

Irreversible Change of NO/Pt(111) after High-Pressure NO Exposure

It is essential to bridge the pressure gap between surface reactions on model catalysts under ultrahigh vacuum (UHV) conditions and practical catalytic reactions under “realistic” conditions in order to understand the reaction mechanism of heterogeneous catalysis. In this study NO adsorption on Pt(111), a model system for automobile catalysis, was studied under 1×10^{-7} Torr NO and after high-pressure (1 Torr) NO exposure at room temperature (RT) by means of N K-edge near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Under 1×10^{-7} Torr NO at RT, NO molecules adsorb not only at the most stable fcc-hollow sites but also partially at energetically unfavorable atop sites. NO at atop sites reversibly desorbs after evacuation. After 1 Torr NO exposure, the adsorption state changes drastically and irreversibly.

NO adsorption on platinum group metal surfaces has been intensively studied because of the important role of the catalytic conversion of NO_x species to N₂ and CO₂ by three-way catalysts for automotive exhaust gases. Surface science studies using electron spectroscopy have been conducted under UHV conditions. Recently, however, the pressure gap between the model system and “realistic” system for heterogeneous catalysis has attracted much attention because a high-pressure atmosphere may induce various surface processes like bond breaking, high-density chemisorption and lateral shifts of adsorption sites. For understanding solid surfaces under realistic conditions it is important to study surface phenomena induced by high pressure. In this report, we present high-pressure effects on a NO/Pt(111) system studied by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy [1].

The experiments were performed at BL-7A using a UHV chamber where a small preparation chamber is attached for ambient-pressure doses. To investigate the NO adsorption behavior, we measured N K-edge NEXAFS spectra by the partial electron-yield method. All the measurements were performed at room temperature (RT).

N K-edge NEXAFS spectra of saturated NO adlayers on Pt(111) at RT were measured under UHV and in the presence of 1×10^{-7} Torr NO as shown in Figs. 1(a) and (b), respectively. Figure 1(a) shows a single peak at 401.1 eV due to the N 1s \rightarrow π^* resonance, which indicates that NO adsorbs only at fcc-hollow sites with the molecular axis aligned perpendicularly (Fig. 2(a)). Under 10^{-7} Torr NO, however, the NEXAFS spectra shown in Fig. 1(b) exhibit discernible changes: energy shift of the π^* peak to 400.7 eV and broadening of the peak width (Insets of Figs. 1(a) and (b)). According to a previous report on saturated NO on Pt(111) at 230 K [2], the peak shift and broadening are explained by the contribution from partial occupation at atop sites with a largely tilted configuration. The large tilting causes a difference in interaction between the NO π^* orbital and the substrate, resulting in the splitting of the π^* orbital into π^*_\parallel and π^*_\perp . The results indicate that 10^{-7} Torr NO induces a high-density chemisorption phase which is composed of fcc-hollow and atop NO species (Fig. 2 (b)). This new species at atop sites disappears after NO evacuation, indicating that the formation of high-density phase under 10^{-7} Torr NO is reversible.

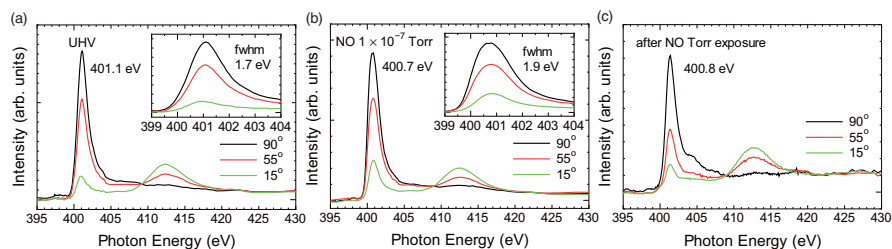


Figure 1
N K-edge NEXAFS spectra taken from NO adsorbed on Pt(111) with different incident angles: (a) saturated at RT under UHV. The full width at half-maximum (fwhm) of the π^* resonance at 55° incidence is 1.7 eV; (b) under 1×10^{-7} Torr NO at RT. The fwhm of the π^* resonance at 55° incidence is 1.9 eV; (c) after 1 Torr NO exposure at RT. The spectra were measured under UHV at RT.

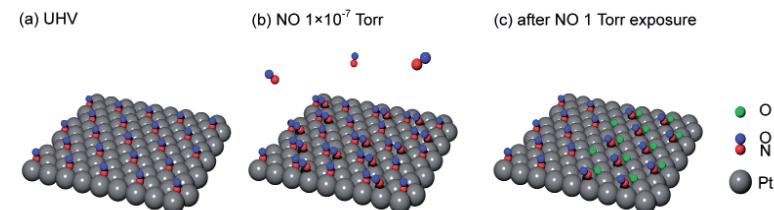


Figure 2
The surface structures of NO adsorbed on Pt(111): (a) saturated at RT under UHV. A (2×2) -NO structure where NO molecules adsorb at fcc-hollow sites; (b) under 1×10^{-7} Torr NO at RT. NO molecules adsorb not only at fcc sites but also at atop sites. The induced high-density phase is reversible concerning the NO evacuation; (c) after 1 Torr NO exposure at RT. A mixed NO + O overlayer is formed via dissociation of NO and removal of atomic nitrogen under the NO high-pressure exposure.

A drastic change was observed after high-pressure (1 Torr) NO exposure. N K-edge NEXAFS spectra taken after high-pressure (1 Torr) NO exposure are shown in Fig. 1(c). In addition to the main peak at 400.8 eV for NO at fcc-hollow sites, new features are observed at 404 and 407 eV, which are irreversibly brought about by the 1 Torr NO dose. We tentatively attribute these peaks to higher lying unoccupied states of NO interacting with atomic oxygen. The atomic oxygen is formed via dissociation of NO on Pt(111), which was supported by ambient pressure XPS measurements. A structure model taking into account the STM results for this surface [1] is depicted in Fig. 2(c).

In summary, we observed not only high-density chemisorption but also an unexpected irreversible surface change for NO/Pt(111) at elevated NO pressures. It is interesting to note that NO does not dissociate on the Pd(111) surface under the same condition [3], although it is regarded as a more active surface. Further studies on high-pressure induced adsorption states will provide rich and novel surface chemistry.

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