



Digest paper

Application of solid-state early-transition metal clusters as catalysts

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ABSTRACT

Metal cluster compounds are expected to be catalysts for new reactions because of synergistic effect of the metal atoms. In solid-state halide clusters and sulfide clusters, metal cluster frameworks are linked in two- or three-dimensions to form a cluster network. Halogen- or sulfur-deficient metal sites in an octahedral metal cluster framework are retained intact and act as catalytically active sites even at high temperatures of 400–700 °C. This review reports recent advances in the development of coordinatively unsaturated metal atoms on solid-state clusters with an octahedral metal framework and their application to organic catalytic reactions.

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Introduction

The development of new reactions by the use of new catalysts is one of the most challenging topics in catalysis chemistry. Catalytic reactions are generally determined by the types of catalysts. Heterogeneous catalysts such as transition metals, transition metal oxides, main-group metal oxides including mesoporous materials and zeolites, and metal salts have been intensively applied to a wide variety of reactions by using characteristic features of each type. Exploration of new types of catalysts will lead to the development of new catalytic reactions, and hence new interdisciplinary research between organic, inorganic, and catalysis chemistry.

Metal clusters contain a discrete group of more than three metal atoms directly bonded to one another.¹ The clusters are expected to catalyze new reactions by taking advantage of the synergistic effect of their multimetallic sites. Electron-rich late-transition metals favorably back-donate their valence electrons to π -accepting carbon monoxide ligands to form molecular carbonyl clusters. However, excess electrons remain in the antibonding orbitals of the metal–metal bonds, resulting in cleavage of the bonds below 200 °C. Therefore, carbonyl clusters do not serve as catalysts with retention of the metal framework of the cluster.^{2,3} By contrast, electron-poor early transition metals favorably accept electrons from π -donating halogen and chalcogen ligands to form halide and chalcogenide clusters, respectively.^{4,5} The electrons moderately fill the bonding orbitals of the metal–metal bonds and stabilize the metal framework, which allows these clusters to be used

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as catalysts with retention of the framework, even at high temperatures.

Most halide and chalcogenide clusters have a hexanuclear octahedral metal framework (M_6).^{4–7} They are classified into two groups. One group includes molecular clusters with an M_6 unit (or rarely a dimer^{8–11} or a tetramer¹² of the M_6 unit). A typical example is $[(Mo_6X^i_8)X^a_6]^{2-}$ ($X = Cl, Br, \text{ or } I$) (Fig. 1a), where X^i (inner) is a ligand coordinating to a face of a Mo_6 octahedron in a μ_3 mode while X^a (außer) is a ligand coordinating terminally to a molybdenum atom.¹³ Another group includes solid-state clusters in which the units are linked in two- or three-dimensions to form a cluster network. In solid-state molybdenum clusters $[Mo_6X^i_8]X^a_2X^{a-a}_{4/2}$ ($X = Cl$ (1), Br (2), or I (3)) (Fig. 1b), octahedral Mo_6 units are connected with intercluster X^{a-a} ligands.¹³ In this review, we focus on the application of solid-state halide clusters and sulfide clusters to catalysis.

Molecular cluster

We have reported the application of molecular halide clusters of Group 5, 6, and 7 metals to a wide variety of organic catalytic reactions.^{14,15} For example, in the case of a neutral molybdenum chloride cluster $[(Mo_6Cl^i_8)Cl^a_4(H_2O)_2]$, the cluster has two aqua ligands (Fig. 2). Thermal activation of the cluster in a hydrogen or helium stream above 200 °C partially removed the chlorido ligand and a proton of the aqua ligand as hydrogen chloride, leading to the formation of a hydroxo ligand and a coordinatively unsaturated metal atom. The hydroxo ligand has Brønsted-acidity and is catalytically active for many organic reactions.

Solid-state cluster

Compared with molecular clusters, solid-state clusters have advantages for the retention of the ligand-deficient site on the octahedral M_6 cluster core for the following three reasons.^{6,7,16} A cluster network is thermally stable, as expected from the high temperature required for its synthesis (over 600 °C). A cluster unit

has no aqua ligands. The number of electrons used for the metal–metal bonds in the cluster core is changeable based on nonstoichiometric metal–ligand ratios. Therefore, coordinatively unsaturated metal atoms are sterically, chemically, and electronically stabilized in the solid-state clusters, and act as catalytically active sites.

Solid-state halide cluster

Studies on the solid-state halide clusters have concentrated on their syntheses, structures, and physical properties.⁶ There have been no reports on the application of these clusters to catalysis. The molybdenum halide clusters **1**, **2**, and **3** are coordinatively saturated compounds by the coordination of halogen ligands. When these clusters were progressively heated in a stream of hydrogen, there were no substantial changes in the Mo_6 cluster cores or the crystal structure up to 400 °C, which was confirmed by Raman spectra and X-ray diffraction (XRD) patterns. However, these clusters showed a weight loss of about 0.4% and a decrease of halogen content of about 1%, as detected by thermogravimetric analyses (TGA) and elemental analyses.¹⁷ Therefore, the halogen ligands were partially eliminated by the thermal activation, with the retention of the Mo_6 core and the linkage mode of the cluster network (Fig. 3).

When a mixture of piperidine and methanol was allowed to react over activated clusters **1**, **2**, or **3**, in a stream of hydrogen at 400 °C, dehydrogenative C-methylation proceeded to yield 3-methylpyridine (Eq. 1; space time yields for each equation are not optimized).¹⁷ To investigate the reaction mechanism, piperidine and related compounds were allowed to react over the iodide cluster **3** under the same reaction conditions. The reaction of piperidine with methanol did not afford 3-methylpiperidine (Fig. 4, a1), and 3-methylpiperidine did not yield 3-methylpyridine (Fig. 4, a2), demonstrating that 3-methylpiperidine was not an intermediate. When piperidine was allowed to react alone, 3,4,5,6-tetrahydropyridine was afforded exclusively (Fig. 4, b1), while pyridine was not formed (Fig. 4, c1). The reaction of pyridine with methanol did not yield 3-methylpyridine (Fig. 4, c2), indicating that pyridine was not an intermediate. Therefore, the dehydrogenative C-methylation of piperidine proceeds via 3,4,5,6-tetrahydropyridine and its methylation (Fig. 4, b2), followed by its subsequent dehydrogenation (Fig. 4, b3). A plausible reaction mechanism is illustrated in Fig. 5. 3,4,5,6-Tetrahydropyridine is stabilized as an η^3 -1-azaallyl intermediate, which is methylated at the 3-position with the methyl cation formed from methanol. The resulting electron-rich methylated azaallyl species releases two hydrogen molecules to yield 3-methylpyridine.

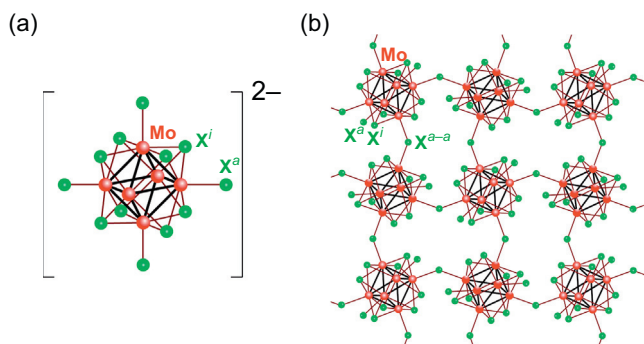


Fig. 1. Typical (a) molecular cluster $[(Mo_6X^i_8)X^a_6]^{2-}$ ($X = Cl, Br, \text{ or } I$) and (b) solid-state cluster $[Mo_6X^i_8]X^a_2X^{a-a}_{4/2}$ ($X = Cl$ (1), Br (2), or I (3)).

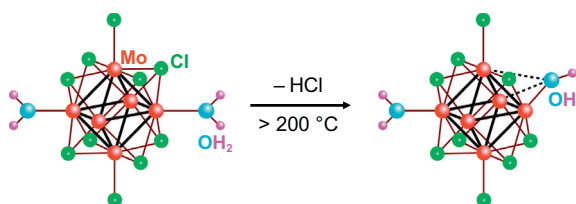
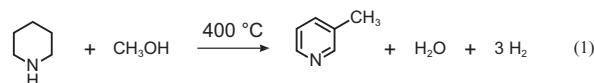


Fig. 2. Thermal activation of a neutral molybdenum halide cluster $[(Mo_6Cl^i_8)Cl^a_4(H_2O)_2]$ to yield hydroxo ligand and coordinatively unsaturated metal atom.



- 1: 77 mg h⁻¹ g-cat⁻¹
 2: 144 mg h⁻¹ g-cat⁻¹
 3: 107 mg h⁻¹ g-cat⁻¹

When the reaction of piperidine with methanol was conducted over a molecular molybdenum halide cluster $(H_3O)_2[(Mo_6Cl^i_8)Cl^a_6] \cdot 6H_2O$ (**4**), the selectivity for *N*-methylation affording *N*-methylpiperidine increased (Eq. 2).¹⁸ The product selectivity of the solid-state clusters **1–3** differed from that of the molecular cluster. The coordination of the nitrogen atom of the azaallyl intermediate on the coordinatively unsaturated molybdenum atom of **1–3** prevented the binding of the methyl cation to the nitrogen atoms and the subsequent formation of *N*-methylpiperidine.

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