First-Principle Study of Pt_{55} and Core-Shell $Ru_{13}@Pt_{42}$ Catalysts for Oxygen Reduction Reaction

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[Abstract] First-principle calculations were performed to investigate the preferential site on the Pt_{42} surface of icosahedron-like $Ru_{13}@Pt_{42}$ and Pt_{55} for interaction with O_2, OOH, O, and OH. $Ru_{13}@Pt_{42}$ has weaker binding ability for O_2 than Pt_{55}. The O-OH bond cleavage of OOH-containing species occurs with small barrier for Pt_{55} and $Ru_{13}@Pt_{42}$. Both of $OH(OH^{Pt})$ and OHH^{Pt} formation reactions participate in rate-determining process in $Ru_{13}@Pt_{42}$ catalyst. On the other hand, $OH(OHH^{Pt})$ formation reaction is rate-determining step (RDS) in Pt_{55} catalyst. The barrier of RDS in the case of $Ru_{13}@Pt_{42}$ is smaller than that of Pt_{55}, suggesting that $Ru_{13}@Pt_{42}$ could serve as a promising ORR heterogeneous catalyst like Pt_{55}.

[Introduction] Pt-based clusters/particles are one of efficient catalysts for oxygen reduction reaction (ORR) at the cathode in proton exchange membrane fuel cells (PEMFCs) because of their incomparable catalytic activity. However, the limited resource and high cost of Pt, as well as the slow reaction of ORR, have remained as the major hurdles for commercialization of PEMFCs. Pt alloys with core-shell structure (M@Pt) have been shown great promise as next generation ORR catalysts due to their superior catalytic performance and lower cost than pure Pt. M@Pt catalyst can significantly improve the Pt utilization by depositing a thin Pt shell outside the M core. The structural and electronic effects of M element in the core play crucial roles in weakening the ability to bind with oxygen species. In general, an ideal catalyst should exhibit a moderate interaction between Pt surface and oxygen species. O_2 activation and electron transfer will be hampered if the ability to bind with oxygen-containing adsorbates is too weak. Conversely, if such binding ability is too strong, the subsequent H_2O formation will be sluggish.

Previously, the stability of icosahedron-like $Pt_{42}Ru_{13}$ cluster were investigated in our group. The core-shell structure ($Ru_{13}@Pt_{42}$) is much more stable than these non-core-shell structures ($PtRu_{12}@Pt_{41}Ru^{edge}$ and $PtRu_{12}@Pt_{41}Ru^{vert.}$). However, further theoretical insights into the catalytic performance of $Ru_{13}@Pt_{42}$ and Pt_{55} catalysts toward ORR is limited and highly desirable. Our purposes are to elucidate the ORR mechanism and rate-determining step (RDS) in $Ru_{13}@Pt_{42}$ and Pt_{55} catalysts.

[Methods] All the spin-polarized calculations were performed with the Vienna Ab initio Simulation Package (VASP). The PBE-D3 method was adopted for geometry optimization
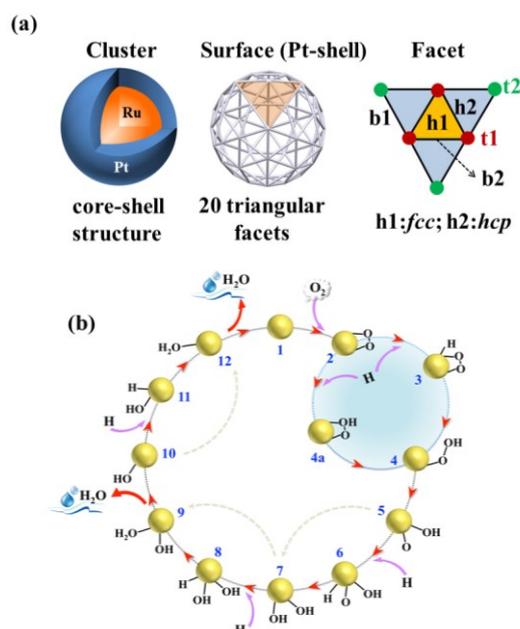
Scheme 1. (a) Binding sites on the surface of icosahedron-like Pt_{42}. (b) Schematic illustration of reaction pathways for ORR.

with an energy cutoff of 400 eV. The cluster was placed in a sufficiently large supercell (25 Å × 25 Å × 25 Å) to ensure enough separation by vacuum. The thresholds for energy and force were set at 0.0001 eV and 0.01 eV/Å, respectively. The reaction energy barrier was calculated using Nudged Elastic Band (NEB) method with VASP Transition State Tools (VTST). To estimate the solvent effect, an implicit solvation model, which describes the effect of electrostatic interaction between solute and, was used in VASP.

[Results and Discussion] The adsorption sites on the Pt_{42} surface of icosahedron-like 55-atom clusters are shown in Scheme 1a. The preferential sites for O_2, OOH, and O-binding on the Pt_{42} surface of $Ru_{13}@Pt_{42}$ and Pt_{55} are b1, t2, and h1, respectively. For OH-binding, the b1 and t2 sites are preferable in Pt_{55}, while only t2 is the most favorable in $Ru_{13}@Pt_{42}$. $Ru_{13}@Pt_{42}$ has a weaker ability than Pt_{55} to bind with O_2, OH, and so on. It can be reasonably explained via lower energy shift of d-band center for $Ru_{13}@Pt_{42}$ due to compressive strain effect of Pt_{42} surface and charge transfer from Pt_{42} shell to Ru_{13} core. The calculated d-band center for $Ru_{13}@Pt_{42}$ is -2.18 eV, which is lower than that for Pt_{55} (-2.02 eV).

The full catalytic cycle of ORR is described in Scheme 1b. For both catalysts, the O-OH bond cleavage occurs with small barrier. For $Ru_{13}@Pt_{42}$, the $OH(OH^{Pt})$, $OH(OHH^{Pt})$, and OHH^{Pt} formations need barriers of 0.86 eV, 0.76 eV, and 0.89 eV, respectively. For Pt_{55}, the $OH(OH^{Pt})$, $OH(OHH^{Pt})$, and OHH^{Pt} formations need barriers of 0.57 eV, 1.10 eV, and 0.91 eV, respectively. Thus, $OH(OH^{Pt})$ and OHH^{Pt} formation reactions participate in rate-determining process in $Ru_{13}@Pt_{42}$ catalyst. $OH(OHH^{Pt})$ formation reaction is the RDS in Pt_{55} catalyst. The barrier of RDS in the case of $Ru_{13}@Pt_{42}$ is smaller than that of Pt_{55}.

Note that the direct H addition to O of oxygen containing species is also possible and much easier than H addition to Pt shell. The full catalytic cycle can be easily described without H^{Pt} containing species **3**, **6**, **8**, **11** (Scheme 1b). Our results verify that $Ru_{13}@Pt_{42}$ could serve as a less expensive ORR catalyst with desirable performance and a similar ORR mechanism to Pt_{55} catalyst.
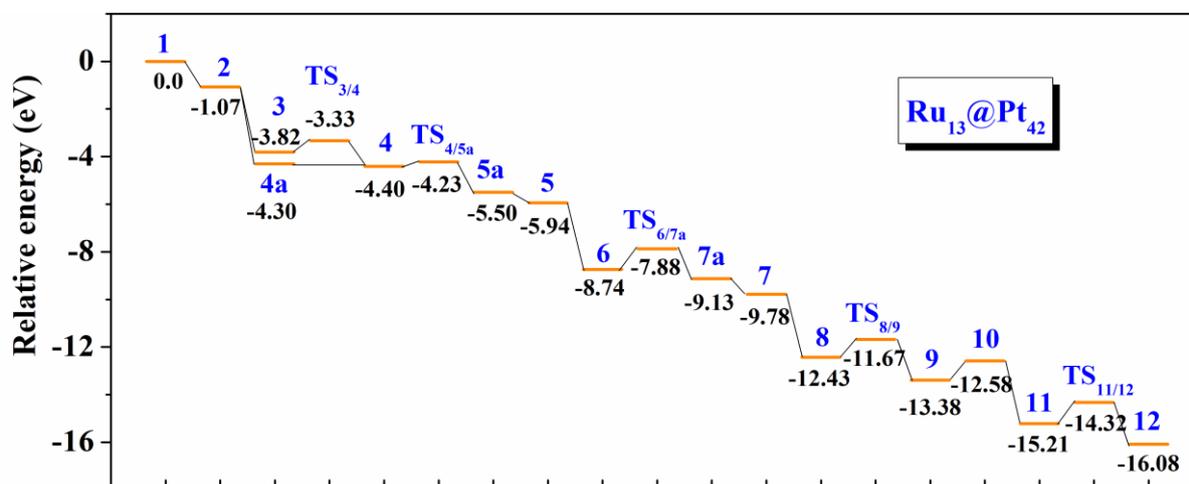

Fig. 1. Potential energy surfaces in the cases of $Ru_{13}@Pt_{42}$ in solution.

[References]
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