

# An Infrared Study on the Formation of Isocyanate in the NO + CO Reaction on Supported Ir Catalyst

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The formation of isocyanate surface species in the NO + CO reaction was investigated on supported iridium catalyst as a function of temperature and composition of the reacting gas mixture. On reduced Ir/Al<sub>2</sub>O<sub>3</sub> samples absorption bands due to isocyanate were observed at 2260–2240 cm<sup>-1</sup>. The isocyanate band was first detected at 200°C, and its maximum intensity was registered at 280–300°C. It is stable below 200°C but decomposes rapidly above 300°C *in vacuo* producing CO<sub>2</sub>, CO, and N<sub>2</sub>. Isocyanate species was also formed on oxidized surfaces but with considerably lower intensities. The reaction between preadsorbed NO and gaseous CO also resulted in the formation of isocyanate, but it was not identified when NO was admitted onto preadsorbed CO. During the surface interaction of NO and CO a large downscale shift of the NO band occurred which was explained by the perturbing effect of adsorbed CO. It is assumed that the primary step in the formation of isocyanate is the dissociation of NO on the reduced centers. It is postulated that isocyanate formed on the iridium migrates to the acceptor sites of the support. This explanation is backed by the observations that the different supports markedly influence the location, formation, and stability of the isocyanate band.

## INTRODUCTION

Considerable experimental attention has recently been devoted to the formation of surface isocyanate on supported Pt, Pd, Rh, and Ru catalysts (1–13). It is hoped that a better understanding of its formation and reactivity may help in the elucidation of the mechanism of the NO + CO reaction and particularly the mechanism of ammonia formation during the catalytic treatment of automobile exhaust gases. An interesting application of these results is to develop a new catalytic route for the production of ammonium isocyanate and isocyanic acid (14–17).

Apart from exploratory work (1), the behavior of supported iridium in the formation of isocyanate has received little attention. Relatively few papers have been published so far on the catalytic properties of supported iridium in the reduction of NO. Recently, however, it has been reported that Ir/alumina can selectively catalyze the NO + CO reaction even in the presence of

excess oxygen (18). This behavior, which is unique among the supported noble metals, will possibly result in a greater importance of iridium in the catalytic chemistry of NO.

In the present work we report on the formation and stability of isocyanate on supported iridium. In the course of this work we examined in detail the formation of isocyanate on reduced and oxidized iridium, the reactions of adsorbed NO with CO, the decomposition of isocyanate species, and the effect of the nature of the support on the above processes.

## EXPERIMENTAL

### Materials

The preparation of supported iridium samples was carried out using the impregnation method. The supports used in this work were Al<sub>2</sub>O<sub>3</sub> (Degussa P110Cl), SiO<sub>2</sub> (Cab-O-Sil), TiO<sub>2</sub> (Degussa P25), and MgO (DAB 6). For the infrared studies the powdered material was pressed into a disk using a pressure of 1670 kp/cm<sup>2</sup> (1 kp/cm<sup>2</sup> =

0.981 · 10<sup>5</sup> Pa). Before each experiment the catalyst disk was pretreated in the infrared cell as follows: (i) evacuation for 90 min at 400°C; (ii) oxidation for 30 min with 100 Torr of O<sub>2</sub> at 400°C; (iii) evacuation for 15 min at 400°C; (iv) reduction for 30 min with 100 Torr of H<sub>2</sub> at 400°C; and (v) evacuation for 15 min at 400°C.

The gases used were of commercial purity. NO was further purified by fractional distillation before use. The purity of the gases was periodically checked by mass spectrometry. The composition of the reacting gas mixture used in the experiments was the following: NO (5%), CO (10%), and N<sub>2</sub> (85%).

### Methods

The infrared spectrometer and the cell used for this work have been described previously (4, 19). All spectra reported here were obtained at room temperature. Mass-spectrometric analysis was performed with a MS 10 mass spectrometer. The ion source of the mass spectrometer was connected to the infrared cell.

## RESULTS

### 1. ADSORPTION OF NO + CO GAS MIXTURE

#### Reduced Surfaces

When 50 Torr reacting gas mixture was adsorbed on reduced Ir/Al<sub>2</sub>O<sub>3</sub>, strong bands not observed during the adsorption of any of the reacting gases (NO, CO) or products (N<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>) of the NO + CO reaction appeared in the spectra at 2260 cm<sup>-1</sup> and a band or a shoulder at 2240 cm<sup>-1</sup> (Fig. 1). Their intensities and behaviors were almost the same; both were very stable against room-temperature evacuation. They were first detected at 200°C. It is to be mentioned that in many cases we obtained only one strong band at 2240–2260 cm<sup>-1</sup>, and it was not possible to separate this into two peaks.

The positions of these bands agree very well with those observed by Unland under

the same conditions at 400°C, who attributed them to surface isocyanate species (1). This assignment is backed by the reaction of this surface species. When 10 Torr H<sub>2</sub>O was admitted into the cell, the intensities of these bands decreased rapidly even at 100°C. Mass-spectrometric analysis at the same time revealed the formation of NH<sub>3</sub>.

With the increase of the adsorption temperature the initial intensities of both bands became higher; after 5–10 min, however, the intensities of the bands, particularly above 300°C, decreased, approaching the low values obtained at 200°C (Fig. 2).

In Fig. 3 we have plotted the maximum intensity values observed at different temperatures. Accordingly, the optimum temperature for the formation of NCO bands is between 280 and 300°C.

It is instructive to examine the appearance and the behaviors of the bands observed previously during the separate adsorption of NO and CO (Table 1) (19). Of the NO bands detected before, only a small band at 1890–1900 cm<sup>-1</sup> can be traced in the

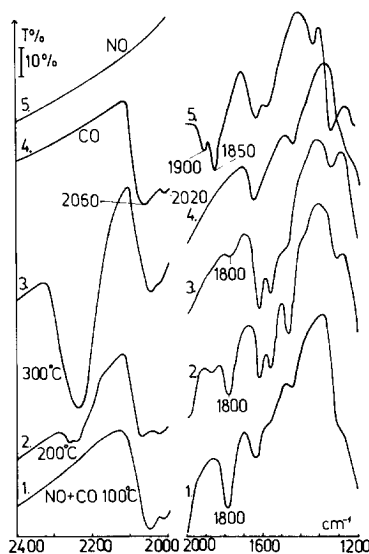


FIG. 1. Infrared spectra observed at room temperature after dosing the reduced 5% Ir/Al<sub>2</sub>O<sub>3</sub> with 50 Torr of a 5% NO, 10% CO, and 85% N<sub>2</sub> (1–100°C; 2–200°C; 3–250°C) and after the adsorption of CO (4–10 Torr at room temperature) and of NO (5–10 Torr at room temperature).

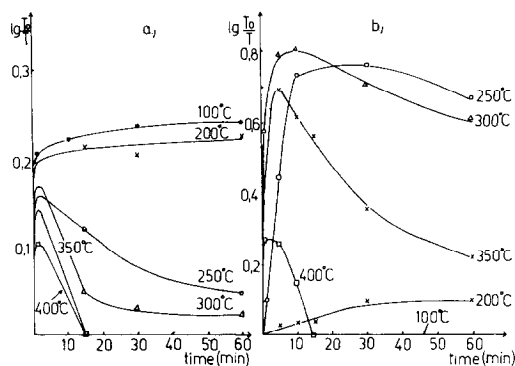


FIG. 2. Intensities of the bands at  $1800\text{ cm}^{-1}$  (a) and  $2260\text{ cm}^{-1}$  (b) vs time during the interaction between the reduced 5% Ir/Al<sub>2</sub>O<sub>3</sub> and 50 Torr of a reacting gas mixture at different temperatures.

spectra below  $250^\circ\text{C}$ . At higher temperatures this band was missing. A new strong band appeared at  $1790\text{--}1800\text{ cm}^{-1}$ , however, after adsorption of the reacting gas mixture, even at  $25^\circ\text{C}$  (Fig. 1).

Both CO bands appeared in the spectra at  $25\text{--}200^\circ\text{C}$ . At  $250\text{--}300^\circ\text{C}$  the band at  $2020\text{ cm}^{-1}$  was detected only in the first minute of the reaction.

The bands between  $1400$  and  $1700\text{ cm}^{-1}$  ( $1620$ ,  $1575$ , and  $1470\text{ cm}^{-1}$ ), possibly due to surface carbonate and nitrate groups, also appeared in the spectra; their intensities increased quickly, but in the later period they were practically unchanged at the temperatures investigated.

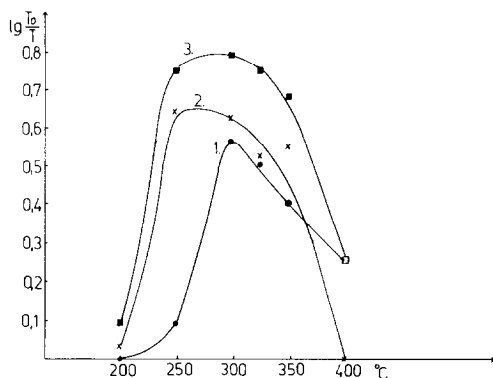


FIG. 3. Dependence of the intensities of the band at  $2260\text{ cm}^{-1}$  on the temperature of dosing 5% Ir/Al<sub>2</sub>O<sub>3</sub> with 50 Torr of a reacting gas mixture. (1) Adsorption time 1 min; (2) adsorption time 15 min; (3) maximum value observed at given temperature.

TABLE 1

Infrared Bands Due to Adsorbed Gases on Ir/Al <sub>2</sub> O <sub>3</sub>			
Adsorbate	Frequency (cm <sup>-1</sup> ) and structure		
CO	2070–2060 Ir–CO on site A	2020 Ir–CO on site B	
NO	1950  O <sup>+δ</sup>   O <sup>2-</sup> –N / \	1900 Ir–NO <sup>+δ</sup> on site A	1850 Ir–NO <sup>+δ</sup> on site B
N <sub>2</sub> O without evacuation	2220 Ir–NNO		
CO <sub>2</sub>	1660 CO <sub>3</sub> <sup>2-</sup> on Al <sub>2</sub> O <sub>3</sub>	1450 CO <sub>3</sub> <sup>2-</sup> on Al <sub>2</sub> O <sub>3</sub>	
NO + CO at 25°C	2060 Ir–CO on site A	2020 Ir–CO on site B	1800 Ir–NO perturbed by CO <sub>ads</sub>
NO + CO at 200°C	2260 and 2240 Al–NCO	2070 and 2020 Ir–CO	1800 Ir–NO perturbed by CO <sub>ads</sub>

Figure 4 shows the results when doses of 20 Torr NO + CO mixture (without N<sub>2</sub>) were admitted successively onto the sample at  $325^\circ\text{C}$ . The highest intensity of the  $2260\text{-cm}^{-1}$  band was always produced immediately after admission of the doses, and then the intensity decreased to a very low value. The  $1800\text{-cm}^{-1}$  band behaved similarly, while the intensity of the  $2060\text{-cm}^{-1}$  band changed only little. Mass-spectrometric analysis revealed that at  $325^\circ\text{C}$  the NO + CO reaction producing N<sub>2</sub>, CO<sub>2</sub>, and a small amount of N<sub>2</sub>O is very fast. When the intensity of the isocyanate band decreased, almost 90% of the NO had reacted.

#### Oxidized Surfaces

On oxidized surfaces the bands due to the surface isocyanate appeared at higher temperatures. Weak bands at  $2260$  and  $2240\text{ cm}^{-1}$  were detected first at  $250^\circ\text{C}$  after a relatively long reaction time. At higher temperatures the intensities of these bands approached the values observed on re-

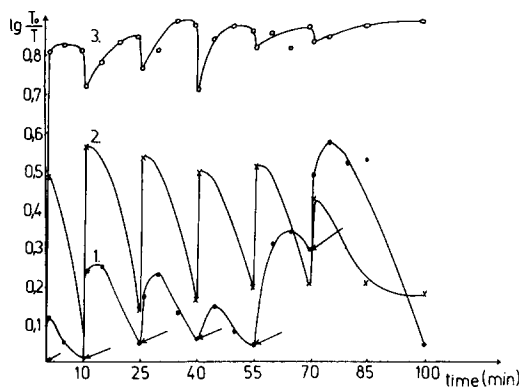


FIG. 4. Change of the intensities of the bands at  $2260\text{ cm}^{-1}$  (1),  $1800\text{ cm}^{-1}$  (2), and  $2060\text{ cm}^{-1}$  (3) with time during the interaction between 5% Ir/ $\text{Al}_2\text{O}_3$  and subsequent doses of 20 Torr of a reacting gas mixture at  $32.5^\circ\text{C}$ . The arrows indicate when the new doses were admitted.

duced iridium and their behaviors were also similar. Bands due to adsorbed CO appeared at  $2060\text{ cm}^{-1}$ . No bands due to adsorbed NO were detected below  $250^\circ\text{C}$ . Above  $300^\circ\text{C}$  a weak band at  $1800\text{--}1795\text{ cm}^{-1}$  was observed only at the very beginning of the reaction.

## 2. EFFECT OF THE GAS COMPOSITION

Experiments were performed at  $300^\circ\text{C}$ . In a NO excess, the formation of the bands due to isocyanate was not detected. They appeared, however, at a NO:CO ratio of 1:1. Figure 5 shows that a large excess of CO stabilizes the NCO band.

## 3. REACTION OF PREADSORBED NO AND CO

In the first series of experiments NO (5 Torr) was adsorbed *on reduced surface* at room temperature for 1 hr, then evacuated for 15 min, and subsequently 10 Torr CO was admitted at different temperatures ( $150\text{--}400^\circ\text{C}$ ). On the action of CO, at first a gradual attenuation in the intensities of the NO bands ( $1900$  and  $1850\text{ cm}^{-1}$ ) was observed at all temperatures, accompanied by the appearance of a band at  $1800\text{ cm}^{-1}$ . At the same time the bands due to adsorbed

CO developed; their intensities increased with increasing temperature and time. The position of the high-frequency band due to CO was slightly shifted at  $150\text{--}200^\circ\text{C}$ , to  $2092\text{ cm}^{-1}$ . In addition, a weak band at  $2160\text{ cm}^{-1}$ , not observed before, appeared in the spectra at  $150\text{--}250^\circ\text{C}$ . At  $200^\circ\text{C}$  a band at  $2265\text{ cm}^{-1}$ , attributed to surface isocyanate, was also detected. With the development of the  $2265\text{ cm}^{-1}$  band, the intensity of  $1800\text{ cm}^{-1}$  band decreased. Some spectra are shown in Fig. 6.

Qualitatively similar results were obtained when 50 Torr NO was adsorbed at  $400^\circ\text{C}$  and after evacuation at  $25^\circ\text{C}$  10 Torr CO was admitted. The isocyanate band at  $2265\text{ cm}^{-1}$  appeared first in this case at  $300^\circ\text{C}$ .

Similar experiments were carried out *with adsorbed CO and gaseous NO*. When NO was introduced then, depending on the temperature, an attenuation of the intensity of the CO bands was observed, and a strong band appeared at  $1790\text{--}1800\text{ cm}^{-1}$ . On elevation of the reaction temperature to  $150^\circ\text{C}$  the NO band at  $1880\text{--}1900\text{ cm}^{-1}$  developed. At  $250^\circ\text{C}$  the  $1800\text{ cm}^{-1}$  band disappeared, and another NO band appeared at  $1950\text{ cm}^{-1}$  in the spectra. *No isocyanate band was detected even when the temperature was raised to 300 or  $400^\circ\text{C}$ .*

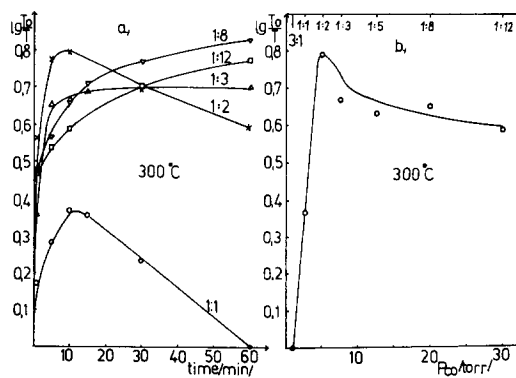


FIG. 5. The effect of gas composition on the intensity of the band at  $2260\text{ cm}^{-1}$ . (a) Intensity vs time curves; (b) intensity in the 10th min vs  $p_{\text{CO}}$  ( $p_{\text{NO}}$  = constant,  $T = 300^\circ\text{C}$ , 5% Ir/ $\text{Al}_2\text{O}_3$  was initially reduced).

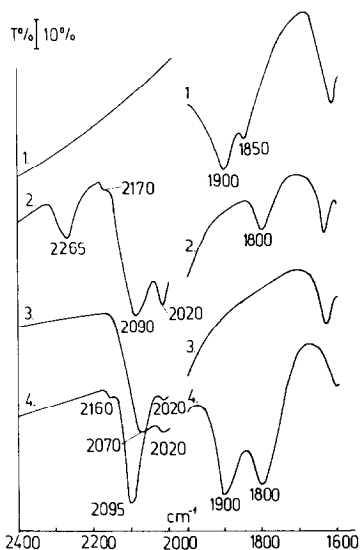


FIG. 6. Infrared spectra obtained at room temperature showing the interaction between preadsorbed NO and CO and between preadsorbed CO and NO. (1) NO adsorbed at 25°C on reduced surface; (2) CO added to preadsorbed NO at 200°C; (3) CO adsorbed at 150°C on reduced surface; (4) NO added to preadsorbed CO at 200°C.

#### 4. THE STABILITY OF THE ISOCYANATE BAND

Isocyanate complex was produced at 300°C. The results are shown in Fig. 7. The intensities of the bands at 2260 and 2240  $\text{cm}^{-1}$  decreased simultaneously at very similar rates. The band due to adsorbed CO at 2060–2080  $\text{cm}^{-1}$  was more stable than in the absence of isocyanate.

In some cases we analyzed the gas phase during the decomposition by mass spectrometry. At the beginning of the decomposition,  $\text{CO}_2$  and  $\text{N}_2$  were evolved. After cessation of  $\text{CO}_2$  evolution, only CO and  $\text{N}_2$  were found; their ratio corresponded to that in NCO.

We note that when a catalyst of lower iridium content, 1 or 0.2 wt%, was used, the band at 2260–2240  $\text{cm}^{-1}$  was more stable than for 5 wt% Ir/ $\text{Al}_2\text{O}_3$ .

#### 5. EFFECT OF THE SUPPORT

Figure 8 shows the spectra observed after dosing the different iridium catalysts

with 50 Torr reacting gas mixture at 300°C. Strong bands indicating the formation of isocyanate complexes appeared for all the catalysts. The location of the isocyanate bands, however, varied with the support. They appeared at 2210  $\text{cm}^{-1}$  on Ir/ $\text{TiO}_2$ , 2230–2240  $\text{cm}^{-1}$  on Ir/ $\text{MgO}$ , 2310  $\text{cm}^{-1}$  on Ir/ $\text{SiO}_2$ , and at 2270 and 2240  $\text{cm}^{-1}$  on Ir/ $\text{Al}_2\text{O}_3$ , at somewhat higher frequencies than on the 5 wt% Ir/ $\text{Al}_2\text{O}_3$  sample.

Figure 9 shows the intensities of the isocyanate band against the reaction time. The formation of isocyanate depended on the support; it was fast on Ir/ $\text{TiO}_2$ , whereas it was extremely slow on Ir/ $\text{SiO}_2$ . In this case, the band due to isocyanate appeared only in the presence of a high pressure (120 Torr) of NO + CO mixture without the use of  $\text{N}_2$  diluent.

The stabilities of the isocyanate complexes were also found to be sensitive to the support (Fig. 9). Decomposition occurred rapidly on Ir/ $\text{TiO}_2$ . The decomposition was slower on Ir/ $\text{Al}_2\text{O}_3$  and Ir/ $\text{MgO}$ . Isocyanate was very stable on Ir/ $\text{SiO}_2$ ; complete decomposition was not obtained below 400°C.

#### DISCUSSION

##### Adsorption of NO and CO

Before discussing the results obtained and proposing a mechanism for the forma-

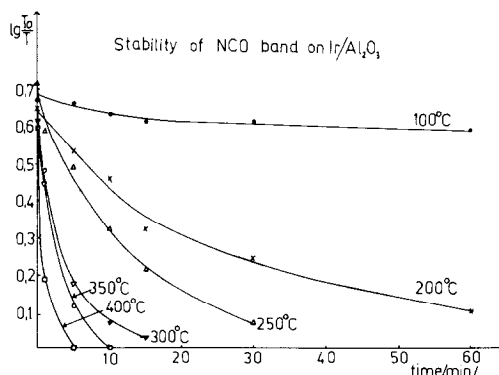


FIG. 7. Change of the intensity of the isocyanate band at 2260  $\text{cm}^{-1}$  with time in continuous evacuation at different temperatures. The isocyanate was produced at 300°C by the interaction of the reduced sample and 50 Torr of a reacting gas mixture.

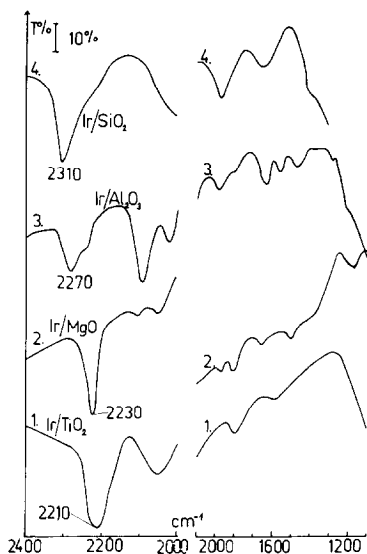


FIG. 8. Infrared spectra obtained at room temperature after dosing the different Ir catalysts with 50 Torr of a reacting gas mixture at 300°C. The spectrum for 1% Ir/SiO<sub>2</sub> was recorded after dosing the sample with 120 Torr of a NO + CO gas mixture (mole ratio 1:2) without nitrogen.

tion of surface isocyanate species, we should summarize the main points of the study of NO and CO adsorption (19). In harmony with the proposals of Howe (20), we distinguished two different adsorption sites. *Site A* represents larger iridium crystallites in which iridium atoms accessible to gas molecules have contact only with each other; *Site B* consists of a small number of iridium atoms influenced strongly by the support.

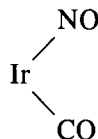
The adsorption of CO produced two bands at 2060–2070 and 2020 cm<sup>-1</sup>; the former was attributed to CO linearly bonded to site A and the latter to CO linearly bonded to site B. The adsorption of NO on reduced surfaces also caused two bands, at 1900 and 1850 cm<sup>-1</sup>, which were assigned to the vibration of M–NO<sup>+</sup> species on site A and on site B. With the oxidation of the surfaces, with either NO or O<sub>2</sub>, a new band appeared at 1950 cm<sup>-1</sup>, assigned to M–NO<sup>+</sup> on oxidized iridiums (Table 1).

When a NO + CO mixture of 1:2 composition was adsorbed on reduced Ir/Al<sub>2</sub>O<sub>3</sub>,

the NO bands recorded during the adsorption of NO alone could hardly be detected. A new band was produced, however, at 1800 cm<sup>-1</sup> (Fig. 1). This band appeared even during the adsorption of NO + CO gas mixture at 25°C, when there was no catalytic reaction between NO and CO, and during the surface interaction of adsorbed NO and gaseous CO and vice versa (Fig. 6).

Above 200°C, when the formation of isocyanate occurred, the highest intensity was observed at the beginning of the reaction. On oxidized surfaces it was detected only transiently at 350 and 400°C, when the oxidized centers were reduced, and before the formation of isocyanate species set in. In order to determine the nature of this band, spectra were taken using isotopically labeled <sup>15</sup>NO. The frequency shift obtained ( $\Delta\nu = -35$  cm<sup>-1</sup>) agreed well with the calculated shift ( $\Delta\nu = -32$  cm<sup>-1</sup>) assuming that the band observed at 1800 cm<sup>-1</sup> is due to the stretching vibration of adsorbed NO.

On the basis of the above behavior we propose that during the surface interaction of NO and CO, similarly as on the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst (8, 12), an



surface species is formed, and the band at

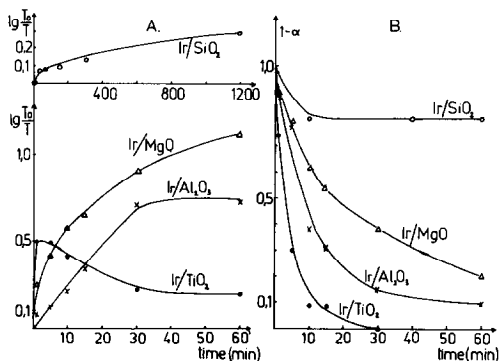


FIG. 9. Change of the intensity of the isocyanate bands on different Ir catalysts with time. (A) During the NCO formation; (B) during the continuous evacuation at 300°C.

1800  $\text{cm}^{-1}$  is that of  $\nu$ -NO in the above structure. The large downscale shift of the NO band is a reflection of the partial transfer of an electron from CO through an Ir atom into the antibonding orbital of NO. The formation of this surface species, however, should also lead to an upscale shift of the CO band due to a decrease of the back donation of  $d$  electrons from Ir to CO, caused by the NO. We could not resolve a new CO band, probably because of the large broad band at 2060–2080  $\text{cm}^{-1}$ , but we observed that when the 1800- $\text{cm}^{-1}$  band appeared in the spectra the high-frequency band of CO was shifted to higher frequencies, 2090–2095  $\text{cm}^{-1}$ . This shift was not experienced when the extent of CO adsorption was increased in the absence of NO (19), and thus a “coverage effect” can be ruled out.

#### *Isocyanate Formation*

When a NO + CO mixture of 1 : 2 composition was adsorbed on reduced Ir/Al<sub>2</sub>O<sub>3</sub> at higher temperatures, a band at 2240–2260  $\text{cm}^{-1}$ , not observed during the adsorption of the reacting gases, appeared in the spectra. As we mentioned in some cases it was possible to distinguish two bands, or a band at 2260  $\text{cm}^{-1}$  and a shoulder at 2240  $\text{cm}^{-1}$ . Mass-spectrometric analysis revealed that the NO + CO reaction proceeded at a measurable rate at this temperature. We attributed these bands to the surface isocyanate species. The positions of these bands are in good agreement with the results of Unland, who observed new bands at 2267 and 2239  $\text{cm}^{-1}$ , formed in the NO + CO reaction at 400°C. The former was assigned to covalently bonded -NCO and the latter to anionic isocyanate, NCO<sup>-</sup> (1).

As concerns the formation of isocyanate complex, the following results are worth mentioning:

(i) Isocyanate complexes form on reduced Ir/Al<sub>2</sub>O<sub>3</sub> at relatively low temperature, 200°C; the formation is sensitive to the composition of the reacting gases.

(ii) Similarly as in former studies with Pt, Pd, Ru, and Rh (3, 4, 6, 12), isocyanate forms on oxidized surfaces, but with considerably lower intensities.

(iii) The reaction between preadsorbed NO and CO also results in the formation of isocyanate, but it was not detected when NO was admitted onto preadsorbed CO. This observation suggests that in the formation of isocyanate on supported Ir the activation of NO is required. This is in contrast to the results obtained for CuO/SnO<sub>2</sub> catalyst when the dissociation of CO was assumed as the dominant step (21).

(iv) It is stable below 200°C, but decomposes rapidly above 300°C *in vacuo* producing CO<sub>2</sub>, CO, and N<sub>2</sub>.

(v) The support exerted a marked influence on the location of the isocyanate band and on the rates of its formation and decomposition.

#### *Location of Isocyanate*

We should deal first with the question of the location of the isocyanate species. Since the exploratory studies of Unland (1, 2) the formation of isocyanate on alumina-supported noble metals has been the subject of many detailed investigations. Very strong absorption bands were observed in all studies; these were attributed to the vibration of isocyanate located *on the metal*. A characteristic feature of the data is that the positions of the isocyanate bands hardly depend on the metal and, even including the results for Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (22), they fall in a very narrow frequency range, 2259–2272  $\text{cm}^{-1}$ .

Dalla Betta and Shelef (23) first suggested that isocyanate resides on the support. Shortly afterward we showed that the number of surface isocyanate groups formed on Pt/Al<sub>2</sub>O<sub>3</sub> greatly exceeds the number of surface metal atoms (10). These results, as well as the great influence of the support on the location of the isocyanate band and on the formation and stability of the isocyanate species, led us to the strong

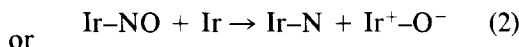
belief that isocyanate is located not on the Pt but rather on the support (11).

In our opinion a similar conclusion can also be drawn in the present case. One of the most convincing arguments for this is that the position of the isocyanate band ( $2210\text{ cm}^{-1}$  on Ir/TiO<sub>2</sub>,  $2230\text{--}2240\text{ cm}^{-1}$  on Ir/MgO,  $2260\text{ cm}^{-1}$  on Ir/Al<sub>2</sub>O<sub>3</sub>, and  $2310\text{ cm}^{-1}$  on Ir/SiO<sub>2</sub>) and the reactivity of the surface isocyanate depend sensitively on the support. The observation that isocyanate was the most stable on Ir/SiO<sub>2</sub> is in harmony with the high stability of Si-NCO species (24).

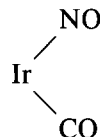
Further proof for this explanation comes from a study of the adsorption of isocyanic acid, HNCO, on Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, and SiO<sub>2</sub> supports (25). We obtained almost exactly the same absorption bands ( $2212\text{ cm}^{-1}$  on TiO<sub>2</sub>,  $2223\text{ cm}^{-1}$  on MgO,  $2272\text{ cm}^{-1}$  on Al<sub>2</sub>O<sub>3</sub>, and  $2313\text{ cm}^{-1}$  on SiO<sub>2</sub>) as found in the present study on differently supported iridium. In addition, the stability orders of isocyanate on the supports and on the supported Ir were also the same.

We should mention here that in the interaction of preadsorbed NO and gaseous CO a weak band was detected at  $2160\text{ cm}^{-1}$ . It disappeared soon after evacuation at  $150\text{--}200^\circ\text{C}$ , without producing any new band. A concrete assignment of this band was not possible due its low intensity. Attempts to enhance its intensity were not successful. A possible assignment of the  $2160\text{-cm}^{-1}$  band is to CO adsorbed on an oxidized Ir atom. In the case of Ru catalyst the formation of such a surface species resulted in a band at  $2150\text{ cm}^{-1}$  (6, 26). However, since the adsorption of CO on Ir/Al<sub>2</sub>O<sub>3</sub> oxidized with either O<sub>2</sub> or NO at  $400^\circ\text{C}$  did not produce this band, such an explanation seems unlikely. Taking into account that the adsorption of HCN on Ir/SiO<sub>2</sub> produced almost the same band (27) we tentatively assign the weak  $2160\text{-cm}^{-1}$  band to an Ir-CN species.

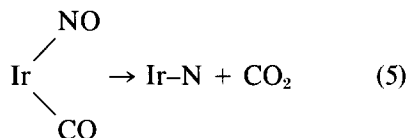
On the basis of the above considerations, we describe the formation of isocyanate on supported Ir in the following way:



We assume that the primary step in the reaction is the dissociation of NO on the reduced centers (Eqs. (1)–(3)), resulting in an adsorbed N atom, which will react with CO to yield isocyanate (Eq. (4)). Adsorption and desorption measurements clearly indicated that dissociation of NO on the Ir/Al<sub>2</sub>O<sub>3</sub> sample used in the present study occurred at the rather low temperature of about  $100^\circ\text{C}$  (19). This is in agreement with the recent ESCA studies; accordingly, NO adsorbs molecularly at 170 K on the Ir (111) face, but dissociates above 323 K (28). Taking into account the interpretation of the appearance of the  $1800\text{-cm}^{-1}$  band we assume that CO, forming the

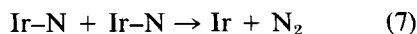
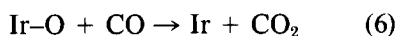


surface species with NO, reacts with NO

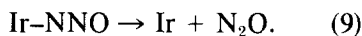
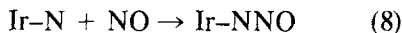


and thereby contributes to the formation of adsorbed nitrogen atoms, and thus also to the formation of isocyanate complex. We propose that these steps occur first of all on site B, i.e., on the finely dispersed Ir, which is mainly surrounded by the ions of the support.

Steps (5)–(9) describe the formation of the products observed during the catalytic reaction of NO + CO in parallel with the formation of the isocyanate species:







The NCO species formed migrates from site B onto the neighboring acceptor site of the support (Eq. (10)):



M is the metal ion of the support.

The fact that the formation of isocyanate produced two bands on Ir/Al<sub>2</sub>O<sub>3</sub>, and also on other alumina-supported noble metals, is not surprising if we take into account that differently coordinated adsorption sites exist on alumina surface (29).

The migration of the isocyanate should be very fast at elevated temperature: there was no indication of the existence of an Ir-NCO species. It is very likely that the slowest step in the formation of isocyanate is the dissociation of NO.

On oxidized surfaces the formation of isocyanate at lower temperatures proceeds more slowly and to a smaller extent. No isocyanate species was detected at 200°C. The adsorbed NO formed on a partially oxidized surface (band at 1950 cm<sup>-1</sup>) is less reactive (the N-O bond is stronger) and, due to the absence of the adjacent free Ir atoms required for the dissociation of NO, the formation of an adsorbed N atom is much more restricted. In addition on oxidized surfaces we could not detect the 1800-cm<sup>-1</sup> band (below 300°C) indicative of the occurrence of the surface interaction between NO and CO.

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