

실리카 지지 전이원소 금속촉매의 일산화탄소 흡착에 미치는 알칼리 촉진제의 영향

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Effect of Alkali Promoter on the CO Adsorption of Silica Supported Transition Metal Catalysts

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요 약. 실리카지지 전이금속 촉매에 의한 일산화탄소의 화학흡착에 있어서 알칼리 촉진제의 효과를 조사하기 위하여 실리카지지 니켈을 칼륨으로 입힌 경우와 입히지 않은 경우 니켈에 화학흡착된 일산화탄소의 적외선 스펙트럼을 $1800\sim 2100\text{cm}^{-1}$ 영역에 걸쳐 여러가지 니켈농도와 일산화 탄소 압력하에서 조사하였다. 칼륨을 입히지 않은 계의 경우에는 적외선 흡수띠의 세기가 니켈 농도에 크게 좌우되지만 띠의 위치는 거의 영향을 받지 않는다. 또한 물리흡착된 $\text{Ni}(\text{CO})_4$ 에 의한 2057cm^{-1} 띠도 확인되었다. 아울러 일산화탄소의 화학흡착에 대한 온도의 효과도 조사하였다. 칼륨을 입혔을 경우 일산화탄소의 적외선 스펙트럼의 흡수띠가 $2\sim 10\text{cm}^{-1}$ 정도 장파장 쪽으로 이동하고 $\text{Ni}(\text{CO})_4$ 의 형성이 억제되며 니켈표면 위에서 불균화반응 ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$)이 일어날 수 있음을 확인하였다.

ABSTRACT. In order to elucidate the effect of alkali promoter on chemisorption of carbon monoxide on silica supported transition metal catalysts we have investigated the infrared spectra for carbon monoxide chemisorbed on silica supported nickel with and without potassium coating within the frequency range of $1800\sim 2100\text{cm}^{-1}$ at various nickel concentrations and CO pressures. For the system without potassium coating the IR band intensities are found to greatly depend on the nickel concentration although the band positions are scarcely affected. The band positions are nearly coincident with those reported by other people, but we have clarified that the 2057cm^{-1} band arises from $\text{Ni}(\text{CO})_4$ molecules physisorbed on silicagel. Besides this, the effect of temperature on CO chemisorption has also been investigated. On coating with potassium we have found that all the bands observed for the system without potassium coating suffer red shifts by $2\sim 10\text{cm}^{-1}$ and the formation of $\text{Ni}(\text{CO})_4$ is inhibited. Furthermore, we have recognized that on the nickel surface with potassium coating a disproportionation may occur to yield carbon dioxide molecules.

INTRODUCTION

It is common that catalysts of industrial

importance contain transition metals or their compounds. For example, nickel and iron are being used as the reaction catalyst for the Fischer-Tropsch synthesis, and basic and applied researches for these catalysts are considered

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to be very important from the standpoint of efficient utilization of energy and natural resources.

In the Fischer-Tropsch reaction the first step is considered to be the chemisorption of carbon monoxide on metal surface and in the next step thus adsorbed CO is to react with H_2 . For investigation of chemisorption phenomena several techniques such as IR, ESCA, EELS, LEED, AES, TPD, electron microscope, work function measurements are being used. Among them the IR method is regarded as a powerful tool in that it can give direct informations about the change of nature of chemical bonds occurring in the chemisorbed molecules.

Since Eischens *et al.*¹ first observed the IR spectra of carbon monoxide chemisorbed on nickel surface, a great deal of investigations has been carried out by O'Neill,² Yates,³ Garland,^{4,5} Blyholder,⁶ and many others.⁷⁻¹¹ The carbonyl stretching vibration in gaseous carbon monoxide occurs at 2143cm^{-1} ; however, when the carbon monoxide gas is chemisorbed on transition metal surface, one can observe a band at $2000\sim 2100\text{cm}^{-1}$ and a few more below 2000cm^{-1} . There have been some controversies over the origin of these bands. O'Neill and Yates² have discussed the origin of these bands in terms of linear and bridge bonded structure of CO. However, such reasoning has been denied by Blyholder¹² who has shown that, for example, the bands at 1940cm^{-1} and 2080cm^{-1} observed for the CO gas chemisorbed on nickel surface resulted from linear forms of chemisorbed CO on two different types of metal sites. Blyholder's view rather supports the assumption by Eischens and Pliskin¹³ that infrared bands assigned to the stretching mode of CO above 2000cm^{-1} are due to CO adsorbed on centers of high surface coordination while those at wave numbers below 2000cm^{-1} originate from

CO adsorbed on surface centers of low surface coordination. Such view is nowadays generally accepted as a correct one and it is also believed that CO adsorbed on centers of low surface coordination is generally more tightly bound to the metal due to increased back donation from the *d*-orbitals of the metal into the antibonding π^* orbitals of CO.¹⁴

It is also known that coating of the surface of Ni or Fe by small amounts of alkali metals such as K, Na, Cs *etc.* enhances the formation of long chain hydrocarbons in the Fischer-Tropsch synthesis.¹⁵⁻¹⁹ Such promoter effect has mostly been studied by making use of single crystals or thin films of metals of interest,^{20,21} but to the knowledge of present authors not much investigation has been performed using supported metals due to the complexity of the latter systems.

In this research we have investigated the IR spectra of adsorbed CO as a function of w/w percentage of Ni in silica supported Ni, CO pressure and temperature of the system, respectively, to understand the nature of chemical bond in adsorbed CO as well as the chemical state of nickel on the surface of supporting material. We have also observed the change in the IR spectra of CO when the surface of silica supported Ni is covered with potassium as a function of CO pressure to gain some insight into how the chemical bonds in this system is affected by the addition of alkali promoters.

EXPERIMENTAL

To prepare the adsorbent an adequate amount of $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chem. Co., Reagent Grade) was dissolved in distilled water and silicagel (HDK Wacker N 20, BET surface area $200\text{m}^2/\text{g}$) was added to it so that a thin slurry was produced. The resulting

slurry was stirred until a homogeneous mixture was obtained. This then was dried at 80~90°C for 72 hrs. and was grounded to a fine consistency using an agate mortar and pestle. After grinding, 30~40mg of the sample was pressed into a pellet, 2cm in diameter, using a pressure of 400kg/cm². This pellet was then reduced at 400°C for 10hrs. under the stream of H₂. After the reduction process was completed the sample was cooled in a hydrogen atmosphere and then evacuated. After this was accomplished, the sample was placed in a cell connected to the vacuum system and adsorption experiment was performed.

For covering the sample with a thin coat of potassium we had the carrier gas (Ar) flow over the metallic potassium in a pot heated at 350~370°C to reach the sample pellet.

The amount of potassium coated over the sample was later analyzed by a conventional wet analysis method and by the atomic absorption spectrophotometry. Hydrogen gas used in this experiment was a domestic product of 99.99 % in purity and the CO gas was purchased from the Matheson Gas Products Co., a product of 99.95% in purity. These gases were used without further purification.

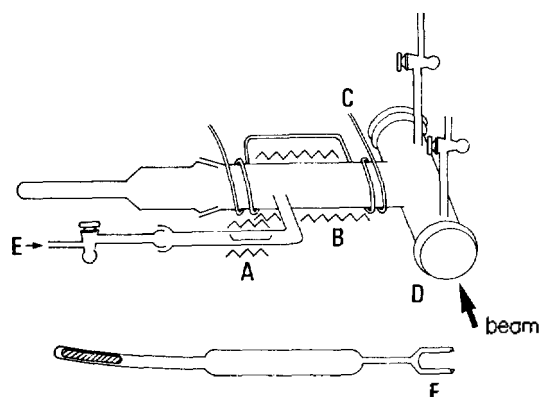


Fig. 1. Cell for infrared study. A alkali metal evaporator, B heating coil, C cooling coil, D KBr window, E carrier gas, F sample supporter.

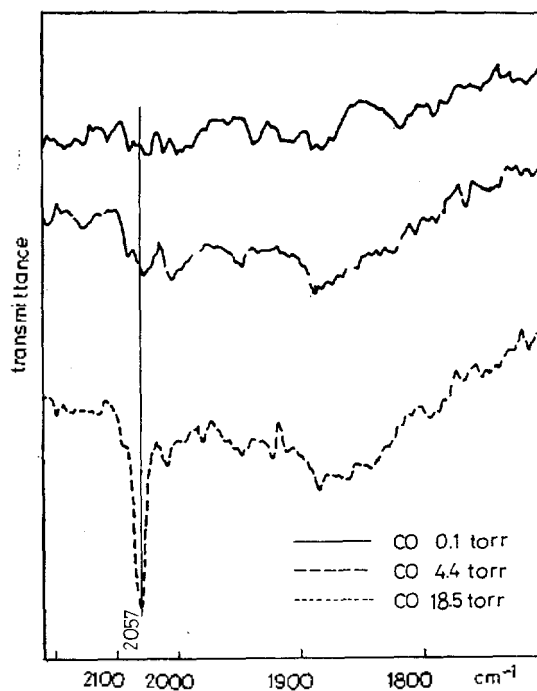


Fig. 2. IR spectra of increasing CO on 3% Ni sample at 20°C.

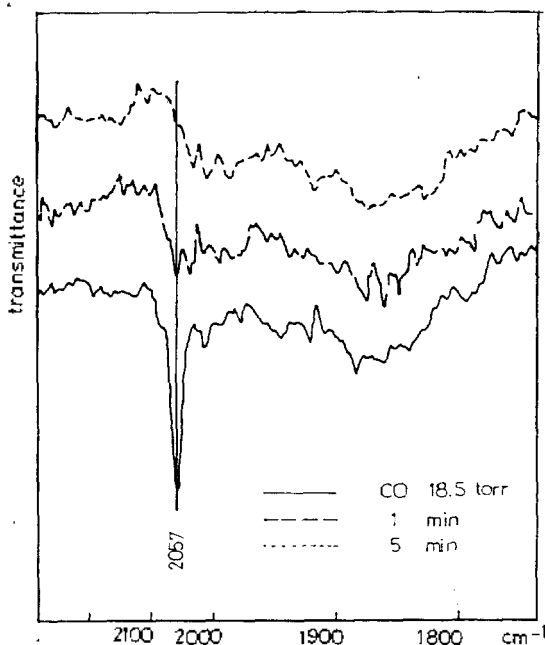


Fig. 3. IR spectra for 3% Ni sample after pumping.

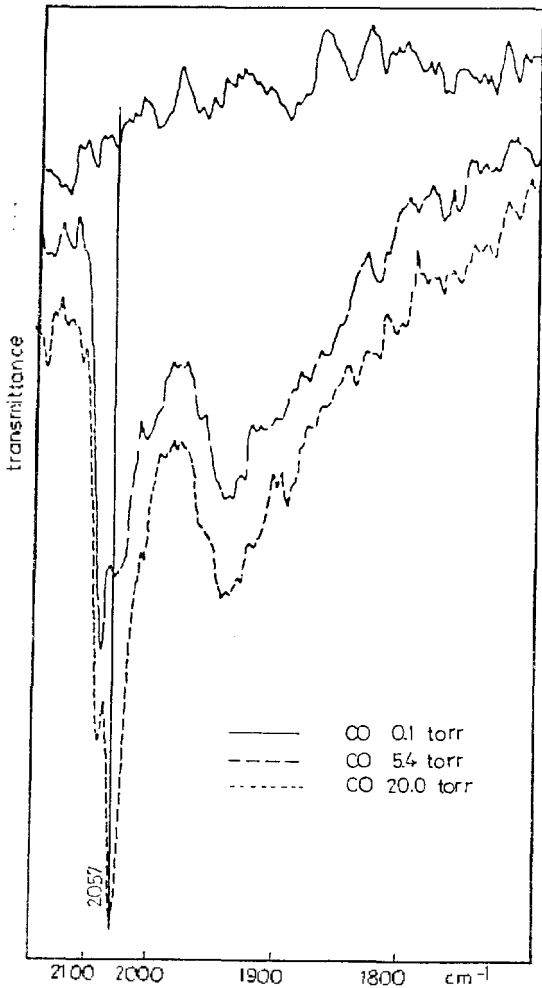


Fig. 4. IR spectra of increasing CO on 6% Ni sample at 20°C.

All the IR spectra were taken on a Perkin-Elmer Model 283 double beam infrared spectrophotometer using an *in situ* cell shown in Fig. 1. To obtain the IR spectra we have used the so-called differential technique in which a replica of the sample pellet was employed as a filter for the reference beam.

RESULTS

(A) Adsorption of CO on Silica-Supported Nickel Without Potassium Coating.

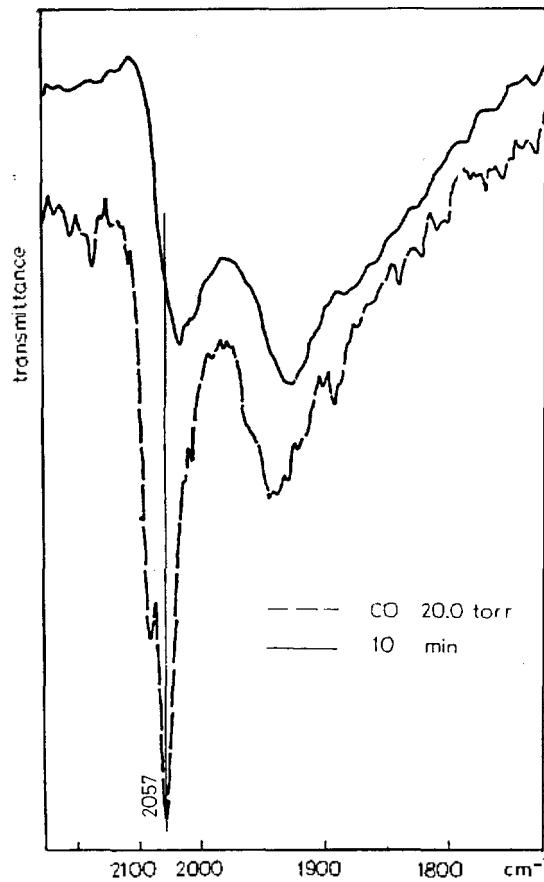


Fig. 5. IR spectra for 6% Ni sample after pumping.

Shown in Fig. 2 through Fig. 11 are the IR spectra taken at 20°C under varying CO pressure using the sample of several different Ni contents. Also shown in the same figures are those IR spectra obtained when pumped to vacuum (10^{-5} torr). In Fig. 12 the IR spectra for 9.5% Ni sample obtained at 20, 90, and 140°C under the CO pressure of 0.7 torr are shown. Fig. 13 shows us the IR spectra for $\text{Ni}(\text{CO})_4$ adsorbed on silicagel at various temperatures.

As shown in Figs. 2, 4, 6, 8, and 10, when the CO pressure is low three bands above 2000cm^{-1} (2080, 2057 and 2032cm^{-1}) can be observed for all the Ni contents investigated.

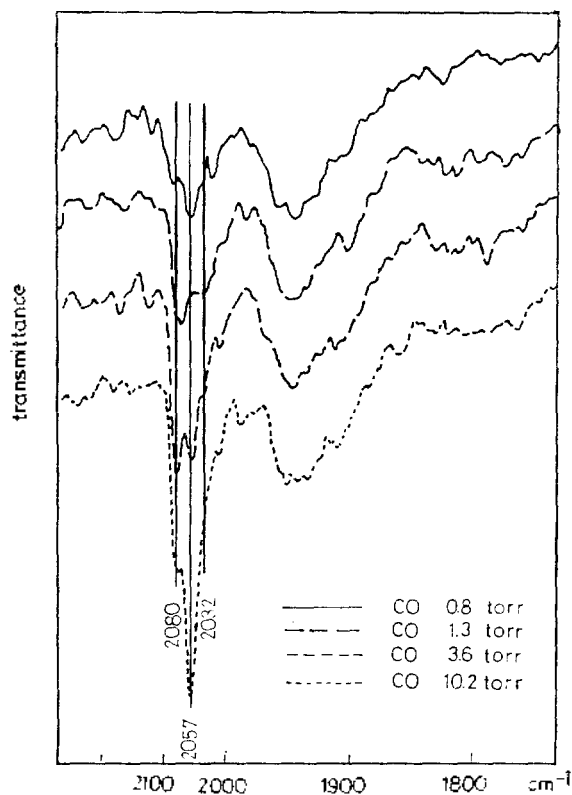


Fig. 6. IR spectra of increasing CO on 9.5% Ni sample at 20°C.

As the CO pressure increases, both of the bands at 2080 and 2057 cm^{-1} grow in intensity, but at higher pressure 2057 cm^{-1} band outgrows the 2080 cm^{-1} band gradually. Nickel content does not appear to give any noticeable effect on the positions of observed bands.

Below 2000 cm^{-1} there appear two bands at 1955 and 1925 cm^{-1} , respectively, and as the CO pressure goes up, the relative intensity of the latter band decreases until a collapsed broad band peaked near 1955 cm^{-1} is formed.

When pumped to vacuum, it is found that above 2000 cm^{-1} two bands at 2080 and 2057 cm^{-1} gradually disappear, leaving the 2032 cm^{-1} band alone. Below 2000 cm^{-1} the broad band at 1955 cm^{-1} gradually changes to a band at 1925 cm^{-1} .

From Fig. 13 one can see that $\text{Ni}(\text{CO})_4$

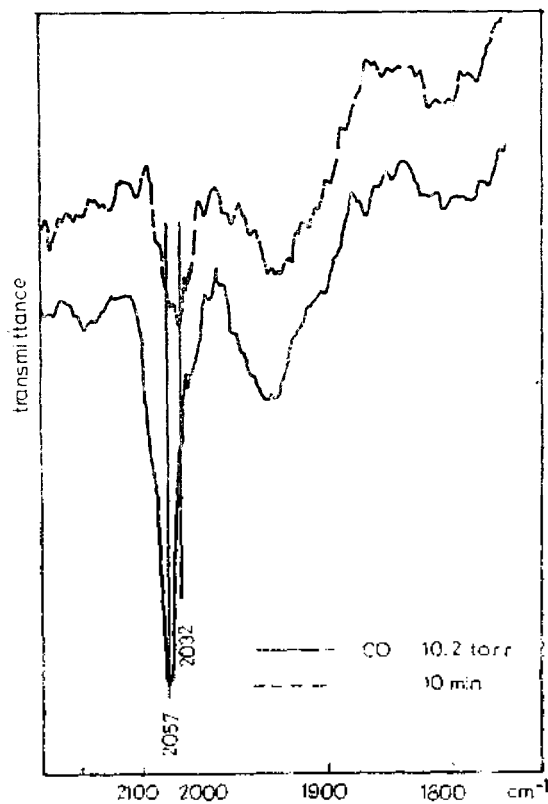


Fig. 7. IR spectra for 9.5% Ni sample after pumping.

adsorbed on silicagel gives rise to a band at 2057 cm^{-1} and temperature dependence of this band quite resembles that of 2057 cm^{-1} band observed for the silica-supported Ni system.

(B) Adsorption of CO on Silica-Supported Nickel with Potassium Coating.

Shown in Figs. 14 and 15 are the IR spectra for the silica-supported Ni (9.5% content) coated with potassium (11 $\mu\text{g}/1\text{mg}$ of Ni) taken under varying CO pressure. The change of adsorption bands when pumped to vacuum is also shown in the same figures.

For the potassium coated system there appear two broad bands peaked at 2077 and 1945 cm^{-1} under the CO pressure of 0.2 torr, and the intensity and band position of these bands show almost no change under pressure variation up

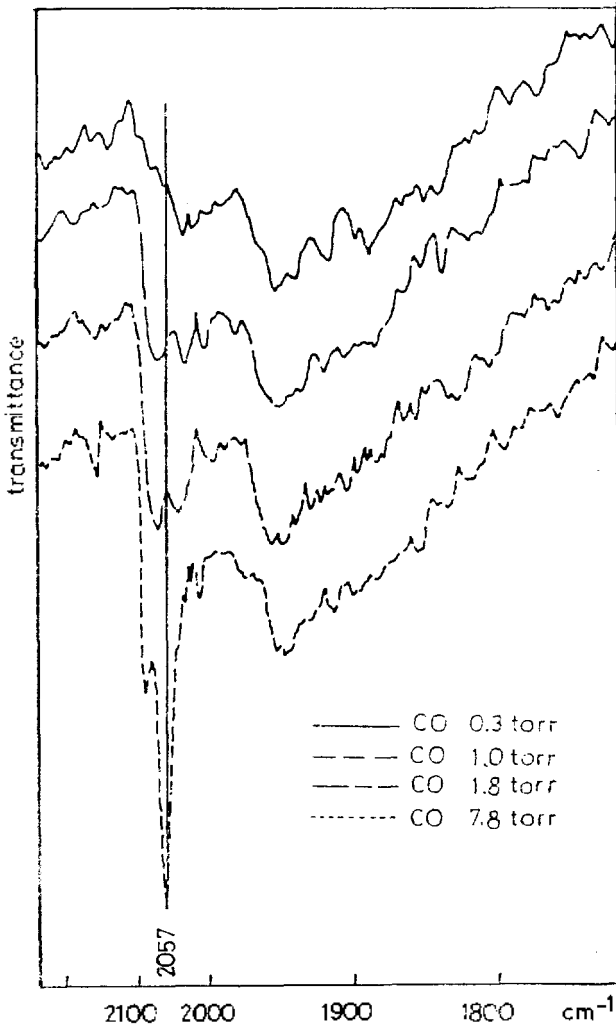


Fig. 8. IR spectra of increasing CO on 14% Ni sample at 20°C.

to 20 torr. In contrast to the case of system without potassium coating, above 5 torr the CO pressure was found to be much lower than expected from the amount of CO added and a band due to the gaseous CO₂ molecules appears at 2349cm⁻¹.

When pumped to vacuum, only a broad band at 2025cm⁻¹ survives above 2000cm⁻¹, and below 2000cm⁻¹ intensity of the 1945cm⁻¹ band gradually decreases, leaving eventually a band at 1915cm⁻¹ alone. The rate at which the

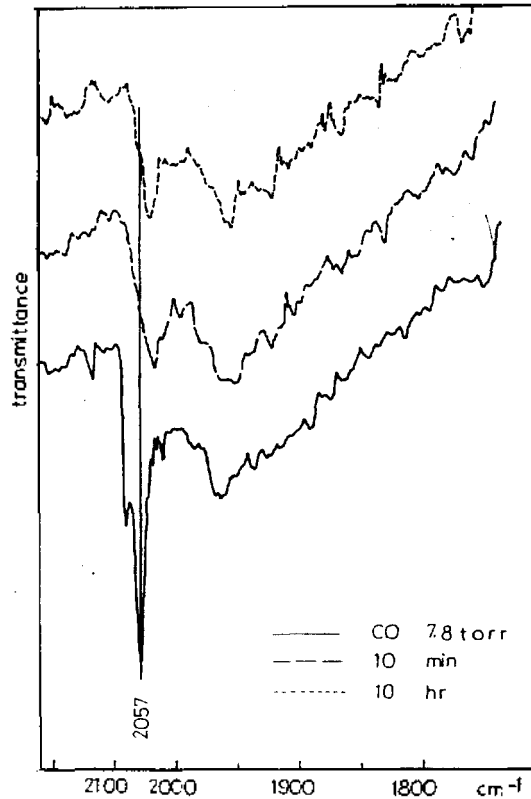


Fig. 9. IR spectra for 14% Ni sample after pumping.

intensity of 1945cm⁻¹ band decreases was found to be much slower than that for the corresponding band in the system without potassium coating.

DISCUSSIONS

IR band positions observed in our experiment for CO chemisorbed on silica-supported Ni without potassium coating are in good agreement with those reported by Pliskin,²² Yates,³ Garland,⁵ and Rochester.²³ The 2032cm⁻¹ band is observable even when the pressure is as low as 0.2 torr and cannot be removed by pumping. Furthermore, the intensity of this band does not change much even up to 140°C. These facts and other evidences such as the EELS spectra, work functions,²⁴ MO calculations,

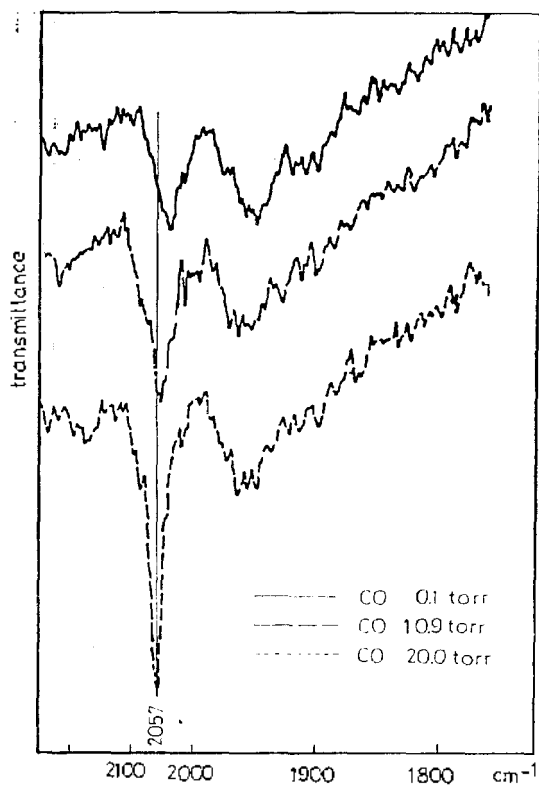


Fig. 10. IR spectra of increasing CO on 20% Ni sample at 20°C.

etc. indicate that the 2032cm^{-1} band comes from one CO molecule linearly (and tightly) bound to one Ni site.

The 2080cm^{-1} band grows much more rapidly than the 2032cm^{-1} band as the CO pressure goes up and can be easily removed by pumping. Therefore, the former probably arises from several CO molecules less tightly bound to one nickel site. Since no bands can be observed below 2100cm^{-1} when silicagel alone is allowed to contact with CO gas, it is obvious that the 2080cm^{-1} band is not due to the CO molecules physisorbed on silicagel.

The 2057cm^{-1} band also grows as the CO pressure is increased and its band position is very close to that of F_2 vibration mode for CO in gaseous $\text{Ni}(\text{CO})_4$ (2057.6cm^{-1}). Moreover,

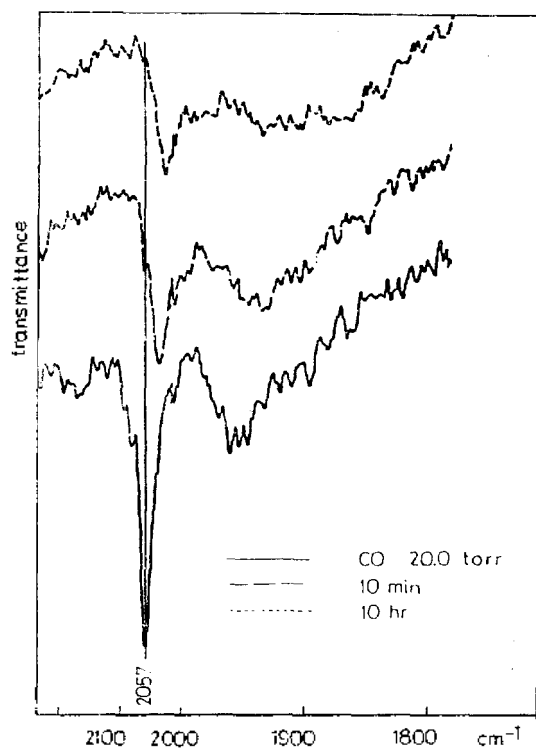


Fig. 11. IR spectra for 20% Ni sample after pumping.

its temperature dependence was found to be quite similar to that of CO band in $\text{Ni}(\text{CO})_4$ physisorbed on silicagel. Thus one may conclude that $\text{Ni}(\text{CO})_4$ molecules physisorbed on silicagel are responsible for this band.

Among two bands appearing below 2000cm^{-1} (1925 and 1955cm^{-1}) the 1925cm^{-1} band is more prevailing than the other only at low pressure (<0.5 torr) and as the CO pressure increases the 1955cm^{-1} band overwhelms the other. Furthermore it was observed that the 1925cm^{-1} band could not be removed easily by pumping. Therefore one may speculate that some kind of molecular species tightly bound to Ni site is responsible for the 1925cm^{-1} band. One may be tempted to accept the above facts as evidences that the 1925cm^{-1} band arises from the CO stretching vibration in a bridged bond like

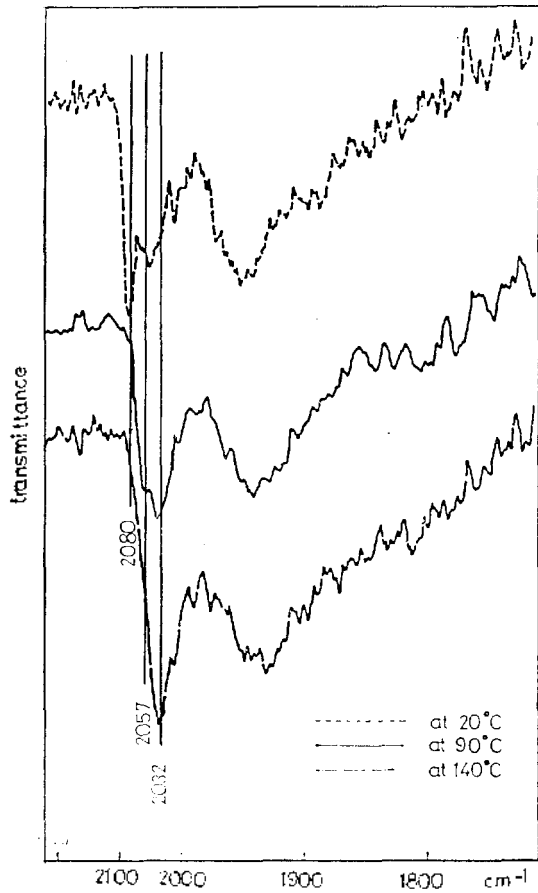


Fig. 12. IR spectra for 9.5% Ni sample at 0.7 torr of CO.

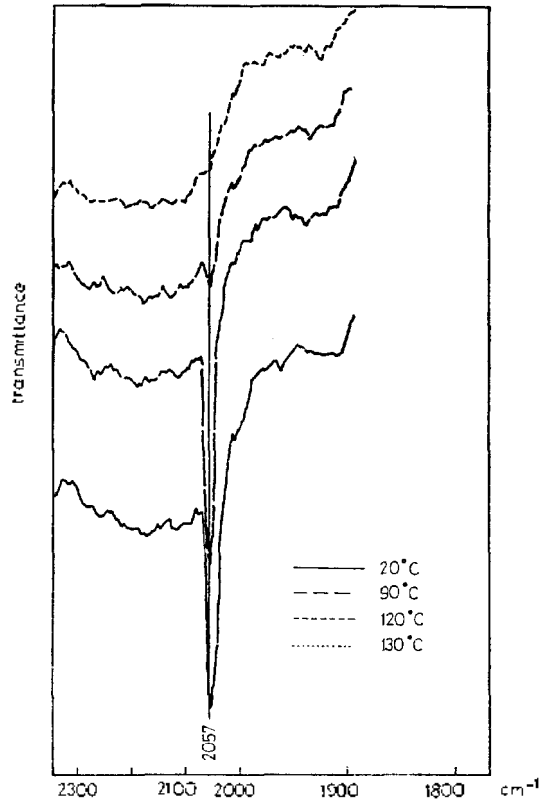
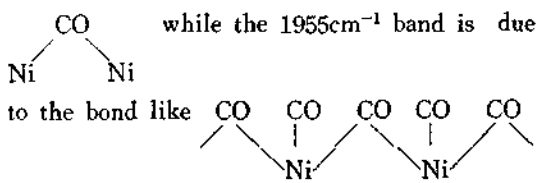


Fig. 13. IR spectra of Ni(CO)₄ adsorbed on silica gel.



as Yates has indicated. Unfortunately, however, the answer does not seem to be as simple as this, because, as Blyholder¹² and DeKock²⁵ pointed out, the bridging carbonyl groups should have much lower infrared frequencies. Thus, these two bands must be subjected to further investigations.

For silicagel-supported Ni coated with potassium variation of the CO pressure within the

range of 0.2 to 20 torr did not produce any noticeable change in the IR spectra except in the positions of absorption bands. On coating with potassium all the bands were found to shift toward longer wavelength side (red shift) as shown below:

without K coating	with K coating
2080cm ⁻¹	2077cm ⁻¹
2032cm ⁻¹	2025cm ⁻¹
1955cm ⁻¹	1945cm ⁻¹
1925cm ⁻¹	1915cm ⁻¹

It is generally believed that these red shifts are caused by electrons back donated by alkali metal because such electrons would occupy the antibonding π* orbitals of CO molecule, thereby weakening the bond strength in CO. Also,

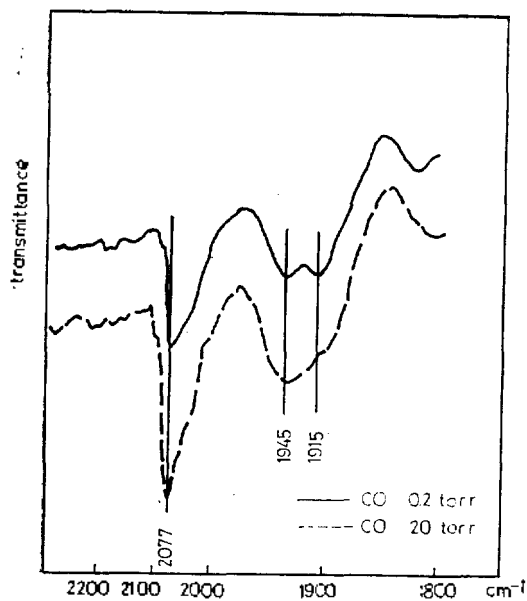


Fig. 14. IR spectra for K-promoted 9.5% Ni sample at 20°C.

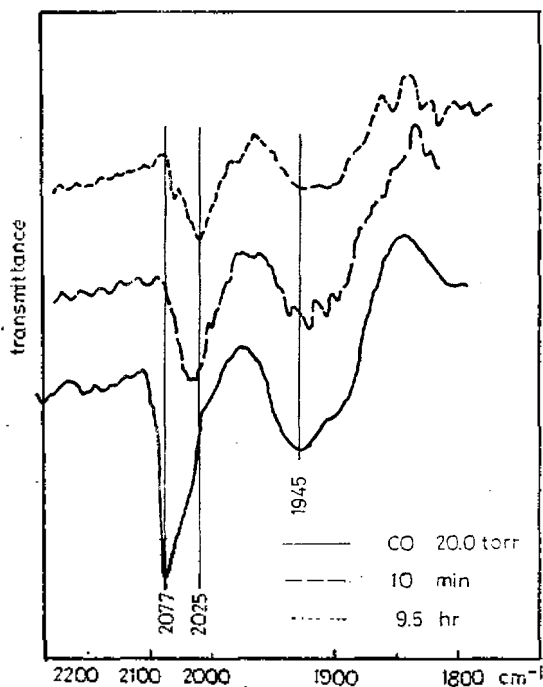


Fig. 15. IR spectra for K-promoted 9.5% Ni sample after pumping.

on coating with potassium 1945 and 2077cm^{-1} band have strong intensity even at pressure as low as 0.2 torr in contrast to the case of no potassium coating. This is probably due to the fact that back donated electrons from alkali metal increase the Ni-C bond energy.

One remarkable phenomena we can observe for the system with potassium coating is that the CO pressure becomes much lower than would be expected from the added amount of CO and that the 2349cm^{-1} band originating from gaseous CO_2 appears with appreciable intensity. This fact suggests that the reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ may occur on the catalyst surface. In fact there has been a report²¹ that on coating the Ni surface with potassium both work function and bond properties of Ni substantially change and that the activation energy necessary for producing carbidic carbon is much lowered. Our observation is of course well consistent with such reported results.

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