Structure of a p-Xylene Adlayer Formed on a Rh(111) Surface in Solution and in Vacuum
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Introduction
Understanding the structure of organic adsorbates on metal surfaces in solution is a major subject of modern interfacial electrochemistry. We have investigated the adsorption of simple aromatic molecules such as benzene, naphthalene, and anthracene on Rh(111), Pt(111), and Cu(111). In this paper, we describe the adlayer structure of p-xylene adsorbed on Rh(111) both in 0.01M HF solution and in ultrahigh vacuum (UHV) by using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). High-resolution STM images provide the internal molecular structure of each p-xylene molecule.

Experimental
Single-crystal electrodes of Rh were made by the crystallization of a molten ball formed at the end of a Rh wire in a hydrogen-oxygen flame. Electrochemical and in situ STM measurements were carried out in 0.01 M HF prepared from Suprapur grade HF and ex situ STM and LEED measurements in a UHV system that consisted of analysis and preparation chambers with a base pressure of 1 × 10⁻¹⁰ Torr. The analysis chamber was equipped with an STM and a retarding-field optics for LEED and Auger electron spectroscopy. All potentials are reported with respect to RHE.

Results
After observing the hexagonal arrangement of Rh atoms on Rh(111) in HF by in situ STM, a small amount of 0.1 mM solution of p-xylene was injected into the STM cell at 0.3 V. The average concentration of p-xylene was ca. 10 μM. Figure 1 shows an STM image of a p-xylene adlayer on Rh(111). Each molecule appeared as an elongated shape because of the existence of two methyl groups at the para position of the benzene ring.

A precise comparison between the image of Figure 1 and that of Rh(111)-(1 × 1) revealed that the structure of p-xylene molecules adsorbed on Rh(111) form a c(2√3 × 4)rect structure in HF solution. Subsequently, the Rh(111) electrode was emersed, and LEED was carried out on the surface. The adlayer structure obtained by ex situ LEED was consistent with that determined by in situ STM. However, this surface symmetry was different from that previously reported by Somorjai and coworkers.

We carefully re-examined the structure of a p-xylene adlayer formed in UHV to understand the discrepancy. Figure 2 shows a height-shaded surface plot of an adlayer of p-xylene obtained in UHV after exposing Rh(111) to p-xylene at 5 × 10⁻⁶ Torr for 60 s (30 L). The elongated shape of each molecule was clearly seen. The same c(2√3 × 4)rect structure was obtained by STM in UHV as well as in solution.

To confirm the adlayer structure, we carried out LEED after the ordered adlayer of p-xylene was imaged by STM. Figure 3 shows a well-ordered LEED pattern for the p-xylene adlayer with regularly arrayed small spots. This LEED analysis confirmed that the adlayer structure of p-xylene was c(2√3 × 4)rect.

References

Figure 1. STM image of an ordered p-xylene adlayer on Rh(111) in HF solution.

Figure 2. STM image of an ordered p-xylene adlayer on Rh(111) in UHV. 4 × 4 nm².

Figure 3. LEED pattern for the ordered adlayer of p-xylene after the STM observation.