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Water on well-defined platinum surfaces : an ultra high vacuum and electrochemical study

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Истина приобретается, как зопото,
не тем, что оно приращается, а тем,
что отмывается от него все то, что не
зопото.

Лев Николаевич Толстой
(1903), Дневник

7

Tuning hydrophobicity of platinum by small changes in substrate morphology

Abstract *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).*

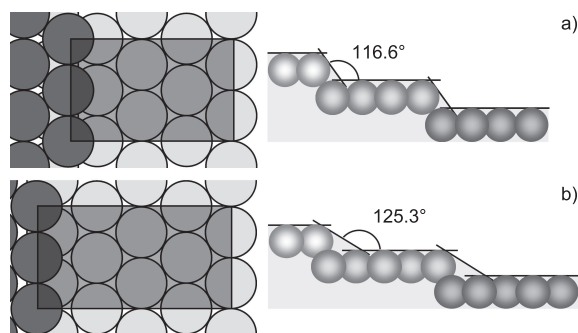


Figure 7.1 Top and side views of a) Pt(533) and b) Pt(553)

Water molecules at an interface find themselves torn between interacting mostly with other water molecules or with the substrate. This competition lies at the origin of, *e.g.*, wetting behavior, micelle formation, and protein folding.¹⁴² The resulting hydrophobicity or hydrophilicity is often determined by the material properties of the substrate^{143,144} In addition, the space available for water may affect its physical behavior. Confinement to very small spaces, such as carbon nanotubes, has been shown to affect physical behavior and may result in hydrophobic interactions.¹⁴⁵ In this chapter, we show that apparently small changes to substrate morphology at an atomic level without changing its chemical identity or confinement size may determine how water molecules adsorb to that surface. This is apparent from drastic changes in both water's physical and chemical response. Our results impact on general thinking about long-range ordering of water molecules at interfaces and poses opportunities for tailoring chemistry occurring on nanoparticles as used in 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 figure 7.1 with every circle representing a Pt atom. The unit cell characterizing these surfaces is emphasized by the red rectangle in the top view. 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 angle that the single-atom high steps make with the terraces is, 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 chapter 2. Low energy electron diffraction (LEED) confirms the atomic ordering of the surface as depicted in figure 7.1.

The cleaned platinum surfaces are first exposed to D₂ by background dosing until no more dissociation occurs. To minimize contamination by H, this is done

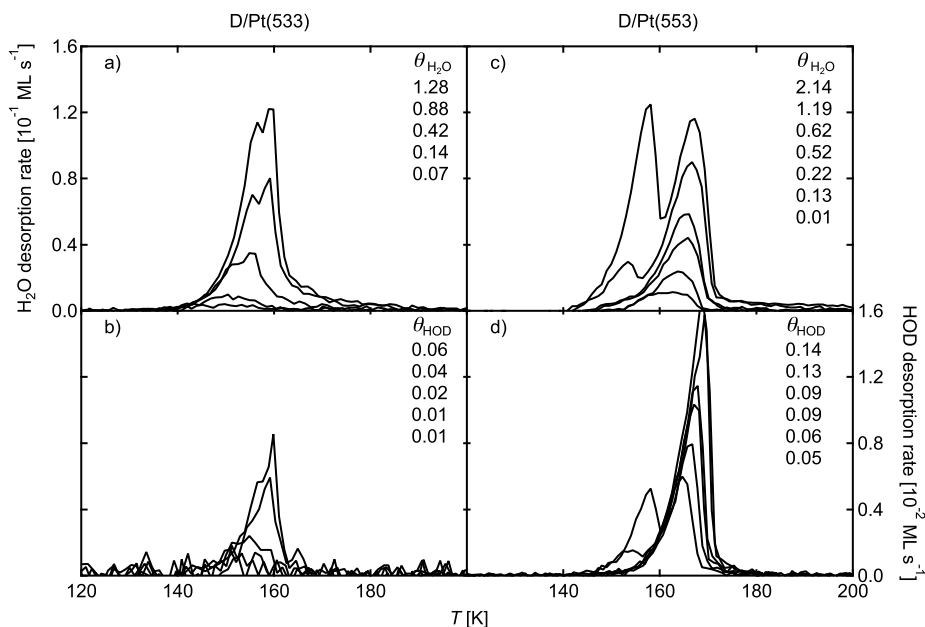


Figure 7.2 TPD spectra of varying amounts of H_2O and HOD desorbing from $\text{Pt}(533)$ and $\text{Pt}(553)$ surfaces that have been fully pre-covered with D_{ad} . a) H_2O from $\text{Pt}(533)$, b) HOD from $\text{Pt}(533)$, c) H_2O from $\text{Pt}(553)$, and d) HOD from $\text{Pt}(553)$.

by exposing the single crystals to relatively high D_2 pressures while cooling them from ~ 500 K to ~ 150 K. We have studied D adsorption and desorption from these surfaces in detail in chapter 3. 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 pre-covered) surfaces in temperature programmed desorption (TPD) experiments.²⁷ The clean surfaces have been shown to be hydrophilic and both step types stabilize water adsorption relative to the (111) terrace (chapter 3).^{26,27}

Figure 7.2 shows TPD spectra of water taken at a temperature ramp of 1.0 K/s 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 $\text{D}/\text{Pt}(533)$, whereas panels c and d show the same for water desorbing from $\text{D}/\text{Pt}(553)$. Comparing the H_2O spectra for the two surfaces, we notice that the desorption traces are remarkably different. The absence of peaks at 188 K for $\text{Pt}(533)$ and 197 K for $\text{Pt}(553)$ informs us that pre-deuteration removes the stabilizing effect that steps have on water adsorption (see chapter 3). For both surfaces we do not observe the stabilization of water observed by pre-deuterating $\text{Pt}(111)$.⁹⁰ In fact, on both surfaces the peak temperatures are located below 171 K, indicating a destabi-

lization compared to water adsorption on the (111) terraces.

Multilayer water desorption is independent of substrate¹⁴⁶ and starts at 140 K.²⁴ This is exactly what we observe for the only peak visible on D/Pt(533): from the lowest coverages onwards we already observe desorption at 140 K, growing in as a zero order desorption peak. The deflection at ~ 158 K for $\theta_{\text{H}_2\text{O}} \geq 0.42$ ML is located at the exact same temperature as where the crystallization from amorphous solid water (ASW) to crystalline ice is observed for 25 bilayers of ASW on Pt(111).^{21,24} The desorption temperature of this peak and the visibility of the deflection suggest that water forms multilayers at sub-monolayer coverages on D/Pt(533), implying a hydrophobic surface. We find the exact same behavior on the 6-atom wide Pt(755) surface, indicating that for small terrace widths terrace length does not influence hydrophobicity.

In contrast to the one peak observed on D/Pt(533), we observe a clear two peak structure on D/Pt(553) (figure 7.2c). The peak at 151 K shows zero order desorption kinetics and is located at the same temperature at which water multilayer desorption from bare Pt(553) starts (chapter 3). Therefore, we ascribe this peak to water multilayer desorption. We ascribe the other peak at ~ 162 K to desorption of water still or also interacting with D/Pt(553), indicating that the hydrophobicity is not as pronounced as on D/Pt(533).

Next, we focus on the HOD signal (figure 7.2b and d). Here, we observe similar structures as for the H₂O spectra: only one peak for D/Pt(533) and a two peak structure for D/Pt(553). On Pt(553), relatively little water desorbs in the multilayer peak for the HOD spectra compared to the H₂O spectra. The exchange between H and D atoms to form HOD mainly takes place directly at the Pt(553) surface, but not between water layers on this surface. The water mobility between the first and second layer is limited, indicating that the coupling between them is poor. This is in stark contrast to the good coupling observed for a (partially) deuterated Pt(533) surface (chapter 8).

The most striking effect however, is the amount of H/D exchange on the two surfaces, especially for low water coverages: $\sim 27\%$ on Pt(553) vs. only $\sim 8\%$ on Pt(533). The exchange is significantly less on the Pt(533) surface. For higher coverages this effect is masked by the poor coupling to the multilayer on Pt(553). This is explained straight forwardly by the morphology of the water overlayer: on the hydrophobic D/Pt(533) surface far less water is in direct contact with the surface, in contrast to the more hydrophilic D/Pt(553) surface.

The HD and D₂ desorption traces from the same experiments identify the location of the 'droplets' on D/Pt(533) and confirm the formation of a completed 'sheet' of water on D/Pt(553). In figure 7.3, 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. Surprisingly enough, these TPD experiments suggest that on Pt(553) hydrogen binds

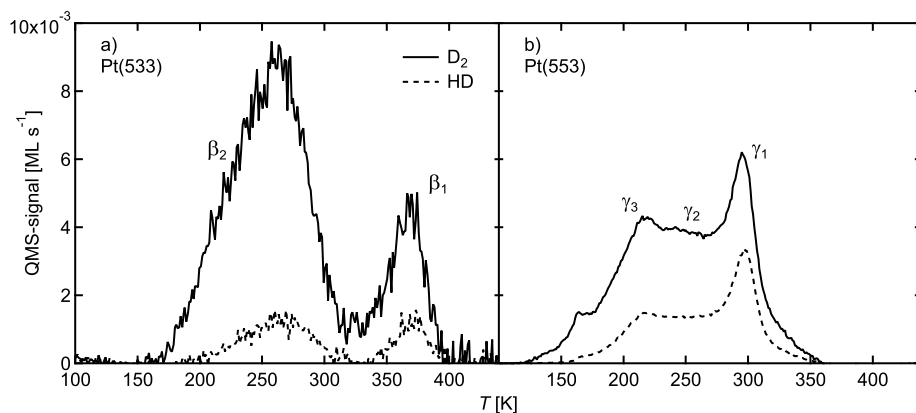


Figure 7.3 TPD spectra of HD and D₂ desorbing from a Pt(533) surface a) or Pt(553) surface b) that has been fully pre-covered with D_{ad} prior to the adsorption of ~ 1 ML H₂O.

stronger to terrace than (110) step sites. The γ_1 and γ_2 peaks are associated with desorption from terrace sites, whereas γ_3 is associated with desorption from step sites (see chapter 3). On D/Pt(533) the deuterium spectra show a clear bias towards exchange in the β_1 peak, *i.e.* at step sites. Therefore, the water ‘droplets’ are likely located there. We do not observe such a pronounced effect on Pt(553), where we observe little difference in the relative peak heights between the HD and D₂ spectra other than a scaling factor. The γ_3 peak is slightly smaller in the HD spectra compared to the D₂ spectra. If a bias exists, it is towards exchange on the D/Pt(553) terrace sites. This could imply that water is primarily adsorbed at terraces on D/Pt(553), but in the next paragraph we will argue that water is also present at step sites from the lowest coverages onwards.

Figure 7.4 shows the sum of the HD and D₂ TPD spectra from Pt(553) for various water coverages. We compare these to D₂ desorbing from bare Pt(553) (dashed lines). The co-adsorption TPD spectra are very similar to those on bare Pt(553). If we look at the spectra with the highest $\theta_{\text{H}_2\text{O}}$, the only significant difference between the spectra is that deuterium desorption from the H₂O post-covered surface starts a little later and subsequently gives a small additional peak at 163 K. At higher temperatures, the spectra are identical within our margin of error. The onset of deuterium desorption coincides with the start of water desorption in the high temperature peak in the corresponding water TPD spectra. This behavior is reminiscent of the ‘molecular volcano’ observed for water adsorbed on top of CCl₄ on Au(111), where CCl₄ desorption is blocked by the water overlayer and occurs abruptly when holes are formed in the overlayer by water desorption.¹⁴⁷ We also observe a delay in the onset of deuterium desorption, indicating that the water overlayer blocks

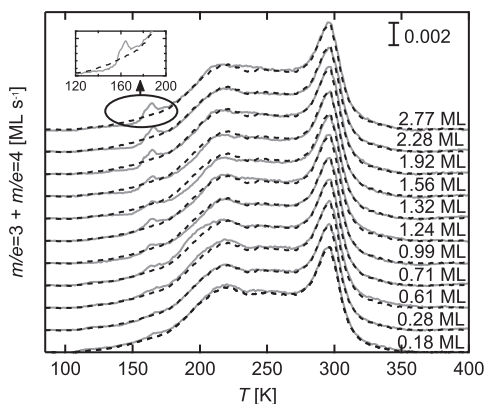


Figure 7.4 TPD spectra of HD and D₂ desorbing from a Pt(553) surface that has been fully pre-covered with D_{ad} after which varying amounts of H₂O were dosed on the surface. The dashed lines show 1 ML D_{ad} desorbing from bare Pt(553).

deuterium desorption. Once the water from this overlayer starts to desorb, the underlying D_{ad} can desorb as well, causing a temporarily higher D₂ desorption rate compared to the bare surface.

For $\theta_{\text{H}_2\text{O}} \leq 1.92$ 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 H₂O spectra. The additional peak remains visible for the lowest water coverages, implying that at low water coverages H₂O has to be adsorbed at the sites associated with γ_3 , which are (110) step sites. Since we concluded from figure 7.3 that H₂O must be present at terrace sites and from figure 7.4 that it is also located at step sites at low coverage, we conclude that H₂O has no preferential adsorption site on D/Pt(553) and wets the entire surface, forming a complete ‘sheet’ of water. This is in stark contrast to the similar Pt(533) surface where pre-adsorption of D induces hydrophobicity (see chapter 8).

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). One difference between the two hydrogenated surfaces is the ‘anomalous’ H-adsorption behavior on Pt(553), *i.e.* H binds stronger to terrace than defect sites (see chapter 3). Perhaps the weaker bound H_{step} on Pt(553) influences the adsorption energies less than the stronger bound H_{step} on Pt(533). However, a more intuitive origin of the effect might be found in the more slanting nature of the Pt(553) surface compared to the Pt(533) surface, which could make it possible for hydrogen bonded networks to form over the (110) steps, whereas the steeper surface angle on Pt(533) results in a discontinuity in the hydrogen bonded network.

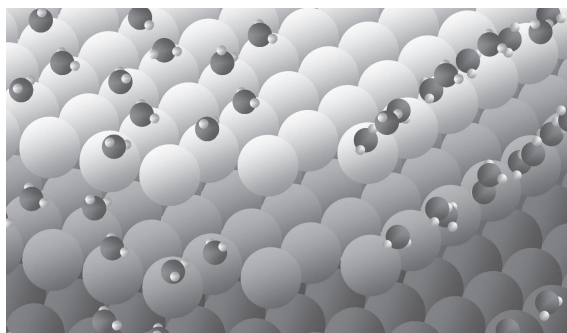


Figure 7.5 Schematic representation of the transition from (100) to (110) steps on a nanoparticle and the proposed morphology of the water on a hydrogenated particle. Pre-adsorbed hydrogen/deuterium atoms are not shown for clarity.

Macroscopic roughening has been shown to induce macroscopic hydrophobicity at the leaves of a lotus plant.¹⁴⁸ The same principle is applied for self-cleaning materials.¹⁴⁹

The difference in morphology and, consequently, reactivity we observe for the two surfaces may have large implications for catalysis, when we extrapolate this to actual catalyst nanoparticles. On nanoparticles both the (100) and (110) step geometries are present, often next to one another. Figure 7.5 gives a schematic representation of the transition on such a nanoparticle, as well as the proposed morphology of the water overlayer on a hydrogenated platinum nanoparticle. Parts of the nanoparticle are hydrophobic, whereas other parts are not. This actually causes some parts to be much more active in hydrogenation reactions than other parts. This is not induced by the morphology of the terraces, but by the geometry of the transition between these terraces. Currently, when ‘designing’ nanoparticles the total amount of (111), (100), or (110) sites is usually determined and taken as a ‘guide’ for the activity. When it comes to hydrophobicity, however, it might turn out that the total amount of sites is less important than the transitions between those sites.

