The Electron Energy Loss Spectrum of Isocyanic Acid on the Pt(111) Surface[1]

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High-resolution, electron energy loss spectra (EELS) and temperature-programmed desorption (TPD) spectra show that isocyanic acid is molecularly adsorbed in multilayers on the Pt(111) surface at 100 K. Heating to 150 K desorbs the multilayers and shifts the asymmetric ν_a (NCO) vibrational frequency from 2270 to 2160 cm^{-1}, but the adsorption remains molecular. By 250 K, most of the isocyanic acid has decomposed on the platinum surface to form CO and nitrogen-containing surface fragments. No CO_2, H_2O, or HCN is found to desorb from the surface, and we find no evidence for cleavage of the bond between the carbon and oxygen atoms. The data indicate that an "isocyanate" species is unlikely to be stable on a platinum surface above room temperature under low-pressure conditions. Also, isocyanates on supported platinum catalysts are probably formed by the reaction of CO with a nitrogen species on the surface.

INTRODUCTION

The reaction between NO and CO on supported catalysts has been found by infrared spectroscopy to give an isocyanate species on the surface. This species has been implicated in the formation of NH_3 in the automotive catalyst and has been the object of extensive research (*1*). Although isocyanate has been found to form on many different catalytic surfaces, including supported platinum (*1–7*), palladium (*1, 8–10*), ruthenium (*1, 11, 26*), rhodium (*1, 12*), iridium (*1, 10*), nickel (*13*), tin oxide

(*14, 15*), chromium oxide (*16*), and cuprous oxide (*17*), it has already been shown for supported noble metal catalysts that the isocyanate exists predominantly on the catalyst support (*18, 27*). However, isocyanate is not formed unless a catalytic metal is present. To determine the nature and stability of isocyanate on the metal surface, we studied the adsorption of isocyanic acid (HNCO) on the Pt(111) surface with electron energy loss spectroscopy (EELS) and temperature-programmed desorption (TPD). We find that HNCO is unstable on the platinum surface above 250 K and therefore it is unlikely that any isocyanate exists on the metal surface in the temperature regime in which the reaction takes place. Further, HNCO decomposes mostly into CO and nitrogen surface species, with no fracture of the carbon–oxygen bond. This suggests that isocyanate is formed by the reaction of CO with a nitrogen surface species.

EXPERIMENTAL

The high-resolution electron energy loss spectrometer (EELS) and UHV system have been described elsewhere (*19*). Typical operating pressures in the vacuum system were 5×10^{-11} Torr. The platinum (111) crystal was cleaned by alternately heating to 1170 K in 1×10^{-8}-Torr oxygen and annealing at 1370 K under vacuum until the Auger spectrometer detected no impurities and EELS spectra showed no losses attributable to impurities.

Isocyanic acid was produced by the reaction of a saturated KNCO–water solution with 85% H_3PO_4 at 273 K and collected in a 195-K cold trap (*20*). The cold trap was then evacuated to remove CO_2, N_2, and other noncondensable gases. The gas-phase infrared and the mass spectra agreed with published spectra and indicated that the sample was isocyanic acid (*21, 22*). The sample was kept at 195 K to prevent polymerization, and the vapor pressure at this temperature was used to dose the crystal through a stainless-steel capillary array directed at the crystal. Multilayer coverages of isocyanic acid were formed on the crystal at 100 K without substantially increasing the background pressure of the vacuum system (pressure $< 1 \times 10^{-9}$ Torr during dosing).

Thermal desorption runs were made monitoring masses 44 (CO_2), 43 (HNCO), 30 (NO), 28, 27 (HCN), 18 (H_2O), 17 (NH_3), 14, 12, and 2 amu on the mass spectrometer. No CO_2, HCN, or H_2O was observed desorbing from the surface. Energy loss spectra were taken at 100 K and after heating to several temperatures as high as 473 K. All vibrational spectra were taken after the crystal again cooled to 100 K. The energy loss spectrometer used a 7.5-eV beam of 1.5×10^{-10} A current measured at the crystal. Under these beam conditions, electron-induced decomposition is negligible. While the resolution varied between 65 and 80 cm^{-1}, peak maxima were reproducible to within 10 cm^{-1}, and we believe the

frequencies we report are accurate to within 20 cm^{-1}.

RESULTS AND DISCUSSION

Thermal Desorption Results

Thermal desorption spectra for the isocyanic acid are shown in Fig. 1. Physically adsorbed multilayers of isocyanic acid are desorbed before 125 K and a small amount of the monolayer surface desorbs at 250 K. Above room temperature, most of the HNCO desorbs as CO, N_2, H_2, and NH_3. (The N_2 and CO desorption peaks were distinguished with 12- and 14-amu desorption experiments.) These fragmentation products desorb in two regimes. The desorption peaks below 470 K for H_2, CO, and NH_3 occur at the same temperature as
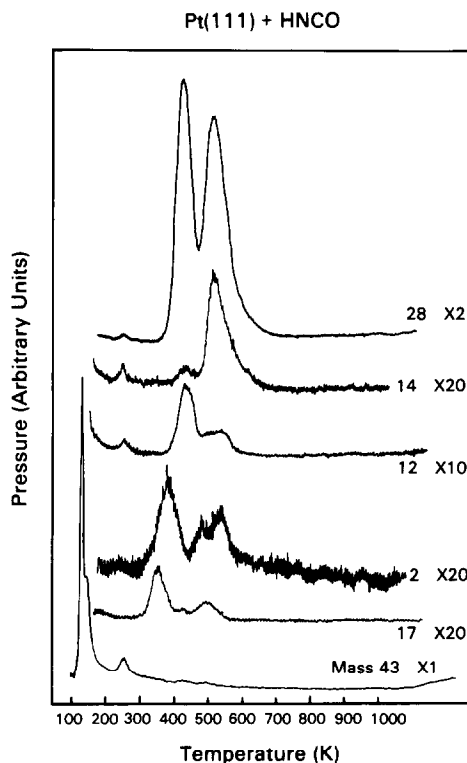
Pt(111) + HNCO

FIG. 1. Thermal desorption curves for the masses shown were obtained after HNCO adsorption at 100 K. The heating rate was 9 K/s. The desorption curves for masses other than 43 amu are not shown below 150 K since they only show the cracking pattern of the HNCO.
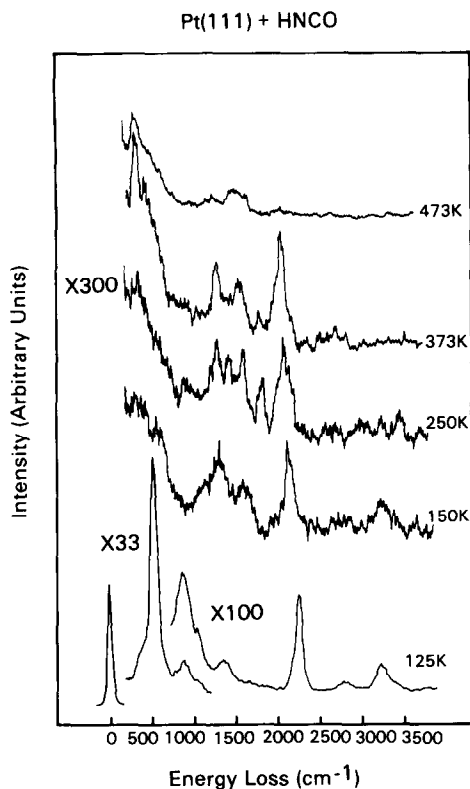
Pt(111) + HNCO

FIG. 2. Shown are the energy loss spectra obtained after adsorbing HNCO on Pt(111) at 100 K and then heating to the given temperatures. All spectra were then taken after the crystal cooled back to 100 K.

they do when these gases are adsorbed alone on the Pt(111) surface (23, 24). Therefore, some of the HNCO must have decomposed at a temperature lower than the desorption temperature for these peaks. The other fragmentation products desorb between 470 and 570 K, above the normal desorption temperatures for any of these species. They are reaction rate limited and are probably formed by the decomposition of the HNCO fragments. The coverage in this temperature regime is still approximately one monolayer since almost all of the N_2 from the HNCO desorbs in this region.

Energy Loss Results

The energy loss spectra for the surface saturated with isocyanic acid are given in

Fig. 2 and the vibrational frequencies obtained are tabulated in Table 1 along with literature values for gas-phase HNCO. The first spectrum is that obtained after heating the crystal to 125 K to remove the multilayers of isocyanic acid. The multilayer surface showed peaks at the same energies as observed in the spectrum at 125 K; however, the low-frequency peaks were somewhat broader and not as intense. This spectrum shows that a single species of molecular isocyanic acid is adsorbed in the surface at 125 K. Stretching frequencies at 3240 and 2270 cm^{-1} correspond to the ν (NH) and the ν_a (NCO) asymmetric vibration, respectively. The corresponding gas-phase frequencies are 3531 and 2274 cm^{-1} (21). Three low-energy peaks at 530, 870, and 1360 cm^{-1} are interpreted as a hindered rotation, a bending mode of the isocyanic acid, and the symmetric ν_s (NCO) vibration, respectively. Peaks at 1060, 2800, and 3790 cm^{-1} are combinations of fundamental vibrations caused either by the loss of energy from the intense peak at 530 cm^{-1}, or by the excitation of two different modes during single scattering events. They are displaced 530 cm^{-1} from corresponding fundamental vibrational frequencies. There should be another double-loss peak at 1400 cm^{-1}, but this is probably obscured by the small peak at 1360 cm^{-1}. From this spectrum, it is not possible to determine how the molecule is bound to the surface since Pt–adsorbate stretching frequencies lie between 300 and 600 cm^{-1} and would be obscured by the peak at 530 cm^{-1}.

When the crystal was heated to 150 K, the elastic peak decreased by more than an order of magnitude, evidence that the adsorbate had disordered. The asymmetric ν_a (NCO) vibration shifted from 2270 to 2160 cm^{-1}, indicating that there was a change in the bonding to the surface. However, the surface is still molecular isocyanic acid, and no desorption occurred in this temperature range. The frequency 2160 cm^{-1} is still considerably higher than 2090 cm^{-1}, corresponding to CO, and thermal desorption

TABLE 1

Vibrational Modes of HNCO (cm^{-1})

HNCO Pt(111)	Bending modes	Pt–adsorbate stretches	ν (Pt–CO)	ν_s (NCO)	Unidentified frequencies	ν (CO)	ν_a (NCO)	ν (N–H)
125 K	530 (hindered rotation) 870			1360			2270	3240
150 K		370					2160	3280
250 K		370			1310 1450 1620 1850	2090		
373 K		350	460		1310 1590 1820	2090		
Gas-phase HNCO	572 670 797			1327			2274	3531

shows isocyanic acid still desorbs at temperatures as high as 250 K. The ν (NH) stretching frequency is still present at 3280 cm^{-1}, and the ratio of the intensities of ν (NH) and the asymmetric ν_a (NCO) vibration remain the same as they did in the spectrum taken at 125 K. The low-frequency modes from 500–1000 cm^{-1}, which we have interpreted as the bending and rotation of the isocyanic acid molecule, have almost disappeared, again showing that the bonding to the surface has changed.

By 250 K, the ν_a (NCO) peak has almost disappeared indicating that the isocyanic acid has fragmented into new surface species. All that can be seen of this ν_a (NCO) band is a small shoulder on the new 2090-cm^{-1} peak. The peak at 2090 cm^{-1} is at the same frequency that Froitzheim *et al.* (25) reported for CO on Pt(111). Identification of this as adsorbed carbon monoxide also agrees with the thermal desorption results. The height of this peak gives the approximate coverage of CO. The peak is about one-third the height obtained for a surface saturated

with CO, indicating a CO coverage of about one-third monolayer. Assignments for the other vibrational bands are impossible to make with any certainty and are probably due to several types of fragments on the surface.

When the surface was further heated to 370 K, just below the CO desorption temperature, a peak at 460 cm^{-1} due to ν (Pt–CO) was resolved (25). At 470 K, this CO band plus the 2090-cm^{-1} peak completely disappear in agreement with the thermal desorption results that CO has desorbed by this temperature. We also observe that the shoulder at 2160 cm^{-1} is completely removed by 370 K; therefore, no isocyanate remains on the surface above this temperature.

While supported platinum and the (111) single crystal may not be catalytically identical, our results show that an isocyanate species is unlikely to be stable on the platinum surface in significant coverages at the temperatures at which these catalysts are usually operated. This agrees with the results of Dalla Betta and Shelef (27) and Solymosi and Bansage (18), who showed

evidence that isocyanate was bound to the oxide support rather than the metal. Solymosi et al. (4) and Lorimer and Bell (28) have observed isocyanate bands at 2148 and 2190 cm^{-1}, respectively, for supported platinum catalysts, which is close to 2160 cm^{-1}, the frequency we see for the ν_a (NCO) stretch above 150 K. However, they have only seen this peak grow at much higher temperatures (near 670 K), and it is unlikely to be due to isocyanate on platinum.

The fact that isocyanic acid decomposes into CO and nitrogen-containing species, with no HCN or CO_2 formation, suggests an isocyanate formation reaction in which CO reacts with a surface nitrogen species. We see no evidence for any bond breakage between the carbon and oxygen atoms.

In summary, we find no evidence for isocyanate bound to platinum above room temperature. While the isocyanate observed on supported platinum catalysts must be formed on the platinum, it does not reside there as a stable species. Assuming that decomposition of HNCO is the reverse of the formation of isocyanate, we find no evidence for CO dissociation in the isocyanate formation reaction.

ACKNOWLEDGMENTS

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