V.G.10 Atomic-Scale Design of Metal and Alloy Catalysts: A Combined Theoretical and Experimental Approach

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Program Scope

This program combines theory, inorganic synthesis, and catalytic reaction kinetics experiments in an integrated approach towards identifying metal and alloy catalysts with high activity and selectivity for high-impact reactions. Theoretical calculations identify the most promising catalyst structures and compositions for novel controlled synthesis, while reaction kinetics experiments evaluate the as-synthesized catalysts for their activity and stability. Potential applications involve low-temperature fuel cells, hydrogen production and purification, and liquid fuels production, which all strongly support the DOE's mission.

FY 2016 Highlights

Shape-Selected Alloy Nanocatalysts for the Oxygen Reduction Reaction (ORR) [1-4]

Depositing ultrathin Pt layers onto a Pd template of controlled shape is an attractive approach to reducing the content of precious Pt while improving its activity for the ORR, which is limited by strong binding of adsorbed O and OH intermediates. We have deposited a controlled number of Pt layers onto nanostructured Pd cubes, octahedra, and icosahedra, and the measured ORR activities surpassed those of a commercial Pt catalyst by two, three and four times, respectively, on the basis of Pt-mass. Density functional theory (DFT) calculations reliably predicted the experimentally-observed activity trends as a function of number of Pt overlayers deposited on the Pd template. The calculations attributed the enhanced activity to the compressive strain imposed on the Pt overlayers by the Pd substrate, which weakened the binding of O and OH. We also identified a unique atomic arrangement of the Pt overlayers in the icosahedral catalysts, in which tensile strain on the underlying Pd lattice facilitated the incorporation of extra Pt atoms in the overlayers relative to the Pd template and therefore led to a net beneficial compressive strain on the Pt overlayers.

Additionally, we have shown that the Pd templates can be selectively etched to yield hollow Pt nanocage structures, which exhibited more than double the activity of their Pd@Pt core@shell counterparts. DFT calculations on novel "membrane" models attributed the enhanced activity to a further shortened Pt-Pt interatomic distance relative to the already-compressed core@shell structure.

Formation Mechanism of Hollow Nanocage Structures [4]

In addition to predicting catalyst activity toward ORR, DFT calculations also elucidate the mechanisms by which the hollow nanostructures form. Rigorous DFT calculations demonstrate that Pd can only be etched through vacancies in the Pt shell. We show that these vacancies can be readily formed by removal of Pd atoms dispersed in the Pt shell during the core@shell formation process. As shown in Figure 1, it is energetically more favorable for Pt adatoms (deposited from solution) to substitute into the Pd template, thus yielding a mixed surface composition as Pt is continually deposited in a layer-by-layer fashion. It is therefore possible for contiguous Pd channels to form; these enable the etching of the core to yield the hollow structure. We further identified an optimal Pt shell thickness of four to six layers. Thinner than this would allow for too many channels to form, which jeopardizes the mechanical stability of the hollow structure. On the contrary, thicker layers would inhibit the formation of contiguous Pd channels. This optimal shell thickness was confirmed by experimental observations that hollow structures could only be successfully formed from Pt-Pd core@shell catalysts with four to six overlayers of Pt.

Reaction Mechanism for Electro-Oxidation of Ammonia [5]

We have constructed a free energy diagram (see Figure 2) for two mechanisms for NH_3 electro-oxidation on Pt(111). The two mechanisms differ in the extent of dehydrogenation needed before making an N-N bond, with the N+N mechanism requiring full dehydrogenation to atomic N before N-N bond formation, while the *Gerischer-Mauerer* mechanism allows for this bond to form between
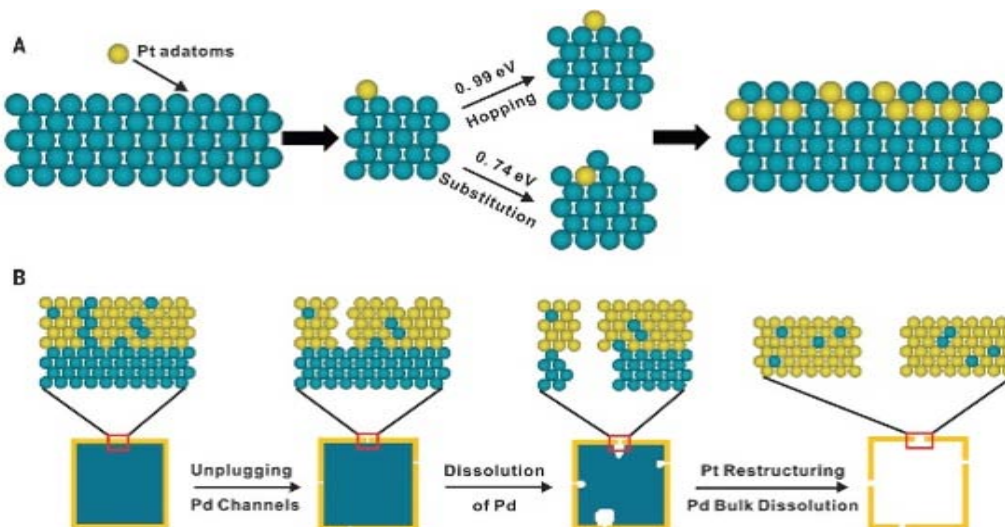
FIGURE 1. Mechanistic details involved in the deposition and etching processes. (A) Pt atoms deposited on the Pd surface may "hop" across the surface or substitute into the surface (activation barriers are shown), leading to a mixed outer-layer catalyst composition. (B) Schematic of the major steps involved in the continuous dissolution of Pd atoms from a Pd@Pt4L nanocube to generate a Pt cubic nanocage.
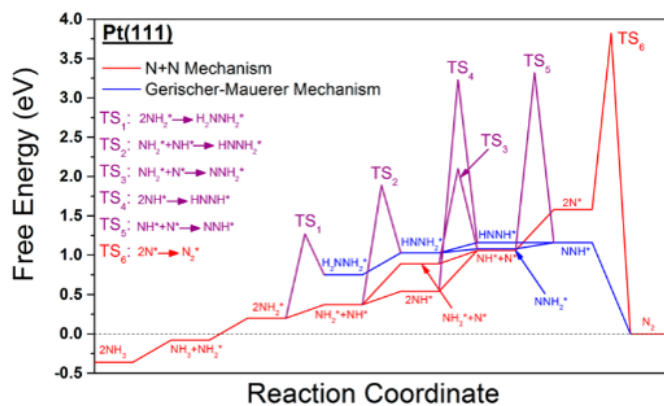

FIGURE 2. Free energy diagram for two mechanisms of N_2 formation on Pt(111) at 0 V_{RHE}. Stoichiometry is implicitly balanced by H^+, OH^-, H_2O, and e^-.

References

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hydrogenated NH_x species. Our calculations explain the experimentally-observed narrow active operating window of potentials for Pt(111), which starts with activating the _Gerischer-Mauerer_ mechanism, and ends with poisoning the surface with N adatoms at the onset of the N+N mechanism. Similar studies were performed on 11 other close-packed monometallic surfaces, and reinforced the need to avoid the N+N mechanism for avoiding N poisoning. A simple Sabatier analysis shows Pt to be most active, followed by Ir and Cu. Hence, improved catalysts should bind atomic N weaker than Pt, but stronger than Cu.