JOURNAL OF CATALYSIS 71, 219–222 (1981)

Infrared Study of the Formation and Stability of Isocyanate Species on Some Unsupported Noble Metals

Infrared spectroscopic measurements in the recent past revealed that during the NO + CO reaction on supported noble metals an isocyanate surface species is formed (*1, 2*). As this surface complex very probably plays an important role in some undesired side reactions during automobile exhaust catalysis, great attention has been paid to the evaluation of its properties and the mechanism of its formation.[1] Recently, strong evidence was obtained that the observed absorption band stems from an NCO species located not on the noble metal, but rather on the support (*2, 4–7*).

Most of the data reported so far on the stability and reactions of NCO species on supported noble metals therefore reflect the properties of NCO primarily interacting with the support and only very little information can be inferred regarding the behavior of the NCO species on metals, as even its absorption band has not yet been unambiguously established. As NCO can accumulate to a large extent on the support, yielding an intense absorption band, this may mask the absorption band due to the NCO bonded to the metal, or the lifetime of NCO on noble metals at high temperatures is too short to permit its identification, due either to its fast migration to the support, or to its high instability on metals.

In the present work we report on an attempt to produce an NCO species on Pt without using an oxidic support, and on the determination of its infrared spectrum and thermal stability. Some observations on the NCO species bonded to other noble metals are also described.

The samples were prepared by the spraying of fine droplets of $H_2PtCl_6 \cdot 6H_2O$ (Reanal), $H_2IrCl_6 \cdot 6H_2O$ (Hicol), $RuCl_3 \cdot 1\text{–}3H_2O$ (Pierce Co.), $RhCl_3$ (Hicol), and $PdCl_2$ (Koch-Light) dissolved in methanol onto a 1-mm-thick NaCl disk. After evaporation of the methanol in air, the samples were treated in an ir cell: (i) evacuation at 473 K for 2 h; (ii) reduction with 13.3 kPa H_2 at 473 K for 2 h; (iii) evacuation at 298 K for 30 min.

The thickness of the metal films was estimated as 3 mg metal/cm^2. The gases used were of high purity. NO was further purified by distillation. HNCO was prepared by the reaction of H_3PO_4 and KOCN (BDH) (*7*).

The spectra were taken with a Specord 71 IR (Carl Zeiss, Jena) spectrophotometer fitted with a unit for ordinate extension. This device permitted 10-fold extension of the ordinate scale. The low-temperature measurements were carried out in a special infrared cell. The sample holder made from stainless steel could be cooled by liquid air to 140 K.

Adsorption of CO on Pt reduced at 473 K produced a band at 2030 cm^{-1} (Fig. 1). The same band was observed in the case of CO adsorption on evaporated Pt film (*8*). Its intensity hardly changed with the increase of CO pressure in the range 0.67–6.7 kPa and, as expected, were much less than on supported Pt (*1, 2*).

Adsorption of NO (1.3 kPa) gave no detectable spectral changes at 298 K. This is not surprising, as the adsorption of NO on supported Pt yielded a much weaker absorption band than that of CO (*1, 2*). Recent infrared reflection absorption spectroscopic (IRRAS) studies showed that the adsorption of NO on a low-area Pt surface gives very weak absorption bands even under high pressure of NO (*9*).

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[1] An interesting application of these studies is to develop a new catalytic route for the production of ammonium isocyanate and isocyanic acid (*3*).

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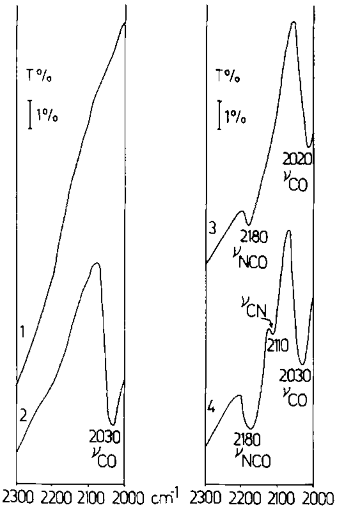

FIG. 1. Infrared spectra recorded on Pt after: (1) NO adsorption; (2) CO adsorption; (3) NO preadsorption and CO addition; (4) adsorption of NO + CO gas mixture (molar ratio 1 : 2) at 298 K. Spectra were taken at 298 K.

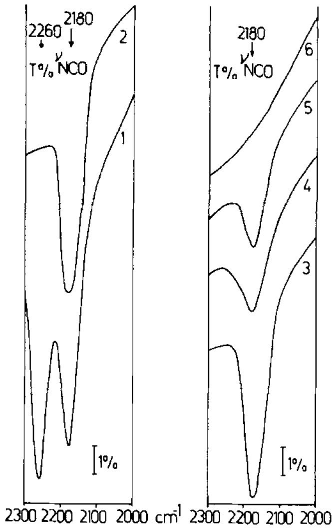

FIG. 2. Infrared spectra recorded on Pt, (1) in HNCO vapor at 140 K; and after evacuation: (2) at 140 K; (3) at 243 K; (4) at 273 K; (5) at 303 K; (6) at 343 K. Spectra were taken at the temperatures of evacuation.

Surprisingly, however, when CO was introduced onto the reduced sample, predosed with NO at 298–473 K, and evacuated at 298 K, in addition to the previously recorded CO band, a new weak band appeared at 2180 cm^{-1} (Fig. 1). This band was also identified with almost the same intensity during the coadsorption of NO + CO (molar ratio 1: 2) at 373 K. Its intensity did not change with the increase of the adsorption temperature up to 473 K. This band disappeared quickly at 310–330 K, when the reacting gas mixture was pumped off.

In order to identify the nature of the species responsible for the 2180-cm^{-1} band, the ir spectra of the possible products of the NO + CO reaction[2] were also taken. Since neither the adsorption of the reactants nor that of the possible reaction products produced a band at 2180 cm^{-1}, we tentatively assign this band to the asymetric stretching vibration of NCO bonded to Pt. As this species was produced when CO was admitted onto the surface predosed with NO, we have to assume that the surface contained either adsorbed N, due to the dissociation of NO, or adsorbed NO in sufficient concentation to react with CO to yield NCO.

In an attempt to confirm this assignment, we used labeled NO and CO. From the shifts observed ($\Delta\nu = -17$ cm^{-1} in ^{15}NO + CO and $\Delta\nu = -22$ cm^{-1} in NO + ^{13}CO, respectively), it may be concluded that the species giving the 2180-cm^{-1} band contains both N and C atoms.[3]

In the subsequent experiments the adsorption of HNCO was investigated at different temperatures. Some spectra are shown in Fig. 2.

The admission of HNCO onto the sample cooled to 140 K produced relatively intense bands at 2180 and 2260 cm^{-1}. The latter band, which is due to the vibration of gaseous (or weakly held) HNCO (*10*), can easily be eliminated by evacuation at 140 K. The appearance of the 2180-cm^{-1} band after adsorption of HNCO at 140 K may

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[2] CO_2, N_2, N_2O, HCN.

[3] The very small band at 2110 cm^{-1}, possibly due to CN species, was shifted in ^{15}NO + ^{12}CO to 2078 cm^{-1} ($\Delta\nu = -32$ cm^{-1}) and in ^{14}NO + ^{13}CO to 2068 cm^{-1} ($\Delta\nu = -42$ cm^{-1}).

indicate that part of the HNCO is adsorbed dissociatively on Pt at this temperature:

$$\text{HNCO} + 2\,\text{Pt} = \text{Pt–H} + \text{Pt–NCO}$$

The 2180-cm^{-1} band underwent very little change up to 243 K, but its intensity decreased markedly above this temperature. The band disappeared at 310–330 K. (On the NaCl window alone, without the Pt film, no adsorption of any gases used in this study occurred, or it was so limited that no detectable absorption bands were produced.)

To summarize these results, it can be concluded that NCO is formed on Pt in the NO + CO reaction, and also in the dissociative adsorption of HNCO without using oxidic supports. Its characteristic vibration, however, appeared at a much lower frequency (2180 cm^{-1}), than on titania (2210 cm^{-1}), magnesia (2241 cm^{-1}), alumina (2272 cm^{-1}), and silica (2318 cm^{-1})-supported Pt, proving that in these cases the NCO is located on the support (*2, 5, 6*). On the other hand, NCO on Pt behaved as an unstable species, as in the absence of the reacting gas mixture (NO + CO) or HNCO its characteristic absorption band disappeared at 310–330 K, very probably as a result of its surface decomposition. It is noteworthy that the band due to the NCO species on supported Pt remained unchanged even at 473–673 K.

The high instability of the NCO species on unsupported polycrystalline Pt is in harmony with the recent results obtained on the Pt(110) surface under ultrahigh vacuum conditions (*11*). From Auger, LEED, electron energy loss and thermal desorption spectroscopic measurements it was concluded that the NCO species exists on this surface, but dissociates completely to adsorbed N and CO at 320–330 K:

$$\text{Pt–NCO} = \text{Pt–N} + \text{Pt–CO}$$

As the band at 2180 cm^{-1} was not detected on any of the alumina, magnesia- or titania-supported Pt samples, we may conclude that in the presence of these oxidic supports the migration of NCO from the Pt onto the support is a very fast process. The driving force of this migration is possibly the formation of a strong bond with the electron acceptor Lewis centers on the oxidic support.

It should be pointed out, however, that a weak absorption band in the region 2180–2195 cm^{-1} was previously observed in the low-temperature reaction of NO + CO on Ru/SiO$_2$ (*12, 13*), and during HNCO adsorption on silica-supported noble metals at 298 K (*7, 14*). The results of the present study confirm that this band is indeed due to an NCO species, and that in these cases most of the NCO formed remained bonded to the metal. Accordingly, the migration of NCO onto silica is hindered at 298 K, very probably due to the high OH concentration.

Finally, it should be mentioned that attempts were made to produce NCO species on other noble metals, using the preparation method applied for Pt. Unfortunately, in these cases we did not succeed in prepar-

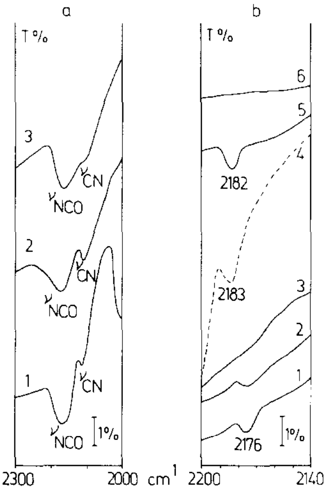

FIG. 3. Infrared spectra recorded: [a] in NO + CO gas mixture (molar ratio 1 : 2) at 298 K: (1) on Ir; (2) on Ru; (3) on Rh. [b] (1) After HNCO adsorption at 213 K and subsequent evacuation at 213 K on Ir; (2) after evacuation at 243 K on Ir; (3) after evacuation at 298 K on Ir; (4) in HNCO vapor at 298 K on Ru; (5) after HNCO adsorption at 213 K and subsequent evacuation at 213 K on Rh; (6) after evacuation at 243 K on Rh.

ing metals in a sufficiently finely dispersed state, and thus even the adsorption of HNCO produced only very weak bands at 2176–2183 cm^{-1} (Fig. 3), which did not allow more detailed studies. It can be safely concluded, however, that the vibration frequency of the NCO, and very probably the stability of the NCO species on other noble metals, are nearly the same as on Pt.

Note added in proof: Recent high resolution electron energy loss spectroscopic measurements on a Pt(111) surface also indicated the instability of the NCO species on Pt (*15*). In this case the NCO band, indicative of the dissociation of HNCO, appeared at 150 K and disappeared above 250 K.

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Received February 19, 1981; revised April 29, 1981