JOURNAL OF CATALYSIS 49, 225–235 (1977)

Interaction of CO_2, CO, and NiO Studied by Infrared Spectroscopy

A. UENO, J. K. HOCHMUTH, AND C. O. BENNETT

Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06268

Received January 13, 1977; revised May 2, 1977

By means of infrared spectroscopy for unsupported NiO catalyst, the rate of the reaction of CO(g) with CO_3(ads) on the catalyst as well as that of the desorption of CO_2 was observed at various temperatures as a function of CO_3(ads) surface coverage. Activation energies for these processes are ~14 and ~7 kcal/mole, respectively, for all surface coverages of CO_3(ads) studied. Infrared spectra also show that the amount of CO_2 adsorbed and its surface structure are sensitive to the oxidation state of the catalyst.

INTRODUCTION

There have been numerous studies on the reaction mechanism of CO oxidation over metal oxide catalysts. Dell and Stone (*1*) postulated that carbonate complexes are formed when CO is added to NiO on nickel. El Shobaky *et al.* (*2*) studied the reaction on NiO by a microcalorimetric technique and suggested a pathway proceeding through a carbonate species on the catalyst surface as the reaction intermediate.

Recently, Conner and Bennett (*3*) found evidence by employing the isotopes carbon-13 and oxygen-18 that the oxidation of CO on NiO passes through a two-carbon complex formed by the interaction of CO in the gas phase with carbonate on the surface of the catalyst. The purpose of the present work is to study the reaction of CO(g) with CO_3(ads) on NiO as well as the adsorption and desorption of CO_2 by means of infrared spectroscopy.

Infrared spectroscopy is a powerful tool for the investigation of adsorbed species. Eischens and Pliskin (*4*) were the first to show the presence of carbonate groups on NiO during the oxidation of CO. Teichner and Morrison (*5*) are of the opinion that there is some difference in surface characteristics between bulk nickel oxide and nickel oxide on nickel. The difference in the surface properties of nickel oxides prepared at different temperatures was confirmed by Courtois and Teichner (*6*) using infrared spectroscopy for the adsorption of CO and CO_2. The amount of oxygen on NiO changes with the temperature at which the catalyst is prepared, and the surface properties of the oxide seem to depend on surface oxygen.

The oxidative power distributions of NiO obtained at various temperatures were measured by Uchijima *et al.* (*7*), and those of MnO_2 by Kobayashi and Kobayashi (*8*). The surface properties of oxide catalysts could be observed by the measurements of their electrical conductivities (*9*), which have a relationship with infrared reflection and transmission (*10*). Infrared spectroscopy, therefore, can also be used to monitor the conductivity changes during gas adsorptions and desorptions by following the changes in the background transmission of the catalyst. This attempt was made by using ZnO for hydrogen (*11*) and carbon monoxide (*12*) adsorption, and CoO for

ISSN 0021-9517

carbon monoxide adsorption (*13*). We are also interested in the measurement of the infrared transmission changes of NiO as related to the oxidation state of the catalyst.

All the investigators who studied NiO by infrared spectrometry have used silica as a support because of its inactivity and the increased infrared transmission of the catalyst. The effects of supports on the surface properties of NiO, however, were observed by carbon monoxide adsorption characteristics (*14*). O'Neil and Yates (*14*) employed alumina, silica, and titania as carriers of NiO and found that the carrier effects were specific to each system and were too strong to ignore in any comparisons.

A feature of the present work lies in using unsupported NiO catalysts for infrared spectroscopic measurements. This allowed us to avoid the complication of support effects on the surface properties of the catalyst during reaction; our catalyst is bulk NiO, not NiO on Ni, as confirmed by X-ray diffraction.

The results of this work are discussed in terms of the sequence of steps proposed previously (*3*):

1. $O_2 + 2\alpha \rightarrow 2O\alpha$.

2a. $CO + O\alpha \rightarrow CO_2\alpha$.

2b. $CO_2\alpha + O\beta \rightleftarrows CO_2O\beta + \alpha$.

3. $CO_2O\beta \rightleftarrows CO_2 + O\beta$.

4a. $CO_2O\beta + CO \rightarrow C_2O_3O\beta$.

4b. $C_2O_3O\beta + O\alpha \rightarrow CO_2 + O\beta + \alpha$.

Although not specifically indicated in the above equations, there is strong evidence that some of the active centers are charged; for example, the adsorption of oxygen as O^- increases the electrical conductivity of NiO, a *p*-type semiconductor. The symbol α is associated with a nickel atom and $O\beta$ represents a quasi-lattice oxygen on the surface among Ni atoms. $CO_2O\beta$ is also written as CO_3(ads).

EXPERIMENTAL METHODS

1. Sample Preparation

Finely divided samples are needed to increase the available surface area for adsorption and to decrease the particle size below the wavelength of the infrared radiation so as to minimize the scattering losses. Self supported NiO disks of adequate strength made in a press in the usual way gave insufficient transmission. However, the following method proved adequate. A suspension of NiO, which was obtained by the decomposition of nickel nitrate at 250°C in an oven, was prepared in water. Some of the finest part of the suspension was pipetted onto a stainless steel mirror covered with a vacuum deposited gold film, and then dried at 75°C to remove water. The largest particle size of the sample prepared was 15 μm, and its mean value about 1 μm, measured by optical microscopy.

After weighing the catalyst, it was placed in the reaction cell and heated at 280°C for 16 hr with oxygen flow at a partial pressure of 100 kPa. If the sample is heated at less than 250°C some residue of nitrate ion will be observed in the infrared spectrum. Heating the catalyst above 300°C caused sintering and a drastic reduction in its infrared transmission.

Besides nickel nitrate, its formate, carbonate, and hydroxide were tested as sources of finely divided particles of the oxide. In the case of the formate and carbonate, infrared spectra showed some residue of formate ion or carbonate ion, respectively, even after heating at 300°C for 16 hr. On the oxide from the hydroxide, one of the best catalysts for CO oxidation reaction, no adsorption of CO and CO_2 were observed from the infrared spectra.

2. Reaction Cell

The optics of the infrared spectrometer used is shown in Fig. 1. The infrared cell is

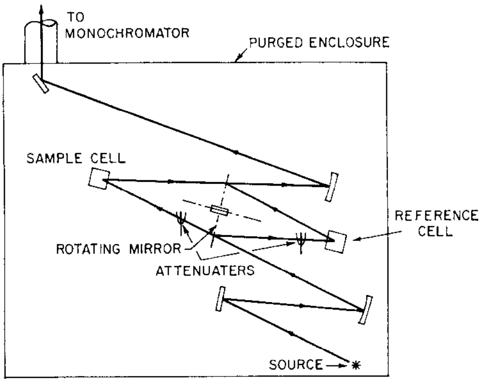


FIG. 1. Optics of the infrared spectrometer.

made of stainless steel with an IRTRAN6 CdTe infrared window, which can be used up to 300°C and transmits infrared radiation well in the region from 4000 to 400 cm^{-1}. The window was glued into a stainless steel holder with Vacuseal and the holder was sealed against the body by a gold gasket. The window is arranged perpendicular to the incident radiation to avoid difficulty caused by reflection from the surface of the window. Gases can be introduced to the catalyst adhering to the mirror; the residence time is 0.2 s when the flow rate is 1 ml/s, which is usually used in the present study. The cell is covered with a heating tape and insulation, and an iron–constantan thermocouple is located close to the mirror. Details of the reactor are shown in Fig. 2.

3. Chemicals

The gases used in the present experiment were obtained from Matheson and were used directly from their cylinders, except Ar and CO. For Ar, a Hydrox purifier was used to remove water and oxygen. Eischens (*15*) reported that carbon monoxide may produce metal carbonyls such as $Fe(CO)_5$ and $Ni(CO)_4$ in its cylinder, so an activated carbon bed was used to purify the CO.

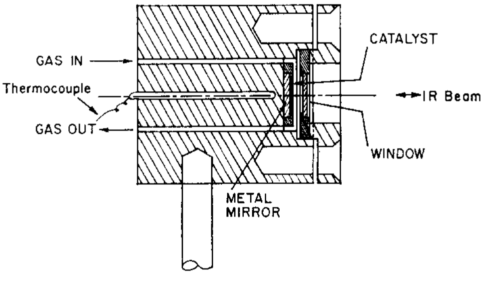


FIG. 2. Reactor schematic.

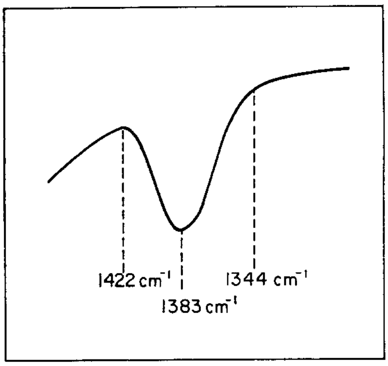


FIG. 3. Absorption peak of adsorbed CO_2.

4. Procedure for Measurements of Optical Densities of Adsorbed Species

The rates of the adsorption and desorption of CO_2 as well as that of the reaction of CO(g) with CO_3(ads) on NiO are rapid. In order to obtain these rates under transient conditions, the wave numbers of the adsorption spectrum were fixed at 1344, 1422, and 1383 cm^{-1}, respectively, and the changes in their transmission were recorded separately for every experimental run. These wave numbers correspond to the background on both sides of the absorption peak of adsorbed CO_2 and the bottom of its peak, as shown in Fig. 3.

Not only the transmission at 1383 cm^{-1}, but also those at 1422 and 1344 cm^{-1} change significantly by the addition of CO_2 and by the interaction of CO(g) with adsorbed CO_2 on NiO. Moreover, the transmission at 2000 cm^{-1} changes with the addition of gases. Since no absorption peaks are expected or observed at 2000 cm^{-1}, the change in the infrared transmission at this wave number reflects the changes of a surface property of the

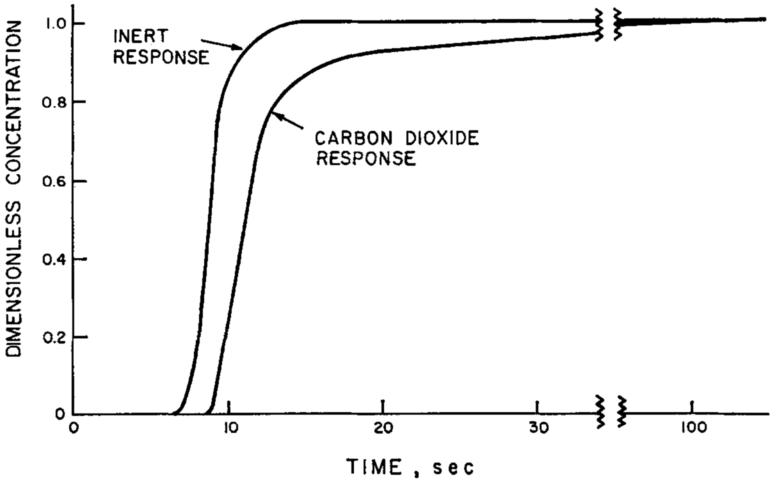


FIG. 4. Typical result used for the measurement of the reversible adsorption of CO_2.

catalyst caused by the introduction of gases. The transmission changes at 1422 and 1344 cm^{-1} could be considered to represent the surface property changes of the catalyst as well.

The optical density was calculated every 5 s during the reaction by using these three wave numbers. The peak shape was invariant, so it was sufficient to use the peak height as a measure of peak area.

5. *Determination of Concentration of Adsorbed Carbon Dioxide*

The gas phase concentration changes corresponding to the dynamic adsorption of carbon dioxide could not be measured during the infrared experiment because of the small amount of catalyst used, about 1.7 mg. Therefore the equilibrium concentration of adsorbed carbon dioxide was measured in a separate experiment. Mixtures of known composition were prepared and introduced to a tubular reactor containing 0.42 g catalyst by means of a Carle 4-way switching valve. The composition of the reactor exit gas was monitored by a DuPont cycloidal mass spectrometer. Prior to each adsorption measurement the reactor response to a step change in feed composition was determined by switching from an inert nitrogen stream to a mixture con-

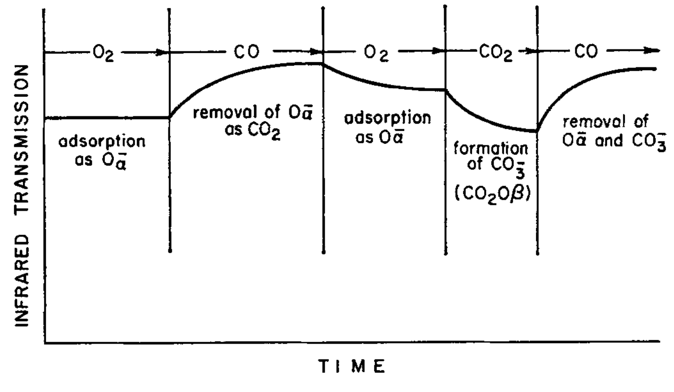


FIG. 5. Changes of the infrared transmission at 2000 cm^{-1} by adsorption of gases at 99°C.

taining nitrogen and argon. The catalyst was then pretreated in the same manner as the infrared catalyst. The quantity of adsorbed carbon dioxide was then estimated using a procedure similar to that described by Kobayashi and Kobayashi (*8*). Typical mass spectrometer traces for the carbon dioxide and inert argon responses are shown in Fig. 3.

The catalyst was prepared using the same conditions as the infrared catalyst. The average particle size was 1 mm. The surface area, measured by BET, was found to be 122 m^2/g for both catalysts.

RESULTS

When various gases adsorb on the surface of NiO, its background transmission changes depending on the electric properties of the adsorbed species. In Fig. 5 the transmission changes at 2000 cm^{-1} are given when pure oxygen, carbon monoxide, or carbon dioxide adsorbs on the catalyst at room temperature. For these gases flow rates are 1.1 ml/s, and the sample weight is 1.7 mg.

Figure 6 shows the results obtained when pure CO_2 was added to NiO at 100°C. The background transmission could be varied by the reduction of the catalyst using CO at 100°C, because CO did not adsorb on NiO but reacted with oxygen atoms on the surface to form CO_2 (*3*). The coverage of CO_3(ads) or CO_2–$O\beta$ (*3*) at equilibrium decreases as the surface oxygen is removed.

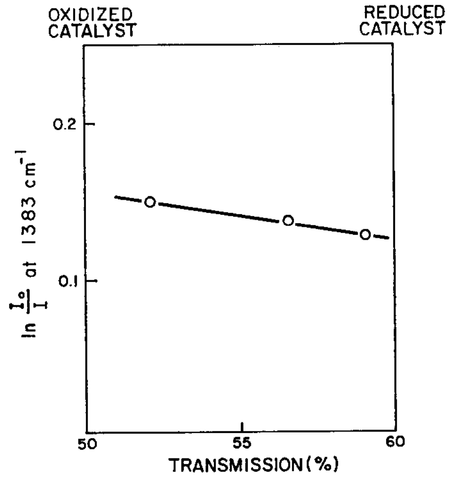
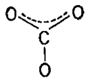
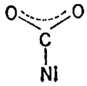


FIG. 6. Adsorption of CO_2 as function of oxidation state of NiO; P_{CO_2} = 100 kPa; T = 100°C; wave number, 1383 cm^{-1}.

TABLE 1

Band Assignments (*4*)

Wave number (cm^{-1})	Species
1344 1422 2000	Background
1383 1620	 carbonate
1276 1545	 carboxylate

The infrared spectrum of reversibly adsorbed CO_2 on NiO is given in Fig. 7a. Two absorption bands were observed, at 1620 and 1383 cm^{-1}, which are assigned to carbonate ion on the oxide (*4*).

When the catalyst was exposed to CO at 200°C for a long time, the carboxylate ion was observed on the surface by infrared spectroscopy. This has two absorption bands, at 1545 and 1276 cm^{-1} (in Fig. 7b). The band could not be removed by subsequent exposure to Ar at 200°C or even 100 kPa O_2 at 200°C. Table 1 summarizes the band assignments of the preceding discussion.

After a few weeks the activity of a given sample often began to decrease, so it would be replaced by a freshly prepared one. It is thus important to be sure that the optical density [the amount of CO_3(ads)] is proportional to the weight—i.e., the thickness of the catalyst layer. Figure 8 shows that the absorbance at 1383 cm^{-1} is proportional to the catalyst weight at 100°C for 100 kPa CO_2.

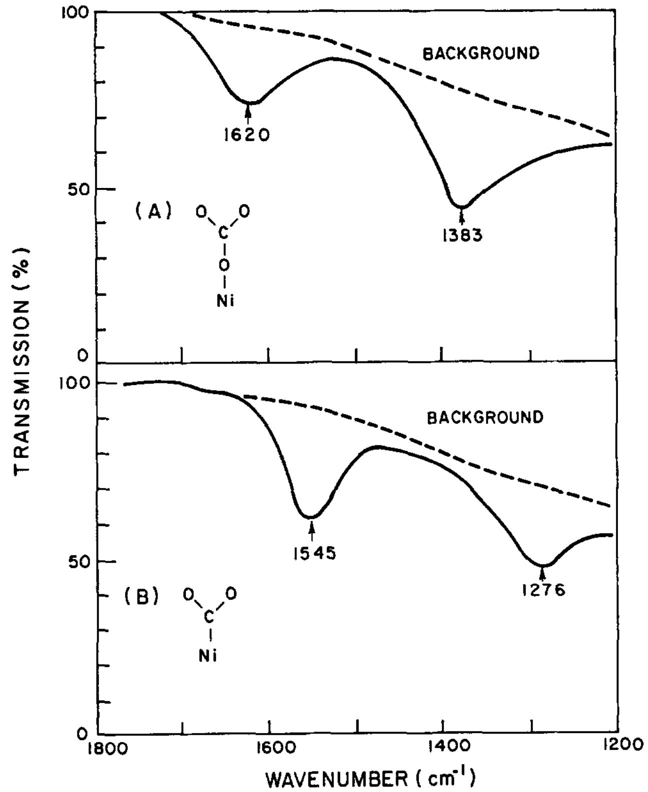


FIG. 7. Infrared spectrum of adsorbed CO_2 at room temperature: (a) Spectrum of carbonate ion on NiO; (b) spectrum of carboxylate ion.

The area of the mirror to which the catalyst adheres is 1 cm^2 and the area irradiated by the infrared beam is 0.4 cm^2. Only 40% of the catalyst is, therefore, effective for the present investigation. However, the values of the sample weight given in this paper refer to the total weight of the sample on the mirror.

The rate of CO_2 adsorption was too fast to be followed by infrared spectrometry under most of the experimental conditions employed. A few results are given in Fig. 9.

The amount of CO_2 adsorbed at the equilibrium state is displayed for the infrared experiments at various temperatures and pressures in Fig. 10 along with selected data from the equilibrium adsorption experiments. The extinction coefficient relating the concentration of adsorbed CO_2 to the absorption intensity was found to be 6.14×10^{15} molecules/cm^2 at 100°C and 50 kPa CO_2. This value is in good agreement with that reported by Wexler (*17*) for carbonate. For example, at an absorption intensity of 0.3, the concentration of adsorbed CO_2 is calculated as 1.84×10^{15} molecules/cm^2 using our extinction coefficient and 3.15×10^{15} molecules/cm^2 using Wexler's.

The observed absorbances have been transformed into surface coverages (based on the BET area) by using the conversion factor found at 100°C and 50 kPa as described above. There is a satisfactory agreement between the isotherm found by infrared and by mass spectrometry. From the data of Fig. 10, the variation of equilibrium CO_2 pressure at constant coverage

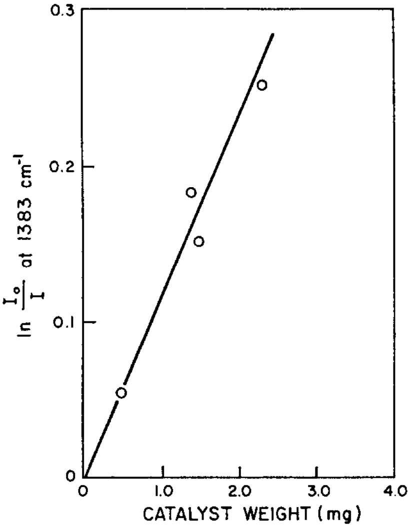


FIG. 8. Relationship between absorbance at 1383 cm^{-1} and catalyst weight at 100°C and 100 kPa CO_2.

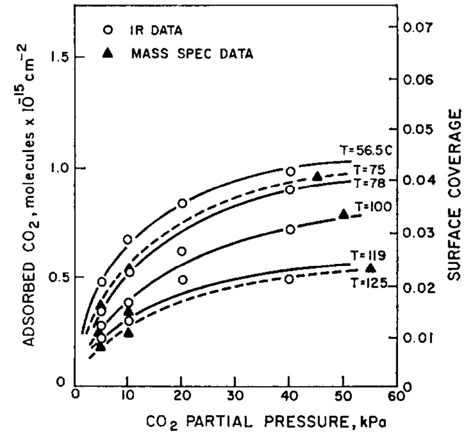


FIG. 10. Adsorption isotherms of CO_2; (○) data obtained from infrared measurements; (▲) data from separate measurements of equilibrium concentration of adsorbed CO_2.

with varying temperature is obtained. The resulting isosteric heats of adsorption are reported in Fig. 11.

The rate of desorption for carbonate ion on NiO was measured by Ar flushing at various temperatures. The flow rate of Ar is the same as that of CO_2, 1.1 ml/s. Fig. 12 shows the curves obtained for the initial rate of desorption, the slope of ln $[I_0/I]$ vs t at $t = 0$. From this result, the activation energy for CO_2 desorption on the catalyst was calculated graphically as a function of the carbonate surface coverage (Fig. 13). If all the data are considered together, a least-squares analysis leads to an activation energy of 5.8 kcal/mole with a correlation coefficient of 0.97.

By using a certain partial pressure of CO as a flushing gas for adsorbed CO_2, the initial rate of decrease of CO_3(ads) was obtained and is reported in Fig. 14. This rate contains both the rate of desorption

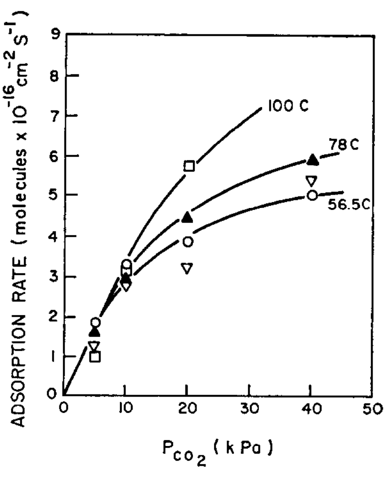


FIG. 9. Rate of CO_2 adsorption; (○) 56.5°C, (▲) 78°C, (□) 100°C, (▽) 119°C.

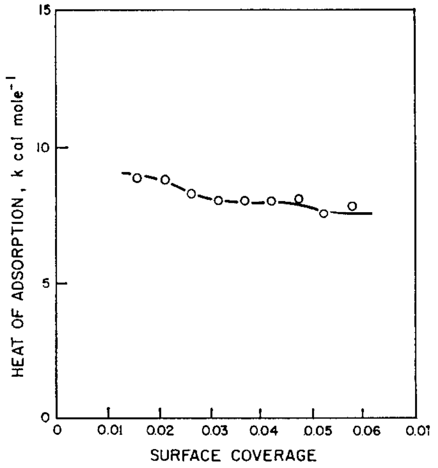


FIG. 11. Isosteric heat of adsorption for CO_2 on NiO as a function of surface coverage.

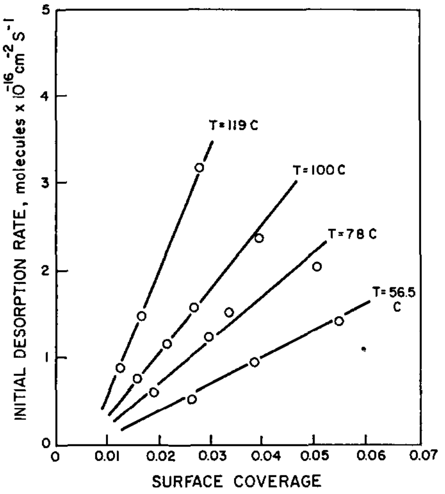


FIG. 12. Initial rate of desorption of adsorbed CO_2 on NiO.

of CO_3(ads) and that of reaction between CO_3(ads) and gaseous CO. As the desorption rate was known from Fig. 12, the rate of this reaction could be calculated by the subtraction of the rate in Fig. 11 from that in Fig. 14 at the same absorbance, i.e., CO_2 surface coverage. The result is shown in Fig. 15. The activation energy for this reaction was found to be 13.8 kcal/mole from these results, using the method of least squares. The correlation coefficient was 0.99. By changing the partial pressure of gaseous CO, the relationship of the reaction rate and CO pressure at 100°C was obtained in Fig. 16. The pressures employed were 60 and 30 kPa CO diluted by Ar to a total pressure of 100 kPa.

When CO is added to the oxidized catalyst, no carbonate band is produced at the gas flow rates used, corresponding to 0.2 s residence time. Conversion to CO_2 is very small, and the rate of CO_2 desorption is intrinsically high so that no CO_3(ads) accumulates on the surface. For example, at 100°C, for 30 kPa CO, the rate of oxidation (CO + Oα) (*3*) is 7.40×10^{12} molecules/cm^2 s. The rate of desorption from Fig. 12 is 8.19×10^{15} molecules/cm^2 s. Since CO_3(ads) is formed so slowly compared to the desorption rate of CO_2, or the

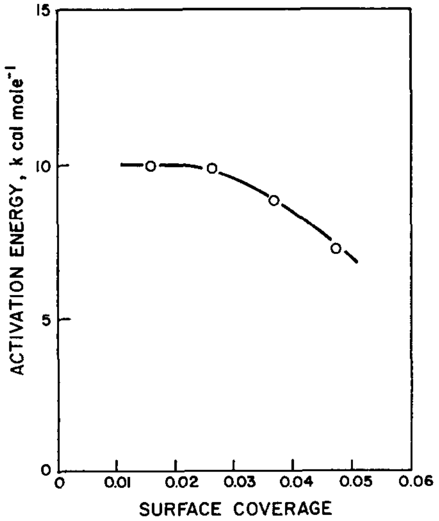


FIG. 13. Activation energy for desorption of CO_2.

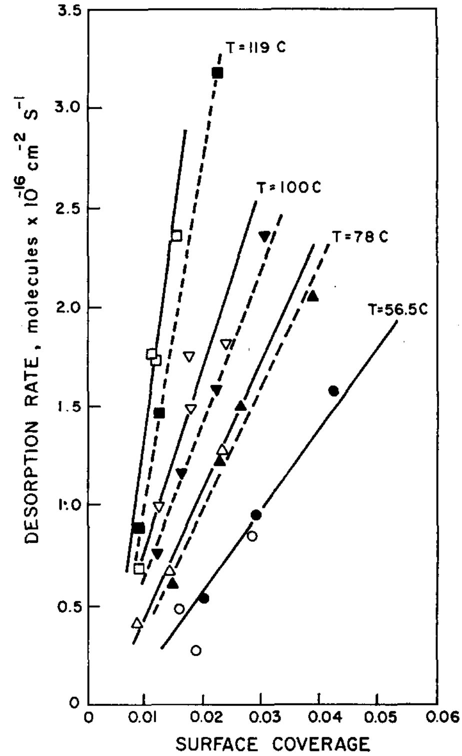


FIG. 14. Initial rate of desorption and reaction between CO and CO_3(ads); (– – –) 100 kPa Ar flushing, (—) 30 kPa CO, 70 kPa Ar flushing.

reaction of CO and CO_3(ads), it is correct to compute the rate of the latter step as described above. Some experiments were made in a stopped-flow mode, converting the cell to a batch reactor. In this case the CO_2 gaseous absorption bands and the CO_3(ads) bands develop concurrently. Measurements of this type, steady-state oxidation measurements, and the effect of CO_2 on the oxidation rate will be reported in a separate paper.

It is important to note that between each adsorption, desorption, or reaction the catalyst was exposed to pure oxygen at 100°C and 100 kPa. Thus the initial state of the catalyst is always the same, since oxygen is irreversibly adsorbed (*3*). Figure 6 shows that the initial state of the catalyst influences the amount of CO_2 adsorbed, for example.

DISCUSSION AND CONCLUSIONS

Nickel oxide is a typical *p*-type semiconductor. Its electric conductivity changes with the adsorption of many gases, and so does its infrared transmission. The transmission changes shown in Fig. 5 can be explained by the changes of the oxidation state of the catalyst caused by adsorption.

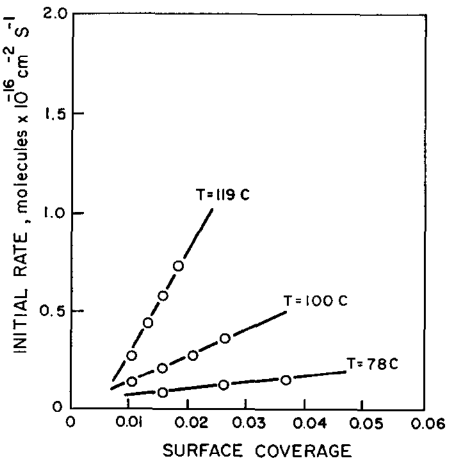


Fig. 15. Initial rate of reaction of CO and CO_3(ads) with 30 kPa CO.

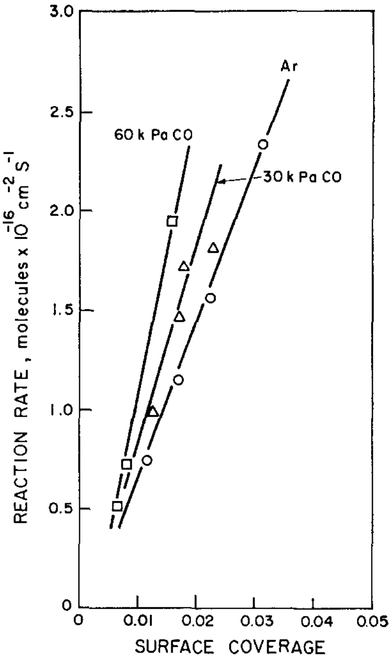


Fig. 16. Rate of removal of CO_3(ads) as a function of CO partial pressure at 100°C.

Carbon monoxide reacts with oxygen on the NiO surface to reduce the oxidation state of the catalyst, and this results in an increase of the background infrared transmission of the sample. In other words, it is possible to estimate the oxidation state of the catalyst by the measurement of the infrared transmission at a certain wave number where there is no specific absorption. Figures 5 and 6 show that Oα and $CO_2O\beta$ are adsorbed as negative ions; CO seems to increase the transmission by removing $O\alpha^{-\delta}$ rather than adsorbing as $CO^{+\delta}$. Conner and Bennett (*3*) suggested that CO_2 adsorbs on the surface lattice oxygen of NiO rather than on the Ni atoms, and the infrared studies confirm this. The number of Oβ sites greatly exceeds the α sites, so that the adsorption of CO_2 on Oα is a small fraction of that adsorbed on Oβ. The former amount was not detected by mass spectrometry, but the decrease in CO_3(ads) shown in Fig. 5 may be due to the removal of Oα. As reduction is carried further, lattice oxygen surrounding Ni atoms may also be removed, so that eventually CO_2 formed from CO is irreversibly adsorbed on these sites as carboxylate as shown in Fig. 6.

No bands for adsorbed CO as such were observed in the 1800–2000 cm^{-1} region. Probably the supported catalysts used by previous investigators had more exposed low-coordination Ni atoms, either because of smaller crystallite sizes or because supported Ni is not completely oxidized to NiO. To study this case of structure sensitivity it is probably necessary to introduce the complication of using supported NiO. Recall that CO_2 is adsorbed and exchanges on SiO_2 (*3*).

The above discussion can be summarized as follows.

A. As suggested by Conner and Bennett (*3*), the reaction,

$$CO_2O\beta + O\alpha + CO(g) \rightarrow 2CO_2 + O\beta + \alpha,$$

does occur; its rate is given by,

$$r = k_4(CO_2O\beta)(CO),$$

where

$$k_4 = A_4 e^{-E_4/RT} = 5.06 \times 10^{23} e^{-13777/RT} \text{ molecules cm}^{-2}\text{ s}^{-1}\text{ kPa}^{-1}.$$

The oxygen coverage $O\alpha$ has not been varied.

B. The chemisorption,

$$CO_2 + O\beta \rightleftarrows CO_2O\beta,$$

occurs rapidly and reversibly.

The desorption rate is given by

$$r = k_3(CO_2O\beta),$$

where

$$k_3 = A_3 e^{-E_3/RT} = 6.40 \times 10^{21} e^{-6798/RT} \text{ molecules cm}^{-2}\text{ s}^{-1}.$$

C. No $CO_2\alpha$ is formed on the normal (oxidized) catalyst.

D. The rate of CO oxidation is 3–4 orders of magnitude slower than the rates of interaction of CO_2 with the catalyst at 100°C.

E. The simplified sequence for the oxidation is then, at 100°C:

1. $O_2 + 2\alpha \rightarrow 2O\alpha.$
2. $CO + O\beta + O\alpha \rightarrow CO_2O\beta + \alpha.$
3. $CO_2O\beta \rightleftarrows CO_2 + O\beta.$
4. $CO + CO_2O\beta + O\alpha \rightarrow 2CO_2 + O\beta + \alpha.$

The number of steps is reduced from (*3*) because of the low coverage of $CO_2\alpha$ and $C_2O_3O\beta$. From other work in progress, the rate determining step is the second one, and it has already been mentioned that steps 3 and 4 are not kinetically significant, at least at low concentrations of $CO_2(g)$.

The apparently simple oxidation of CO on NiO presents many complexities when studied in detail. Work continues on this system and will be reported in a subsequent paper.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation.

REFERENCES

1. Dell, R. M., and Stone, F. S., *Trans. Faraday Soc.* **50**, 501 (1954).
2. El Shobaky, G., Gravelle, P. C., and Teichner, S. J., *J. Catal.* **4**, 4 (1969).
3. Conner, W. C., and Bennett, C. O., *J. Catal.* **41**, 30 (1976).
4. Eichens, R. P., and Pliskin, W. A., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky, and P. B. Weisz, Eds.), Vol. 9, p. 662. Academic Press, New York, 1957.
5. Teichner, S. J., and Morrison, J. A., *Trans. Faraday Soc.* **51**, 961 (1955).
6. Courtois, M., and Teichner, S. J., *J. Catal.* **1**, 121 (1962).
7. Uchijima, T., Yoneda, Y., and Takahashi, M., *J. Catal.* **9**, 403 (1967).
8. Kobayashi, M., and Kobayashi, H., *J. Catal.* **27**, 100 (1972).

9. Wolkenstein, T., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 12, p. 189. Academic Press, New York, 1960.
10. Martin, D. H., *Advan. Phys.* **14**, 39 (1965).
11. Scholten, J. J. F., and Van Montfoort, A., *Proc. Int. Congr. Catal., 5th, 1972,* 22–385 (1973).
12. Hertl, W., *J. Catal.* **31**, 231 (1973).
13. London, J. W., and Bell, A. T., *J. Catal.* **31**, 32 (1973).
14. O'Niel, C. E., and Yates, D. J. C., *Spectrochim. Acta* **17**, 953 (1961).
15. Eischens, R. P., *Accounts Chem. Res.* **5**, 74 (1972).
16. Kobayashi, H., and Kobayashi, M., *Catal. Rev.* **10**, 139 (1974).
17. Wexler, A. S., *Appl. Spec. Rev.* **1**, 29 (1967).