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Research of the behaviour of O chemisorption on the (110) surface of Rh_x–Pt_{1-x} alloy*

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An atomic group model of the disordered binary alloy Rh_x–Pt_{1-x} has been constructed to investigate surface segregation. According to the model, we have calculated the electronic structure of the Rh_x–Pt_{1-x} alloy surface by using the recursion method when O atoms are adsorbed on the Rh_x–Pt_{1-x}(110) surface under the condition of coverage 0.5. The calculation results indicate that the chemical adsorption of O changes greatly the density of states near the Fermi level, and the surface segregation exhibits a reversal behaviour. In addition, when $x < 0.3$, the surface on which O is adsorbed displays the property of Pt; whereas when $x > 0.3$ it displays the property of Rh.

Keywords: chemisorption, surface segregation, recursion method, density of states
PACC: 7320, 6822, 7120

1. Introduction

The adsorption of O on Rh and Pt surfaces has been studied extensively in the past.[1,2] Apart from a fundamental intrinsic interest, such studies have been motivated by the fact that Rh and Pt catalyse several important heterogeneous oxidation reactions such as the oxidation of poisonous automotive exhaust gases NO and CO and the oxidation of NH_3 in the nitric acid synthesis. Compared with pure metals, alloys are the more important catalysts,[3,4] so the investigation of Rh_x–Pt_{1-x} alloy surface is very important.

Surface segregation is a typical phenomenon of alloys besides surface relaxation and surface reconstruction.[5] The surface segregation influences the chemisorption of adsorbent, which in turn influences the process of surface segregation, so there is strong coupling between chemisorption and surface segregation.[6,7] To obtain catalysts with different properties and efficiency, one kind of adsorbent was chosen to study the chemisorption by changing the component concentration. In this study, we have constructed the models of Rh_x–Pt_{1-x} alloy with different bulk Rh concentrations x for a close investigation of the mutual influence between chemisorption and multiplayer surface segregation. We hope that it can provide a certain theoretical basis for further studies on the design of alloys for various catalysts.

2. The model and methodology

2.1. The model of the (110) surface of the Rh_x–Pt_{1-x} alloy before and after chemisorption

The atomic structure model of the disordered binary alloy (DBA) Rh_x–Pt_{1-x} is constructed for different bulk Rh concentrations under the condition of whether the surface segregation exists or not. The method of constructing the model and the model parameters are described as follows. Each model is a big cubic cluster which contains 512 crystal cells and 1241 atoms. Three perpendicular basic vectors of the crystal cell $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ are all equal to the crystal lattice constant a ($a = x \times a_{\mathrm{Rh}} + (1-x) \times a_{\mathrm{Pt}}$). The O atoms are adsorbed on the interstitial sites of the (110) surface of the Rh_x–Pt_{1-x} cluster consisting of many unit cells. The basic vectors of this unit cell, $\boldsymbol{a}_{\mathrm{s}}$ and $\boldsymbol{b}_{\mathrm{s}}$, are $\boldsymbol{a}/\sqrt{2}$ and $\boldsymbol{a}$, respectively. The coverage of the O/Rh–Pt system is 0.5. The adsorbed structure of O on the (110) surface of Rh_x–Pt_{1-x} cluster is $\boldsymbol{c}(2\times2)$. The distance between the absorbed O and the (110) surface atom is 0.085nm. Using the stochastic distribution

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computer program, we construct two surface models: the first model is constructed for the case that original surface segregation is considered, the second one is constructed for the case that chemisorption induced surface segregation is considered. Figure 1 shows the atomic structure model before and after adsorbing O, where (a) is the multilayer projection of the model in Z direction before adsorbing O, (b) is the monolayer projection of the model in Z direction after adsorbing O.

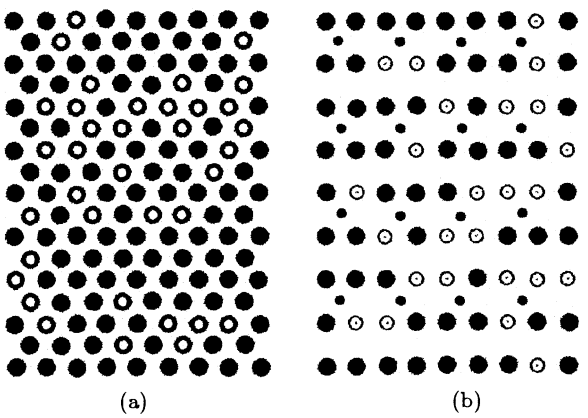


Fig.1. Atomic structure model of the (110) surface of Rh_x–Pt_{1-x} (The projection of the model in Z direction; Where ● refers to Rh atoms, ⊙ refers to Pt atoms, • refers to O atoms).

2.2. Theoretical method

According to the recursion method and the tight-binding approximation, the structural energy at some site i is the integral of $n_{\alpha i}(E)$, namely $U_i = \sum_{\alpha} \int_{-\infty}^{E_f} E n_{\alpha i}(E)\,\mathrm{d}E$, and the total energy of the system can be given by the sum of U_i, namely, $U = \sum_i U_i$. The Fermi level of the system is determined by $Z = \sum_{\alpha i} \int_{-\infty}^{E_f} n_{\alpha i}(E)\,\mathrm{d}E$. The environmental sensitive inlaid energy E_{ses} of the atoms in the surface layers can be written as: $E_{ses} = \frac{1}{mn}\left[E^i - E^{cl} + nE_f^i - nE_f\right]$, where m is the total number of atoms we calculate, E^i and E^{cl} are respectively the total structural energy when some atom (e.g. Rh) enrichments on the alloy surface are considered or not. "n" is the difference in number of that kind of atoms in the two cases. E_f^i and E_f are the free energy of the two types of atoms respectively. The more detailed formula can be seen in Refs.[8–10].

3. Results and discussion

3.1. Density of states (DOS)

The local density of states (LDOS) of single Rh and Pt atoms in the first three layers before and after chemisorption are compared to reveal the influence of O atom adsorption on the Rh_x–Pt_{1-x} (110) by the energy curve. The model of Rh_x–$Pt_{1-x}$with the bulk Rh concentration 0.7 is chosen. We assume that the relative positions of the Rh and Pt atoms on the surface are unchanged when O atoms are adsorbed on the surface. The LDOS curves of Rh atoms in the first three layers before and after chemisorption are given in Fig.2. Comparing Figs.2(a) and 2(b), we can see that the chemisorption of O make the LDOS curves of Rh atoms lowered, and changed from three inconspicuous peaks to two big clear peaks near the Fermi level (E_F). At the same time, the LDOS curve of O atom displays a clear double-peak structure, but for a single O atom, the curve must be a gentle one. So we can conclude that the Rh atom must have lost electrons, and the O atom must obtain electrons, and there is strong coupling between them. Figure 3 is the LDOS curves of Pt atoms in the first three layers, the trend of the curves are similar with that of Rh atoms.

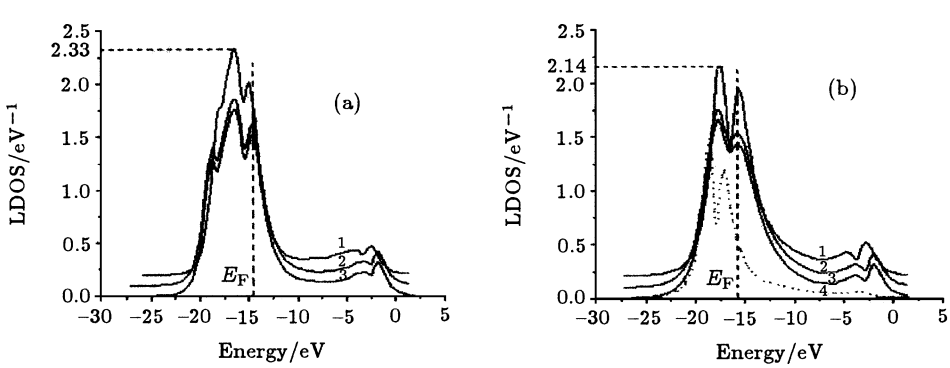


Fig.2. LDOS of Rh atoms before (a) and after (b) chemisorption. 1, 2 and 3 refer to the Rh atoms in the first, second and third layer. 4 refers to the LDOS of O atom after chemisorption.

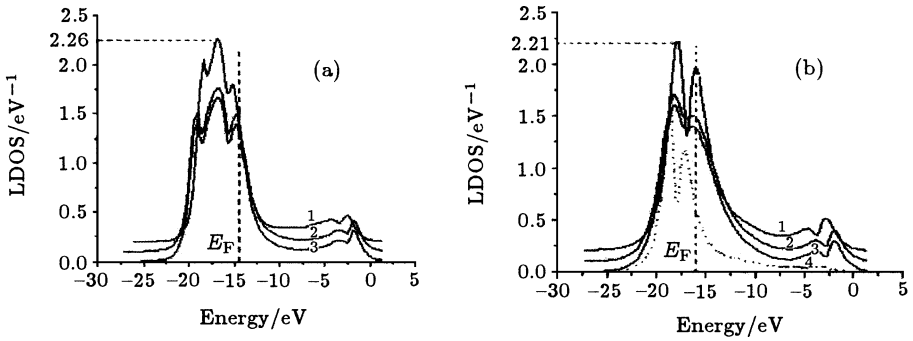


Fig.3. LDOS of Pt atoms before (a) and after (b) chemisorption. 1, 2 and 3 refer to the Pt atoms in the first, second and third layer. 4 refers to the LDOS of O atom after chemisorption.

3.2. Environment sensitive inlaid energy (E_{ses})

Tables 1 and 2 show the environment sensitive inlaid energy (E_{ses}) for the Rh_x–Pt_{1-x} alloy before and after chemisorption corresponding to the Rh bulk concentration x=0.7. In the case of no chemisorption, the E_{ses} of Rh atom is greater than that of Pt atom in the first and third layer, but smaller in the second layer, which means that the Rh_x–Pt_{1-x} alloy possesses an enriched Pt concentration in the first and third layer, and an enriched Rh concentration in the second layer. In the case of chemisorption, the situation is just the opposite, so the chemisorption of O causes a reversal of the surface segregation of the Rh_x–Pt_{1-x} alloy. By comparing the ΔE_{ses} of Rh and Pt atoms in the first three layers in Tables 1 and 2, we can see that the ΔE_{ses} in the first layer is the biggest, so we can conclude that the phenomenon of surface segregation mainly takes place in the first layer. The results are in agreement with Ref.[11].

Table 1. The E_{ses} of Rh and Pt atoms in the first three layers before chemisorption.

E_{ses}/eV	Rh	Pt	ΔE_{ses}
The first layer	0.0948	–2.3772	2.4720
The second layer	–1.9158	–0.1117	1.8041
The third layer	–2.3349	–2.3510	0.0161

Table 2. The E_{ses} of Rh and Pt atoms in the first three layers after chemisorption.

E_{ses}/eV	Rh	Pt	ΔE_{ses}
The first layer	–2.3562	–1.0424	1.3138
The second layer	–1.9804	–2.3475	0.3671
The third layer	–2.3238	–2.3045	0.0193

3.3. Total structural energy

In order to discuss the relationship between the chemisorption of O and the surface property of Rh_x–Pt_{1-x} alloy for x over 0–1, we calculate the total structural energies of O/Rh–Pt system in four cases: namely, when the segregation of the non-adsorbed surface exists or not, and when the chemisorption-induced surface segregation is taken into account or not. The total structural energy in each case is the sum of the structural energies of all atoms in a cuboid. The method to determine the cuboid of the O/Rh–Pt system is as follows. The XOY plane on the Rh_x–Pt_{1-x} (110) surface is built according to a coordinate shifting program we wrote. For the interstitial site chemisorption, the cuboid centre is set on a site on top of which there is an O atom. The length, width and height of the cube are 0.139nm, 0.197nm and 0.278nm, respectively. The cube includes 10 atoms among which there are one O atom and different numbers of Rh and Pt atoms over all the x range.

Figure 4 shows that the total structural energy increases with the increasing bulk Ph concentration x since the free energy of Rh (–136.03eV) is larger than that of Pt (–155.80eV). When segregation is not considered before chemisorption, the curve of the structural energy displays nearly linear behaviour (curve A). When segregation is considered, the energy of the Rh_x–Pt_{1-x} system increases slowly at first, but when $x > 0.6$, the energy increases quickly as shown by curve B, thus the property of the Rh_x–Pt_{1-x} surface is insensitive to the bulk Rh concentration below $x < 0.6$. Similar to curve B, when the interaction between chemisorption and surface segregation is not considered (curve C), the total structural energy decreases because of the negative energy of O atom. When the interaction between chemisorption and surface segregation is considered, the increase of the total structural energy can be observed in curve D, which means an enrichment of the Rh concentration in the surface layers. Furthermore, when $x < 0.3$, the system of O/Rh–Pt displays the property of Pt atom, whereas when $x > 0.3$ the property of Rh atom.

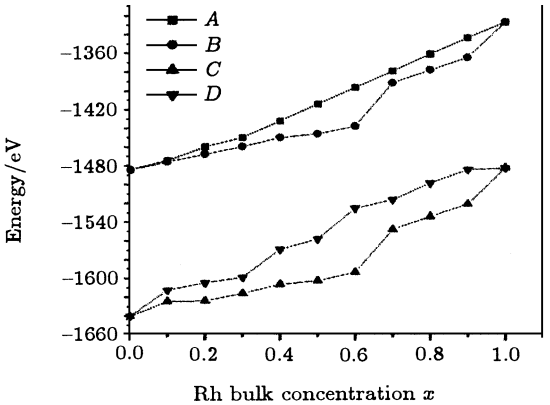


Fig.4. Total structural energies corresponding to the bulk Rh concentration x=0–1. Curve A refers to the situation when surface segregation before chemisorption is not considered, and B when it is considered. Curve C refers to the situation when chemisorption-induced surface segregation after chemisorption is not considered, and curve D when it is considered.

4. Summary and conclusions

We have built the atomic structural models of the Rh_x–Pt_{1-x} (x=0–1) disordered binary alloy for the cases when surface segregation exists or not. Then the modes of chemisorption of O on the alloy Rh_x–Pt_{1-x} surface were constructed. Using the computer program, we calculated the electron structure, the environmental sensitive inlaid energy and the total structural energy . It is found that for the O/Rh–Pt system, chemisorption of O makes the curve of the density of states change greatly near the Fermi level, and the surface segregation exhibits a reversal behaviour. In addition, when $x < 0.3$, the surface on which O adsorbed displays the property of Pt; whereas when $x > 0.3$ the property of Rh.

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