Interface quantum trap depression and charge polarization in the CuPd and AgPd bimetallic alloy catalysts

Chang Q. Sun,*ab Yan Wang,a Yan Guang Nie,a B. R. Mehta,c M. Khanuja,c S. M. Shivaprasada, Yi Sun,e Ji Sheng Pan,e L. K. Panf and Zhuo Sunf

Received 29th October 2009, Accepted 13th January 2010
First published as an Advance Article on the web 10th February 2010
DOI: 10.1039/b922677j

The ability of a catalyst to accept or donate charge is the key to the process of catalytic reaction. However, the determination of the catalytic nature of a specimen as yet remains a great challenge. Here we report an effective yet simple method for this purpose based on the tight binding theory and XPS monitoring of the evolution of valence and core electrons upon alloy formation. Firstly, we measured the valence and core band charge density of the constituent elements of Cu, Ag, and Pd and then the respective states upon alloy formation. A subtraction of the resultant spectrum of the alloy by the composed elemental spectra gives the residual that shows clearly the occurrence of charge trapping or polarization. We found that the valence and the core electrons of the CuPd alloy shift positively to deeper energies, opposite to the occurrences in the AgPd alloy. Findings clarify for the first time that CuPd serves as an acceptor due to quantum trapping and the AgPd as a donor because of charge polarization, which also explain why AgPd and CuPd perform very differently as important catalysts.

1. Introduction

Bimetallic alloy interfaces have been a subject of extensive study because the formation of interfacial metal–metal bonds can produce large perturbations to the Hamiltonian, binding energy density, atomic cohesive energy, and hence the catalytic, electronic, dielectric, optic, mechanical, and thermal properties, making them completely different from those of the constituent metals.1,2 The study of the interface alloys is motivated by their use in many industrial applications, such as in searching for new catalysts,3,4 sensors and testing electronic devices. Varying the composition or thermal annealing upon continuous deposition of dissimilar metals5,6 has provided an effective method to modify interatomic strain and redistribute charge around the bonded atoms.7,8

Ag and Cu are often paired with Pd because their interaction typically results in an improved heterogeneous catalyst.9–11 But AgPd and CuPd alloys behave quite differently in catalytic reactions.12 CuPd is active for CO and alkene oxidation, CO, benzene, toluene, and 1,3-butadiene hydrogenation and ethanol decomposition.13 CuPd alloys are also promising catalysts for NO reduction with CO. AgPd alloy is a good candidate for hydrogen reaction and permeation.14,15 Both Ag and Cu grow on Pd in a layer-by-layer fashion at room temperature without any apparent signatures of alloy formation.5,16,17

In the process of catalytic reaction, the direction of charge transfer is a key concern because the reactivity depends on the degree of filling of antibonding states and the degree of orbital overlapping between the catalyst and the adsorbate.18,19 Although the catalytic behavior of CuPd and AgPd bimetallic alloys have been extensively investigated,5,12,20–23 the laws governing the energetic behavior of the core and valence electrons and their catalytic nature are yet to be established. This communication aims to show a simple method that determinine the catalytic nature of these two alloys as exemplars. We found that the opposite directions of the valence and core charge polarization determines why AgPd and CuPd perform differently and that the concepts of quantum trapping (QT) and charge polarization are necessary when one deals with the interface electrons.

2. Principles

The principles for quantum trap depression and charge polarization at atomic sites of an impurity or at the heterojunction interfaces are very simple. The distribution of the density of states (DOS) in the valence and a core band of a material is determined by two factors. One is the interatomic interaction represented by the periodic crystal potential, V_{eff}(r, B), experienced by electrons in the specimen, which determines the energy shift and the allowed states in a particular band. The other is the actual occupation of the allowed states.
The presence of nonbonding electrons such as the nonbonding lone pairs and antibonding dipoles in oxides\textsuperscript{24} and nitrides,\textsuperscript{25} the nonbonding unpaired \pi-electrons in carbon,\textsuperscript{26} and the otherwise conducting electrons in the half-filled s-shell of noble metals such as Au and Rh,\textsuperscript{27} will generate new states in the otherwise conducting electrons in the half-filled s-shell of noble metals. In the interface region, if the atomic coordination number, \( n_\text{cryst} \), becomes large, the bond nature alteration associated with charge repopulation becomes significant.\textsuperscript{28} If the QT or polarization proceeds in the interface region, the crystal potential for each constituent will become more energy dependent than that of the alloy.\textsuperscript{29} In the interface region, the constituent materials produce a mixture of charge densities of the constituent elements. The bond energy, \( E_\text{B} \), is the cohesive energy per bond. For an alloy or a compound, the core band may be subject to change due to the modification of the crystal potential resulting from bond nature alteration and possible strains. However, the valence DOS is a mixture of valence charges of the constituent elements, and the resultant spectrum of the alloy should give fingerprints of such processes.

In the interface region, the constituent materials produce a mixture of chemical composition due to the diffusion of the constituent atoms.\textsuperscript{29} If the QT or polarization proceeds in the interface region, the crystal potential for each constituent will become more energy dependent than that of the alloy.\textsuperscript{29} Under equilibrium conditions, \( V_{\text{cryst}}(r, B) = E_\text{B} \) is the cohesive energy per bond. For an alloy or a compound, the core band may be subject to change due to the modification of the crystal potential resulting from bond nature alteration and possible strains. However, the valence DOS is a mixture of valence charges of the constituent elements, and the resultant spectrum of the alloy should give fingerprints of such processes.

The energy shift of a band is governed by the overlap and exchange integrals.\textsuperscript{28} Under equilibrium conditions, \( V_{\text{cryst}}(r, B) = E_\text{B} \) is the cohesive energy per bond. For an alloy or a compound, the core band may be subject to change due to the modification of the crystal potential resulting from bond nature alteration and possible strains. However, the valence DOS is a mixture of valence charges of the constituent elements, and the resultant spectrum of the alloy should give fingerprints of such processes.

In the interface region, the constituent materials produce a mixture of chemical composition due to the diffusion of the constituent atoms.\textsuperscript{29} If the QT or polarization proceeds in the interface region, the crystal potential for each constituent will become more energy dependent than that of the alloy.\textsuperscript{29} Under equilibrium conditions, \( V_{\text{cryst}}(r, I) = \gamma V_{\text{cryst}}(r, B) \), where \( \gamma \) is the bond energy reduced by that of the ideal bulk constituent. The energy shift of the resultant valence charge and the core electrons of the alloy will increase, rendering that of the \( B \) as the total number of electrons in the particular level is conserved. The intensity evolution reflects the extent of alloy formation.

3. Experiment

In order to verify the proposed mechanism of the interface QT and charge polarization, we first deposited Cu (2 nm) and Ag (2 nm) thin films, respectively, onto a Pd (10 nm) substrate on an Si wafer using a physical vapor-deposition system.\textsuperscript{6} The deposition was achieved by alternating thermal evaporation of Pd (99.99\%) and Cu (99.99\%), and Ag (99.99\%), at a base pressure of 2.7 \texttimes 10^{-4} \text{ Pa} from respective alumina-coated tungsten boats. A single-crystal quartz sensor interfaced with deposition controller (Heviac) was used to monitor the film thickness, and the evaporation rate was 0.1 nm s\textsuperscript{-1}.

XPS measurements were then performed in an ultrahigh vacuum chamber (PHI 1257) with a base pressure of 5.3 \times 10^{-8} \text{ Pa}. The XPS spectrometer is equipped with a...
high-resolution hemispherical electron analyzer (279.4 mm diameter with 25 meV resolution) and Al Kα (hv = 1486.6 eV) X-ray anode as the photon source. All XPS data were corrected for electrostatic charging using the XPS lines of remnant C (1s) as internal reference energy.

To investigate the DOS evolution of the AgPd and the CuPd interface alloying states, XPS spectra were collected upon sample cooling to 300 K as a function of isochronal annealing (1 min) at increasingly high temperature for CuPd (up to 940 K) and for AgPd (573 K) until the 2 nm adlayers show complete alloying. Each spectrum was deconvoluted into two Gaussian components. The valence band was measured under the same conditions. Before measuring the valence and core DOS of the alloys, we had measured the corresponding spectrum for the pure constituent for comparison purposes.

4. Results and discussion

4.1 Valence charge evolution

Fig. 2 compares the normalized valence DOS of pure Ag, Cu, and Pd. The valence DOS of Pd is in the energy range of 0–6 eV and the DOS of Cu covers 2–6 eV. The DOS for Ag is in the range of 4–7 eV. These DOS are very much the same as reported in refs. 20–22. In order to gain information about the valence charge polarization, we averaged the valence DOS spectra of the pairing constituents, for instance, [(n(Cu) + n(Pd))/2, and then subtracted the average from the resultant DOS of the alloy: \( \Delta n(CuPd) = n(CuPd) - (n(Cu) + n(Pd))/2 \). This spectral difference (solid lines) exhibits clearly the direction of valence charge polarization upon alloy formation, as denoted by arrows in Fig. 3. Ideally, the sum of the area covered by the solid line and the x-axis should be zero if the net charge density is conserved. It is exciting to note that for the CuPd alloy, the valence charge migrates from the upper to the bottom edge of the valence band while for the AgPd alloy the valence charge polarizes in an opposite direction. We can call the former quantum trapping and the latter charge polarization. Applying the same process to the valence DOS of Cu, Pd, and CuPd alloy collected by Matensson et al.,20 Rochefort et al.,21 and Barnes et al.23 attained the same result and conclusion. The QT generates electronic holes in the upper edge of the valence band, thus the CuPd can serve as a charge acceptor in the process of catalytic reaction. Comparatively, the polarization of AgPd shifts the valence DOS up to generate excessive electrons at the upper edge, which makes AgPd alloy to serve as a charge donor in the process of catalytic reaction. The distinctive directions of valence charge polarization should differentiate the catalytic performance of these alloys.

It is noted that the QT in the CuPd disobey the rule of electronegativity difference. This contradiction suggests that interface QT does occur due to the lattice strain and alloy bond formation. Low-energy electron and photoelectron diffraction studies confirmed that the Cu–Pd distance contracts up to \( \pm 2.5\% \).23,32,33 This finding favors the explanation\(^1\) that the under-coordinated Cu atom, having a half occupied 4s\(^1\) band, accepts charge from the Pd 4d\(^{10}\) valence band that is fully occupied, though the electronegativity of Cu (1.9) is lower than that of Pd (2.2). However, the electronegativity of Ag (1.9) is the same as Cu, but the AgPd shows charge polarization, instead. The possible reason for the polarization direction difference could be the number of electron shells. Electrons in the half-filled s-orbit of Ag (5s\(^1\)) tends to be polarized more readily than those in the Cu (4s\(^1\)). The charge polarization also happens to Au (6s\(^1\)) and Rh (5s\(^1\)) but not...
the Pt(6s\(^6\)) as we found recently,\(^27\) at sites with localized strain. Nevertheless, the discrepancy in the charge transferring direction of Cu and Ag upon alloy formation is an interesting issue that needs further investigation.

### 4.2 Core band DOS evolution

Fig. 4 shows the intensity evolution of the Cu 2p\(_{3/2}\), Ag 3d\(_{5/2}\), and Pd 3d\(_{5/2}\) spectra collected after annealing at two typically given temperatures in the respective alloys. The intensity inversion of the I and the B components at the given temperatures indicate the completeness of interface alloying of the 2 nm-thick surface layers.

Table 1 summarizes the information about the XPS spectrum evolution during CuPd and AgPd alloy formation. Only three of five measurements at different temperatures are shown. For the CuPd alloy, the core bands shift from the B to the I component positively while for the AgPd alloy the core bands shift negatively, being consistent with the valence charge polarization directions. The separation between the I and the B component represents the additional QT depth.

In order to extract quantitative information about the absolute values of the QT depth from the XPS data, we need the values of \(\Delta E_n(B)\) for each constituent. In the previous theoretical reproduction of the measured size dependence of the Cu 2p\(_{3/2}\)\(^34\) and the Pd 3d\(_{5/2}\)\(^35\) core level shift, we have derived that the \(\Delta E_n(B)\) for Cu 2p\(_{3/2}\) and Pd 3d\(_{5/2}\) are 1.70 and 3.98 eV, respectively. These data allow us to estimate the \(\gamma\) values for the QT with the resolved \(\Delta E_n(I) - \Delta E_n(B)\), as listed in Table 1. Results in Table 2 indicate that the \(\gamma\) values for Pd and Cu in the CuPd are \(~1.40\) and \(~1.94\), respectively. The corresponding core level shift are 5.53 and 3.28 eV in comparison to the bulk values of 3.98 and 1.70 eV for Pd 3d and Cu 2p levels. Similarly, the \(\gamma\) values for Pd and Ag in the AgPd alloy are estimated to be 0.69 and 0.56. The potential barrier heights of Ag and Pd in the AgPd alloy are 3.98 \(\times\) 2.76 = 1.22 eV and 1.18 eV. According to the tight binding approximation, the core level shift is proportional to the equilibrium bond energy. The findings indicate that the CuPd interface bond become stronger while the AgPd interface bond weaker.

![Fig. 4](image_url) Thermally-driven spectral evolution of (a) Cu 2p\(_{3/2}\) and (b) Pd 3d\(_{5/2}\) BE in the CuPd interface upon annealing at 540 and 940 K and (c) Ag 3d\(_{5/2}\) and (d) Pd 3d\(_{5/2}\) BE in the AgPd interface upon annealing at 300 K and 573 K and their decompositions. The CuPd alloy demonstrates QT, while the AgPd alloy polarization.
Table 2  Summary of the relative depths $\gamma$ and the interface energy shift $\Delta E_{i}(B)$ for the Pd 3d$^{3/2}$, Ag 3d$^{3/2},$ and Cu 2p$^{3/2}$ core levels in the CuPd and the AgPd alloy interfaces

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E$-levels</th>
<th>$E_{c}(I)$</th>
<th>$\Delta E_{i}(B)$</th>
<th>$\Delta E_{i}(B) - \Delta E_{i}(I)$</th>
<th>$\gamma$</th>
<th>$\Delta E_{i}(I)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Pd</td>
<td>Cu 2p$^{3/2}$</td>
<td>1.70$^{34,37}$</td>
<td>931.00</td>
<td>1.58</td>
<td>1.94</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>Pd 3d$^{3/2}$</td>
<td>3.96$^{35,37}$</td>
<td>330.34</td>
<td>1.55</td>
<td>1.38</td>
<td>5.53</td>
</tr>
<tr>
<td>Ag-Pd</td>
<td>Pd 3d$^{3/2}$</td>
<td>-1.22</td>
<td>2.69</td>
<td>0.69</td>
<td>2.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag 3d$^{3/2}$</td>
<td>332.86</td>
<td>-1.18</td>
<td>0.56</td>
<td>1.51</td>
<td></td>
</tr>
</tbody>
</table>

5. Conclusion

In summary, we have developed an effective yet a simple approach of identifying the direction of valence and core charge polarization and the interfacial QT depth of the CuPd and AgPd bimetallic alloys. It is discovered that a positive shift occurs to the valence and core electrons of CuPd alloy due to the QT effect but the electrons in the AgPd alloy shift in an opposite direction due to the charge polarization. The rule of electronegativity difference may not always be followed in bimetallic alloys. The different directions of polarization may distinguish the CuPd from the AgPd in their catalytic functionality. The CuPd is suggested to serve as an acceptor and the AgPd as a donor in the process of catalytic reaction. The concepts of QT and charge polarization are essential for one to deal with bimetallic alloy interfaces.

Acknowledgements

Financial supports from Nanyang Technological University and A*Star, Singapore, Nature Science Foundation (Nos.10772157) of China, are all gratefully acknowledged.

References