JOURNAL OF CATALYSIS **179,** 277–282 (1998)
ARTICLE NO. CA982208

The Effect of Adsorbed Oxygen on the Stability of NCO on Rh(111) Studied by Reflection Absorption Infrared Spectroscopy

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Received June 9, 1998; revised June 9, 1998; accepted June 15, 1998

The interaction of HNCO with Rh(111) has been studied with reflection absorption infrared spectroscopy. HNCO adsorbs dissociatively on Rh(111) at 150 K to yield adsorbed H and NCO species. On clean Rh(111) the NCO species was found to decompose readily to adsorbed CO and N on warming to room temperature. Preadsorbed oxygen atoms result in an increase in the relative amount of NCO, shifts the dominant vibrational band of NCO from 2160 to 2182 cm^{-1}, and significantly stabilizes the NCO species on Rh(111). The possible relevance of the stabilization of NCO in the NO + CO reaction is discussed. © 1998 Academic Press

Key Words: **NO + CO reaction; adsorption of HNCO; NCO surface complex; decomposition of NCO; effects of coadsorbed oxygen; stabilizing effect of oxygen adatoms; reflection absorption infrared spectroscopy.**

INTRODUCTION

In the clarification of the mechanism of catalytic reactions it is of fundamental importance to establish the nature and the reactivity of surface complexes formed on the catalyst surface. In the case of the NO + CO reaction the formation of isocyanate (NCO) surface species was observed on supported metals (1,2). Due to the great technological importance of the reaction this observation was followed by extensive research with the aim to disclose more details on the formation of isocyanate complex and on its role in the catalytic reduction of NO. The results obtained strongly suggested that isocyanate plays an important role in the undesired formation of ammonia during automobile exhaust catalysis (1–6).

Subsequent studies, however, revealed several surprising features of adsorbed NCO species, namely that the amount of NCO greatly exceeds the number of surface metal atoms available (6), and the location of NCO bands in the infrared spectra (6–11), together with the reactivity of NCO species (6,10,11), are primarily determined by the nature of the support. These observations led to the conclusion that although isocyanate is formed on the metals, it migrates onto the support and becomes stabilized there (6–13). This conclusion was confirmed by IR spectroscopic measurements (14–17). As a consequence of this finding, isocyanate was no longer considered as a reaction intermediate of the NO + CO reaction (18–20). This is obviously true for isocyanate located and stabilized on the support, but it remains an open question whether NCO primarily formed on and bonded to the metals cannot participate in the NO-CO reaction.

In harmony with the behaviour of a real reaction intermediate, this NCO species should have a short lifetime at high temperatures and low concentration; its identification, as well as the study of its chemistry, should therefore require sensitive spectroscopic techniques. This was clearly demonstrated in results obtained on unsupported metals, Cu{111} (21), Pt{111} (22), Pt{110} (23), Rh{111} (24), which showed that NCO (produced by the dissociation of HNCO) on these metals is unstable and decomposes to adsorbed CO and N at around room temperature.

This observed instability of the isocyanate complex is rather surprising and apparently in contradiction with the experimental fact that both the NO + CO reaction and the NCO formation proceed on supported Pt metals above 473–573 K. This implies a significant lifetime and stabilization of NCO on Pt metals, even at such a high temperatures, before its migration onto the support where it accumulates. We assume that the key species in this phenomenon is adsorbed oxygen atoms formed in the NO + CO reaction. The primary object of this work is to establish the effect of adsorbed oxygen on the vibrational characteristics and thermal stability of NCO species on Rh (111). For this purpose reflexion absorption infrared spectroscopy (RAIRS) is applied which—taking into account its high resolution and sensitivity—can be considered as an excellent method.

EXPERIMENTAL

The experiments were performed in a two-level UHV system with a base pressure of 5×10^{-10} mbar. The lower part of the chamber had facilities for Auger electron

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0021-9517/98 $25.00

spectroscopy (AES) and temperature-programmed desorption (TPD). The upper part was equipped with a single beam Fourier transform infrared spectrometer (Mathson Unicam, Research Series), which was used for RIAS measurements. All IR spectra were averaged over 512 scans using a MCT detector at 2–4 cm^{-1} resolution. Sample spectra were ratioed against a background taken immediately after the sample by flashing the crystal to 1270 K. The scan was initiated after the crystal temperature had returned to 95 K.

The Rh(111) single crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1–2 kV, 1×10^{-4} Pa argon, 3 μA for 10–30 min) and by annealing at 1270 K for several minutes. Surface cleanliness was confirmed by AES. The Rh sample was resistively heated, and the temperature was measured with a chromel–alumel thermocouple spot-welded to the edge of the crystal. For low-temperature measurements the sample was cooled via a tantalum attached to a liquid-nitrogen-cooled stainless steel tube. The adsorption of oxygen was performed at 300 K. The surface concentration of oxygen on Rh(111) at saturation corresponds to 0.5 monolayer, $\Theta_O = 0.5$. The lower coverage oxygen overlayers were prepared by exposing the Rh(111) crystal to O_2 for varying times at 300 K. The amount of the surface oxygen was monitored by AES.

HNCO was prepared by the reaction of 95% H_3PO_4 and saturated KOCN (8). It was degassed and purified by freeze-pump-thraw cycles.

RESULTS AND DISCUSSION

The RAIR spectrum of the Rh(111) surface exposed to various amounts of HNCO at 95 K is shown in Fig. 1A. At low exposure only one absorption band could be detected at 2267 cm^{-1}. With the increase of the HNCO exposure the 2267 cm^{-1} band shifted to 2277 cm^{-1} and other absorption bands appeared at 3373, 3240, 1444, 1419, 1322, 1245 cm^{-1}. Taking into account the vibrational characteristics of vapour and solid HNCO and those of adsorbed HNCO on oxides surfaces (8,11,25), the strong band at 2267–2277 cm^{-1} is no doubt due to the asymmetric stretch of molecular adsorbed HNCO. The assignment of the other bands are given in the Table 1. It is remarkable that the bands due to N-H vibration appeared only at higher exposure, which may indicate that in the submonolayer the H-N axis (but not the N-C-O group) is paralell to the surface. It is also possible that the absence of the ν(N-H) band at low coverage could be due to its lower intensity, compared to other bands. Note that a weak band at 2160 cm^{-1} also appeared, which was attributed in our previous works to the asymmetric vibration of adsorbed NCO formed in the dissociation of HNCO (8,11). Alternatively, it may belong to the molecularly adsorbed HNCO, as this weak band was also seen in the IR spectrum of HNCO vapour (25). When the sample was heated to 150–175 K, the 2267 cm^{-1} band (ν_a, NCO), and the band at 3240 cm^{-1} (νN-H), both indicative of the presence of molecularly adsorbed HNCO, were completely eliminated. At the same time the peak at 2160 cm^{-1} intensified and a new peak developed at ~2020 cm^{-1}. There is no doubt that this 2160 cm^{-1} band is due to NCO species, while the band at 2020 cm^{-1} is the vibration of adsorbed CO produced by the decomposition of NCO complex. Further increase in the annealing temperature led to the attenuation of the 2160 cm^{-1} band and to the intensification of the CO band. In agreement with the results of previous works, the band indicative of the presence of the adsorbed NCO completely disappeared between 300–330 K (24).

TABLE 1

Frequencies (cm^{-1}) and Assignments of the Fundamental Vibrations of Vapour, Solid and Adsorbed HNCO

Assignment		Vapour	Solid	Submonolayer on Rh(111)	Multilayer on Rh(111)
ν_1 (a′)	ν(NH)	3531	3133	—	3373; 3240
ν_2 (a′)	ν_a(NCO)	2274	2246	2267	2277
$\nu_4 + \nu_6$		1480	1460	—	1444
$\nu_4 + \nu_5$		1371	1377	—	1419
ν_3 (a′)	ν_s(NCO)	1327	1326	—	1322
ν_4 (a′)	δ(NCO)	797	—	—	—
ν_5 (a′)	hindered rotation	572	—	—	—
ν_6 (a″)		670	—	—	—

Note. Data for HNCO in vapour and solid phase were taken from Ref. (25). $\nu_4 + \nu_6$; $\nu_4 + \nu_5$ correspond to combinations of fundamental vibrations.

TPD measurements indicated that the weakly adsorbed HNCO desorbed with a peak temperature of 118 K, which shifted to 125 K at higher exposures. This peak cannot be saturated, which is the sign of the formation of a condensed layer. In addition to HNCO, the formation of CO with $T_p =$ 440 K, and N_2 with $T_p = 630$ and 720 K also occurred. These peak temperatures agree well with those found following the adsorption of CO (27) and N atoms (28) on Rh(111) surface, suggesting that the evolution of these compounds is desorption limited reaction. TPD data are collected in Table 2.

The same experiments have been performed on oxygen-dosed Rh. The molecularly adsorbed HNCO gave identical spectral features as obtained for the clean surface. The position of the NCO species, however, shifted to higher frequencies. In order to see more clearly, the adsorption of HNCO was performed at 150 K, above the desorption temperature of HNCO. The effect of oxygen coverage is shown in Fig. 2A. At lower oxygen coverages, two peaks can be distinguished at 2160 and 2180 cm^{-1}. At the highest oxygen coverage we obtained only one peak at 2182 cm^{-1}. The

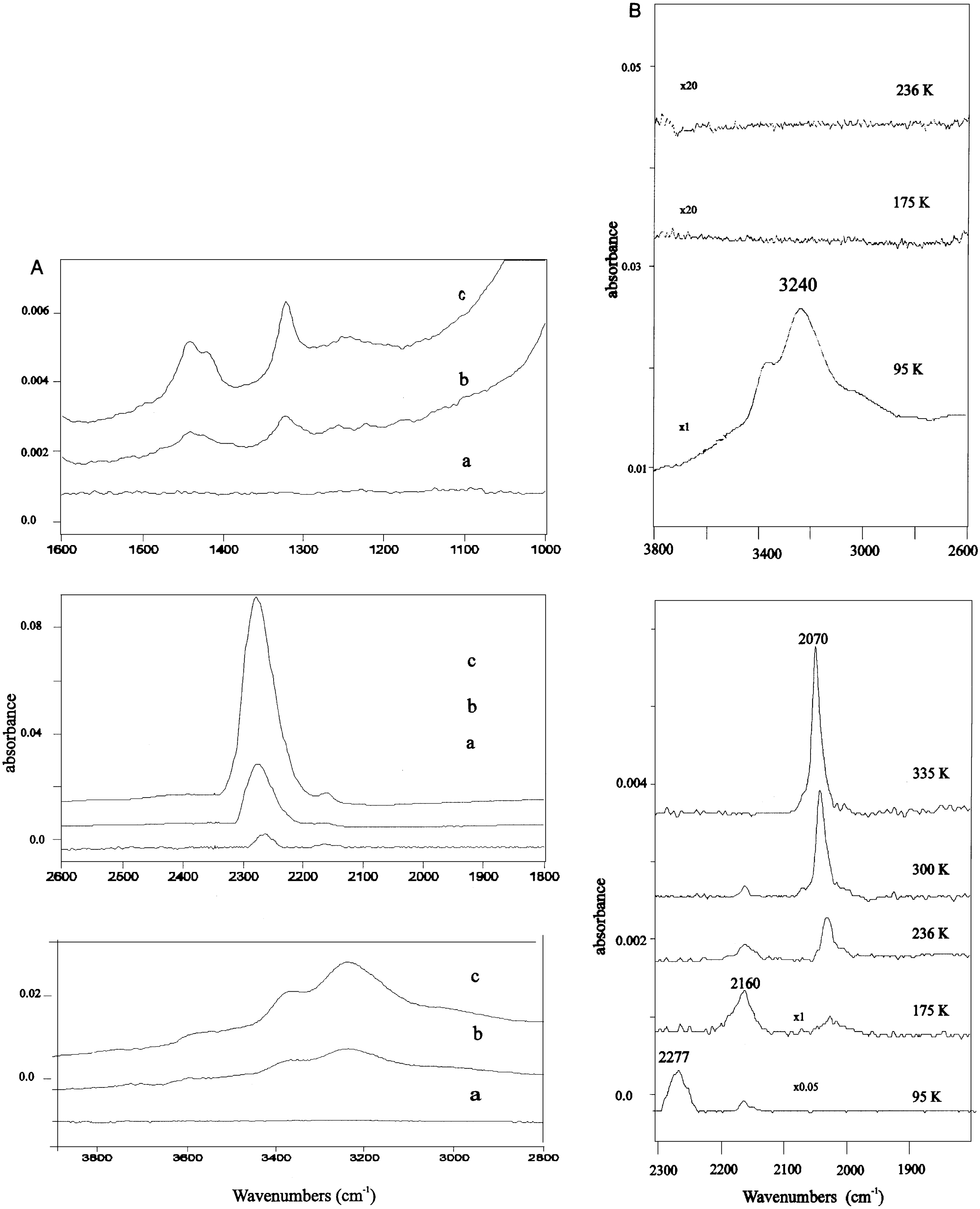

FIG. 1. (A) RAIR spectrum of adsorbed HNCO as a function of HNCO exposures on a clean Rh(111) at 95 K: (a) 6L; (b) 18L; (c) 30L. (B) Effects of annealing of the adsorbed layer.

TABLE 2

Characteristic TPD Data Following the Adsorption of HNCO on Clean and O-Dosed Rh(111) at ~95 K

	Peak temperature (K)	
Product	Clean Rh(111)	Oxygen covered Rh(111) $\Theta_O \sim 0.5$
HNCO	118–125	118–125
CO	440	460
N_2	630; 720	630; 720
H_2	420	—
CO_2	—	390
H_2O	—	185

effect of annealing is displayed in Fig. 2B. Around 200 K, an intense CO band appeared at 2060 cm^{-1}. On further heating of the sample, the NCO band attenuated and the CO band became more intense. The spectral feature centered at 2182 cm^{-1} disappeared only at 373 K, a significantly higher temperature than in the case of a clean surface. This suggests that preadsorbed oxygen enchances the stability of the isocyanate complex on Rh surface. This is clearly demonstrated by the intensity data versus annealing temperature in Fig. 3.

By means of TPD we detected the same desorbing products, CO and N_2, as for the clean surface. In addition, the release of H_2O ($T_P = 185$ K) and CO_2 ($T_P = 390$ K) was also established. Taking into account that above 300 K both the NCO and CO are present on the surface it is likely that both compounds participate in the reaction with adsorbed O. The formation of CO_2 is clearly a reaction-limited process, as CO_2 desorbs from a clean Rh(111) far below 300 K (29).

For the stabilizing effect of adsorbed O atoms several reasons can be considered: (i) The NCO species is affected by a strong electric field induced by adsorbed oxygen atoms (30–32). Recently Kreuzer (31–32) has shown that the binding of adsorbed species to the surface can be strongly influenced in an external field. As a result of this effect, NCO species can be converted into a more ionic form, leading to higher stability. Previous IR data show that the increasing stability of surface NCO adsorbed on a series of oxides is reflected in an increase in NCO frequency (8,11). (ii) Oxygen adatoms could block sites for the formation of the dissociation products, CO(a) and N(a). It is conceivable that the combined influence of these factors lead to the stabilization of the NCO species. It is also possible that preadsorbed oxygen changes the adsorption sites for NCO. The direction and the extent of the shift of the NCO vibrational band due

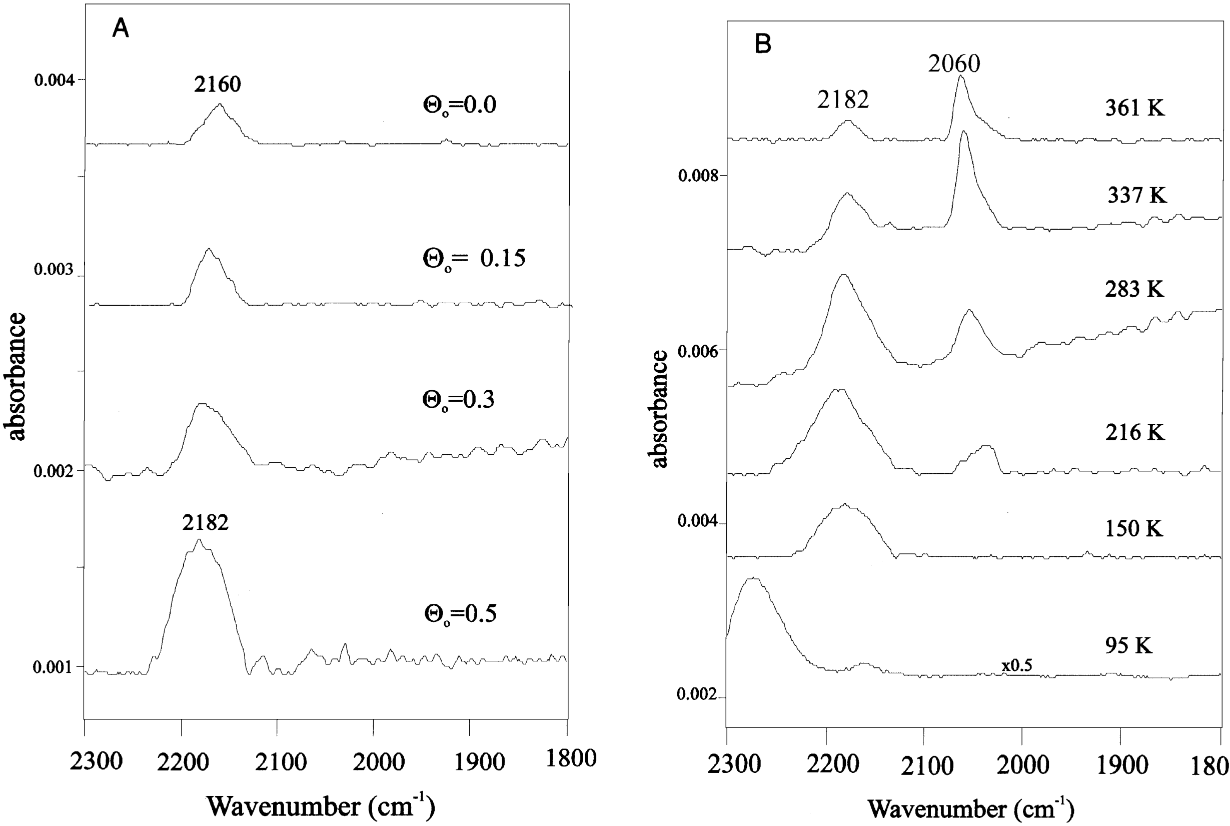

FIG. 2. (A) Effects of oxygen coverage on the RAIR spectrum of adsorbed NCO on Rh(111) at 150 K. (B) Effects of annealing of HNCO + O/Rh(111) system ($\Theta_O \approx 0.5$). Adsorption temperature was 95 K.

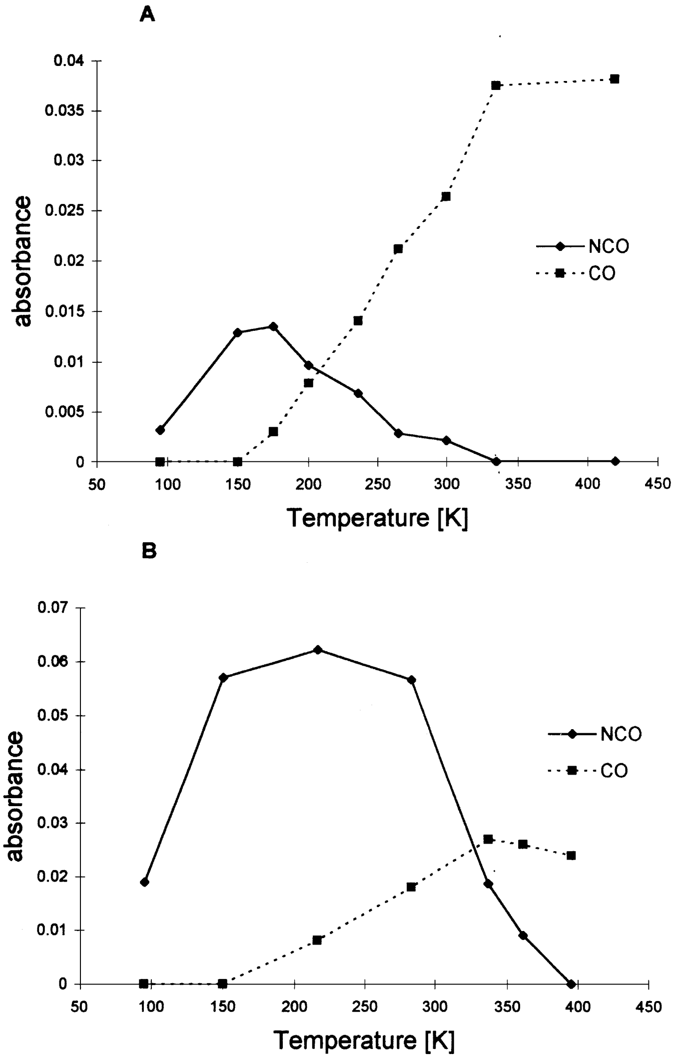

FIG. 3. The intensity changes of vibrational bands at 2160–2182 cm^{-1} (NCO) and 2020–2070 cm^{-1} (CO) after heating the clean (A) and oxygen-dosed samples (B) saturated with HNCO at 95 K. All vibrational spectra were taken after the crystal again cooled to ca 95 K.

to adsorbed oxygen atoms, however, do not support this assumption.

We may compare the features observed with those established recently by Menzel *et al.* (33,34). They succeeded for the first time to produce NCO species by the NO + CO reaction on a single crystal, Ru(001), under UHV conditions. The NCO gave a vibrational band at 2170 cm^{-1} in the HREEL spectrum. An important finding of this work is that the presence of adsorbed oxygen is a necessary condition for the production of NCO. For pure (N + CO) layers isocyanate formation was not observed. Furthermore, the production of NCO depended strongly on the structure of the preadsorbed (N + O) layer. In explaining these results, the influence of an electrostatic field due to O-induced dipoles on the (N(a) + CO(a)) layer, and the O-induced changes of the adsorption properites of Ru(001) were taken into account. In the light of our results, it is very likely that the stabilizing effect of oxygen atoms also contributes to the existence and identification of the NCO species on Ru(001). Interestingly, when NCO was produced under optimum conditions (heating of the disordered (N + CO) layer), NCO gave a vibrational band at 2190 cm^{-1} and of higher intensity; this loss was detectable at a higher temperature than the 2170 cm^{-1} loss observed following heating of the ordered layer (33,34). These features are in agreement with our findings and we feel they are strongly associated with the effects of adsorbed oxygen atoms established in this work.

Finally, we mention that the NCO surface complex has also been detected in the reduction of the NO pollutant with saturated and unsaturated hydrocarbons on supported Cu catalysts. Yoshida *et al.* (35,36) found a correlation between the efficiency of NO_x reduction and the formation of the NCO species. They concluded that the NCO intermediate and/or its reaction with NO are a key to efficient NO reduction in the presence of oxygen. In a recent study it was also shown that NCO is more stable on copper that on Pt metals, and the migration onto the support is more restricted (37). Isocyanate species were also identified on oxidized Pt metals in the catalytic reaction of NH_3 and CO, which is connected with the synthesis of compounds important for the fertilizer industry (16,17). We believe that in both cases the stabilizing effect of adsorbed oxygen plays an important role in the appearance and identification of NCO species.

On summing up we can assume that, under dynamic conditions, due to this stabilizing effect, the NCO surface species has a sufficient lifetime on Rh, even at a higher temperature, for it to function as a surface intermediate in the main and side-reactions during automobile exhaust catalysis. Further studies are clearly required under dynamic conditions.

CONCLUSIONS

HNCO adsorbs dissociatively on a clean Rh(111) surface above 150 K. The NCO species formed is characterized by an intense loss feature at 2160 cm^{-1} on a clean and 2182 cm^{-1} on an oxygen-dosed Rh(111) surface in the RAIR spectrum. The NCO surface complex decomposes almost completely on clean Rh at around 300 K under UHV conditions. Oxygen adatoms enhance its stability region at least by 60 K. Although the detailed reaction kinetics of the CO/NO oxidation reaction to CO_2 over Rh can be described with a scheme involving NO dissociation (38), where NCO plays no part, it is likely that under dynamic conditions NCO exists on the Rh catalysts even at higher temperatures and may be involved in important side reactions.

ACKNOWLEDGMENTS

This work is supported by Hungarian Academy of Sciences and by the OTKA Grant 23023.

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