Mode of Migration of Isocyanate from Palladium to Silica

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The reaction of CO and NH_3 over preoxidized Pd/SiO_2 has been studied using infrared spectroscopy to identify surface species. An isocyanate (NCO) surface intermediate on Pd providing an infrared band at 2168 cm^{-1} was detected after heating to 500 K and subsequent cooling to ambient temperature. No migration of NCO from Pd to the SiO_2 support was observed. However, the decomposition of formamide over preoxidized Pd/SiO_2 at ambient temperature did produce an NCO species which migrated to the SiO_2 via the formation of HNCO gas. It was concluded that an amide species is not an intermediate in the CO/NH_3 reaction over preoxidized Pd/SiO_2, although it may be for the reaction over preoxidized Pd/Al_2O_3. © 1989 Academic Press, Inc.

INTRODUCTION

Recent work in these laboratories has focused on the reaction of CO with NH_3 over supported transition metal catalysts. This reaction is potentially of importance to the fertilizer industry in the production of the nitrification inhibitor dicyandiamide. Several very interesting observations have been made concerning the reaction using infrared spectroscopy as a diagnostic tool. For example, both isocyanate (NCO) and cyanate (OCN) surface species have been detected for the reaction over preoxidized Rh/SiO_2 (*1*), and NCO has been shown to be produced by two different mechanisms during the reaction over Ru/Al_2O_3 (*2*). In the current paper, the CO/NH_3 reaction over Pd/SiO_2, as well as the mode of migration of NCO from Pd to the support during the decomposition of formamide over Pd/SiO_2, is discussed. It is shown that NCO remains bonded to Pd for the CO/NH_3 reaction, thus eliminating an amide surface species as a viable consideration as a possible intermediate in the production of NCO on Pd/SiO_2.

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EXPERIMENTAL

The infrared cell reactor and catalyst preparation procedures used in this study have been described in detail elsewhere (*3–5*). Briefly, a suspension of $PdCl_2$ solution (Johnson Matthey), SiO_2 (Cabosil M5, 200 m^2 g^{-1}, Cabot Corp.), acetone, and water was sprayed onto a heated 20-mm CaF_2 infrared plate so as to obtain a final Pd/SiO_2 film having 2.2% weight Pd. The sample plate was positioned in the infrared cell reactor and pretreated by evacuation overnight at ambient temperature, evacuation to 10^{-6} Torr for 1 h at 513 K, exposure to 5-, 5-, 10-, and 20-min cycles of 78 Torr O_2 (or, in some cases, H_2) at 523 K with each exposure being followed by evacuation to 10^{-5} Torr, and then 1-h evacuation to 10^{-6} Torr at 533 K. Previous work in these laboratories (*1–5*) has established that the four timed reduction cycles under the indicated conditions provide films for which reproducible results in accord with those from other laboratories can generally be obtained. Following evacuation overnight at 10^{-6} Torr at ambient temperature, the sample was exposed to a reactant gas (2/1 CO/NH_3, HNCO, or formamide) at a known

pressure (MKS Baratron capacitance manometer), and the IR spectra were monitored (IBM 32/AT FTIR operating at a resolution of 4 cm^{-1}) as a function of temperature and/or reaction time. The HNCO gas was prepared from aqueous KOCN and 95% H$_3$PO$_4$ at 283 K and purified by trap-to-trap distillation. Formamide (Aldrich Chemical Co.) was purified by vacuum distillation. Ammonia and CO were obtained from Matheson at a purity of 99.999%; the CO was passed through molecular sieves and a trap at 196 K to remove iron carbonyls. All isotopically labeled gases were obtained from Cambridge Isotope Laboratories, Inc., and used without further purification.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra for a preoxidized 2.2% Pd/SiO$_2$ film exposed first to 30 Torr of CO followed by evacuation (Fig. 1a) and then a 2/1 mixture of CO and NH$_3$ at a total pressure of 15 Torr as a function of time and temperature (Figs. 1b–f). After preoxidation and exposure to CO, bands at 2163, 2112, 2004, and 1963 cm^{-1} were produced. An analogous sample prereduced gave bands only at 2087 and ca. 1963 cm^{-1} (not shown). Therefore, it is evident that the 2163 cm^{-1} band for the preoxidized surface corresponds to CO bonded to oxidized Pd (Pd$^{+\delta}$), quite possibly to a carbonyl oxide species; the 2112 cm^{-1} band also must refer to CO on a Pd site influenced by oxidation since it shifts down to 2087 cm^{-1} upon prereduction. The 1963 cm^{-1} band for both preoxidized and prereduced Pd/SiO$_2$ may be assigned to a bridged Pd$_2$CO species (6). Upon introduction of the CO/NH$_3$ mixture to the preoxidized Pd/SiO$_2$ film at ambient temperature, the adsorbed CO species seen in Fig. 1a were largely suppressed; broad bands near 2080 and 1800–2000 cm^{-1} were observed which grew as the temperature was increased, indicating the probable enhanced reduction of the Pd/SiO$_2$ in the presence of the CO/NH$_3$ reducing atmo-
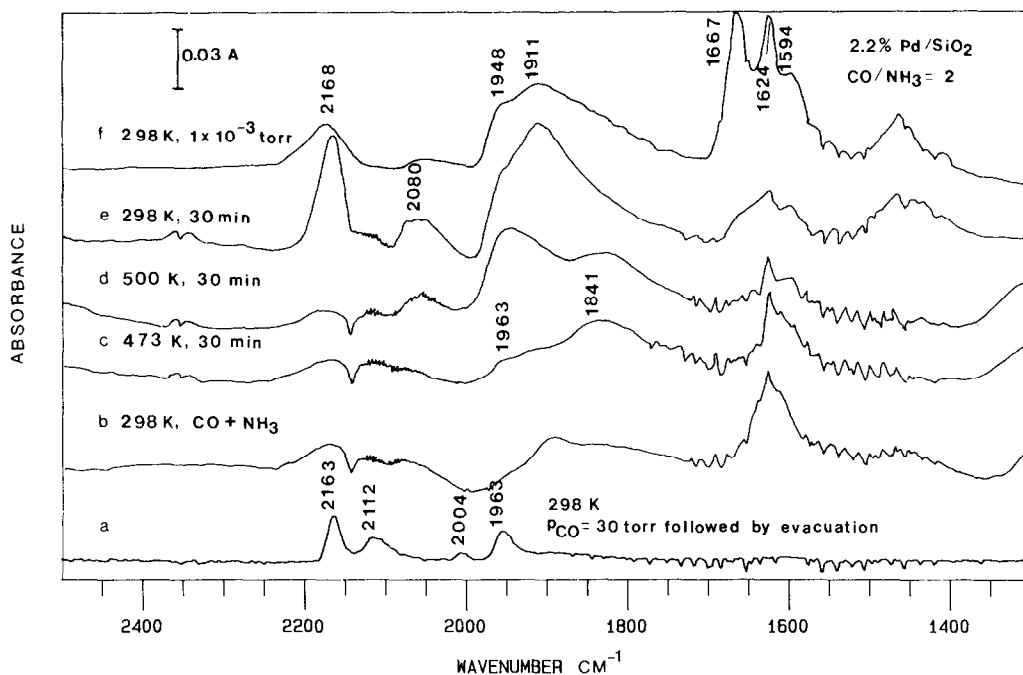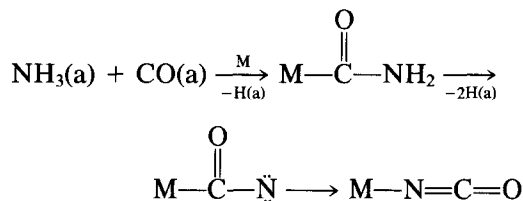

FIG. 1. Infrared spectra for the reaction of CO and NH$_3$ over a preoxidized 2.2% Pd/SiO$_2$ film (4.3 mg cm^{-2}) at a total pressure of 15 Torr.

sphere. The production of CO_2 gas was evidenced by the weak band near 2350 cm^{-1} which was observed upon heating (Figs. 1b–e). This CO_2 may result from decomposition of the oxidized PdCO species which caused the 2163 cm^{-1} band at ambient temperature. The broad band near 1625 cm^{-1} refers to NH_3 gas and NH_3 adsorbed on Pd/SiO_2. The most interesting feature in Fig. 1 is the intense band at 2168 cm^{-1} seen upon cooling after heating to 500 K. The band remains upon evacuation, indicating that it corresponds to a surface species. It is not observed following prereduction of Pd/SiO_2, so preoxidation is a necessary condition for its formation.

We suspected that the 2168 cm^{-1} band could be attributed to a PdNCO species, since other workers had postulated the existence of NCO surface species during the reaction of NO and CO over Pd (7, 8), Pd/Al_2O_3 (9, 10), and Pd/X (X = Al_2O_3, TiO_2, MgO, SiO_2, and Y zeolite) (11–14). Solymosi and Raskó have reported a band at 2180 cm^{-1} which formed during the decomposition of HNCO over preoxidized Pd/SiO_2 which they attributed to a PdNCO species. They suggested that such a species is not stable on a prereduced Pd surface, but is stabilized as a result of preoxidation (15). However, we can find no other report of a PdNCO species on Pd/SiO_2 with an infrared band near 2168 cm^{-1}. Therefore, several experiments were performed to confirm our tentative assignment. First, isotopically labeled gases were employed (ND_3, ^{13}CO, $^{15}NH_3$, and $C^{18}O$) in the CO/NH_3 reaction over preoxidized Pd/SiO_2 films. The band appeared at 2168, 2013, 2150, and 2158 cm^{-1}, respectively, for these labeled compounds. The shifts of 0, 55, 18, and 10 cm^{-1}, respectively, indicate that C, N, and O, but not H, are present in the surface species and are consistent with the postulated PdNCO species, as we have shown previously for RhNCO using isotopic labeling and high-quality *ab initio* computations (1). It should be noted that the 2168 cm^{-1} band is not observed for the

reaction of CO with NH_3 over SiO_2 alone; Pd must be present, so the NCO is formed initially on Pd. However, it was deemed possible that the 2168 cm^{-1} band referred to NCO which had migrated to the SiO_2 support, although the probability of this seemed unlikely since Solymosi and coworkers had reported the presence of a 2317 cm^{-1} band assigned to NCO on the support for the reaction of NO with CO over 1% Pd/SiO_2 (11) and a band at 2313 cm^{-1} for the decomposition of HNCO gas over SiO_2 (16). Thus, we decomposed HNCO gas over preoxidized 2.2% Pd/SiO_2 and SiO_2 alone; the results are shown in Fig. 2. One can see that bands at 2170 and 2305 cm^{-1} were produced for the preoxidized Pd/SiO_2 film, but only the 2305 cm^{-1} band was produced for SiO_2 alone. Thus, it is obvious that the 2168 cm^{-1} band seen for the CO/NH_3 reaction must refer to PdNCO, and that NCO does *not* migrate to the SiO_2 support during this reaction under the conditions of our experiments.

The mechanism of formation of PdNCO during the CO/NH_3 reaction is of interest. We have recently demonstrated that an amide intermediate is possible for the reaction over Rh/SiO_2 (1) and Ru/Al_2O_3 (2), so we considered this possibility for Pd/SiO_2. It is conceivable that CO may insert into an N–H bond of NH_3 on a transition metal to form an amide surface species which undergoes rearrangement through a nitrene intermediate as in the well-known Hofmann amide degradation from organic chemistry (17).

$$NH_3(a) + CO(a) \xrightarrow[-H(a)]{M} M\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!NH_2 \xrightarrow{-2H(a)}$$

$$M\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!\ddot{N} \longrightarrow M\!-\!N\!=\!C\!=\!O$$

Figures 3 and 4 show the infrared spectra resulting from the decomposition of formamide (HCONH$_2$) over a preoxidized 2.2% Pd/SiO_2 film. From Fig. 3 it can be seen that the amide bands at 1690, 1600, 1395, and
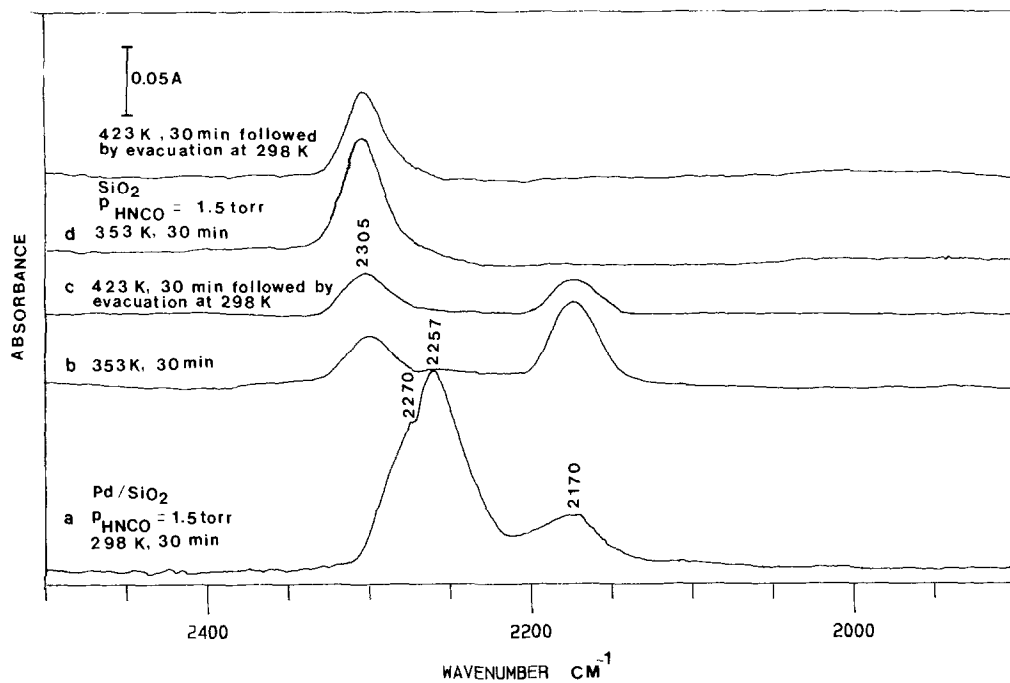
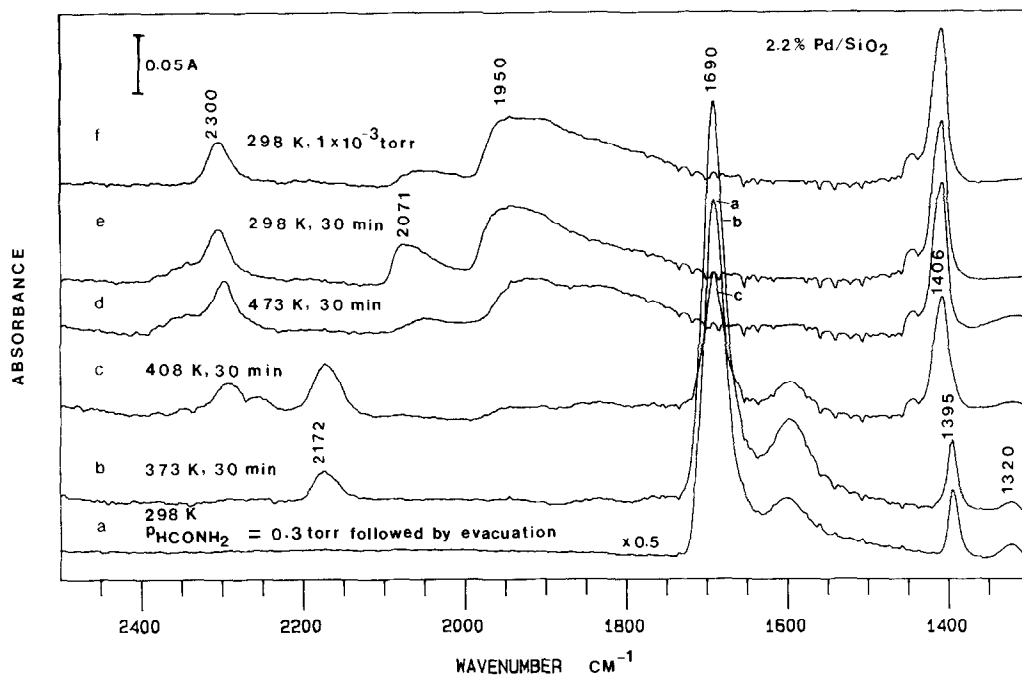FIG. 2. Infrared spectra for the decomposition of HNCO over preoxidized 2.2% Pd/SiO₂ and SiO₂ films (4.3 mg cm⁻²).

FIG. 3. Infrared spectra for the decomposition of formamide over a preoxidized 2.2% Pd/SiO₂ film (4.3 mg cm⁻²).
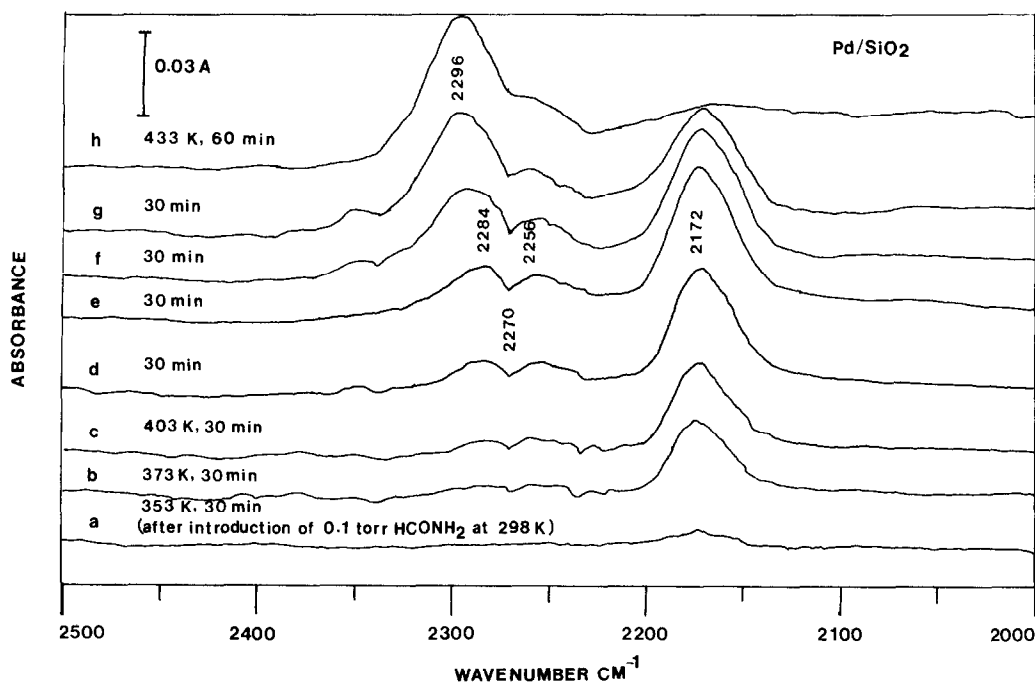
FIG. 4. The isocyanate region of the infrared spectra for the decomposition of formamide over a preoxidized 2.2% Pd/SiO₂ film (4.3 mg cm⁻²) showing migration of NCO from Pd to SiO₂ via an HNCO gas intermediate.

1320 cm⁻¹ disappear with the concomitant formation of a band at 1406 cm⁻¹ (NH₄⁺/SiO₂), PdCO and Pd₂CO bands at 2071 and 1950 cm⁻¹, and NCO bands at 2172 cm⁻¹ (PdNCO) at low temperature and 2300 cm⁻¹ (NCO on SiO₂) at higher temperature. The minor shift in frequency (4 cm⁻¹) for PdNCO produced by formamide decomposition relative to the CO/NH₃ reaction is not considered to be significant because it could result from coverage effects and/or error in band center measurement. It is unlikely that an amide intermediate is involved in the CO/NH₃ reaction to form PdNCO since no spillover to the support is observed (no 2300 cm⁻¹ band) for that process as is the case for formamide decomposition. Thus, for the CO/NH₃ reaction over Pd/SiO₂ a mechanism involving decomposition of NH₃ at 500 K forming adsorbed N [as for decomposition of NH₃ over Pd films (18)] followed by reaction with CO to produce NCO is more likely. A number of re-

ports have suggested this type of mechanism to account for NCO formation in the NO/CO reaction at high temperature over supported metal catalysts (19).

The expanded-scale spectra in Fig. 4 show that during decomposition of formamide over preoxidized Pd/SiO₂, as the PdNCO (2172 cm⁻¹ band) species spills over to the support (2296 cm⁻¹ band), an intermediate species having an IR band center at 2270 cm⁻¹ results. This 2270 cm⁻¹ band which contains rotational structure (P branch, 2256 cm⁻¹; Q branch, 2270 cm⁻¹; R branch, 2284 cm⁻¹) may be assigned to gas-phase HNCO. Thus, the mode of migration from Pd to SiO₂ seems to involve the formation of HNCO gas on Pd and the subsequent decomposition of HNCO on the support. Lorimer and Bell once proposed the formation of HNCO from NCO on Pt/SiO₂ to account for the appearance of NCO on their SiO₂ reference disk in a double-beam IR cell containing a Pt/SiO₂ disk and an

SiO$_2$ reference disk (20). Our experiment would seem to support their proposal.

CONCLUSION

In conclusion, our experiments have shown that a PdNCO species is produced at 500 K over preoxidized 2.2% Pd/SiO$_2$ during the CO/NH$_3$ reaction. This isocyanate species produced on Pd does not migrate to the support and is not formed through an amide intermediate. Formamide does decompose over preoxidized Pd/SiO$_2$ at low temperature to give a PdNCO species; the NCO in this case migrates to the SiO$_2$ support at higher temperatures via the formation of HNCO gas. In contrast, recent work here has shown that for the CO/NH$_3$ reaction over preoxidized Pd/Al$_2$O$_3$, NCO is produced on Pd at ambient temperature which rapidly migrates to the Al$_2$O$_3$ support as evidenced by a strong infrared band at 2246 cm^{-1}, but no band at 2170 cm^{-1}. A similar result was obtained at ambient temperature for the decomposition of formamide over Pd/Al$_2$O$_3$, indicating that an amide intermediate is probable for the CO/NH$_3$ reaction over Pd/Al$_2$O$_3$. Thus, the nature of the support material is quite significant for the CO/NH$_3$ reaction over supported Pd.

ACKNOWLEDGMENTS

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