Interface atom mobility and charge transfer effects on CuO and Cu$_2$O formation on Cu$_3$Pd(111) and Cu$_3$Pt(111)

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We bombarded Cu$_3$Pd(111) and Cu$_3$Pt(111) with a 2.3 eV hyperthermal oxygen molecular beam (HOMB) source, and characterized the corresponding (oxide) surfaces with synchrotron-radiation X-ray photoemission spectroscopy (SR-XPS). At 300 K, CuO forms on both Cu$_3$Pd(111) and Cu$_3$Pt(111). When we increase the surface temperature to 500 K, Cu$_2$O also forms on Cu$_3$Pd(111), but not on Cu$_3$Pt(111). For comparison, Cu$_2$O forms even at 300 K on Cu(111). On Cu$_3$Au(111), Cu$_2$O forms only after 500 K, and no oxides can be found at 300 K. We ascribe this difference in Cu oxide formation to the mobility of the interfacial species (Cu/Pd/Pt) and charge transfer between the surface Cu oxides and subsurface species (Cu/Pd/Pt).

Metal oxides have long attracted researchers’ attention, particularly the role of metal valence electrons in determining structure and properties\cite{1,2}. Manganese (Mn) in Mn oxides, for example, can take on more than one oxidation state (mixed valency). MnO$_2$ exhibit better catalytic activity than MnO\cite{3}. Copper (Cu) oxides also attract particular attention, due to their utility, industrial applications, abundance, low-cost, and non-toxicity. Cu$_2$O and CuO, two of the most common forms of Cu oxides, find applications as anodes in lithium ion battery\cite{4} and solar cells\cite{5}. Copper oxides are also expected to be used as catalysts for CO\cite{6}, NO dissociation\cite{7}, and O$_2$ adsorption, as compared to Cu(111)\cite{8–11}. Similarly, the catalytic reactivities of Cu oxides vary with the Cu oxidation state. Several factors determine oxide formation on the surface, e.g., translational and internal (vibration and rotation) energies of impinging O$_2$, surface temperature, and surface electronic state\cite{12,13}. Alloying allows for a simple way to vary the surface electronic state and the corresponding reactivity. For example, by alloying Cu with gold (Au) and tuning the surface composition, previous studies tried to enhance the activity and selectivity of Cu–Au nano-particle catalysts for CO\cite{14} reduction, NO dissociation\cite{15}, and O$_2$ adsorption, as compared to Cu(111)\cite{16–20}. At surface temperature $T_s = 300$ K, Au-rich layers, formed between the bulk and surface, prevent Cu oxide formation further into bulk. Atom diffusion at $T_s = 500$ K promotes Cu$_2$O formation, but leaves a protective Au-rich layer that prevents further oxidation into the bulk. On the other hand, Cu–palladium (Pd) alloys synergistically enhanced CO$_2$ hydrogenation to alcohol, as compared to mono-metallic catalysts\cite{21,22}. Cu–platinum (Pt) alloys, viz., Pt$_{34.5}$Cu$_{65.5}$, also showed superior methanol oxidation and oxygen reduction performance\cite{23}. Moreover, single Pt atoms at the Cu metal-oxide interface promote the reduction of Cu$_2$O by H$_2$ exposure\cite{24}. These results indicate that choosing the right alloy components strongly affect reactivity. Here, we report on how alloying Cu with Pd and Pt, elements known to be more reactive than Au, affects oxidation of the corresponding surfaces. We bombarded Cu$_3$Pd(111) and Cu$_3$Pt(111) with a 2.3 eV hyperthermal oxygen molecular beam (HOMB) source, and characterized the corresponding (oxidized) surfaces using X-ray photoemission spectroscopy (XPS) in conjunction with synchrotron radiation (SR). We found that the presence of interfacial Pd and Pt, between surface Cu oxides and bulk, suppresses atomic diffusion and induces charge transfer near the interface. These result in the formation of protective layers that prevent Cu oxidation further...
into the bulk. These also account for the difference in Cu valencies and resulting oxidation states (Cu oxide species formed) on Cu₃Pd(111) and Cu₃Pt(111), as compared to Cu(111) and Cu₃Au(111).

**Results**

**Pd and Pt (surface) concentration profiles.** In Table 1, we show the corresponding experimental and calculated layer concentration profiles xₙ (in units of %Pd or %Pt) for clean Cu₃Pd(111) and Cu₃Pt(111). To experimentally determine the corresponding Pd and Pt layer concentrations xₙ, of the n-th layer from the vacuum, we followed the method described in previous studies, using the photoelectron detection angle dependence of the intensities of the bulk (B-) and surface (S-) components of the Pd-3d and Pt-4f XPS spectra. (For more details on the procedures, analyses, and calculations, cf., Section S.1 in the supplementary information.)

On the Cu₃Pd(111), our experimental analyses (calculation results) show a Pd concentration of x₁ = 44 (50) (cf., first two rows, Table 1), which is greater than the bulk value of x.bulk = 25. This indicates Pd segregation onto the surface, resulting in a Pd-rich surface.

On the Cu₃Pt(111), our experimental analyses show x₁ = 23, x₂ = 33, and x₃ = 88 (cf., third row, Table 1). This indicates Pt segregation onto the 2nd and 3rd layers (Pt-rich 2nd and 3rd layers). Previous studies using low energy ion scattering (LEIS) report similar results, viz., x₁ = 20, x₂ = 31 (cf., fourth row, Table 1). For comparison, low energy electron diffraction (LEED) studies report x₁ = 28, x₂ = 8, x₃ = 48, and x₁ = 8 (cf., fifth row, Table 1). On the other hand, calculation results show 100%-Pd segregation onto the 1st (surface) layer, and 50%-Pt segregation onto the 3rd layer. Regardless, both experiment and theory show (on the average) similar Pd concentrations from the 1st to the 3rd layer, viz., 48% and 50%, respectively.

**LEED patterns.** The clean Cu₃Pd(111) exhibits a (2 x 2) LEED pattern with some spot splittings (cf., Fig. S.4(a) in the supplementary information), which we ascribe to the presence of structural anti-phase domains on the surface (considering the 44%-Pd surface segregation and three rotationally symmetric domains). For comparison, the clean Cu₃Pt(111) exhibits a (1 x 1) LEED pattern, indicating random distribution of 23%-Pt atoms on the 1st layer.

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Table 1. Layer concentration profiles xₙ (in units of %Pd or %Pt) for clean Cu₃Pd(111) and Cu₃Pt(111).

| Sample          | 1st layer x₁ | 2nd layer x₂ | 3rd layer x₃ | 4th layer x₄ |
|-----------------|-------------|-------------|-------------|-------------|
| Cu₃Pd(111)     | Experiment  | 44          | 22          | Bulk(25)    | Bulk(25)    |
| Theory          | 50          | 25          | Bulk(25)    | Bulk(25)    |
| Cu₃Pt(111)     | Experiment  | 23          | 33          | 88          | 20          |
| Experiment²⁵   | 20          | 31          | Bulk(25)    | Bulk(25)    |
| Experiment²⁶   | 28          | 8           | 48          | 8           |
| Theory          | 100         | 0           | 50          | Bulk(25)    |

*This work.*

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Figure 1. O uptake curves for Cu₃Pd(111) and Cu₃Pt(111) after 2.3 eV HOMB irradiation at Tₛ = 300 and 500 K. For reference, O uptake curves taken after thermal O₂ exposure, and O uptake curves for Cu(111) and Cu₃Au(111) after 2.3 eV HOMB irradiation, are also shown.
Figure 2. (a) Cu-L_{2,3}M_{4,5}M_{4,5} AES and (b) Cu-2p XPS spectra of Cu_3Pd(111) and Cu_3Pt(111), taken after 2.3 eV HOMB irradiation at T_s = 300 K and 500 K, at a photoelectron detection angle θ = 70° from the surface normal. For Cu_3Pd(111), corresponding AES spectra for O-coverages of 0 ML (clean), 0.76 ML at 300 K, and 1.8 ML at 500 K, are shown. Similarly, for Cu_3Pt(111), corresponding AES spectra for O-coverages of 0 ML (clean), 0.49 ML at 300 K, 0.53 ML at 500 K, are shown. Bulk Cu_2O spectra also shown in (a) for reference, with dashed vertical line indicating characteristic Cu_2O peak position.

Table 2. Oxides species formed on Cu and Cu-based alloys after 2.3 eV HOMB irradiation at T_s = 300 K.

|          | Cu_3Pd(111) | Cu_3Pt(111) | Cu(O)(111) | Cu(O)_{Au}(111) |
|----------|-------------|-------------|------------|-----------------|
| 300 K    | CuO         | CuO         | Cu_2O      | Only chemisorbed O |
| 500 K    | Cu_2O       | Cu_2O       | Cu_2O      | Cu_2O           |

Oxygen uptake curves. In Fig. 1, we show the O uptake curves for Cu_3Pd(111) and Cu_3Pt(111) produced by integrating a series of O-1s XPS spectra measured after 2.3 eV HOMB irradiation at T_s = 300 and 500 K (also cf., Fig. S6 in supplementary information). We determined the oxygen coverage by comparing Cu(100)-(2√2×2)-O and Cu(110)-(2×1)-O^{27} and also cross-checked by using the intensity ratios of O-1s/Pd-3d and O-1s/Pt-4f. For comparison, we also show the O uptake curves taken after thermal O_2 exposure, and the O uptake curves for Cu(111) and Cu_3Au(111) taken after 2.3 eV HOMB irradiation. Comparing the results of HOMB irradiation and thermal O_2 exposure, we confirm the need for higher translational energies to realize effective oxide formation. However, following procedures previously reported for determining Au concentrations on the oxidized Cu_3Au(111)^{27}, we were not able to consistently obtain the Pd and Pt concentrations. This may be due to the presence of Cu oxide islands on the corresponding surfaces, whereas only homogeneous adsorbed-O forms on Cu_3Au(111)^{27}

Cu-L_{2,3}M_{4,5}M_{4,5} and Cu-2p spectra. In Fig. 2, we show the Cu-L_{2,3}M_{4,5}M_{4,5} AES (Auger electron spectroscopy) and Cu-2p XPS spectra of the corresponding Cu oxides formed on Cu_3Pd(111) and Cu_3Pt(111). For reference, note the Cu_O features appearing at ca. 917 eV kinetic energy (cf., bulk Cu_2O peak, Fig. 2a). From Fig. 2a, we find prominent Cu_2O formation only for Cu_3Pd(111) oxidized at T_s = 500 K. On the other hand, in Fig. 2b, we find characteristics of Cu(O) (cf., shoulder at ca. 396 eV and satellite peaks between ca. 393 eV and 946 eV^{28}) for both Cu_3Pd(111) and Cu_3Pt(111) oxidized at T_s = 300 K. We also see that these CuO features persist at T_s = 500 K for Cu_3Pt(111), but disappear for Cu_3Pd(111). On Cu_3Pt(111), AES spectra analyses indicate CuO formation only, both at T_s = 300 K and 500 K. On Cu_3Pd(111), AES spectra analyses indicate CuO formation at T_s = 300 K and Cu_2O formation at T_s = 500 K. (Pd-3d and Pt-4f XPS spectra analyses also indicate that only...
Cu oxidation occurs on both Cu_{3}Pd(111) and Cu_{3}Pt(111), cf., Section S.4 in supplementary information). In Table 2, we show a summary of oxides formed on the Cu and Cu-based alloy surfaces studied.

In Fig. 3, we show the effect of annealing on the corresponding Cu-L_{3}M_{4,5}M_{4,5} AES and Cu-2p spectra of Cu_{3}Pd(111) and Cu_{3}Pt(111) oxidized at T_{S} = 300 K. We see enhanced CuO features from the Cu-L_{3}M_{4,5}M_{4,5} spectra, and diminished CuO features from the Cu-2p. (The fitted O-1s XPS spectra also show enhanced CuO features and diminished CuO features, cf., Fig. S.9 in supplementary information). This suggests the reduction of CuO to Cu_{2}O at high T_{S}. However, a lingering CuO peak remains on Cu_{3}Pt(111), even after the annealing at T_{S} = 600 K, which we no longer see on Cu_{3}Pd(111). We found that annealing at T_{S} = 650 K completes the reduction from CuO to Cu_{2}O on the Cu_{3}Pt(111). Therefore, we conclude more stable CuO formation on Cu_{3}Pt(111) as compared to Cu_{3}Pd(111). Similar effect can be observed for Cu(410) oxidation at lower T_{S}. After 2.2 eV HOMB irradiation, CuO forms on Cu(410) at T_{S} = 100 K^{30}. Annealing at T_{S} = 273 K reduces CuO into Cu_{2}O. Alloying increases the corresponding transition temperature from CuO to Cu_{2}O. CuO persists even at T_{S} = 300 K.

**Discussions.**

\(O_2\) Dissociation, CuO and Cu_{2}O formation on Cu and Cu alloys in the early stage of oxidation.\n
The position of the surface \(d\)-band center relative to the Fermi level^{31,32} has often been used to qualitatively discuss reactivity of dissociative adsorption. The deeper the surface \(d\)-band center, the less reactive the surface. From XPS measurements, in order of increasing depth with respect to the vacuum level (viz., in order of decreasing reactivity), we have Cu_{3}Pd (~2.7 eV), Cu_{3}Pt (~2.9 eV), Cu (~3.1 eV), and finally Cu_{3}Au (~3.7 eV) (also cf., Fig. S.10 in supplementary information, and Ref^{33}). However, the uptake curves in Fig. 1 show different tendency of reactivity. We see O-coverages lower than what we would expect from the \(d\)-band for both Cu_{3}Pd(111) and Cu_{3}Pt(111).

Now, let us consider what the uptake curves taken at T_{S} = 300 K and 500 K tell us (cf., Fig. 1). Here, we discuss the early stage of oxidation where only the dissociative adsorption of \(O_2\) occurs on Cu(111). Note that on Cu(111) and Cu_{3}Au(111), previous HOMB irradiation studies at 2.3 eV^{34} report that direct \(O_2\) dissociative adsorption dominates at the early stage of oxidation, and Cu oxide (CuO) subsequently forms above \(\sim 10^{17}\) molecules cm\(^{-2}\). In comparison, Cu_{3}Pd(111) and Cu_{3}Pt(111) show Cu oxide (CuO) formation above ca. 8-60 \times 10^{15} molecules cm\(^{-2}\) as shown in Fig. S.8 in supplementary information. In other words, Cu oxide forms earlier on Cu_{3}Pd(111) and Cu_{3}Pt(111) than on Cu(111). Taking this into account, we can interpret the reactivity below \(\sim 10^{17}\) molecules cm\(^{-2}\) as follows. The inactive CuO formed at an early stage of oxidation makes Cu_{3}Pd(111) and Cu_{3}Pt(111) more robust to further oxidation of bulk Cu, while further bulk Cu is lost.
through Cu$_2$O formation on Cu(111). The earlier CuO formation at ca. $8 \times 10^{13}$ molecules cm$^{-2}$ further indicates a more robust Cu$_3$PtPt(111) than Cu$_3$Pd(111). So, based on the corresponding O uptake curves, we have Cu(111), Cu$_3$Pd(111), Cu$_3$Au(111)35, and Cu$_3$Pt(111), in order of decreasing susceptibility to Cu loss (i.e., Cu$_2$O formation).

**The protective layer.** The difference in efficiency of oxide formation between Cu and Cu alloy surfaces can be ascribed to the resulting protective layer of Pd (Pt) layer formed at the interface between the bulk and surface Cu oxide (cf., e.g., Cu$_3$Au(111)35). As mentioned in S.4 in supplementary information, only Cu oxidation occurs on Cu$_3$Pd(111) and Cu$_3$Pt(111). Previous studies also show that only Cu oxide forms on Cu-Pt alloy28 and Cu deposited on Pt(111)35. The selective Cu oxidation results in Pd- and Pt-rich interface layers. We see a steep O diffusion further into the bulk to realize the CIA process. It also prevents Cu diffusion from the bulk to the surface CuO.

**Mobility/diffusion.** At $T_S = 500$ K, we expect that the increased temperature would enhance atom diffusion, allowing for Cu oxide formation further into the bulk. On Cu$_3$Au(111), Cu$_3$O forms at 500 K19, Cu$_3$Pd(111) also has a steeper O uptake curve at 500 K than 300 K (cf., above $10^{17}$ molecules cm$^{-2}$ in Fig. 1). However, Cu$_3$Pt(111) remains relatively reactive, even at 500 K. This is because of the presence of less mobile Pt at the interface. In Cu, Pd has an activation/diffusion barriers of ca. 0.88 eV37, Au has 1.1 eV38, and Pt has 1.51 eV39. This is consistent with the reactivity observed above ca. $10^{17}$ molecules cm$^{-2}$ at 500 K, i.e., the region where mainly CuO forms. The interface Pt suppresses Cu oxide growth into the bulk even at 723 K. Cu diffusion through the Pd (Pt) interface would also be unlikely considering the high Cu diffusion barriers (ca. 2.5 eV in Pd, 2.75 eV in Pt, and 2.0 eV in Au)40. As expected, these differences in diffusion barriers affect the kind of Cu oxides formed on the Cu alloy surfaces.

At 100 K, metastable CuO forms on Cu(111)40. The low temperature suppresses O diffusion from the surface to the bulk (and also Cu diffusion from the bulk to the surface), while collision induced absorption (CIA) allows for a continuous supply of O atoms to the surface. We can expect similar effects on the Cu-Pd and Cu-Pt alloy surfaces.

At 300 K, the presence of Pd or Pt at the corresponding interfaces suppresses the diffusion of O and Cu, while CIA allows for a continuous supply of O atoms on the surface. Similarly, on Cu$_3$Au(111) at 300 K, O atoms adsorbed on surface cannot diffuse into bulk due to the interface Au17,18. As a result, no Cu oxides form on Cu$_3$Au(111) at 300 K.

At 500 K, enhanced diffusion allows oxidation further into the bulk of Cu$_3$Au(111) and Cu$_3$Pd(111), and we find growth of the thermodynamically more stable Cu$_2$O. On the other hand, CuO persists on Cu$_3$Pt at 500 K because of the higher Pt diffusion barrier. As shown in Fig. 3, Cu$_2$O forms after annealing (after the HOMB irradiation at 300 K). Higher $T_S$ enables O diffusion further into the bulk and further Cu supply to the surface CuO. This occurs at $T_S = 650$ K on Cu$_3$Pt, and $T_S = 600$ K on Cu$_3$Pd. The less diffusive Pt present at the interface prevents further Cu$_2$O formation as compared to Pd. At $T_S = 723$ K, Cu$_2$O islands grow on Cu-Pt alloy. However, the oxide does not grow deeper into bulk even at high temperature because of less diffusivity of Pt41.

**Charge distribution.** In Fig. 4, for 0.5 ML-O adsorbed on Cu$_3$Pt(111), we see that in the early stage of oxidation, Cu segregates to the surface and oxidized to form CuO. The charge distribution also shows that the more electronegative Pt competes with O for the Cu electrons. This, together with the mobility arguments presented earlier, accounts for why Cu$_2$O easily forms on Cu(111) and not on Cu-alloys. Note that this could also consistently explain previous reports for that electron transfer from the metal substrate (Au, Ni, Mo, Cu, V) to the metal oxide resulted in Mo$^{4+}$ reduction to Mo$^{3+}$ and/or Mo$^{2+}$ near the interface41. Conversely, in our case, electron transfer results in Cu$^{+}$ oxidation to Cu$^{2+}$ as shown in Fig. S.11 in supplementary information. Additionally, the presence of single Pt atoms at the Cu metal-oxide interface weakens Cu-O bond42, consistent with the preferential formation of CuO (Cu–O: 0.188 and 0.196 nm) than Cu$_2$O (Cu–O: 0.185 nm) on Pt interface42.

**Summary and conclusions**

In conclusion, we studied the oxidation of Cu$_3$Pd(111) and Cu$_3$Pt(111), using 2.3 eV hyperthermal oxygen molecular beam (HOMB) source, and synchrotron radiation X-ray photoemission spectroscopy (SR-XPS) for surface characterization. We determined the Pd- and Pt- layer profiles of Cu$_3$Pd(111) and Cu$_3$Pt(111) from the corresponding Pd-3$d$ and Pt-4$f$ spectra. At 300 K, we found mainly (only) the presence of CuO on both Cu$_3$Pd(111) and Cu$_3$Pt(111). At 500 K, we found Cu$_2$O on Cu$_3$Pd(111), and only CuO on Cu$_3$Pt(111). For comparison, at 300 K, Cu$_3$O forms on Cu(111), and no oxides form on Cu$_3$Au(111). The early formation of Cu oxides on Cu$_3$Pd(111) and Cu$_3$Pt(111) results in hindered reactivity (susceptibility) to further oxidation into the bulk (resulting in the formation of Cu$_2$O) as compared to Cu. Cu oxide formation depends on the Cu alloy component and temperature. We ascribe this difference/preference of Cu oxide species to the mobility of the interfacial Cu/Pd/Pt, and the charge transfer between the initial (pre-oxidized) surface (Cu) and subsurface (Cu, Pd, or Pt) species. The presence of Cu$_2$O and metastable CuO at the Pd and Pt interface could play an important role in catalytic reactions. We showed that we can control the oxidation state of the surface metal oxide by alloying, which in turn would allow us to control the catalytic reactivity of the oxides.
Method
Experiments. We performed all experiments with the surface reaction analysis apparatus (SUREAC 2000) built at BL23SU in SPring-8, with the base pressure of < 2 × 10⁻⁸ Pa. Briefly, our surface reaction analysis chamber has an electron energy analyzer (OMICRON EA125-5MCD) and a Mg/Al-Kα twin-anode x-ray source (OMICRON DAR400). We also have a quadrupole mass spectrometer, for monitoring the molecular beam, located opposite to the HOMB (hyperthermal oxygen molecular beam) source. We purchased Cu₃Pd(111) and Cu₃Pt(111) samples from SPL and MaTeck, respectively. We cleaned the Cu₃Pd(111) and Cu₃Pt(111) samples by repeated sputtering with Ar⁺ and annealing for 20 min (Cu₃Pd(111): 1.0 keV, 723 K, Cu₃Pt(111): 0.5 keV, 773 K), until the impurities were no longer detectable by SR-XPS (synchrotron-radiation X-ray photoelectron spectroscopy). We generated a HOMB by the free expansion of mixed gas of O₂, He and/or Ar from a nozzle with a small orifice. The translational energy of HOMB, E_{SG}, can be expressed as:

\[ E_{SG} = S^2 \cdot R \cdot T_0 \cdot \frac{m_{SG}}{m_r}, \]  

where \( S \) (≈ 1.557) is a factor that is expressed by using the Mach number, \( R \) (≈ 8.617 × 10⁻⁵ eV · K⁻¹) is gas constant, \( T_0 \) is the nozzle temperature, \( m_{SG} \) is the mass of the reactant gas (O₂) and \( m_r \) is the reduced mass of the mixed gas (He and/or Ar). By changing the gas mixing ratios at the nozzle and nozzle temperature \( T_0 \), we can control the kinetic energy of the incident HOMB, \( E_{SG} \). The detailed explanation for HOMB generation is shown in Refs.45,46. We set the nozzle temperature to 1400 K, obtaining a 2.3 eV HOMB. We irradiate the sample surface with a HOMB (along the surface normal) at \( T_S = 300 \) and 500 K. The pressure during the HOMB irradiation is about \( 1 \times 10^{-3} \) Pa. The oxidation by the scattered O₂ which causes the pressure increase is not important because the percentage of O₂ in the gas is only 1% for the 2.3 eV HOMB, and the oxidation by thermal O₂ is less reactive than by HOMB as shown in Fig. 1. After each irradiation, we then obtained the corresponding high-resolution SR-XPS spectra at \( T_S = 300 \) K, at detection angles of \( \theta = 0° \) and 70° from the surface normal, using a monochromatic SR beam with a photon energy of 1100 eV. We performed the HOMB irradiations at \( T_S = 300 \) and 500 K.

Theoretical calculations. We performed density functional theory (DFT)-based total energy calculations as implemented in the Vienna Ab Initio Simulation Package\(^{47,48}\), within the generalized gradient approximation (GGA)\(^{49}\), using plane waves (600 eV cutoff energy) and the projector augmented wave method\(^{50}\). To model Cu₃Pd(111) and Cu₃Pt(111), we used slabs. Each slab has seven fcc(111) layers, separated by ca. 1.50 nm (Cu₃Pd) and 0.7 nm (Cu₃Pt) vacuum, repeated in a supercell geometry (shown in Fig. S.2). We also applied dipole corrections. Each layer in the slab contains 4 atoms, so that the composition (of Pd or Pt) can be varied in steps of 25%. Convergence tests for \( k \)-point meshes and cutoff energy values were performed (cf., Table. S.1). We have chosen sufficiently large supercells so as to avoid interaction between adsorbates in the neighboring super-
cells. We performed Brillouin zone integration using the Monkhorst-Pack special k-point sampling technique\(^1\), with \(8 \times 8 \times 1\) (Cu-Pd) and \(6 \times 6 \times 1\) (Cu-Pt) sampling meshes. We kept the bottom five (four) layers of Cu-Pd (Cu-Pt), which comprise the unsegregated layers having bulk stoichiometry, viz., 25%-Pd (or Pt) 75%-Cu in the \(1 \times 1\) ordered structure, fixed to the optimized theoretical bulk lattice constant 0.3723 nm (0.3730 nm). We allowed the top three layers, which constitute the segregated layers, viz., the first surface layer, the second-, and third-(sub-surface) layers, to relax. In addition to calculations for the slab, we also carried out similar calculations for bulk Cu, bulk Pd, bulk Pt, bulk Cu3Pd and bulk Cu3Pt.

Data availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information. Additional data related to this paper may be requested from the authors.

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Author contributions
M.O. conceived and directed the research, Y.T., T.M., A.Y. and M.O. performed all the experiments. Y.T. and M.O. carried out the data analyses. Y.T., J.S.G. and W.A.D. performed the theoretical calculations. All authors contributed to the manuscript preparation.

Competing interests
The authors declare no competing interests.

Additional information
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