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Aniline Hydrogenolysis on the Pt(111) Single Crystal Surface: Mechanisms for C-N Bond Activation

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INTRODUCTION

Hydrogenolysis of C-N bond on transition metals is a crucial step in hydrodenitrogenation (HDN) reactions. Despite the overall complexity of HDN processes, the details of important surface reactions can be characterized using model reactions of organonitrogen compounds on single crystal model catalysts. The structure and reactivity of well characterized aniline monolayers on the Pt(111) surface both in vacuum and in the presence of hydrogen is discussed here. Adsorption and reactions of aniline were studied by Gland and Somorjai on the Pt(111) and Pt(100) surfaces (1), and more recently by Benziger's group on the Ni(111) and Ni(100) surfaces (2). On both Pt and Ni surfaces, aniline π bonds through the aromatic ring with its ring parallel to the substrate surface.

DISCUSSION

A combination of temperature programmed reaction spectroscopy (TPRS) and near edge X-ray absorption fine structure (NEXAFS) have been used to characterize adsorption and hydrogenolysis of adsorbed aniline on the Pt(111) surface. These experiments were performed in an UHV end station on U-1 beamline at National Synchrotron Light Source. The UHV system, described in detail elsewhere previously (3), is equipped with facilities for NEXAFS measurements using both electron yield and fluorescence yield detection with

low-energy electron diffraction (LEED), Auger electron spectroscopy, and multiple mass TPRS. The symmetry of the surface was verified using LEED, while surface cleanliness was verified with Auger. Aniline (99%) was obtained from Aldrich® and purified by freeze-pump-thaw cycles. Reference NEXAFS spectra were recorded for solid multilayers of aniline. A saturated monolayer was prepared by briefly annealing the multilayer to 210 K. The NEXAFS spectra are normalized to the carbon continuum edge jump to facilitate quantitative comparison. The photon

energy reported here were calibrated against the CO/Pt(111) π^* resonance.

Following aniline adsorption on the clean Pt(111) surface at 95 K, molecular desorption from the multilayer occurred at 200 K. Molecular desorption from the monolayer occurred at 240 K (Figure 1). No significant aniline decomposition was observed by NEXAFS below 250 K, thus molecular aniline must remain intact up to 250 K, the temperature where monolayer aniline desorbs. Large hydrogen peaks are observed at 350 K and 470 K, indicating that partial aniline dehydrogenation is occurring with increasing temperature. As successive desorption of phenyl hydrogens continues above 500 K, several unresolved hydrogen peaks were observed.

Hydrogenolysis of aniline by adsorbed hydrogen from aniline dehydrogenation yields a small benzene peak at 400 K, and an ammonia peak at 500 K. The yield of ammonia from a monolayer coverage of aniline increases substantially as the amount of coadsorbed hydrogen increases. In the presence of 1.5 L post-adsorbed hydrogen, the yield of ammonia increased almost fivefold as indicated by the integrated ammonia areas in the 400 to 900 K temperature range (see middle spectra Figure 1). The structure and bonding of the species responsible for these hydrogenolysis reactions were examined both in vacuum and in hydrogen using NEXAFS.

The NEXAFS spectrum of multilayer aniline (Figure 2) provides a reference spectrum with good signal-to-noise for resonance identification and assignment (Table 1). The

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Figure 1. TPD spectra of aniline on Pt(111) for an initial coverage of ≤ 1 ML. Shown here are the spectra with and without the postadsorbed hydrogen, respectively.

Figure 2. Carbon K-edge NEXAFS spectra for aniline on the Pt(111) surface. The resonance assignment is discussed below, and listed in Table 1.

spectra of multilayer aniline and multilayer benzene on Pt(111) contain many similar resonances (5). Additional resonances are observed for the aniline case because the -NH_2 group lifts the degeneracy of several molecular orbitals in the aromatic ring. The magnitude of splitting (1.3 eV for $\pi_{1,2}^*$ peak) is a direct result of the binding energy shift of the C atom bonded to nitrogen from the rest of the C atoms in the phenyl ring. The π^* resonances at 288.0 eV and 289.4 eV overlapped in energy with a $\sigma^*(\text{C-H})$ resonance (6). These resonance assignments are in good agreement with those for aniline on the Ag(110) surface (7).

The assignment of the resonances for the aniline monolayer spectra are directly derived from the multilayer spectra above. For monolayer aniline annealed to 370 K, the ring is oriented almost parallel ($< 31^\circ$) to the Pt(111)

surface (Figure 3). The orientation turns the p-lobes in the aromatic π -system toward the surface, suggesting π -bonding of the ring with the surface. The strong nitrogen-metal bond may be the cause of the 30° tilt of aniline away from the surface. At normal incidence, a strong resonance at 291.4 eV is observed and attributed to a σ shape-resonance due to the C-N bond. We made this assignment by comparing with NEXAFS spectra for a variety of pure aromatic hydrocarbons on Pt(111), which do not have $\sigma_{\text{C-N}}^*$ (5), and with species which have $\sigma_{\text{C-N}}^*$ (8). Using dipole selection rules, the spectra indicate that the C-N bond is almost parallel to the Pt(111) surface at 370 K. A parallel C-N bond may activate the C-N bond by facilitating the π^* orbital overlap with metal d orbital. Since benzene from aniline hydrogenolysis desorbs at 400 K, the adsorbed intermediate species at 370 K are believed to be the

primary intermediates for C-N bond activation. These spectroscopic results indicate that this intermediate species is bonded to the surface through both the phenyl π electrons as well as nitrogen lone pair.

Annealing a monolayer of aniline on Pt(111) in 0.001 Torr of hydrogen flow gives an NEXAFS spectrum (Figure 3) significantly different from that in vacuum. The $\pi_{1,2}^*(\text{C}_{2,3,4})$ resonance is shifted by -0.2 eV to 284.2 eV from that at multilayer coverage. This downward shift is believed to be an indication of new bonding between platinum and C₂, C₃, C₄ on the phenyl ring (9). The most noticeable spectral changes are the larger σ^* to π^* resonance ratio at both normal and grazing incidence compared to those observed in vacuum. The substantial change in σ^* intensity indicates a loss of aromatic character. We suggest that this may be the result of partial

Figures 3a and 3b. Carbon K-edge NEXAFS spectra for monolayer aniline annealed in vacuum and in hydrogen flow. The sample is prepared by annealing the monolayer aniline to 370 K briefly, and quenching down to 100 K. The resonance (*) at 287.4 eV arises from carbon monoxide contaminant adsorbed when sites are left by desorbing aniline during annealing.

hydrogenation of the aromatic ring at this temperature in flowing hydrogen. Also noticeable is a stronger and broadened $\pi_2^*(C_1)$ resonance at 285.7 eV for the aromatic carbon atom bonded to the nitrogen atom. The peak broadening indicates stronger molecule-surface interactions caused by hybridization of benzene π^* orbitals with metal states and/or reduced lifetime of π^* state due to delocalization (5). Further observation reveals that σ_{C-N}^* resonance becomes more

dominant at normal incidence, possible only when C-N bond is parallel to the surface. We believe that this configuration is critical for activating the C-N bond and promoting hydrogen addition to the ends of the C-N bond.

CONCLUSION

In conclusion, C-N bond activation is substantially enhanced in the presence of hydrogen. After annealing to 370 K, the adsorbed aniline is

oriented with the C-N bond almost parallel to the Pt(111) surface. This configuration is believed to facilitate the activation of the C-N bond, especially in the presence of surface hydrogen. When the surface hydrogen supply is sufficiently high, hydrogenolysis will be favored over competing surface processes like dehydrogenation and decomposition.

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Table 1.
NEXAFS Resonance Assignment of Multilayer Aniline/Pt(111)

Benzene (5)	$\pi_{1,2}^*(e_{2u})$	$\pi_3^*(b_{2g})$	$\sigma_1^*(e_{2u})$	$\sigma_2^*(e^*_{2g}a_{2g})$		
Multilayer/Pt(111)	285.0	288.9	293.3	300.1		
Aniline	A	B	C	D	E	F
Multilayer/Ag(110)(7)	285.6	287.0	289.2	290.7	295.1	302
Multilayer/Pt(111)	284.4	285.7	288.0	289.4	293.1	300
Assignment	$\pi_1^*(C_{2,3}) + \pi_2^*(C_{2,4})$	$\pi_2^*(C_1)$	$\pi_3^*(C_{2,3,4})$ or CH^*	$\pi_3^*(C_1)$ or CH^*	σ_1^*	σ_2^*

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