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Ab initio simulation of the interaction of hydrogen with the {111} surfaces of platinum, palladium and nickel. A possible explanation for their difference in hydrogenation activity

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Density functional theory calculations have been performed on Pt, Pd and Ni {111} surfaces showing a considerable difference in adsorption energies for different sites on Pd and Ni while Pt shows an almost uniform adsorption energy which may be linked to the difference in activity of the these metals for hydrogenation.

Platinum, palladium and nickel, despite their close structural relationship and their proximity in the periodic table, show several significant differences in their chemistry. For example, for a given olefin the ease of hydrogenation over metal catalysts decreases in the order Pd > Rh > Pt > Ni >> Ru.[1] Under low hydrogen pressure conditions olefin isomerisation can also occur. Pt shows little isomerisation activity while Pd (together with Ni) promotes double bond migration *via* the formation of π-allyl intermediates. The degree of isomerisation over metal catalysts tends to decrease in the following order: Pd > Ni > Rh > Ru > Os ≅ Pt .[2,3] From this data it is clear that there are significant differences in the interaction of olefins and/or hydrogen with the metal surfaces. In this study we focus on one aspect of these differences, the interaction of hydrogen.

Molecular hydrogen adsorbs dissociatively on most transition metal surfaces with heats of chemisorption of between 30 and 60 kJ mol^{-1} (per H atom). Owing to its small size it can enter a metal surface fairly deeply leading to strong perturbations of the electronic structure. In most cases, including Pt and Ni, this only results in a relaxation of the first few atomic layers. However, some metals, including Pd, undergo a surface reconstruction which can lead to bulk absorption and the formation of PdH. The presence of sub-surface hydrogen in Pd has been illustrated by both temperature programmed desorption (TPD)[4] and H–D exchange reactions.[5]

Here, we consider the energertic differences between hydrogen atoms adsorbed at alternative sites of the clean {111} surfaces of Ni, Pd and Pt. We have employed the periodic plane wave pseudopotential density functional theory (DFT) method as implemented in the code VASP (Vienna *Ab initio* Simulation Program).[6] The Kohn–Sham equations are solved self consistently within the generalised gradient approximation, using the parameterisation derived by Perdew *et al.*[7] *k*-Point sampling, obtained using the Monkhorst–Pack scheme,[8] was used to treat the extended electronic states of the metal band structure with convergence accelerated using second order Methfessel–Paxton smearing[9] with a width of 0.1 eV. In this study a *k*-point grid of 5 × 5 × 1 was used which has been shown to provide accurate results.[10]

The {111} surfaces were constructed using the calculated equilibrium lattice constants of 3.990 Å (Pt), 3.950 Å (Pd) and 3.526 Å (Ni). These compare well with the experimental values of 3.924 Å (Pt), 3.891 Å (Pd) and 3.524 Å (Ni). A p(2 × 2) surface unit cell with three atomic layers, containing 12 metal atoms, was constructed. A vacuum gap equivalent to three layers was introduced to create the surfaces (one each side of the slab) with one hydrogen atom placed on one side of the slab corresponding to a surface coverage of 0.25 of a monolayer. The position of the hydrogen atom at each adsorption site was optimised with the metal surface held rigid. The adsorption energy is defined as the energy released on adsorption and is given by

$$E_{\mathrm{ads}} = -\left[E(\mathrm{M} + \mathrm{H}) - \mathrm{E(M)} - \tfrac{1}{2}\,E(\mathrm{H_2})\right]$$

Where E(M + H) is the energy of the hydrogen adsorbed on the metal, E(M) is the energy of the bare metal slab and $E(\mathrm{H_2})$ is the energy of a gas phase H_2 molecule. A positive value of E_{ads} implies that chemisorption from gas phase H_2 is thermodynamically favourable.

Fig. 1 shows a plan view of the {111} surface illustrating the four adsorption sites examined, the atop, bridge, fcc hollow and hcp hollow. Table 1 lists the adsorption energies and structures of hydrogen adsorbed onto each on these sites on the {111} surfaces of Ni, Pd and Pt. The differences in the influence of the H coordination on the adsorption energy for different metals is striking.

The adsorption onto the {111} surface of Ni increase with the coordination number of the hydrogen atom. The most stable site is the three-fold hcp hollow site (63.8 kJ mol^{-1}) closely followed by the three-fold fcc site (63.6 kJ mol^{-1}). The least stable is the atop site (10.1 kJ mol^{-1}) with the two-fold bridge site having an intermediate value (51.4 kJ mol^{-1}). The Ni–H bond lengths also follows the coordination number with the singularly coordinated atop site having the shortest bond and the three-fold hollow sites the longest bonds. Table 1 also lists the height Z(h) of the H atom above the first surface layer, clearly demonstrating that the atop hydrogen is significantly above the surface.

The results for Ni are in good agreement with experiment. Christmann *et al.*[11] found an adsorption energy of 49 kJ mol^{-1} while the stability of the hcp and fcc sites is consistent with the observed c(2 × 2)-2H structure.[12] Previous *ab initio* calculations[13] at a coverage of $\theta = 1$, gave rise to the same trend in the adsorption energy with the higher coordinated sites having the largest adsorption energies.

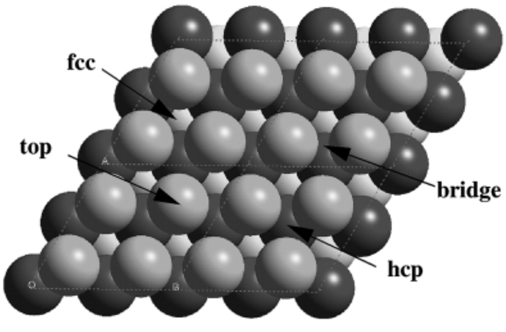

Fig. 1 Schematic illustration of the four adsorption modes for hydrogen investigated on the {111} surfaces of nickel, palladium and platinum. The one-fold atop site, the two-fold bridge site and the three-fold hollow sites (hcp and fcc) with the metal atoms not shown to scale so that the top, second (dark) and third (light) metals layers are clearly visible.

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Table 1 Comparison of the adsorption energies, bond lengths and height of the hydrogen atom above the surface for hydrogen adsorption on the {111} surfaces of nickel, palladium and platinum. The numbers in parentheses indicate the coordination number of the hydrogen atoms in each case

	Nickel			
	Atop	Bridge	hcp hollow	fcc hollow
E_{ads}/kJ mol^{-1}	10.1	51.4	63.8	63.6
Ni–H distance/Å	1.469 (×1)	1.626 (×2)	1.708 (×3)	1.708 (×3)
Z(H)/Å	1.47	1.04	0.92	0.92
	Palladium			
E_{ads}/kJ mol^{-1}	3.1	36.4	45.2	49.1
Pd–H distance/Å	1.552 (×1)	1.725 (×2)	1.818 (×3)	1.818 (×3)
Z(H)/Å	1.552	1.012	0.840	0.838
	Platinum			
E_{ads}/kJ mol^{-1}	44.8	42.4	43.2	43.9
Pt–H distance/Å	1.565 (×1)	1.772 (×2)	1.876 (×3)	1.875 (×3)
Z(H)/Å	1.565	1.071	0.927	0.922

Adsorption on the Pd {111} surface follows closely the results obtained for Ni {111} but with slightly lower adsorption energies. In this case the fcc hollow site (49.1 kJ mol^{-1}) is slightly more stable than the hcp hollow site (45.2 kJ mol^{-1}). The bridge site is again slightly less stable (36.4 kJ mol^{-1}) and the atop site the least stable (3.1 kJ mol^{-1}). These results are consistent with thermal desorption spectroscopy,[14] which gave an adsorption energy of 43.4 kJ mol^{-1}, and low energy electron diffraction[15] (LEED) which suggests that the hydrogen occupies the fcc hollow site with a Pd–H distance of 1.78–1.80 Å. Previous calculations[13.16,17] also identified the hcp hollow site as the most stable with the stability reducing as a function of the coordination of the hydrogen. In the previous computational studies, the effect of surface relaxation was also investigated and found to be very small thus justifying our use of rigid surfaces.

For the Pt {111} surface the results are significantly different. All four adsorption sites have very similar energies, around 44 kJ mol^{-1} which is also in good agreement with microcalorimetric experiments on hydrogen adsorption to Pt powders[18] (45 kJ mol^{-1}). Although there is no relationship between the adsorption energy and the coordination number, surprisingly, the Pt–H distance follows the same trend as for the Ni and Pd with the atop site the shortest and the hollow sites the longest. For Pt {111} there are no previous *ab initio* calculations with which to compare.

From this it is clear that the interaction of hydrogen with the surface of Pt is significantly different to Pd and Ni. This is likely to have significant implications for reactions involving hydrogen on the surfaces of these metals. The atop will be more accessible for reacting with other adsorbed species and for Pd and Ni it is clear that hydrogen will not occupy this site. For Pt the atop site is in fact the most stable (although only marginally) implying that both the atop site and the hollow sites will be significantly populated and thus hydrogen will be more accessible for reaction.

More significantly the similar adsorption energies for all sites on Pt imply that the diffusion of hydrogen across the surface will be more rapid than for the other two metals. Recent experimental evidence to this effect has been obtained from quasi-elastic helium scattering.[19] If a hydrogen atom is located on a fcc hollow site on the {111} surface it will have to pass through either an atop or bridge site to diffuse across the surface. For Pt {111}, the energy of these sites is almost identical, and thus the energy barriers to diffusion are likely to be small. For Pd and Ni, the lowest energy pathway is through the bridge site, which is less stable than the fcc hollow site by 12 kJ mol^{-1} for Ni and 13 kJ mol^{-1} for Pd, compared to a difference of only 1.5 kJ mol^{-1} on Pt {111}. Diffusion over the Pd and Ni {111} surfaces will thus be hindered since H adsorbates have to pass through the bridge site creating a significant energy barrier compared to that on Pt. Evidence for this effect can be found in the isomerisation data presented earlier. At low partial pressure of hydrogen Pd and Ni allow olefin isomerisation while Pt does not. This can be explained by the rate of the hydrogenation reaction on Pd and Ni being limited by the transport of hydrogen to the reaction site. On Pt, owing to the faster diffusion, hydrogen transport will not be a significant factor.

The results presented indicate that there are fundamental differences in the interaction of hydrogen on the surfaces of platinum, paladium and nickel, and that these differences may contribute to the differences in the hydrogenation activity. While we have not considered sub-surface hydrogen in our calculations on Pd, the similarity of our results for Pd and Ni, where sub-surface hydrogen is known to be less important, suggest that our conclusions regarding the surface hydrogen species are valid.

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