

deuterium exchange between adsorbed C_6H_6 and C_6D_6 [in the case of Ni(100), annealing to 150°C of the surface with a chemisorbed mixture of C_6H_6 and C_6D_6 gave no evidence of hydrogen–deuterium exchange between chemisorbed benzene molecules].

In dehydrogenation of $c-C_6H_{10}$ and $c-C_6D_{10}$ on the platinum surfaces, a mixture of all possible $C_6H_xD_{6-x}$ molecules were observed in both the thermal desorption and the displacement reactions, conducted at $\sim 125^\circ\text{C}$ and $\sim 100^\circ\text{C}$, respectively, for the stepped and (111) surfaces. Since hydrogen–deuterium exchange was not observed² between adsorbed C_6H_6 and C_6D_6 on Pt(111) up to $\sim 130^\circ\text{C}$, the hydrogen–deuterium exchange process in the cyclohexene dehydrogenation on Pt(111) must occur at some intermediate state before chemisorbed benzene is formed. A similar intermediate exchange probably occurs for cyclohexene on the stepped platinum surface.

Cyclohexane did not react with any of the nickel surfaces at room temperature or above. The residence time of cyclohexane was probably too short for any significant dehydrogenation to occur under these conditions. Only the Pt 6(111)×(111) surface displayed a high activity for the dehydrogenation of cyclohexane to benzene. Dehydrogenation of cyclohexane to benzene had a higher activation energy than the dehydrogenation of cyclohexene to benzene on this surface. Evidence of hydrogen–deuterium exchange between adsorbed $c-C_6H_{12}$ and $c-C_6D_{12}$ on the Pt 6(111)×(111) was obtained from a thermal desorption study subsequent to an attempted trimethylphosphine displacement whereby all possible $C_6H_xD_{6-x}$ molecules were desorbed at 170–190°C—a feature similar to that observed for benzene chemisorbed on the stepped platinum surface.

Dehydrogenation reactions were studied over carbon-contaminated surfaces (submonolayer coverage). The Ni(110)-C surface was far more reactive in dehydrogenating both cyclohexene and cyclohexadiene than the clean Ni(110)

surface. A substantial carbon effect on the chemistry of the other surfaces was not detected.

Rate data for the dehydrogenation to benzene establish the cyclohexadiene transformation as the most facile process, cyclohexene next and cyclohexane least. Thus, the data are not inconsistent with *chemisorbed* intermediates of cyclohexadiene in the cyclohexene transformation and of cyclohexene and cyclohexadiene in the cyclohexane transformation. In the cyclohexadiene and cyclohexene reactions, it is presumed that the initial chemisorption states primarily involved an interaction of appropriate metal surface orbitals with the π and π^* orbitals of the olefinic or diolefinic systems. This necessarily places one C–H hydrogen atom of the saturated CH_2 centers proximate to the metal surface, thus enabling C–H bond scission at these sites and the subsequent generation of chemisorbed benzene. Reversible C–H bond breaking was not detectable for any of the nickel surfaces *under the ultrahigh vacuum conditions*, but was for platinum—a result consistent with the relative electronic properties of nickel and platinum.

There is some generality to the metal surface conversion of a cyclic hydrocarbon to a chemisorbed C_nH_n species. Exploratory experiments have demonstrated the conversion of 1, 5-cyclo-octadiene to cyclo-octatetraene on Pt(111).

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¹C. M. Friend and E. L. Muetterties, *J. Am. Chem. Soc.* **103**, 773 (1981).

²M.-C. Tsai and E. L. Muetterties, *J. Am. Chem. Soc.* (in press).

Summary Abstract: CO on Ru(001): Formation and dissolution of islands of CO at low coverages

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Upon adsorption on the basal plane of ruthenium, CO forms a $(\sqrt{3} \times \sqrt{3})R 30^\circ$ superstructure,^{1–3} hereafter referred to as the $\sqrt{3}$ structure. Results of thermal desorption⁴ and infrared⁵ measurements on this system indicate that there is an attractive second-neighbor interaction between CO molecules. This should cause the CO molecules to order into islands of the $\sqrt{3}$ structure at low coverages if the temperature

is sufficiently low. The size and mechanism of formation of islands has been studied for this system using low-energy electron diffraction (LEED). Measurements of the temperature and coverage dependence of the $\sqrt{3}$ beam profile have been performed using a standard Varian LEED system, modified by the installation of a channel electron multiplier into the Faraday cup.⁶ Electron multiplication in the detec-

tor allowed the use of low incident beam currents (1–10 nA) which prevented significant electron beam damage⁷ during the course of the measurements.

At 100 K, the $\sqrt{3}$ structure is observed easily with LEED at fractional coverages as low as $\frac{1}{3}$. (The optimum coverage for the $\sqrt{3}$ structure is $\theta = \frac{1}{3}$.) This confirms the prediction of island formation. If there were no attractive second-neighbor interaction causing island formation, no ordered $\sqrt{3}$ structure would form below a coverage of approximately $\theta = 0.28$ at any temperature.^{8,9} The coverage dependence of the island size was monitored by measuring the width of the $\sqrt{3}$ beam profile for five coverages between $\theta = 0.10$ and $\theta = \frac{1}{3}$ at 100 K. The results are shown in the upper curve of Fig. 1. The true widths, shown in the lower curve of Fig. 1, were determined by a Fourier transform deconvolution of the measured profiles with the instrument response function.^{10,11} There is a strong increase in the full width at half maximum (FWHM) with decreasing coverage, indicating the formation of smaller islands at lower coverages. This rapid increase in the FWHM is inconsistent with a strict step-limited model of island formation, for which there should be a linear change in island size with coverage. To generate the coverage dependence shown in Fig. 1, there must be increasing numbers of islands at low coverages. This indicates that other limitations on surface mobility, in addition to step edges, constrain island formation, causing there to be more than one island per terrace at low coverages.

The temperature dependence of the $\sqrt{3}$ beam profiles at three coverages is shown in Fig. 2. As indicated by the arrows, at $\theta = 0.14$ and $\theta = \frac{1}{6}$ an abrupt onset of beam broadening is observed after the intensity has decreased by approximately 20%. This delayed onset of beam broadening with respect to intensity decrease is a result of the distribu-

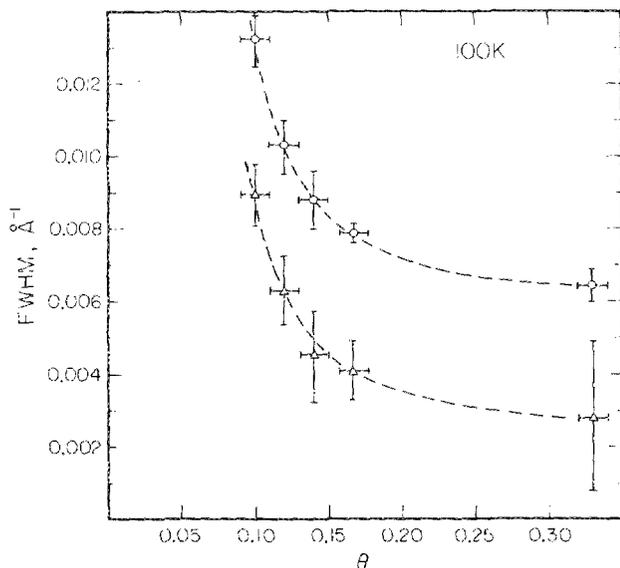


FIG. 1. Full width at half maximum of the $\sqrt{3}$ LEED beam as a function of coverage of CO. Circles \circ are measured values. Error bars are the standard deviation from multiple measurements. Triangles \triangle are the true widths obtained from the measured values by deconvolution of the instrumental width. Dashed lines are empirical.

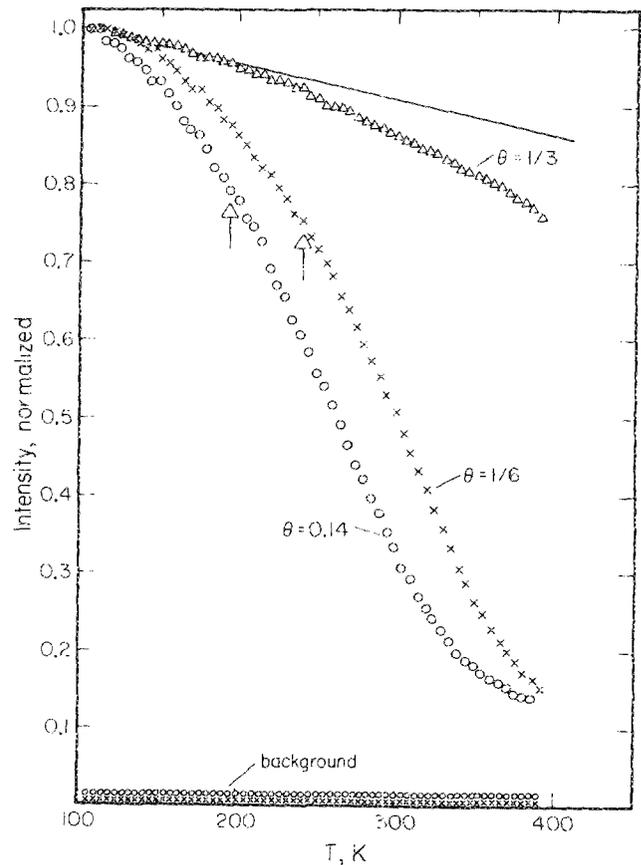


FIG. 2. Variation of intensity with temperature at $\theta = \frac{1}{3}$, triangles; $\theta = \frac{1}{6}$, \times 's; and $\theta = 0.14$, circles. Each curve has been normalized to unity at 100 K. Arrows indicate the onset of beam broadening at $\theta = \frac{1}{6}$ and 0.14. The solid curve is the intensity decrease calculated for the frustrated translational mode of CO parallel to the surface with a frequency of 45 cm^{-1} .

tion of island sizes. Although many different size distributions are consistent with the measured FWHM's, the observed intensity-width behavior can occur with only one size distribution.¹¹ This size distribution was determined by modeling the equilibrium between the ordered phase (islands) and the disordered phase. Once the size distribution was found, it was used in conjunction with the measured FWHM's to calculate the mean island size as a function of coverage. At $\theta = \frac{1}{6}$ the mean number of CO molecules per island is 1000; it is 500 at $\theta = 0.14$, 300 at $\theta = 0.12$, and 160 at $\theta = 0.10$.

It is not possible to make a determination of the island size from the width of a diffracted beam profile unless the size distribution is known by some other method. For CO on Ru(001), the temperature dependence of the disordering has allowed a determination of the size distribution and thus the island sizes. In addition, the coverage dependence of the FWHM indicates that island formation is not strictly step limited, i.e., there is more than one island per terrace at low coverages for CO on Ru(001).

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