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Vacancy dynamics on CO-covered Pt(111) electrodes

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Supporting Information

Experimental Section

The experiments were performed at controlled potential at room temperature (≈298 K), using a homebuilt video-STM for in situ measurements in electrochemical environment.[1] The video sequences were obtained in the ''constant height'' mode, which enables fast measurements. Because the image contrast in this mode results from local variations in the tunneling current, which has a strongly non-linear current–distance characteristic, the atomic lattices is much better resolved in those areas where the tip is closer to the sample. In areas with large tip–sample distances, e.g. at the bottom terrace near a step, the contrast may be completely lost. Although the instrument allows image acquisition rates up to 30 images per second, usually lower rates were used for higher stability and lower distortions of the images. All images presented in this work were obtained from videos of 1–3 min duration recorded at a rate of 10 images per second (For better visualization of the vacancies, only a part of the actually recorded images is shown).

STM tips were etched from tungsten wire and covered with polypropylene (PP), leaving only the very end of the tip exposed. That way, the faradaic currents at the tip can be reduced to an extent that they are much lower than the tunneling currents.

Prior to the measurements, the Pt(111) electrode (Mateck) was annealed in an induction oven for 30 min at ≈1000°C in Ar containing 2% CO (a slightly reducing atmosphere to prevent surface oxidation) and then cooled down to room temperature in the same atmosphere. The use of adsorbing gas (CO) as cooling gas has been shown to increase the surface mobility, which helps in healing surface defects on Pt(111).[2] The electrode was subsequently brought into contact with ultrapure water to avoid contamination, and then transferred into the electrochemical cell. In the experiments an Ag/AgCl (KCl sat.) reference electrode was used and an initial potential of -0.15 V was applied to the sample. Tip and sample potentials were independently kept under potentiostatic control, and a constant bias of 50 to 200 mV was used. 0.1 M H_2SO_4 saturated with CO was used as electrolyte solution, prepared from ultrapure H_2SO_4 (Merck) and ultrapure water.

Supplementary STM data

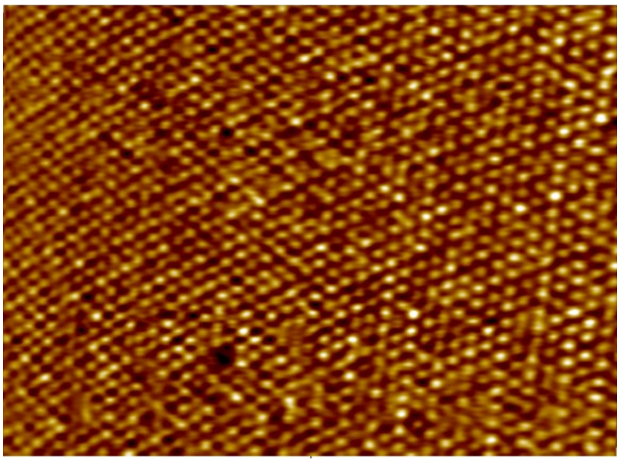

Figure 1S. *In situ* video STM image of Pt(111) in CO-saturated 0.1 M H2SO4 solution at 0.3 V, showing a larger surface area of the apparent (1x1)-CO adlayer (12 × 8.3 nm^2) with one Pt(111) surface vacancy (bottom, center).

Identification of the defects as surface vacancies

In the following, we justify in more detail the assignment of the observed mobile point defects to surface vacancies and, specifically, discuss why those cannot be explained by surface contaminations. We first recall the requirements for such a hypothetical contamination species. According to our STM data, such a species would need to a) be strongly chemisorbed in order to not be replaced from the surface by the high coverage CO adlayer, b) reside on the atop sites of the Pt surface layer, c) be sufficiently small to enable CO adsorption on a neighboring Pt atom (i.e. at 0.277 nm distance) and d) would need to be adsorbed from solution, as these species are only found on the surface upon increasing the potential into the regime of the apparent (1 x 1)-CO phase (i.e. above 0.2 V). These restrictions rule out all organic contaminations and most molecular species as well as metal cations, which would desorb rather than adsorb upon an increase in potential. Small anions, such as halides, can be excluded because they typically occupy hollow sites on metal surfaces and already have too large steric demands. Theoretically possible could be small linearly adsorbed molecules, such as cyanide or thiocyanide, but contamination of the ultrapure sulfuric acid solution by those can be safely excluded. Furthermore, this hypothetical species would have to appear lower than the CO adsorbates in the STM images. Taking into account that even strongly electronegative adsorbate such as oxygen atoms exhibit a larger apparent height than adsorbed CO,[3] very few adsorbates at all could account for our observations. Thus, we can safely rule out that the defects correspond to adsorbed contaminants. In contrast, surface vacancies in the top Pt layer easily can account for all of the above observations.

References

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