Chemisorption on inverse-supported catalysts: H–ZnO/Ni*

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The chemisorption energy of hydrogen on a semiconductor/metal composite substrate is investigated using the complex-energy-plane integration approach. The electronic properties of the interfacial substrate are described via a Green–function formalism. The tight-binding approximation is employed to model the semiconductor catalysts by a finite chain of alternating s- and p-orbitals, while the semi-infinite metal support is represented by a linear chain of d-orbitals. Specific calculations are performed for the H–ZnO/Ni system.

Key words: Chemisorption energy — Supported catalysts — Green function

1. Introduction

Nowadays, most industrially important catalytic reactions employ supported catalysts of the synergetic type [1]. However, as was pointed out in a previous paper [2], there is a dearth of quantum-mechanical studies on such composite systems. Indeed, in the case of *inverse-supported catalysts*, not a single quantal investigation appears to have been made of the chemisorption properties of these important interfacial systems. The present paper is the first attempt to remedy this situation.

Calculations have been performed for hydrogen chemisorption on a ZnO catalyst supported by a Ni base. Specifically, results are presented showing the variation of the hydrogen chemisorption energy (ΔE) with the thickness (N_{sc}) of the ZnO film. Unlike the earlier treatment [2] of the H–Ni/ZnO case, ΔE is obtained via

the complex-energy-plane integration technique, while the electronic properties of the composite substrate are again described by using a Green–function (GF) method within the framework of the tight-binding approximation.

2. Chemisorption energy and complex energy formulation

Similar to the one-electron model of Einstein and Schrieffer [3], we shall describe our chemisorption system by $H_0 + V$, where $H_0 = H_s + H_a$ is the Hamiltonian of the substrate and an isolated atom (energy E_a), and V is the adatom–substrate interaction. If V is modelled by a bond of strength β between the adatom and the surface atom, the chemisorption energy can be written as [3]

$$E = \frac{2}{\pi} \operatorname{Im} \int_{-\infty}^{E_F} \ln\left[1 - \beta^2 G_{aa}(E + i0^+) G_{00}(E + i0^+)\right] dE, \tag{2.1}$$

where the adatom GF $G_{aa}(E + i0^+) = (E - E_a + i0^+)^{-1}$ and $G_{00}(E)$ is the substrate GF at the surface site. For real E, depending on the complexity of $G_{00}(E)$, the integrand of (2.1) can exhibit sharp peaks due to resonances. Furthermore, for large values of β, there exist localized states whose energy E_s satisfies $E_s - E_a - \beta^2 \operatorname{Re} G_{00}(E_s) = 0$ outside the substrate band, which must be located numerically in general. Thus, the direct numerical evaluation of (2.1) can become rather cumbersome. However, if we allow the energy E to become complex, its imaginary part will damp out the resonances and isolate any singularities due to localized states, rendering the integrand for ΔE a smooth function of energy and the resulting integral very easy to evaluate.

To proceed, let

$$f(z) = \ln\left[1 - \beta^2 G_{aa}(z) G_{00}(z)\right] \tag{2.2}$$

which is analytic in the complex z-plane, except along the branch-cut and at singularities located on the real axis. Since the GF's satisfy $G(z^*) = G^*(z)$, it follows that $2i \operatorname{Im} f(E + i0^+) = f(E + i0^+) - f(E - i0^+)$, so that (2.1) becomes

$$\Delta E = -(\pi i)^{-1} \int_{C_1} dz\, f(z), \tag{2.3}$$

where C_1 is the path in the complex z-plane shown in Fig. 1, which starts from $E_F + i0^+$, goes around the branch-cut and singularities of $f(z)$ and ends up at $E_F - i0^+$. By Cauchy's theorem, the path C_1 can be deformed into any path which avoids the singularities on the real axis [4]. A particularly convenient path for the present tight-binding model is the semi-circular path C_2 indicated in Fig. 1 [5]. Since $G(z) \sim z^{-1}$ as $z \to \infty$, $f(z) \sim z^{-2}$ as $z \to \infty$ and the contribution from the semi-circle at infinity to the integrand is zero by Jordan's lemma. Thus, we only have to evaluate the integral along the straight path $E_F + iy$ for $-\infty < y < \infty$.

Furthermore, using the reflection symmetry of $f(z)$ about the real axis, the expression for ΔE becomes

$$\Delta E = -2\pi^{-1} \int_0^\infty \operatorname{Re} f(E_F + iy)\, dy. \tag{2.4}$$
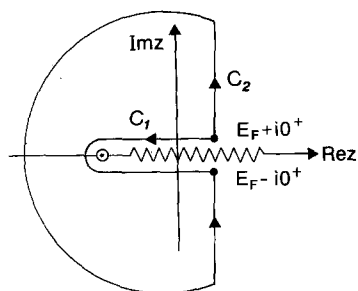
Fig. 1. Contour path in complex plane for integration of (2.3)

In actual computation, the integral of (2.4) is transformed into one with finite limits by the substitution $y = x/(1-x)$, and then evaluated with standard Gaussian quadrature.

3. Substrate Green function

The metal supported-semiconductor substrate will be described by the one-dimensional tight-binding model shown in Fig. 2, which is essentially the one used by Davison et al. [2], except that the roles of the semiconductor and the metal are reversed. The substrate GF at the surface site, which enters the expression for ΔE [see (2.3) and (2.4)], can be derived from the Dyson equation approach [2] as

$$G_{00}(z) = g_2(0, 0) + \gamma^2 g_2(0, n) g_2(n, 0)[g_1^{-1}(n+1, n+1) - \gamma^2 g_2(n, n)]^{-1}, \quad (3.1)$$

where $g(i, j)$ is the GF between the ith and jth sites of the isolated αth component of the substrate ($\alpha = 1$ for the semi-infinite metal, $\alpha = 2$ for the infinite semiconductor), the energy dependence being suppressed.

For the semi-infinite metal, we have for complex energy z,

$$g_1(n+1, n+1) = [z_1 - (z_1^2 - 1)^{1/2}]/\beta_1, \quad (3.2)$$

where $z_1 = (z - \alpha_1)/\beta_1$ and the branch-cut of $(z_1^2 - 1)^{1/2}$ is taken to be between ± 1. It can easily be shown that g_1 in (3.2) reduces to that given by Ueba [6] when $z = E + i0^+$.

Expressions for the GF's of the finite semiconductor $g_2(n', n)$ are more complicated. They can, however, be written in terms of the GF's of the infinite semiconductor $G_2(m, n)$ by the Dyson equation approach [2]. After some algebra,
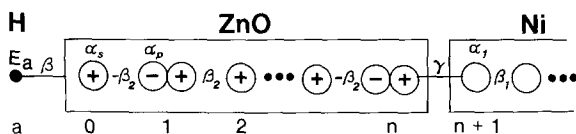

Fig. 2. Diagrammatic representation of H–ZnO/Ni system showing hydrogen adatom a of electronic energy ε_a with bond energy β to the Zn surface atom at $m = 0$. The ZnO film, lying between $0 \le m \le n$, is depicted by a chain of alternating (Zn)s- and (O)p-orbitals with corresponding site energies α_s and α_p and bond energies $\pm\beta_2$. The bond of energy γ attaches film to first ($m = n+1$) Ni atom in semi-infinite Ni support containing atoms of site energy α_1 and bond energy β_1

we obtain

$$g_2(0, 0) = [DG_2(0, 0) - BG_2(0, n)]/\Delta \tag{3.3}$$

$$g_2(n, 0) = [AG_2(0, n) - CG_2(0, 0)]/\Delta \tag{3.4}$$

$$g_2(0, n) = [DG_2(0, n) - BG_2(n, n)]/\Delta \tag{3.5}$$

$$g_2(n, n) = [AG_2(n, n) - CG_2(0, n)]/\Delta, \tag{3.6}$$

where

$$A = 1 + \beta_2 G_2(0, -1) \tag{3.7}$$

$$B = \beta_2 G_2(0, n+1) \tag{3.8}$$

$$C = \beta_2 G_2(n, -1) \tag{3.9}$$

$$D = 1 + \beta_2 G_2(n, n+1) \tag{3.10}$$

and

$$\Delta = AD - BC. \tag{3.11}$$

Since we assume that the ZnO film (thickness N_{SC}) is bonded to the Ni base via an oxygen atom, $n = 2N_{SC} - 1$.

Explicit expressions of $G_2(m, n)$ have been given by Bose and Foo [7]; the derivation is summarised in the Appendix and their analytic continuation into the complex-energy plane is discussed. The diagonal GF's can be written explicitly as

$$G_2(n, n) = (z - \alpha_s)/\beta_2^2 b(z) \tag{3.12a}$$

and

$$G_2(0, 0) = (z - \alpha_p)/\beta_2^2 b(z), \tag{3.12b}$$

where

$$\beta_2^2 b(z) = [(z - \alpha_s)(z - \alpha_p)(z - \alpha_s - w)(z - \alpha_p - w)]^{1/2} \tag{3.13}$$

with $w = (\varepsilon^2 + 4\beta_2^2)^{1/2} - \varepsilon$ and $\varepsilon = \frac{1}{2}(\alpha_s - \alpha_p)$. The function $b(z)$ has branch-cuts along the real axis from $\alpha_p - w$ to α_p and from α_s to $\alpha_s + w$, i.e., across the valence and conduction band energies. The off-diagonal GF's appearing in (3.3) to (3.10) can be expressed in terms of $G_2(0, 0)$ as

$$G_2(0, 1) = \beta_2 G_2(0, 0)[1 + u_<(z)]/(z - \alpha_p) \tag{3.14}$$

$$G_2(0, n) = \beta_2[G_2(0, n+1) - G(0, n-1)]/(z - \alpha_p) \tag{3.15}$$

with

$$G_2(0, n \pm 1) = G_2(0, 0)u_<(z)^{n \pm 1/2} \tag{3.16}$$

and

$$G_2(n, -1) = (z - \alpha_s)(z - \alpha_p)^{-1}G_2(0, n+1), \tag{3.17}$$

where

$$u_<(z) = \frac{1}{2}[\alpha + b(z)], \qquad \alpha = 2 - (z - \alpha_s)(z - \alpha_p)/\beta_2^2. \tag{3.18}$$

Note that $b(z)$ defined by (3.13) is also equal to $(\alpha^2 - 4\beta_2^2)^{1/2}$. By symmetry, and noting n is odd, $G_2(n, n+1) = G_2(-1, 0) = G_2(0, -1)$, so that $A = D$. We can also show by substituting (3.12), (3.16) and (3.17) into (3.4), (3.5), (3.8) and (3.9) that $g_2(0, n) = g_2(n, 0)$.

Finally, we notice that, since $|u_<| < 1$, the off-diagonal GF's $G_2(0, n)$ and $G_2(0, n \pm 1)$, as given by (3.15) and (3.16), vanish as $n \to \infty$, so $g_2(0, n)$ also vanishes. In this limit, the substrate surface GF (3.1) reduces properly to

$$G_{00}(z) = g_2(0, 0) = G_2(0, 0)[1 + \beta_2 G_2(0, -1)]^{-1}, \qquad n \to \infty \qquad (3.19)$$

which is the surface GF for a pure semiconductor substrate.

4. Results and discussion

We have calculated values of ΔE for a model of hydrogen chemisorption on the ZnO/Ni substrate as a function of the number of layers of ZnO $N_{sc} = \frac{1}{2}(n+1)$. The energy zero was chosen to be at the Fermi level of bulk Ni, for which the parameters $\alpha_1 = -1.7$ eV and $\beta_1 = 0.95$ eV were used [2, 8], while for ZnO, we chose [2] $\alpha_s = 0.0$ eV, $\alpha_p = -3.4$ eV and $\beta_2 = 3.755$ eV, giving a bandwidth $w = 6$ eV. The Ni-ZnO bond $\gamma = \frac{1}{2}(\beta_1 + \beta_2) = 2.35$ eV [2]. The adatom level is approximated by the formula [9] $E_a = -\frac{1}{2}(I + A)$, where I and A are the ionization energy and affinity level of the adatom, respectively. For hydrogen, $E_a = -2.7$ eV, which lies within the range of the effective adatom level ε_σ determined self-consistently within the Hartree-Fock approximation [2]. Finally, the H-ZnO bond β was chosen to be 3.0 eV, so that the resulting ΔE for a pure ZnO substrate [calculated by using (3.19) in (2.4)] is very close to the experimental value of -2.67 eV [10].

Fig. 3 shows a plot of the integrand of (2.4), $\mathrm{Re}\, f(E_F + iy)$ [where $f(z)$ is given by (2.2)] as a function of y for the case $N_{sc} = 4$, which demonstrates clearly that $\mathrm{Re}\, f(E_F + iy)$ is a smooth decreasing function of y. In Table 1, we present the main results of our calculation, the values of ΔE for different number of layers of ZnO. For $N_{sc} < 3$, $\Delta E(N_{sc})$ is higher than $\Delta E(\infty)$, the value for a pure ZnO substrate. At $N_{sc} = 4$, ΔE is lower than $\Delta E(\infty)$. For $N_{sc} > 5$, ΔE rises from the minimum value $\Delta E(4)$ to $\Delta E(\infty)$. However, even at $N_{sc} = 15$, $\Delta E(N_{sc})$ still differs from $\Delta E(\infty)$ slightly.

One possible interpretation of the presence of a minimum in the behaviour of ΔE with N_{sc} is the following. Since the work function of metals is generally less
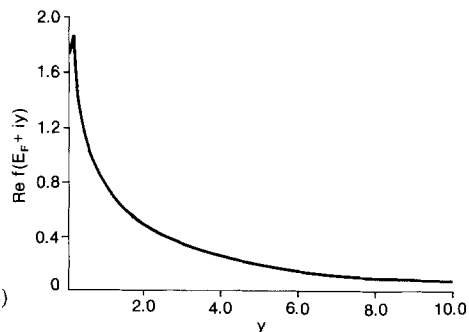

Fig. 3. Plot of the integrand $\mathrm{Re}\, f(E_F + iy)$ of (2.4) as a function of y for $N_{sc} = 4$

Table 1. Variation of ΔE
with N_{sc} for $\gamma = 2.35$ eV
and $\beta = 3.0$ eV. For $N_{sc} =$
∞ (pure ZnO substrate),
$\Delta E = -2.675$ eV

N_{sc}	ΔE (eV)
1	-2.409
2	-2.468
3	-2.545
4	-2.776
5	-2.756
6	-2.736
7	-2.715
8	-2.709
9	-2.702
10	-2.694
15	-2.687

than that of semiconductors, before contact $E_F^M > E_F^{sc}$. Consequently, during the *initial stages* of the ZnO film growth on the Ni support, electrons pass from the Ni to the ZnO and provide a "source" of charge for transfer *to* the H adatom, thus enhancing bond formation and increasing $|\Delta E|$. Subsequently, however, a *threshold point* is reached ($N_{sc} = 4$), when the thickness of the ZnO film becomes such as to provide a "sink" for electrons coming from the Ni and, to a lesser extent from the H adatom, thus reversing the flow of charge *away from* the H adatom, so that $|\Delta E|$ now decreases with increasing N_{sc} until it attains the $\Delta E(\text{ZnO})$ value.

5. Concluding remarks

The above results are encouraging, and provide insight into the possible charge-transfer mechanisms involved in chemisorption on inverse-supported catalysts. It is indeed interesting to see that, as the ZnO film grows on the Ni support, the charge-transfer process between the H adatom and the ZnO/Ni substrate changed from an *acceptor* to a *donor* type and, in so doing, reflects the desired aspect of approaching the correct $\Delta E(\text{ZnO})$ value. While the present treatment has ignored such features as surface and interface states, and the problem of self-consistency, the calculations do provide acceptable values of ΔE for H on the ZnO/Ni substrate. Further work is in progress to include these features, and improve the findings of these initial calculations.

Appendix: Green's function for a one-dimensional infinite s–p atomic chain

Consider a one-dimensional infinite chain of alternating s- and p-atoms. Let the orbital energies of the $s(p)$ atoms be denoted by α_s (α_p) with $\alpha_s > \alpha_p$, and the bond between adjacent atoms by $\pm \beta_2$. The Hamiltonian for this tight-binding model can then be written as

$$H_0 = \sum_r [\alpha_s |2r \times 2r| + \alpha_p |2r+1 \times 2r+1| + \beta_2(|2r \times 2r+1| - |2r-1 \times 2r| + \text{h.c.})], \tag{A1}$$

where we assume that the $s(p)$ atoms occupy the even (odd) sites. Forming the Bloch states

$$|ks\rangle = \frac{1}{\sqrt{N}} \sum_r e^{ikr} |-2r\rangle$$

$$|kp\rangle = \frac{1}{\sqrt{N}} \sum_r e^{ik(2r+1)/2} |2r+1\rangle$$

(A2)

the Hamiltonian in these basic functions becomes a 2×2 matrix

$$H_0(k) = \begin{pmatrix} \alpha_s & 2i\beta_2 \sin\dfrac{k}{2} \\ -2i\beta_s \sin\dfrac{k}{2} & \alpha_p \end{pmatrix}.$$

(A3)

For notational convenience, we shall define the energy zero to be midway between α_s and α_p, and let

$$\alpha_s = -\alpha_p = \varepsilon.$$

(A4)

Diagonalizing (A3) gives the band energies

$$E_k = \pm\sqrt{\varepsilon^2 + 2\beta_2^2 - 2\beta_2^2 \cos k}.$$

(A5)

The GF matrix in the Bloch representation of (A2) is

$$G(k, z) = [z\mathbf{1} - H_0(k)]^{-1} = \frac{1}{\beta_2^2(2 \cos k - \alpha)} \begin{pmatrix} z + \varepsilon & 2i\beta_2 \sin\dfrac{k}{2} \\ -2i\beta_2 \sin\dfrac{k}{2} & z - \varepsilon \end{pmatrix},$$

(A6)

where $\alpha = 2 - (z^2 - \varepsilon^2)/\beta_2^2$ has already appeared in (3.18). The GF's in the site-representation can then be obtained by inverting (A2) and using (A6). Thus,

$$\langle 2r'|G(z)|2r\rangle = \int_{-\pi}^{\pi} \frac{dk}{2\pi} e^{ik(r'-r)} \frac{z+\varepsilon}{\beta_2^2(2 \cos k - \alpha)}$$

(A7)

$$\langle 2r'+1|G(z)|2r+1\rangle = \int_{-\pi}^{\pi} \frac{dk}{2\pi} e^{ik(r'-r)} \frac{z-\varepsilon}{\beta_2^2(2 \cos k - \alpha)}$$

(A8)

$$\langle 2r'|G(z)|2r+1\rangle = \int_{-\pi}^{\pi} \frac{dk}{2\pi} e^{ik(r'-r-1/2)} \frac{2i\beta_2 \sin k/2}{\beta_2^2(2 \cos k - \alpha)}$$

(A9)

and

$$\langle 2r+1|G(E)|2r'\rangle = \int_{-\pi}^{\pi} \frac{dk}{2\pi} e^{ik(r-r'+1/2)} \frac{(-2i\beta_2 \sin k/2)}{\beta_2^2(2 \cos k - \alpha)}.$$

(A10)

Defining

$$I_{|r'-r|}(z) = \frac{1}{\beta_2^2} \int_{-\pi}^{\pi} \frac{dk}{2\pi} \frac{e^{ik(r'-r)}}{2 \cos k - \alpha}$$

(A11)

(A7) becomes

$$\langle 2r'|G(z)|2r\rangle = (z+\varepsilon) I_{|r'-r|}(z)$$

(A12)

and all other GF's can be expressed in terms of this GF as

$$\langle 2r'+1|G(z)|2r+1\rangle = \frac{z-\varepsilon}{z+\varepsilon} \langle 2r'|G(z)|2r\rangle$$

(A13)

$$\langle 2r'|G(z)|2r+1\rangle = \frac{\beta}{z+\varepsilon}[\langle 2r'|G(z)|2r\rangle - \langle 2r'|G(z)|2r+2\rangle]$$

$$= \langle 2r+1|G(z)|2r'\rangle. \tag{A14}$$

Equations (A13) to (A14) agree with (10) of [7].

The integral of (A11) can readily be evaluated by making the substitution $u = e^{ik(r'-r)}$ for $r' > r$ [and $u = e^{ik(r-r')}$ if $r > r'$, which gives the same result, so the integral depends only on $|r'-r|$, as indicated by the LHS of (A11)], and applying the residue theorem. The result is

$$I_{|r'-r|}(z) = \frac{u_<^{|r'-r|}}{\beta^2(u_< - u_>)}, \tag{A15}$$

where $u_>$ and $u_<$ are the roots of the quadratic equation

$$u^2 - \alpha u + 1 = 0 \tag{A16}$$

such that $|u_>| > 1$ and $|u_<| < 1$. (Note that $u_> u_< = 1$). It can be shown that

$$u_> = \tfrac{1}{2}[\alpha - b(z)], \qquad u_< = \tfrac{1}{2}[\alpha + b(z)], \tag{A17}$$

where

$$b(z) = (\alpha^2 - 4\beta^2)^{1/2} = [(z^2 - \varepsilon^2)(z^2 - \varepsilon^2 - 4\beta^2)]^{1/2} \tag{A18}$$

with branch-cuts $[-\varepsilon - w, -\varepsilon]$ and $[\varepsilon, \varepsilon + w]$, and $w = \sqrt{\varepsilon^2 + 4\beta^2} - \varepsilon$. Note that, if $z = E + iO^+$ and E lies within the valence or conduction band, so that $\varepsilon^2 < E^2 < \varepsilon^2 + 4\beta^2$, then $b(E + i0^+) = i \, \text{sgn} \, (E)\sqrt{4\beta^2 - \alpha^2}$. Substituting (A17) into (A15) yields

$$I_{|r'-r|}(z) = \frac{u_<^{|r'-r|}}{\beta^2 b(z)} \tag{A19}$$

which, together with (A12) to (A14), generates the expressions used in Sect. 3.

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10. Gopel W (1985) Prog Surf Sci 20:9. The chemisorption energy ΔE is related to the heat of adsorption q by $E = -\tfrac{1}{2}(D + q)$, where D is the dissociation energy of H_2. With $D = 4.48$ eV and $q = 8.3$ KJ/mole $= 0.86$ eV, $\Delta E = -2.67$ eV