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Isocyanate Intermediates in the Reaction of NO and CO Over Noble Metal Catalysts

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A comparative study of the infrared spectra of reaction intermediates and chemisorbed species during the reaction of NO + CO over Pt, Pd, Rh, Ir, and Ru-on-alumina catalysts at elevated temperatures has been made. A strong band which is assigned to a surface isocyanate species has been found in the 2260–2270 cm^{-1} region on all the noble metals except Ru where the band is either quite weak or entirely absent. The weakness of the band on Ru/Al_2O_3 seems to correlate with its unique low ammonia-forming properties during NO_x removal from automobile exhaust. Hydrolysis of the surface isocyanate species provides a pathway to NH_3 which does not involve reduction of NO directly with hydrogen already present in the exhaust stream or generated via a water-gas shift mechanism. No assessment of the relative importance of this mechanism with respect to other mechanisms for ammonia formation in actual automobile exhaust can be made from the present results.

Sulfur poisoning of the Rh and Ru catalysts is observed to inhibit the formation of the isocyanate species. However, this poisoning is temporary and the -NCO sites can be regenerated by oxidation treatment.

INTRODUCTION

Because of concern over $NO_x(NO + NO_2)$ emissions from automobile exhaust, the search for suitable methods of catalytically controlling NO_x has become more intense in recent years. While entirely suitable NO_x catalysts have not yet been found, it appears that one of the noble metals, Ru, is rather unique (*1–4*) in not forming large amounts of ammonia under the reducing conditions necessary for NO_x removal. It was believed that a comparative infrared study of the NO + CO reaction over noble metal-on-alumina catalysts such as had been carried out for Pt/Al_2O_3 (*5*) would give some insight into the unique behavior of Ru/Al_2O_3 as well as more general insight into the problems of NO_x removal from automobile exhaust using noble metal catalysts. A preliminary report of this study has been published (*6*) and we will here amplify and add new material to those results.

EXPERIMENTAL METHODS

The infrared cell, method of sample preparation, sample treatment procedures, and instrumental details have been described (*5, 6*) earlier. The Pt and Ir samples were prepared from chloroplatinic acid and iridium trichloride, respectively, while the Rh, Ru, and Pd samples were prepared from the corresponding nitrate salts. All samples contained a nominal 5% metal on alumina after calcination and reduction. The sample "thickness" is estimated as 1.0–1.5 mg/cm^2. All spectra were run at temperatures $\leq 50°C$ at 1 Torr gas pressure after dosing the cleaned (*5*) sample at 400°C with 100 Torr of the desired gas for a period of 30 min. XRD spectra and transmission electron microscope pictures of these samples showed that the noble metals on these supports were highly dispersed with an average crystallite size of less than 40 Å. The crystallite size of the fibrillar Al_2O_3 is of the order of 50 Å.

INFRARED RESULTS

Chemisorption of CO, CO_2 NO and N_2O

In order to aid the interpretation of the spectra observed when using a reactive gas mixture of NO and CO, runs were made on each sample with the individual reactant and product gases CO, NO, CO_2 and N_2O. With the exception of N_2O all the gases produced some changes in the sample spectrum when compared against a blank run in vacuum. Apparently, N_2O is not strongly adsorbed on any of the samples as prepared and studied in this work.

The results of CO chemisorption on the noble metal samples are presented in Fig. 1. While all of the samples show some evidence of bands in the carbonyl stretching region from 1800 to 2200 cm^{-1} only Rh, Ir, and Pt show strong bands in this region. However, one must be aware of the possibility that differences in defect structure, crystallite size, oxidation state and active surface area can play an important part in the nature of the observed spectrum and, therefore, that firm conclusions should not be drawn from the presence or absence of bands from a single sample using a single gas. In fact, reasonably strong CO bands have been reported in the literature for all the noble metals (*7*). This, of course, points out the necessity of running reference spectra on the particular sample of interest and of making sample preparation and treatment procedures as uniform as possible in a comparative study.

The results of using the other reactant gas, NO, are presented in Fig. 2. With the above reservations about possible sample differences, this set of samples appears to chemisorb NO in the order Ru > Rh > Pd > Ir > Pt based on relative intensities of the bands in the 1700–1900 cm^{-1} region. The strong NO band on Ru is not surprising since it is generally recognized (*8*) that NO complex formation is an important feature of ruthenium chemistry.

The region 1200–1700 cm^{-1} in Fig. 2 is quite complex and the possible adsorbed species giving rise to adsorption bands in this region include NO_3^-, NH_4^+, and NH_3 (deformation mode). The NH_3 species could be formed from H_2 left in the metal since samples were in all cases reduced with H_2 prior to evacuation and dosing with

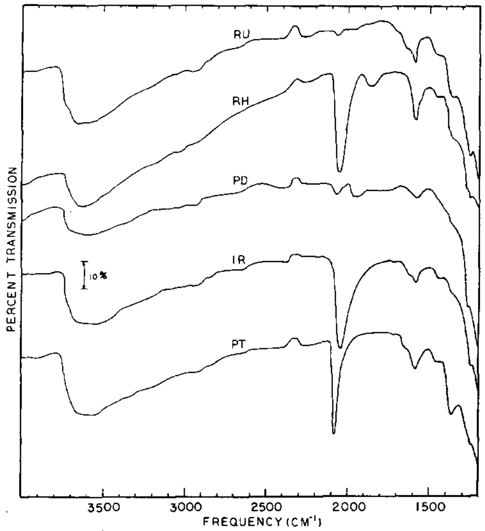


FIG. 1. Spectra observed at room temperature and 1 Torr pressure after dosing the clean 5% noble metal/Al_2O_3 sample at 400°C with 100 Torr of CO.

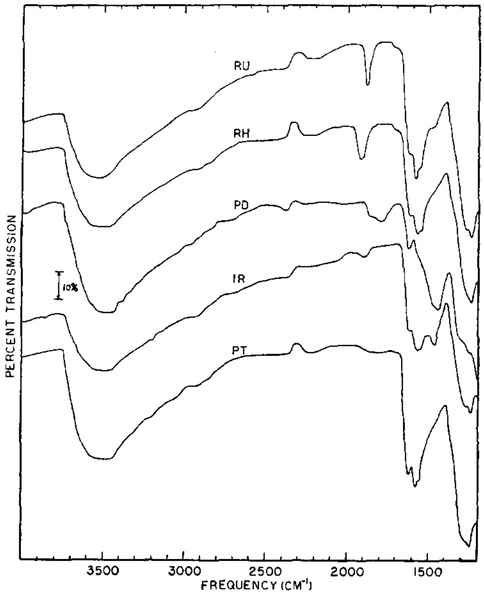


FIG. 2. Spectra observed at room temperature and 1 Torr pressure after dosing the clean 5% noble metal/Al_2O_3 sample at 400°C with 100 Torr of NO.

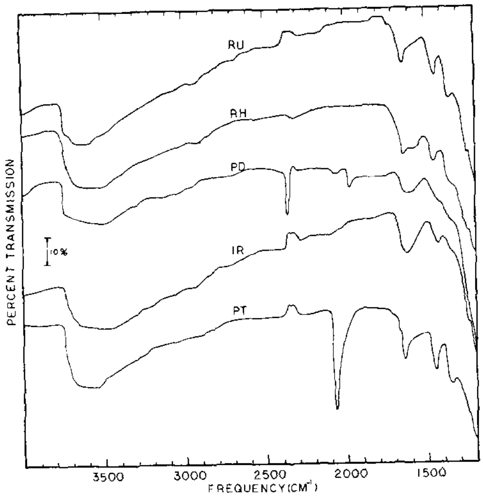


FIG. 3. Spectra observed at room temperature and 1 Torr pressure after dosing the clean 5% noble metal/Al_2O_3 sample at 400°C with 100 Torr of CO_2.

NO at 400°C. The band system in the 3300–3700 cm^{-1} region in the spectra in Fig. 2 does appear to be more intense than in Figs. 1, 3, and 4, and may well arise from –NH stretching modes if appreciable NH_3 formation has occurred on the sample surface.

Of possible infrared active products of the NO + CO reaction only CO_2 produced changes in the sample spectra when compared against a blank run (clean sample under vacuum at room temperature). The results of the CO_2 reference runs are displayed in Fig. 3. Of the noble metals studied only Pt/Al_2O_3 dissociatively adsorbed CO_2 as evidenced by the strong CO band at 2075 cm^{-1}. On the majority of the samples, carbonate bands appear at ~1630 and ~1450 cm^{-1}, although the lower frequency band is very weak or absent in the Pd/Al_2O_3 sample. Palladium also seems to be somewhat unique in that a fairly strong physical adsorption of CO_2 occurs as indicated by a band at ~2360 cm^{-1} which could be removed by pumping for 1 hr at room temperature.

Reaction Mixture Spectra

Figure 4 shows the spectra obtained using the same samples as in Figs. 1–3 when 100 Torr of a gas blend containing 10% CO, 5% NO, and 85% N_2 was used. The location of the major bands in Fig. 4 are given in Table 1. The lower frequency bands around 1630, 1570, and 1465 cm^{-1} seem to be more or less common to the whole series and, as discussed in the earlier detailed study (*5*) of Pt/Al_2O_3, these are tentatively assigned to imine, bidentate carbonate, and carbonate anion or monodentate carbonate complexes, respectively.

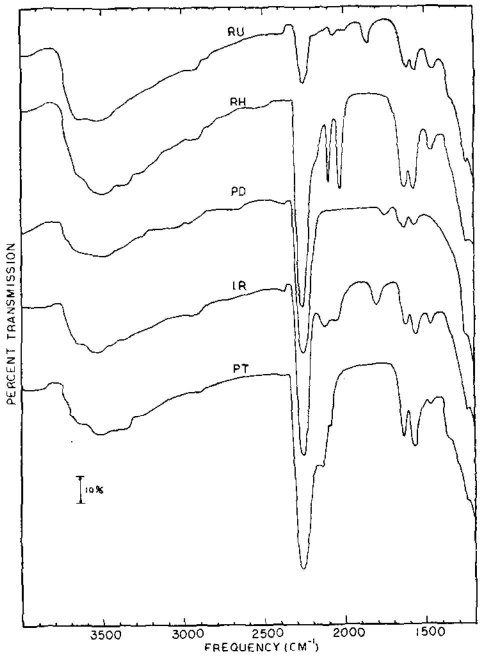


FIG. 4. Spectra observed at room temperature and 1 Torr pressure after dosing the clean 5% noble metal/Al_2O_3 sample at 400°C with 100 Torr of a blend containing 10% CO, 5% NO, and 85% N_2.

The main features and points of interest in Fig. 4 are the prominent bands between 2260 and 2270 cm^{-1} in each of the spectra. From earlier studies (*5*) on Pt/Al_2O_3 which included temperature, concentration, and isotopic labeling experiments, it was concluded that these intense bands arise from either a covalently bonded –NCO species or an anionic $[NCO^-]$ species.

Sulfur Poisoning

The antiseptic conditions used in this study bear little relation to actual auto-

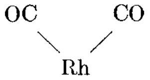
TABLE 1

Major Bands in Fig. 4 (Frequency in cm^{-1})

Metal	-NCO	$([NCO]^-)^a$	-CO	CO	-NO	$\left(>C=N-\right)^a$	CO_3^{2-}	$(CO_3^{2-})^a$
Ru	2259	2238	2070	2009	1856	1620	1568	1457
Ru[b]	—	—	—	—	1882, 1861, 1715	1610	1575	1536, 1445
Rh	2269	2175	2106[c]	2036[c]	—	1633	1570	1466
Pd	2264	—	—	—	1751	1635	1571	—
Ir	2267	2239	2126	2050	1807	1627	1568	1475
Pt	2267	2148	2090	—	—	1631	1570	1465

[a] The assignments in parentheses are considered tentative.

[b] Spectrum not shown in Fig. 4. This was the same sample after it had been heated under a variety of gases a number of times. The experiment was identical but it is obvious the sample has changed. Ru/Al_2O_3 was the only sample which changed under repeated runs.

[c] Assigned to  $(OC)_2Rh$ species as per Ref. (9).

mobile exhaust which contains hydrocarbons, sulfur, lead, water and other components which can act as either permanent or temporary catalyst poisons. While it was not feasible in the present study to employ real exhaust mixtures, an attempt was made to observe the effect of preadsorbed sulfur on the infrared spectra. The procedure was to clean the catalyst as before but to contact the hot sample with a small amount of SO_2 prior to admitting the 10% CO + 5% NO mixture to the cell. Examples of low and high NH_3 forming NO_x reduction catalysts, Ru/Al_2O_3 and Rh/Al_2O_3, were studied in this manner. In addition, the effect of water vapor at room temperature on the -NCO bands on both catalysts was observed. Figures 5 and 6 show the results obtained on Ru and Rh samples.

The effect of preadsorbing SO_2 on the Ru/Al_2O_3 surface can be seen by comparing B and C in Fig. 5. The problem of sintering of the Ru/Al_2O_3 samples noted in Table 1 was avoided by using freshly prepared samples in B and C. It is evident that the SO_2 has been strongly adsorbed in scan C and has prevented the formation of both the -NCO and -CO groups as well as hindering the chemisorption of NO. It is interesting that two distinct -NO bands are observed after preadsorption of SO_2. Either the NO is now adsorbed on two different sites or at least in two slightly different forms. The presence of a small carbonate band at ~1577 cm^{-1} is taken as evidence that the preadsorbed SO_2 did not completely inhibit the reaction between NO and CO. After scan B of Fig. 5 was completed, 5 Torr of water vapor were added at room temperature and allowed to equilibrate for 1 hr. The spectrum at 0.5 Torr is shown in Fig. 5D. The decreased intensity of the -NCO band at 2258 cm^{-1} and the increased intensity in the -OH region ~3500 cm^{-1} are readily apparent. The decrease in intensity of the 2258 cm^{-1} band is consistent with a reaction between -NCO and H_2O and the increased intensity of the band at 1630 cm^{-1} is probably due to adsorbed H_2O, but a contribution from adsorbed NH_3 may also be present.

The results of a similar series of experiments on Rh/Al_2O_3 are shown in Fig. 6. In this case the same sample was used for all experiments since earlier experience indicated that the "cleaning" procedure described in the notes to Fig. 6 brings the Rh/Al_2O_3 samples back to the same state as far as can be determined by infrared analysis. Spectrum B of Fig. 6 shows the strong -NCO band at 2270 cm^{-1} and the

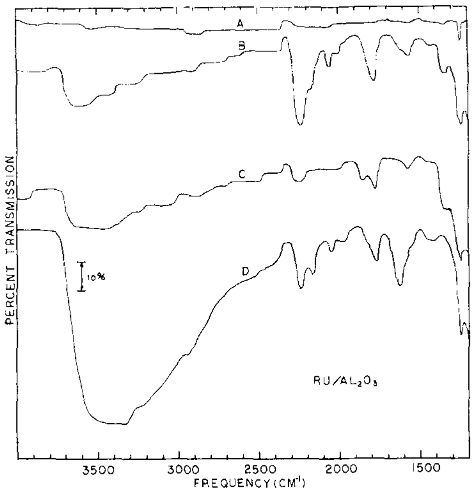


FIG. 5. 5% Ru/Al_2O_3 infrared spectra: (A) evacuated cell, sample out; (B) fresh, reduced sample treated at 400°C with 100 Torr 10% CO + 5% NO. Scan at $P = 1$ Torr, $T \leq 50°C$. (C) Fresh, reduced sample treated at 400°C with 10 Torr 10% SO_2/N_2 plus 90 Torr 10% CO + 5% NO. Scan at $P = 1$ Torr, $T \leq 50°C$. (D) Sample B evacuated and treated with 5 Torr H_2O. Scan at $P = 0.5$ Torr, $T \leq 50°C$. NOTE: The "fresh, reduced" samples were prepared by calcining *in vacuo* for 4 hr at 400°C then reducing in 100 Torr H_2 for 1 hr at 400°C before evacuating for 30 min.

doublet at 2104 and 2035 cm^{-1} associated with two CO molecules adsorbed on the same Rh atom.

This type of CO adsorption is believed (*9*) to occur primarily on highly dispersed and irregular Rh surfaces. From Fig. 6C the strong effect of preadsorbing SO_2 on the catalyst is apparent. All bands are either much weaker or totally absent and the CO is no longer adsorbed on the Rh primarily in a two-on-one fashion but rather in a linear configuration. These results show that SO_2 has completely covered the highly energetic sites needed for -NCO formation and adsorption of two CO molecules per Rh atom. Also, the absence of carbonate bands in Fig. 6C may indicate that the SO_2 has completely inhibited the reaction under these conditions. Spectrum D of Fig. 6 is a recheck of the Rh/Al_2O_3 sample after SO_2 poisoning and an oxidation-reduction treatment at 400°C. The -NCO band has reappeared but the dicarbonyl doublet in B is absent. The single band for CO in Fig. 6D may indicate that the surface is still partially poisoned with sulfur or that sintering of the noble metals has occurred. From Fig. 6E, it is noted that the effect of H_2O on the -NCO band at 2270 cm^{-1} is quite pronounced for Rh as it was in the case of Ru and Pt (*5*).

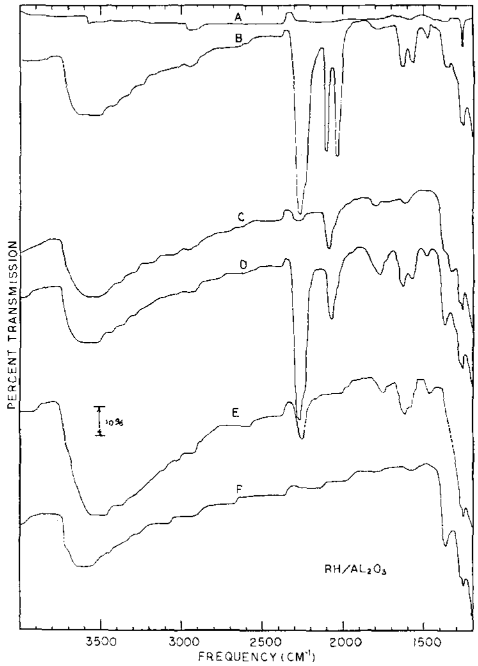


FIG. 6. 5% Rh/Al_2O_3 infrared spectra: (A) evacuated cell, sample out; (B) cleaned sample treated with 100 Torr 10% CO + 5% NO at 400°C. Scan at $P = 1$ Torr, $T \leq 50°C$. (C) Cleaned sample treated with 10 Torr 10% SO_2/N_2 plus 90 Torr 10% CO + 5% NO at 400°C. Scan at $P = 1$ Torr, $T \leq 50°C$. (D) Cleaned sample treated with 100 Torr 10% CO + 5% NO at 400°C. Scan at $P = 1$ Torr, $T \leq 50°C$. (E) Sample D treated at room temperature with 7 Torr H_2O and evacuated before scan. (F) Cleaned sample. Scan at $P = 0$ Torr, $T \leq 50°C$. NOTE: "Cleaning" the sample involves the following steps: (1) Heat to 400°C while pumping (minimum 1 hr). (2) Treat with 100 Torr O_2 at 400°C (minimum 30 min). (3) Evacuate at 400°C (minimum 15 min). (4) Treat with 100 Torr H_2 at 400°C (minimum 30 min). (5) Evacuate at 400°C (minimum 15 min).

Further experimentation on Rh/Al_2O_3 showed that if the SO_2/N_2 mixture is evacuated for 5–10 min at 400°C before adding the NO + CO mixture, the –NCO species will still be formed. Furthermore, when 10 Torr of a 1% SO_2/N_2 mixture was used instead of the 10% SO_2/N_2 as in Fig. 6, the isocyanate band was observed but with much lower than normal intensity. These results indicate that the effect of SO_2 is temporary in that it can be rapidly removed from the heated Rh surface and that the strong effects observed above are in part due to strong competitive chemisorption of SO_2 with the other reactants.

If one supposes for the moment that the –NCO intermediate were connected with the formation of NH_3 in actual auto exhaust, then the above results suggest that certain sites important to NH_3 formation could be blocked by selective poisoning. This selective poisoning of NH_3 formation sites might be accomplished by a temporary poison such as SO_2 or with a permanent poison which is intentionally added to the catalyst composition. While it certainly does not prove the above speculation, it has been confirmed in our laboratories (*10*) that the presence of a small amount of SO_2 in a synthetic exhaust stream will keep Ru/Al_2O_3 catalysts in a "low ammonia" state.

Discussion

The mechanism of surface isocyanate formation is not clear. Certainly it must involve the breaking of an N–O bond but whether this occurs through direct dissociation of NO on the surface or during the formation of a reaction intermediate involving CO cannot be determined from the present study. Kinetic data on the NO + CO reaction over a copper chromite catalyst (*11*) indicates a dual-site mechanism which would favor the reaction intermediate postulate, but it must be pointed out that the connection between experimental conditions in that study and the present one is remote. London and Bell (*12*) have reported observing isocyanate intermediates during the reaction of NO + CO over CuO/SiO_2 catalysts. In their discussion of reaction mechanism they postulate the formation of a copper nitride species by the following mechanism:

$$Cu + NO \rightarrow Cu^+NO^-, \qquad (1)$$

$$Cu^+NO^- + Cu^+ \rightarrow CuN + Cu^{2+}O^-. \qquad (2)$$

The CuN can then go to give N_2O by reaction with NO or to form CuNCO by reaction with CO. Their proposed NO + CO reaction mechanism is quite complex and involves copper in three different oxidation states. Since ESCA results illustrate the ability of surface noble metal atoms to change oxidation state readily, it would seem that a mechanism similar to that proposed for CuO/SiO_2 (*12*) might also be postulated for the noble metal-on-alumina catalysts of the present study. By whatever mechanism, once the formation of a surface isocyanate has occurred, one can envision both gas phase and surface interactions (*5*) which lead to NH_3 in the presence of H_2O. The interesting point here is that the intensity of the isocyanate band (2260–2270 cm^{-1}) as observed on the different noble metals in Fig. 4, seems to correlate with the ammonia-forming tendencies of these metals in actual NO_x removal situations. That is, all the noble metals, except Ru, promote the formation of appreciable amounts of NH_3 from auto exhaust when the exhaust is overall reducing in nature. From Fig. 4 the Ru/Al_2O_3 sample spectrum shows the weakest –NCO band of all the noble metals. It was also noted that only on a freshly prepared and reduced Ru/Al_2O_3 catalyst was the –NCO band observed at all. After several cycles the catalyst seemed to sinter or become oxidized so that no –NCO band was observable. This correlates with observations by Klimisch and Taylor (*2*) who found that Ru can exist in a "high NH_3 (reduced)" form and a "low NH_3 (oxidized)" form. If only the correlations mentioned above were considered, it would be tempting to speculate that the –NCO is an intermediate in the formation of NH_3 in NO_x removal from auto exhaust using noble metal catalysts. However, the direct reduction of NO both with molecular hydrogen in the exhaust and with atomic hydrogen from the water–gas shift reaction is certainly important and, indeed, under the conditions which obtain in auto exhaust, may be the preferred route to ammonia. As was noted in an earlier report (*6*) we have found conditions in the laboratory in which reaction mixtures containing NO, CO, and H_2O (no H_2) produced NH_3, but under which no water–gas shift was observed with only CO and H_2O present. We take these observations as evidence that hydrolysis of -NCO to NH_3 can occur at least in some instances.

Thus, the problem of ammonia formation in auto exhaust is quite complex and there are a number of competing reactions which can occur. In addition, the decomposition of NH_3 over these same catalysts must be considered. It is a fact that the catalysts which show good NH_3 decomposition activity also show low overall NH_3 production especially at higher temperatures (*3*). During ammonia decomposition the ammonia is probably not desorbed into the gas phase (*13*) but, rather, ammonia fragments as they are formed, pair up and react on the surface, to form the resultant N_2 and H_2 species. The following reactions illustrate the complexity of the situation for NH_3 formation.

$$(\text{-NCO}) + 2H_2O \rightarrow NH_3 + CO_2 + (\text{-OH}) \quad \text{(isocyanate hydrolysis)}, \quad (3)$$

$$NO + \tfrac{5}{2}H_2 \rightarrow NH_3 + H_2O \quad \text{(direct formation)}, \quad (4)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \xrightarrow{NO} NH_3 \quad \text{(direct formation via water–gas shift)}, \quad (5)$$

$$NH_3 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \quad \text{(ammonia decomposition)}, \quad (6)$$

In addition, the other oxidation–reduction reactions which occur over noble metal catalysts will have an effect on the reactants in (3)–(6) above and, therefore, on the oxidation state or mixture of states of the catalyst under operating conditions. If it were possible to examine the state of the catalyst under realistic reaction conditions, one could better understand the interconnection of reaction (3)–(6). Certainly the observation of Klimisch and Taylor (*2*) and Otto and Shelef (*14*) suggest that the oxidation state of a catalyst plays an important role in its activity and selectivity toward certain reactions and one might expect that the mechanism of ammonia formation during the reduction of NO_x in automobile exhaust is also a function of catalyst oxidation state.

In conclusion, we have observed isocyanate species on the surface of certain noble metal catalysts during the reaction of NO + CO. We believe that hydrolysis of this isocyanate group can lead to NH_3 formation and that this route to NH_3 should be considered when dealing with the problem of NH_3 formation over NO_x reduction catalysts for purifying automobile exhaust.

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