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Chemisorption on composite systems

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Abstract. The chemisorption energy of hydrogen on composite systems, such as $\text{Cu/Ni}_x\text{Cu}_{1-x}$ and $\text{ZnO/Ni}_x\text{Cu}_{1-x}$, is investigated using the complex-energy-plane integration approach. The electronic properties of the composite substrate are described by using the Green function method within the framework of the tight-binding approximation. The coherent-potential approximation is used to cope with the alloys. The results are as follows. (1) The Cu (or ZnO) film which grows on the Ni or $\text{Ni}_x\text{Cu}_{1-x}$ substrates can weaken (or strengthen) the chemisorption of H. (2) The chemisorption properties can be modified by the alloy concentration. (3) A Cu (or ZnO) film of ten layers thickness can be taken as bulk Cu (or ZnO).

1. Introduction

It has been known that the most industrially important catalytic reactions employ supported catalysts, such as Ni/ZnO, Pt/ZnO and Ni/Al₂O₃ [1], and bimetallic catalysts [2, 3], such as Pt/W, Ru/Cu, Au/Pt, Cu/Pt and Cu/Ni. Therefore, the study of chemisorption of an atom on these composite systems is of particular interest. Many workers studied the composite systems by using experimental techniques. Prigge *et al* [4] studied the adsorption of CO and O on the Pd/W(110) system and found that the adsorption behaviours are quite different from that on bulk Pd. Shek *et al* [5] studied CO adsorption on the Cu/Pt system by using photoemission spectroscopy and thermal desorption spectroscopy. Paffett *et al* [6] studied the properties of Cu adsorption on Pt(111) and measured the work function of the Cu/Pt(111) system for different Cu coverages. Sachtler *et al* [7, 8] found that a Pt(100) surface covered with one monolayer of Au has a sixfold enhancement in reactivity with regard to cyclohexene dehydrogenation, while Au itself is inert for this reaction. However, very few quantum-mechanical studies on such composite systems have been performed, especially on the chemisorption on bimetallic systems. The Green function (GF) method and the Anderson–Newns theory have been used by Davison *et al* [9] to study the chemisorption of hydrogen on an Ni/ZnO composite substrate. They found that the chemisorption energy and the charge transfer depend on both the thickness of the Ni film and the Ni–ZnO coupling strength. The chemisorption on the inverse-supported catalyst ZnO/Ni was first studied by Liu and Davison [10]. Using the Green function method and the one-electron chemisorption theory of Einstein and Schrieffer (ES) [11], Zhang *et al* [12] studied the impurity effects on the chemisorption of hydrogen on supported catalysts, and found that impurities can weaken (e.g. Cu and Pt impurities) or strengthen (e.g. Co and W impurities) the chemisorption. Recently, the

present authors [13] studied the properties of CO chemisorption on $\text{Cu}/\text{Ni}_x\text{Cu}_{1-x}$ composite systems using the GF method and the coherent-potential approximation (CPA) [14] and found that the chemisorption properties could be modified by the thickness of the metal film and the concentration ratio of the two components in the alloy support. The present paper attempts to study the properties of hydrogen chemisorption on two kinds of composite system: $\text{Cu}/\text{Ni}_x\text{Cu}_{1-x}$ and $\text{ZnO}/\text{Ni}_x\text{Cu}_{1-x}$. These models can be used to study the H/Cu , $\text{H}-\text{ZnO}/\text{Cu}$ (for $x = 0$) and $\text{H}-\text{Cu}/\text{Ni}$, $\text{H}-\text{ZnO}/\text{Ni}$ (for $x = 1$) systems. When x changes from 0 to 1, we can see the effect of the alloy concentration on the chemisorption process.

We know that one particularly important phenomenon which occurs at alloy surfaces is surface segregation. In particular, for $\text{Ni}_x\text{Cu}_{1-x}$ alloy, the amount of Cu in the surface layer is substantially greater than that in a bulk layer. Such Cu enrichment has considerable theoretical and experimental support [15–17]. The present model, $\text{Cu}/\text{Ni}_x\text{Cu}_{1-x}$, can also be used to study the $\text{Ni}_x\text{Cu}_{1-x}$ system with Cu enrichment at the surface.

The one-electron chemisorption theory of ES [11] and the CPA [14] are used to calculate the chemisorption energy of H on these systems. The formalism is presented in section 2; the results and brief discussion are given in section 3.

2. Formalism

The model of the $\text{H}-\text{ZnO}/\text{Ni}_x\text{Cu}_{1-x}$ and $\text{H}-\text{Cu}/\text{Ni}_x\text{Cu}_{1-x}$ composite systems are shown in figure 1. The Hamiltonian for these systems can be written

$$H = E_a |a\rangle\langle a| + \beta (|a\rangle\langle 1| + |1\rangle\langle a|) + H_s \quad (1)$$

where E_a is the effective energy level of the adatom and β the hopping integral between the adatom and the surface atom of the substrate. H_s is the Hamiltonian for the substrate systems. Within the CPA [14] and the surface–bulk approximation (SBA) [18], H_s can be written as follows.

(a) For the $\text{ZnO}/\text{Ni}_x\text{Cu}_{1-x}$ system,

$$\begin{aligned} H_s = & \sum_{i=1}^{N_{sc}} [\alpha_s |2i-1\rangle\langle 2i-1| + \alpha_p |2i\rangle\langle 2i| + (\beta_2 |2i\rangle\langle 2i+1| - \beta_2 |2i-1\rangle\langle 2i| + \text{HC})] \\ & + (\gamma - \beta_2) (|n\rangle\langle n+1| + |n+1\rangle\langle n|) \\ & + \sum_{m=n+1}^{\infty} [(\alpha_v + \sigma_b) |m\rangle\langle m| - \beta_1 (|m\rangle\langle m+1| + |m+1\rangle\langle m|)] \\ & + (\sigma_s - \sigma_b) |n+1\rangle\langle n+1|. \end{aligned} \quad (2)$$

(b) For the $\text{Cu}/\text{Ni}_x\text{Cu}_{1-x}$ system,

$$\begin{aligned} H_s = & \sum_{m=1}^n \alpha_2 |m\rangle\langle m| - \sum_{m=1}^{n-1} \beta'_2 (|m\rangle\langle m+1| + |m+1\rangle\langle m|) \\ & + \sum_{m=n+1}^{\infty} [(\alpha_v + \sigma_b) |m\rangle\langle m| - \beta_1 (|m\rangle\langle m+1| + |m+1\rangle\langle m|)] \\ & + (\sigma_s - \sigma_b) |n+1\rangle\langle n+1| + \gamma (|n\rangle\langle n+1| + |n+1\rangle\langle n|). \end{aligned} \quad (3)$$

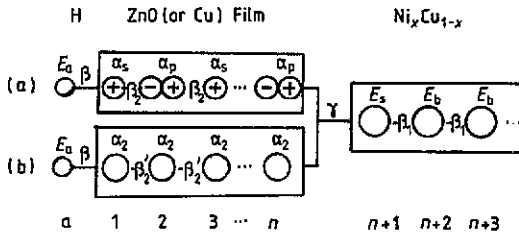


Figure 1. (a) The H-ZnO/Ni_xCu_{1-x} and (b) the H-Cu/Ni_xCu_{1-x} systems. $E_a = \alpha_v + \sigma_s$; $E_b = \alpha_v + \sigma_b$.

In equations (2) and (3), $\alpha_{s(p)}$ is the energy level of the s(p) orbital of the Zn(O) atom, $\pm\beta_2$ is the bond energy between Zn and O atoms, $N_{sc}(=n/2)$ is the number of layers of ZnO film, α_2 is the energy level of the Cu atom, $-\beta'_2$ is the bond energy between nearest-neighbour atoms in the Cu film, γ is the hopping integral between the ZnO (or Cu) film and Ni_xCu_{1-x}, α_v is the site energy level of the virtual crystal (VC) corresponding to Ni_xCu_{1-x}, $-\beta_1$ is the effective bond energy between nearest-neighbour atoms in Ni_xCu_{1-x}, and σ_b and σ_s are the coherent potentials introduced in Ni_xCu_{1-x} within the CPA, which can be determined self-consistently [14]. The surface GF in the Wannier representation is given by [9, 10]

$$G_{11}(Z, \sigma_b, \sigma_s) = g_2(1, 1) + \gamma^2 g_2(1, n) g_2(n, 1) / D \tag{4}$$

$$D = g_1^{-1}(n + 1, n + 1) - \gamma^2 g_2(n, n) \tag{5}$$

where $g_1(n + 1, n + 1)$ is a matrix element of the GF for the semi-infinite alloy [14] and $g_2(i, j)$ is a matrix element of the GF for the finite ZnO (or Cu) chain, which can be found in [9, 10]. Using the ES [11] theory and the complex-energy-plane integration approach [10], we can write the chemisorption energy as

$$\Delta E = -\frac{2}{\pi} \int_0^\infty \text{Re} f(E_F + iy) dy \tag{6}$$

where E_F is the Fermi level of the composite substrate,

$$f(Z) = -(Z - E_F)(\partial/\partial Z)\{\ln [1 - \beta^2 G_{aa}(Z)G_{11}(Z, \sigma_b, \sigma_s)]\} \tag{7}$$

where $G_{aa}(Z) = (Z - E_a)^{-1}$ is the GF of the adatom.

3. Results and discussions

The energy zero is chosen to be at the vacuum level. For the specific systems H-ZnO/Ni_xCu_{1-x} and H-Cu/Ni_xCu_{1-x}, the effective energy level of the adatom H is at -7.15 eV [10]. The parameters for ZnO are [9, 10, 19] $\alpha_s = -4.50$ eV, $\alpha_p = -7.90$ eV, $E_{F2} = -4.7$ eV and $\beta_2 = 3.755$ eV. The parameters for pure Cu and Ni are listed in table 1. The parameters for the Ni_xCu_{1-x} alloy are given by [14]

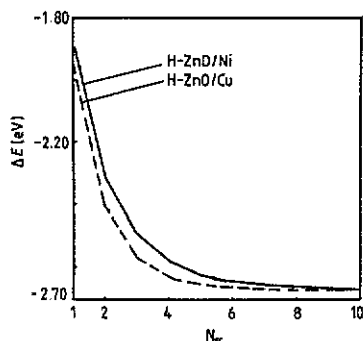
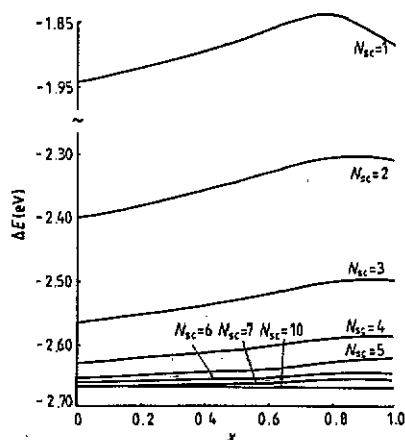
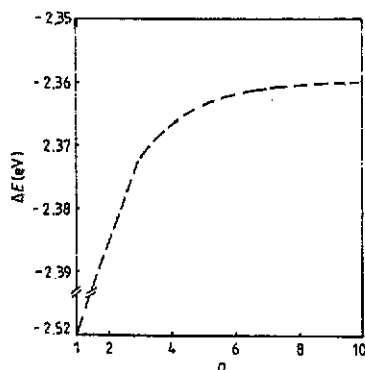
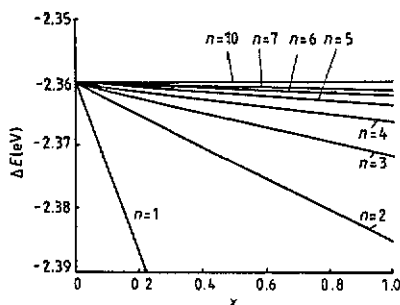
$$E_{F1} = xE_{FA} + (1 - x)E_{FB}$$

$$\beta_1 = x\beta_A + (1 - x)\beta_B.$$

The ZnO (or Cu)-Ni_xCu_{1-x} bond $\gamma = [\beta_1 + \beta_2 \text{ (or } \beta'_2)]/2$. The H-ZnO (or Cu) bond β is chosen to be such a value that the resulting ΔE for H chemisorption on the pure ZnO (or Cu) substrate is very close to the experimental value. The calculated results are shown in figures 2-5.

Table 1. Parameters for pure metals [14].

	Ni	Cu
$\alpha_{A(B)}$	-6.26	-7.37
$E_{FA(B)}$	-4.50	-4.46
$\beta_{A(B)}$	0.95	0.675

Figure 2. ΔE for the system H-ZnO/Ni (or Cu) versus N_{sc} , the number of layers of ZnO film.Figure 3. ΔE for the system H-ZnO/Ni_xCu_{1-x} versus x for different N_{sc} .Figure 4. ΔE for the system H-Cu/Ni versus n , the number of layers of Cu film on the Ni substrate.Figure 5. ΔE for the system H-Cu/Ni_xCu_{1-x} versus x for different n .

The chemisorption energy ΔE of atomic hydrogen on the ZnO/Ni (or Cu) substrate as a function of the number of layers of ZnO ($N_{sc} = n/2$) is shown in figure 2. It shows that the chemisorption properties of atomic hydrogen on the ZnO/Ni and ZnO/Cu composite systems are similar to each other; the chemisorption energy decreases with increase in thickness of the ZnO film and gradually approaches that of pure ZnO case.

Figure 3 shows ΔE for the system H-ZnO/Ni_xCu_{1-x} versus x , the bulk Ni concentration in the Ni_xCu_{1-x} alloy, for different N_{sc} . When x is very close to 1, the

system H-ZnO/Ni_xCu_{1-x} is similar to the H-ZnO/Ni (Cu impurity) system of Zhang *et al* [12], and the chemisorption energy is higher than that of H-ZnO/Ni system; this means that Cu impurities contained in the Ni substrate can weaken the chemisorption, in agreement with the results of Zhang *et al* [12]. For higher Cu concentrations ($x < 0.8$), the chemisorption can be strengthened on increase in the Cu concentration. We can also find that, the smaller N_{sc} , the more important are the effects of the concentration x on the chemisorption. For a definite x , the chemisorption energy decreases with increase in N_{sc} , corresponding to stronger chemisorption. When N_{sc} reaches 10, ΔE is independent of x . When $x = 0.8$, there are maxima in some of the ΔE versus x curves. We can predict that the chemisorption is relatively unstable there, and this will be discussed further later.

Figure 4 shows the chemisorption energy ΔE of H on the Cu/Ni system for different n , the number of layers of Cu film. We find that the chemisorption energy increases and gradually approaches that of H on bulk Cu ($\Delta E(\infty)$) with an increase in n . This means that the chemisorption can be weakened as the Cu film grows on the Ni support. For $n \geq 10$, we find that $\Delta E = \Delta E(\infty)$; therefore a Cu film of ten layers thickness can be taken as bulk Cu. Figure 5 shows the curves of ΔE versus the bulk Ni concentration x for different n . They show that

- (1) when $x = 0$, $\Delta E = -2.36$ eV for all different n , corresponding to H on a pure bulk Cu substrate,
- (2) when $x = 1$, the results are the same as those shown in figure 2,
- (3) for a definite n , ΔE decreases with increase in the Ni concentration x , corresponding to stronger chemisorption,
- (4) for a definite x , ΔE increases with increase in n , which means that the chemisorption was weakened as the Cu film grows on the Ni_xCu_{1-x} alloy substrate, similar to that of H on segregated Ni_xCu_{1-x} [14] and
- (5) when $n \geq 10$, ΔE does not change with x and so we can also predict that a Cu film of ten layers thickness can be taken as bulk Cu.

These results are similar to those on CO-Cu/Ni_xCu_{1-x} in [13].

From the discussion above, we can summarize our results as follows.

- (a) The ZnO film which grows on the Ni, Cu or Ni_xCu_{1-x} substrates can strengthen the chemisorption of H; a Cu film which grows on the Ni or Ni_xCu_{1-x} substrates can weaken the chemisorption.
- (b) The chemisorption properties of the H on ZnO/Ni_xCu_{1-x} system can be modified by the alloy concentration, and the chemisorption of H on Cu/Ni_xCu_{1-x} system can be strengthened by increasing the Ni concentration in Ni_xCu_{1-x}.
- (c) A ZnO (or Cu) film of ten layers thickness can be taken as bulk ZnO (or Cu).

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