

The Effect of the Support on the Formation and Stability of Surface Isocyanate on Platinum

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The effects of different carriers (SiO_2 , MgO , Al_2O_3 , and MgO) on the formation and stability of isocyanate complexes in the $\text{NO} + \text{CO}$ reaction on a platinum catalyst were investigated. The method used was infrared spectroscopy combined with mass spectrometry. Isocyanate formed with great ease on Pt/TiO_2 , whereas its formation on the other catalysts, particularly on Pt/SiO_2 , was much slower. The supports markedly influenced the location of the band due to isocyanate: It appeared at 2210 cm^{-1} on Pt/TiO_2 , 2241 cm^{-1} on Pt/MgO , 2272 cm^{-1} on $\text{Pt/Al}_2\text{O}_3$, and 2318 cm^{-1} on Pt/SiO_2 . The stability of the isocyanate depended sensitively on the support. Whereas it decomposed very rapidly on Pt/TiO_2 even at 300°C , it was extremely stable on Pt/SiO_2 . This latter behavior is in harmony with the high stability of the Si-NCO species. The results led to the conclusion that the isocyanate complex is located on the support which basically determines its properties. It was assumed that either the isocyanate formed on the Pt migrated to the acceptor sites of the support, or the nitrogen atoms formed in the dissociation on the Pt migrated to the support and reacted with gaseous or adsorbed CO yielding isocyanate species. The phenomenon observed forms a special case of the spillover.

INTRODUCTION

A number of recent papers concerned the study of the chemistry of surface isocyanate formed on supported platinum catalysts in the $\text{NO} + \text{CO}$ reaction (1-7). The easy identification of the isocyanate complex by infrared spectroscopy made possible many interesting investigations on the properties and role of a surface complex.

Recent quantitative measurements showed that in certain cases the number of surface isocyanate species greatly exceeds the number of surface Pt atoms (8, 9). This result strongly supports the idea that at least a part of the isocyanate complex is located on the alumina support (7, 10). We have further observed that isocyanate complexes can also be formed on the non-metallic catalyst chromia/alumina (11).

In the light of these findings it is very likely that the oxidic support may contribute to the observed characteristics of the formation and reaction of the isocyanate complex on the noble metals.

Up to now no detailed work has been done on the role of the support (in most cases alumina was used). In the present work we report how the support influences the formation and the stability of isocyanate complexes on platinum catalysts.

EXPERIMENTAL

Materials

For the preparation of the supported Pt, 1 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 ml of doubly distilled water. The calculated volume of the Pt-containing solution was added to an appropriate amount

TABLE 1
Some Characteristic Data for the Catalysts^a

Supports	Area of the supports (m ² /g)	The amount of Pt	Method ^b	Pt dispersion (%)	Metallic surface area (m ² /g of catalyst)	Average particle size (Å)
Al ₂ O ₃ (Degussa P 110 Cl)	100	0.5 mol%	A	25.3	0.69	39.4
		1.0 wt%	B	25.6	0.71	33.1
SiO ₂ (Aerosil 200)	240	0.5 mol%	A	12.7	0.56	66.9
		1.61 wt%	B	16.0	0.72	52.0
MgO (DAB 6)	170	0.5 mol%	A	23.8	1.55	35.5
		2.37 wt%	A	23.9	1.56	35.4
TiO ₂ (Degussa P 25)	150	0.5 mol%	A	(30.0)	(1.02)	(28.2)
		1.21 wt%				

^a The dispersity of Pt was determined by O₂-H₂ titration (19) according to the equations proposed by Boudart *et al.* (20). Due to the slight surface reduction of TiO₂ by H₂, the dispersity of Pt on TiO₂ support can not accurately be determined.

^b A: chemisorption of H₂ at 25°C on the oxidized surfaces; B: chemisorption of H₂ at 25°C on reduced surfaces. The surface area of one Pt atom was taken as 8.9 Å².

of support with constant stirring. The homogenized suspension was dried for 16 hr at 100°C and then powdered in an agate mortar. The origins and surface areas of the catalysts used are shown in Table 1.

Coherent 30 × 10-mm self-supporting tablets, satisfactorily transparent to infrared light, were prepared from 30 mg of finely powdered material at high pressure. The sample thickness was estimated as 10 mg/cm². Before adsorption and infrared spectroscopic measurements, the solid sample was treated as follows: (i) evacuation for 90 min at 400°C; (ii) oxidation for 30 min with 100 Torr of O₂ at 400°C; (iii) evacuation for 30 min at 400°C; (iv) reduction for 30 min with 100 Torr of H₂ at 400°C; and (v) evacuation for 30 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 N₂ (85%).

Methods

Infrared spectra were recorded with a Specord 71 ir double-beam spectrophotometer. A greaseless vacuum infrared cell was constructed and combined with an MS 10 mass spectrometer. Details of the spectrophotometers and the cell have been described elsewhere (4, 8).

The particle size of the supported Pt was determined by O₂-H₂ titration. There was no great difference in the dispersity of the Pt (Table 1).

RESULTS

Formation of Isocyanate Complexes

In the case of Pt/Al₂O₃ Unland (1, 2) found two bands due to isocyanate complexes, at 2267 and 2148 cm⁻¹. The first was assigned to covalently bonded isocyanate [-NCO]; the second one was assigned tentatively to anionic isocyanate [NCO⁻].

The formation of isocyanate complexes was first investigated at 250°C; 45 Torr of a reacting gas mixture was admitted to

the pretreated catalysts at the reaction temperature. From time to time the solid sample was moved to the cold part of the cell. The spectra were taken at the temperature of the infrared beam (about 50°C) in the presence of the reacting gases or after a brief evacuation of the cell. The spectra obtained are shown in Fig. 1. The characteristic peaks observed are shown in Table 2.

In the presence of the reacting gas mixture very intense bands appeared in all the spectra in the range 2318–2210 cm^{-1} . No such absorption bands were produced in this range in the presence of any of the individual reactants (NO, CO) or products of the NO + CO reaction (N_2O , N_2 , CO_2).

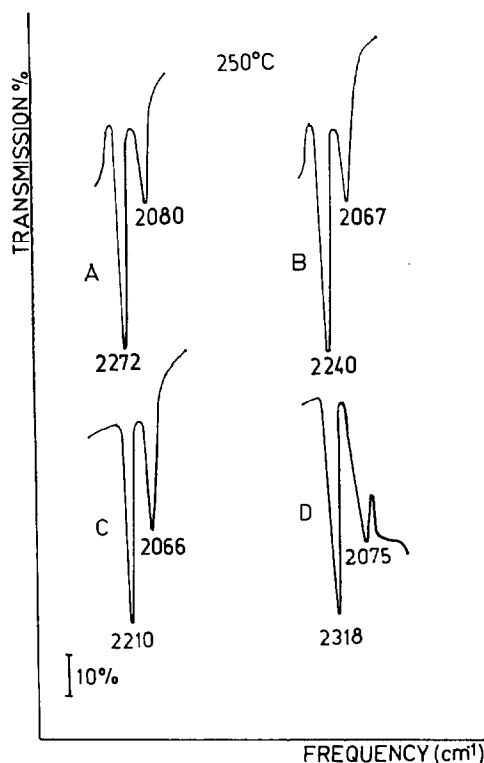


FIG. 1. Infrared spectra observed at room temperature after dosing the different Pt contacts with 45 Torr of a 10% CO, 5% NO, and 85% N_2 mixture at 250°C. (A) Pt/ Al_2O_3 : reaction time, 10 min; (B) Pt/ MgO : reaction time, 10 min; (C) Pt/ TiO_2 : reaction time, 2 min; (D) Pt/ SiO_2 : reaction time, 300 min.

TABLE 2
The Positions of the Bands due to Surface Isocyanate and Carbon Monoxide

Catalyst	Reaction temperature (°C)	Frequency (cm^{-1})		
		–NCO	[NCO [–]]	–CO
Pt/ Al_2O_3	250	2272	—	2080
	400	2272	2138 ^a	2080
Pt/ SiO_2	250	2318	—	2075
	400	2318	—	2075
Pt/ MgO	250	2241 ^b	—	2067
	400	2241 ^b	2213 ^a	2067
Pt/ TiO_2	250	2210	—	2066
	400	2210	—	2066

^a Shoulder.

^b At high coverages.

On this basis of the former studies on platinum, we attribute these bands to surface isocyanate complexes. *It is to be noted that we could not detect these bands in the absence of platinum on any of the supports used in this work.*

Apart from this general behavior, the rate of formation of the isocyanate band varied with the support. It formed at the highest rate on Pt/ TiO_2 , whereas on Pt/ SiO_2 the rate of formation was very slow (Fig. 2). The details of the spectra also varied with the supports.

In the case of Pt/ Al_2O_3 a band due to an isocyanate complex appeared at 2272 cm^{-1} (covalently bonded isocyanate). The presence of adsorbed CO was indicated by a band at 2080 cm^{-1} (linearly bonded CO). A shoulder at 2138 cm^{-1} indicating the presence of anionic isocyanate [NCO[–]] was observed at 350°C. It is to be noted that on 5% Pt/ Al_2O_3 these bands appeared at 2267, 2140, and 2080 cm^{-1} , respectively (4). The reason for this shift is possibly the difference in the dispersities of the Pt in the two samples.

On Pt/ SiO_2 only one band due to isocyanate was detected at 2318 cm^{-1} . A strong CO band appeared at 2075 cm^{-1} .

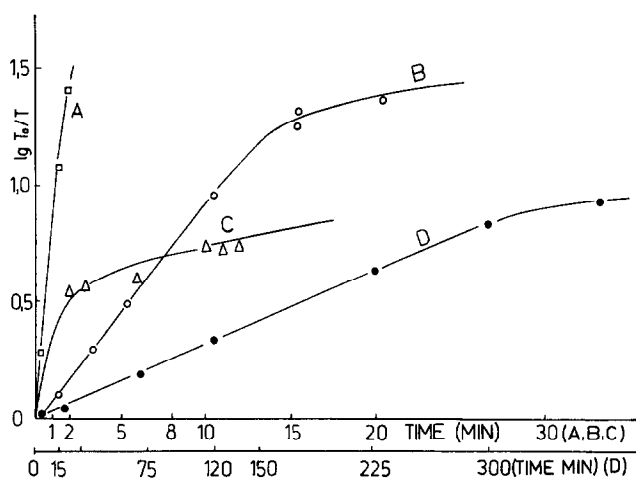


FIG. 2. Change of the intensity of the isocyanate bands with time observed at room temperature after dosing the different Pt contacts with 45 Torr of a 10% CO, 5% NO, and 85% N₂ mixture at 250°C. (A) 2210 cm⁻¹ on Pt/TiO₂; (B) 2225 to 2241 cm⁻¹ on Pt/MgO; (C) 2272 cm⁻¹ on Pt/Al₂O₃; (D) 2318 cm⁻¹ on Pt/SiO₂.

The isocyanate band was located at 2241 cm⁻¹ on Pt/MgO. A medium intense band due to adsorbed CO appeared at 2067 cm⁻¹. At 350°C a shoulder was also observable on the spectra at 2213 cm⁻¹. We note that in this case the location of the isocyanate band seems to depend on the coverage. At low coverage it appeared at about 2220–2227 cm⁻¹. With the increase of the surface concentration of isocyanate the band was shifted to higher frequencies, up to 2241 cm⁻¹ (Fig. 3).

The formation of isocyanate on Pt/TiO₂ was indicated by a band at 2210 cm⁻¹. The adsorbed CO gave a very strong band at 2066 cm⁻¹.

As in former studies with Pt/Al₂O₃ (2, 4), bands due to adsorbed NO were very weak or did not appear at all on any of the catalysts under the conditions applied.

The formation of isocyanate was also investigated at 400°C. The location of the isocyanate band was practically the same as at 250°C with the difference that the band or shoulder attributed to [NCO⁻] became more intense.

Effect of Support on Stability of Isocyanate Complexes

The stability of the isocyanate complex on supported Pt samples was investigated at 300–450°C. In all cases the isocyanate complex was produced at 250°C. To obtain more comparable data, the initial intensity of the isocyanate band was adjusted to practically the same value. This was achieved by variation of the reaction time and the pressure of the reacting gases.

The stabilities of the isocyanate complexes proved to be very sensitive to the support. Whereas they decomposed very rapidly on Pt/TiO₂ at 300°C, they were surprisingly stable on Pt/SiO₂ and Pt/MgO. The decomposition on these surfaces was relatively slow even at higher temperatures. Some results obtained at 300 and 400°C are shown in Fig. 4. Interestingly, the stability of the CO band (linearly bonded CO) was influenced only slightly by varying the carrier.

In the case of Pt/MgO it was observed that during the decomposition of isocyanate at 450°C the position of the isocyanate

band shifted to lower frequencies with the progress of the decomposition (Fig. 5).

Analysis of the Gas Phase during the Formation and Decomposition of Surface Iso-cyanate

No products of the surface reactions between NO and different Pt catalysts were detected below 100°C. Small amounts of N₂O appeared first in the gas phase at 100°C. At 250°C N₂O, O₂, and N₂ also formed. No significant difference was found among the behaviors of the Pt samples.

Catalytic reaction between the NO and CO was first observed at 200°C yielding N₂O, CO₂, and N₂. The lowest temperature for the formation of isocyanate was also 200°C on all the catalysts, with the exception of Pt/TiO₂; in this case formation of isocyanate was detected even at 150°C.

At the beginning of the decomposition of

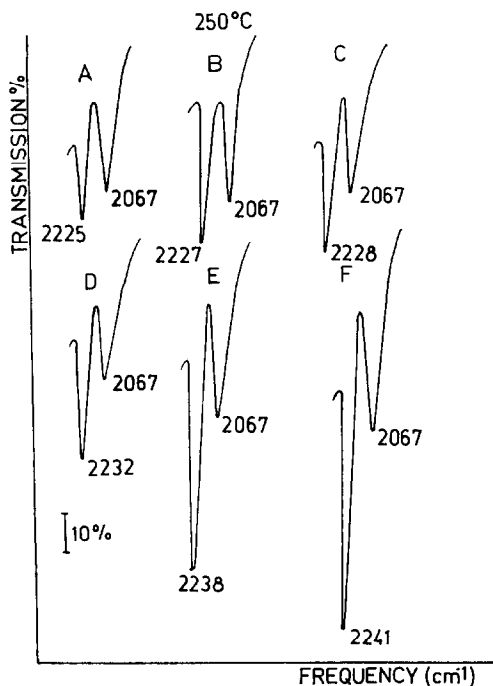


Fig. 3. Change in the infrared spectra with the progress of the formation of isocyanate on Pt/MgO at 250°C. (A) 1 min; (B) 3 min; (C) 5 min; (D) 10 min; (E) 20 min; (F) 30 min.

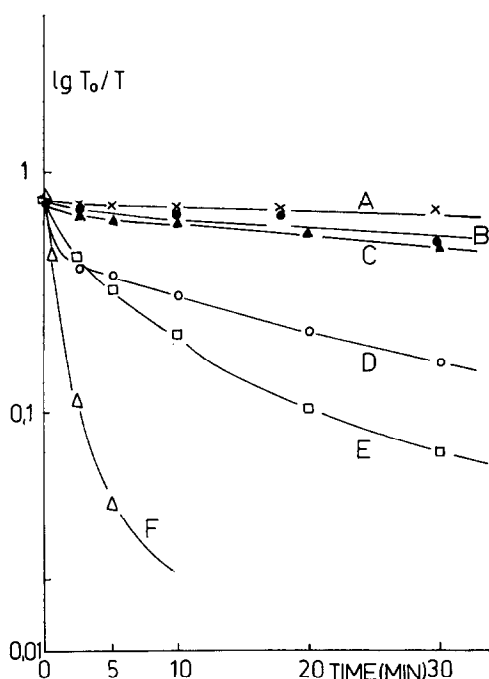


Fig. 4. Change of the intensity of the isocyanate bands with time in continuous evacuation at 300 and 400°C. (A) Pt/SiO₂ at 300°C; (B) Pt/MgO at 300°C; (C) Pt/SiO₂ at 400°C; (D) Pt/MgO at 400°C; (E) Pt/Al₂O₃ at 300°C; (F) Pt/TiO₂ at 300°C.

isocyanate at 350 to 400°C, CO₂ and N₂ evolved. The ratio CO₂/N was 1.2 to 1.5 in this stage. After this short initial period (3-6 min) only CO and N₂ were evolved. The ratio CO/N was somewhat larger than 1.0.

DISCUSSION

The results obtained unequivocally show that the supports influence the location of the isocyanate band and markedly affect the formation and the stability of the isocyanate complex. The bands due to isocyanate appeared at 2210 cm⁻¹ on Pt/TiO₂, 2241 cm⁻¹ on Pt/MgO, 2272 cm⁻¹ on Pt/Al₂O₃, and 2318 cm⁻¹ on Pt/SiO₂.

Before interpreting these findings in term of the "carrier effect," we deal briefly with the possible effect of the dispersity of the Pt. In the case of NO adsorption it

was observed that the stretching vibration of NO irreversibly adsorbed on supported Pt is particle size-dependent: the larger the size, the lower the $\gamma(\text{NO})$ vibration (12). This result was interpreted by assuming that the extent of the back-donation to the π^* orbitals of NO^+ depends on the collective properties of the crystallites.

Investigating the effect of the particle size of platinum supported by alumina on the formation of isocyanate, we found that, with the increase of the Pt dispersity, the position of the isocyanate band was also shifted to higher frequency (8, 13). This dependence, however, although in our opinion a real one, was very slight, $\Delta\gamma$ never exceeding 15 cm^{-1} in the dispersity range 9 to 30%.

In the present study the difference in the dispersity of Pt was less, but nevertheless the variation of the position of the surface isocyanate with the supports was much larger: $\Delta\gamma$ amounts to 108 cm^{-1} . On the basis of this we feel that the variation of the dispersity of Pt on the different supports is not the primary reason for the large shift observed in the location of the $-\text{NCO}$ band.

We may attempt to interpret the results in terms of the carrier effect. As has been demonstrated in several cases, due to the chemical and electronic interactions between the metal and the oxides, particularly semiconducting oxides, the properties of the metal can be changed, which influences its chemisorptive and catalytic properties (14). As the bonding of NO, CO, and very probably NCO is very sensitive to the electronic state of the metal, it can be expected that variation in the electronic properties of the platinum induced by supports with different electric properties affects its bonding with CO, NO, and also NCO.

Figueras *et al.* recently found that the location of the CO band was almost the same on Pd supported by MgO, Al_2O_3 , and SiO_2 ; however, a shift ($\Delta\gamma = 40\text{--}50\text{ cm}^{-1}$)

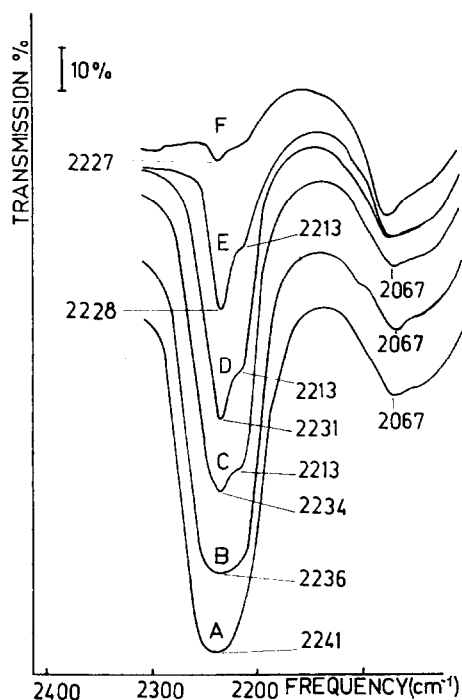


Fig. 5. Change in the infrared spectra of isocyanate on Pt/MgO during its decomposition *in vacuo* at 450°C . (A) 0 min; (B) 2.5 min; (C) 10 min; (D) 20 min; (E) 30 min; (F) 40 min.

of the CO vibration toward higher frequencies was observed when supports possessing electron-acceptor sites were used (15). The shift reflected a decrease in the back-donation of electrons from palladium to CO. The effect was interpreted in terms of an electronic interaction between the metal and oxidizing sites of the supports modifying the electronic state of the palladium.

In agreement with the above results, the supports used in the present work influenced the position of the bands due to adsorbed CO relatively only slightly, and thus it does not seem very likely that the large variation of the NCO vibration with the nature of the support could be attributed to the change of the electronic properties of Pt induced by interaction with the support.

There are a number of observations, however, which suggest that the large shift of

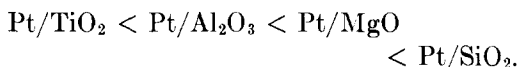
γ NCO is due to the fact that the isocyanate species are located not on the Pt but rather on the support. These are the following:

(i) Dalla Betta and Shelef (7) pointed out that the band area for adsorbed CO was almost independent of whether the surface was treated with CO or CO/NO mixtures. Assuming that the surface of the Pt is covered with adsorbed CO near its saturation coverage in both cases, the intense isocyanate band observed on the adsorption of CO/NO mixtures was attributed to the isocyanate adsorbed on the alumina.

(ii) Investigating the decomposition of the isocyanate complex on Pt/Al₂O₃ by the quantitative determination of the reaction products, we found that at low Pt content the number of isocyanate species greatly exceeded the number of surface Pt atoms (8, 9). From this it was concluded that the isocyanate (or part of it) formed on the Pt migrated from the Pt to the alumina carrier.

(iii) This explanation seems to be supported by the fact that the isocyanate gave an absorption maximum at 2313 cm⁻¹ on silica (16) and 2232 cm⁻¹ on magnesia (17). These values are almost the same as those observed on Pt/SiO₂ and Pt/MgO.

(iv) The stability of isocyanate on supported Pt is markedly influenced by the support (Fig. 4), increasing in the following order:



On the other hand, the stability of the CO band at 2067 to 2080 cm⁻¹ (linearly bonded CO) was affected only slightly by changing the support (Fig. 5). The extent of the difference in the stability of the isocyanate on the different catalysts was so large that it can not be accounted for by the "carrier effect." While isocyanate decomposed rapidly on Pt/TiO₂ even at 300°C, it was extremely stable on Pt/SiO₂, where com-

plete decomposition cannot be attained even at 450°C.

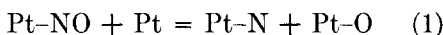
Investigating the decomposition of surface isocyanate on Pt/Al₂O₃, we found that the dispersity of the Pt influences the stability of the isocyanate (8). In the present case, however, the stability of the isocyanate differed even in when the dispersity of the Pt was almost identical (Pt/Al₂O₃ and Pt/MgO). The adsorbed gases present on the surfaces may also exert an influence on the properties of the isocyanate complexes. A prominent role is played by the chemisorbed oxygen, Pt-O, formed in the dissociation of NO, which can react with NCO groups (9). We found that when the Pt-O surface species had previously been reacted with CO, the stability of the Pt-NCO was greatly increased (9). The fact that a large amount of CO₂ was detected by mass spectrometry in the decomposition of isocyanate proved that the Pt-O groups were present on all the solid samples. To exclude the effect of adsorbed oxygen, this was reacted with CO before the decomposition of NCO. This treatment did indeed influence the stability of the isocyanate, in the present cases, as well, but qualitatively the pattern remained the same.

The most probable reason for the large difference in the stability is that the isocyanate is located on the support, and when all other factors are nearly the same, its stability is primarily determined by the chemical properties of the support. The relative insensitivity of the stability of the CO band to the nature of the support may indicate that the CO is bonded to the platinum. The fact that isocyanate was found to be the most stable on Pt/SiO₂ is in harmony with the high stability of Si-NCO (16).

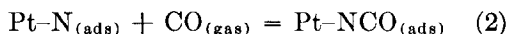
The stability of isocyanate on Pt/TiO₂ was less. In this case it is very likely that the reaction of isocyanate with the surface oxygens of TiO₂ also contributes to the observed instability of isocyanate.

In view of these considerations, the question arose of the role of the metal in the surface chemistry of the isocyanate complex. The fact that the formation of isocyanate from a gas mixture of NO and CO was not observed in the absence of Pt on any support indicates the essential role of the Pt in the formation of the isocyanate.

In a former paper we dealt in detail with the possible mechanism of the formation of isocyanate species on Pt/Al₂O₃ (4). We came to the conclusion that the primary step is the dissociation of NO on the Pt:



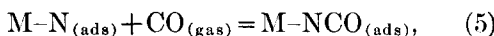
Especially at lower temperature, this may be promoted by CO through the transient formation of a molecular complex between NO and CO. This is followed by the reaction of an adsorbed N atom and gaseous CO:



In light of the results of the present work it seems likely that either the isocyanate formed on the Pt migrates to the carrier,



or the atomic nitrogen formed on Pt migrates to the support and reacts with gaseous or adsorbed CO,



where M = metal ion of the carrier.

If this proves to be the case, the phenomenon observed is a special case of the spillover [for review see (18)]. We may assume that the carbon formed in the dissociation of CO may serve as bridges which connect the platinum particles with the support particles.

On the basis of the available data it is difficult to say more about the possible modes of occurrence of isocyanate on the support. There are some observations, however, which might be useful in this

respect. The most important one is that the support *markedly affects the formation of the isocyanate complexes.*

Considering the extremely large difference in the formation of isocyanate, especially on Pt/TiO₂ and Pt/SiO₂, it is unlikely that this feature could be attributed to interactions of different extents between Pt and the carriers. It seems also less likely that the large difference in the formation of isocyanate can be accounted for by their influence on the migration of isocyanate species from the Pt to the support. If this were the dominant mode of effect of the support, one would expect to observe a band due to isocyanate on metal, assuming that the vibration of isocyanate is different on Pt and the support. However, even in the case of Pt/SiO₂, where the formation of isocyanate was exceptionally slow, we observed only the isocyanate band at 2318 cm⁻¹, attributed to Si-NCO. Therefore we tend to believe that the adsorbed nitrogen atom [N_(ads)] is the migrating species; its diffusion from the Pt to the acceptor sites is influenced by the surface structure and properties of the support, and this influence may modify the formation of isocyanate on the support. The fact that isocyanate formed with great ease on Pt/TiO₂ (TiO₂ is an *n*-type semiconductor), whereas the formation was the slowest on Pt/SiO₂ (SiO₂ is an insulator), is in agreement with the expectation that the higher ionic and electronic conductivity of the support promotes the migration of the adsorbed species.

Investigations are in progress to disclose more details on these processes and to evaluate the possible mechanism of migration of the adsorbed species.

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