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Tuning Hydrophobicity of Platinum by Small Changes in Surface Morphology

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Stepped platinum surfaces can become hydrophobic when they are hydrogenated. Even though the Pt(533) and Pt(553) surfaces have similar geometries, the hydrophobicity on the deuterated surface is surprisingly different: on Pt(533) the surface is hydrophobic with water clustering at steps, whereas the entire surface is wet on Pt(553).

Groups of water molecules at an interface have the choice between interacting mostly with the substrate or with each other. This competition lies at the heart of a large variety of phenomena with wetting behavior of surfaces likely being the most well-known example. Contact angle studies date at least as far back as Thomas Young's work from the start of the 19th century [1]. Other important areas where such competition governs physical behavior are, e.g., protein folding and micelle formation [2].

For solid surfaces, hydrophilic vs hydrophobic behavior appears difficult to predict. A recent study of water interacting with carbon nanotubes shows that in such confined spaces small changes in temperature may cause a switch between hydrophilic and hydrophobic interaction [3]. Also, minute details of the substrate appear to be of great relevance. A single molecular layer of amorphous solid water is hydrophilic [4], whereas the same layer of crystalline ice is hydrophobic [5].

In this Letter, we show that a small change at the atomic level in substrate morphology without changing chemical identity or confinement size may also affect how water molecules adsorb to a surface. A switch from hydrophobic to hydrophilic behavior is not only apparent from drastic changes in H_2O's desorption characteristics, but also in the chemical reactivity toward H-D exchange at well-ordered platinum surfaces. Our results impact on general thinking on long-range ordering of water molecules at interfaces and pose opportunities in tailoring chemistry occurring on nanoparticles as used in, e.g., heterogeneous catalysis and electrochemistry.

As a substrate, we use single crystalline platinum discs, cut and polished to expose either the (533) or (553) surface. Schematic representations of these surfaces for top and side views are shown in Fig. 1 with every circle representing a Pt atom. The only difference between these surfaces is the step type that separates the 4-atom wide (111) terraces. The (533) surface contains the steeper (100) step type, whereas the (553) surface has the more gently sloped (110) step type. The angles that the single-atom high steps make with the terraces are, respectively, 116.6° and 125.3°. Our platinum surfaces are cleaned and studied under ultrahigh vacuum (UHV) conditions. Details

on experimental procedures can be found in the Supplemental Material [6]. Low energy electron diffraction (LEED) confirms the atomic ordering of the surface as depicted in Fig. 1.

The cleaned platinum surfaces are first exposed to D_2 by background dosing until no more dissociation occurs. To minimize contamination by H, this is done by exposing the single crystals to relatively high D_2 pressures while cooling them from ~ 500 K to ~ 150 K. We have previously studied D adsorption and desorption from these surfaces in detail [7]. Subsequently, H_2O is dosed onto the D-saturated surface at a temperature ≤ 110 K. We define 1 monolayer (ML) of H_2O as the sum of the two peaks associated with water desorption from step and terrace sites from the bare (i.e., not D precovered) surfaces in temperature programmed desorption (TPD) experiments [7–9]. Both clean Pt surfaces have been shown to be hydrophilic and both step types stabilize water adsorption relative to the (111) terrace [7,8,10].

Figure 2 shows TPD spectra of water taken at a temperature ramp of 1.0 K s^{-1} corresponding to various amounts of H_2O dosed onto the D-saturated surfaces. Panels (a) and (b) show the spectra of, respectively, H_2O and HOD desorbing from D/Pt(533), whereas panels (c) and (d) show the same for water desorbing from D/Pt(553). In the H_2O spectra, dashed lines show desorption of water from the bare Pt surfaces. Comparing the H_2O spectra for the two surfaces, we notice that the desorption traces are remarkably affected by predeuteration, but in dissimilar manners. For both surfaces, the removal of
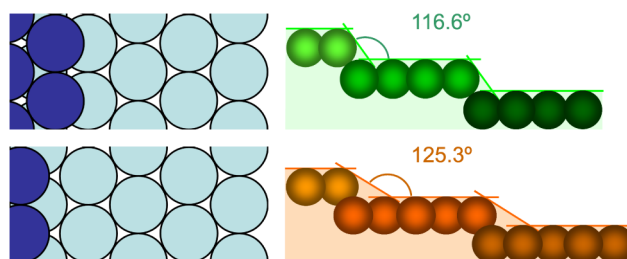

FIG. 1 (color online). Top and side views of (a) Pt(533) with (100) step type and (b) Pt(553) with (110) step type.
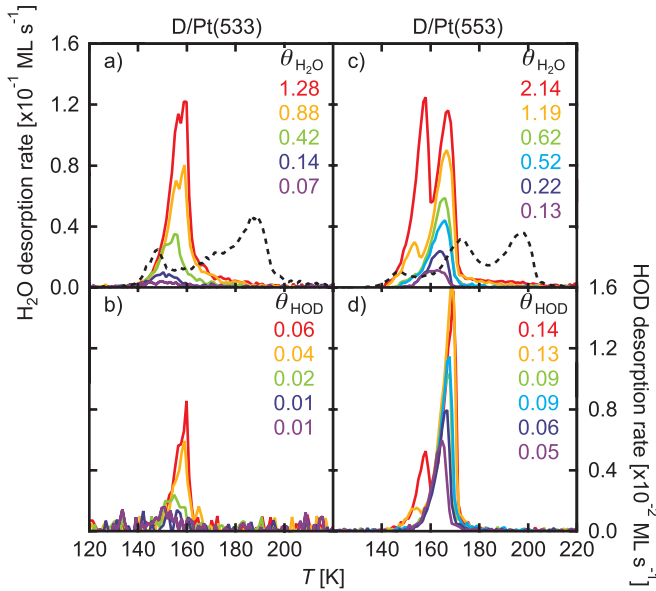
FIG. 2 (color online). TPD spectra of varying amounts of H_2O and HOD desorbing from Pt(533) and Pt(553) surfaces that have been fully precovered with D_{ad}. (a) H_2O from Pt(533), (b) HOD from Pt(533), (c) H_2O from Pt(553), and (d) HOD from Pt(553). The dashed lines in the H_2O spectra show ~1 ML H_2O desorption from the bare surfaces.

higher temperature peaks at 188 K for Pt(533) and 197 K for Pt(553) informs us that predeuteration removes the stabilizing effect that steps have on water adsorption (see Ref. [7]). This observation is in contrast to the stabilization of adsorbed water observed by predeuterating Pt(111) [11]. In fact, on both surfaces the peak temperatures are located below 171 K, indicating a destabilization compared to water adsorption on the (111) terraces [7].

Next, we compare the desorption of water from both deuterated surfaces. Multilayer water desorption is independent of the substrate [12] and starts at ~140 K [13]. This is exactly what we observe for the single desorption peak visible on D/Pt(533): from the lowest coverages onwards we observe desorption at 140 K. The peak shows typical characteristics of zero order desorption kinetics. Also, the deflection at ~158 K for $\theta_{H_2O} \geq 0.42$ ML is located at the exact temperature where crystallization from amorphous solid water (ASW) to crystalline ice is observed for 25 ML of ASW on Pt(111) [13,14]. The formation of ASW under these conditions was also concluded from the Reflection Absorption Infrared Spectra we published earlier for this system [9]. The desorption temperature of this peak and the presence of the deflection due to crystallization show that water forms a multilayered structure at submonolayer coverages on D/Pt(533). This surface is therefore clearly hydrophobic. Desorption studies on the 6-atom wide D-saturated Pt(755) surface show identical behavior, indicating that terrace length does not influence hydrophobicity for small terraces separated by (100) steps (see Supplemental Material [6]).

In contrast to the single peak observed on D/Pt(533), we clearly observe two peaks for water desorption from D/Pt(553) [Fig. 2(c)]. The peak at 151 K again shows characteristics of zero order desorption kinetics and is located at the same temperature at which water multilayer desorption from bare Pt(553) starts [7]. Therefore, we ascribe this peak to water multilayer desorption. The other peak at ~162 K strongly resembles desorption from the bare hydrophilic surface, although it appears at a slightly lowered peak temperature. The size of this feature in comparison to that of 1 ML H_2O desorbing from the bare Pt(553) surface suggests that almost the entire D/Pt(553) surface was covered by H_2O. Therefore, D/Pt(553) seems to be hydrophilic and the first wetting layer is almost completed prior to formation of the multilayer. We shall return to this point in the discussion of the H-D isotope exchange.

The different interactions between water and these two surfaces are also reflected in the isotope exchange between H_2O and D. In the HOD signal [Figs. 2(b) and 2(d)], we observe the same structures as for the H_2O spectra: a single peak for D/Pt(533) located at the temperature where water multilayers desorb and a two-peak structure for D/Pt(553) indicating two distinguishable water layers of which the first one is nearly completed before the second grows in. Interestingly, we note that on Pt(553), relatively little HOD desorbs in the multilayer peak compared to the H_2O spectra. Although the initial exchange between H and D atoms to form HOD must obviously take place at the interface, little H-D exchange takes place between the first and subsequent water layers.

The more striking effect however, is the absolute amount of H-D exchange on the two surfaces, especially for low water coverages: ~27% on Pt(553) vs only ~8% on Pt(533). If the suggested difference in hydrophobic vs hydrophilic character is correct, it provides a straight forward explanation: compared to the more hydrophilic D/Pt(553) surface, far less water is in direct contact with the hydrophobic D/Pt(533) surface. However, beyond this simple geometric argument, we also note that the spectrum of bond strengths for D on Pt(553) reaches lower values than on Pt(533) [7]. Weaker D-Pt bonds may assist in reaching the $H_2O + D \leftrightharpoons HOD + H$ equilibrium more rapidly.

The HD and D_2 desorption traces from the same experiments will identify the location of the "droplets" on the hydrophobic D/Pt(533) surface and will confirm the formation of a completed "sheet" of water on, and therefore the hydrophilicity of, D/Pt(553). In Fig. 3, we show these desorption traces for Pt(533) [panel (a)] and Pt(553) [(panel (b)]. The β_1 and β_2 peaks on Pt(533) are associated with the recombinative desorption from, respectively, step and terrace sites, whereas on Pt(553) the γ_1 and γ_2 peaks are associated with desorption from terrace sites and γ_3 is associated with desorption from step sites [7]. As
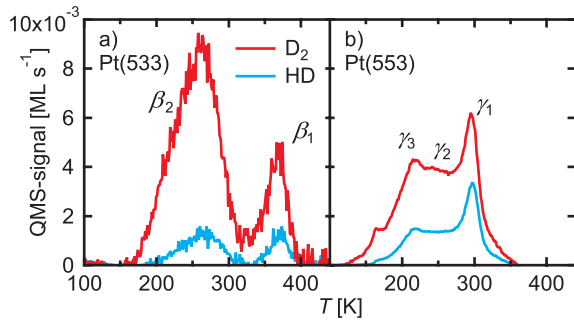
FIG. 3 (color online).   TPD spectra of HD and D_2 desorbing from a Pt(533) surface (a) or Pt(553) surface (b) that has been fully precovered with D_{ad} prior to the adsorption of ~1 ML H_2O.

mentioned, these spectra qualitatively indicate that hydrogen binds weakly to (110) step sites in comparison to (100) steps. A more quantitative comparison of these spectra indicate that on D/Pt(533) a clear bias exists for H-D exchange in the β_1 peak, i.e., at step sites. We have concluded that on this hydrophobic surface, water "droplets" must therefore be located mostly at steps [9].

For Pt(553), we do not observe such a pronounced bias in Fig. 3. Very little difference in the relative peak heights between the HD and D_2 spectra exist and a simple scaling factor turns one spectrum nearly exactly into the other. Only the γ_3 peak is slightly smaller in the HD spectra compared to the D_2 spectra. Therefore, if a bias exists, it is towards exchange on the D/Pt(553) terrace sites and H_2O must have been present at terrace sites at $\theta_{H_2O} \approx 1$ ML.

Figure 4 shows the sum of the HD and D_2 TPD spectra from Pt(553) for various water coverages. We compare
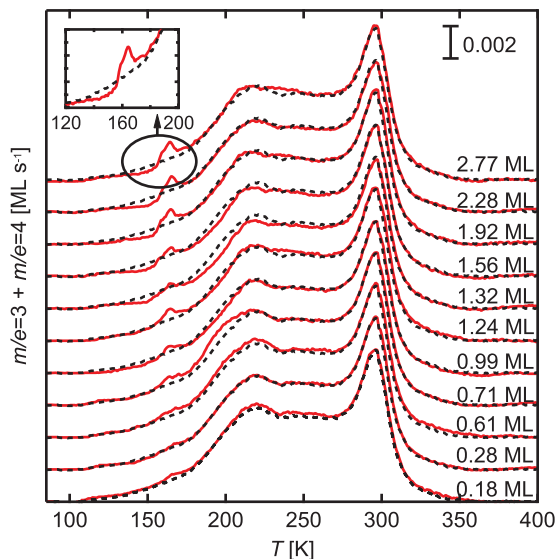

FIG. 4 (color online).   TPD spectra of HD and D_2 desorbing from a Pt(553) surface that has been fully precovered with D_{ad} after which varying amounts of H_2O were dosed on the surface. The dashed lines show 1 ML D_{ad} desorbing from bare Pt(553).

every trace to D_2 desorbing from bare Pt(553) (dashed lines). The coadsorption TPD spectra are very similar to those on bare Pt(553). The inset in Fig. 4 shows that for the highest θ_{H_2O}, the only difference is a minor but significant delay in deuterium desorption from the H_2O post-covered surface followed by a small additional peak at 163 K. At higher temperatures, the spectra are identical within our margin of error. The onset of deuterium desorption in the inset coincides with the start of water desorption in the high temperature peak in the corresponding water TPD spectra of Fig. 2. This behavior is reminiscent of the "molecular volcano" observed for ASW adsorbed on top of CCl_4 on Au(111), where CCl_4 desorption is blocked by the ASW overlayer and occurs abruptly when cracks are formed in the overlayer when the ASW crystalizes [15]. We explain our observation as follows: once the water from our overlayer starts to desorb, the underlying D_{ad} can associatively desorb, causing a temporarily higher D_2 desorption rate compared to the bare surface. The formation or desorption of D_2 is inhibited by (less than) a single monolayer of water.

For $\theta_{H_2O} \lesssim 1.92$ ML the additional peak at 163 K becomes less pronounced and shifts to higher temperatures with decreasing water coverage, following the zero order desorption kinetics of the corresponding H_2O spectra. However, the additional peak remains visible for the lowest H_2O coverages. This implies that at low coverages H_2O is preferentially adsorbed at the sites associated with D_2 desorption in γ_3, which are (110) step sites. Since we also concluded that at 1 ML H_2O is present at terraces and the peak at 162 K is of a size of ~1 ML, H_2O must be present across the entire Pt(553) surface. The H_2O overlayer appears to grow from the steps onto the terraces, ultimately forming a complete single layer "'sheet" of water. On the Pt(533) surface, water initially wets (part of) the step sites, but then grows three-dimensional clusters without wetting the terraces fully [9]. As mentioned, the formation of these three-dimensional clusters is in agreement with our earlier RAIRS measurements [9]. We also note that we have performed LEED studies on H_2O and $H_2O + D$ coadsorbed systems. LEED images unfortunately yield no information as they show no more than the split-spot patterns characteristic of the Pt substrates published previously [9].

In providing clues for a plausible interpretation of this unanticipated difference in hydrophilicity of deuterated Pt(533) and Pt(553), let us outline the main geometrical and energetic differences between these two surfaces, in the absence and presence of deuteration, realizing that ultimately also geometrical differences must impact on the energetics of water adsorption to explain the differences in hydrophilicity.

As the main difference between the two surfaces is the step geometry, it seems likely that the structure of water at step edges is different. For water adsorbing on undeuterated

Pt, STM studies have shown that on (100) step edges, water initially forms one-dimensional chains along the steps, whereas for (110) steps these are not clearly adsorbed [16]. On deuterium-covered Pt, the interaction of water with such surfaces will be driven by the (in)ability of water to form relatively stable two-dimensional hydrogen-bonded networks extending onto the terraces, versus the tendency of water to be structured into solvation shells of the adsorbed deuterium. We note that from density-functional theory (DFT) calculations, the interaction of water layers with Pt(111), i.e., the water-Pt bonding, is known to be very weak and its stability on such surfaces is mainly determined by the two-dimensional hydrogen bonding network [16]. Therefore, we expect that the fact that adsorbed deuterium inhibits the direct interaction of water with the platinum surface atoms, will have only a minor effect on its stability. Apparently, hydrogen in a (110) step edge on platinum causes a corrugative smoothening in terms of water adsorption, whereas hydrogen in a (100) step edge leads to an enhanced corrugation causing localized growth of water ''droplets'' near or at the step sites. Perhaps this could be related to the steepness of the step site (see Fig. 1), but we would like to point out another difference in the properties on these two surfaces related to their interaction with atomic hydrogen in the absence of water. The preferred binding site of hydrogen and deuterium at the (100) step site appears to be the bridge site between two Pt atoms along the step (i.e., the two dark blue step atoms in the top panel of Fig. 1), according to DFT calculations of the similar Pt(211) surface [17]. The same step-bridge site has been computed to be the preferred binding site on Pt(331), a stepped surface with a (110)-type step, but with the interesting difference that the binding energy difference between step-bound hydrogen and terrace-bound hydrogen is larger for the (100)-type step than for the (110)-type step [18]. In fact, according to the DFT calculations, the H binding energy surface on Pt(331) with a (110)-type step is almost flat, whereas H clearly prefers the step site on Pt(211) with a (100) step [18]. This agrees qualitatively well with our UHV experiments that show deuterium binds stronger to (100) step sites in Pt(533) than to (110) step sites in Pt(553), even to the extent that we concluded from TPD experiments that on Pt(553) terraces are preferred binding sites for deuterium compared to step sites [7]. If the more strongly bound hydrogen somehow acts as an anchoring point for water molecules, than this could relate to the induced corrugation of Pt(533) in the presence of adsorbed hydrogen.

Although at this moment we can really only speculate about the exact molecular origin of the observed differences in wetting of deuterium-covered Pt(553) and Pt(533), our results impact on the molecular thinking of interfacial water. The experiments discussed herein show that small changes in the atomic-level structure of edges and steps may have a dramatic effect on how water organizes around such surface perturbations, leading to either two-dimensional wetting or three-dimensional cluster growth. This may influence the chemical reactivity of such interfaces, as clearly demonstrated by the delay in D_2 associative desorption from Pt(553) when the surface is (partially) covered by a wetting layer of water, whereas no such phenomenon is observed on Pt(533). In a related though admittedly more remote setting, these effects may affect the reactivity of platinum under aqueous electrochemical conditions, since step sites often feature as the active sites for many catalytic reactions, as for instance taking place in fuel cells [19].

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