The present experiments indicate that even those products that appear with high translational energy in the isolated system (F^-, CF_3^-) are formed thermally when CF_4^- is generated within an aggregate. Multiple-scattering events in the ionized complex, strongly controlled by short-range attractive interactions between the additional charge and the induced dipoles, prevent the ejection of fragment ions with high kinetic energy.

Conclusion

Electron capture by CF_4 clusters yields a variety of larger negatively charged products such as M_n^-, $M_n{\cdot}F^-$, and $M_n{\cdot}CF_3^-$, $n = 1, 2, \ldots$. The ion yield curves of these products suggest that the initial step of electron capture proceeds via formation of CF_4^- within the cluster. While the isolated temporary ion immediately decomposes into the complementary channels $F^- + CF_3$ and $F + CF_3^-$ with high translational excess energy release, intramolecular interaction in the aggregates results in the formation of various product ions, among them the monomeric anion CF_4^- in its relaxed configuration, not accessible in electron impact to isolated CF_4. It is suggested that CF_4^- represents a weakly bound ion molecule adduct $CF_3{\cdot}F^-$ in a metastable state with respect to autodetachment. The TOF spectra indicate that all ionic products formed in electron capture by CF_4 clusters (including F^- and CF_3^-) appear with low kinetic energy.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (through Sonderforschungsbereich 337) and the Fonds der Chemischen Industrie.

Influence of Oxidation of Pd/Al_2O_3 for the Reactions of CO with NH_3 and Formamide Decomposition

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The reaction of CO with NH_3 and the decomposition reactions for HNCO and formamide over Pd/Al_2O_3 films have been investigated by infrared spectroscopy. The formation of isocyanate species (NCO) was observed during all of these reactions over preoxidized Pd/Al_2O_3, but not over prereduced surfaces. These NCO species were formed on Pd but spilled over to the Al_2O_3 support. Palladium became reduced during the course of the reaction of CO with NH_3. A mechanism is proposed in which the reduction of $Pd^{\delta+}$ and the formation of a Pd formamide species are key features.

I. Introduction

The pioneering infrared studies of Unland[1-3] concerning the reaction of NO with CO over supported transition-metal catalysts to generate surface isocyanate species have led to considerable interest in the investigation of such species for the NO/CO reaction[4] as well as, recently, for the NH_3/CO system in these laboratories.[5-8] Fourier transform infrared spectroscopy has revealed the presence of RhNCO and RhOCN, simultaneously, during the reaction of CO with NH_3 over preoxidized Rh/SiO_2,[5] the migration of NCO from Pd to SiO_2 via the formation of HNCO gas,[6] two mechanisms of formation of NCO on Ru/Al_2O_3,[7] and the effect of support material on NCO formation over M/X (M = Rh, Ru, Pd; X = Al_2O_3, SiO_2, TiO_2).[8] The present work addresses the changes in the oxidation state of Pd for Pd/Al_2O_3 during the course of the NH_3/CO reaction and the decomposition of formamide. It will be demonstrated that Pd becomes reduced during the course of the reaction in which CO in the presence of NH_3 is oxidized to isocyanate via the formation of a formamide intermediate.

II. Experimental Section

Al_2O_3-supported Pd catalyst samples were prepared[9-11] in a slurry containing $PdCl_2$ solution (Johnson & Mathey) and Al_2O_3 (Degussa aluminum oxide C, 100 m^2/g) in the appropriate ratio to produce 2.2 wt % Pd/Al_2O_3. The slurry was suspended in a liquid consisting of 9 parts of spectroscopic grade acetone and 1 part doubly distilled water and was sprayed with an atomizer onto a 2.0-cm-diameter CaF_2 disk maintained on a hot plate at approximately 360 K. The solvents evaporated rapidly, leaving a thin film of $PdCl_2{\cdot}xH_2O/Al_2O_3$ adhered to the CaF_2 disk. A total sample weight of $(1.3-1.6) \times 10^{-2}$ g was deposited in the preparations, yielding a final surface density (Pd/Al_2O_3) of $(4.3-5.0) \times 10^{-3}$ g/cm^2 for the various samples. The catalyst sample was then mounted inside a specially designed infrared cell,[9,11] which was subsequently evacuated by a bakable all-metal vacuum system employing a mechanical pump and a 20 L/s ion pump. The sample was outgassed under vacuum at ambient temperature for approximately 10 h, heated at 513 K for 1 h at 1×10^{-6} Torr, and subjected to 5-, 5-, 10-, and 20-min cycles of exposure to 80 Torr of H_2 (or O_2) at 523 K, each cycle being terminated by evacuation to 1×10^{-5} Torr. The reduced or oxidized sample was allowed to remain under vacuum (1×10^{-6} Torr) at 533 K for 1 h. Following evacuation overnight at 1×10^{-6} Torr at 298 K, the IR spectrum of the sample (background spectrum) was recorded. The sample was then exposed to reacting gases, and the IR spectra were monitored as a function of time and temperature during the reaction.

Infrared spectra were obtained from a N_2-purged IBM FTIR 44 spectrometer with a DTGS detector coupled with a data acquisition system. Measurement capability below the 10^{-3} absorbance level was achieved with adequate signal-to-noise ratios and resolution by using the multiple-scan data accumulation feature. The spectra reported here are the differences between the samples before and after exposure to reactants. The IR cell was securely mounted throughout the course of data acquisition, thus minimizing artifacts in the subtraction technique. Smoothing

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(1) Unland, M. L. *J. Catal.* **1973**, *31*, 459.

(2) Unland, M. L. *J. Phys. Chem.* **1973**, *77*, 1952.

(3) Unland, M. L. *Science* **1973**, *179*, 567.

(4) See the numerous references quoted in ref 5-8.

(5) Paul, D. K.; McKee, M. L.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *J Phys. Chem.* **1989**, *93*, 4598.

(6) Paul, D. K.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *J. Catal.* **1989**, *120*, 272.

(7) Paul, D. K.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *Surf. Sci.* **1989**, *223*, 509.

(8) Paul, D. K.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *Chem. Phys. Lett.* **1989**, *160*, 559.

(9) Dai, C. H.; Worley, S. D. *J. Phys. Chem.* **1986**, *90*, 4219.

(10) Henderson, M. A.; Worley, S. D. *J. Phys. Chem.* **1985**, *89*, 1417.

(11) Dai, C. H.; Worley, S. D. *Langmuir* **1988**, *4*, 326.

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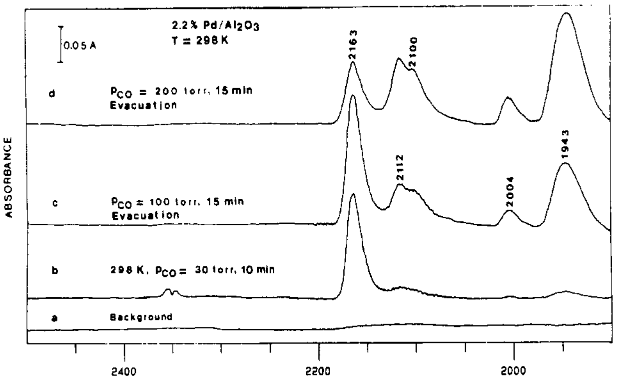

Figure 1. Infrared spectra for the interaction of CO with a preoxidized 2.2% Pd/Al_2O_3 film.

functions were not used during data handling and manipulation. The spectrometer was operated from 4000 to 1000 cm^{-1}, coadding 500 interferograms at a resolution of 4 cm^{-1}.

The NH_3 and CO were obtained from Matheson at a purity level of 99.99%. The CO was passed through molecular sieves and a dry ice/acetone trap to remove iron and nickel carbonyls. The O_2 and H_2 gas (Matheson) were obtained with a purity level of 99.999%. The isotopically labeled gases (^{13}CO, ^{13}C atom, 99%; $C^{18}O$, ^{18}O atom, 98%; ND_3, D atom, 99.5%; $^{15}NH_3$, ^{15}N, atom 99%) were obtained from Cambridge Isotope Laboratories, Inc., in break-seal glass flasks and were used without further purification. The $HCONH_2$ (Aldrich Chemical Co., purity >99%) was transferred to a glass bulb filled with dry molecular sieves fitted with a high-vacuum Teflon stopcock inside a drybox purged constantly with dry N_2 gas. THe reagent was purified with several freeze–pump–thaw cycles using a glass vacuum line operating at a base pressure of 1×10^{-6} Torr. The HNCO was prepared from aqueous KOCN and 85% H_3PO_4 at 283 K and purified by trap-to-trap distillation.[12] After repeated distillation (2–3 times), the HNCO obtained was stored in a preevacuated glass tube immersed in liquid N_2.

III. Results and Discussion

A. Interaction of CO with Preoxidized and Prereduced Pd/Al_2O_3. The fact that $Pd^{\delta+}$ is reduced by CO is illustrated by the results shown in Figure 1. A 2.2% Pd/Al_2O_3 film was exposed to O_2 in a pretreatment procedure as described in the previous section. Then the surface was exposed to 30 Torr of CO for 10 min at 298 K; the infrared spectrum following this treatment is shown in Figure 1b. An intense band was observed at 2163 cm^{-1} with weaker bands at 2112, 2004, and 1943 cm^{-1}. A weak band at 2352 cm^{-1} corresponding to CO_2(g) was also observed, indicating that CO was oxidized by $Pd^{\delta+}$. Then the surface was exposed to 100 Torr of CO for 15 min at 298 K followed by evacuation, and the spectrum in Figure 1c was recorded. Finally, additional exposure to 200 Torr of CO for 15 min at 298 K followed by evacuation led to the spectrum in Figure 1d.

In contrast, for a sample provided a prereduction treatment, the spectrum recorded in Figure 2A was recorded after exposure to 30 Torr of CO for 15 min at 298 K followed by evacuation. In the latter spectrum the 2163-cm^{-1} band does not appear, and the other three bands are all shifted to lower wavenumber. In accord with previous studies for CO adsorbed on supported Pd,[6,13-16] the 2163-cm^{-1} band may be assigned to a linear CO bound to $Pd^{\delta+}$ (probably Pd^{2+} since $PdCl_2$ was used as the precursor), with the 2112–2100-cm^{-1} band system being assigned to linear CO on a Pd site influenced by oxidation since it shifted to 2090 cm^{-1} following prereduction. The bands at 2004 and 1943 cm^{-1} (preoxidation) which shifted to 1975 and 1928^{-1} cm^{-1} upon prereduction can be assigned to bridged Pd_2CO species, those resulting after preoxidation being influenced by surface oxygen. These assignments are in accord with infrared reflection studies for single crystals (2090 cm^{-1} for linear CO on Pd(100) and Pd(111); 1975 and 1928 cm^{-1} for bridged CO on Pd(100) and Pd(111), respectively).[17,18] Palazov and co-workers[16] have pointed out that oxygen treatment of a Pd/Al_2O_3 catalyst causes an oxide phase[19] which is partially reducible at 298 K by subsequent CO exposure in accord with our observations in this work. Thus, it is clear that CO causes the reduction of preoxidized Pd/Al_2O_3.

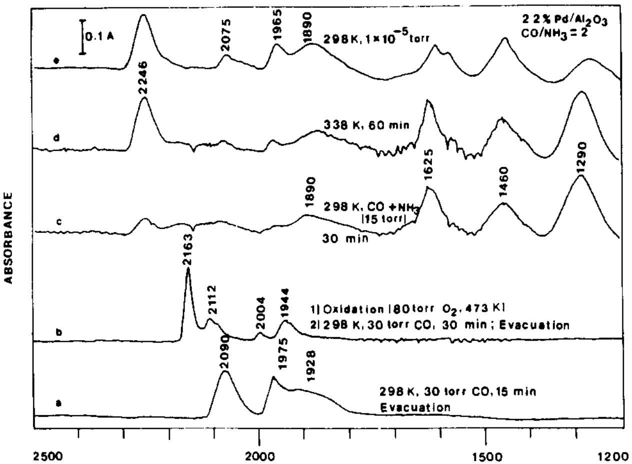

Figure 2. Infrared spectra for the interaction of CO and NH_3 (c–e) over a preoxidized 2.2% Pd/Al_2O_3 film following prereduction (a) and then preoxidation (b) with subsequent exposure to CO in each case.

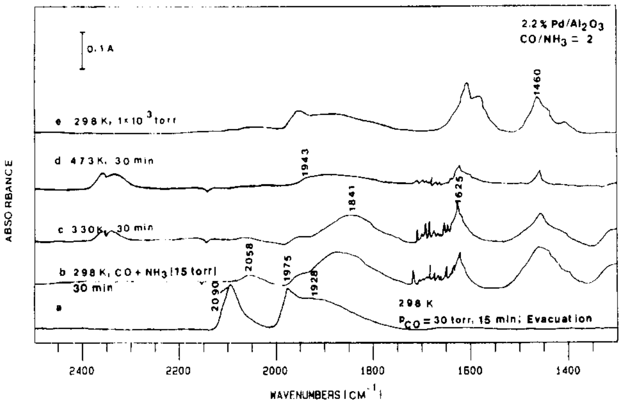

Figure 3. Infrared spectra for the interaction of CO and NH_3 over a prereduced 2.2% Pd/Al_2O_3 film.

B. Interaction of CO and NH_3 over Pd/Al_2O_3. Figure 2b rather dramatically shows the effect on the Pd/CO species following oxidation of a prereduced sample. In fact, exposure to CO following the oxidation treatment (80 Torr at 473 K for 30 min) gave rise to an infrared spectrum very similar in appearance to that in Figure 1c. The intense 2163-cm^{-1} band and the high wavenumbers of the other three bands in Figure 2b indicated an oxygenated surface which contained $Pd^{\delta+}$. Upon exposure of this surface to 15 Torr of a CO/NH_3 mixture (2:1) at 298 K for 30 min, dramatic spectral changes occurred (Figure 2c). All Pd/CO bands were suppressed, the weak band at 2143 cm^{-1} indicated the presence of CO(g), and new bands were observed at 2246, 1890, 1625, 1460, and 1290 cm^{-1}. Little change was noted upon heating at 338 K for 60 min except that the 2246-cm^{-1} band was enhanced in intensity (Figure 2d). Upon evacuation at 298 K all bands

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[12] Ashby, R. A.; Werner, R. L. *J. Mol. Spectrosc.* **1965**, *18*, 184.

[13] Palazov, A.; Chang, C. C.; Kokes, R. J. *J. Catal.* **1975**, *36*, 338.

[14] Kember, D. R.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1309.

[15] Palazov, A.; Kadinov, G.; Bonev, Ch.; Shopov, D. *J. Catal.* **1982**, *74*, 44.

[16] Palazov, A.; Kadinov, G.; Bonev, Ch.; Dimitrova, R.; Shopov, D. *Surf. Sci.* **1990**, *225*, 21.

[17] Bradshaw, A. M.; Hoffmann, F. M. *Surf. Sci.* **1975**, *52*, 449.

[18] Bradshaw, A. M.; Hoffmann, F. M. *Surf. Sci.* **1978**, *72*, 513.

[19] Lieske, H.; Völter, J. *J. Phys. Chem.* **1985**, *89*, 1841.

TABLE I: Vibrational Frequencies in cm^{-1} and Mode Assignment of Chemisorbed Formamide on Ru(001), of $HCONH_2$ and/or HCONH on Pd/Al_2O_3 and Al_2O_3, and of Gas-Phase and Liquid Formamide

	$HCONH_2(g)$[a]	$HCONH_2(l)$[b]	$HCONH_2/Pd/Al_2O_3$[c]	$HCONH_2/Ru(001)$[d]	$HCONH/Al_2O_3$[e]
υ(CO)	1734	1681	1684[f]	1660	1685
$\delta(NH_2)$	1572	1611	1600	1585	n.o.[g]
υ(CN)	1255	1309	1315	1360	n.o.
δ(CH)	1378	1391	1385	n.o.	n.o.
υ_a(CONH)			1600		1600
δ_s(CONH)			1360		1375

[a] See refs 34 and 35. [b] See refs 34 and 36. [c] This work. [d] See ref 37. [e] See ref 38. [f] Probably a mixture of $HCONH_2$ and HCONH (see text). [g] n.o. = not observed.

except that for CO(g) remained (Figure 2e). The bands at 2075, 1965, and 1890 cm^{-1} can be assigned to the Pd/CO species on a highly reduced surface as discussed in the last section. The bands at 1625 and 1290 cm^{-1} can be assigned as $\delta_a(NH_3)$ and $\delta_s(NH_3)$ for NH_3 interacting with Lewis acid sites on the support (Al^{3+}), while that at 1460 cm^{-1} is characteristic of NH_2^- bonded to the support as pointed out previously.[20,21] Control experiments in which the CO/NH_3 mixture as well as NH_3 alone were exposed to Al_2O_3 produced the same three infrared bands, indicating that the bands are not due to Pd/NH_3 or other Pd surface species.

Figure 3 shows a series of spectra recorded for the CO/NH_3 (2:1) interaction over a 2.2% Pd/Al_2O_3 film which was prereduced only. In this case the band at 2246 cm^{-1} observed for the oxidized surface was completely absent throughout, indicating that preoxidation is a necessary condition for formation of the surface species causing that band.

Given prior observations in these laboratories[5-8] and elsewhere for the CO/NO system[1-3,22-31] and the CO/NH_3 system,[32,33] it is probable that the 2246-cm^{-1} band can be assigned to an isocyanate species (NCO) on the Al_2O_3 support. Solymosi and co-workers have shown that the NCO band position for isocyanate bonded to the metal during the NO/CO reaction and for HNCO decomposition is almost independent of transition metal (ca. 2170 cm^{-1} for Rh, Ru, Pt, and Pd) but markedly dependent upon the nature of the support (2200–2320 cm^{-1}) for NCO bonded to it.[22-24] Prior work in these laboratories for HNCO decomposition over preoxidized Pd/SiO_2 showed that NCO formed initially on Pd (infrared band at 2170 cm^{-1}) but then spilled over to the SiO_2 support (band at 2305 cm^{-1}).[6] To confirm this 2246-cm^{-1} band assignment, we performed two additional experiments.

In the first HNCO was decomposed over preoxidized 2.2% Pd/Al_2O_3 and Al_2O_3 films. The results are shown in Figure 4. For Al_2O_3 alone at 298 K a broad infrared band centered at 2270 cm^{-1} (Figure 4a) corresponding to HNCO(g) and surface NCO was obtained. Following heating to 338 K and evacuation (Figure 4b), the band shifted to ca. 2259 cm^{-1}, indicative of surface NCO. For the sample containing Pd (Figure 4c,d), two bands were detected at 298 K. The weak band at 2170 cm^{-1} corresponds to NCO bonded to Pd, while the intense band at 2259 cm^{-1} following evacuation refers to NCO on the Al_2O_3 support. The support band position at 2259 cm^{-1} is higher than that observed in the NH_3/CO reaction (2246 cm^{-1}) because of higher coverage due to enrichment of NCO from the HNCO starting material and probable image forces due to the presence of NH_3 on the support for the NH_3/CO reaction. Furthermore, it was observed (Figure 4d) that the weak PdNCO band disappeared upon evacuation, indicating that the bonding interaction between Pd and NCO is weak; this rationalizes the absence of a 2170-cm^{-1} band for the CO/NH_3 system for which NCO coverages were much lower.

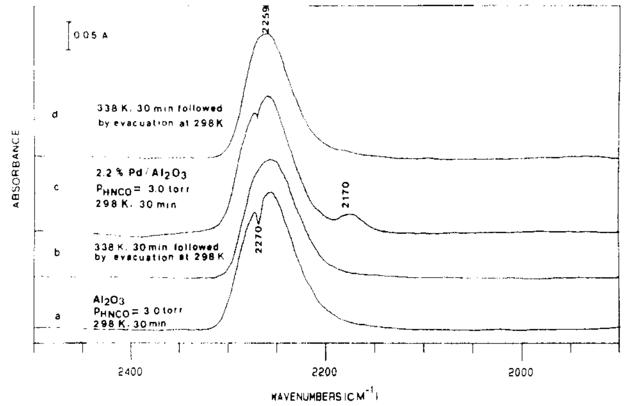

Figure 4. Infrared spectra for the decomposition of HNCO over preoxidized Al_2O_3 (a, b) and preoxidized 2.2% Pd/Al_2O_3 (c, d) films.

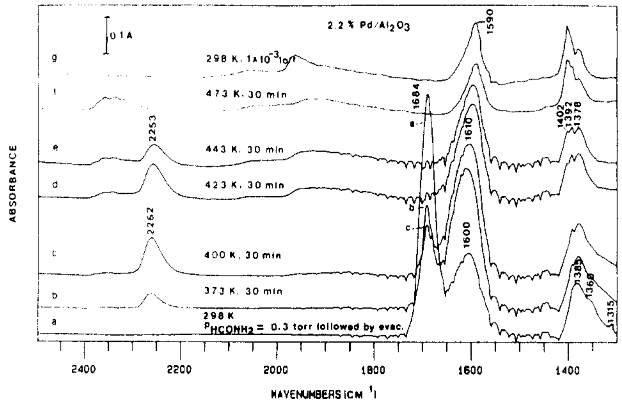

Figure 5. Infrared spectra for the decomposition of formamide over a preoxidized 2.2% Pd/Al_2O_3 film.

In the second experiment the CO/NH_3 reaction was performed over preoxidized 2.2% Pd/Al_2O_3 using each of the isotopically labeled reagents $^{14}ND_3$, ^{13}CO, $^{15}NH_3$, and $C^{18}O$. The shifts to lower wavenumbers for the suspected NCO band at 2246 cm^{-1} were as follows: 0 for ND_3, 18 for $^{15}NH_3$, 66 for ^{13}CO, and 8 for $C^{18}O$. The zero shift for $^{12}C^{16}O/ND_3$ indicates that hydrogen is not present in the surface species. The other shifts are consistent with an NCO species on the Al_2O_3 surface.[5-8]

It should be noted that a 2246-cm^{-1} band was not obtained when the CO/NH_3 reaction was run over preoxidized Al_2O_3 alone. Thus, NCO must initially form on Pd or the Pd/Al_2O_3 interface and then rapidly spill over to the Al_2O_3 support.

C. Decomposition of Formamide over Pd/Al$_2$O$_3$. An obvious candidate for a surface intermediate in the formation of NCO from CO/NH_3 is an amide. Thus, experiments were performed

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(20) Bulgakov, O. V.; Uvarov, A. V.; Antipina, T. V. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1970**, *44*, 9.
(21) Kiselev, A. V.; Lygin, V. I. In *Infrared Spectra of Surface Compounds*; Wiley: New York, 1975; p 245.
(22) Solymosi, F.; Völgyesi, L.; Raskó, J. *Z. Phys. Chem.* **1980**, *120*, 79.
(23) Solymosi, F.; Völgyesi, L.; Sárkány, J. *J. Catal.* **1978**, *54*, 336.
(24) Solymosi, F.; Sárkány, J.; Schauer, A. *J. Catal.* **1977**, *46*, 297.
(25) Brown, M. F.; Gonzalez, R. D. *J. Catal.* **1976**, *44*, 477.
(26) Raskó, J.; Solymosi, F. *J. Catal.* **1981**, *71*, 219.
(27) Hecker, W. C.; Bell, A. T. *J. Catal.* **1984**, *85*, 389.
(28) Hecker, W. C.; Bell, A. T. *J. Catal.* **1984**, *88*, 289.
(29) Dictor, R. *J. Catal.* **1988**, *109*, 89.
(30) Solymosi, F.; Sárkány, J. *Appl. Surf. Sci.* **1979**, *3*, 68.
(31) Schuth, F.; Wicke, E. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 813.
(32) Sheets, R. W.; Blyholder, G. *J. Phys. Chem.* **1975**, *79*, 1572.
(33) Gutschick, D.; Meissner, H. *React. Kinet. Catal. Lett.* **1983**, *22*, 221.
(34) Evans, J. C. *J. Chem. Phys.* **1954**, *22*, 1228.
(35) King, S. T. *J. Phys. Chem.* **1971**, *75*, 405.
(36) Suzuki, I. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1359.
(37) Parmeter, J. E.; Schwalke, U.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 1876.
(38) Krietenbrink, H.; Knozinger, H. *Z. Phys. Chem.* (*Munich*) **1976**, *102*, 43.

in which formamide ($HCONH_2$) was decomposed over the preoxidized and prereduced Pd/Al_2O_3 films. The infrared spectra in Figure 5 indicate that no decomposition of formamide to NCO occurred at 298 K. Bands were observed at 1684, 1600, 1385, 1360, and 1315 cm^{-1}; comparative data for $HCONH_2(g)$, $HCONH_2(l)$, $HCONH_2/Ru(001)$, and $HCONH/Al_2O_3$, and corresponding band assignments are presented in Table I. However, upon heating to 373 K for 30 min, formamide band positions and intensities began to change and a new band at 2262 cm^{-1} indicating that presence of NCO on the Al_2O_3 support began to form. The band obtained maximum intensity upon heating at 400 K for 30 min and then declined in intensity at higher temperature, disappearing completely at 473 K. Thus, in the low-temperature regime (<400 K) studied for CO/NH_3 (although not shown in Figure 2, the 2246-cm^{-1} band remains at 400 K and vanishes near 450 K for the CO/NH_3 system), formamide decomposition also produces NCO over preoxidized Pd/Al_2O_3. It should be noted that, following heating to 423 K, bands at 1590, 1392, and 1378 cm^{-1} characteristic of a formate species on Al_2O_3[39-42] and one at 1402 cm^{-1} corresponding to NH_4^+ on the support[8] were observed.

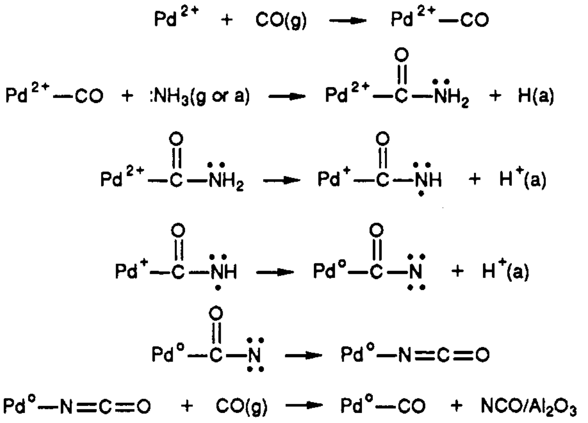
When the analogous experiment was run for formamide decomposition over prereduced Pd/Al_2O_3 or preoxidized Al_2O_3 alone, the NCO band at 2246–2260 cm^{-1} was not observed at any temperature. Thus, in contrast to our earlier observations for the CO/NH_3 reaction over Pd/SiO_2 for which an amide intermediate did not seem to be involved,[6] an amide intermediate is probable for the reaction over Pd/Al_2O_3.

D. Proposed Mechanism of CO/NH$_3$ Reaction. Although Gutschick and Meissner have reported isocyanate production for reduced Rh/Al_2O_3 and Rh/NaY catalysts for the CO/NH_3 reaction,[33] it is evident from this work that the production of NCO is optimized for preoxidized Pd/Al_2O_3. Stern and Spector have produced alkyl isocyanates in solution reactions of $PdCl_2$ with CO and primary amines at 1 atm and 338–358 K as shown below:[43]

$$PdCl_2 + CO + RHN_2 \rightarrow [\text{Pd complex}] \rightarrow RNCO + Pd^0 + 2HCl$$

Furthermore, it has been demonstrated that reactions of amines with CO in solution catalyzed by transition-metal complexes can lead to the formation of *N*-alkyl formamides (HCONHR).[44,46]

Thus, on the basis of the data described herein, we propose the following mechanism for the reaction of CO with NH_3 over preoxidized Pd/Al_2O_3.



$$Pd^{2+} + CO(g) \longrightarrow Pd^{2+}\text{—}CO \tag{1}$$

$$Pd^{2+}\text{—}CO + {:}NH_3(\text{g or a}) \longrightarrow Pd^{2+}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\ddot{N}H_2 + H(a) \tag{2}$$

$$Pd^{2+}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\ddot{N}H_2 \longrightarrow Pd^{+}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\underset{\bullet}{\ddot{N}}H + H^{+}(a) \tag{3}$$

$$Pd^{+}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\underset{\bullet}{\ddot{N}}H \longrightarrow Pd^{\circ}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\underset{\bullet\bullet}{\ddot{N}} + H^{+}(a) \tag{4}$$

$$Pd^{\circ}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\underset{\bullet\bullet}{\ddot{N}} \longrightarrow Pd^{\circ}\text{—}N{=}C{=}O \tag{5}$$

$$Pd^{\circ}\text{—}N{=}C{=}O + CO(g) \longrightarrow Pd^{\circ}\text{—}CO + NCO/Al_2O_3 \tag{6}$$

Step 1 corresponds to adsorption of CO(g) on an oxidized Pd site (probably Pd^{2+} by analogy with the solution chemistry results discussed above). Step 2 represents a nucleophilic attack by NH_3 on the carbonyl carbon of the adsorbed CO to form an amide species. Steps 3–5 are analogous to the well-known Hofmann amide degradation reaction from organic chemistry,[47] with steps 3 and 4 being the redox steps. This mechanism appears to rationalize the observations in this work in that (a) isocyanate is only produced over preoxidized Pd/Al_2O_3, (b) although CO does reduce some $Pd^{\delta+}$ sites, formamide is only converted to isocyanate over oxidized Pd/Al_2O_3, (c) bands at 1684, 1600, and 1360 cm^{-1} indicate the probable presence of a PdCONH surface species as well as the $PdCONH_2$ species (see literature assignment[38] in Table I), (d) once PdNCO is formed, the NCO spills over to the Al_2O_3 support, and (e) at the conclusion of the reaction the $Pd^{\delta+}$ sites have been reduced to Pd metal.

IV. Conclusions

The following conclusions can be drawn from this work.

1. In order to optimize the production of NCO during the reaction of NH_3 and CO over Pd/Al_2O_3, it is necessary that Pd have an oxidation state higher than 0 (probably +2).
2. The NCO produced in the reaction of NH_3 and CO over preoxidized Pd/Al_2O_3 rapidly spills over from Pd to the Al_2O_3 support.
3. Palladium becomes reduced to Pd^0 metal during the course of the reaction.
4. A key intermediate in the reaction is almost certainly an amide species which forms on the oxidized Pd.

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(39) Basu, P.; Ballinger, T. H.; Yates, J. T. *Langmuir* **1989**, *5*, 502.

(40) Noto, Y.; Fukuda, K.; Onishi, T.; Tamaru, K. *Trans. Faraday Soc.* **1967**, *63A*, 2300.

(41) Greenler, R. *J. Chem. Phys.* **1962**, *37*, 2094.

(42) Ito, K.; Bernstein, H. J. *Can. J. Chem.* **1956**, *34*, 170.

(43) Stern, E. W.; Spector, M. L. *J. Org. Chem.* **1966**, *31*, 596.

(44) Rosenthal, A.; Wender, I. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. 1, p 405.

(45) Rempel, G. L.; Teo, W. K.; James, B. R. Plackett, D. V. *Adv. Chem. Ser.* **1974**, *No. 132*, 166.

(46) Dombek, B. D.; Anjelici, R. J. *J. Catal.* **1977**, *48*, 433.

(47) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; pp 1003–1004.