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	Project Information	Project Number : 22H04971 Keywords : mononuclear metalates, multinuclear active site structures, small molecules, highly difficult reactions	Project Period (FY) : 2022-2026

Purpose and Background of the Research

● Outline of the Research

In this study, based on our design strategies for molecular oxide catalysts, metal nanoparticle catalysts, and cluster catalysts from mononuclear metalates (such as $[MO_x]^{n-}$ species consisting of one metal), we will establish and generalize methodologies for designing multinuclear active site structures with orderliness in terms of metal species, number, arrangement, structure, and size. In addition, we will target highly difficult reactions involving small molecules as shown in **Figure 1**, design truly potent inorganic catalytic materials to realize these reactions, and aim to construct catalytic reaction systems at practical levels.

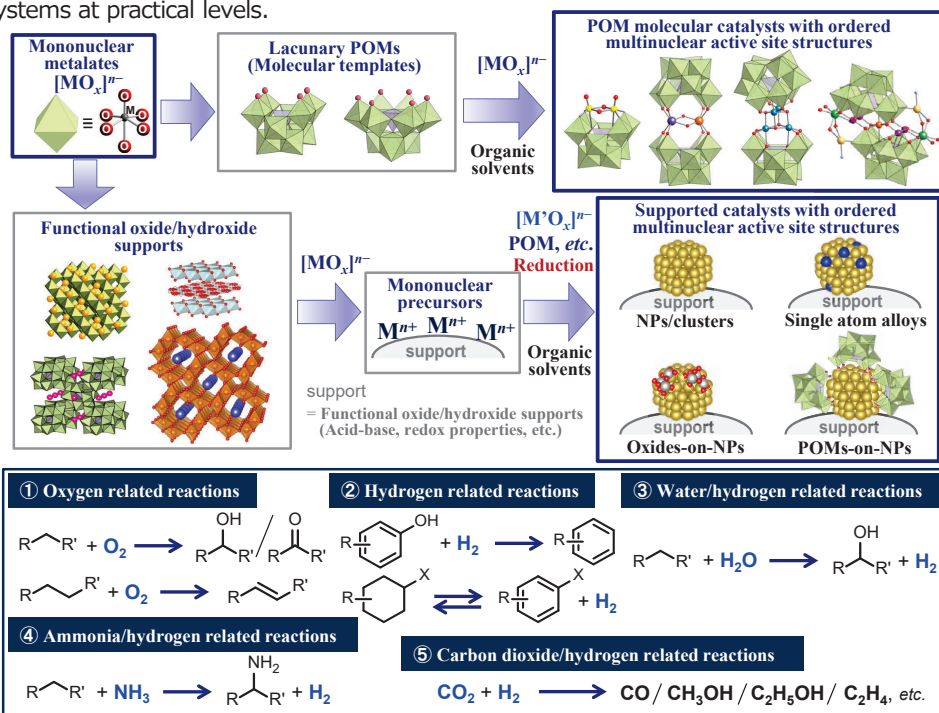


Figure 1. Catalyst design strategies and reactions involving the small molecules targeted in this study. POM = polyoxometalate, a metal oxide cluster composed of multiple metal oxide units; NP = nanoparticle.

● Background to the Research Proposal

The development of highly efficient material conversions that take into account the need to address energy, environmental, and resource issues is an important research topic. In particular, the development of highly efficient chemical synthesis using small molecules such as oxygen, hydrogen, water, ammonia, and carbon dioxide, as well as energy conversion, storage, and transportation technologies, would greatly advance the realization of a carbon neutral society. To efficiently activate these molecules, it is essential to precisely

design multinuclear active site structures. Furthermore, it is desirable to develop inorganic catalytic materials with high durability. However, construction of multinuclear active site structures with controlled number and arrangement of metals and active site structures consisting of multiple metal species has been extremely difficult to achieve using existing inorganic synthetic methods.

The principal investigator's group has succeeded in precisely designing multinuclear active site structures using polyoxometalates (lacunary POMs), metal oxide clusters composed of multiple metal oxide units, as molecular templates (**Figure 1 upper**), nanosized hydroxides, crystalline oxides, and nanoparticles with unique structures composed of different metal species (**Figure 2**). Furthermore, we have succeeded in developing various environmentally benign functional group transformations using catalysts with precisely designed active site structures (**Figure 3**). We have come up with this proposal in the hope that we can develop highly difficult reactions involving small molecules (**Figure 1 lower**) and previously unexplored reactions by further deepening our original catalyst design strategies.

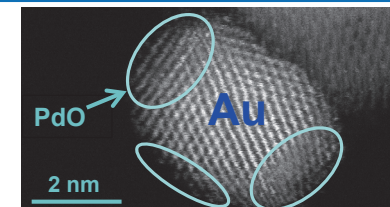
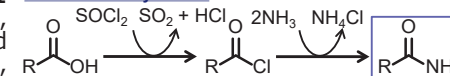


Figure 2. Palladium oxide (PdO)-on-gold (Au) nanoparticle structures. Activation of various substrates at heterometallic interfaces.

Conventional synthesis



Green amide synthesis

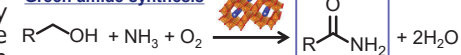


Figure 3. Amide synthesis methods. The conventional synthesis uses highly toxic reagents and generates wastes. Our green amide synthesis co-produces only water. This research aims to develop such reactions.

Expected Research Achievements

● Design of Molecular Templates and Functional Supports

We establish and generalize methods to design lacunary POMs consisting of various structures and constituent elements that can be used as molecular templates, and crystalline oxides and hydroxides that can be used as functional supports (**Figure 1**).

● Design of Catalysts with Multinuclear Active Sites Structures

By utilizing precise sequential reactions in organic solvents between mononuclear metalates and lacunary POMs, we develop methods for designing multinuclear active site structures with orderliness in metal species, number of metals, arrangement, structure, and size (**Figure 1**). We also develop methods for designing ordered metal nanoparticles/clusters by supporting mononuclear metalates on functional supports and using appropriate reducing agents in organic solvents (**Figure 1**).

● Development of Highly Difficult Reactions Using Small Molecules

Using the catalysts designed in this way, highly difficult reactions using small molecules such as oxygen, hydrogen, water, ammonia, and carbon dioxide are realized. For oxygen-related reactions, we aim to achieve selective oxygenation, oxidative functionalization, and dehydrogenative oxidation by activation of an oxygen molecule and C-H bonds at specific positions of substrates. Hydrogen-related reactions include C-O bond cleavage and highly efficient dehydrogenative aromatization and hydrogenation. Dehydrogenation and hydrogenation can be used for synthesis of key compounds (phenol, aniline, etc.) with hydrogen production (**Figure 4**). We also develop reactions using water as an oxygen source and ammonia as a nitrogen source, and highly efficient multielectron carbon dioxide reduction reactions.

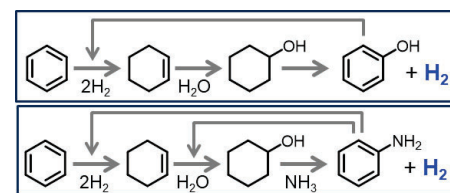


Figure 4. Synthesis of key compounds with hydrogen production.

We establish and generalize new guidelines and scientific principles for the above catalyst design and development of highly difficult reactions, as well as gain knowledge for future implementation of the developed highly difficult reactions.