Control of Structure of Oxide Cluster and

the Application to Catalytic Technology

Noritaka MIZUNO*

*Department of Applied Chemistry, School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku Tokyo 113-8656 Japan
E-mail : tmizuno@mail.ecc.u-tokyo.ac.jp

The active sites for selective oxidation can be synthesized on polyoxometalates (oxide clusters). For example, Keggin-type di-iron-substituted silicotungstate, γ-SiW$_{10}${Fe(OH$_2$)}$_2$O$_{38}^{6-}$ (I), was synthesized by the reaction of the lacunary γ-SiW$_{10}$O$_{36}^{8-}$ with Fe(NO$_3$)$_3$ in an acidic aqueous solution and isolated as the tetra-n-butylammonium salt (TBA- I). It was characterized by various analyses and the structure with the oxo-bridged di-iron site was clarified. TBA- I was stable and catalyzed selective oxidation of various alkanes and alkenes with hydrogen peroxide: Cyclohexane, adamantane, n-hexane, and n-pentane were catalytically oxidized. Even lower alkanes such as methane, ethane, propane, and n-butane were catalytically oxidized. It was remarkable that the efficiency of hydrogen peroxide utilization to oxygenated products reached up to ca. 100% for the oxidation of cyclohexane and adamantane. Alkenes were mainly epoxidized with hydrogen peroxide. In addition, it was demonstrated that the TBA- I showed high turnover numbers for the oxygenation of cyclohexane and epoxidation of alkenes with 1 atm oxygen.

Key Words : Oxide, Cluster, Synthesis, Selective oxidation, Hydrocarbons

1 INTRODUCTION

Catalytic function of polyoxometalates has attracted much attention because their acidic and redox properties can be controlled at atomic or molecular levels [1-4]. The strong acidity or oxidizing p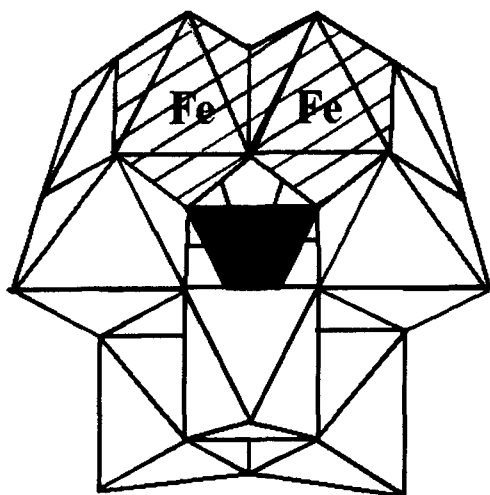roperty of polyoxometalates has induced a lot of studies on the heterogeneous and homogeneous catalysis. An additional attractive and technologically significant aspects of polyoxometalates in catalysis are their inherent stability towards oxygen donors such as molecular oxygen and hydrogen peroxide. Therefore, polyoxometalates could be useful catalysts for liquid-phase oxidation of various organic substrates with hydrogen peroxide.

Iron compounds are known to exhibit significant catalytic activity in biological and synthetic systems. Di-iron-containing ribonucleotide reductase and methane monooxygenase are the prominent examples of the redox-active enzymes. The active site of methane monooxygenase has a μ-hydroxo di-iron structure [5].

Iron-containing polyoxometalates include *mono-* and *tri*-iron-substituted Keggin-type silicotungstates, Fe$_2$ Ni-substituted Keggin-type phosphotungstate, and *tetra*-iron-containing Dawson- and Keggin-derived sandwich compounds. However, di-iron-substituted silicotungstate (I), of which the structure of iron site is similar to that of methane monooxygenase, has never been reported.

Here, our recent work on the synthesis and liquid-phase selective oxidation catalysis of γ-SiW$_{10}${Fe(OH$_2$)}$_2$O$_{38}^{6-}$ (Figure 1) is reported [6-14].

2 SYNTHESIS OF γ-SiW$_{10}${Fe(OH$_2$)}$_2$O$_{38}^{6-}$ AND STABILITY [6,7]

TBA- I was synthesized by the reaction of the lacunary γ-SiW$_{10}$O$_{36}^{8-}$ with Fe(NO$_3$)$_3$ in an acidic aqueous solution and isolated as the tetra-*n*-butylammonium salt. TBA- I has been characterized

Figure 1. Polyhedral representation of γ-SiW$_{10}${Fe^{3+}(OH$_2$)}$_2$O$_{38}^{6-}$ polyoxometalate; species 1. The two iron atoms are represented by shaded octahedra. The WO$_6$ occupy the white octahedra, and an SiO$_4$ group is shown as the internal black tetrahedron.

by infrared, Raman, ^{183}W NMR, UV-*visible*, Mösbauer, and ESR spectroscopy, TG/DTA, FAB-mass, and magnetic susceptibility measurements, elemental analysis, and acid/base titration. The ^{183}W NMR, infrared, Raman, and UV-*visible* spectroscopy indicated that I has a γ-Keggin structure with C_{2v} symmetry. It was shown by the magnetic susceptibility measurement and Mösbauer, ESR, and UV-*visible* spectroscopy that TBA- I shows an antiferromagnetic coupling of the two high-spin Fe^{3+} centers.

3 APPLICATION TO CATALYTIC TECHNOLOGY [8-14]

3.1 Oxidation of Alkanes and Alkenes with Hydrogen Peroxide [8-12]

The oxidation of various alkanes with hydrogen peroxide was carried out in the presence of TBA- I in acetonitrile at 305 K. The main products were the corresponding alcohols, ketones, aldehydes, and acids. Cyclohexane, *n*-hexane, *n*-pentane, and adamantane were catalytically oxygenated with high efficiency of hydrogen peroxide utilization. The turnover numbers for the oxidation of methane, ethane, propane, and *n*-butane were 25, 64, 42, and 36, respectively, showing that even lower alkanes are catalytically oxidized. The turnover number of 25 for oxidation of methane with hydrogen peroxide was the highest among those of di-iron containing model complexes having organic ligands.

Various alkenes were also catalytically epoxidized by TBA- I. For example, cyclooctene, 2-octene, and cyclohexene were catalytically oxidized with $\geq$ =92% efficiency of hydrogen peroxide utilization. The conversion and efficiency decreased for the oxidation of 1-octene because the double bond is more electron-deficient.

3.2 Oxidation of Alkanes and Alkenes with Molecular Oxygen [13,14]

TBA- I catalyzed the oxidation of cyclohexane with 1 atm molecular oxygen at 365 K. The main products were cyclohexanol and cyclohexanone and an induction period was observed. The selectivities changed little with time. The conversion was 1.1% after 96 h and was increased to 2.4% by increasing the amount of catalyst by a factor of two. The turnover number of γ-SiW$_{10}$ {Fe(OH$_2$)}$_2$O$_{38}^{6-}$ reached up to 135-147 after 96 h, of which the value is much higher than 18 and 5 reported for K[Ru^{III}(saloph) Cl$_2$] (saloph = *bis*(salicylaldehyde-*o*-phenylene diiminato) and P W$_9$O$_{37}${Fe$_{3-x}$Ni$_x$(OAc)$_3$}$^{(9+x)-}$ (x = predominantly 1), respectively, with 1 atm molecular oxygen.

TBA- I has been used as catalysts for the oxygenation of alkenes in homogeneous reaction media using molecular oxygen as an oxygen donor. It is remarkable that selectivity to cyclooctene oxide and turnover number reached up to 98% and 10000, respectively, for the oxygenation of cyclooctene. The value is more than 100 times higher than those so far reported for epoxidation of cyclooctene with 1 atm molecular oxygen alone as shown in Table 1. Not only cyclooctene but also cyclododecene, 1-octene, 2-octene, 2-heptene and 2-hexene were catalytically oxygenated with high turnover numbers and high selectivity to the corresponding epoxides. It was also suggested that di-iron-substituted polyoxometalate was stable under the conditions used. The results of infrared studies with ^{18}O$_2$, reaction stoichiometry, kinetic studies, effects of radical scavenger, stereoselectivity, oxygenation of adamantane show that the reaction mainly proceeds with non-radical processes, an iron-oxygen intermediate species being formed. The catalyst is thus able to use molecular oxygen as an oxidant, and raises a prospect of using this type of inorganic catalyst for industrial epoxidation processes.

Table 1. Comparison of turnover numbers for epoxidation of cyclooctene with molecular oxygen

catalyst	TON[a]
γ-SiW$_{10}${Fe(OH)$_2$}$_2$O$_{38}^{6-}$	10000
WZnRu$_2$(OH)(H$_2$O)(ZnW$_9$O$_{34}$)$_2^{11-}$	50
Ru(TMP)O$_2$ (TMP : tetramesitylporphyrinato)	26
Ru(dpp)O$_2$ (dpp : dodecaphenylporphyrinato)	24

[a](Mol of products) / (mol of catalyst used).

4 FUTURE OPPORTUNITIES [15]

Micro/meso porous materials containing heteropolyanions or related to heteropoly compounds are interesting because these compounds are expected to condense hydrocarbons and to be active in the selective catalysis: Keggin-type polyoxometalate, Si W$_{12}$O$_{40}^{4-}$, and Cr(III) trinuclear cation, Cr$_3$O(OOCH)$_6$(H$_2$O)$_3^+$, assembled in the presence of K$^+$ to create a channeled complex K$_3$[Cr$_3$O(OOCH)$_6$(H$_2$O)$_3$]SiW$_{12}$O$_{40}\cdot$16H$_2$O with an opening of 0.5 $\times$ 0.8 nm (scheme 1). The three kinds of ions line up by Coulomb force forming a neutral column. Only van der Waals force works among the columns to arrange them in a hexagonal pattern, creating a one-dimensional channel. The large size (about 1 nm) of the ions (SiW$_{12}$O$_{40}^{4-}$ and Cr$_3$O(OOCH)$_6$(H$_2$O)$_3^+$) is crucial to the complexation. The complex absorbs small polar molecules such as H$_2$O and CH$_3$OH reversibly with change in the distance between the columns.

$$K_3[Cr_3O(OOCH)_6(H_2O)_3]SiW_{12}O_{40} \cdot 16H_2O$$
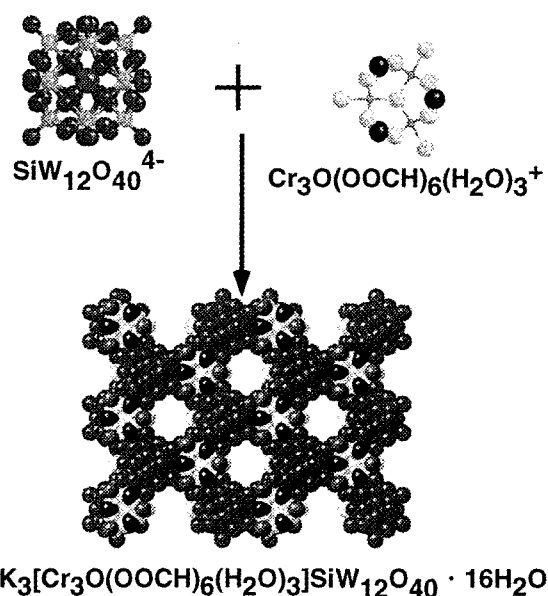
Scheme 1. Micro/meso structured material containing heteropolyanion

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