Transition Metal Heterogeneous Catalysis Towards Applications in Sustainable Energy: Leveraging Rational Design Principles for Activity, Stability, and Stereoselectivity
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As global demand grows for renewable energy storage and conversion technologies, novel methods of storing energy and providing portable power are a necessity to accommodate variability in energy resources. Heterogenous catalysis is a fundamental driver in the development of direct liquid fuel cells, water electrolyzers, and other sustainable energy storage applications including liquid organic hydrogen carriers (LOHCs).

The methanol oxidation reaction (MOR) is a multistep reaction comprised of methanol dehydrogenation leading to CO adsorbed on the catalyst surface, followed by CO oxidation. Incorporation of an oxophilic material that facilitates the formation of OH groups on the surface is highly effective for improving CO oxidation and MOR performances. Thus in addition to the enhanced MOR activity through incorporation of the carbide core beneath the monolayers of Pt, the performance of these catalysts is expected to increase further by adding Ru atoms to the Pt shell. The performance of this core-shell nanoparticles with carbide cores and PtRu alloy shells can be tailored by multiple approaches. First, the degree of electronic interaction between core and shell and the corresponding CO adsorption energy are altered by changing the thickness of PtRu shell. Second, modification of electronic structure of Pt, which has significant influence on the strength of CO adsorption, and facilitation of OH species formation near CO on the surface of catalysts was carried out by modifying the ratio between Pt and Ru, resulting in an overall 10 times enhancement in mass activity compared to commercial DMFC catalysts.

Metal hydroxide organic frameworks (MHOFs) comprise edge-sharing metal hydroxide octahedra layers interconnected by carboxylate linkers which utilize π-π stacking to impart additional stability for electrochemical applications including the oxygen evolution reaction (OER). However, we discovered that there are definitive limits to this stability. This work explored the underlying processes causing loss of MHOF-specific motifs, which lead to phase transformations from MHOF to $NiOOH_{2-x}$-like phase during OER, providing insight into the phase stability of these types of materials in base. During extended electrochemical OER cycling, linkers leach from the MHOF structure, exposing more electrochemically active Ni sites, thereby increasing the geometric OER activity. The linker leaching was observed to be accelerated by Ni^{2+} to $Ni^{3+/4+}$ oxidation, which leads to a phase transformation from MHOF to $NiOOH_{2-x}$ structure. A phase transformation mechanism is proposed where mono-μ-oxo bridge motifs found only in the MHOF structure convert to di-μ-oxo bridge motifs in the $NiOOH_{2-x}$-like phase. MHOFs with the weaker π-π interaction L1 linker underwent full transformation to $NiOOH_{2-x}$-like phases. Meanwhile, the MHOFs with the stronger π-π interaction L4 linker showed transformations to $NiOOH_{2-x}$-like phases only at near surface regions, where the MHOF can remain as a less active core, thereby identifying $NiOOH_{2-x}$ as the OER active phase, but highlights the potential of stability these MHOF materials for alkaline water oxidation.

Finally, MHOFs present unique opportunities as sacrificial templates for thermocatalysis, with adjustable metal centers, structural robustness, and heteroatom incorporation through linker selection. In this thesis I present a model for using MHOFs and analogous MOFs to generate catalysts with unique catalytic properties which differentiate them from typical Ni hydrogenation catalysts. The MHOF-based catalysts perform similarly to other Ni-based catalysts in naphthalene and tetralin to decalin conversion rates per active site, however with a notable stereoselectivity toward cis-decalin across compared to the other Ni catalysts. This work highlight Ni-MHOFs as precursors for transition metal catalysts that emulate the stereoselectivity of NM catalysts, thereby reducing energy requirements in LOHC dehydrogenation.

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