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Subsurface Hydrogen Exciton-Like States in Solid Catalysts

By

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Subsurface hydrogen electronic levels are discussed in terms of exciton-like states generated by vacancy–hydrogen interaction in transition-metal catalysts. Trapped hydrogen atoms have binding energies that depend exponentially on the density of electronic states at the Fermi level.

Die Elektronenniveaus von Sub-Oberflächenwasserstoff werden mit Exziton-ähnlichen Zuständen diskutiert, die durch Leerstellen–Wasserstoff-Wechselwirkung in Übergangsmetallkatalysatoren gebildet werden. Die angehafteten Wasserstoffatome haben Bindungsenergien, die exponentiell von der Dichte der Elektronenzustände am Ferminiveau abhängen.

1. Introduction

The importance of adsorbed hydrogen in the active surface layers of a working catalyst is now well-recognized [1]. Several surface hydrogen states can be distinguished. Mostly, however, only indirect methods such as temperature programmed desorption [2, 3], radio-tracer studies [4], and selective dehydrogenation measurements [5] have been used for their detection.

Some experiments — especially using temperature programmed desorption — point to the existence of subsurface hydrogen. Adsorbed hydrogen can cause reconstruction of surfaces of nickel and palladium single crystals [6, 7] which could be the initial step in the sintering of these catalysts in hydrogen [1].

2. Exciton-Like States

Vacancies in a crystalline material originate at the surface, with the system as a whole in a non-equilibrium state. Large concentration gradients cause diffusion perpendicular to the surface, while self-diffusion occurs along the surface and parallel to it for a few subsurface layers.

The structure of the surface layer can be described by using a two-dimensional lattice gas based on the Ising model [8]. A "quasi-binary" vacancy–atom system can then be constructed, layer by layer, from the surface, with a transition or interface region between the surface layer and the true bulk material. In this transition region a gradient of the vacancy concentration occurs in opposite direction to the gradient of the atomic concentration. The sum of the vacancy concentration and the atomic concentration in this quasi-binary transition phase is constant at all depths.

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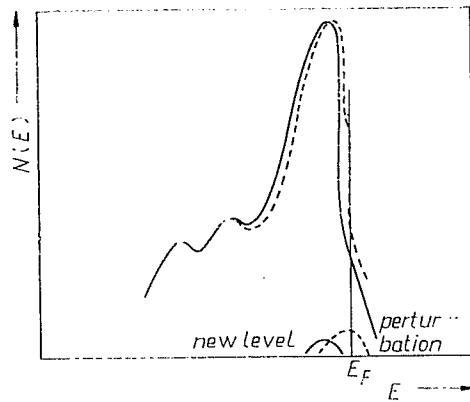[2]) 48 North Portland Str., Glasgow G1 1XN, Great Britain.

Fig. 1. Effect on the density of electronic states $N(E)$ at E_F, around the exciton-like state formed by a hydrogen–vacancy pair. An enhancement of $N(E)$ is required to screen the trapped hydrogen atom. The effect is non-localized and can extend as far as 12 nm from the hydrogen–vacancy pair [14]

Several experiments [9, 10] tend to support the view that hydrogen atoms can be trapped by the vacancies. The electron-energy distribution around such a vacancy-trapped hydrogen atom will be different from that around an interstitial hydrogen [11, 12] and this has important implications for adsorbed hydrogen [13].

It can be shown for many transition metals, using the coherent potential approximation (CPA) in the Hartree picture that despite their high density of states at the Fermi energy, $N(E_F)$, a bound state appears for a hydrogen trapped by a vacancy in the host metal. The capture of an electron by this bound state produces an exciton-like hydrogen state [14]. The electron "hole" in this exciton-like state is not a real hole in the conduction band (its lifetime would then be too short) but is a hole bound to a screened hydrogen, whose charge is then less than one.

The electronic energy of the exciton-like state depends exponentially on $N(E_F)$ [14]. This exciton-like surface hydrogen–vacancy state is not the same as the surface exciton that occurs for semiconductors [15 to 17]; our proposed hydrogen–vacancy state has a high degree of delocalization and a low internal binding energy. It can form weak bonds with surface species, as is implied experimentally in autocatalytic processes [18]. Overlap of exciton-like surface states creates a new level near to E_F, with consequent charge transfer which causes the Fermi level to shift to slightly higher energy (Fig. 1). The additional positive charge on the trapped hydrogen atom perturbs the electron valence band in its vicinity and causes an enhancement of $N(E_F)$, near to the hydrogen–vacancy pair (screening it to restore neutrality). The overlap will give rise to the well-known surface reactivity of transition metals and their alloys. The formation of a hydrogen–vacancy state is also consistent with the observed partial depopulation of d-levels of the host metal in cluster calculations [13].

The role of the d-electrons in dissociation of hydrogen at transition-metal surfaces is recognized in the Harris and Andersson model [19]. However, we suggest that the interaction of the metal d-electrons is not directly with hydrogen s-electrons, as proposed by Harris and Andersson, but with exciton-like surface hydrogen states; these being non-localized and extending over a small region around the hydrogen–vacancy interaction from which they are generated. This, in our view, appears more plausible than a direct interaction of hydrogen s-electrons with strongly localized metallic d-orbitals. The 1s-orbital of a physisorbed hydrogen atom cannot readily overlap with the localized metal d-orbitals but the much more delocalized wave function of a hydrogen–vacancy (exciton-like) state could easily do so, permitting entry of the hydrogen into the chemisorbed region.

3. Surface Catalysts

By far the largest class of gas-phase catalytic reactions involve hydrogen-containing reactants. The essential question, in understanding their mechanism, is how do the surface atoms of a solid catalyst [20] control a gas-phase reaction. We believe that exciton-like hydrogen states have a role in generating active sites. Surface intermediates involving exciton-like states decrease the energy barrier for a given process, promoting the catalysis. Moreover this chemisorbed hydrogen, in the form of an exciton-like surface state, can exchange with hydrogen atoms of the reactants.

If a surface hydrogen is removed, by a reactant or by desorption, the metal can obtain a replacement hydrogen atom more easily if an exciton-like hydrogen state exists — because of its delocalization. On nickel, for example, an exciton-like state extends some 12 nm into the bulk and over the surface of the metal [14]. Thus, one chemisorbed hydrogen atom can affect the surface properties of the catalyst over a relatively large area, making it energetically favourable for further hydrogen atoms to stick to the surface. Metal–hydrogen active sites, consisting of several surface atoms, have been proposed as "landing sites" by Frennet et al. [21]. We interpret these landing sites as the delocalization of the hydrogen–metal bond in our exciton-like state extending to several atoms.

The concept of a landing site has become widely invoked in catalytic systems involving hydrogen. We propose it to be the region of the surface where an exciton-like interaction of metal with a hydrogen atom occurs. For example, the primary adsorption reactions detected in hydrogen–deuterium studies of hydrocarbon systems [22, 23] can be explained by the existence of surface (or subsurface) exciton-like hydrogen atoms. They explain also the ease of sintering of catalysts in hydrogen and the "quasi-liquid" platinum–hydrogen surface layer [24] needed for sintering of platinum in hydrogen.

It is known that an active surface for the dissociation of hydrogen is produced only after an initial incubation process, which is experimentally observable as some form of electrode process [25, 26]. We propose this to be adsorption of hydrogen into the host material, producing sensitive exciton-like states which then provide sinks for s-electrons of hydrogen [19]. Exciton-like states would also give rise to the indirect collective long-range interactions invoked by Lau and Kohn [27] and more recently by Christmann [28].

Hydrogen-induced rearrangement of the surfaces of single crystals has been observed [29] at temperatures between 470 and 770 K, during thermal desorption of hydrogen. This too is a long-range effect involving subsurface hydrogen in a metal–hydrogen reaction. We propose that a particle, such as an adsorbate atom, attaches to an exciton-like surface hydrogen state, its effect then extending over a relatively large region of the surface. For example, when phosphorus is incorporated into amorphous nickel phosphide glassy alloys [14] the interaction traps the phosphorus atoms in non-equilibrium positions, giving rise to the amorphous structure.

Exciton-like quasi-particles would obey Bose-Einstein statistics. Like a condensed state, they may all be in the ground state. Thus, they can overlap to a high degree and create a sensitive (continuous) surface. While not directly supporting theories attributing catalytic activity to individual active atoms, the delocalized exciton-like state explains the ligand-field state invoked to explain the behaviour of complex catalysts; the surface atom in the exciton-like state plays the role of the active ligand or central atom. The proposal agrees too with theoretical calculations [30] of adsorbed hydrogen atoms mutually interacting at the surface.

Surface electronic structure studies by UV photoemission [31] also support the concept of an exciton-like surface state. A narrow UPS peak observed just below E_F

for a catalytically active (metastable) surface is found to disappear on reconstruction (stabilization) of the surface, which becomes also less chemically active. The enhanced $N(E_F)$ promotes, in our model, the catalytic activity. This is increased also by a larger vacancy concentration in the metastable state. We believe, for example, that hydrogenation of benzene [32, 33] to form cyclohexane (clearly a hydrogen-promoted process) occurs through formation of exciton-like states.

4. Subsurface Hydrogen

The vacancy-trapped hydrogen atom, in our proposed exciton-like surface state is a subsurface one and therefore surrounded by atoms of the bulk metal. It will behave as a two-dimensional hydrogen–metal binary, similar to the subsurface-trapped hydrogen atom proposed by Rieder et al. [6, 7] for nickel and more recently by Yates et al. [34] for ruthenum, with an energy between chemisorbed and physisorbed [28]. Yates et al. proposed three possible models for these subsurface hydrogen states but preferred an endothermic model. We calculate for nickel [14] a value of ≈ 3 kcal g-atom^{-1} (≈ 0.13 eV) for the binding energy of hydrogen in an exciton-like subsurface state. For ruthenium [35], with lower $N(E_F)$, the binding energy would be ≈ 2 kcal g-atom^{-1} (≈ 0.8 eV). We therefore support the endothermic model preferred by Yates et al.

Subsurface hydrogen atoms can move easily into surface sites [29] and are thus difficult to distinguish experimentally from surface hydrogen. Evidence has been cited [34, 36, 37] for the presence of subsurface hydrogen in the high-density planes of transition metals, as well as against their existence at such planes [28, 38]. With our exciton-like model, subsurface hydrogen can occur at densely packed interfaces. Although the capture of H atoms by vacancies at such interfaces may be slower, the local density of electronic states will vary for different absorbed species and depend sharply on co-ordination and surface structure [39]. Thus the presence of hydrogen at subsurface high-density planes will depend on several structural factors and on the presence of other adsorbed species. Similarly, $N(E_F)$ for "flat" surface planes (as for densely packed surface planes) is small [40], reducing the formation of exciton-like states and causing the decrease in catalytic activity observed [41] for such surfaces.

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