Condensed Matter Physics, 1998, Vol. 1, No 2(14), p. 383–388

Models of the adsorbtion-catalytic centers on transition metals

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Received May 21, 1998

The models of adsorbo-catalitic centers for transition metals, which use the peculiarities of the electron-orbital structures as insulated and bounded atoms, have been analized. The important role of the unfilled d-orbitals, their orientation, changing of the occupation of d-shalls, and influence of the ligands with completely occupied d-orbitals were considered in connection with the catalytic activity of the transient metals. The new approach for enhanced catalytic properties, based on the film alloys of catalytic metals, was proposed.

Key words: *adsorbtion, catalys, transition metals and alloys*

PACS: *05.70.Ce, 65.50.+m*

1. Introduction

Characteristics of hydrogen on the surface of transition metals (adsorption, catalytic decomposition, transport etc.) are the subject of a precise scientific investigation and play an important role in determining the parameters of solid-state gas sensors of H-containing molecules. Decomposition and subsequent transport of a proton (or atomic hydrogen) occur strongly depending on the interconnection of the neighbouring adsorption centers for protons, the shape of the barrier, dynamic parameters (determined by a barrier electron–phonon coupling) etc.

A thorough theoretical analysis of the proton properties within the H-bond model, (transfer, orientational hopping between the neighbouring bonds etc.) has been made in a number of works by I.V. Stasyuk and co-authors [1,2]. In particular, an analysis within the framework of a 1-dimensional chemical model with taking into consideration a tunnelling effect, demonstrates the orientation motion effect which strongly depends on the energy spectrum of the H-bonded proton system. This leads to the redistribution of protons in a chain-cluster and, hence, the ground state (i.e., barriers, wells) is changed. The external electric field can also influence the general thermodynamic functions of the system containing hydrogen. For the effect of the surface charging induced by adsorption, which is the basis of semiconductor gas sensors, the proton (H_a) polarization is the principal phenomenon. Earlier calculations performed for small molecular complexes by Zundel and Eckert [2] exhibit an anomalously large proton polarizability which is in contradiction with the experimental data. To consider a more realistic situation, I.V. Stasyuk with co-authors have proposed a new approach (a pseudo-spin based model) for the description of H-bonded molecular systems which give reasonable values of energy levels and the degree of polarization. We believe that this model, at least in a qualitative way, can be used for analysing the catalytic processes of H-containing molecules on transition metals (decomposition, transport etc.) and can also be used for the study of the layered structures "metal-insulator-semiconductor" (MIS).

2. General features of the transition metal catalysts

The enhanced catalytic activity of the definite transition metals is based on the fundamental characteristics of the electron shell configuration. Indeed, in the case, when a d-orbital plays an important role in the formation of chemical bonds (especially surface bonds), all those atoms are candidates for the creation of highly catalytic systems. The reason for this is that d-orbitals (in comparison with s– and even p–, as well as sp–hybrid–orbitals) are long–range active, so they can create a small barrier for adsorption (V_d–barrier $\ll$ V_s–barrier), and due to this the activation energy for a catalytic process ε_{cat} decreases drastically, whereas the reaction cross–section $S_{cat.}\sim r$, and therefore, the catalytic reaction yield have to be increased considerably. Figure 1 demonstrates the Lennard–Jones configuration diagram for s– and d– bonds and illustrates the above formulated statement. Because the energy of the bonds $E = E_{\min} - E_{\max}$ also becomes small, the products of the catalytic reaction more easily leave the surface. On the other hand, the bond energy E_b is often nearly the same as, for example, for H on Cu, Zn, Ag, Ni and Pd [3–5]). So, chemosorption of H_2 on Ni and Pd proceeds rather quickly, but on Cu, Zn and Ag chemosorption of H_2 is nearly absent.

Let us compare electron configurations for a set of transition and semitransition metals.

In all of these cases the role of d-orbitals is important. It is known that the most expanded chemical bonds create either pure d-orbital (as in Pd) or atoms where d-orbitals are near to saturation and only one s-orbital (Pt) or two (Fe, Co) give a nondominant share and lead to some symmetrisation of the bonds.

3. Catalysis and the influence of external impurities or alloys

The role of promoters or inhibitors of catalysis has been long known. In particular, alkali metals were known as promoters for the synthesis of ammonia on Ru($4d^7 5S^1$) and on Ro ($4d^8 5S^1$), but the inhibition of the CH_4 on Ni catalysis by S and P and other reactions of such type were observed.

Table 1. Electron configurations for different d-elements

Elements	Electron configuration	Group
Fe	$(2d^6 4s^2)$	4^a-th
Ni	$(2d^8 4s^2)$	4^a
Cu	$(3d^{10} 4s^1)$	4^b
Zn	$(3d^{10} 4s^2)$	4^b
Co	$(3d^6 4s^2)$	4^b
Pd	$(4d^{10})$	5^a
Ag	$(4d^{10} 5s^1)$	5^b
Pt	$(5d^9 6s^1)$	5^a

Table 2. Electronegativity of elements

K	Ti	Fe	Ni	Cu	Sn	Pd	Pt
0.8	1.6	1.8	1.8	2.0	1.7-1.8	2.1-2.3	2.1-2.4

3.1. Electrostatic model

The comparison with electronegativity seems to indicate a local electrostatic mechanism of the adsorption-catalytic promotion. In accordance with this conception, highly electropositive alkali metals considerably decrease the electrostatic potential of a catalytic substrate. In this case the potential well of the adsorption state increases and, consequently, decreases the barrier for desorption. On the other hand, the electronegative elements (like O, S, P, Cr, F, Cl etc.) lead to the weakening of chemical bonds. As a result, the depth of the pre-chemosorption well decreases. It causes a decrease of the barrier for chemosorption and an increase of one for desorption. The reason of this is the redistribution of the electron density of chemical bonds – accepting in the case of electronegative elements and adding – in the electropositive elements case. So for H_2 (and H-related molecules) dissociative reaction, it is possible to propose the following set of elements for enhancing the catalytic activity:

In accordance with the known relation for sticking coefficient S

$$S \sim (1 - A\exp(E_a - E_d)/kT).$$

From this relation it is possible to see that at $E_d > E_a$ we have an activated adsorption (like for H_2 on Cu) and at $E_d < E_a$ – a nonactivated adsorption (H_2 on Pt, Pd). The changing of the electron density on the Fermi surface of Me is the most important factor of the electrostatic mechanism.

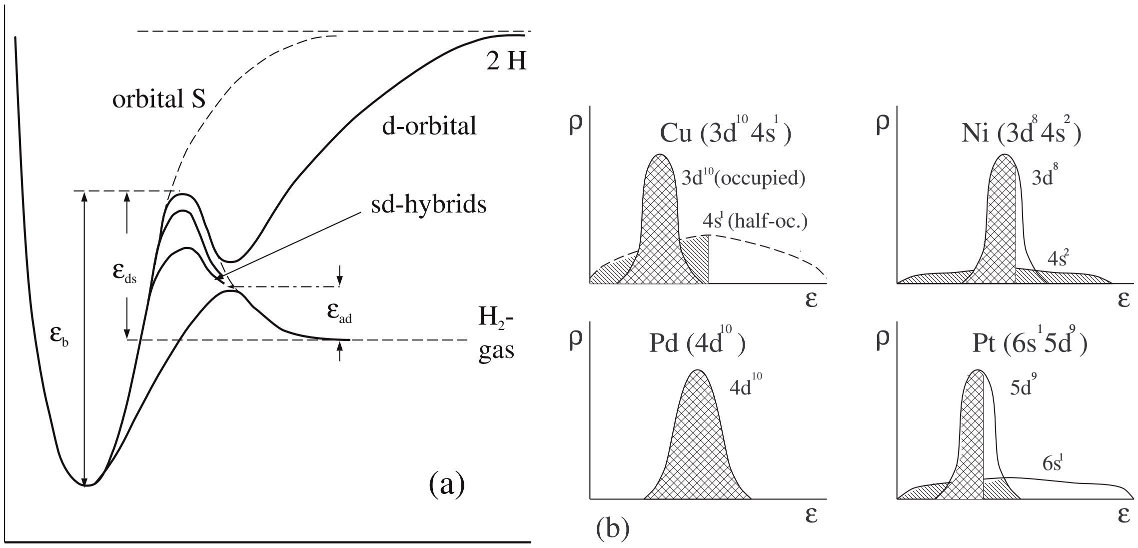

Figure 1. (a) The curves of potential energy vs. distance M–H of the dissociative adsorbtion of H_2 molecule in a l-dimentional model on non-transition metals (upper curve–energy activation ε_{as}) and transition metals (bottom curve, $\varepsilon_d \ll \varepsilon_a$). (b) Electron density ρ distribution for d and s orbitals for Cu, Ni, Pd, Pt.

3.2. Molecular bond model

For isolated transition Me atoms there are 5 linearly independent d-orbitals (taking into account a spin, a fully occupied d-shell contains 10d electrons): d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{x^2}, which have the same energy (with the quantum number, correspondingly, 1=2; m=0, ±1; ±2). Orbitals $d_{x^2-y^2}$, d_{z^2} have the maximum electron density along the coordinate axis x, y, z, and orbitals d_{xy}, d_{yz}, d_{xz} are directed along bisectors. The latter are denoted as t_{2g} (or d_e) orbitals, the former are known as e_g orbitals. The t_{2g} orbitals overlap and create metallic conductivity bands, e_g orbitals do not overlap, and are low localized. For a face centered cubic lattice, plane (100), orbital e_g (field) is directed along the normal to the surface, and 4 bonds t_{2g} are oriented at 45°. For an octahedron (III) face, both types of orbitals are not normally directed, but, correspondingly, at 35° and 55° to the surface. For (110)–t_{2g} (filled) are normal, but e_g are oblique at 45° to the surface. As more normally directed and filled orbitals are catalytically active, the (III) plane is more preferable.

In the crystal lattice field the degeneration is removed and we have a splitting of the energy levels. For example, in the octahedral field the energy of orbital e_g becomes larger, and of t_{2g} – lower. Because the value of splitting is different for different crystal planes, we have a variation for the values of splitting and, hence, for polycrystalline samples we have a catalytically heterogeneous surface.

As a model of adsorption let us consider the adsorption of H_2 on the non-catalytic (Cu) and catalytic (Ni) substrate, [5], figure 2. The energy levels at the moving of H_2 to the surface become shifted in a different manner: the anti-bonding (non-occupied) IS^2 level (H_2) shifts down and $4S^2$ (Cu and Ni) – shifts up; this determines the crossover position at a definite small distance. These values are

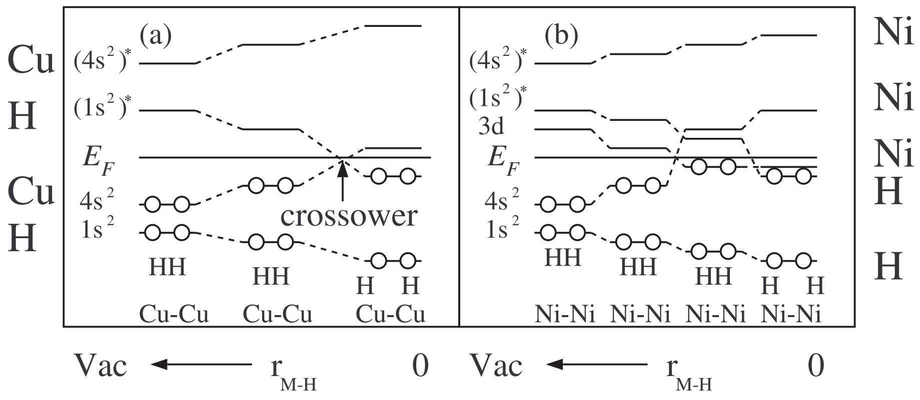

Figure 2. Energy levels shift under dissociative chemoadsorbtion molecule H_2 on Cu (a) and Ni (b) in the model of surface clusters H_2Cu_2 and H_2Ni_2, respectively [5].

ordinarily deposited slightly below the Fermi energy. So, here we have a change of the anti-bonding orbital to slight bonding – at moving to the substrate. The decrease of the energy of H-M complex and the increase of the filling energy of Me ($4S^2$–bonding) mean that after the crossover point we have a decompositional adsorption of H_2-molecule. For Ni the repulsion barrier near the surface decreases due to the influence of anti-bonding 3d orbitals, for which the crossover takes place at a much larger distance. Here E_a becomes rather small and $E_a \sim E_d$.

3.3. Ligands and alloys

For ligands (mixtures) negatively charged (electronegative elements), we have an increasing energy of d–level (due to the repulsion force). Depending on the position of the ligand atoms (1 atom – spherical symmetry field, 4 – tetrahedral, 5 – pyramid, 6 – octahedral etc.), splitting becomes more and more complicated and grows, the higher positions have, starting from octahedral, e_g orbitals. The latter are more directed than t_{2g}, so they are more preferable for the creation of long-acting chemical bonds with relatively low desorption barriers.

Mixed orbitals can be estimated from the theory of the ligand field (based on the molecular orbital method).

If bonds are created due to a non-paired ligand, electrons and vacant orbitals of Me, – that gives donor-acceptor bonds. If an electron shifts from the ligand to Me – then Me is an acceptor, and the ligand is a donor; in the opposite case Me is a donor (dative bonds). For such bonds more acceptable are the elements with a fully (or nearly) occupied d-orbital configuration (d^{10-n}, n=1, 2, 3 ...) namely, Cu, Ag, Cd, Hg. In particular, Cu repulses the d-orbital of Pd, and in a circular configuration leads to the creation of a more normal direction of d-bonds, stimulating in such a manner their catalytic activity. Indeed, the change of the adsorption and catalytic properties of Pd by Cu (and other semitransition metals

[5-8]) was observed. Desactivated Pd (Pt) atoms in relation to CO chemosorption, and, on the contrary, activation of H_2 adsorption take place. The similar type of phenomena is observed for extended values of Cu. Castro et al. [7-8] have shown that for CuPt–alloys (Cu_3Pt (III) etc.) the adsorption energy of CO decreases in comparison with pure transition Me. For alloys a cut sp-band configuration is important for obtaining a high adsorption position. For CO-adsorption on NiAl (110), the effect of decreasing E_a is treated as an additional filling of a d-band of Ni and changing in a sp-d hybridization, which leads to increasing the role of d-orbitals. On the Cu_3Pt alloy the adsorption H_2 does take place almost as for pure Pt, and at the same time oxygen can be blocked by Cu atoms. Catalytic processes take place, whereas CO and larger molecules prevent the adsorption of H_2 molecules on Pt (Pd) atoms [7].

References

1. I.V.Stasyuk, O.L.Ivankiv // Modern Phys. Let., 1992, vol. B6, p. 85.
2. I.V.Stasyuk, O.L.Ivankiv, N.I.Pavlenko // J. of Phys. Studies, 1997, vol. 1, No 3, p. 418.
3. O.Krylov, V.Kiselev Adsorption and catalysis on transition metals and their oxides. Springer, Surf. Sci., vol. 9, 1989.
4. V.G.Litovchenko, A.A.Efremov, T.I.Gorbanyuk, I.P.Lisovskii, D.Schipanski, Z.Gerginchen, P.Kornezky // J. Phys. Low. Dimensional structures, 1995, vol. 12, p. 193.
5. A.Zangwill Physics of surfaces. Cambridge Univ. Press, 1988.
6. J.A.Rodrigues, R.Campbell, D.Goodman // Surf. Science, 1994, vol. 307-309, p. 377.
7. M.O.Castro, G.Dooyen // Surf. Science, 1994, vol. 307-309, p. 384; p. 412.
8. R.Linke, V.Shneider, H.Bussee et al // Surf. Science, 1994, vol. 307-309, p. 407.

Моделі адсорбо-каталітичних центрів перехідних металів

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Отримано 21 травня 1998 р.

Проаналізовано моделі адсорбо-каталітичних центрів перехідних металів, враховуючи електронні орбіталі як ізольованих, так і сконденсованих у тверде тіло атомів. Відзначається домінуючий вплив на каталітичну активність незаповнених d-оболонок. Запропоновано новий підхід для підвищення каталітичної активності, що базується на використанні плівкових сплавів перехідних металів.

Ключові слова: *адсорбція, каталіз, перехідні метали та сплави*

PACS: *05.70.Ce, 65.50.+m*