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Correlation between the Surface Electronic Structure and CO-oxidation Activity of Pt Alloys

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KEYWORDS

Alloy catalysts, CO oxidation, CO adsorption, surface electronic structure, d-band center
ABSTRACT

The surface electronic structure and CO-oxidation activity of Pt and Pt alloys, Pt₃T (T = Ti, Hf, Ta, Pt), were investigated. At temperatures below 538 K, the CO-oxidation activities of Pt and Pt₃T increased in the order Pt < Pt₃Ti < Pt₃Hf < Pt₃Ta. The center-of-gravity of the Pt d-band (the d-band center) of Pt and Pt₃T was theoretically calculated to follow the trend Pt₃Ti < Pt₃Ta < Pt₃Hf < Pt. The CO-oxidation activity showed a volcano-type dependence on the d-band center, where Pt₃Ta exhibited a maximum in activity. Theoretical calculations demonstrated that the adsorption energy of CO to the catalyst surface monotonically decreases with the lowering in the d-band center because of diminished hybridization of the surface d-band and the lowest-unoccupied molecular orbital (LUMO) of CO. The observed volcano-type correlation between the d-band center and the CO oxidation activity is rationalized in terms of the CO adsorption energy which counterbalances the surface coverage by CO and the rate of CO oxidation.
1. INTRODUCTION

The development of environmental-remediation technologies is of paramount importance to balance the growth in economy and the natural environment. One of the key objectives of the current environmental-purification technologies is reduction of expensive precious-group metals (PGMs: Pt, Pd and Rh) in automobile catalysts.\(^1\)\(^2\) There have been numerous approaches to alloy PGMs and more abundant metals such as Ni or Co to achieve high performance and low materials costs (alloy catalysts).\(^3\)\(^4\)\(^7\) However, it still remains a challenge to adequately design alloy catalysts for exhaust purification, because of the lack of understanding in correlation between the catalytic activity and experimentally measureable or theoretically calculable parameters of the alloys, such as a center-of-gravity of the Pt \(d\)-band (the \(d\)-band center).\(^8\)\(^14\)

Furthermore, surface segregation, which readily occurs on alloy surfaces in harsh conditions including high-temperature exhaust, makes it difficult to interrelate the apparent activity with the electronic and/or atomic structure of unperturbed surfaces.\(^15\) To evaluate an inherent alloying effect on the exhaust-purification activity of alloy catalysts, it is required to investigate thermally stable alloys with high melting points (> 2000 K), such as early-\(d\)-Pt alloys (Pt-\(T\): \(T\) = early \(d\)-metals), because their high ordering enthalpies can inhibit surface segregation and segregation-induced changes on the electronic or atomic structure of the surface.\(^16\)\(^18\)

Here we report that a simple correlation can be established between the apparent exhaust-purification activity and the surface electronic structure of early-\(d\)-Pt alloys, Pt\(_3\)\(T\) (\(T\) = Ti, Ta of Hf). X-ray photoemission spectroscopy using synchrotron radiation (Hard X-ray Photoemission Spectroscopy: HX-PES) demonstrated that the surface of Pt\(_3\)\(T\) was free from segregation when exposed to a simulated exhaust (a 2:1 mixture of carbon monoxide (CO) and O\(_2\) gases, 10 kPa) at temperatures below 598 K. At temperatures lower than 538 K, the catalytic activity of Pt and
Pt$_3$T for the oxidation of CO increased in the order Pt < Pt$_3$Ti < Pt$_3$Hf < Pt$_3$Ta. This trend leads to a volcano-type dependence of the CO oxidation activity on the theoretically calculated center-of-gravity of the Pt $d$-band (the $d$-band center) which increases in the order Pt < Pt$_3$Hf < Pt$_3$Ta < Pt$_3$Ti. Theoretical calculations have further demonstrated that the adsorption energy of CO to the catalyst surface monotonically decreases with the lowering in the $d$-band center because of diminished hybridization of the surface $d$-band and the lowest-unoccupied molecular orbital (LUMO) of CO. The observed volcano-type correlation between the $d$-band center and the CO oxidation activity is accounted for in terms of the CO adsorption energy which counterbalances the surface coverage by CO and the rate of CO oxidation. This established correlation allows us to understand and even predict the exhaust-purification activity of unknown Pt-based alloys by theoretically calculating and/or experimentally determining the $d$-band center, which will be a guiding principle in the quest for efficient alloy catalysts for exhaust purification.
2. EXPERIMENTAL SECTION

2.1 Sample preparation.

Polycrystalline samples of intermetallic Pt$_3$T ($T =$ Ti, Ta, and Hf) were synthesized in a pure Ar atmosphere (99.9999 %) with an arc furnace. Prior to the synthesis, the arc furnace was evacuated to a vacuum level with a pressure lower than $10^{-3}$ Pa and backfilled with pure Ar. All starting materials were purchased from Furuya Kinzoku Co. An aliquot of 1 g of Pt powder (99.9 %) was pelletized with a stainless-steel die and melted with the arc furnace into an ingot. Titanium (sponge, 99 %) and Ta (wire, 99 %) metals were used as received. As-purchased Hf metal (chunk, 98 %) was first melted with the arc furnace to remove surface oxides. The ingots of Pt and the other metals were weighed such that the molar ratio was Pt:$T = 3$:1 and melted together in the arc furnace. The ingot obtained, with a combined weight of approximately 3 g, was cut into two halves with a diamond saw. One of the halves was ground with an agate mortar for powder X-ray diffraction ($p$XRD), Brunauer–Emmett–Teller (BET) surface area measurements and catalytic CO oxidation measurements. Slices that were 0.5 mm thick were cut from the other half and polished to a mirror finish for hard X-ray photoemission spectroscopy (HX-PES) measurements.

2.2 Characterization.

$p$XRD (RIGAKU RINT 2000, Cu-K$_\alpha$ radiation, $\lambda$ = 1.541 Å) was used to examine the powdered samples of the Pt$_3$T alloys. The specific surface area of each sample was determined using the BET method. A Micromeritics ASAP 2020 was used to collect a partial adsorption isotherm at liquid-nitrogen temperature (77 K) using krypton as the adsorption gas. HX-PES was performed at room temperature under ultra-high vacuum using synchrotron radiation (5.95 keV, SPring-8, beamline BLXU15) and an electron energy analyzer (VG SCIENTA R4000). A 0.3 mm-thick
Pt plate (99.9 %, Furuya Kinzoku Co.), a 0.3 mm-thick Ti plate (99.9 %, Nilaco Co.) and slices of Ta and Hf taken from button-shaped ingots prepared in the arc furnace were used as references for HX-PES. All samples for HX-PES were fixed with carbon adhesives to grounded Cu sample holders. The HX-PES data were referenced to the Fermi edge of an Au film that was electrically connected to the samples via the sample holder.

2.3 Catalytic measurements.

A fixed-bed flow micro-reactor (Ohkura Riken) equipped with a gas chromatograph (GL Sciences) was used to evaluate the catalytic activities of the samples for the oxidation of CO. An aliquot of 150 mg of Pt or Pt₃T powder was introduced in the micro-reactor and subjected to a constant flow (100 ml min⁻¹) of a reactant gas that consisted of CO, O₂ and He at a molar ratio of 2:1:97 (Sumitomo Seika Chemicals). The BET surface areas of the powders were determined prior to the catalytic measurements. The composition of the outlet gas from the micro-reactor was analyzed at different sample temperatures ranging from 473 to 573 K.

2.4 Theoretical calculations.

Theoretical calculations of the electronic structures of the catalyst were performed using density-functional theory. The exchange-correlation energy functional was represented by the Perdew–Burke–Ernzerhof generalized gradient approximation. Projector-augmented wave pseudopotentials were employed as implemented in the VASP code. The valence configurations of the pseudo-potentials were 5d⁶6s¹ for Pt, 3p⁶3d³4s¹ for Ti, 5p⁶5d³6s² for Ta and 5p⁶5d²6s² for Hf. The energy cutoff for the plane-wave basis set expansion was set at 500 eV. Monkhorst–Pack k-point sets of 12×12×12 and 10×10×10 were used for the 1-atom and 4-atom unit cells for Pt and Pt₃Ti, respectively, whereas an 8×8×8 set was used for the 16-atom unit cells of Pt₃Ta and Pt₃Hf. The optimized lattice constants were as follows: \( a = 3.98 \) Å for Pt; \( a = 3.95 \) Å for Pt₃Ti, \( a = 3.98 \) Å for Pt₃Ta and \( a = 3.95 \) Å for Pt₃Hf.
Å for Pt₃Ti; \(a = 4.93\, \text{Å}, b = 5.61\, \text{Å}, c = 9.40\, \text{Å}, \beta = 100.56^\circ\) for Pt₃Ta; and \(a = 5.71\, \text{Å}, b = 5.71\, \text{Å}, c = 9.32\, \text{Å}, \gamma = 119.99^\circ\) for Pt₃Hf, using the reported crystallographic parameters.²⁴-²⁶

The unit cells were extended for the creation of slab models of the Pt(111), Pt₃Ti(111), Pt₃Ta(001) and Pt₃Hf(001) surfaces. The Pt(111) slab model consisted of 15 layers of Pt planes, including 120 atoms in total, and a vacuum of the same thickness as the Pt slab. The 7-9th layers were fixed during the surface relaxations to represent the bulk region. The 120-atom slab model of Pt₃Ti(111) was created in the same manner as that of Pt(111). The Pt₃Ta(001) slab model consisted of 12 layers of Pt₃Ta planes, including a total of 96 atoms, and a vacuum of the same thickness as the Pt₃Ta slab. The 5-8th layers were fixed during the surface relaxations. A similar model was constructed for the Pt₃Hf(001) surface. For the surface calculations, the \(k\)-point sampling was set at \(2\times2\times1\). The atomic positions of the slab modes were fully relaxed except for the fixed layers. The total density of states (DOS) was plotted with a smearing factor of 0.05 eV.

The \(d\)-band centers were evaluated by applying the following formula to the calculated DOS:

\[
d\text{-band center} = \frac{\int E \, \text{DOS}(E) \, dE}{\int \text{DOS}(E) \, dE}
\]

Where \(\text{DOS}(E)\) is the density of states of the occupied \(d\)-states.

For the calculation of the CO adsorption energy on each surface, a CO molecule was placed above a Pt atom with the C–Pt distance fixed at 1.94 Å (Figure S1).²⁷ The total energy of a single CO molecule, \(E_{\text{tot}}(\text{CO})\), was also computed using the same size supercell to evaluate the CO adsorption energy according to

\[
E_{\text{ads}} = E_{\text{tot}}(\text{CO-Metal}) - E_{\text{tot}}(\text{Metal}) - E_{\text{tot}}(\text{CO}),
\]
where $E_{\text{tot}}(\text{CO-Metal})$ and $E_{\text{tot}}(\text{Metal})$ are the total energies of the slabs with or without a CO molecule on the surface, respectively.

### 3. Results and Discussion

![Crystal structures of Pt and Pt$_3$T](image)

**Figure 1.** Crystal structures of Pt and Pt$_3$T. 

- **a.** Ball-and-stick model for a Pt$_{12}T$ cubo-octahedron (left) and the crystal structures of Pt and Pt$_3$Ti as a polygonal model (right). The grey polyhedra correspond to the Pt$_{12}$Pt and/or Pt$_{12}T$ cubo-octahedra.
- **b.** Ball-and-stick model for a structural derivative of the Pt$_{12}T$ cubo-octahedron (left) and a polygonal model for Pt$_3$Ta (right). The grey and white polyhedra correspond to the cubo-octahedral Pt$_{12}T$ and its structural derivative, respectively.
- **c.** Polygonal model for Pt$_3$Hf.

Figure 1 presents the structural models for Pt and Pt$_3$T: Pt, $Fm\bar{3}m$, $a = 3.9200$ Å; Pt$_3$Ti, Cu$_3$Au type, $Pm\bar{3}m$, $a = 3.9040$ Å; Pt$_3$Ta, Pt$_3$Nb type, $P2_1/m$, $a = 4.8690$ Å, $b = 5.5370$ Å, $c = 9.2690$ Å,
$\beta = 100.62^\circ$; and Pt$_3$Hf, Ni$_3$Ti type, $P6_3/mmc$, $a = 5.6360$ Å, $c = 9.2080$ Å, $\beta = 120^\circ$.\textsuperscript{24-26} The Pt and/or Pt$_{12}$Ti cubo-octahedron depicted by the stick-and-ball model and grey polyhedra in Figure 1a share the six square planes of the neighboring polyhedra in forming the framework of Pt and/or Pt$_3$Ti. The crystal structures of Pt$_3$Ta and Pt$_3$Hf, unlike that of either Pt or Pt$_3$Ti, are constructed from two types of Pt$_{12}$T polyhedra with different configurations (Figure 1b and 1c). One of the two types of Pt$_{12}$T polyhedra is isomorphic with the Pt$_{12}$Ti cubo-octahedron. The other type of Pt$_{12}$T polyhedron, which is depicted by a stick-and-ball model and white polyhedra, is a structural derivative obtained by rotating one of the eight Pt triangles of a Pt$_{12}$T cubo-octahedron by $180^\circ$. The monoclinic structure of Pt$_3$Ta is constructed by face- and edge-sharing of the Pt$_{12}$T cubo-octahedron and its structural derivative. The hexagonal structure of Pt$_3$Hf is also constructed by face- and ledge-sharing of the two types of Pt$_{12}$T polyhedra, but in a different sequence (Figure 1c).
Figure 2. $p$XRD profiles for $\text{Pt}_3\text{Ti}$ (a), $\text{Pt}_3\text{Ta}$ (b) and $\text{Pt}_3\text{Hf}$ (c). Simulated diffraction patterns are indicated as solid bars.

Figure 2 shows the $p$XRD profiles for $\text{Pt}_3T$, together with the diffraction patterns simulated using the reported crystallographic parameters. The $p$XRD profiles for $\text{Pt}_3\text{Ti}$, $\text{Pt}_3\text{Ta}$ and $\text{Pt}_3\text{Hf}$ are consistent with the simulated patterns. The synthesized samples of $\text{Pt}_3T$ were single-phase ordered alloys with the desired compositions and crystal structures.
**Figure 3.** HX-PES profiles for the core levels of the $T$ elements in Pt$_3$T. a. Ti 2$p$ levels of Pt$_3$Ti and pure Ti. b. Ta 4$f$ levels of Pt$_3$Ta and pure Ta. c. Hf 4$f$ levels of Pt$_3$Hf and pure Hf.

Figure 3 shows the HX-PES profiles for the core levels of the $T$ elements in Pt$_3$T. The Ti 2$p$ levels of Pt$_3$Ti were shifted by 1.0 eV toward high binding energies relative to those of pure Ti (Figure 3a). Similar shifts were observed for the other Pt$_3$T (Figures 3b and 3c). Both the Ta 4$f$ levels of Pt$_3$Ta and the Hf 4$f$ levels of Pt$_3$Hf were shifted by 1.5 eV toward high binding energies relative to those of the corresponding pure metals (Table 1).
Table 1. Core Levels of the $T$ Elements in Pt$_3T$

<table>
<thead>
<tr>
<th>Material</th>
<th>Binding energy (eV)</th>
<th>Binding energy (eV)</th>
<th>spin-orbit splitting $\Delta^a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_3$Ti</td>
<td>Ti 2$p_{3/2}$</td>
<td>Ti 2$p_{1/2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>454.82±0.20</td>
<td>460.92±0.20</td>
<td>6.10</td>
</tr>
<tr>
<td></td>
<td>(455.2)$^b$</td>
<td>(461.3)$^b$</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>453.82±0.20</td>
<td>460.02±0.20</td>
<td>6.20</td>
</tr>
<tr>
<td></td>
<td>(454.0)$^c$</td>
<td>(460.0)$^c$</td>
<td></td>
</tr>
<tr>
<td>Pt$_3$Ta</td>
<td>Ta 4$f_{7/2}$</td>
<td>Ta 4$f_{5/2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23.22±0.20</td>
<td>25.27±0.20</td>
<td>2.05</td>
</tr>
<tr>
<td>Ta</td>
<td>21.67±0.20</td>
<td>23.57±0.20</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>(21.7)$^d$</td>
<td>(23.7)$^d$</td>
<td></td>
</tr>
<tr>
<td>Pt$_3$Hf</td>
<td>Hf 4$f_{7/2}$</td>
<td>Hf 4$f_{5/2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.37±0.20</td>
<td>17.07±0.20</td>
<td>1.70</td>
</tr>
<tr>
<td>Hf</td>
<td>14.22±0.20</td>
<td>15.87±0.20</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>(14.31)$^e$</td>
<td>(15.98)$^e$</td>
<td>(1.67)$^e$</td>
</tr>
</tbody>
</table>

Note: Literature values are indicated in parentheses.

a. $\Delta$: spin-orbit splitting.

b. ref. 28-30.

c. ref. 31,32.

d. ref. 33,34.

e. ref. 35.
Figure 4. HX-PES profiles for the Pt core levels of pure Pt and Pt\textsubscript{3}T.

The HX-PES profiles for the Pt 4\textit{f} levels of pure Pt and Pt\textsubscript{3}T are presented in Figure 4. The Pt 4\textit{f}_{7/2} and 4\textit{f}_{5/2} levels were, in descending order, Pt, Pt\textsubscript{3}Ti, Pt\textsubscript{3}Ta and Pt\textsubscript{3}Hf, where the amplitude of the spin-orbit splitting was 3.35±0.20 eV irrespective of the identity of T (Table 2). In summary, the synthesized Pt\textsubscript{3}T samples were ordered alloys that exhibited different crystal structures and electronic structures from those of the constituent elements.

Table 2. Pt Core Levels of Pure Pt and Pt\textsubscript{3}T

<table>
<thead>
<tr>
<th>Material</th>
<th>Pt 4\textit{f}_{7/2} binding energy (eV)</th>
<th>Pt 4\textit{f}_{5/2} binding energy (eV)</th>
<th>spin-orbit splitting $\Delta$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>70.97±0.20</td>
<td>74.32±0.20</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>(71.30)\textsuperscript{b}</td>
<td>(74.23)\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td>Pt\textsubscript{3}Ti</td>
<td>71.37±0.20</td>
<td>74.72±0.20</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>(71.3)\textsuperscript{c}</td>
<td>(74.65)\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>Pt\textsubscript{3}Ta</td>
<td>71.52±0.20</td>
<td>74.82±0.20</td>
<td>3.30</td>
</tr>
<tr>
<td>Pt\textsubscript{3}Hf</td>
<td>71.62±0.20</td>
<td>74.92±0.20</td>
<td>3.30</td>
</tr>
</tbody>
</table>

\textit{a.} $\Delta$: spin-orbit splitting.

\textit{b.} ref. 36.

\textit{c.} ref. 28-30.
Prior to the catalytic testing, the chemical stability of each Pt$_3$T surface was examined at elevated temperatures in a reactant gas that consisted of CO, O$_2$ and He at a molar ratio of 2:1:97. Each Pt$_3$T surface was exposed to the reactant gas for 1 hour in a fixed-bed flow micro-reactor at a temperature of 548, 598 or 823 K. After exposure to the reactant gas, the Pt$_3$T samples were transferred to the UHV chamber for HX-PES measurements.

**Figure 5.** HX-PES profiles for the Pt$_3$T surfaces subjected to different atmospheres. *a.* Pt 4f (left) and Ti 2p levels (right) of the Pt$_3$Ti surface. *b.* Pt 4f (left) and Ta 4f levels (right) of the Pt$_3$Ta surface. *c.* Pt 4f (left) and Hf 4f levels (right) of the Pt$_3$Hf surface. Colored profiles correspond to
the as-prepared surfaces (blue) and to the surfaces heated in the reactant gas at 548 K (light blue), 598 K (green) or 823 K (red). Black profiles indicated in the left panels from a. through c. correspond to the Pt 4f levels of the pure Pt surface.

The left panel of Figure 5a shows Pt 4f profiles for the Pt₃Ti surfaces subjected to different atmospheres. Both of the Pt 4f profiles for the Pt₃Ti surfaces heated at 548 K (light-blue profile) or 598 K (green profile) were identical to that for the as-prepared Pt₃Ti surface (blue profile). The Pt 4f emission peaks for the Pt₃Ti surface heated at 823 K (red profile), however, exhibited large shoulders at 71.02±0.20 and 74.36±0.20 eV. These values were consistent with the Pt 4f emission peaks for the pure Pt surface at 70.97±0.20 and 74.32±0.20 eV, respectively (black profile). The Pt₃Ti surface, when heated to 823 K in the reactant gas mixture, precipitated pure Pt.

The right panel of Figure 5a shows the Ti 2p profile for the Pt₃Ti surfaces. The Ti 2p₃/2 (454.87±0.20 eV) and Ti 2p₁/2 (460.97±0.20 eV) levels of the as-prepared surface were consistent with those of the surfaces heated at 548 K or 598 K, though an additional peak was observed at 458.85±0.20 eV for the heated surfaces. This peak was attributed to the adsorption of oxygen to the surface Ti to form a suboxide, TiO₂₋ₓ (ₓ > 0). For the sample heated at 823 K, the Ti emission peaks for Pt₃Ti and TiOₓ (ₓ < 2) nearly vanished. Two peaks appeared at 459.25±0.20 and 465.00±0.20 eV instead, corresponding to the Ti 2p₃/2 and Ti 2p₁/2 emissions, respectively, from titanium dioxide, Ti⁴⁺O₂⁻. The Pt₃Ti surface retained its chemical composition when heated in the reactant gas at temperatures below 598 K but was decomposed at 823 K into pure Pt and TiO₂.

The left and right panels of Figure 5b show the Pt 4f and Ta 4f profiles, respectively, for the Pt₃Ta surfaces. The Pt 4f profiles for the Pt₃Ta surfaces heated at 548 or 598 K were virtually identical to that of the as-prepared surface (left panel) and the Ta 4f profiles for the Pt₃Ta
surfaces heated at 548 or 598 K were similar to that for the as-prepared surface (right panel). A shoulder at 26.0 eV and a weak peak at 28.0 eV on the Ta 4f profile for the as-prepared Pt₃Ta surface (blue profile in the right panel) correspond to a surface contamination that was removed by heating in the reactant gas. The Pt₃Ta surface retained the chemical composition of the as-prepared surface when heated to temperatures ranging from 548 to 598 K. At a temperature of 823 K, the emission peaks that correspond to pure Pt (red profile in the left panel) and Ta⁵⁺O₅ (red profile in the right panel) became clearly visible.³³,³⁴ At 823 K, the Pt₃Ta surface decomposed into pure Pt and Ta₂O₅, similar to the behavior of the Pt₃Ti surface.

The left and right panels of Figure 5c show the Pt 4f and Hf 4f profiles for the Pt₃Hf surface. The Pt emission peaks for the surfaces heated to 548 K or 598 K, 71.60±0.20 and 74.90±0.20 eV, respectively, were consistent with those observed for the as-prepared Pt₃Hf surface, at 71.62±0.20 and 74.92±0.20 eV, respectively (left panel). The Hf emission peaks for the surfaces heated at 548 K or 598 K, 15.35±0.20 and 17.00±0.20 eV, respectively, were also consistent with those for the as-prepared Pt₃Hf surface, 15.37±0.20 and 17.07±0.20 eV, respectively (right panel).

The Pt 4f and Hf 4f emission peaks for the Pt₃Hf surfaces heated at 548 or 598 K, unlike those for the as-prepared surface, exhibited shoulders at lower binding energies. The binding energies for the shoulders of the Pt 4f emission peaks were revealed by deconvolution to be at 71.15±0.20 and 74.46±0.20 eV. These values were not consistent with the Pt 4f levels of the pure Pt surface, 70.97±0.20 and 74.32±0.20 eV. The binding energies for the shoulders of the Hf 4f emission peaks, 14.98±0.20 and 16.66±0.20 eV, were also inconsistent with the values for HfO₂ (16.60±0.20 and 18.10±0.20 eV), Pt₃Hf (15.37±0.20 and 17.07±0.20 eV) or pure Hf (14.22±0.20 and 15.87±0.20 eV).³⁵
Morant et al. reported that a suboxide of Hf, HfO$_{2-x}$ ($x > 0$), was formed on a Hf surface at room temperature at an early stage of adsorption of oxygen ($\leq 5$ L). The reported binding energies for the Hf 4f emissions from HfO$_{2-x}$, 15.1 and 16.8 eV, are similar to the values for the shoulders of the Hf 4f emissions from Pt$_3$Hf surfaces heated at 548 or 598 K, 14.98±0.20 and 16.66±0.20 eV, respectively. The observed shoulders of the Hf 4f peaks for the Pt$_3$Hf surfaces heated at 548 or 598 K are assigned to a suboxide of the surface Hf that may accompany a core-level shift for the surface Pt.

The Pt 4f profile for the Pt$_3$Hf surface heated at 823 K (red profile in the left panel of Figure 5c) was different from that for the surface heated at either 548 or 598 K and was similar to that for the pure Pt surface. The Hf 4f profile for the surface heated at 823 K (red profile in the right panel of Figure 5c) showed two peaks that corresponded to Hf$^{4+}$O$_2$ at 16.60±0.20 and 18.10±0.20 eV. The Pt$_3$Hf surface retained the chemical composition of the as-prepared surface when heated to temperatures ranging from 548 to 598 K but decomposed into pure Pt and HfO$_2$ when heated at 823 K.

Summarizing the HX-PES data in the core-level region, we conclude that the Pt$_3$T surfaces retain their chemical compositions when exposed to the O$_2$-containing reactant gas, as long as the temperature is lower than 598 K. When the temperature exceeds 823 K, the Pt$_3$T surfaces decomposed into pure Pt and a transition-metal oxide of $T$ in its highest available oxidation state. Indeed, the O1s emission peaks for the Pt$_3$T surfaces heated at 823 K were more intense than those for the surfaces heated below 598 K (see supporting information, Figure S2). Catalytic tests were performed at temperatures below 598 K to establish a reliable correlation between the catalytic activity and the surface electronic structure of Pt$_3$T.
Figure 6. Catalytic CO oxidation over the Pt and Pt$_3$T surfaces. The specific activities for CO oxidation over Pt (○), Pt$_3$Ti (□), Pt$_3$Ta (■) and Pt$_3$Hf (▼) are plotted as functions of temperature.

Figure 6 shows the temperature dependence of the catalytic activities of Pt and Pt$_3$T toward the oxidation of CO. The specific CO oxidation activity of Pt increased monotonically with increasing temperature (open circles in Figure 6). The specific CO oxidation activities of Pt at 473 and 573 K were $1.35 \times 10^{-5}$ and $1.38 \times 10^{-3}$ mols$^{-1}$m$^{-2}$, respectively. The specific CO oxidation activity of Pt$_3$Ti also increased with increasing temperature but at a higher rate. The specific activity of Pt$_3$Ti at 473 K was $1.66 \times 10^{-5}$ mols$^{-1}$m$^{-2}$, which was higher than the value of Pt at the same temperature. At 573 K, however, the specific activity of Pt$_3$Ti was $2.91 \times 10^{-3}$ mols$^{-1}$m$^{-2}$, which was double that observed for Pt. Pt$_3$Ta showed the highest specific CO oxidation activity at low temperatures. The specific activity of Pt$_3$Ta at 473 K, $8.62 \times 10^{-5}$ mols$^{-1}$m$^{-2}$, was 5-fold
higher than the values for Pt or Pt$_3$Ti. The specific activity of Pt$_3$Hf at each temperature was between those of Pt$_3$Ta and Pt. The specific CO oxidation activities of Pt and Pt$_3$T were Pt < Pt$_3$Ti < Pt$_3$Hf < Pt$_3$Ta at temperatures below 538 K and Pt < Pt$_3$Hf < Pt$_3$Ta < Pt$_3$Ti above 538 K.

**Figure 7.** HX-PES profiles and calculated density-of-states (DOS) for Pt and Pt$_3$T in the valence region. *a.* Pt. *b.* Pt$_3$Ti. *c.* Pt$_3$Ta. *d.* Pt$_3$Hf. The blue, red and black profiles correspond to the experimental HX-PES data and the DOS components of Pt and T, respectively.

Figure 7 shows the HX-PES profiles for the pure Pt and the as-prepared Pt$_3$T surfaces in the valence region, together with the calculated DOS for Pt and T. Both the HX-PES and the DOS profiles for pure Pt exhibit a large peak immediately below the Fermi level, assigned to the Pt 5$d$ orbital (Figure 7a). In contrast, the HX-PES profile for Pt$_3$Ti exhibits no corresponding peak below the Fermi level (Figure 7b). Theoretical calculations have shown that the Pt 5$d$ and Ti 3$d$ orbitals are hybridized to split into anti-bonding and bonding states located above and below the
Fermi level. The valence band of Pt$_3$Ti is a bonding state of Pt and Ti that consists mostly of the Pt $5d$ state with a small Ti $3d$ component. As with Pt$_3$Ti, neither Pt$_3$Ta (Fig. 7c) nor Pt$_3$Hf (Figure 7d) shows any predominant peaks immediately below the Fermi level in the HX-PES or DOS profiles: the Ta $5d$ orbital and the Hf $5d$ orbital are hybridized with the Pt $5d$ orbital and split into anti-bonding and bonding states.

![Diagram](image)

**Figure 8.** Calculated $d$-band centers for Pt and Pt$_3T$. Insets show schematic energy diagrams for Pt (top left) and Pt$_3T$ (bottom right).

The calculated gravity centers of the filled Pt $d$-band ($d$-band center) for Pt and Pt$_3T$ were ordered as Pt$_3$Ti < Pt$_3$Ta < Pt$_3$Hf < Pt (Figure 8). Pure Pt has the highest energy $d$-band center because the $d$-band in pure Pt is mostly filled by electron pairs, as shown in the top-left inset. In Pt$_3T$, however, few electrons are donated by the $T$ element, and only the bonding states are occupied, which results in a downshift in the $d$-band center (bottom-right inset). The energy level of the $d$-band center of Pt$_3T$ is determined by the energy gap between the $d$-orbitals of Pt and $T$: a smaller energy gap results in a lower $d$-band center due to a larger energy splitting. The energy
levels of the $d$-orbitals were calculated as -5.52 eV (Pt), -4.12 eV (Ti), -3.55 eV (Ta), and -2.64 eV (Hf). These values are consistent with the trend presented in Figure 8.

**Figure 9.** Correlation between the CO oxidation activity and the $d$-band center. Specific CO oxidation activities of Pt and Pt$_3T$ at 473 K are plotted as a function of the $d$-band center.
The CO oxidation activities at the lowest temperature in the measurement range, 473 K, were plotted against the calculated \(d\)-band centers (Figure 9). The CO oxidation activity exhibited a volcano-type dependence on the \(d\)-band center with \(\text{Pt}_3\text{Ta}\) at the top. The CO oxidation activities of \(\text{Pt}_3\text{Ti}\) and \(\text{Pt}_3\text{Hf}\) were higher than that of pure Pt, but lower than that of \(\text{Pt}_3\text{Ta}\).

Figure 10 shows the theoretically calculated CO adsorption energy on the catalyst surface of Pt and \(\text{Pt}_3T\). The amplitude of CO adsorption energy decreases monotonically as the \(d\)-band center decreases. The CO adsorption energy on the \(\text{Pt}_3\text{Ti}\) surface is 30% lower than that on the pure Pt surface. This trend is attributed to poor electron back-donation from the \(\text{Pt}_3T\) surfaces to CO admolecules, which is caused by the increased energy gap between the \(d\)-band center and the lowest unoccupied \(2\pi^*\) molecular orbital (LUMO) of the CO admolecules.\(^{27,39,40}\)

The volcano-type correlation established in this work may be assigned to a downshift in the \(d\)-band center of \(\text{Pt}_3T\) relative to that of Pt, which is accompanied by a weakening of the CO
adsorption. The CO adsorption to the Pt surface is so strong that the catalysis is blocked by the CO adlayer. In contrast, CO oxidation is poorly promoted by Pt$_3$Ti at low temperatures because CO admolecules readily desorb from the surface.$^{41-45}$ Pt$_3$Ta, which exhibits an intermediate $d$-band center, achieves the highest CO oxidation activity because of an optimum balance in the adsorption and desorption of CO.

**CONCLUSIONS**

In conclusion, we have demonstrated that ordered early $d$-metal alloys, Pt$_3$T ($T =$ Ti, Ta and Hf), exhibit catalytic activities that are superior to that of pure Pt for the oxidation of CO. The specific CO oxidation activities of Pt and Pt$_3$T showed a volcano-type correlation with the $d$-band center of the catalyst. The observed volcano-type correlation has been interpreted as a result of the weakening of CO adsorption to the catalyst surface caused by a downshift in the $d$-band center of Pt$_3$T relative to that of Pt.

Outstanding issues and potential limitations to be addressed include the chemical composition of the catalyst surface at work, the surface dynamics of the reaction intermediates and how the atomic arrangement on the surface affects the apparent activity. The Pt$_3$Ta catalyst, which exhibited a very high CO oxidation activity, should be synthesized in the form of nanoparticles for practical use. These issues are challenging, yet worthy of effort, because the high activity and the reduced precious-metal content of alloy catalysts will strongly promote the future development of such metal catalysts for environmental and/or energy applications.

**ASSOCIATED CONTENT**

Supporting Information.
HX-PES profiles in the O1s and Pt 4p\textsubscript{3/2} regions for the surfaces of Pt\textsubscript{3}Ti, Pt\textsubscript{3}Ta and Pt\textsubscript{3}Hf that were heated at different temperatures in the reactant gas. This material is available free of charge via the Internet at http://pubs.acs.org.

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The CO-oxidation activity of Pt and Pt alloys, Pt3T (T = Ti, Hf, Ta, Pt), shows a volcano-type dependence on the d-band center of the catalysts.