

## Nonlinear Island Growth Dynamics in Adsorbate-Induced Restructuring of Quasihexagonal Reconstructed Pt{100} by CO

Andrew Hopkinson, Josephine M. Bradley, Xing-Cai Guo, and David A. King

*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*  
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We have made the first dynamic measurement of the  $(1 \times 1)$ -CO island growth rate and the simultaneous CO coverage on the quasihexagonal reconstructed (hex-*R*) phase during the CO-induced hex-*R*  $\rightarrow$   $(1 \times 1)$  phase transformation on Pt{100}. The island growth rate is described by a strongly nonlinear power law with respect to the local CO coverage on the hex-*R* phase at surface temperatures between 380 and 410 K, with an apparent reaction order of  $4.5 \pm 0.4$ . These kinetics manifest themselves as a strongly flux dependent net sticking probability.

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Numerous observations have now been made of surface structural phase changes induced by the presence of adsorbates. Despite this, there are no studies available which establish the growth mechanism of the islands of the new phase from the stable clean surface phase. In this Letter we present a study of the conversion of the stable surface of clean Pt{100}, described as hex-*R*, to a  $(1 \times 1)$  configuration during CO adsorption. It represents the first dynamic measurement of the  $(1 \times 1)$ -CO island growth rate and the simultaneous CO coverage on the hex-*R* phase during the surface structural transformation. The results show that 4 to 5 CO molecules are involved in the restructuring process, leading to a strongly nonlinear growth dependence. This is crucial to the understanding of the nucleation and growth mechanism and also oscillatory reactions involving CO on Pt{100} [1,2].

The most stable phase of the clean Pt{100} surface is a reconstructed phase in which the surface layer of Pt atoms has a quasihexagonal structure. Following Heilmann, Heinz, and Müller [3], we will refer to this surface as Pt{100}-hex-*R*0.7° or simply hex-*R*. A metastable  $(1 \times 1)$  clean surface (the bulk truncation structure) can be prepared which reconstructs irreversibly above  $\approx 400$  K [4,5] to form the "hex" surface, which in turn reconstructs to form the hex-*R* surface at  $\approx 1100$  K. The hex and hex-*R* surfaces differ by a rotation of the hexagonal layer by  $\approx 0.7^\circ$  with respect to the bulk. The hex and hex-*R* reconstructions are lifted by the adsorption of CO, NO, O<sub>2</sub>, and other adsorbates to yield the  $(1 \times 1)$  phase. The driving force of the CO-induced hex  $\rightarrow$   $(1 \times 1)$  surface phase transition was identified by Thiel *et al.* [6] from a low energy electron diffraction (LEED) study to be the higher heat of adsorption of CO on the  $(1 \times 1)$  phase than on the reconstructed phase. Thiel *et al.* also proposed that the transformation occurs by *sequential* steps of adsorption on the reconstructed surface followed by migration and "trapping" of CO onto growing "islands" of the  $(1 \times 1)$  surface, initially formed by nucleation. It is known that a critical CO coverage of ca. 0.05 monolayer (ML) on the hex phase is required to induce the hex  $\rightarrow$   $(1 \times 1)$  phase transformation [7,8] [where

1 ML is equal to the Pt atom density in the ideal  $(1 \times 1)$  surface].

The progress of the CO-induced hex  $\rightarrow$   $(1 \times 1)$  phase transformation has been followed by LEED [6,7,9,10], work function measurement [7,8,11], Rutherford backscattering spectroscopy [4,8], nuclear microanalysis [8], electron energy loss spectroscopy [7], and scanning tunneling microscopy (STM) [12,13]. However, none of the above techniques can be used to follow the CO coverage on the hex or hex-*R* phase during the phase transformation. In principle, reflection-absorption infrared spectroscopy (RAIRS) could be used to follow the CO coverage on the hex or hex-*R* phase during the transformation, but high resolution (and therefore a long data acquisition time) is required to resolve the adsorption band of CO on the hex-*R* phase from that of CO in an island on  $(1 \times 1)$  surface [14]. A further problem with RAIRS is the possibility that the absorption band of CO at the edges of the small monatomic Pt islands on the  $(1 \times 1)$  surface, which are created in the phase transformation [12,13], overlaps the absorption band of CO on the hex-*R* phase.

During the CO-induced hex-*R*  $\rightarrow$   $(1 \times 1)$  phase transformation, the local CO coverage on the  $(1 \times 1)$  phase is high, approximately 0.5 ML [6], while on the remaining areas of hex-*R* surface the local CO coverage is low, typically less than 0.03 ML. At surface temperatures above ca. 350 K, desorption of CO from the hex-*R* phase is significant and competes with island growth. If CO on the hex-*R* phase is in equilibrium with CO on the  $(1 \times 1)$  phase, which is a reasonable assumption considering the high mobility of CO on either phase at ambient temperatures, then the desorption rate from unit area of the hex-*R* phase is much greater than that from the  $(1 \times 1)$  phase, even though the local coverage on the  $(1 \times 1)$  phase is greater than that on the hex-*R* phase. The relative desorption rates actually equate to the relative absolute sticking probabilities on the two phases, which are  $s_a \approx 0.78$  on the hex-*R* phase at low local CO coverage and  $s_a \approx 0.04$  on the  $(1 \times 1)$  phase at a local coverage of 0.5 ML [15]. We therefore conclude that during the CO-induced hex-*R*  $\rightarrow$   $(1 \times 1)$  phase transformation, CO

desorption is primarily from the hex-*R* phase, until most of the reconstruction is lifted.

We have measured the dynamic desorption rate indirectly during the phase transformation, by measuring the *net sticking probability* as a function of total CO coverage using the King and Wells (KW) molecular-beam reflectivity technique [16]. We define the net sticking probability  $s_n$  at time  $t$  by

$$s_n(t) = s_a(t) - \frac{r_d(t)}{z}, \quad (1)$$

where  $z$  is the impingement rate (beam flux),  $s_a$  is the absolute sticking probability (the ratio of chemisorption rate to  $z$ ), and  $r_d$  is the total desorption rate. We assume that at any total CO coverage  $\theta$ ,  $s_a$  is independent of surface temperature  $T_s$ , and take

$$s_a(\theta, T_s) \approx s_a(\theta, 315 \text{ K}). \quad (2)$$

At  $T_s = 315 \text{ K}$ , desorption is negligible and the KW technique measures the absolute sticking probability. The assumption Eq. (2) is reasonable, at least until most of the reconstruction is lifted, because the initial sticking probability of CO on the hex-*R* surface is independent of  $T_s$  [15]. Substituting for  $s_a$  in Eq. (1) using Eq. (2) leads to an expression for the desorption rate  $r_d$ ,

$$r_d(\theta, T_s) \approx z[s_a(\theta, 315 \text{ K}) - s_n(\theta, T_s)]. \quad (3)$$

Since desorption is primarily from the hex-*R* phase (until most of the reconstruction is lifted) the CO coverage on the hex-*R* phase is  $\approx r_d/k_d$ , where  $k_d$  is the first order desorption rate constant for CO on the hex-*R* surface. The *local* CO coverage on the hex-*R* phase is obtained by dividing the total CO coverage on the hex-*R* phase by the area of hex-*R* phase, estimated from the total CO coverage assuming a local CO coverage on the  $(1 \times 1)$  phase of 0.5 ML. We determined  $k_d$  from desorption isotherms at different surface temperatures  $T_s$ . At  $T_s$  between 380 and 420 K, a single molecular beam pulse of CO was used to dose the hex-*R* surface and the decay in desorption rate after dosing was followed by measuring the CO pressure in the main UHV chamber using a conventional quadrupole mass spectrometer (QMS). At  $T_s$  between 590 and 620 K, a 50% duty chopped CO beam was employed and the desorption rate was monitored by a line-of-sight double-differentially pumped QMS. In both temperature ranges, the CO coverage was kept below 0.01 ML to prevent the formation of the  $(1 \times 1)$  phase. A linear Arrhenius plot was obtained from which the desorption activation energy ( $E_d = 105 \text{ kJ/mol}$ ) and preexponential factor ( $\nu = 3.7 \times 10^{12}$ ) were determined. The energy is slightly lower than  $E_d = 115 \text{ kJ/mol}$  obtained by Thiel *et al.* [9] on the hex as opposed to the hex-*R* surface.

In addition, since the CO coverage on the hex-*R* phase remains small, the increase in total CO coverage during the phase transformation must be attributed to the trap-

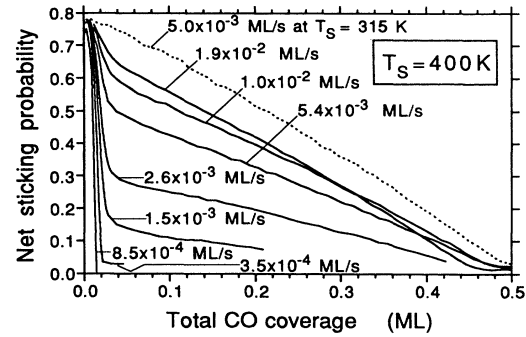


FIG. 1. Net sticking probability of CO on an initial Pt{100}-hex-*R* clean surface at 400 K as a function of total CO coverage at different molecular beam fluxes. The sticking probability at 315 K is also shown as an estimate of the absolute sticking probability at 400 K.

ping of CO onto growing islands of  $(1 \times 1)$  phase, on which the local CO coverage is  $\approx 0.5 \text{ ML}$ . The island growth rate  $r_g$ , in terms of the rate of incorporation of CO into islands, is given by

$$r_g(\theta, T_s) \approx z s_n(\theta, T_s). \quad (4)$$

Figure 1 shows the net sticking probability  $s_n$  as a function of total CO coverage at  $T_s = 400 \text{ K}$ . Total CO coverages were calibrated against the saturation coverage of 0.75 ML at  $T_s = 315 \text{ K}$  [4]. In the low coverage limit  $s_n \approx 0.78$  and is independent of beam flux and surface temperature between 285 and 420 K [15]. With increasing total CO coverage,  $s_n$  decreases rapidly as desorption from the hex-*R* phase increases until, at all but the lowest beam fluxes, island growth, competing with desorption, prevents the continued increase in CO coverage on the hex-*R* phase. This leads to the characteristic break in the  $s_n$  data. *The net sticking probability is clearly flux dependent.* We also obtained similar data to that shown in Fig. 1 at  $T_s = 380, 390,$  and  $410 \text{ K}$  [15]. For a given beam flux,  $s_n$  decreases with increasing  $T_s$ .

Using Eqs. (3) and (4) and the measured values of  $k_d$ , we have extracted from Fig. 1 and the data at different surface temperatures, the island growth rate as a function of the *local CO coverage on the hex-*R* phase* at an arbitrarily selected total CO coverage of 0.05 ML (Fig. 2). *The island growth rate is a very nonlinear function of the local CO coverage on the hex-*R* phase*, but with no surface temperature dependence within experimental error. The island growth rate is approximated by a power law with respect to the local CO coverage on the hex-*R* phase. The apparent reaction order is  $4.5 \pm 0.4$ .

Figure 3 shows the island growth rate, relative to the estimated area of remaining hex-*R* phase, and the local CO coverage on the hex-*R* phase as a function of total CO coverage during the CO-induced phase transformation at different beam fluxes, extracted from Fig. 1. The trend illustrated in Fig. 3 is representative of data at the

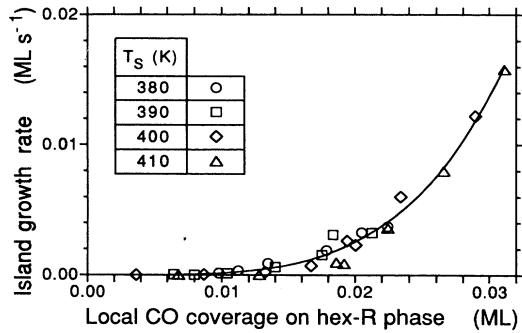


FIG. 2.  $(1 \times 1)$ -CO island growth rate as a function of the local CO coverage on the hex- $R$  phase ( $\theta_{\text{hex-}R}$ ) for an initial Pt{100}-hex- $R$  clean surface at different temperatures. The line depicts a rate proportional to  $(\theta_{\text{hex-}R})^{4.5}$ .

different surface temperatures [15]. The analysis cannot be extended to total CO coverages approaching 0.5 ML because the assumption that CO desorption is primarily from the hex- $R$  phase becomes invalid as this phase becomes eliminated from the surface at high total coverages. Figure 3 shows that *both the island growth rate and the local CO coverage on the hex- $R$  phase are virtually independent of the area of hex- $R$  phase transformed*. The absence of a continued increase in the island growth rate or a sudden decrease in the local CO coverage on the hex- $R$  phase after the onset of island growth is unexpected considering the nucleation process.

Nucleated processes sometimes show history-dependent behavior. To investigate a possible dependence of the island growth rate on CO pressure history, we performed KW experiments in which we changed the beam flux part way through the surface phase transformation. Figure 4 shows a typical result of such an experiment. We measured  $s_n$  at  $T_s = 400$  K with a beam flux of 0.0053 ML/s (curve *a*). When the total CO coverage had increased to 0.2 ML, the molecular beam was switched off for a while. The local CO coverage on the  $(1 \times 1)$  phase decreases slightly due to some desorption in this beam-off period, but remains sufficiently high to stabilize the areas of  $(1 \times 1)$  phase. A molecular beam with a lower flux of 0.0015 ML/s was allowed to impinge on the surface, still at  $T_s = 400$  K. At this lower beam flux,  $s_n$  is initially quite high because of the decrease in the desorption rate during the beam-off period. However, as the local coverages on both phases and the desorption rate increase,  $s_n$  drops below that measured with the higher beam flux for the same total CO coverage of 0.2 ML. In fact, it drops to the same value as measured with a beam flux of 0.0015 ML/s on an initial hex- $R$  clean surface. *The net sticking probability, and therefore the island growth rate, is determined only by the instantaneous beam flux and not by the beam flux history in this experiment.* This behavior is also unexpected considering the nucleation process.

In summary, the island growth rate can be described

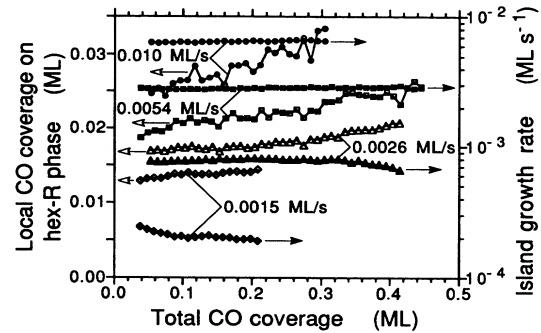


FIG. 3. Local CO coverage on the hex- $R$  phase, and  $(1 \times 1)$ -CO island growth rate relative to the remaining area of hex- $R$  phase, as a function of the total CO coverage on an initial Pt{100}-hex- $R$  clean surface at 400 K, at the molecular beam fluxes indicated.

by a power law with respect to the local CO coverage on the hex- $R$  phase at  $T_s$  between 380 and 410 K, with no dependence on  $T_s$  within experimental error, and with no dependence on either the area of hex- $R$  phase transformed or the CO beam flux (pressure) history. We conclude that the  $(1 \times 1)$  islands are heterogeneously nucleated from the hex- $R$  phase, and then grow at a rate determined by the power law. Isotropic growth is unlikely, because a rapid increase in the length of growing island edge after the onset of nucleation is not consistent with a constant local CO coverage on the hex- $R$  phase—it would be expected to decrease rapidly in this case. In a STM study, Ritter *et al.* [13] observed anisotropic growth for the NO-induced hex- $R \rightarrow (1 \times 1)$  phase transformation—the favorable growth direction was along the “furrows” in the corrugated hex- $R$  surface. The condensed phase analogy of anisotropic island growth on a surface is the growth of cylinders in the axial direction only [17].

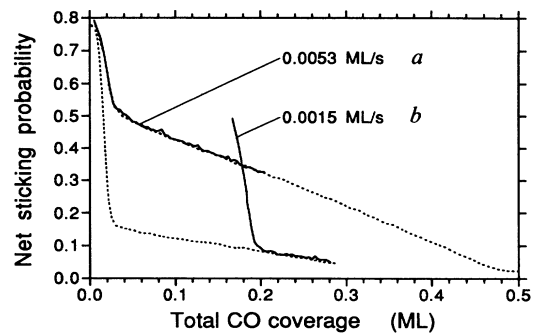


FIG. 4. Net sticking probability of CO on an initial Pt{100}-hex- $R$  clean surface at 400 K as a function of total CO coverage with a beam flux of 0.0053 ML/s (curve *a*) and subsequently 0.0015 ML/s (curve *b*). The broken lines show equivalent results at similar beam fluxes, but starting from an initial Pt{100}-hex- $R$  clean surface for both beam fluxes.

The power law precludes CO diffusion across the hex-*R* surface being the rate limiting step. We speculate that 4 or 5 CO molecules (based on the reaction of  $4.5 \pm 0.4$ ) are involved in a concerted reaction step resulting in growth of the (1×1) phase from the hex-*R* phase. We cannot, however, rule out the possibility that the islands are themselves nucleated at a rate described by the power law, subsequent growth being terminated at some sort of defect. A very nonlinear dependence of the nucleation rate on the local CO coverage on the hex-*R* phase is consistent with nucleation phenomena in general [17].

In conclusion, the first dynamic measurement of the island growth rate and the simultaneous CO coverage on the hex-*R* phase during the CO-induced hex-*R* → (1×1) phase transformation has yielded a strongly nonlinear dependence of the rate on the CO coverage on the hex-*R* phase. This result provides important input for modeling the observed oscillatory reactions involving CO on Pt{100} [2].

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