micelles was embedded in epoxy resin (Epon), and thin sections of ~60 nm in thickness were obtained by microtoming the resin sample at room temperature. In order to increase the contrast between the PAA and the PS regions, the sections were stained with CsOH (aq) and washed with deionized water to remove excess CsOH.

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Calorimetric Measurement of the Energy Difference Between Two Solid Surface Phases

Y. Y. Yeo, C. E. Wartnaby, D. A. King

A recently designed single-crystal surface calorimeter has been deployed to measure the energy difference between two solid surface structures. The clean Pt{100} surface is reconstructed to a stable phase in which the surface layer of platinum atoms has a quasi-hexagonal structure. By comparison of the heats of adsorption of CO and of C_2H_4 on this stable Pt{100}-hex phase with those on a metastable Pt{100}-(1×1) surface, the energy difference between the two clean phases was measured as 20 ± 3 and 25 ± 3 kilojoules per mole of surface platinum atoms.

Phase transitions in bulk systems can be readily characterized by their enthalpy change by using calorimetric measurements. Although surface phase transitions are well known, their energetics have been inferred indirectly, either through kinetics measurements (*1*) or by theoretical studies (*2*), or both. Recently we have developed a surface calorimeter that allows heats of adsorption to be measured directly (*3*). Because chemisorption can induce or lift surface reconstructions, such studies can be used to construct thermodynamic cycles that allow the heat of the surface reconstruction to be determined directly. Because of recent developments in the theoretical treatment of metal surfaces, it is of great importance to obtain such high-quality experimental data, which can serve as a testing ground for theory.

The clean Pt{100} surface can be prepared in a metastable ideal bulk termination (1×1) structure, stable at 300 K. On heating above 500 K, the surface restructures to a more stable structure, in which the top layer adopts a quasi-hexagonal structure and the second layer retains the square array of the {100} surface. This phase is referred to as Pt{100}-hex, following Heilmann *et al.* (*4*). Adsorption of several gases, including CO, NO, and H_2, induces a reversal of this surface to the (1×1) phase, a process that plays a critical role in the catalytic reactions on this surface, including the phenomena of bistability and kinetic oscillations (*5*). Recently, the growth rate of (1×1) islands on the hex phase was found to follow a strongly nonlinear power law dependence on the CO (*6*) and H (*7*) coverages on the hex phase. The energetics of the hex and (1×1) phases of Pt{100} have recently been computed with the use of density functional theory (*8*), making this an appropriate system for experimental study.

Our methodology for determining the surface phase transition energy is as follows. The clean metastable Pt{100}-(1×1) and the stable Pt{100}-hex surfaces are prepared by the standard procedures (*9*), and the calorimetric heats of adsorption of CO and of C_2H_4 are measured on each of these surfaces, in turn, as a function of surface coverage. The term "differential heat of adsorption" refers to the heat released in an incremental adsorption following a path in which no work is performed; as in our calorimetric experiments, it is identical to the isosteric heat defined by constant-coverage pressure-temperature equilibrium (*10*). The integral heat of adsorption ΔH_{in} can then be calculated from the differential heat ΔH_{diff} by summing the coverage-differential heat product and then normalizing this result against the coverage θ

$$\Delta H_{\text{in}} = \frac{\int \Delta H_{\text{diff}} d\theta}{\int d\theta}$$

At 300 K, adsorption on the hex phase leads to rapid conversion to the (1×1) structure, such that the final state at θ_{co} = 0.5 monolayer (ML) is the same in each case. Evidence for this conclusion is provided by the loss of the hex pattern and the appearance of a c(4×2) low-energy electron diffraction (LEED) pattern (*11*). Confirmation is provided in an infrared study carried out by Martin *et al.* (*12*) in which identical bands were observed at 1869 cm^{-1} (weak) and 2088 cm^{-1} (sharp) after adsorption of 0.5 ML of CO onto both the hex and (1×1) surfaces. The differential heats of adsorption also coincided, within experimental error, at CO coverages exceeding 0.5 ML, further substantiating the conclusion that the same final state was attained. The difference between the two heats of adsorption is therefore the difference in surface energies between the (1×1) and the hex phases of the clean surface. The CO differential heats of adsorption $-\Delta H_{\text{diff}}$ are shown in Fig. 1. Because the heats are expressed per mole of CO molecules and because, for a total coverage θ_{co} = 0.5 ML, there are two surface Pt atoms (Pt_s) for each adsorbed CO molecule, the integral adsorption heats of CO are halved to represent the heat per mole of Pt_s atoms

$$\begin{aligned} \mathrm{Pt_s\{100\}\text{-}hex + CO(g)} &\rightarrow \mathrm{Pt\{100\}\text{-}(1\times1)} \\ &\quad - \mathrm{CO}(\theta_{\text{co}} = 0.5) - \Delta H_{\text{in}}^{\text{hex}} \\ &\quad = 85 \pm 2\ \mathrm{kJ\ (mol\ Pt_s)^{-1}} \end{aligned}$$

$$\begin{aligned} \mathrm{Pt_s\{100\}\text{-}(1\times1) + CO(g)} &\rightarrow \mathrm{Pt\{100\}\text{-}(1\times1)} \\ &\quad - \mathrm{CO}(\theta_{\text{co}} = 0.5) - \Delta H_{\text{in}}^{1\times1} \\ &\quad = 105 \pm 2\ \mathrm{kJ\ (mol\ Pt_s)^{-1}} \end{aligned}$$

where $-\Delta H_{\text{in}}^{\text{hex}}$ is the integral heat of adsorption on the hex phase at $\theta_{\text{CO}} = 0.5$ ML and $-\Delta H_{\text{in}}^{1\times1}$ is the integral heat of adsorption on the (1×1) phase at $\theta_{\text{CO}} = 0.5$ ML. Thus, the energy difference between the two clean surface phases is 20 ± 3 kJ (mol $Pt_s)^{-1}$. This can also be expressed as 0.43 J m^{-2} or 0.21 eV per (1×1) area.

Any adsorbate that efficiently converts the hex phase of Pt{100} to the (1×1) phase should give the same result for the surface energy difference. In Fig. 2, we show calorimetric (that is, differential) adsorption heat measurements for C_2H_4 adsorption on Pt{100} hex and (1×1) phases. As for CO adsorption, there is a significant difference at low coverages, and the heats become

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Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK.

coincident at a fractional coverage of 0.5 ML. Regardless of the state of the adlayer, which is discussed elsewhere (*13*), the difference between the integral heats on the two surfaces up to a coverage of 0.5 ML should yield the surface energy difference between the (1×1) and hex phases; in this case, we obtain 25 ± 3 kJ (mol Pt$_s$)$^{-1}$, a value within the experimental error limit of that obtained by CO adsorption.

At very low coverages of CO on Pt{100}-hex, the rate of transformation to the (1×1) phase becomes negligibly small as a result of the nonlinear growth power law, $r_g = c(\theta_{hex}^{CO})^{4.1}$ (*15*), where r_g is the rate of (1×1) island growth and c is the rate constant. Thus, at coverages $\theta_{hex}^{CO} \leq$ 0.02 ML, the growth rate is negligible and it is possible to measure the isosteric heat (*6*) or the desorption energy (*14*) for CO on the hex phase; a value of 115 kJ (mol CO)$^{-1}$ has been obtained (*15*) for the hex phase. The fact that the adsorption heat on the (1×1) phase (Fig. 1) is much larger, at −225 ± 5 kJ (mol CO)$^{-1}$, than that on the hex phase therefore represents the driving force for the adsorbate-induced lifting of the hex reconstruction, as first deduced by Thiel *et al.* (*15*). Because the activation barrier for the conversion of the clean surface from (1×1) to hex has been determined by LEED intensity measurements (*15*) as 115 kJ (mol Pt$_s$)$^{-1}$, it is now possible to construct a potential energy diagram associated with the clean surface phases and the two CO-covered surface phases (Fig. 3). The energy gained in converting Pt{100}-hex with 0.5 ML of CO to Pt{100}-(1×1) with 0.5 ML of CO is 27 kJ (mol Pt$_s$)$^{-1}$, which provides the driving force for the lifting of the reconstruction. In the calorimetric experiment, we did not measure the adsorption heat for CO on hex without the lifting of the reconstruction at low coverages because the adsorption of CO from the background after cleaning the crystal, before initiating the experiments, led to a rapid (1×1)-island growth rate upon further adsorption of CO. The background CO partial pressure was about 5 × 10^{-11} mbar, and the time taken to cool the crystal before dosing with CO was ~1800 s; we therefore estimate an uptake of θ_{CO} ~ 0.03 ML before the first calorimetric measurement was made.

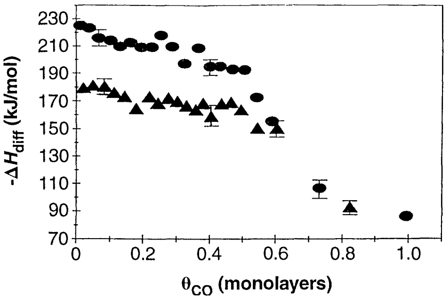

Fig. 1. The coverage-dependent differential heats of adsorption ΔH_{diff} of CO on Pt{100}-hex (triangles) and Pt{100}-(1×1) (circles) at 300 K. The heat shown was obtained as an average of seven experiments, and the error bars indicated are given by the standard deviation of these independent experiments. A coverage of θ_{CO} = 1 ML corresponds to the Pt atom density in the ideal (1×1) surface, which is 1.3 × 10^{15} cm^{-2}.

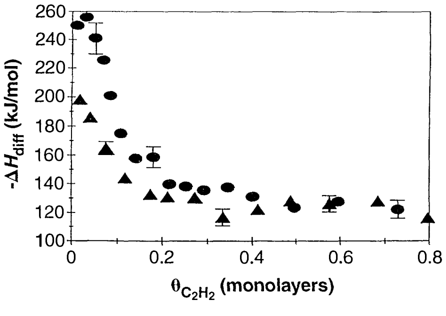

Fig. 2. The coverage-dependent differential heats of adsorption ΔH_{diff} of C_2H_4 on Pt{100}-hex (triangles) and Pt{100}-(1×1) (circles) at 300 K. The heat shown was obtained as an average of seven experiments, and the error bars indicated are given by the standard deviation of these independent experiments.

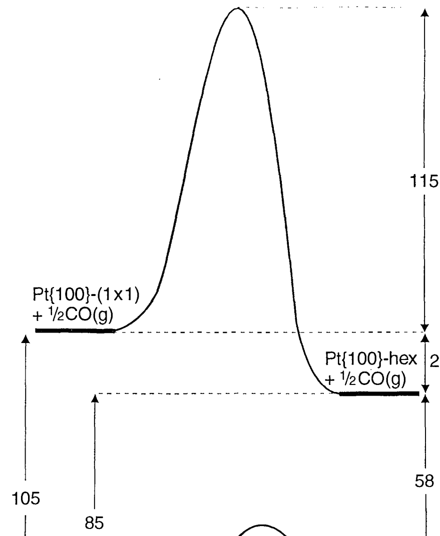

Fig. 3. Schematic energy diagram illustrating the clean hex ↔ (1×1) phase transition, with the activation energy barrier, and the adsorption of CO on both surfaces, demonstrating the reversed relative stability of the two surfaces in the presence of CO. The activation barrier between the adsorbate-covered phase has not been determined, but it is known to be low because it proceeds even at 100 K. All units are quoted in kilojoules per mole of surface platinum atoms.

There are only two points of comparison for the present data in the literature available to date. Thiel *et al.* (*15*) made an estimate of the energy difference between the two clean surface phases of Pt{100}, as 46 ± 8 kJ (mol Pt$_s$)$^{-1}$, based principally on thermal desorption experiments. Given the assumptions made in that work, we believe there is reasonable agreement with the present measurement. Recently, Fiorentini *et al.* (*8*) calculated the surface energy difference between the (1×1) and the (1×5) phases of Pt{100} as −3 ± 5 kJ (mol Pt$_s$)$^{-1}$ using density functional theory. The (1×5) phase was taken to simulate the hex phase because the large (5×20) unit mesh of the latter prohibits calculation. However, from the present study, we see that the result is not a perfect representation of the hex to (1×1) phase transition energy. Fiorentini *et al.* (*8*) have estimated the surface energy of Pt{100}-(1×1) to be 115 kJ (mol Pt$_s$)$^{-1}$. The present experiment thus indicates that formation of the clean reconstructed hex phase from the ideal (1×1) surface lowers the total surface energy by about 17%.

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