

## WHEN LANGMUIR IS TOO SIMPLE: H<sub>2</sub> DISSOCIATION ON Pd(111) AT HIGH COVERAGE

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Under operating conditions, heterogeneously catalyzed chemical reactions take place on surfaces with dense layers of adsorbates. In order to adsorb on such a surface the reactant molecules must find empty surface sites (active sites) created either by one missing adsorbate (vacancy) or by aggregates (ensembles) of vacancies. In the case of H<sub>2</sub> dissociation on Pd - a process of interest in many industrial reactions, including hydrogenation and fuel cell technologies - a recent Scanning Tunnelling Microscopy (STM) study<sup>1</sup> has revealed that the classically assumed mechanism where diatomic molecules require ensembles of two empty sites is too simplistic. Indeed, Mitsui et al.<sup>1,2</sup> have found that near saturation coverage the sites for the facile molecular dissociation on Pd(111) require ensembles of three or more H-free nearest neighbours fcc sites. Holloway<sup>3</sup> has suggested that such an unexpected result could be due to chemical self-poisoning of the surface originated by adsorbed hydrogen, further hindering the activity by increasing the dissociation barrier. An alternative mechanism involves the suppression of energy dissipation channels of the exothermic dissociation reaction<sup>iError! Marcador no definido.</sup>. This in turn could be due to: a) modification of the *d*-band occupation by adsorbed H that would alter the rate of electron-hole pair generation or b) by surface stiffening, which would reduce phonon excitations. Clearly, the structure and electronic properties of the hydrogen-free ensembles and their effect on the molecular dissociation are fundamental questions that have not been addressed until now.

To gain a fundamental understanding of the chemical properties of ensembles of vacancies we carried out Density Functional Theory (DFT) calculations. Various configurations of non-interacting vacancies on a  $p(3 \times 3)$  Pd(111) surface are modelled. Hydrogen was adsorbed on one side of the slab with correction for the resulting dipole moment in the vacuum region. The following systems were employed: a) fully H-covered surface; b) surface with separated 1 H-free site (1V), equivalent to 0.11 ML of vacancies; c) surface with 0.22 ML of vacancies forming di-vacancies (2V); and d) 0.33 ML of vacancies forming a contiguous trimer (3V). The lifetime of 3V or 2V aggregates is of the order of seconds to minutes in the temperature range investigated, large enough compared to the time scale for hydrogen interacting with the potential well, ( $\sim 1 \mu\text{s}$ ).<sup>iError! Marcador no definido.</sup>

The present first principles calculations provide a theoretical understanding of the observation that H<sub>2</sub> dissociation on Pd(111) requires ensembles of at least three empty adjacent fcc sites. The dissociation site involves not only two empty fcc sites as proposed in the Langmuir model, but three empty fcc sites in a special configuration where a Pd atom exists that is not directly bound to any adsorbed H atom. H<sub>2</sub> impinging on Pd atoms already bound to H encounter a higher barrier for dissociation due to chemical poisoning. Such results are in agreement with the predictions from the *d*-band model. Our results demonstrate also that the concept of "active site" should be refined since these can be ensembles of sites larger and more complex in structure than usually assumed.

### References:

[1] T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree and M. Salmeron, *Nature*, **422** (2003) 705

[2] T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree and M. Salmeron, *Surf. Sci.* **540** (2003) 705

[3] S. Holloway, *Surf. Sci.* **540** (2003) 1