

Site-selective adsorption and influence of subsurface atoms : an STM and X-ray study of Pt₉₀Co₁₀(110)-(1x3)

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ABSTRACT

Scanning tunneling microscopy was used to study the clean and CO covered Pt₉₀Co₁₀(110)-(1x3) surface. The clean sample reconstructs with a (1x3) missing row (MR) arrangement forming alternating ridges and valleys [1], in the manner of Pt(110) and of similar Pt-metal alloys [2-3]. While LEED and LEIS [1] reveal that the atoms exposed to vacuum in the ridges and the slopes are almost exclusively Pt, STM images reveal the presence of two different sites (Fig. 1, top left): they cannot be explained but by a mixed Pt-Co composition in the buried row of the third layer (36% Pt from LEED calculations). First-layer Pt atoms residing on Pt in layer 3 appear higher than those sitting on Co as already found for Pt₈₀Fe₂₀(111) [4]. The corrugation difference results from 1/ the large difference (10%) in the atomic radii and possibly 2/ from ligand effects.

Comparison of STM images of the same area upon adsorption shows that, at low dose, CO adsorbs exclusively on the Pt/Pt sites and never on Pt/Co ones (Fig. 2, 3). Saturation of these sites occurs around 0.3 L. The one to one correspondence between the CO positions and that of Pt/Pt sites lets room for only one possibility: the molecules reside, upright, on top of these latter sites.

At higher exposure, CO also adsorbs on the Pt/Co sites, still upright, in on top position up to ~3 L (Fig. 3a). Saturation of the surface occurs around 4 L with a marked change in the adsorption mode (Fig. 3b). The coverage in the Pt/Co zones becomes twice as large, with CO sitting on top of every Pt/Co sites, but with nearest-neighbours tilted, in opposite directions, by about 20 degrees off normal: the molecules are now arranged in a zigzag fashion due to CO-CO repulsion as observed on pure Pt(110) [5]. Note that a few holes, created by atom mobility from the ridge to the troughs, have appeared on the (1x3) terraces (Fig. 2).

There are several remarkable differences with CO adsorption on Pt(110). i/ On the alloy, CO molecules are visible at very low coverages ($\theta_{CO} \leq 0.07$ L) in contrast to pure Pt where they appear at $\theta_{CO} = 1$ only [5-6]. ii/ up to saturation there is no structural change in the alloy whereas deconstruction of the surface starts at ~1 L on Pt(110). iv/ finally, and this is the main change, the (1x3) ridge and valley structures is mainly preserved in the present case whereas massive deconstruction towards a rough (1x1) occurs, at room temperature, on Pt(110) [7-8].

Recent grazing x-ray measurements confirm this particular resistance of the alloy to deconstruction: while a gas dose of 1 L yields only little changes in the structure factors with respect to those of the clean surface, changes certainly associated with moderate changes in surface atom positions due to CO binding, the (1x3) reconstruction remains unchanged from up to 500 L (highest dose used) at room temperature [9]. This has important consequences with respect to catalytic properties. Indeed, in the case of Pt(110), the deconstruction strongly changes the morphology and the distribution of active sites – which means modifying markedly the activity as a function of the gas dose [5]- as opposed to the more stable behaviour of the present alloy.

Ab initio calculations allow to clearly disentangle the contributions of ligand effects due to the presence of Pt and Co in layer 3 and of simple geometrical effects due to different heights. They also confirm that adsorption on top of Pt/Pt is always more favourable than any other configuration – bridge or on top of Pt/Co. (cf. the oral presentation of M. Schmid).

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