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Disproportionation of Carbon Monoxide on Supported Nickel Catalysts[1]

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The disproportionation of carbon monoxide was investigated mainly on a 5.5% Ni/Al_2O_3 catalyst by infrared spectroscopy and temperature-programmed desorption. The reaction was found to be of first order with respect to the surface concentration of CO below 200°C, while at 450°C the reaction proceeded as a second order reaction for the pressure of CO. Results obtained with predeposited carbon indicated that the disproportionation reaction requires an ensemble of several nickel atoms. In agreement with this result, the disproportionation did not take place readily on a 1.1% Ni/Al_2O_3 catalyst on which a high dispersion of the metal was indicated by both infrared spectroscopy and the chemisorption of hydrogen. In the temperature-programmed desorption (TPD) carbon monoxide desorbed in a single peak before 300°C. Some of the carbon monoxide, however, underwent disproportionation during TPD and a carbon dioxide peak appeared at about 220°C. Furthermore, carbon thus deposited on the surface was oxidized to carbon monoxide by oxygen supplied from the catalysts and gave a second peak of CO in TPD at temperatures higher than 300°C. Possible sources of the oxygen were discussed.

INTRODUCTION

The methanation of carbon monoxide has been extensively studied and a number of works published recently (*1–8*) indicates, at least on nickel catalyst, that the reaction occurs through carbon formed by the dissociation of carbon monoxide. When carbon monoxide alone is contacted with nickel catalysts, the disproportionation of CO (Boudouard reaction) takes place

$$2CO \rightleftharpoons C + CO_2.$$

Rostrup-Nielsen (*9*) reported that the equilibrium constant of the reaction varied depending on the crystallite size of nickel. Recently several investigators studied the disproportionation reaction mainly in connection with the methanation of carbon monoxide (*5, 7, 10, 11*). Further study is, however, necessary since the dissociation of CO could be the rate-determining step of methanation under certain conditions as discussed previously (*8*).

In the present report, the disproportionation of carbon monoxide was investigated on supported nickel catalysts by infrared spectroscopy and temperature-programmed desorption in an attempt to obtain more information on the reaction. Results were obtained mainly on a 5.5 wt% nickel supported on γ-alumina but some other catalysts were also compared.

EXPERIMENTAL METHODS

Apparatus. Two apparatus were used for the present study: One with a high-temperature infrared cell and the other with a sector-type mass spectrometer. Both apparatus have been described previously (*8*). Most of the temperature-programmed desorption (TPD) was carried out with the mass spectrometer system at a heating rate of 18°C/min by pumping the gas through the mass spectrometer, but some qualitative TPD was also done in the infrared cell with a small quadrupole mass spectrometer attached to the system.

Materials. Two different methods were used for the preparation of catalysts. One was the precipitation of basic nickel car-

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bonate on Alon alumina (Cabot Corp., Boston, Mass.) by adding an excess of sodium carbonate to a nickel nitrate solution in which the alumina was suspended. The precipitate was thoroughly washed with doubly distilled water. Two catalysts, 5.5 and 1.1 wt% Ni/Al_2O_3, were prepared by this method. The other method employed was the simple impregnation of support with a nickel nitrate solution. Another 5.5 wt% Ni/Al_2O_3 and a 4.8 wt% Ni/SiO_2 were thus prepared. The catalysts were either pressed into a disk for infrared spectroscopy or crushed to 9–16 mesh particles for TPD.

Before use all catalysts were reduced in the apparatus with hydrogen for 3 hr at 400°C and finally for 1 hr at 450°C. The catalysts were treated after each run with hydrogen at 400°C to remove carbon deposit. After this treatmet they were kept overnight with hydrogen newly introduced, but evacuated at 400°C before each run. The highest temperature of TPD was limited to 400°C except for one or two experiments done at the end of a series. By this procedure no serious sintering occurred as observed by the TPD of hydrogen carried out from time to time.

In preliminary experiments, TPD of carbon monoxide and hydrogen was examined with the alumina support. The amounts of gases adsorbed and desorbed in TPD were all negligible compared with those reported in this paper. Although all the catalysts were examined for comparison, the 5.5% Ni/Al_2O_3 precipitated with sodium carbonate was mainly used in the present study. Results reported in the following sections are those obtained with this catalyst unless otherwise stated.

Gases used were ultrahigh purity hydrogen (99.999%) and research grade carbon monoxide (99.99%), both supplied by Matheson of Canada.

RESULTS

1. Chemisorption and TPD of CO

Carbon monoxide adsorbed on the 5.5% Ni/Al_2O_3 catalyst at temperatures between room temperature and 200°C showed several ir absorption bands between 2400 and 1800 cm^{-1} as represented by spectrum a in Fig. 1. In agreement with the previous authors (*12–17*), the bands at 2030 and 1930 cm^{-1} are the most characteristic of carbon monoxide chemisorbed on nickel as they always appeared with adsorption. The band at 2250 cm^{-1} was observed only when the temperature was higher than 100°C and the pressure higher than 5 Torr (1 Torr = 133.3 N m^{-2}). At low temperature and high pressure, on the other hand, another band appeared at 2070 cm^{-1}. This band usually overlapped with the 2030 cm^{-1} band shifting the latter to higher frequency, but was removed by prolonged evacuation. The intensity of the 1850 cm^{-1} band increased with the temperature of adsorption.

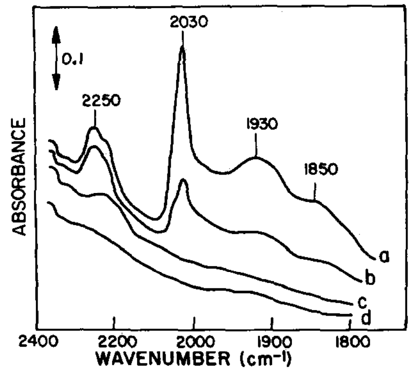

FIG. 1. Infrared spectra of carbon monoxide adsorbed on 5.5% Ni/Al_2O_3. Catalyst disk, 19 mm diameter, 73 mg. After adsorbing CO at 6 Torr and 150°C, spectra a to d were recorded during TPD as indicated by arrows in Fig. 2. Spectra b to d are displaced vertically for clarity.

Curve A in Fig. 2 shows a spectrum of TPD carried out in the infrared cell after adsorbing CO. Carbon monoxide was adsorbed for 1 hr at 6 Torr and 150°C, cooled to room temperature, and the gas was pumped out before TPD. As shown by curve A in Fig. 2, the first peak appeared at 240°C but the desorption of CO started increasing again after 300°C. The heating was stopped at 400°C so that the real peak maximum of the second peak was not

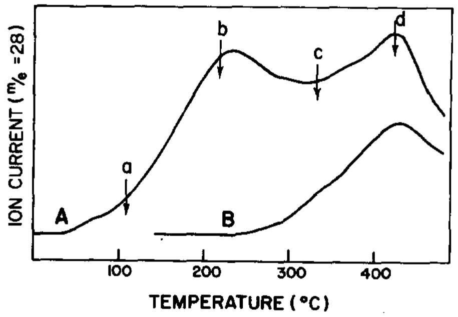

FIG. 2. TPD (in ir cell) of CO adsorbed on 5.5% Ni/Al$_2$O$_3$ (A) CO adsorbed at 6 Torr and 150°C and evacuated at 24°C. Small arrows indicate the start of ir scanning and corresponding spectra are shown in Fig. 1. (B) TPD after the disproportionation of CO and removal of CO$_2$ at 250°C.

known. Also detected but not shown in Fig. 2 was carbon dioxide which desorbed between the two peaks of CO. This matter will be discussed later in more detail. During the TPD infrared spectra were also recorded: The arrows a–d on curve A in Fig. 2 indicate the start of scanning and the corresponding spectra are shown in Fig. 1 with the same symbols. It is seen by comparing Figs. 1 and 2 that all ir bands except that at 2230 cm^{-1} disappeared by 350°C. Most of the 2250 cm^{-1} band was also removed at this temperature and only a weak band remained at 2230 cm^{-1}. Although only the 2400–1800 frequency range was shown in Fig. 1, no other bands were found in the entire range of 4000 to 1200 cm^{-1} scanned in the present work except for hydroxyl groups which did not change during the TPD. Also in another experiment in which CO was adsorbed at room temperature thus giving no band at 2250 cm^{-1}, all ir bands disappeared before 350° during TPD which also gave two peaks of CO similarly to curve A in Fig. 2. Therefore, carbon monoxide desorbed under the second peak of TPD must have come from a surface species which was not detected spectroscopically.

It should be noted here that the experimental conditions used for the TPD in the infrared cell were far from ideal: Heating in vacuum the catalyst disk of 19 mm diameter in a large bore of the cell caused a temperature gradient on the catalyst resulting in the broadening of the peaks. Moreover, the temperature shown in Fig. 2 was that of the furnace, and the real temperature of the catalyst could be considerably lower than the temperature of the furnace. As discussed above, the results of TPD nevertheless gave the useful information when they were compared with the spectroscopic results.

2. *Disproportionation of CO*

The present 5.5% nickel catalyst adsorbed up to about 4 × 10^{19} molecules/g of carbon monoxide almost instantaneously at room temperature giving two conspicuous ir bands at 2030 and 1930 cm^{-1} and a broad one at 1850 cm^{-1} similar to those shown by Fig. 1a. While these adsorption bands stayed unchanged at room temperature, the intensity of the bands decreased with time noticeably at temperatures higher than 100°C. All bands finally disappeared without giving rise to any new ir band in the frequency range used in the present study. At the same time, carbon dioxide was collected in a trap at -195°C connected to the cell, and its amount was always very close to half of the amount of carbon monoxide admitted to the system initially. Apparently, the disproportionation of carbon monoxide, $2CO \rightarrow C + CO_2$, took place stoichiometrically.

The bands at 1930 and 1850 cm^{-1} were so broad that their absorbance could not be measured accurately. However, the 1930 cm^{-1} band disappeared roughly at the same rate as that of the 2030 cm^{-1} band while perhaps the 1850 cm^{-1} band went slightly slower. In any case, the latter band was very weak compared to the other bands particularly when the amount of carbon monoxide adsorbed was small. Therefore, the rate of the consumption of carbon monoxide on the surface was examined by following the peak absorbance of the 2030 cm^{-1} band with time as shown in Fig. 3.

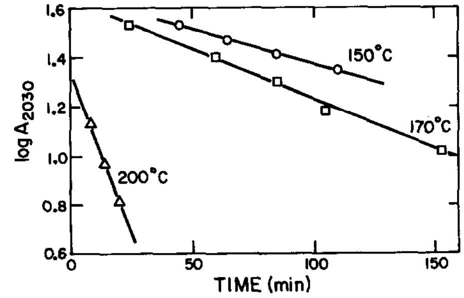

FIG. 3. First order plot of the peak absorbance of the 2030 cm^{-1} band during CO disproportionation.

Carbon dioxide formed was removed by the trap during the reaction and an initial portion of the time course where appreciable pressure of CO was present was omitted from the figure. As is clear in Fig. 3, the disproportionation reaction takes place without CO in the gas phase and proceeds as a first order reaction with respect to the surface concentration of carbon monoxide. The results indicate that the rate-determining step is the dissociation of CO on the surface. The rate constant was obtained from Fig. 3 as $k = 9.68 \times 10^3 \exp(-15400/RT)$ sec^{-1}.

While the reaction is of first order below 200°C as described above, the plot of the reciprocal of carbon monoxide pressure against time was found to be linear at 450°C. Therefore, the disproportionation reaction takes place as a second order reaction at high temperatures where the rate-determining step probably shifts to the surface combination of oxygen and carbon monoxide.

3. *TPD of Carbon Deposit*

A temperature-programmed desorption was carried out after the disproportionation of CO was completed at 250°C and carbon dioxide was removed from the surface. The TPD spectrum thus obtained is shown by curve B in Fig. 2. No ir bands due to the surface CO were detected before the TPD and the amount of CO_2 removed was half of the carbon monoxide admitted within experimental error. As seen in Fig. 2, the carbon deposited on the surface by the disproportionation desorbed as CO and the desorption pattern coincided with the second peak of spectrum A. Since the stoichiometric amount of CO_2 had been removed before TPD, the oxygen of the carbon monoxide desorbed under curve B in Fig. 2 must have come from the catalyst instead of the carbon monoxide introduced. When carbon monoxide is adsorbed at low temperature (curve A, Fig. 2), CO desorbs at relatively low temperatures under the first peak. Before all carbon monoxide desorbs, however, some disproportionation occurs as the temperature rises producing carbon dioxide and carbon. As the temperature rises still higher, the carbon thus deposited on the surface is oxidized to carbon monoxide which gives the second CO peak. As already pointed out, carbon dioxide desorbed between the two peaks of CO of curve A.

In some experiments $C^{18}O$ was adsorbed at room temperature. Carbon monoxide desorbed in the first peak of TPD subsequently carried out was almost exclusively $C^{18}O$, while the second peak of carbon monoxide consisted of more than 90% of $C^{16}O$. Although the exchange of oxygen occurs between carbon monoxide and alumina very slowly at high temperature (*18*), the large fraction of $C^{16}O$ found in the second peak supports the view that the catalyst oxygen oxidizes deposited carbon. Also high atom fractions of ^{18}O (up to 75%) were found in the carbon dioxide desorbed, but no definite conclusion could be drawn from this result since extremely fast exchange of oxygen takes place between carbon dioxide and alumina (*19*).

4. *Effect of Carbon Deposit on Disproportionation*

Figure 4a shows a TPD spectrum of carbon monoxide obtained with the mass spectrometer system. An amount of 0.201 g of the 5.5% Ni/Al_2O_3 catalyst was loaded in the inner tube of a trap-type reactor (*19*) and the temperature of the catalyst was

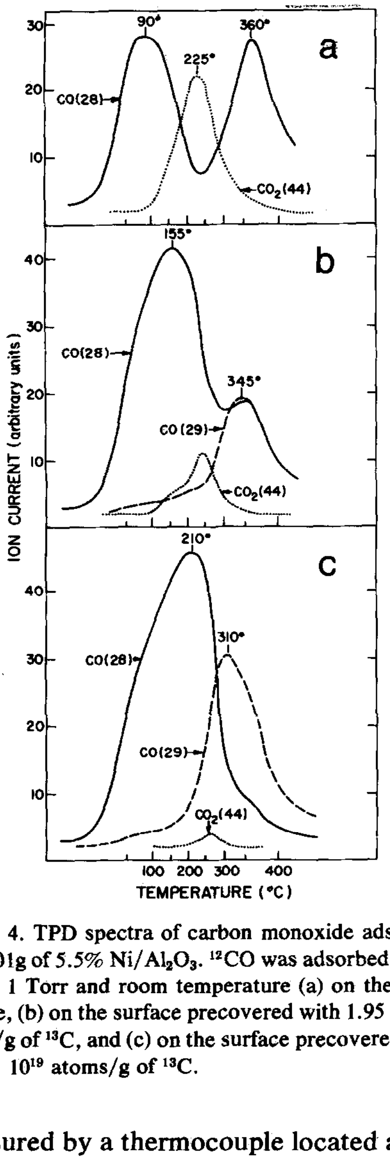

FIG. 4. TPD spectra of carbon monoxide adsorbed on 0.201g of 5.5% Ni/Al_2O_3. ^{12}CO was adsorbed for 30 min at 1 Torr and room temperature (a) on the fresh surface, (b) on the surface precovered with 1.95×10^{19} atoms/g of ^{13}C, and (c) on the surface precovered with 4.17×10^{19} atoms/g of ^{13}C.

measured by a thermocouple located at the center of the catalyst bed. Carbon monoxide was adsorbed at 1 Torr and room temperature and evacuated for 30 min at the same temperature before TPD. As seen in Fig. 4a, the TPD spectrum thus obtained was similar to that in Fig. 2 but with better resolution. As already mentioned, the CO_2 peak was formed by the disproportionation of CO and the second peak of CO appearing at about 360°C resulted from the oxidation of carbon deposit produced by the disproportionation. Again the heating was stopped at 400°C so that the second peak of CO could not be finished. In Fig. 4, the carbon monoxide peaks were corrected for the contribution of fragmental ions (m/e = 28) of carbon dioxide, but the correction for the difference in the sensitivity of detecting carbon monoxide and carbon dioxide was not made. Therefore, the real ratio of CO_2/CO is larger than it appears in Fig. 4.

In a series of experiments, various amounts of carbon were predeposited by the disproportionation of ^{13}CO. The reaction was carried out at increasing temperature up to 300°C and the amount of ^{13}C deposited was calculated from the $^{13}CO_2$ collected in a trap at −195°C. The amount of ^{13}CO left on the surface, if any, was negligible. ^{12}CO was then adsorbed under the same conditions employed for Fig. 4a and TPD was carried out. Some of the results thus obtained are shown in Figs. 4b and c where the peak of ^{13}CO (m/e = 29) resulting from the oxidation of the predeposited carbon increased with the amount of ^{13}C deposited as expected. On the other hand, the amount of $^{12}CO_2$ (m/e = 44) decreased sharply from a to c in Fig. 4 with increasing amount of ^{13}C. As a result, the amount of ^{12}CO desorbed under the first peak increased and the peak maximum shifted to higher temperature. The amount (area) of $^{12}CO_2$ desorbed was taken as an approximate measure of the reaction conversion and plotted in Fig. 5 as various functions of the surface coverage of ^{13}C predeposited. The surface coverage, θ_c, was calculated by dividing the amount of ^{13}C deposited by the monolayer amount of hydrogen (1.1×10^{20} atoms/g). Figure 5 shows clearly that a straight line was obtained against $(1 - \theta_c)^4$ rather than $(1 - \theta_c)$. The results indicate that the disproportionation of carbon monoxide requires an ensemble of several nickel atoms. The amount of $^{12}CO_2$ plotted was, however, a rough approximation since the reaction took place at varying temperature during TPD. Therefore, the results of Fig. 5 should not be interpreted to mean that the ensemble consists of four nickel atoms.

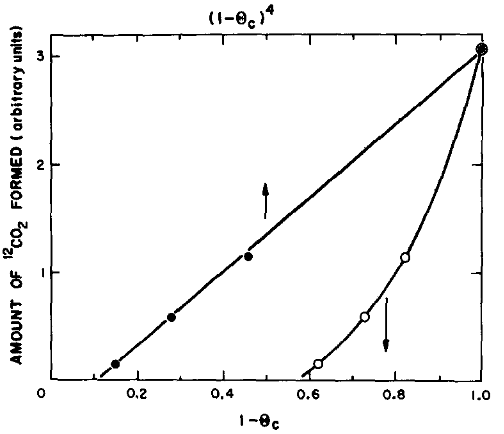

FIG. 5. Amount of $^{12}CO_2$ formed during TPD vs $(1-\theta_c)^n$.

Figure 6 shows infrared spectra observed with carbon monoxide adsorbed on the fresh surface (a) and on the surface precovered extensively with carbon deposit (b). It is seen that the bands at 2035 and 1930 cm^{-1} were greatly suppressed by the presence of carbon deposit and a new band appeared at 2065 cm^{-1}. The 2065 cm^{-1} band is probably due to carbon monoxide adsorbed in a linear form on nickel sites left sparsely after the deposition of carbon.

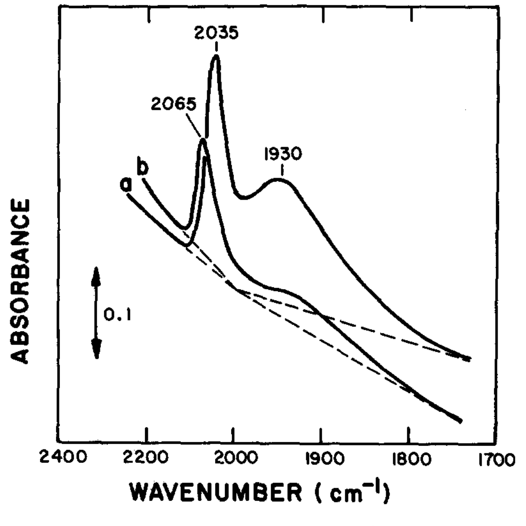

FIG. 6. ir spectra of carbon monoxide adsorbed at room temperature (a) on the fresh surface and (b) on the surface precovered extensively with carbon deposit. Catalyst 5.5% Ni/Al_2O_3.

5. *TPD of Carbon Monoxide on Other Catalysts*

As reported so far, a considerable fraction of carbon monoxide adsorbed on the 5.5% nickel catalyst underwent disproportionation during TPD. The disproportionation during TPD was, however, almost negligible on the 1.1% Ni/Al_2O_3 as demonstrated in Fig. 7 where the ratio of CO_2 to CO was much smaller than that in Fig. 4a. Although the second peak of carbon monoxide appeared before the CO_2 peak, this peak seems to be due to the oxidation of carbon since the TPD of carbon deposit showed a CO peak at the same temperature. Also when $C^{18}O$ was adsorbed, the carbon monoxide peak at 320°C was mostly $C^{16}O$.

The ir spectrum of carbon monoxide adsorbed on the 1.1% nickel catalyst at room temperature was similar to spectrum b in Fig. 6, namely, a band at 2065 cm^{-1} was the only band observed at low pressure indicating a high dispersion of the metal. The TPD of hydrogen also showed a dispersion of nickel of 34% compared to 19% on the 5.5% Ni/Al_2O_3 catalyst. The poor activity of this catalyst for the disproportionation reaction seems to be due to a high dispersion of the metal in agreement with the results shown in Fig. 5. The saturation of the 1.1% Ni/Al_2O_3 with hydrogen, however, required higher temperatures while

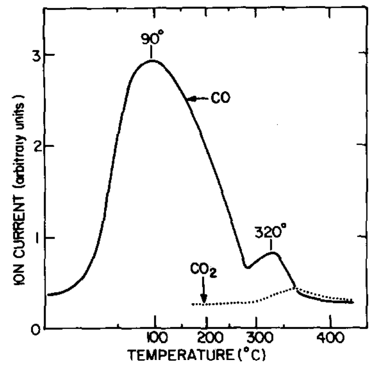

FIG. 7. TPD spectrum of carbon monoxide adsorbed on 0.248 g of 1.1% Ni/Al_2O_3. Carbon monoxide was adsorbed at 2.4 Torr and room temperature.

the 5.5% Ni/Al_2O_3 was almost saturated by hydrogen at room temperature. It is possible that the diluted nickel catalyst is more difficult to be reduced. In that case, too, the active sites would be more dispersed and the catalyst will show a poor activity for the disproportionation reaction.

Unreduced nickel oxide was thought to be the most likely source of oxygen which oxidized carbon deposit during TPD. Since there was the possibility that the sodium carbonate used in the preparation of the catalysts or the alumina support itself made it difficult to reduce the nickel, other nickel catalysts, 5.5 wt% Ni/Al_2O_3 and 4.8 wt% Ni/SiO_2, were examined. These catalysts were both prepared by impregnation as described in the Experimental section. Results obtained were essentially the same as those on the 5.5% Ni/Al_2O_3 precipitated with Na_2CO_3, that is, TPD spectra of carbon monoxide consisted of two peaks of CO and a peak of CO_2 appearing at almost the same temperatures as observed in Fig. 4a. Finally all catalysts used in the present study were reduced with hydrogen more extensively at 550°C, but there was no sign of reducing the second peak of CO.

DISCUSSION

The assignment of the ir bands is not the objective of this paper, nor is it possible at this stage. Nevertheless, we add some notes on the adsorption bands, particularly the 2250 cm^{-1} band observed in the present work. Carbon monoxide adsorbed on metal catalysts usually gives most conspicuous bands between 1900 and 2100 cm^{-1} but sometimes gives additional bands at higher frequencies. These bands appearing between 2100 and 2200 cm^{-1} were discussed in detail by Little (*20*). The highest frequency band was observed on the present 5.5% nickel catalyst at 2250 cm^{-1} which was beyond the above range and situated between the frequencies of gaseous carbon monoxide and carbon dioxide. Borello *et al.* (*21*) and Della Gatta *et al.* (*22*) found a band at 2240 cm^{-1} with carbon monoxide adsorbed on alumina at room temperature and the former authors assigned it to CO molecule adsorbed on tetrahedral Al^{+3} ions. However, this band appeared only when alumina was degassed at temperatures higher than 500°C and it was removed by evacuation rather easily. The present 2250 cm^{-1} band was formed above 100°C at high pressures of carbon monoxide but was removed only at high temperatures as already pointed out. The adsorption of carbon dioxide did not give this band nor did carbon monoxide on the oxidized catalyst. When hydrogen was present together with carbon monoxide (methanation reaction), no 2250 cm^{-1} band was observed despite much higher temperatures and CO pressures employed. The 2250 cm^{-1} band may be due to a species, O=C=O, formed by an interaction between adsorbed CO and oxygen atoms produced by the disproportionation. Similar species were considered first by Eischens and Pliskin (*23*) for a band observed at 2193 cm^{-1} during the oxidation of CO on a nickel catalyst. Actually the 2250 cm^{-1} band is a doublet as seen in Fig. 1 although the frequency split seems to be too small for the symmetric and asymmetric stretching vibrations. It is also unlikely that this species is an intermediate of the disproportionation reaction since this band is rather stable. Certainly, more information is necessary for a definite assignment.

For carbon monoxide adsorbed on metal catalysts, bands appearing above and below 2000 cm^{-1} have been usually assigned to CO adsorbed in linear and bridge forms, respectively, since the work of Eischens *et al.* (*24*) with few exceptions (*25*). Recently, Martin *et al.* (*11*) assigned a band at 1830 cm^{-1} observed with CO adsorbed on a nickel/silica catalyst to carbon monoxide bonded to four nickel atoms. However, no attempt will be made here to identify the bands observed in this work.

As described in the preceding sections, the disproportionation of carbon monoxide below 200°C was found to be of first order for the surface concentration of CO with an activation energy of 15 kcal/mole. The rate-determining step would be the dissociation of carbon monoxide as already pointed out. Tøttrup (*10*) also found on a 9.9 wt% Ni/Al_2O_3 catalyst that the rate was expressed between 280 and 400°C by a Langmuir–Hinshelwood equation derived by assuming that the dissociation of adsorbed carbon monoxide was the rate-determining step. The apparent activation energy found in his study was, however, 31 kcal/mole which apparently included the heat of adsorption of CO. The activation energy of the dissociation of CO, therefore, could be still greater. We cannot explain this large difference in the activation energy between the two studies at this moment. Martin *et al.* (*11*) investigated the dissociation of carbon monoxide by ir and saturation magnetization and postulated that CO adsorbed on nickel in linear and bridged form (2035 and 1935 cm^{-1}) were irreversibly transformed to Ni_4–CO (1830 cm^{-1}) before the dissociation. In the present experiments, however, all ir bands disappeared at similar rates as described earlier, and no clear selectivity toward dissociation was observed among the adsorbed species of CO during the reaction.

The results shown in Fig. 5 indicated that the dissociation of carbon monoxide requires an ensemble of several metal atoms as mentioned. Similar conclusion has been obtained by previous investigators (*1, 7, 11*). A poor activity of the 1.1% nickel catalyst for the disproportionation was also explained in terms of ensemble. This view was actually supported by the spectroscopic observation that the 2065 cm^{-1} band became predominant when the metal was poisoned by carbon or dispersed. Results obtained by Yates and Garland (*12*) also indicated the predominance of 2057 and 2082 cm^{-1} bands of CO when nickel was highly dispersed on alumina. Although the disproportionation of CO during the TPD on the 5.5% nickel catalyst was almost completely blocked by predeposited carbon at a concentration of 4.2 × 10^{19} atoms/g (Fig. 4c), much more carbon could be deposited when carbon monoxide was contacted with the catalyst at temperatures higher than 300°C. Probably carbon would become mobile on the surface at these temperatures and multisite centers are formed from place to place.

As seen in Fig. 4, the first peak of CO (*28*) became larger and the peak maximum shifted to higher temperature as the surface was blocked with larger amounts of carbon. This is due to the fact that, with carbon predeposited on the surface, more carbon monoxide molecules survive and desorb as CO at high temperature region of the first peak where CO would have otherwise dissociated into carbon. There is another factor to be considered for the shape of the peak: The metal sites would not be homogeneous and the disproportionation reaction should occur on high energy sites preferentially. The similarity of the peak temperature of the first peaks of Figs. 4a and 7 may indicate that the CO of the first peak of Fig. 4a desorbed mostly from highly dispersed nickel on which no disproportionation occurred. In any case, we will never see the complete peak of CO desorbed from the unpoisoned surface. The CO (*28*) peak in Fig. 4c was obtained almost without disproportionation, but about 40% of the metal surface was covered by carbon. Therefore, the CO peak *on the clean surface* would extend still higher temperatures.

The adsorption of carbon monoxide on unsupported nickel, single crystal, or polycrystalline has been studied extensively by the flash desorption technique (*26–30*). Those results mostly show that carbon monoxide desorbed in a single peak before 200°C when CO was adsorbed at room temperature. Recently carbon monoxide chemisorbed on supported nickel catalysts was investigated by using the technique of temperature-programmed desorption by Zagli *et al.* (*5*) and Wentrcek *et al.* (*31*).

Their results of TPD are in general agreement with those of the present work: Two peaks of carbon monoxide appeared in temperature regions similar to those in Fig. 4a. Zagli *et al.* also found that a large fraction of CO adsorbed underwent disproportionation during TPD, and that a second peak appeared at high temperatures after a CO_2 peak (*5*). While Wentrcek *et al.* (*31*) interpreted the two CO peaks as different states of adsorption, Zagli *et al.* suggested that the high temperature CO peak was likely due to carbon–oxygen recombination although they also pointed out the possibility that CaO and carbon in one of the supports or a component of kieselguhr used might be responsible for the CO peak desorbed above 600°C (*5*). The present results clearly demonstrated that the second peak of carbon monoxide appearing at high temperature in TPD resulted from the oxidation of carbon on the surface by oxygen supplied from the catalyst. Since the second peak did not finish in TPD, the total amount of the oxygen available was not measured. The oxidation reaction of carbon was rather slow below 400°C and only about 30% of carbon deposited on the surface was recovered as CO in the second CO peak of TPD.

The source of oxygen which oxidized carbon on the surface is not known definitely at this stage. There are a couple of possibilities: (1) Unreduced nickel oxide as already suggested; (2) A leak of air between runs; (3) The accumulation of moisture degassed from the walls of the apparatus; (4) Oxygen of alumina or support itself. These possibilities are discussed individually in the following.

(1) As described in 5 in the Results section, the comparison of various catalysts and the results obtained on the catalysts reduced extensively did not show any sign indicating that unreduced NiO played an important role in the oxidation of carbon. In a TPD of carbon monoxide, say in Fig. 4a, a minimum of 1×10^{19} oxygen atoms/g was desorbed in the second peak of CO. This amount of oxygen as NiO corresponds to about 2% of the total nickel in the 5.5% nickel catalyst, and at least a dozen of these TPD were repeated without decreasing the high temperature CO peak. Although the possibility of unreduced nickel cannot be excluded completely, it seems difficult to explain all the oxygen involved by the unreduced nickel alone.

(2) Although a small amount of leak could occur, the catalysts were kept with hydrogen and reduced with the hydrogen at 400°C before each run as described earlier. Moreover, if air leaked in overnight, it is likely that the surface nickel is oxidized preferentially. The same calculation used above shows that at least 10% of the nickel surface would have been oxidized before each experiment. Results of infrared spectroscopy did not indicate such a large fraction of oxide surface.

(3) The presence of moisture desorbed from the walls of the apparatus is rather possible. In fact, some weak ir bands were observed at 1590 and 1370 cm^{-1} as well as those due to chemisorbed CO when carbon monoxide was adsorbed at high temperatures. Similar bands were observed on alumina during the water–gas conversion reaction and ascribed to formate ion which was proved to be the intermediate of the reaction (*32*). Therefore, water seems to exist on the surface to some extent. The direct oxidation of nickel by water is again improbable, instead the water may be retained on the surface of the support mainly as hydroxyl groups.

(4) Oxygen atoms on the alumina surface are exchangeable with carbon dioxide and some of them are quite reactive (*19*). The Alon alumina used as a support in the present study was found to have similar exchangeable oxygen, the density of which was 1.2×10^{20}, 2.3×10^{20}, and 2.9×10^{20} atoms/g at 220, 350, 400°C, respectively (*33*). These oxygen may be involved in the oxidation of carbon particularly in the presence of nickel. Since hydroxyl groups are a part of the exchangeable oxygen (*18*), the moisture from the walls could replenish the

oxygen consumed. The determination of definite source of the oxygen, however, has to wait for further investigations.

Finally, it has been pointed out that some carbon monoxide might be adsorbed in a form which is infrared inactive, for example, CO lying horizontally on the surface (*17*). The present results showed that the stoichiometric amount of CO_2 was formed when all infrared bands due to chemisorbed CO disappeared, and the CO desorbed after that was due to the oxidation of carbon deposit. Therefore, it is unlikely that there was another form of chemisorption of CO which was not detected by infrared spectroscopy.

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