High-throughput computational-experimental screening protocol for the discovery of bimetallic catalysts

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To accelerate the discovery of materials through computations and experiments, a well-established protocol closely bridging these methods is required. We introduce a high-throughput screening protocol for the discovery of bimetallic catalysts that replace palladium (Pd), where the similarities in the electronic density of states patterns were employed as a screening descriptor. Using first-principles calculations, we screened 4350 bimetallic alloy structures and proposed eight candidates expected to have catalytic performance comparable to that of Pd. Our experiments demonstrate that four bimetallic catalysts indeed exhibit catalytic properties comparable to those of Pd. Moreover, we discover a bimetallic (Ni-Pt) catalyst that has not yet been reported for H2O2 direct synthesis. In particular, Ni61Pt39 outperforms the prototypical Pd catalyst for the chemical reaction and exhibits a 9.5-fold enhancement in cost-normalized productivity. This protocol provides an opportunity for the catalyst discovery for the replacement or reduction in the use of the platinum-group metals.

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INTRODUCTION

One of the important roles of computer simulations in materials science is to predict and/or design materials prior to experiments. In particular, first-principles calculations using density functional theory (DFT) have played a vital role in the field of catalysis1–3. The computational framework enables the prediction or understanding of reaction pathways on catalyst surfaces, which is undoubtedly useful for experimentalists. However, the accurate estimation of some crucial properties such as the reaction barriers on catalytic surfaces is extremely time-consuming in first-principles calculation schemes. In this regard, obtaining a full understanding of the catalytic reaction mechanism via first-principles calculations is often considered rather inefficient. In our experience, although dependent on computing power, a time cost of several months is required for computing a full energetics picture of even one metallic catalyst system. The efficiency of the search of catalysts via first-principles calculations has therefore been questioned because carrying out experimental tests without the aid of computer simulations can often be even faster.

To maximize the efficiency of catalyst discovery using combined computational and experimental studies, the descriptors or features that bridge these two areas should be wisely chosen. Specifically, a simple but physically reasonable descriptor or feature enabling the representation of catalytic properties is critical. A representative example of such a descriptor is the d-band center theory, which correlates between the d-band center, i.e., the average energy of electronic d-states projected onto a surface atom of the catalyst, and the gas adsorption energy, which is widely accepted in the field of metallic catalysis. Coupled with the volcano relationship between catalytic activity and adsorption energy7, it is theoretically possible to predict catalytic activity from the d-band center without exploration of the full reaction mechanism. Later, along with the d-band center theory, consideration of the d-band shapes describing higher moments of the d-band as well as the sp-band properties describing local Pauli electronegativity were also suggested to capture the surface reactivity of transition metal alloys5–8. These studies indicate that the electronic density of states (DOS) patterns themselves projected onto the surface atoms of catalysts can serve as an improved descriptor for the development of metal catalysts because they include more comprehensive information on not only d-states but also sp-states (both their values and shapes). Nonetheless, the full DOS patterns themselves have never been used as a descriptor in combined computational-experimental screening processes.

As electronic structures are key to determining the physical/chemical properties of materials, materials with similar electronic structures tend to exhibit similar properties. Indeed, a DFT study revealed that a solid-solution Ir50Au50 alloy can exhibit catalytic properties for the H2 dissociation reaction with an activity comparable to that of Pt, and this result is attributed to the similar electronic structures (DOS patterns) of the Ir50Au50 alloy and Pt9. In another example, the similar electronic structures of Rh50Ag50 and Pd were experimentally verified for hydrogen storage10. The similar electronic structural characteristics enable the Rh50Ag50 alloy to exhibit hydrogen storage properties superior to those of Pd11, although neither Rh nor Ag alone shows hydrogen storage properties9. Thus, bimetallic alloys with a DOS pattern similar to that of Pd, which is a well-known representative metal catalyst, should exhibit catalytic performance similar to that of Pd, which is a good hypothesis for the high-throughput development of bimetallic catalysts.

Here, we used the full DOS pattern as a key descriptor in high-throughput computational-experimental screening protocols. As a
demonstration in the high-throughput search of bimetallic catalysts, we selected palladium (Pd), the prototypical catalyst for hydrogen peroxide (H₂O₂) synthesis from hydrogen (H₂) and oxygen (O₂) gases, as our reference material. Using DFT calculations, we first screened 4350 crystal structures of bimetallic alloys to investigate their thermodynamic stabilities (only closest-packed surfaces were considered). Next, the similarities in the DOS patterns between the alloys and Pd were quantified, and subsequently, their synthetic feasibility was evaluated. Through these processes, we finally proposed eight candidates with high DOS similarities with Pd, which are expected to show catalytic properties comparable to those of Pd. These eight screened alloys were experimentally synthesized and tested for H₂O₂ direct synthesis, and four of them (Ni₅₀Pt₅₀, Au₅₇Pd₄₃, Pt₇₅Pd₂₅, and Pd₅₂Ni₄₈) indeed exhibited catalytic properties comparable to those of Pd. In particular, Pd-free Ni₅₀Pt₅₀ is greatly outperformed prototypic Pd with a 9.5-fold enhancement in cost-normalized productivity (CNP) owing to the high content of inexpensive Ni.

RESULTS

High-throughput computational screening for bimetallic catalysts

Figure 1 shows a schematic diagram of our high-throughput screening protocol for the discovery of bimetallic catalysts. Based on 30 transition metals in periods IV, V, and VI, we considered a total of 435 (50×50) binary systems with a 1:1 (50:50) composition. For each alloy combination, 10 ordered phases that are available for 1:1 composition were investigated, namely, B₁, B₂, B₃, B₄, B₁₁, B₁₉, B₂₇, B₃₃, L₁₀, and L₁₁, leading to a screening of 4350 (435×10) crystal structures. Using DFT calculations, we calculated the formation energy (ΔE) of each phase and determined which crystal structure is most stable in the bulk phase. Here, negative formation energy implies that the phase is thermodynamically favorable (or that the element combination is miscible), and vice versa. Because nonequilibrium alloyed phases can be stabilized by the nanosize effect, although the elemental combinations are immiscible in the bulk phases, a margin of ΔE<0.1 eV was considered when screening the thermodynamic stabilities of the bimetallic systems. The alloyed structures with ΔE>0.1 eV could be readily synthesized; however, such structures would be easily transformed into phase-separated structures during chemical reactions (two-phase structures of the pure elements), which is not suitable for their practical uses as catalysts. Eventually, a total of 435 binary systems and 249 alloys were filtered at the thermodynamic screening step.

For the 249 thermodynamically screened alloys, we calculated the DOS pattern projected on the close-packed surface for each structure and compared it with that of the Pd(111) surface. To quantitatively compare the similarity of two DOS patterns, we defined the following measure:

\[ \Delta \text{DOS}_{2,1} = \left( \int [\text{DOS}_2(E) - \text{DOS}_1(E)]^2 g(E; \sigma) dE \right)^{\frac{1}{2}} \]  

\[ g(E; \sigma) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(E-E_0)^2}{2\sigma^2}} \]  

Here, ΔDOS₂₁ in Eq. (1) indicates the similarity between the DOS of the alloy (DOS₂) and the DOS of the reference Pd(111) (DOS₁) in which a Gaussian distribution function, g(E; σ) in Eq. (2), is considered to compare the two DOS patterns near Fermi energy (E₀) with the high weight. We set the standard deviation, σ = 7 eV because most of the d-band centers for the bimetallic alloys are distributed from -3.5 eV to 0 eV relative to the Fermi energy.

In comparing two DOS patterns, both d-states and sp-states were considered. To clarify the importance of the inclusion of sp-states, we discuss this effect with an example of O₂ adsorption on Ni₅₀Pt₅₀(111), which is one of the elementary steps for H₂O₂ direct synthesis. In Fig. 2, the DOS patterns for d-states and sp-states are shown; the patterns are obtained by the sum of the partial DOSs of the surface Ni and Pt atoms on Ni₅₀Pt₅₀(111). Comparing the DOS patterns before/after O₂ adsorption, the change in the d-band DOS is negligible after O₂ adsorption. On the other hand, the sp-band DOS patterns change more smoothly after O₂ adsorption. This result implies that an O₂ molecule interacts more with the sp-bands of the surface Ni and Pt atoms than with the d-bands on Ni₅₀Pt₅₀(111) in O₂ adsorption. The partial DOSs of O₂ before/after O₂ adsorption on Ni₅₀Pt₅₀(111) are also compared in Fig. 2. An O₂ molecule in the gas phase has a pair of half-occupied orbitals (π*, σ*), which is supportive evidence that the π*, σ* states are fully occupied through the interaction between the metal surface atoms and the O₂ molecule.

The DOS similarity values of the 249 alloy surfaces are shown in Fig. 3. According to the definition of DOS similarity, as the value approaches zero, the electronic structure of the alloy becomes more similar to that of Pd(111), and the material is expected to show catalytic properties similar to those of Pd(111). In Fig. 3, we chose 17 candidates with the low DOS similarity values (ΔDOS₂₁<2.0) to filter: CrRh (ΔDOS₂₁=1.97, B₂ structure), FeCo (1.63, B₂), CoNi (1.71, L₁₀), CoHf (1.89, L₁₀), CoTa (1.96, L₁₀), CoPt (1.78, L₁₀), NiCu (1.11, L₁₀), NiNb (1.96, L₁₀), NiMo (1.87, L₁₀), NiRh (0.98, L₁₀), Ni-Pd (0.84, L₁₀), NiR (1.28, L₁₁), Ni-Pt (1.16, L₁₁), CuPd (1.51, B₂), RhPt (1.67, L₁₁), Pd-Pt (1.16, L₁₀), and PdAu (1.43, L₁₀). Here, owing to the rarity of Hf and Ta, the CoHf and CoTa alloys were excluded from the candidate list. In addition, we excluded NiCu and CrRh from the list because the large reduction potential difference between the elements in the binary system leads to the unfavorable formation of alloyed structures in which the two elements are homogeneously mixed via a wet-chemical method for nanoparticle (NP) synthesis.

Experimental verification of the DFT-guided bimetallic catalysts

For the remaining 13 candidates, we tried to synthesize their alloyed NPs and confirm whether their crystal structures were identical to those (Fig. 3) predicted by DFT calculations. For NP synthesis, we used a butyllithium reduction method. Details of the NP synthesis are found in the Methods section. Because it was assumed in Fig. 3 that the proposed alloys had a composition of 50:50, we intended to synthesize alloys with nearly the same composition. Inductively coupled plasma (ICP) analyses revealed that the compositions of the synthesized alloys (loading ratio of metal precursors = 50:50) were Au₅₇Pd₄₃, Ni₅₀Pt₅₀, Pt₇₅Pd₂₅, Pd₅₂Ni₄₈, Pt₇₅Co₄₂, Pt₇₅Pd₂₅, Rh₅₀Ni₄₈, and Rh₅₀Pd₄₄, however, CoPt, NiMo, NiNi, and NiCo were not alloyed because the reducing power of butyllithium used as a reducing agent was likely insufficient. To confirm whether the alloyed NPs had the same crystal structures as predicted by DFT, their X-ray powder diffraction (XRD) patterns were investigated, as shown in Fig. 4. The samples showed alloyed diffraction patterns without signals from phases of the pure elements that compose each alloy. We also simulated XRD patterns of the alloys on the basis of the DFT crystal structures and found that the simulated patterns matched well with the experimental patterns. This result clearly reveals that we successfully synthesized alloyed NPs with the crystal structures predicted by DFT calculations for eight bimetallic systems.
lattice parameters for the alloyed samples are presented in Supplementary Table 1. In addition, we performed Rietveld refinements of the XRD patterns (Supplementary Figure 1). The synthesized NPs clearly have cubic-based structures as predicted by our DFT calculations, although in the Ni-Pt samples a small amount of non-alloyed Pt (pure Pt) coexists with alloyed Ni$_{72}$Pt$_{28}$. As we used the synthesized Ni-Pt samples themselves when measuring their catalytic performance, we used the ICP composition (Ni$_{61}$Pt$_{39}$).

It was also important to determine whether the synthesized NPs have ordered or disordered structures because the two types of structures can show different catalytic properties$^{19}$. The main role of our descriptor ($\Delta$DOS$_{2-1}$) in the high-throughput protocol for catalyst development is to discover potential catalysts and then transfer the information to experimentalists at high speed. For this purpose, a reference structure for comparison with alloys is required because various structures are possible for random solid-solution structures. In this work, ordered structures were used as a reference and were also validated by comparing simulated and
experimental XRD patterns. From this process, we intended to predict the possibilities and tendencies of alloys for use as H2O2 direct synthesis catalysts. Nevertheless, because the synthesized sample could include random solid-solution structures, there is the potential for discrepancies between theory and experiment.

We further characterized the NP samples by high-angle annular dark-field scanning transmission electron microscopy (Fig. 4 and Supplementary Figure 2–9). The elemental color mapping and overlay clearly indicate the homogeneous mixing of elements in each NP. The mean diameters of the alloyed NPs were 3.4 ± 0.4 nm for the four alloys (Ni50Pt50, Au51Pd49, Pd52Ni48, and Pt52Pd48) showing catalytic properties comparable to those of Pd (Table 1), their NP diameters were in the range of 5.2–11.6 nm, which is similar to the diameter (7.2 ± 1.6 nm) of Pd NPs (Supplementary Figure 10).

To investigate whether the catalytic performance of the eight proposed alloys is comparable to that of Pd, the alloyed catalysts were tested for direct H2O2 synthesis under mild conditions (20°C, 1 atm) in comparison to pure Pd (Table 1). Along with the industrial importance of H2O2 as an eco-friendly oxidizing agent,20,21 the H2O2 direct synthesis reaction can be performed under ambient temperature and pressure conditions, and Pd has been regarded as the archetypical catalyst for the chemical oxygen reduction reaction (ORR) that has been widely used in metallic catalysts. Here, we considered the difference between the d-band centers of the alloys and that of Pd to interpret the catalytic performance, side reactions such as H2O formation should be considered. In other words, the catalytic performance of H2O2 direct synthesis is not dominated by only one catalytic behavior but coupled with multiple behaviors that involve not only H2 conversion but also H2O2 productivity and selectivity. In addition, we compared our descriptor of DOS similarity (ΔDOS2−1) with the d-band center that has been widely used in metallic catalysts. Here, we considered the difference between the d-band centers of the alloys and that of Pd to interpret the catalytic performance, side reactions such as H2O formation should be considered.

Among the four alloy combinations showing high H2O2 productivity, the Au-Pd systems were previously reported as promising candidates for H2O2 direct synthesis, validating our approach once again. In addition, our approach led to the discovery of a catalyst, a Ni-Pt alloy, which has shown catalytic properties comparable to those of Pd (Table 1).

Fig. 2 Partial DOS for the Ni50Pt50 (111) system before and after O2 adsorption. The s-states (light), p-states (dark), and d-states (patterned) DOS plots are shown. Occupied states are filled in color; unoccupied states are depicted by lines. a–c The shape of states without adsorbed O2 on the Ni50Pt50 (111) surface and O2 gas phase in a vacuum. d–e The shape of states of the Ni50Pt50 (111) surface and O2 in gas phase.
Pd-free Ni-Pt alloy can serve as a more cost-effective option. To identify the cost-effectiveness of the Ni-Pt catalyst, we list the CNP (unit, mmol H₂O₂ $metal^{-1} h^{-1}$) of the assessed materials in Table 1, in which the metal price [unit, U.S. dollar ($)] instead of catalyst mass is used. In terms of this metric, Ni₆₁Pt₃₉ shows a CNP of 69.3, which is not only ~9.5 times higher than that of Pd (7.3) but also much higher than those of the other candidates (Au₅₁Pd₄₉: 7.1, Pd₅₂Ni₴₈: 5.5, and Pt₅₂Pd₴₈: 23.0). As another metric for catalytic activity, we also considered the turnover frequency of the catalysts. In terms of this metric, Ni₆₁Pt₃₉ (98.5) shows a performance superior to that of Pd (58.8). Moreover, for efficient H₂O₂ direct synthesis, the H₂ conversion and H₂O₂ selectivity properties of the catalysts should be considered. It is also interesting that Ni₆₁Pt₃₉ shows an H₂O₂ selectivity similar to that of Pd, although Ni₆₁Pt₃₉ shows higher H₂ conversion. These findings clearly demonstrate that the Ni-Pt bimetallic catalyst is very attractive for H₂O₂ direct synthesis.

When screening bimetallic catalysts by electronic structure calculations, only one composition (50:50) for the bimetallic systems was considered because DFT prediction to determine the optimized composition to provide the best catalytic performance would be challenging and time-consuming. Instead, composition optimization proceeded with the help of experiments, likely providing a faster result than a DFT prediction. Therefore, to optimize the composition of the Ni-Pt bimetallic catalysts, we also explored the effects of the Ni/Pt ratio in NiₓPt₁₀₀₋ₓ NPs on their catalytic properties for H₂O₂ direct synthesis (Supplementary Table 2), and no significant structural changes in the NiₓPt₁₀₀₋ₓ NPs were observed (Supplementary Figure 12 and 13). We found that the best catalytic performance was exhibited by Ni₆₁Pt₃₉ in terms of H₂O₂ productivity, H₂ conversion, and H₂O₂ selectivity.
oxidation process of H₂ on the NP surfaces. We also investigated the mechanism on Ni₅₀Pt₅₀(111) and Pd(111) by DFT calculations where the computational hydrogen electrode method was used along with consideration of implicit water solvents (Fig.5b). On both Pd(111) and Ni₅₀Pt₅₀(111), the ORR processes for H₂O₂ formation are thermodynamically favorable. In particular, although the first protonation is very similar (−1.03 eV for Pd and −1.00 eV for Ni₅₀Pt₅₀), the second protonation is slightly more favorable on Ni₅₀Pt₅₀(111) (−1.40 eV vs −1.58 eV). This mechanism also readily reveals more preferential H₂O₂ production on Ni-Pt surfaces than on Pd surfaces.

In Fig. 5a, it is interesting that Ni₅₀Pt₅₀(111) stabilizes H₂O₂* (III state) more than Pd(111) does, whereas the energetics for OOH* (II state) are comparable on the two surfaces. To clarify this result, we investigated the binding characteristics between the adsorbates (OOH* and H₂O₂*) and catalyst surfaces (e.g., Pd(111) and Ni₅₀Pt₅₀(111)) via projected crystal orbital Hamilton population (pCOHP) analysis (Supplementary Figure 15a), in which we display the pCOHPs according to the typical method, namely drawing negative (i.e., bonding) contributions to the right and positive (i.e., anti-bonding) contributions to the left. For OOH* binding to Pd(111) and Ni₅₀Pt₅₀(111), the bonding contributions are comparable. In other words, there are three energy windows for the bonding contributions: −3 to −4 eV (1st window), −5 to −7 eV (2nd), and −8 to −9 eV (3rd). Here, the bonding energy levels for the first and third contributions are lower (stronger binding) for Ni₅₀Pt₅₀(111), whereas the bonding energy levels for the second are lower for Pd(111). On the other hand, in the case of H₂O₂* binding, all of the bonding contributions for Ni₅₀Pt₅₀(111) are lower than those for Pd(111), which explains why the H₂O₂* adsorbate is more stable on Ni₅₀Pt₅₀(111) than Pd(111). This behavior can be explained by the back-bonding character between H₂O₂* and Ni₅₀Pt₅₀(111). Alloying of Pt and Ni creates electron-rich Ni atoms in the alloy structure, which leads to back-bonding with the adsorbate (the Ni atom donates electrons to an empty orbital in the adsorbate). This effect is significantly enhanced for H₂O₂* compared to OOH* as the O atom in the adsorbate bonded to metal surfaces is more electron-deficient for H₂O₂* than OOH* due to the additional O-H bond in H₂O₂*.
In addition, we discuss the selectivity of H$_2$O$_2$ production on Pd (111) and Ni$_{50}$Pt$_{50}$(111) surfaces by DFT calculations, where we considered the ratio of the O-O bond dissociation barrier at several steps to the corresponding hydrogenation step barrier. This is consistent with the experimental finding that the selectivity for H$_2$O$_2$ production is similar for both Pd (63.0%) and Ni$_{50}$Pt$_{50}$ (61.2%).

**DISCUSSION**

This work demonstrates an efficient computational-experimental screening protocol for the development of bimetallic catalysts to replace conventional Pd catalysts for H$_2$O$_2$ direct synthesis. Using this protocol, a Pd-free bimetallic catalyst, Ni$_{61}$Pt$_{39}$, was successfully developed. Here, we note that Ni and Pt have not usually been considered in the catalysis field for H$_2$O$_2$ direct synthesis because they prefer to dissociate O$_2$ molecules, which prevents H$_2$O$_2$ formation, although Ni-Pd and Pt-Pd bimetallic catalysts have been reported. The success story of our protocol primarily results from the validity of our descriptor, the similarity of electronic DOS patterns, for catalyst screening. Moreover, one can readily extend our screening protocol by updating a reference material. For example, since the Ni-Pt system shows superior catalytic performance in this work, we can discover other catalysts by using the DOS pattern of the Ni-Pt alloy as a reference, which remains as future work. In this regard, this protocol will immediately provide opportunities for catalyst discovery for the replacement or reduction in the use of the platinum-group metals and then enable the further application of these catalysts to other chemical reactions.

**METHODS**

**Computational details for screening bimetallic catalysts**

We generated 10 ordered phases for each bimetallic alloy with a 1:1 composition. Specifically, the crystal structure prototypes were obtained by NaCl (B1), CsCl (B2), zinc blende (B3), wurtzite (B4), TiCu (B11), CdAu (B19), FeB (B27), CrB (B33), AuCu (L1$_0$), and CuPt (L1$_1$) compounds from the Material Project. Here, the initial lattice parameters were replaced by values commensurate with covalent radii of two elements in the target compounds. By means of the DFT optimization process, we collected the most stable bulk phases for 4350 binary alloys. Furthermore, the formation energies of the O atom in H$_2$O$_2$* desorption for H$_2$O$_2$ production as an estimation for the H$_2$O$_2$ selectivity (Supplementary Table 5). We assume that the H$_2$O$_2$ production reaction occurs most frequently at the O-O bond scission step with the lowest reaction barrier among the three possible O-O bond scission reactions. Comparing the ratios for the three O-O bond scission reactions, Pd(111) shows the lowest ratio possible O-O bond scission reactions. Pd(111) shows the lowest ratio possible O-O bond scission reactions.

**H$_2$O$_2$ formation mechanism**

The energy diagrams for H$_2$O$_2$ production on the Ni$_{50}$Pt$_{50}$(111) surface and Pd(111) surfaces were also calculated by the DFT method. The simulations were performed using the VASP with projector-augmented-wave (PAW) pseudopotentials and the revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional. Then, we used a plane-wave kinetic energy cutoff of 400 eV and Monkhorst-Pack k-point meshes of $8 \times 8 \times 8$ for the bulk systems and $4 \times 4 \times 1$ for the slab systems. The bulk of the 1 × 1 × 1 unit cell and the slab of the 2 × 2 unit cell with four layers were used. In the slab systems, a vacuum spacing of 15 Å was used to avoid interactions between slabs. All relaxations were performed until the energy change was $>1 \times 10^{-6}$ eV/Å and the forces on the individual atoms were <0.01 eV/Å.

**Table 1.** Catalytic performances of eight bimetallic NPs proposed by the DFT screening process in comparison with that of pure Pd NPs.

| Catalyst       | H$_2$O$_2$ productivity | H$_2$ conversion (%) | H$_2$O$_2$ selectivity (%) |
|---------------|-------------------------|-----------------------|----------------------------|
|               | Mass-normalized (mmol/gmetal h$^{-1}$) | Cost-normalized (mmol/5gmetal h$^{-1}$) | TOF (h$^{-1}$) |
| Au$_{51}$Pd$_{49}$ (1.43)* | 505.2 | 7.1 | 77.1 | 11.6 | 70.1 |
| Ni$_6$Pt$_{39}$ (1.16) | 880.1 | 69.3 | 98.5 | 22.9 | 61.2 |
| Pd$_{50}$Cu$_{50}$ (1.51) | 49.4 | 1.3 | 4.2 | 1.6 | 50.8 |
| Pd$_{50}$Ni$_{50}$ (0.84) | 218.1 | 5.5 | 18.2 | 2.8 | 99.9* |
| Pt$_{50}$Cu$_{50}$ (1.78) | 87.6 | 4.6 | 12.1 | 11.0 | 12.8 |
| Pd$_{50}$Pt$_{50}$ (1.16) | 1225.6 | 23.0 | 186.9 | 25.0 | 78.7 |
| Rh$_{50}$Ni$_{50}$ (0.98) | 16.8 | 0.1 | 14.0 | - | - |
| Rh$_{50}$Pt$_{50}$ (1.67) | 109.3 | 0.6 | 15.7 | 10.6 | 16.6 |
| Pd | 552.4 | 7.3 | 58.8 | 14.0 | 63.0 |

*The number in parentheses corresponds to $\Delta$DOS$_{2-1}$ for the alloy with a composition of 50:50 shown in Fig. 4.

*The high selectivity is mainly caused by the low H$_2$ conversion property.

15b, we find that Ni atoms on Ni$_{50}$Pt$_{50}$ and O atoms in H$_2$O$_2$* donate electrons (cyan isosurface) while the O atoms in H$_2$O$_2$* also accept electrons (yellow), indicating the back-bonding mode between the metal and H$_2$O$_2$.
on the following reactions:

$$O_{2(g)} \rightarrow \ast O_2$$

(3)

$$\ast O_2 + H^+ + e^- \rightarrow \ast OOH$$

(4)

$$\ast OOH + H^+ + e^- \rightarrow \ast H_2O_2$$

(5)

$$\ast H_2O_2 \rightarrow \ast H_2O_2(\ast)$$

(6)

We also performed pCOHP calculations using the LOBSTER package to understand the binding character between the adsorbates (e.g., OOH$^*$ and H$_2$O$_2^*$) and catalyst surfaces (e.g., Pd(111) and Ni$_{50}$Pt$_{50}$(111)). The differential charge density ($\Delta$$\rho$) of the H$_2$O$_2^*$ adsorbates on the Ni$_{50}$Pt$_{50}$(111) surface was evaluated by the following:

$$\Delta$$\rho = $$\rho_{\text{tot}}$$ - $$\rho_{\text{ads}}$$ - $$\rho_{\text{slab}}$$

(7)

where, $\rho_{\text{tot}}$ is the charge density of the H$_2$O$_2^*$-Ni$_{50}$Pt$_{50}$ system and $\rho_{\text{ads}}$, and $\rho_{\text{slab}}$ are the charge densities of the H$_2$O$_2^*$ adsorbate and metal slab, respectively. The atomic coordinates for $\rho_{\text{ads}}$, and $\rho_{\text{slab}}$ are equal to those in the H$_2$O$_2^*$-Ni$_{50}$Pt$_{50}$ system.

**Chemicals**

Palladium(II) acetate [Pd(CH$_3$COO)$_2$, ≥99.9%], copper(II) acetate [Cu(CH$_3$COO)$_2$, 99.99%], nickel(II) acetylacetonate [Ni(acac)$_2$, 95%], rhodium (III) nitrate hydrate [Rh(NO$_3$)$_3$·XH$_2$O, ~36%], gold(III) chloride trihydrate [HAuCl$_4$·3H$_2$O, 99.9%], chloroplatinic acid hydrate [H$_2$PtCl$_6$·XH$_2$O, ~38%], cobalt acetate tetrahydrate [Co(CH$_3$COO)·4H$_2$O, 99.99%], diocyl ether, oleylamine, and n-butyl lithium solution [2.0 M in cyclohexane] were purchased from Sigma-Aldrich. Ethanol was analytical grade and was used without further purification.

**Catalyst synthesis**

All alloy metal catalysts and Pd catalysts were synthesized using the butyllithium reduction method. To synthesize the bimetallic KY catalysts, 0.017 mmol of X precursor and Y precursor (details are described in Table 3 of Supporting Information) were dissolved in 10 mL of dioctyl ether with 2 mL of oleylamine at 50°C. The solution was then injected into a butyllithium solution containing 15 mL of diocyl ether and 1.2 mL of 2.0 M butyllithium in cyclohexane at 50°C. The colloids were stirred (500 rpm) for 20 min and then heated to 120°C for 1.5 h in an Ar atmosphere. The reaction mixture was further heated to 260°C for 1 h. The mixture was cooled to room temperature, and 1.25 mL of trietylphosphine was injected to protect the colloids. The resulting NPs were washed with ethanol three times.

**Catalyst characterization**

Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectra (EDS) were acquired using a transmission electron microscope (FEI Talos F200X) equipped with scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (Bruker Super-X EDS system). The crystal structure was examined by X-ray diffraction (Rigaku Dmax 2500) with Cu Kα radiation ($\lambda = 1.5406$ Å). The samples for the TEM images and X-ray diffraction patterns were purified by centrifugation three times to remove the surfactants and/or excess reactants. Then, the NPs were dispersed in ethanol. The resulting solution was dropped on a copper grid coated with an amorphous carbon film for the TEM images and a soda-lime-silica glass for the X-ray diffraction pattern. The actual compositions of each alloy catalyst were measured via ICP atomic emission spectrometry using ICAP6500 Duo (Thermo).

**Catalyst performance measurements**

The direct synthesis of H$_2$O$_2$ was performed in a double-jacket glass reactor under stirring at 1200 rpm. The reaction medium (150 mL) was composed of ethanol and water (ethanol:water volume ratio = 1:4) with 0.9 mM sodium bromide (NaBr) and 0.02 M phosphoric acid (H$_3$PO$_4$). The catalyst weight used was 1 mg. The volumetric flow rate of the reactant gas stream was 22 mL/min (H$_2$O$_2$ volume ratio = 1:10). The reaction was performed at 293 K and 1 atm for 1 h. After the reaction, the concentration of H$_2$O$_2$ was calculated using iodometric titration. The concentration of H$_2$ was calculated using gas chromatography (Younglin, 6500GC) equipped with a Molecular Sieve 5 A (Supelco, 60/80 mesh, 6 ft × 1/8 in, 2.1 mm) packed column and a thermal conductive detector. The catalytic properties (H$_2$O$_2$ productivity, H$_2$ conversion, and H$_2$O$_2$ selectivity) shown in Table 1 were calculated with the following equations:

$$H_2 \text{ conversion} (%) = \frac{\text{moles of reacted } H_2}{\text{moles of supplied } H_2} \times 100$$

$$H_2O_2 \text{ selectivity} (%) = \frac{\text{moles of formed } H_2O_2}{\text{moles of reacted } H_2} \times 100$$

$$H_2O_2 \text{ productivity} (\text{mmol/gmetal} \times \text{h}) = \frac{\text{mmoles of formed } H_2O_2}{\text{weight of metal (g)} \times \text{reaction time (h)}}$$

$$\text{TOF} (h^{-1}) = \frac{\text{mmoles of formed } H_2O_2}{\text{mmol of metal} \times \text{reaction time (h)}}$$

**Fig. 5**  

H$_2$O$_2$ direct synthesis mechanisms of Ni$_{50}$Pt$_{50}$(111) and Pd(111) from DFT calculations.  

(a) The Langmuir-Hinshelwood mechanism.  

(b) The electron–proton transfer mechanism. The cyan lines are the energy diagram for Ni$_{50}$Pt$_{50}$(111), and the magenta lines are for Pd(111). The color code for the atoms is as follows: teal = Ni, coral = Pt, red = O, and green = H.
DATA AVAILABILITY
All data needed to evaluate the conclusions of this paper are available within the paper and Supplementary Information.

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AUTHOR CONTRIBUTIONS
S.S.H. conceived the idea. B.C.Y., Hyunji Nam, S.Y.L, and S.S.H. designed the calculations and experiments. B.C.Y. performed the high-throughput DFT calculations. Hyunji Nam and Hyobin Nam performed the synthesis and characterization of NP catalysts. Hyunji Nam, Hyobin Nam, K.-Y.L., S.-C.K., and S.O.W. performed the catalytic performance measurements. M.-C.K., H.W.L, and D.K. performed DFT calculations on the catalytic reaction mechanism. B.C.Y., Hyunji Nam, M.-C.K., H.W.L, S.Y.L, and S.S.H.
analyzed and discussed the results. B.C.Y., Hyunji Nam, M.-C.K., S.Y.L., and S.S.H. drafted the manuscript. S.Y.L. and S.S.H. supervised the research. All the authors approved the final version of the manuscript. B.C.Y. and Hyunji Nam contributed equally to this work.

COMPETING INTERESTS
The authors declare no competing interests.

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