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O₂ activation by core–shell Ru₁₃@Pt₄₂ particles in comparison with Pt₅₅ particles: a DFT study†

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The reaction of O₂ with a Ru₁₃@Pt₄₂ core–shell particle consisting of a Ru₁₃ core and a Pt₄₂ shell was theoretically investigated in comparison with Pt₅₅. The O₂ binding energy with Pt₅₅ is larger than that with Ru₁₃@Pt₄₂, and O–O bond cleavage occurs more easily with a smaller activation barrier (*E_a*) on Pt₅₅ than on Ru₁₃@Pt₄₂. Protonation to the Pt₄₂ surface followed by one-electron reduction leads to the formation of an H atom on the surface with considerable exothermicity. The H atom reacts with the adsorbed O₂ molecule to afford an OOH species with a larger *E_a* value on Pt₅₅ than on Ru₁₃@Pt₄₂. An OOH species is also formed by protonation of the adsorbed O₂ molecule, followed by one-electron reduction, with a large exothermicity in both Pt₅₅ and Ru₁₃@Pt₄₂. O–OH bond cleavage occurs with a smaller *E_a* on Pt₅₅ than on Ru₁₃@Pt₄₂. The lower reactivity of Ru₁₃@Pt₄₂ than that of Pt₅₅ on the O–O and O–OH bond cleavages arises from the presence of lower energy in the d-valence band-top and d-band center in Ru₁₃@Pt₄₂ than in Pt₅₅. The smaller *E_a* for OOH formation on Ru₁₃@Pt₄₂ than on Pt₅₅ arises from weaker Ru₁₃@Pt₄₂–O₂ and Ru₁₃@Pt₄₂–H bonds than the Pt₅₅–O₂ and Pt₅₅–H bonds, respectively. The low-energy d-valence band-top is responsible for the weak Ru₁₃@Pt₄₂–O and Ru₁₃@Pt₄₂–OH bonds. Thus, the low-energy d-valence band-top and d-band center are important properties of the Ru₁₃@Pt₄₂ particle.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a promising candidate for a clean and sustainable energy source to cope with the growing energy consumption and related environmental concerns. Pt particles are used as a catalyst for the oxygen reduction reaction (ORR) at the PEMFC cathode because of their incomparable catalytic activity and stability in acidic solution, as discussed in recent reviews;^{1–6} we cite here reviews

from the last 5 years because many reviews have been published. However, their limited availability on earth and high cost still remain major obstacles for the wide use of PEMFCs. One of the promising methods to solve this problem is the use of core–shell Pt particles (M@Pt) consisting of Pt for the shell and abundant metals (M) for the core, because Pt content can be reduced in the catalyst by the use of a M core but the Pt shell exhibits high catalytic activity and stability in acid solution, as reviewed in the last few years.^{7–14} Also, one can expect to improve the catalytic activity of the Pt shell by tuning the electronic structure of the Pt shell with the M core.

Recently, core–shell Ru@Pt particles have been reported as excellent ORR catalysts.^{15–20} For instance, Adzic and co-workers demonstrated that the catalytic activity of Ru@Pt could be tuned by varying the Pt shell thickness; Ru@Pt_{2ML} with two Pt layers was more active than Ru@Pt_{xML} (*x* = 1 and 3).¹⁵ Jackson and coworkers^{17,19} and Takimoto and coworkers¹⁸ reported that the catalytic activity of Ru@Pt for the ORR exceeded that of a commercial Pt electrode. Jackson and co-workers also interestingly obtained a volcano plot of the catalytic activity against the O binding energy, suggesting that both overly strong and overly weak O binding with the Pt surface is not good for ORR catalysts.¹⁷ However, the relation between electronic structure and origin of the O binding energy has been unclear.

Many theoretical ORR studies reported so far discuss the relation between electronic structure of the catalyst and ORR activity.^{21–39} In particular, the O–O bond activation has been

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† Electronic supplementary information (ESI) available: Possible adsorption structures of 2(O) species and (O)(OH) species (Scheme S1); total energies for Pt₅₅ and Pt₄₂Ru₁₃ in different possible spin states using PBE-D3 method (Table S1); binding energies (*E_b*, in eV) for O₂ and OOH species (Table S2); binding energies (*E_b*, in eV) for O, OH, and H/x-binding species (Table S3); optimized structures of O₂-binding species (Fig. S1), 2O-binding species (Fig. S2), OOH-binding species (Fig. S3), (O)(OH)-binding species (Fig. S4) and Cartesian coordinates of important optimized species discussed in the main text. The effect of box size for periodic calculation on the Fermi level (*E_F*, eV) and the d-valence band top (*E_{VB, top}*, eV) energies (Table S4). d-Valence band top energy (in eV) calculated using several different functionals and basis sets (Table S5). See DOI: 10.1039/d0ra05738j



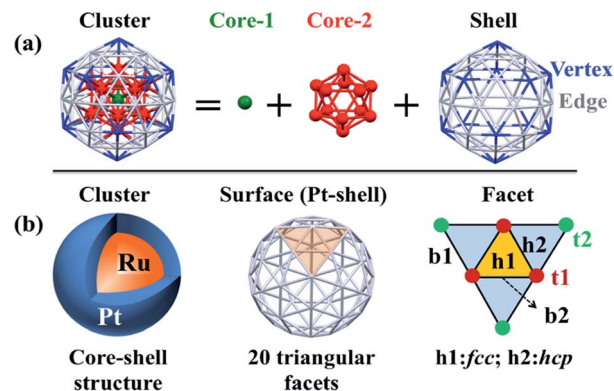
theoretically investigated in many works, as discussed by a recent review⁴⁰ and many works even after this review.^{41–46} However, the theoretical study of Ru@Pt has been limited so far; for instance, the O and OH-binding energies with Ru₁₃@Pt₄₂ and Pt₅₅ have been theoretically investigated,⁴⁷ but the O–O bond cleavage on Ru@Pt has not been investigated, despite the crucial importance of such O–O bond cleavage in the ORR. Considering that the theoretical study of nanoscale metal particles is still challenging and its development is needed even currently,^{48–50} the theoretical study of the O₂ reaction on Ru@Pt and related metal particles is indispensable.

In this work, we theoretically investigated dioxygen (O₂) adsorption and O–O bond cleavage by the Ru₁₃@Pt₄₂ particle in comparison with the Pt₅₅ particle using DFT computations. In the O–O bond cleavage, two reaction courses are plausible; in one, the O–O bond of the adsorbed O₂ molecule is cleaved. In the other reaction course, OOH species are formed on the surface, followed by O–OH bond cleavage, because it is likely that the OOH species are easily formed in the presence of excess protons and enough supply of electrons to the electrode. Our purposes here are to explore O₂ adsorption, O–O bond cleavage, OOH formation, and O–OH bond cleavage, compare the reactivity between Ru₁₃@Pt₄₂ and Pt₅₅, find important factor(s) determining the reactivities of Ru₁₃@Pt₄₂ and Pt₅₅, and present a theoretical understanding of the differences between Ru₁₃@Pt₄₂ and Pt₅₅. We believe that the theoretical findings on these issues are valuable for understanding the chemistry of nanometal particles.

2. Computational methods and models

Spin-polarized periodic DFT calculations were carried out using the Vienna *Ab initio* Simulation Package (VASP),^{51,52} where plane-wave basis sets were employed with an energy cutoff of 400 eV, and the projector-augmented-wave (PAW) pseudopotentials were used to represent core electrons. The PBE-D3 functional was employed in all calculations,⁵³ where “D3” represents the dispersion correction proposed by Grimme’s group.^{54,55} Ru@Pt and Pt particles were placed in a large supercell (25 Å × 25 Å × 25 Å) to ensure enough separation by vacuum. Geometry optimization of equilibrium structure was carried out in gas phase using the energy threshold of 0.0001 eV and force threshold of 0.01 eV Å^{−1}. Optimization of transition state (TS) was carried out using the climbing image nudged elastic band (CI-NEB) method with the VASP transition-state tools (VTST),^{56,57} in which thresholds for convergence were set to 0.0001 eV for energy and 0.02 eV Å^{−1} for force. To evaluate solvent effects, an implicit solvation model, which describes the effect of electrostatic interaction between solute and solvent, was employed as implemented in VASPsol,^{58,59} where optimized geometry in gas phase was used.

Though Pt₅₅ and Ru₁₃@Pt₄₂ particles are not very large compared to real catalysts, we employed these particles here as model nanoparticles because we have to optimize many intermediates and transition states. Also, the use of Pt₅₅ and



Scheme 1 (a) Geometry of the icosahedron (*I_h*) 55-atom particle and (b) binding sites of the Pt₄₂ shell of the *I_h* Ru₁₃@Pt₄₂ core-shell particle.

Ru₁₃@Pt₄₂ particles is not unreasonable, considering that subnanometer-scale metal particles with 55 metal atoms have been employed as model particle in theoretical studies of O₂ adsorption and O–O bond cleavage^{46,60–63} and other catalytic reactions.^{64–69} The number “55” is a magic number for icosahedral (*I_h*) and cuboctahedral (*O_h*) structures. Here, we employed the *I_h*-like structure because the *I_h* structure is more stable than *O_h* in Ru₁₃@Pt₄₂; the relative stabilities of various spin states and comparison between core-shell and non-core-shell structures have been investigated recently.⁴⁷ As shown in Scheme 1, the Pt₄₂ surface of icosahedral Pt₅₅ and Ru₁₃@Pt₄₂ consists of 20 triangular facets. Each facet has three different types of binding sites: top (t), bridge (b) and hollow (h). Adsorptions at these binding sites are classified as follows: (i) adsorption at the top site is denoted as t1 or t2, in which the adsorbate binds with one Pt atom at the edge or the vertex position. (ii) Adsorption in a bridging manner is denoted as b1 or b2, in which the adsorbate binds with two adjacent Pt atoms at either the edge and vertex positions or two adjacent edge positions. (iii) Adsorption at the hollow site is denoted as h1 or h2, in which the adsorbate binds at either the fcc-like position among three edge-Pt atoms or the hcp-like position among two edge-Pt atoms and one vertex-Pt atom. We explored all these possible adsorption sites.

3. Results and discussion

In this work, we firstly discuss O₂ adsorption to Pt₅₅ and Ru₁₃@Pt₄₂, followed by O–O bond cleavage, OOH formation from the adsorbed O₂ molecule, and O–OH bond cleavage on the Pt₅₅ and Ru₁₃@Pt₄₂ surfaces. Next, we show the differences in reactivity between Pt₅₅ and Ru₁₃@Pt₄₂ in these reactions and elucidate the reasons for the differences. Lastly, we unveil the characteristic feature(s) of Ru₁₃@Pt₄₂ in comparison with Pt₅₅.

3.1 Dioxygen (O₂) adsorption

The binding energy $E_b(\text{O}_2)$ of dioxygen molecule (O₂) increases (becomes more negative) following the order O₂-η¹/h1 < O₂-η¹/t1 < O₂-η¹/t2 < O₂-μ₂/b2 < O₂-μ₃/h2 < O₂-μ₃/h1 < O₂-μ₂/b1 for pure Pt₅₅ and O₂-η¹/h1 < O₂-μ₂/b2 < O₂-η¹/t1 < O₂-μ₃/h2 < O₂-μ₃/h1 <



$O_2-\eta^1/t_2 < O_2-\mu_2/b_1$ for $Ru_{13}@Pt_{42}$, as shown in Fig. S1 in the ESI,[†] where $h1$, $t1$ etc., represent the adsorption site shown in Scheme 1 and “A- μ_2/x ” represents the interaction of adsorbate A with Pt at the x binding site in a μ_2 manner, hereinafter. Obviously, O_2 is preferentially adsorbed at the $b1$ site of both Pt_{55} and $Ru_{13}@Pt_{42}$ in a μ_2 -side-on manner ($O_2-\mu_2/b1$). This is the most stable O_2 adsorption structure. The coordination number of the surface Pt atom is one of the important factors for stabilization of O_2 adsorption: because the coordination number of the vertex Pt atom is 6 but that of the edge Pt is 7, the O_2 molecule tends to interact with the vertex Pt atom compared to the edge Pt atom. However, the O_2 molecule cannot interact with two vertex Pt atoms because the vertex Pt is far from the neighboring vertex Pt. Thus, O_2 interacts with one vertex Pt and one edge Pt in a bridging manner, as seen by the $O_2-\mu_2/b1$ structure.

In the most stable $O_2-\mu_2/b1$ -binding species (2), the O–O distance of $Pt_{55}(O_2)$ **2^{Pt}** is moderately longer than that of $Ru_{13}@Pt_{42}(O_2)$ **2^{RuPt}**, and the Pt–O distance of **2^{Pt}** is moderately shorter than that of **2^{RuPt}**, as shown in Fig. 1. The $E_b(O_2-\mu_2/b1)$ value is -1.85 (-1.70) eV for Pt_{55} and -1.07 (-0.95) eV for $Ru_{13}@Pt_{42}$, as shown in Fig. 2, where the figures in parentheses represent the binding energy in gas phase. The larger binding energy of the O_2 molecule with Pt_{55} than with $Ru_{13}@Pt_{42}$ is consistent with such geometrical features as the shorter Pt–O and longer O–O distances in **2^{Pt}** than in **2^{RuPt}**. The reasons for the stronger O_2 adsorption with Pt_{55} than with $Ru_{13}@Pt_{42}$ are discussed below. It is also noted that solvation by water enhances O_2 binding with these metal particles.

3.2 O–O bond cleavage

Starting from **2^{Pt}** and **2^{RuPt}**, O–O bond cleavage occurs *via* transition states **TS2/3a^{Pt}** and **TS2/3a^{RuPt}** to afford $Pt_{55}(O)_2$ **3a^{Pt}** and $Ru_{13}@Pt_{42}(O)_2$ **3a^{RuPt}**, respectively, as shown in Fig. 1. In **TS2/3a^{Pt}**, the O–O distance is considerably elongated to 1.835 Å, by 0.451 Å, and the Pt–O distances become shorter to 1.825 Å and 1.845 Å, by 0.144 and 0.152 Å (Fig. 1). In **TS2/3a^{RuPt}**, the O–O distance is more elongated to 1.939 Å (by 0.565 Å) than in **TS2/3a^{Pt}**, indicating that **TS2/3a^{Pt}** is more reactant-like than **TS2/3a^{RuPt}**. Consistent with the O–O bond elongation, the Pt–O distances become shorter in **TS2/3a**. Though they are almost the same between **TS2/3a^{Pt}** and **TS2/3a^{RuPt}**, the average of Pt–O distances is moderately shorter in **3a^{Pt}** than in **3a^{RuPt}**, suggesting the stronger binding energy of the O atom with Pt_{55} than with $Ru_{13}@Pt_{42}$, as discussed below. The activation barrier (E_a) relative to **2** is 0.31 (0.33) eV and 0.35 (0.49) eV for **TS2/3a^{Pt}** and **TS2/3a^{RuPt}**, respectively, and the reaction energy (ΔE) relative to **2** is -0.90 (-0.83) eV and -0.95 (-0.85) eV, for **3a^{Pt}** and **3a^{RuPt}**, as shown in Fig. 2, where a negative ΔE value represents exothermicity. The smaller E_a for the O–O bond cleavage on Pt_{55} than on $Ru_{13}@Pt_{42}$ is consistent with the more reactant-like **TS2/3a^{Pt}** than **TS2/3a^{RuPt}**. The moderately smaller ΔE in the Pt_{55} case than in the $Ru_{13}@Pt_{42}$ case is seemingly inconsistent with the smaller E_a of the former case than in the latter. But, this is not unreasonable because the O_2 binding energy with Pt_{55} is overly larger than that with $Ru_{13}@Pt_{42}$. It is noted that the E_a is smaller and ΔE is more negative in water than in gas phase, because CT is generally enhanced by polar solvents.

The short Pt–Pt distance of the surface has been discussed as one important factor for high catalytic activity.^{70–73} The surface

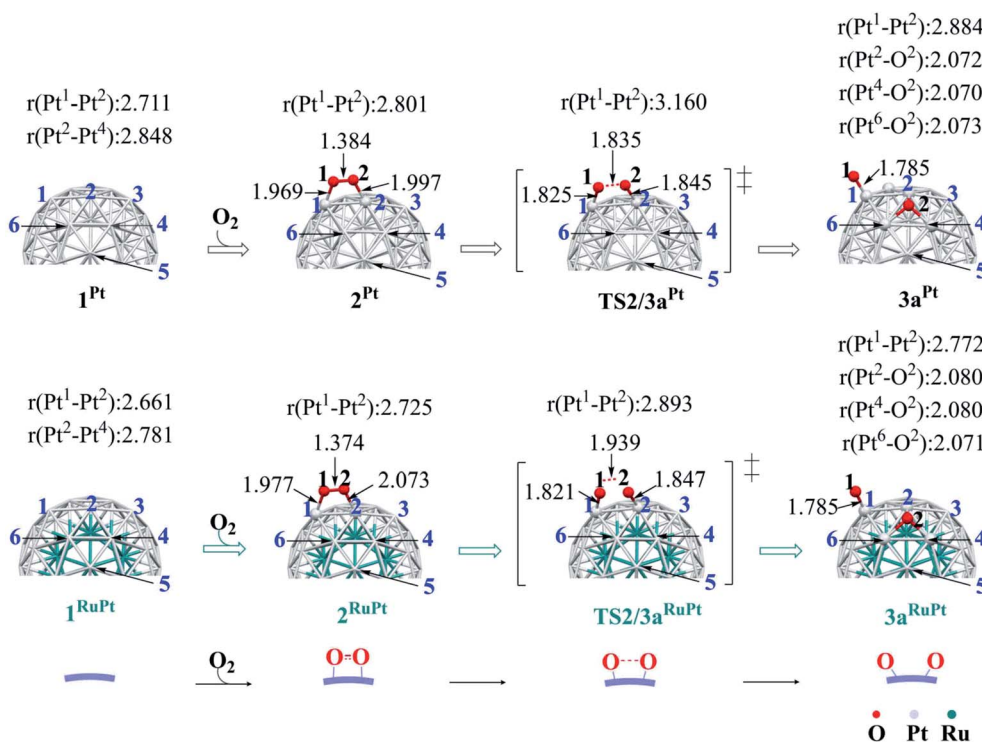


Fig. 1 Geometry changes in O_2 adsorption followed by O–O bond cleavage on Pt_{55} and $Ru_{13}@Pt_{42}$. Values represent bond distance in angstrom.



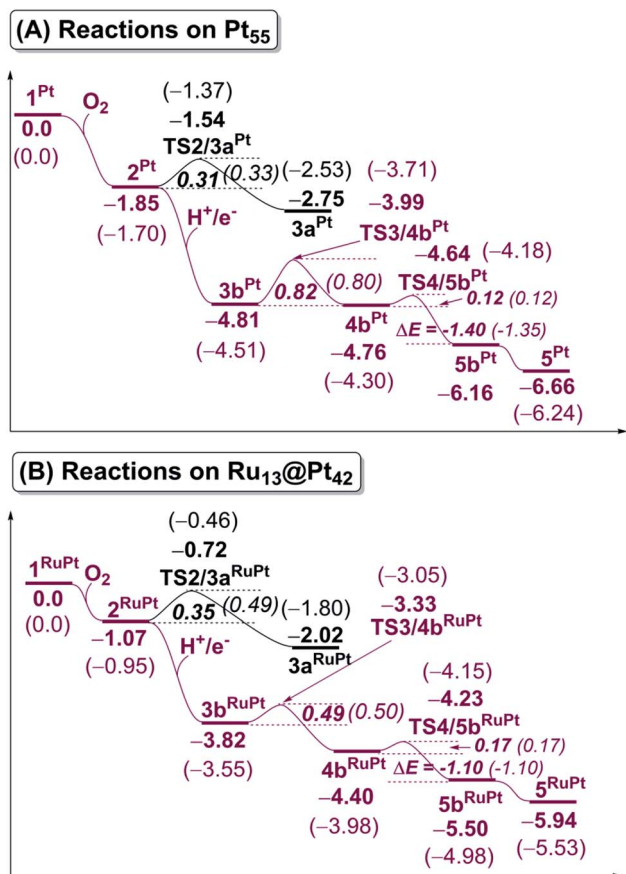


Fig. 2 Energy changes in O₂ adsorption followed by O–O bond cleavage and OOH formation, followed by O–OH bond cleavage, on (A) Pt₅₅ and (B) Ru₁₃@Pt₄₂. Values represent energy (in eV) relative to Pt₅₅ or Ru₁₃@Pt₄₂. In parentheses are values for energy in gas phase.

Pt¹–Pt² distance becomes longer by the O₂ adsorption and the O–O bond cleavage in both Pt₅₅ and Ru₁₃@Pt₄₂ (Fig. 1), suggesting that the short Pt–Pt distance of the surface is not beneficial to these processes. The other important factor is flexibility of the Pt surface. Actually, the energy destabilization of Pt₅₅ is much smaller than that of Ru₁₃@Pt₄₂ when surface Pt–Pt distance is elongated; it is 1.0 kcal mol^{−1} in Pt₅₅ and 7.5 kcal mol^{−1} in Ru₁₃@Pt₄₂ for the Pt–Pt elongation by 0.4 Å, where we employed rather arbitrarily the elongation of 0.4 Å because the Pt–Pt distance is elongated by about 0.3–0.4 Å at TS2/3a^{Pt} of the O–O bond cleavage on Pt₅₅. These results suggest that the longer Pt–Pt distance and the larger flexibility of Pt₅₅ than those of Ru₁₃@Pt₄₂ are favorable for O₂ adsorption and O–O bond cleavage; in other words, the discussion that short Pt–Pt distance is good for high catalytic activity is not useful when these processes are rate-determining. In addition, it should be noted that the flexibility of the Pt surface is a crucially important factor besides Pt–Pt distance.

3.3 OOH formation followed by O–OH bond cleavage

In ORR, it is likely that the proton is adsorbed easily to the cathode surface because protons exist in excess in solution. Also, electrons are always supplied to the cathode. These

features suggest that H species is formed on the cathode surface. Actually, the reactions of adsorbed H atoms with oxygen-containing species were discussed in recent works,^{25,74–76} which indicate they correspond to the Langmuir–Hinshelwood pathway. First, we investigated the formation of OOH species from the adsorbed O₂ molecule and H atom on the surface; the adsorption sites of OOH and H are shown in Fig. S3, Tables S2 and S3 in the ESI.†

The H⁺/e[−] addition occurs with significant exothermicity in 2^{Pt} and 2^{RuPt} to afford Pt₅₅(O₂)(H¹) 3b^{Pt} and Ru₁₃@Pt₄₂(O₂)(H¹) 3b^{RuPt}, as shown in Fig. 2, where one-half of Δ*E* of the eq. 2H⁺ + 2e[−] → H₂, was taken as the energy of H⁺/e[−]; it is noted that this step can be tuned experimentally by the cell voltage. In 3b^{Pt} and 3b^{RuPt}, H¹ takes the position bridging two Pt atoms, as shown in Fig. 3 and 4. Starting from 3b^{Pt} and 3b^{RuPt}, the H¹ reacts with the adsorbed O₂ *via* transition states TS3/4b^{Pt} and TS3/4b^{RuPt} to afford an OOH species adsorbed on the Pt surface Pt₅₅(OOH) 4b^{Pt} and Ru₁₃@Pt₄₂(OOH) 4b^{RuPt}, respectively (Fig. 3 and 4). In the transition state, the H¹ is approaching the O², keeping a bonding interaction with one Pt, and simultaneously, the O² is leaving the Pt₄₂ surface. Though the Pt–O² distance is very long in TS3/4b^{Pt}, the O²–H¹ distance is still long (1.414 Å), and the O¹–O² distance is moderately elongated. In TS3/4b^{RuPt}, the O²–H¹ distance is much longer (2.006 Å) than that of TS3/4b^{Pt}, suggesting that TS3/4b^{RuPt} is more reactant-like than TS3/4b^{Pt}, in contrast to the more product-like TS2/3a^{RuPt} than TS2/3a^{Pt}. This contrast is reasonable according to the Hammond rule because the O–O bond cleavage occurs with smaller *E*_a (relative to 2^{Pt}), but the OOH formation occurs with larger *E*_a on Pt₅₅ than on Ru₁₃@Pt₄₂. In 4b^{Pt} and 4b^{RuPt}, the O¹–O² distance is 1.451 Å and 1.456 Å, respectively, which is moderately shorter than that (1.471 Å, the PBE-D3-optimized value) of free HOOH. The surface Pt¹–Pt² distance becomes longer in this reaction, suggesting that the short Pt–Pt distance of the Pt surface is not favorable for this step, either.

We explored here another OOH formation pathway in which adsorbed O₂ molecule undergoes protonation followed by one-electron reduction, as proposed by several works.^{77–79} This reaction corresponds to the Eley–Rideal pathway. We compared the energy change in this pathway with that of the Langmuir–Hinshelwood pathway, as shown in Scheme 2. In the Pt₅₅ case, the energy changes differ little between these two pathways, suggesting that the OOH formation occurs *via* both pathways. In Ru₁₃@Pt₄₂, the H⁺/e[−] addition to the adsorbed O₂ molecule is more exothermic than that to the Pt₄₂ surface (Scheme 2), indicating that the Eley–Rideal pathway is more favorable than the Langmuir–Hinshelwood pathway from the viewpoint of reaction energy. Also, Scheme 2 strongly suggests that the OOH formation occurs more easily on Ru₁₃@Pt₄₂ *via* the Eley–Rideal pathway than that on Pt₅₅ *via* both the Langmuir–Hinshelwood and Eley–Rideal pathways. Here, we need to mention that the reaction pathway significantly depends on the coverage of Pt surface by O₂ molecules; the Langmuir–Hinshelwood pathway preferentially occurs at low coverage. On the other hand, the Eley–Rideal pathway preferentially occurs at high coverage from the viewpoint of possibility, while the Eley–Rideal pathway becomes less easy at high coverage than at low coverage, from



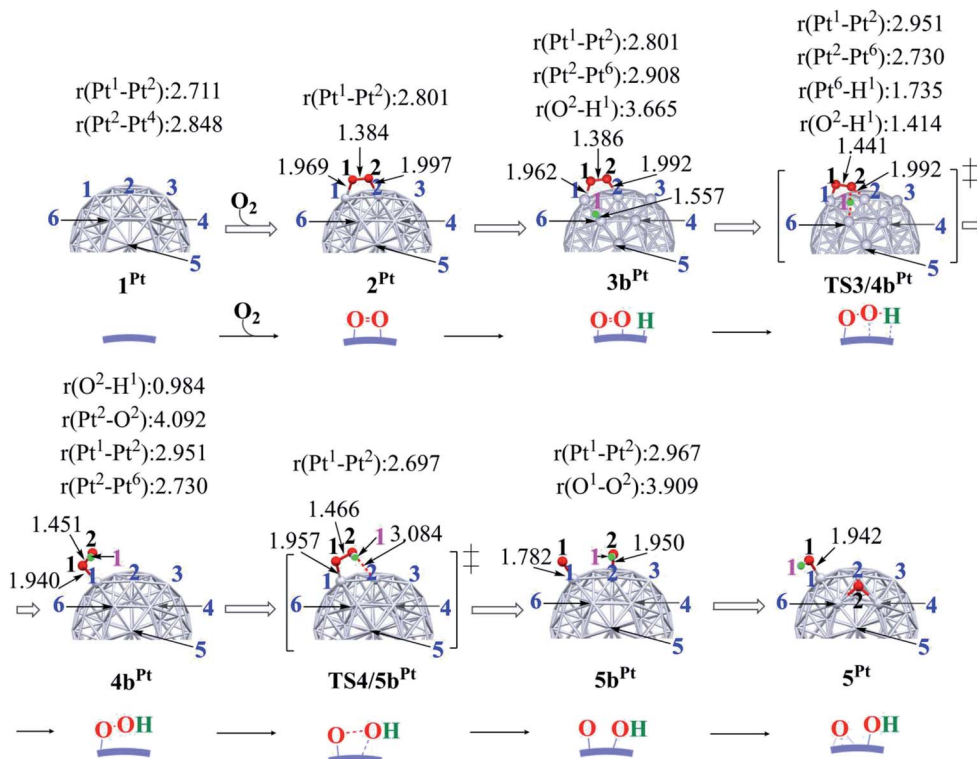


Fig. 3 Geometry changes in OOH formation through the reaction between adsorbed O₂ molecule and H atom, followed by O–OH bond cleavage on Pt₅₅ particle. Numbers represent bond distance in angstrom.

the viewpoint of reactivity of adsorbed O₂ molecule, because the adsorbed O₂ molecule becomes less negatively charged at high coverage. The mechanism of OOH formation significantly depends on reaction conditions, which must be investigated

carefully in the near future. In both pathways, it is reasonably concluded that OOH formation is an easy process on Pt₅₅ and Ru₁₃@Pt₄₂ particles.

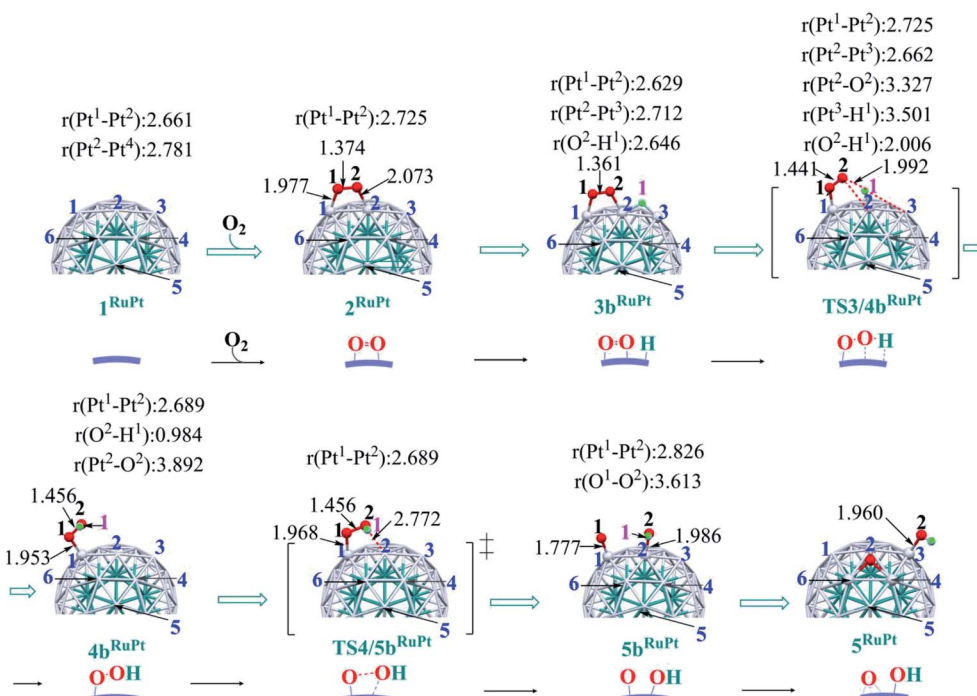
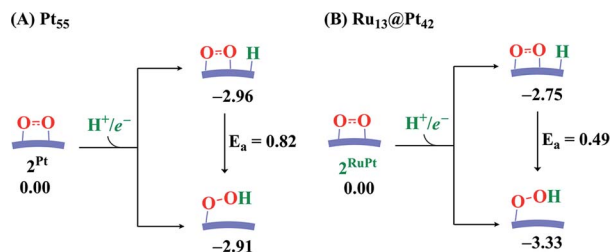


Fig. 4 Geometry changes in OOH formation through the reaction between adsorbed O₂ molecule and H atom, followed by O–OH bond cleavage on Ru₁₃@Pt₄₂ particle. Numbers represent bond distance in angstrom.





Scheme 2 Comparison of energy change between H⁺/e⁻ addition to the Pt₄₂ surface (the Langmuir–Hinshelwood pathway) and the adsorbed O₂ molecule (the Eley–Rideal pathway).

Table 1 Changes of the Bader charges in O₂ adsorption and O–O bond cleavage^a

	2	TS2/3a	3a
Pt₅₅			
O ¹	−0.305 (−0.273) ^b	−0.496 (−0.434)	−0.610 (−0.509)
O ²	−0.300 (−0.259)	−0.480 (−0.406)	−0.706 (−0.684)
Pt ₅₅	+0.605 (+0.532)	+0.976 (+0.840)	+1.316 (1.193)
Δ(CT) ^c	0.0 (0.0)	0.371 (0.308)	0.711 (0.661)
Ru₁₃@Pt₄₂			
O ¹	−0.326 (−0.289)	−0.519 (−0.445)	−0.640 (−0.536)
O ²	−0.320 (−0.268)	−0.506 (−0.427)	−0.719 (−0.689)
Ru ₁₃ @Pt ₄₂	+0.646 (+0.557)	+1.025 (0.872)	+1.359 (+1.225)
Δ(CT) ^c	0.0 (0.0)	0.379 (0.315)	0.713 (0.668)

^a A positive value represents positive atomic charge, and *vice versa*.

^b Values in parentheses represent the Bader charge in gas phase. ^c A positive value represents the increase in charge transfer from the metal particle to O¹ and O² atoms.

Starting from **4b^{Pt}** and **4b^{RuPt}**, the O–OH bond is cleaved through transition states **TS4/5b^{Pt}** and **TS4/5b^{RuPt}** to afford Pt₅₅(O)(OH) **5b^{Pt}** and Ru₁₃@Pt₄₂(O)(OH) **5b^{RuPt}**, respectively (Fig. 3 and 4). In the transition state, the O² is approaching the Pt², while the Pt²–O² distance is still long, and the O¹–O² distance changes little from those in **4b^{Pt}** and **4b^{RuPt}**, indicating that the transition state is reactant-like. These transition states

differ little from each other except for moderately different Pt–O² and O¹–O² distances.

The OOH formation from adsorbed O₂ and H species occurs with a smaller E_a of 0.49 (0.50) eV on Ru₁₃@Pt₄₁ than on Pt₅₅ (E_a = 0.82 (0.80) eV), as shown in Fig. 2. The smaller E_a in the reaction on Ru₁₃@Pt₄₂ than on Pt₅₅ is consistent with the more reactant-like **TS3/4b^{RuPt}** than **TS3/4b^{Pt}**. The O–OH bond cleavage occurs with a very small E_a on both Pt₅₅ (E_a = 0.12 (0.12) eV) and Ru₁₃@Pt₄₁ (E_a = 0.17 (∼0) eV; Fig. 2). The very small E_a for the O–OH bond cleavage is consistent with the reactant-like transition states **TS4/5b^{Pt}** and **TS4/5b^{RuPt}**. Though the E_a is moderately smaller in the reaction on Pt₅₅ than on Ru₁₃@Pt₄₂, the difference is small, and therefore, the geometry of **TS4/5b^{Pt}** differs little from that of **TS4/5b^{RuPt}**.

It should be noted that the O–OH bond cleavage occurs with a smaller E_a than the O–O bond cleavage of the adsorbed O₂ molecule on both Pt₅₅ and Ru₁₃@Pt₄₂. This is not surprising because the O–O bond of the adsorbed O₂ molecule is weaker than the original O–O double bond of free O₂ molecule, as shown by the elongated O–O bond, but still stronger than the O–O single bond of the OOH species. Another result to be noted is that the E_a of the OOH formation from adsorbed O₂ and H species is larger in the Pt₅₅ case than in the Ru₁₃@Pt₄₂ case, but the E_a for O–O bond cleavage is smaller in the Pt₅₅ case than in the Ru₁₃@Pt₄₂ case. These findings are discussed below in more detail on the basis of electronic structure.

3.4 Electronic process in O₂ adsorption, O–O bond cleavage, OOH formation, and O–OH bond cleavage

As shown in Table 1, the O₂ moiety is negatively charged in Pt₅₅(O₂) **2^{Pt}** and Ru₁₃@Pt₄₂(O₂) **2^{RuPt}**, because O₂ adsorption occurs with charge-transfer (CT) from metal particle to O₂ molecule. This CT is enhanced by the polar solvent (water), as expected. Notably, the O₂ molecule is more negatively charged in **2^{RuPt}** than in **2^{Pt}**. Seemingly, this result is inconsistent with the larger adsorption energy of the O₂ molecule with Pt₅₅ than with Ru₁₃@Pt₄₂, which is discussed below. In the O–O bond cleavage (2 → 3a), both O¹ and O² atoms become much more negatively charged, as well known. A moderately larger CT

Table 2 Changes of the Bader charges in OOH formation from adsorbed O₂ and H species and O–OH bond cleavage

	3b	TS3/4b	4b	TS4/5b	5b
Pt₅₅					
O ¹	−0.295 (−0.263) ^a	−0.246 (−0.218)	−0.371 (−0.339)	−0.669 (−0.630)	−1.016 (−0.935)
O ²	−0.289 (−0.250)	−0.252 (−0.197)	−0.624 (−0.575)	−0.384 (−0.349)	−0.615 (−0.511)
H	−0.035 (−0.037)	0.198 (0.204)	0.683 (0.609)	0.727 (0.653)	0.676 (0.610)
Pt ₅₅	0.619 (0.550)	0.300 (0.211)	0.312 (0.305)	0.326 (0.326)	0.955 (0.836)
Ru₁₃@Pt₄₂					
O ¹	−0.312 (−0.261)	−0.260 (−0.235)	−0.401 (−0.367)	−0.945 (−0.671)	−1.182 (−1.138)
O ²	−0.278 (−0.245)	−0.210 (−0.140)	−0.800 (−0.728)	−0.401 (−0.367)	−0.708 (−0.680)
H	0.008 (0.007)	0.069 (0.083)	0.872 (0.782)	1.000 (0.675)	0.822 (0.789)
Ru ₁₃ @Pt ₄₂	0.582 (0.499)	0.401 (0.292)	0.329 (0.313)	0.346 (0.363)	1.068 (1.029)

^a Values in parentheses represent the Bader charge in gas phase.



occurs unexpectedly in $\text{Ru}_{13}@\text{Pt}_{42}$ than in Pt_{55} , despite the larger E_a in $\text{Ru}_{13}@\text{Pt}_{42}$ than in Pt_{55} .

In the OOH formation *via* the reaction between the adsorbed O_2 molecule and H atom ($3b \rightarrow \text{TS3}/4b \rightarrow 4b$), the H atom becomes more positively charged, the O^1 and O^2 atoms become more negatively charged, and the positive charges of Pt_{55} and $\text{Ru}_{13}@\text{Pt}_{42}$ decrease. However, these population changes are not simple. The positive charges of Pt_{55} and $\text{Ru}_{13}@\text{Pt}_{42}$ decrease when going from $3b$ to $\text{TS3}/4b$ but change little after $\text{TS3}/4b$, suggesting that the CT from O_2 and H to the metal particle mostly occurs in step $3b \rightarrow \text{TS3}/4b$ but little after $\text{TS3}/4b$. In this $3b \rightarrow \text{TS3}/4b$ step, the H atomic charge becomes considerably positive, but the O^1 and O^2 atomic charges moderately change, suggesting that the H atom mainly participates in the CT to the metal particle. As it goes from $\text{TS3}/4b$ to $4b$, the O^1 becomes more negatively charged, the O^2 is much more negatively charged, and the H atom becomes much more positively charged. Because the CT occurs little to metal particle in this step ($\text{TS3}/4b \rightarrow 4b$), as discussed above, the change in electron distribution mainly occurs in the O^2H moiety, suggesting that the $\text{O}^{\delta-}-\text{H}^{\delta+}$ polarization becomes strong in this step. It is noted that the positive charges of Pt_{55} and $\text{Ru}_{13}@\text{Pt}_{42}$ change to a lesser extent in this OOH formation than in the O_2 adsorption, O–O bond cleavage, and O–OH bond cleavage, as shown in Tables 1 and 2. These features suggest that not only CT but also some other factors

play important roles in this OOH formation, as discussed below.

In the $\text{O}^1-\text{O}^2\text{H}$ bond cleavage ($4b \rightarrow \text{TS4}/5b \rightarrow 5b$), the O^2H group becomes considerably positive at $\text{TS4}/5b$ and then returns to moderately positive at $5b$, while the negative charge of the O^1 atom and the positive charges of Pt_{55} and $\text{Ru}_{13}@\text{Pt}_{42}$ increase when going from $4b$ to $5b$. These population changes indicate that this step occurs with CT from the metal particle to the OOH moiety. These population changes resemble those by the oxidative addition in organometallic chemistry.⁸⁰ This is reasonable because the σ -bond cleavage needs CT from the metal to the σ^* -antibonding orbital. Because the CT deeply relates to the electronic structure of the metal particle, the next task is to elucidate the electronic structures of Pt_{55} and $\text{Ru}_{13}@\text{Pt}_{42}$.

3.5 Electronic structures of Pt_{55} and $\text{Ru}_{13}@\text{Pt}_{42}$, M–X bond energy ($\text{M} = \text{Pt}_{55}$ and $\text{Ru}_{13}@\text{Pt}_{42}$; $\text{X} = \text{H}, \text{O}, \text{OH}$, and OOH), and their relation to O_2 activation

The 5d-valence band-top and d-band center of the Pt_{42} shell are calculated at higher energy in Pt_{55} than in $\text{Ru}_{13}@\text{Pt}_{42}$, but the d-conduction band-bottom of the Pt_{42} shell is calculated at lower energy in Pt_{55} than in $\text{Ru}_{13}@\text{Pt}_{42}$ (Fig. 5A and B), where the d-band center was calculated using d-valence bands and the DOS energy was corrected according to Baldereschi and coworkers.⁸¹ We checked if the box size for periodic calculation

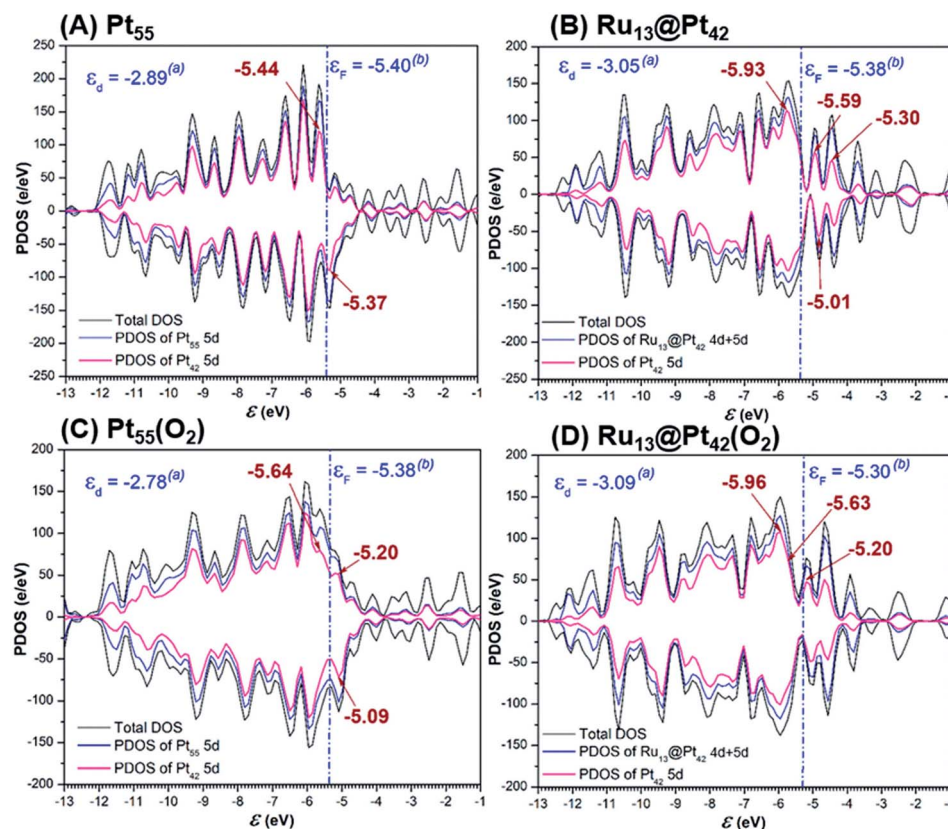


Fig. 5 Density of states (DOS), partial density of states (PDOS) of total d of whole particle and 5d of the Pt_{42} shell in (A) Pt_{55} , (B) $\text{Ru}_{13}@\text{Pt}_{42}$, (C) $\text{Pt}_{55}(\text{O}_2)$, and (D) $\text{Ru}_{13}@\text{Pt}_{42}(\text{O}_2)$.



influences little the Fermi level after the correction, as shown in Table S4 in the ESI (page S10†), and also we wish to note the 5d-valence band-top energy differs moderately from that of our previous work,⁴⁷ because of the different computation method, as explained in the ESI (pages S11 to S12†). The O₂ adsorption decreases the density of the d-valence band-top and that of the d-conduction band-bottom in both Pt₅₅ and Ru₁₃@Pt₄₂, as shown by Fig. 5A, B and C, D, indicating that the d-valence band-top mainly participates in the CT from the Pt₄₂ shell to the O₂, and the d-conduction band-bottom mainly participates in the reverse CT from the O₂ to the Pt₄₂ shell. The higher energy d-valence band-top and the lower energy d-conduction band-bottom induce stronger CT from Pt₅₅ to O₂ than that from Ru₁₃@Pt₄₂ to O₂ and, also, stronger CT from O₂ to Pt₅₅ than that from O₂ to Ru₁₃@Pt₄₂, respectively. Consequently, the binding energy of O₂ molecule with Pt₅₅ is larger than that with Ru₁₃@Pt₄₂, as discussed above, but the O₂ moiety is less negatively charged in Pt₅₅(O₂) than in Ru₁₃@Pt₄₂(O₂); see Table 1. As shown in Fig. 5C and D, the d-valence band-top and d-band center exist at higher energy in Pt₅₅(O₂) than in Ru₁₃@Pt₄₂(O₂). The higher energy d-valence band-top and d-band center in Pt₅₅(O₂) than in Ru₁₃@Pt₄₂(O₂) are the origin of the smaller E_a value of the O–O bond cleavage on Pt₅₅ than on Ru₁₃@Pt₄₂. Considering these results, we mainly employ the d-valence band-top and the conduction band-bottom for discussion; these DOSs correspond to HOMO and LUMO in the frontier orbital theory in molecular theory. Also, we used the d-band center for discussion because it is an important property representing the electronic structure of metal particles.

In OOH formation, on the other hand, the charge distribution changes to a lesser extent than in the O–O bond cleavage, as mentioned above, but the E_a value is considerably different between Pt₅₅ and Ru₁₃@Pt₄₂. This result suggests that some different factor plays an important role in this reaction. One plausible factor is bond dissociation energy (BDE). In OOH formation, M–O₂ and M–H bonds are broken and M–(OOH) and O–H bonds are formed, where M represents Pt₅₅ and Ru₁₃@Pt₄₂. Because the O–H bond formation is common in both Pt₅₅ and Ru₁₃@Pt₄₂ cases, we focus here on M–O₂, M–H, and M–(OOH) bonds. As shown in Scheme 3, the Pt₅₅–(O₂) and Pt₅₅–H bonds are stronger than the Ru₁₃@Pt₄₂–(O₂) and Ru₁₃@Pt₄₂–H bonds, respectively, in the reactant side, while the Pt₅₅–(OOH) bond is stronger than the Ru₁₃@Pt₄₂–(OOH) bond in the product side. Therefore, two strong Pt₅₅–(O₂) and Pt₅₅–H bonds (the sum of BDEs = 4.48 eV) are converted to one strong Pt₅₅–(OOH) bond (BDE = 1.96 eV) in the OOH formation on Pt₅₅, where the energy

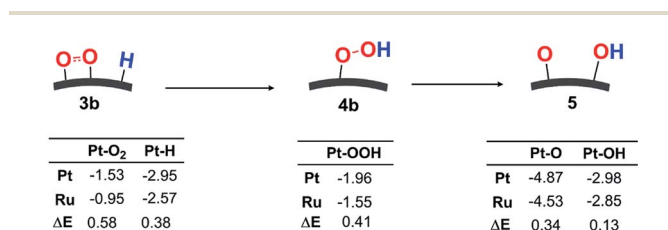
loss is 2.52 eV. In the OOH formation on Ru₁₃@Pt₄₂, on the other hand, two weaker Ru₁₃@Pt₄₂–(O₂) and Ru₁₃@Pt₄₂–H bonds (the sum of BDEs = 3.52 eV) are converted to one weaker Ru₁₃@Pt₄₂–(OOH) bond (BDE = 1.55 eV), where the energy loss is 1.71 eV. Apparently, the reaction occurs more easily on Ru₁₃@Pt₄₂ than on Pt₅₅ because of the smaller energy loss in the reaction by the former than by the latter. These results lead us to the conclusion that the stronger Pt₅₅–(O₂) and Pt₅₅–H bonds than Ru₁₃@Pt₄₂–(O₂) and Ru₁₃@Pt₄₂–H bonds, respectively, are reasons why OOH formation from adsorbed O₂ and H needs a larger E_a on Pt₅₅ than on Ru₁₃@Pt₄₂.

Because the O–OH bond cleavage needs CT from the metal particle to the OOH moiety, the higher energy d-valence band-top and d-band center of Pt₅₅ than those of Ru₁₃@Pt₄₂ are the origin of the smaller E_a on Pt₅₅ than on Ru₁₃@Pt₄₂. In addition, the bond energies relating to this O–OH bond cleavage provide clear understanding of the larger reactivity of Pt₅₅ than that of Ru₁₃@Pt₄₂, as follows: the Pt₅₅–(OOH) bond is stronger than the Ru₁₃@Pt₄₂–(OOH) bond, as shown in Scheme 3, and the Pt₅₅–O and Pt₅₅–(OH) bonds are stronger than the Ru₁₃@Pt₄₂–O and Ru₁₃@Pt₄₂–(OH) bonds, respectively. This means that one stronger bond is broken, but two stronger bonds are formed in the O–OH bond cleavage by Pt₅₅ than by Ru₁₃@Pt₄₂. Thus, Pt₅₅ is more reactive for this reaction than Ru₁₃@Pt₄₂.

As discussed above, the stronger Pt₅₅–(O₂) and Pt₅₅–X bonds (X = H, O, OH, and OOH) than the Ru₁₃@Pt₄₂–(O₂) and Ru₁₃@Pt₄₂–X bonds, respectively, are responsible for the reactivity difference in OOH formation and O–OH bond cleavage between Pt₅₅ and Ru₁₃@Pt₄₂. Also, it has been supposed that the overly strong binding energy of oxygen-containing species with the Pt electrode is unfavorable for ORR activity.¹⁷ Thus, it is of considerable importance to discuss the Pt₅₅–X and Ru₁₃@Pt₄₂–X bond energies and determining factor of these bond energies. Because the Pt₅₅–(O₂) and Ru₁₃@Pt₄₂–(O₂) bond energies were discussed above in terms of the d-valence band-top and d-band center energies, we focus here on Pt₅₅–X and Ru₁₃@Pt₄₂–X bond energies. These bonds are neither pure ionic nor pure covalent, but they are understood to be strongly polarized covalent bonds. Polarized covalent bond energy E_{cov} (A–B) is approximately represented by eqn (1) on the basis of simple Hückel MO theory;⁸²

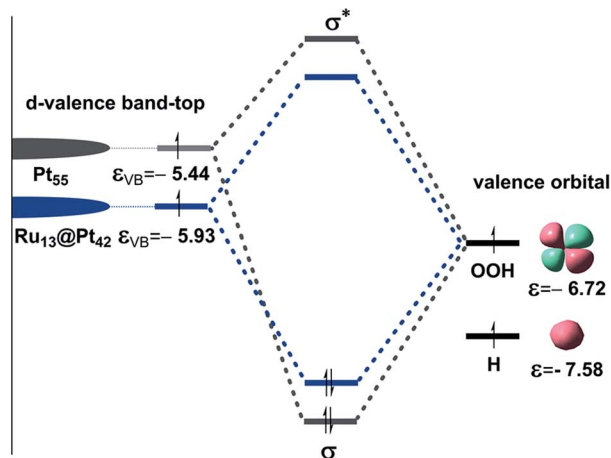
$$E_{\text{cov}}(\text{A} - \text{B}) = \sqrt{(\epsilon_{\text{A}} - \epsilon_{\text{B}})^2 + 4\beta^2}, \quad (1)$$

where ϵ_{A} and ϵ_{B} are the valence orbital energies of A and B, respectively, and β is a resonance integral. This eqn (1) has been employed to discuss the relative bond strengths of various M–R bonds (M = transition metal element and R = alkyl, silyl, etc.).^{83–87} Because the M–R bond is understood to be a polarized covalent bond, it is likely that this eqn (1) can be applied to the present discussion. Actually, this equation has recently been applied to the discussion of binding energies of H, O, and OH species with Pd₅₅ and Rh₅₅ particles.⁶⁶ Eqn (1) indicates that E_{cov} (A–B) becomes larger as the energy difference in valence orbital ($\epsilon_{\text{A}} - \epsilon_{\text{B}}$) increases when the β does not differ. Here, the β value is almost the same between Pt₅₅–X and Ru₁₃@Pt₄₂–X because X is bound with the Pt₄₂ shell in both particles. Thus, the valence



Scheme 3 Bond energy changes (in eV) in OOH formation followed by O–OH bond cleavage on Pt₅₅ and Ru₁₃@Pt₄₂.





Scheme 4 Schematic representation of orbital interaction between X (X = H or OOH) species and the Pt₄₂ shell of Pt₅₅ or Ru₁₃@Pt₄₂ particle.

orbital energies of Pt₅₅ and Ru₁₃@Pt₄₂ play an important role in determining these bond energies. As shown in Scheme 4, the d-valence band-top of the Pt₄₂ shell is calculated at a higher energy (−5.44 eV) in Pt₅₅ than in Ru₁₃@Pt₄₂ (−5.93 eV). Because the 2sp valence orbitals of O, OH, and OOH and the 1s valence orbital of H are at lower energy than these d-valence band-tops due to their larger electronegativities, the energy difference between the d-valence band-top of the Pt₄₂ shell and the valence orbital of X species is larger in Pt₅₅ than in Ru₁₃@Pt₄₂, as apparently shown in Scheme 4; for simplicity, O and OH valence orbitals are omitted in this Scheme. Consequently, the Pt₅₅–X bond is stronger than the Ru₁₃@Pt₄₂–X bond.

It should be clearly concluded that the higher energy d valence band-top of Pt₅₅ than that of Ru₁₃@Pt₄₂ is the origin of the stronger Pt₅₅–X bond than the Ru₁₃@Pt₄₂–X bond. The higher energy d valence band-top of Pt₅₅ than that of Ru₁₃@Pt₄₂ is also responsible for the larger O₂ adsorption energy to Pt₅₅ than to Ru₁₃@Pt₄₂ and smaller *E_a* values of the O–O and O–OH bond cleavages on Pt₅₅ than on Ru₁₃@Pt₄₂. Thus, one of the important characteristic features of Ru₁₃@Pt₄₂ is the presence of the d-valence band-top of the Pt₄₂ shell at lower energy than that of Pt₅₅; here we wish to mention that higher energy d-valence band-top relates to higher energy d-band center in many cases, indicating that the d-band center is also useful for discussion.

4 Conclusions

O₂ adsorption followed by O–O bond cleavage and OOH formation followed by O–OH bond cleavage on Pt₅₅ and Ru₁₃@Pt₄₂ particles were investigated using DFT computations, and comparisons were made between Pt₅₅ and Ru₁₃@Pt₄₂. Several important findings are summarized as follows: (i) O₂ is preferentially adsorbed to the vertex Pt and the neighboring edge Pt atoms in a bridging μ₂-side-on manner. (ii) The O₂ adsorption energy with the Pt₄₂ shell is larger in Pt₅₅ than in Ru₁₃@Pt₄₂. (iii) The O–O bond cleavage occurs with a smaller *E_a* on Pt₅₅ than on Ru₁₃@Pt₄₂. (iv) The OOH formation from the

adsorbed O₂ molecule and H atom occurs with a smaller *E_a* on Ru₁₃@Pt₄₂ than on Pt₅₅. The CT occurs much less in this reaction than in the O–O bond cleavage. The stronger Pt₅₅–(O₂) and Pt₅₅–H bonds than the Ru₁₃@Pt₄₂–(O₂) and Ru₁₃@Pt₄₂–H bonds, respectively, are the origin of the larger *E_a* on Pt₅₅ than on Ru₁₃@Pt₄₂. (v) The OOH formation *via* H⁺/e[−] addition to the adsorbed O₂ molecule also occurs easily in Pt₅₅ similarly to the reaction between adsorbed O₂ molecule and H atom, but more easily in Ru₁₃@Pt₄₂. And, (vi) the O–OH bond cleavage occurs more easily with much smaller *E_a* than the O–O bond cleavage of the adsorbed O₂ molecule.

The abovementioned differences between Pt₅₅ and Ru₁₃@Pt₄₂ are understood on the basis of the PDOS of these metal particles. The d-valence band-top and d-band center of the Pt₄₂ shell are calculated at higher energy in Pt₅₅ than in Ru₁₃@Pt₄₂, but the d-conduction band-bottom of the Pt₄₂ shell is at lower energy in Pt₅₅ than in Ru₁₃@Pt₄₂. Accordingly, the O₂ molecule is adsorbed to Pt₅₅ more strongly than to Ru₁₃@Pt₄₂, because the CT from the Pt₄₂ shell to O₂ and the reverse CT from the O₂ to the Pt₄₂ shell are more strongly formed with Pt₅₅ than with Ru₁₃@Pt₄₂. Because the O–O bond cleavage needs CT from the metal particle to the O₂ moiety, the presence of d-valence band-top at high energy is favorable. Consequently, Pt₅₅ is more reactive than Ru₁₃@Pt₄₂. On the other hand, the reactivity for OOH formation from adsorbed O₂ and H depends on the M–(O₂) and M–H bond energies, as follows: because the Pt₅₅–(O₂) and Pt₅₅–H bonds are stronger than the Ru₁₃@Pt₄₂–(O₂) and Ru₁₃@Pt₄₂–H bonds, respectively, OOH formation on Pt₅₅ needs a larger *E_a* than that on Ru₁₃@Pt₄₂.

The binding energy of oxygen-containing species with Pt-based electrode has been discussed as an important factor for ORR activity. Also, the above discussion suggests that the bond energy is an important property for understanding reactions on the Pt-based electrode. We explored the Pt₅₅–X (X = H, O, OH, and OOH) and Ru₁₃@Pt₄₂–X bond energies and found that the Ru₁₃@Pt₄₂–X bond is weaker than the Pt₅₅–X, and the lower energy d-valence band-top of Ru₁₃@Pt₄₂ than that of Pt₅₅ is the origin of the weaker Ru₁₃@Pt₄₂–X bond than the Pt₅₅–X bond. It is clearly concluded that the lower energy of the d-valence band-top of Ru₁₃@Pt₄₂ than that of Pt₅₅ is one of the important characteristic features of Ru₁₃@Pt₄₂ in comparison to Pt₅₅.

Conflicts of interest

The authors declare no competing financial interest.

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