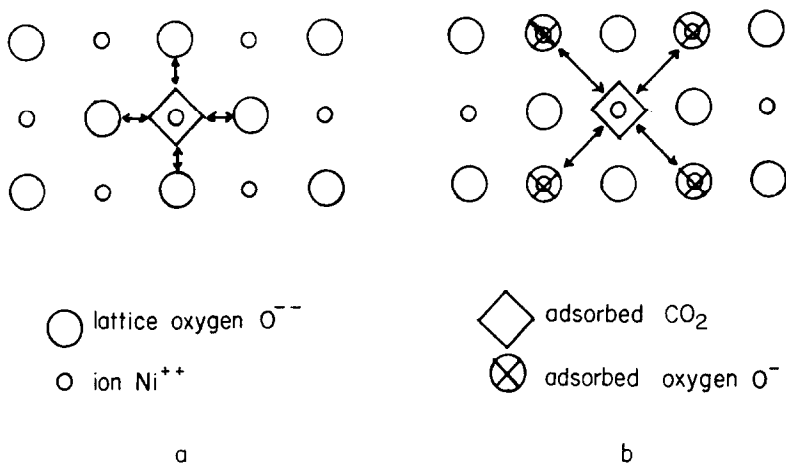


FIG. 12. Resonance structure of adsorbed CO_2 .

the proposed global resonance structure is the same for $\text{CO}_{(\text{ads})}$ and $\text{CO}_{2(\text{ads})}$, these two molecules are differentiated by adsorption bands at 1420 and 1360 cm^{-1} which characterize $\text{CO}_{(\text{ads})}$ and $\text{CO}_{2(\text{ads})}$, respectively.

Step 4: Adsorbed O_2 + Gaseous CO

The black nickel oxide, containing previously adsorbed oxygen, returns to its

peak observed on the background spectrum at 1455 cm^{-1} is a little more intense and enlarged thus revealing the presence at about 1440 cm^{-1} of an absorption band of weak intensity resulting from an excess of adsorbed CO. Thus carbon monoxide reacts principally with adsorbed O^- ions, giving $\text{CO}_{2(\text{ads})}$. This result is in agreement with the reaction established for this step (4-6),

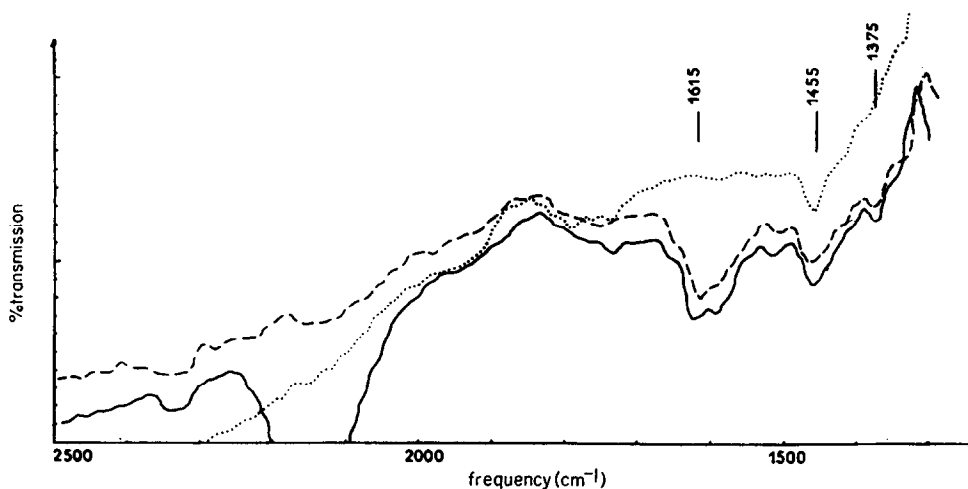
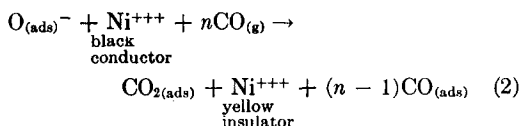


FIG. 13. Interaction of adsorbed O_2 with gaseous CO. Dotted line—10 mm O_2 pressure; solid line— O_2 adsorbed + 40 mm CO pressure; dashed line— O_2 adsorbed + CO adsorbed after evacuation.



Thus, when oxygen is preadsorbed, carbon monoxide coming from the gas phase leads to the formation of CO_{2(ads)} [Eq. (2)] whereas, when carbon monoxide is preadsorbed, oxygen coming from the gas phase leads to the formation of CO_{3(ads)}⁻ complex [Eq. (1)].

Therefore, infrared spectroscopy clearly shows that the steps O_{2(ads)} + CO_(g) and CO_(ads) + O_{2(g)} do not lead to the same adsorbed species. In the first step carbon dioxide is mainly formed. In the second, the infrared spectrum does not reveal any trace of CO_{2(ads)} but can be explained by the presence of a resonance structure of CO with the oxygens, for which structure the other methods have given the formula CO₃⁻ (4-6).

C. Study of the Reaction CO + ½ O₂

To obtain the oxidation reaction on the catalyst, a stoichiometric mixture of carbon monoxide and oxygen was introduced into

with the catalyst surface can thus be continuously regenerated. Because of the high exothermicity of the reaction (134 kcal/mole O₂) (13), it is necessary to introduce the reaction mixture into the cell very slowly, with the help of the Fugassi valve, in order to prevent any overheating of the catalyst. The spectra were recorded 2 hr after the introduction of the reaction mixture. Two types of spectra were obtained.

The first type (Fig. 14) exhibits two bands at 1620 and 1360 cm⁻¹ which are characteristic of adsorbed carbon dioxide, whereas the second type (Fig. 15) presents, in addition to the two preceding bands, a third distinct and intense peak at 1450 cm⁻¹ which would correspond to the band at 1420-1440 cm⁻¹ of adsorbed carbon monoxide. For each of the two types of spectra the reaction repeated after regeneration of the catalysts in vacuum at 200°C in no way modifies the spectra.

For catalysts giving spectra with three absorption bands at 1620, 1450, and 1360 cm⁻¹, it must be assumed that the surface of the catalyst contains CO₂ molecules characterized by the peaks at 1620 and

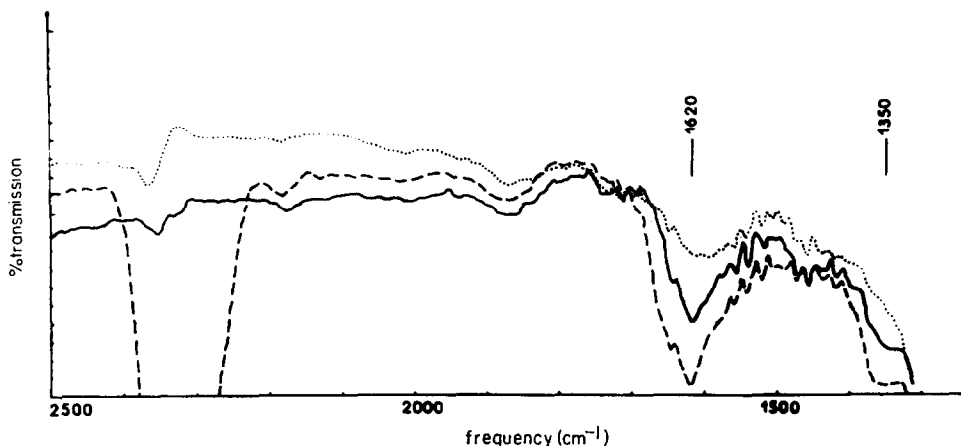


FIG. 14. Reaction CO + ½ O₂. First type of spectrum. Dotted line—background spectrum; solid line—CO + O₂ mixture, 5 mm pressure; dashed line—60 mm CO₂ pressure.

the infrared analysis cell at a pressure of about 5 mm Hg. Under these conditions the carbon dioxide formed during the reaction can diffuse easily in the cell and condense in the liquid nitrogen trap placed near the cell. The gaseous layer in contact

1360 cm⁻¹ and molecules of adsorbed CO with the structure given in Fig. 10(b), that is to say, in resonance with adsorbed oxygen ions. This structure would correspond to the intermediate chemisorbed complex.

When the spectra present only the two

bands of adsorbed CO_2 , at 1620 and 1360 cm^{-1} , one must assume that CO_2 molecules are fixed on the nickel oxide surface and have the resonance structure of Fig. 12(b). From all these results it appears that the infrared study of the oxidation reaction

linear and of bridged CO, differ by the presence of bands at 1620 and/or 1575 cm^{-1} , according to the temperature of the preparation of nickel oxide.

The infrared study of oxygen adsorption on nickel oxide containing preadsorbed CO

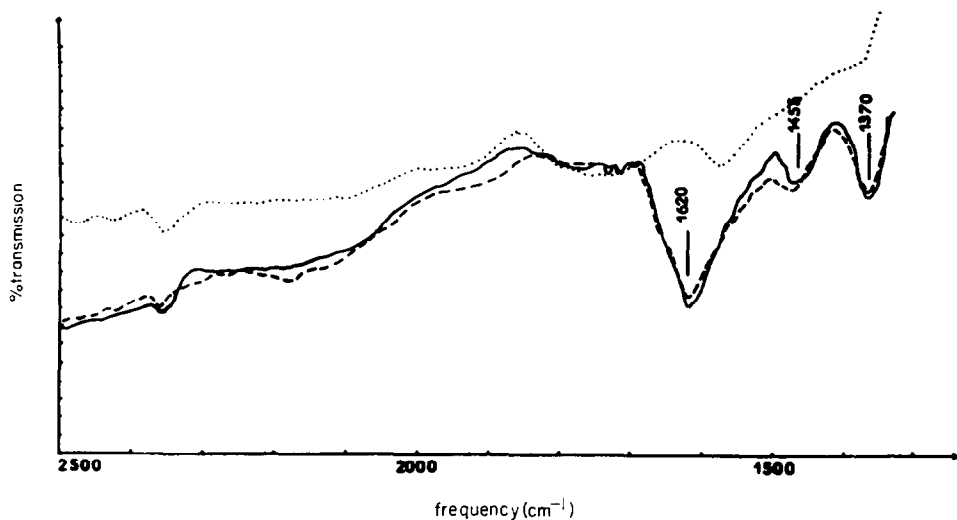


FIG. 15. Reaction $\text{CO} + \frac{1}{2} \text{O}_2$. Second type of spectrum. Dotted line—background spectrum; solid line— $\text{CO} + \text{O}_2$ mixture on fresh sample; dashed line— $\text{CO} + \text{O}_2$ on sample regenerated three times.

itself does not give any additional information on the reaction mechanism beyond that obtained by the study of the different chemisorption steps previously considered.

CONCLUSIONS AND SUMMARY

The aim of the present work was, first, to confirm the presence of an intermediate phase in the oxidation reaction of carbon monoxide on nickel oxide and, second, to obtain further information about the different species adsorbed on the catalyst during the reaction.

The study of the chemisorption of reaction gases CO , CO_2 , O_2 by nickel oxide has shown that the conditions of the preparation of the catalyst, in particular the decomposition temperature of nickel hydroxide into nickel oxide, have an appreciable influence on the spectra of adsorbed gases. Indeed, the infrared absorption spectra of adsorbed CO , all presenting a system of the two bands at 2060 and 1960 cm^{-1} as a result, respectively, of adsorbed

did not show any variation in the spectrum of adsorbed CO beyond the disappearance of the bridged carbon-monoxide band at 1960–1970 cm^{-1} . Now, other methods (4–6) have revealed the formation, under these conditions, of a complex of global formula CO_3^- . Consequently we were led to assume a structural form of adsorbed CO coming into resonance either with lattice oxygen ions in the neighborhood of a Ni^{++} site on which CO has been adsorbed, or with oxygen ions adsorbed on the neighboring metallic ions. The interactions undergone by the CO group would be practically identical in these two structures which could not then be distinguished by infrared spectroscopy.

The study of the adsorption of pure carbon dioxide and then of the successive adsorptions of oxygen and of carbon dioxide, for which the infrared adsorption bands at 1620 and 1360 cm^{-1} are identical, led the authors to suppose the existence of a similar structure of resonance between carbon dioxide adsorbed on Ni^{++} ions and

either oxygen lattice or adsorbed ions. Eischens (1,2) has similarly noted the presence of these two bands for adsorption of CO₂ on NiO obtained by the oxidation of metallic nickel. As this author did not obtain an infrared spectrum of CO adsorbed on NiO, he made an analogy with the spectra of bulk alkaline bicarbonates to justify ascribing the two bands to the presence of a bicarbonate ion at the catalyst surface. This hypothesis, which concerns the adsorption of CO₂, would also lead in the present case to assumption of the formation of bicarbonate ions from adsorbed CO, whose characteristic bands at 1620 and 1420 cm⁻¹ exist likewise in the absorption regions of bulk bicarbonates. However, previous studies (4-6) tend to show that carbon monoxide cannot reduce nickel oxide at room temperature and is for this reason probably adsorbed on Ni⁺⁺ ions. Neither would the formation of a bicarbonate ion, as supposed by Eischens, afford any explanation of the poisoning effect of CO₂ on subsequent chemisorptions of CO and O₂. Finally, Winter (15) did not observe any exchange between lattice labeled oxygen and CO or CO₂ adsorbed at room temperature. This exchange would be possible only if CO and CO₂ were adsorbed on lattice oxygen and formed a bicarbonate or carboxylate ion. For these reasons it has been assumed in this work that all the reagent gases studied are adsorbed on nickel ions without reacting with lattice oxygen. Accordingly we did not consider it possible to compare our infrared spectra of chemisorbed species with the spectra of bulk three-dimensional substances such as carbonates, bicarbonates, formates, or carboxylates. However an explanation was attempted by turning to

resonance structure of species chemisorbed on the surface of the catalyst.

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