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Infrared Studies of Carbon Monoxide and Hydrogen Adsorbed on Silica-Supported Nickel Catalysts

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The interaction of CO and H_2 on silica-supported nickel was studied using infrared spectroscopy. The products occurring in the gas phase, as well as adsorbed CO spectra of the surface species in the frequency range 2300–1700 cm^{-1} for different order of addition of the two reactants was examined. It was found that: (i) CH_4 formation occurred at temperatures above 190 ± 5°C. (ii) A band attributed to linearly held adsorbed CO, at 2080 cm^{-1} when at room temperature, was correlated with CH_4 formation. (iii) Gaseous $Ni(CO)_4$ was formed at room temperature when only CO was present or providing the catalyst was pretreated with CO before the addition of H_2. (iv) A band which occurred at 2055 cm^{-1} was correlated with the formation of $Ni(CO)_4$. (v) Heating the system caused bands attributed to adsorbed CO to shift to lower frequencies. On cooling, the frequency shift occurred in the opposite direction but followed a different path. On further heating and cooling this shift became temperature reversible.

INTRODUCTION

The adsorption of CO and H_2, both individually and as mixtures, on various metals have been the subject of numerous investigations (*1–7*). In these, techniques such as infrared spectroscopy, thermal desorption, LEED and other methods have all been employed.

Eischens *et al.* (8) showed that CO adsorbed on silica-supported nickel gave rise to bands in the infrared at 2041 and 1908 cm^{-1}, and that these bands tended to broaden and shifted to lower frequencies when H_2 was admitted to the system. Similar observations have been made by others (*9, 10*).

The interaction of CO and H_2 on "potassium-promoted" and unpromoted silica-supported nickel catalysts was studied by Ferreira and Leisegang (*11, 16*). By varying the H_2:CO ratio they found that different reactions took place on the surface. At high ratios CH_4 was observed as the main product, whereas at low ratios CO_2 formation was predominant. The reaction mechanism for CH_4 formation was considered to involve "bridged" CO species only, and to proceed via a carbide or by oxygenated alcoholic-type surface intermediates. They also showed that gaseous $Ni(CO)_4$ was formed when CO was left in contact with the nickel surface for long periods, but stated that the reaction may not occur if the catalyst was at room temperature prior to the admission of CO. Very recently CO contained in an otherwise empty stainless steel infrared cell at pressures $\geqslant$50 Torr and at room temperature was shown to give rise to gaseous $Ni(CO)_4$ (*12*).

This paper reports further work on infrared studies of the adsorption and reaction of CO and H_2 with very finely crystalline Ni supported on silica, promoters being omitted. The objective was to investigate the effect of the regularly varying temperature on the adsorption and reaction of CO, alone and with H_2 present both (i) in the gas phase, and (ii) on the catalyst surface. Correlations between the results obtained from (i) and (ii) could then be made.

EXPERIMENTAL METHODS

A Perkin-Elmer model 180 double beam infrared spectrometer was used to measure carbon monoxide and its reaction products both in the gas phase and on the surfaces of Cab-O-Sil–silica-supported nickel catalyst, hereinafter referred to as the catalyst. In one mode of operation spectra were scanned and in the other given species were monitored in time and temperature at constant wavenumber. The slit width was set to correspond to a resolution of 2 cm^{-1}.

In order to follow the composition of reactant and product gases as a function of time, or as a function of time and temperature, a small Pyrex catalyst reactor, containing about 0.7 g of powdered material, was connected to a gas line and to a 10 cm path length infrared cell fitted with CaF_2 windows. The infrared cell was housed in the sample beam of the spectrometer. The reactor was enclosed in a furnace and its temperature could be raised smoothly to 400°C over a period of about 3 hr using a motor driven variable autotransformer. Measurable amounts of CO or H_2, one at a time or as a mixture, were admitted to the reactor and gas cell and infrared analysis was conducted in the following way. A background spectrum (4000–1000 cm^{-1}) was first recorded with the system evacuated. The spectrometer was then set to monitor $Ni(CO)_4$ at 2063.6 cm^{-1}. Gas was admitted and the system was allowed to reach equilibrium at room temperature for 1 hr. After this heating was commenced and either the $Ni(CO)_4$ monitoring continued or the spectrometer was set at 3017.5 cm^{-1} in order to monitor the ν_3 Q branch of CH_4. Once the reactor had reached 400°C the spectrum was recorded again over the whole range.

Secondly, the infrared spectra of the adsorbed species on a pressed catalyst disc were studied in the range 2300–1700 cm^{-1}. This was done using the *in situ* infrared cell described previously (*13*). The cell was connected to the same gas line and was similarly heated. A "blank" silica disc, held in an evacuated cell, was placed in the reference beam of the spectrometer in order to flatten the 100% transmittance line and to establish the more sensitive differential technique.

The background spectrum was first recorded with the cell at room temperature, gas was admitted and the spectrum was again recorded after standing for 1 hr. On those occasions when the cell was evacuated prior to heating, the spectrum was again recorded. During heating either the spectrum was taken at half hourly intervals or one of the three adsorbed species termed A, B, or C, at 1900, 2030, and 2056 cm^{-1}, respectively, was monitored.

Material to be used in the reactor was prepared by mixing silica with a nickel nitrate solution, drying and grinding into a fine powder. The nickel nitrate was decomposed to the oxide in the reactor by heating at 300°C for 4 hr, and then reduced to nickel in flowing hydrogen at the same temperature for up to 18 hr. These catalysts contained 5 wt% Ni.

It was noted that on pressing thin discs of diameter 25 mm and 0.2–0.3 mm thickness for the *in situ* infrared cell using the $Ni(NO_3)_2/SiO_2$ powder, they tended to crumble and had a mottled appearance indicative of inhomogeneity. Silica discs were therefore simply dipped into nickel nitrate solution of appropriate concentration (designed to yield 5–6 wt% Ni), dried, and decomposed and reduced *in situ* under the same conditions (times and temperatures) as for the reactor catalyst.

On reusing a catalyst sample it was first "cleaned" by evacuating at ⩾400°C for at least 0.5 hr. Carbon monoxide and hydrogen were admitted at room temperature in the pressure ranges: (i) 10–15 and 70–80 Torr, respectively, for the reactor experiments; and (ii) 1–2 and 10–15 Torr, respectively, for the *in situ* cell experiments.

RESULTS

1. Reactor Experiments

1.1 Admission of CO followed by H_2: The complete spectrum recorded after the reactor had reached 400°C is shown in Fig. 1. The bands at 2063.6 and 2024 cm^{-1} together with those at 3017.5 and 1305 cm^{-1} clearly indicate the presence of $Ni(CO)_4$ and CH_4, respectively. An increase in the amount of CO_2 is also shown by the increase in intensity of its ν_3 fundamental at 2350 cm^{-1}. A steady decrease in transmittance with time at a frequency of 2063.6 cm^{-1} was observed when the catalyst was allowed to stand in the presence of CO alone at room temperature, thus indicating the formation of $Ni(CO)_4$. The change in absorbance with temperature monitored at 3017.5 cm^{-1}, Fig. 2, shows clearly that no CH_4 was formed below 190 ± 5°C.

1.2 Admission of a CO/H_2 mixture: The spectrum taken when the reactor had reached 400°C showed that, although CH_4 had formed, none or very little $Ni(CO)_4$ and CO_2 had been produced. The absence of $Ni(CO)_4$ was confirmed by monitoring at 2063.6 cm^{-1} while the system was at room temperature for 1 hr. No decrease in transmittance was observed, contrary to that found in 1.1. Once again monitoring at 3017.5 cm^{-1} during heating demonstrated that CH_4 was formed only at temperatures above 190 ± 5°C.

Similar results were obtained when the system was pretreated with H_2 and allowed to stand at room temperature for 0.5 hr before CO was then admitted.

1.3. Admission of CO followed by evacuation for 10 min, and then addition of H_2: During the standing period after the admission of CO, $Ni(CO)_4$ was formed as previously found. Evacuation for 10 min removed this and the CO from the gas phase. After the addition of H_2 and heating

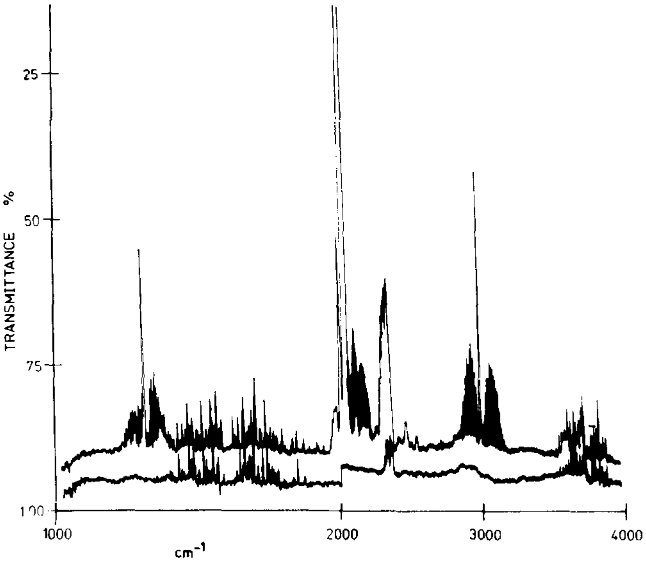

FIG. 1. Spectrum of products at 400°C from CO followed by H_2 adsorbed on Ni/SiO_2, with background offset.

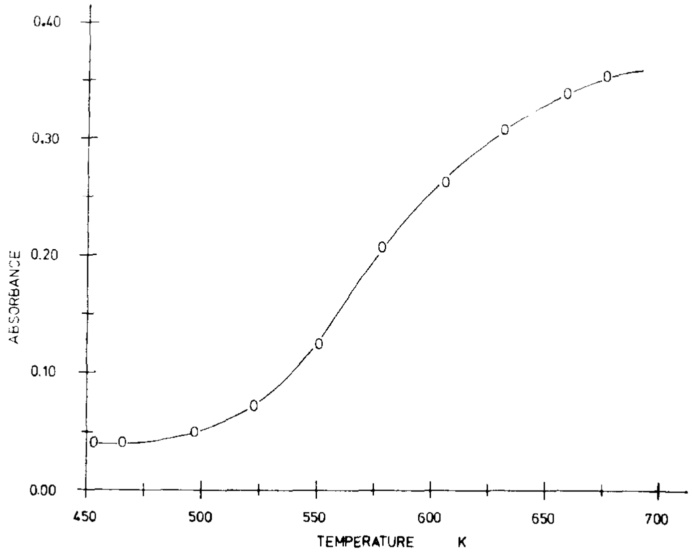

FIG. 2. Plot of absorbance as a function of temperature, at 3017.5 cm^{-1}, from the interaction of CO and H_2 on Ni/SiO_2.

to 400°C the complete spectrum showed CH_4 to be the only product.

1.4. With CO alone in the system: $Ni(CO)_4$ was formed as usual at room temperature and CO_2 during the heating process. The formation of CO_2 was observed by the increasing intensity of its band at 2334.2 cm^{-1} which was monitored during heating. The spectrum taken at 400°C showed that no other species was formed.

1.5. Admission of a CO/H_2 mixture to the reactor when at 430°C: CH_4 was formed from the moment of addition of the gas mixture.

1.6. $Ni(CO)_4$ heated together with H_2 and CO but in the absence of catalyst: This experiment was done to see if $Ni(CO)_4$ had any effect on CH_4 production, and also to investigate the effect of high temperatures on $Ni(CO)_4$. $Ni(CO)_4$ was produced in the reactor by allowing CO to come into contact with the catalyst at room temperature in the absence of H_2. After this, the gas cell containing $Ni(CO)_4$ and CO was then isolated from the reactor by closing the stopcock between them. H_2 was then added to the contents of the gas cell and this cell was heated in the usual way. The band at 2063.6 cm^{-1} which was monitored throughout this experiment showed that decomposition of $Ni(CO)_4$ occurred over the range 150–195°C, Fig. 3. Comparison of the spectra taken at 25 and at 400°C showed the disappearance of the $Ni(CO)_4$ bands at 400°C, but an appreciable increase in the amount of CO at this temperature as compared to that observed at 25°C. No CH_4 was detected.

2. *In situ* Cell Experiments

2.1. Adsorbed CO on a Ni/SiO_2 surface at room temperature gave rise to a very strong broad band in the frequency range 2090–2050 cm^{-1}. Two maxima were observed at 2080 and 2055 ± 2 cm^{-1}, and classified as bands B and C, respectively. A medium very broad band, classified as band A, was also given with its maximum in the region 1925–1935 cm^{-1}. These absorptions agree well with the observations of Ferreira and Leisegang (*16*).

The above was only observed when either CO alone was admitted to the catalyst or alternatively CO was allowed to stand in contact with the catalyst for 1 hr followed

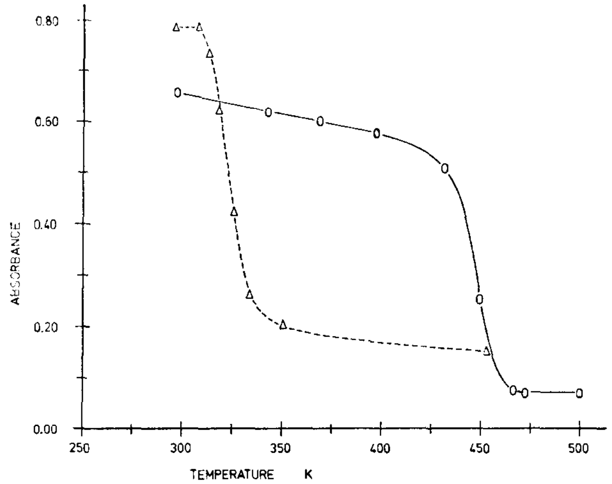

FIG. 3. Plot of absorbance as a function of temperature at 2063.6 cm^{-1} (——); at 2056 cm^{-1} due to adsorbed CO on Ni/SiO_2 (– – –).

by the admission of H_2. However, at room temperature, on pretreatment with H_2 followed by CO or on admission of a CO/H_2 mixture, only band B was observed in the region above 2000 cm^{-1}. This appeared as a strong but narrower absorption with its maximum at 2074 ± 2 cm^{-1}. Band A occurred as before in the range 1925–1935 cm^{-1}.

During heating, after CO pretreatment followed by H_2 or on admission of CO alone only one peak was observed in the region above 2000 cm^{-1} instead of two. Thus at 100°C the only peak given in this region was at 2065 cm^{-1}. On further heating this peak shifted to lower frequencies as the temperature increased. Band B similarly shifted to lower frequencies for those systems in which the catalyst had been pretreated with H_2 and then CO admitted or on treatment with a CO/H_2 mixture. This effect is shown in Fig. 4. The band shifts and reduction in band intensities at elevated temperatures are clearly shown.

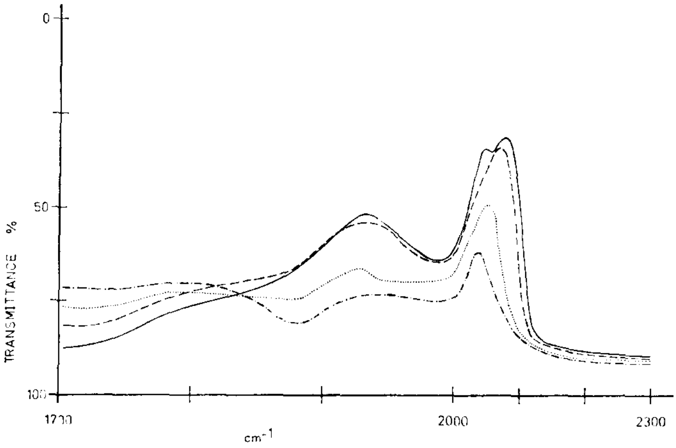

FIG. 4. Spectra of CO adsorbed on Ni/SiO_2 during heating: (——) room temperature; (– – –) 110°C; (····) 260°C; (·–) 375°C.

Generally the shifts observed for band B were as given in Fig. 5. Band A was also seen to shift to lower frequencies as the temperature increased; however, accurate measurements could not be made due to the general very broad appearance of the band.

2.2. Evacuation of each system for 10 min, at room temperature and prior to heating the catalyst, had the following effect. With CO alone or on CO pretreatment followed by H_2 the spectrum recorded after evacuation showed only one peak in the range above 2000 cm^{-1} instead of two. This had its maximum at 2074 cm^{-1}. The effect is shown in Fig. 6 and is similar to that of heating to 100°C (2.1; Fig. 4). With H_2 followed by CO, or with a CO/H_2 mixture the spectrum recorded after evacuation showed that band B had shifted by approximately 6 cm^{-1} to lower frequencies and also decreased slightly in intensity, Fig. 7. Evacuation at room temperature for longer periods up to 1.5 hr had very little further effect on the spectra.

After evacuation and the addition of a further aliquot of H_2 the heating program was commenced. Results of monitoring at 2030 cm^{-1} are given in Fig. 8. The frequency of 2030 cm^{-1} was chosen to demonstrate the effect of temperature on band B in the CH_4 formation temperature range, viz, 190°C. This frequency was possibly a little low but the effect as shown

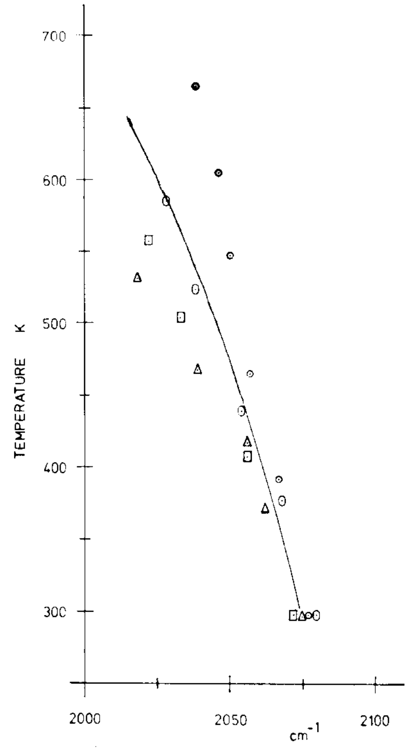

FIG. 5. Plot of band B frequency as a function of temperature: (0) CO followed by H_2; (△) CO/H_2 mixture; (□) H_2 followed by CO; (○) CO alone. The line drawn indicates the general trend (see text).

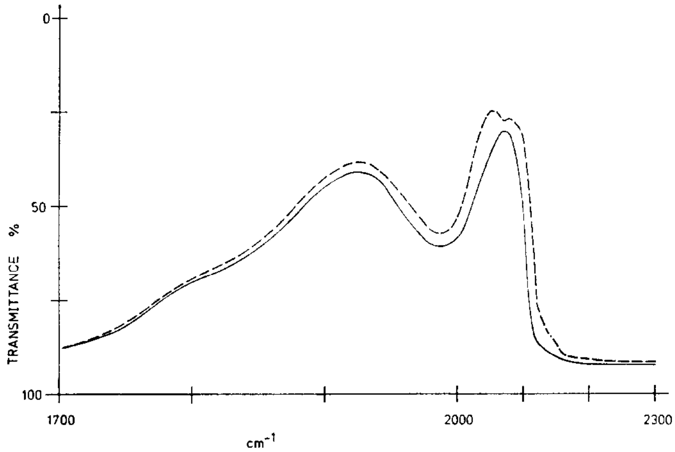

FIG. 6. Effect of evacuation on the spectrum for CO adsorbed on Ni/SiO_2: (- -) before evacuation; (——) after evacuation.

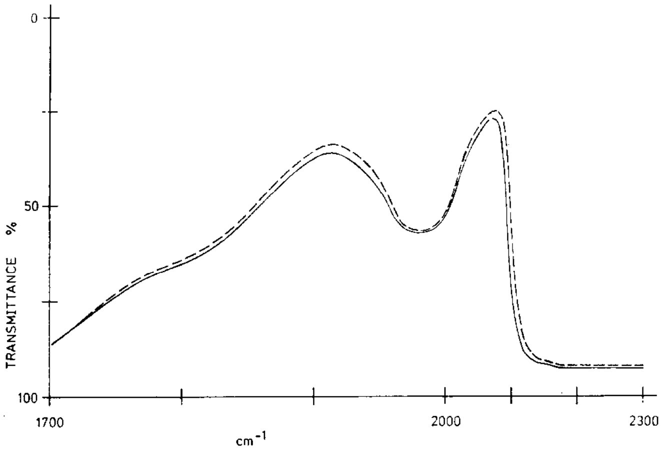

FIG. 7. Effect of evacuation on the spectrum for a CO/H_2 mixture adsorbed on Ni/SiO_2: (- -) before evacuation, (——) after evacuation.

in Fig. 8 was very marked. There was a very sharp decrease in absorbance, which occurred at approximately 190°C in all cases in which CO and excess H_2 were simultaneously present, but which did not occur when only CO was present.

2.3. The effect of heating on band C^- at 2056 cm^{-1}, for the system CO alone is shown in Fig. 3. A substantial decrease in absorbance occurred in the temperature range 35–80°C. Adsorbed CO giving rise to band A, at 1900 cm^{-1}, was firmly held onto the surface and only at temperatures $\geqslant 230°C$ did this band decrease in intensity.

2.4. Another phenomenon observed was that of aging and/or sintering of the catalyst. After repeated use during which the catalyst was often subjected to temperatures in excess of 400°C (necessitated for cleaning the samples, 400–420°C), the high wavenumber bands at 2080 and 2055 cm^{-1}, 2.1, were replaced by a set of four bands, Fig. 9. Well defined maxima were given at 2063 and 2055 cm^{-1} usually with

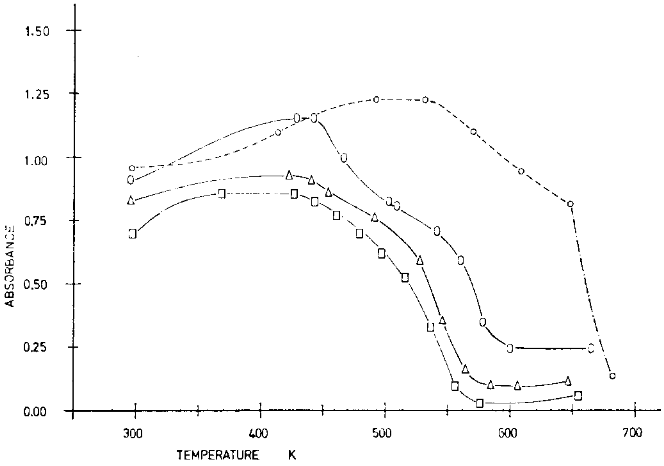

FIG. 8. Plots of absorbance as a function of temperature at 2030 cm^{-1}: (△) CO followed by H_2; (□) a CO/H_2 mixture; (0) H_2 followed by CO; (○ - -) CO alone; (-·) CO alone during evacuation.

shoulders at 2075 and 2051 cm^{-1}. This characteristic was also observed with CO adsorbed on catalysts having a lower nickel content, about 3 wt%. The four bands disappeared either on evacuating the system for 10 min or on heating at 120°C for 1 hr after which one band only was observed, less intense than the others, and occurring in the region 2065–2062 cm^{-1}. The aging/sintering effect is also illustrated in Fig. 8 in which the three full line plots refer to the same catalyst sample. Here the absorbance decreased with age of sample.

2.5. Finally the effect of a heating/cooling procedure was investigated for which only CO was admitted to the catalyst. The system was heated slowly in the usual manner up to 400°C, and then cooled slowly back to room temperature. The position of band B was measured at various temperatures by recording the spectrum frequently and the result is given in Fig. 10. On returning to room temperature only one band and not two occurred at higher frequencies, cf. 2.1. A similar experiment was conducted whereby the CO was admitted when the catalyst was at >400°C. The system was slowly cooled as before, and the position of B was again measured. The result was similar to that given for the cooling curve, Fig. 10. When at room temperature, the system was evacuated for 1 hr and the spectrum then was recorded. No decrease in intensity of band B was observed nor was there a frequency shift. After that the system was heated once more. The shift observed for band B as the temperature increased followed the same curve as was obtained when the system was cooled from the highest to the lowest temperature, Fig. 10.

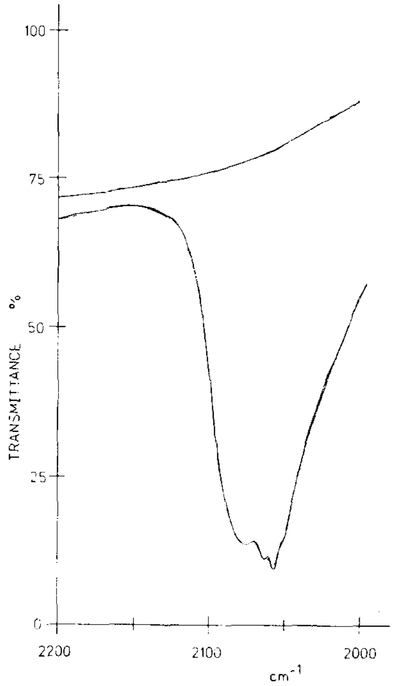

Fig. 9. Spectrum of CO adsorbed on an aged/sintered Ni/SiO_2 disc.

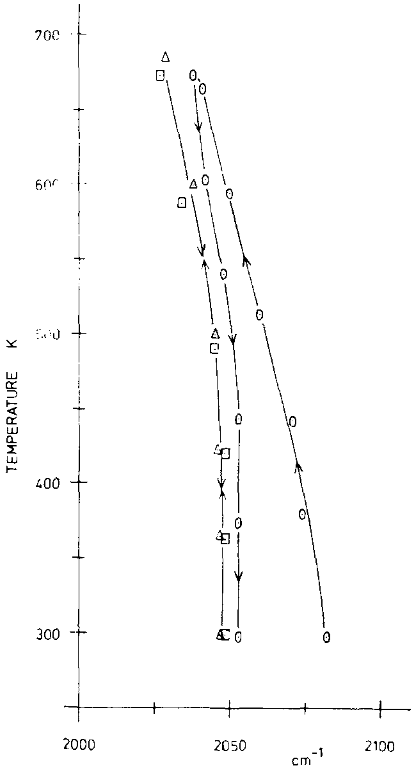

Fig. 10. Plot of band B frequency as a function of temperature for CO adsorbed on Ni/SiO_2: (0) during a heating/cooling cycle; (△) during cooling; and after evacuation (□) on reheating.

DISCUSSION

It has been generally accepted that bridged CO groups, strongly held onto the catalyst surface, give rise to bands at lower frequencies than terminal groups which are less firmly held *(11, 14, 15)*. For nickel catalysts bands below about 2000 cm^{-1} are thus assigned to bridged carbonyls and do not readily disappear on evacuation or heating. In contrast, bands above 2000 cm^{-1}, assigned to terminal groups, are more sensitive to evacuation and heating. Result 2.3 demonstrates this.

Furthermore, the multiplicity of the band structure above 2000 cm^{-1} has been ascribed to variations in crystallinity of the adsorbent *(17–19)*. The carbon-to-metal π bond, which involves the sharing of electrons between a filled $d\pi$ or hybrid $dp\pi$ metal orbital and an empty $p\pi$ (antibonding) orbital of CO, strongly influences the chromophore relative to the σ bond formed between a filled carbon σ orbital and an empty metal σ orbital. As the π character of the metal-to-carbon bond increases, so the bond order of the carbon-to-oxygen bond decreases, which results in a lowering of the CO stretching frequency. Therefore CO adsorbed on metal sites rich in *d* electron density, i.e., edges, corners or sites in crystallographic planes of low coordination number, form a stronger metal-to-carbon bond and give rise to bands at lower frequencies than when adsorbed on sites of high coordination number.

It has been shown by the results that when CO alone or CO followed by H_2 is allowed to contact the surface there occur two main bands in the range above 2000 cm^{-1}, viz, a band at 2080 cm^{-1} and one at 2055 cm^{-1} (result 2.1). The band at 2055 cm^{-1} (band C) does not occur when H_2 is first admitted to the system or when a CO/H_2 mixture is used. Nor under these latter conditions is $Ni(CO)_4$ observed to form (result 1.2). It was also observed that this band was easily removed by evacuation or by heating (results 2.2, 2.3, Figs. 3 and 6). Thus it was concluded that band C must be due to a species which is less firmly bound than is the species which gives rise to band B at 2080 cm^{-1}. It also seems very likely that band C is involved in gaseous $Ni(CO)_4$ formation. The fact that this band is less firmly held than B at 2080 cm^{-1} is contrary to the usual correlation of more strongly held species exhibiting lower frequency; this is indicative that the species which gives rise to band C is not merely CO adsorbed but possibly tending to adsorbed $Ni(CO)_4$. Thus the presence of H_2 in the system prior to the admission of CO blocks those sites on which adsorbed $Ni(CO)_4$ and/or its precursors can be held and thus prevents its formation.

In addition, during a heating/cooling procedure or on admission of CO to the heated catalyst followed by cooling, only one band was observed to occur in the range above 2000 cm^{-1}. This came close to 2053 cm^{-1}, Fig. 10, but its properties were different from those of the original band (C) at 2055 cm^{-1}. Thus, it was not easily removed by evacuation or on heating (result 2.5); instead its frequency merely decreased systematically with increasing temperature with a much smaller rate of decrease in intensity than shown by band C. The heating/cooling experiments can be interpreted in terms of CO being adsorbed at room temperature only on sites of low heat of adsorption and low activation energy. At higher temperatures sites of high heat of adsorption and high activation energy become available and thus the band frequencies decrease, possibly because as the species are more firmly held the stronger metal-to-carbon bond gives rise to bands at lower frequencies. On cooling, the distribution obtained at the higher temperature persists, i.e., the CO becomes "frozen" such that the band observed on returning to room temperature will occur at a lower frequency. Also the frequency shifts on further heating and cooling will be temperature reversible as observed in Fig. 10.

This redistribution of CO on the surface after the heating/cooling treatment seems to be such that the sites which when initially at room temperature were occupied by adsorbed $Ni(CO)_4$ become occupied by adsorbed CO which thus blocks the readsorption of $Ni(CO)_4$ as such. An experiment which has not yet been performed to confirm this would be to add CO at an elevated temperature to the catalyst contained in the reactor, cool the system to room temperature and then examine the gas phase for the presence of $Ni(CO)_4$. None, or very little should be formed.

The major product formed by the interaction of adsorbed CO and H_2 on Ni was CH_4. Its formation as demonstrated by results 1.1 and 1.2 and shown by Fig. 2 only occurred at temperatures above 190 ±5°C, but was still produced, albeit in limited quantities, at temperatures $\geqslant 430$°C (result 1.5).

Strong evidence for the surface species involved in CH_4 formation is obtained from the *in situ* cell experiments. The rapid decrease in absorbance at ±190°C in the absorbance–temperature curve, Fig. 8, on heating systems containing both CO and excess H_2, and the absence of such a decrease in the system containing only CO, indicates that band B, i.e., terminal CO species, is involved in CH_4 formation, contrary to the findings of others (*11*, *16*).

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