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PRIORITY COMMUNICATION

Remarkable Structure Dependence of Intrinsic Catalytic Activity for Selective Oxidation of Hydrocarbons with Hydrogen Peroxide Catalyzed by Iron-Substituted Silicotungstates

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The structures of iron centers remarkably influenced the catalytic activities, the *di*-iron-containing γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$ being specifically the most active and giving high turnover numbers; the catalytic activities for oxidation of cyclohexane, cyclohexene, and *trans*-stilbene were 10^1–10^2 times higher than those of *non*-, *mono*-, and *tri*-iron-substituted silicotungstates. © 1999 Academic Press

Key Words: *di*-**iron site; polyoxometalate; oxidation; hydrocarbons; hydrogen peroxide.**

INTRODUCTION

Catalytic function of polyoxometalates in the solid state as well as in solution has attracted much attention because their acidic and redox properties can be controlled at atomic/molecular levels. The strong acidity or oxidizing properties of polyoxometalates induce a lot of studies on the heterogeneous and homogeneous catalysis (1–8). The additional attractive and technologically significant aspect of polyoxometalates in catalysis is their inherent stability towards oxygen donors such as molecular oxygen and hydrogen peroxide and the possibility of the introduction of various elements into polyoxometalates and the countercations (1–12). For example, high stability to hydrogen peroxide has been reported for manganese or iron-substituted polyoxometalates (9–12). Therefore, polyoxometalate-based catalysts are especially significant as prototype catalysts for investigations of oxidative catalysis, since their oxidative stability minimizes the otherwise complicating issue of catalyst degradation effects upon selectivity, kinetic, and mechanistic studies.

Hydrogen peroxide is a preferable oxidant because of the environmentally friendly nature of coproduct and the high oxygen utilization (13–17). However, little is known of the specificity of iron centers for the oxidation since organic ligands are gradually degraded by the reaction with oxidants (17, 18). For example, while a number of structural models with *di*-iron center have been reported, functional models with *di*-iron center for oxidation of alkanes are fewer in numbers. [Fe(salen)]$_2$O (salen = *N*,*N*-ethylenebis(salicyldeneaminato)) (19), Fe$_2$O[HB(pz)$_3$]$_2$(OAc)$_2$ (pz = 3,5-bis(isopropyl)-pyrazolyl) (20), [(PA)$_2$Fe]$_2$O (PA = 2,6-dicarboxylatopyridine) (21), Fe$_2$O(OAc)$_2$(bpy)$_2$Cl$_2$ (bpy = 2,2′-bipyridine) (22, 23), and [Fe$_2$(TPA)$_2$O(OAc)] (ClO$_4$)$_3$ (TPA = tris(2-pyridylmethyl)amine) (24) are examples.

In this communication, we report that the structures of iron centers shown in Fig. 1 remarkably influence the catalytic activities, *di*-iron-containing polyoxometalate being specifically active.

EXPERIMENTAL

Preparation of polyoxometalates. The following polyoxometalates, α-SiW$_{12}$O$_{40}^{4-}$, α-SiW$_{11}$Fe(OH$_2$)O$_{39}^{5-}$, γ-SiW$_{10}$\{Fe(OH$_2$)\}$_2$O$_{38}^{6-}$, and α-SiW$_9$\{Fe(OH$_2$)\}$_3$O$_{37}^{7-}$ were synthesized as tetrabutylammonium salts as follows.

[(C$_4$H$_9$)$_4$N]$_4$[α-SiW$_{12}$O$_{40}$]. Tetrabutylammonium salt of α-SiW$_{12}$O$_{40}^{4-}$ was precipitated by adding an excess amount of [(C$_4$H$_9$)$_4$N]Br (3.48 g, 11 mmol) to K$_4$[α-SiW$_{12}$O$_{40}$] · 17H$_2$O (3.0 g, 0.9 mmol), according to the published method (25). Elemental analysis: Found (calcd) for [(C$_4$H$_9$)$_4$N]$_4$[α-SiW$_{12}$O$_{40}$]: C, 20.15 (20.00); H, 3.55 (3.78); N, 1.54 (1.46). Infrared spectrum (cm^{-1}): 967 (s), 920 (s), 884 (s), 801 (s, br). UV-*visible* spectrum (nm) in acetonitrile at 296 K: $\lambda_{\max} = 264$ ($\varepsilon = 37200$ M^{-1}cm^{-1}). Both spectra were characteristic of α-Keggin structure.

[(C$_4$H$_9$)$_4$N]$_{4.25}$H$_{0.75}$[α-SiW$_{11}$\{Fe(OH$_2$)\}O$_{39}$]. K$_5$[α-SiW$_{11}$\{Fe(OH$_2$)\}O$_{39}$] · 14H$_2$O was prepared according to Ref. (26). The purity of K$_5$[α-SiW$_{11}$\{Fe(OH$_2$)\}O$_{39}$] · 14H$_2$O was checked by infrared (cm^{-1}) (966 (s), 911 (s), 791 (s, br)) and UV-*visible* ($\lambda_{\max} = 259$ nm ($\varepsilon = 39000$ M^{-1}cm^{-1})) spectra. Tetrabutylammonium salt of α-SiW$_{11}$\{Fe(OH$_2$)\}O$_{39}^{5-}$

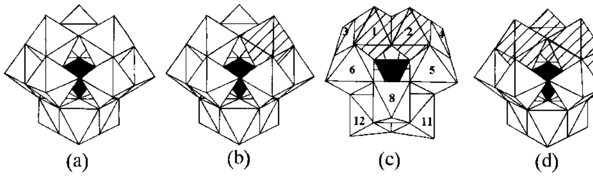

FIG. 1. Polyhedral representation of (a) α-$SiW_{12}O_{40}^{4-}$, (b) α-$SiW_{11}\{Fe(OH_2)\}O_{39}^{5-}$, (c) γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$, and (d) α-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$. Keggin-type polyoxometalates. Iron atoms are represented by hatched octahedra. WO_6 octahedra occupy the white octahedra and an SiO_4 group is shown as the internal black tetrahedron. The numbering is based on IUPAC recommendations.

was precipitated by adding an excess amount of $[(C_4H_9)_4N]Br$ (4.3 g, 13.3 mmol) to aqueous solution of $K_5[\alpha\text{-}SiW_{11}\{Fe(OH_2)\}O_{39}] \cdot 14H_2O$ (2.5 g, 0.78 mmol). The precipitate was purified by repeated reprecipitation from acetonitrile solution with the addition of excess water. Elemental anal.: Found (calcd) for $[(C_4H_9)_4N]_{4.25}H_{0.75}[\alpha\text{-}SiW_{11}Fe(OH_2)O_{39}]$: C, 21.34 (21.61); H, 4.15 (4.15); N, 1.65 (1.58). Infrared spectrum (cm^{-1}): 966 (s), 911 (s), 791 (s, br) in agreement with those of $K_5[\alpha\text{-}SiW_{11}Fe(OH_2)O_{39}]$. Raman spectrum ($cm^{-1}$): 965 (s), 952 (s), 232 (m), characteristic of α-Keggin structure (27). UV-*visible* spectrum (nm) in acetonitrile at 296 K: $\lambda = 261$ (ε 47500 $M^{-1}cm^{-1}$), 473 (ε 19 $M^{-1}cm^{-1}$).

$[(C_4H_9)_4N]_{3.25}H_{3.75}[\alpha\text{-}SiW_9\{Fe(OH_2)\}_3O_{37}]$. α-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$ was prepared according to Ref. (28), where the polyoxometalate was purified by the passing through a cation-exchange column to remove free iron ions. Tetrabutylammonium salt of α-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$ was prepared by adding $[(C_4H_9)_4N]Br$ (16.8 g, 52 mmol) to α-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$ (4.0 mmol) in aqueous solution. The precipitate was purified by repeated reprecipitation from acetonitrile solution with the addition of excess water. Elemental anal.: Found (calcd) for $[(C_4H_9)_4N]_{3.25}H_{3.75}[\alpha\text{-}SiW_9\{Fe(OH_2)\}_3O_{37}]$: C, 18.48 (18.98); H, 3.54 (3.88); N, 1.44 (1.38). Infrared spectrum (cm^{-1}): 966 (s), 912 (s), and 800 (s, br) in agreement with band positions of $K_6H[\alpha\text{-}SiW_9\{Fe(OH_2)\}_3O_{37}] \cdot 8H_2O$ reported in Ref. (28). Raman spectrum (cm^{-1}): 973 (s), 956 (s), 226 (m). UV-*visible* spectrum (nm) in acetonitrile at 296 K: $\lambda = 262$(ε 38000 $M^{-1}cm^{-1}$), 461 (ε 39 $M^{-1}cm^{-1}$). The Raman and UV-*visible* spectra also showed the α-Keggin structure.

$[(C_4H_9)_4N]_{3.5}H_{2.5}[\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}] \cdot H_2O$. Tetrabutylammonium salt of γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ was synthesized by modification of the method reported for the γ-$SiW_{10}Mn_2O_{38}^{6-}$ polyoxometalate (29) as follows. Stoichiometric amounts of $K_8[\gamma\text{-}SiW_{10}O_{36}] \cdot 12H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were mixed under acidic condition. After the solution had been stirred for 5 min, the addition of an excess tetrabutylammonium nitrate (3.1 g, 10 mmol) resulted in a white-yellow precipitate. The precipitate was filtered off and purified by twice dissolving it in acetonitrile (15 mL) and then adding water (300 mL) to reprecipitate the product. The resulting hydrophobic quaternary tetrabutylammonium salt was purified by reprecipitation from acetonitrile/water. The yellow-orange precipitate of tetrabutylammonium salt of γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ is obtained in 37% yield. Elemental anal.: Found (calcd) for $[(C_4H_9)_4N]_{3.5}H_{2.5}[\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}] \cdot H_2O$: C, 19.08 (19.26); H, 3.63 (3.88); N, 1.58 (1.40); Si, 0.80 (0.80); Fe, 3.20 (3.20). Infrared spectrum (cm^{-1}): 1025 (w), 1002 (w), 961 (s), 903 (s), 886 (s), 797 (s), 755 (s, br), 547 (w). ^{183}W NMR spectrum (ppm) in acetonitrile at 296 K: −1334, −1847, with integrated intensities of 2 : 1. Two broad signals with integrated intensities of 2 : 1 were also observed at −1181 and −1700 ppm for the previously known $[\gamma\text{-}SiW_{10}Mn_2^{II,II}O_{38}]^{8-}$ polyoxometalate prepared according to Ref. [29]. According to the assignment of Wn in *di*-vanadium-substituted heteropolyanion, $[\gamma\text{-}SiW_{10}V_2O_{40}]^{6-}$ (30), the lower field signal is assigned to equivalent W9, W10, W11, and W12 atoms and the other signal is assigned to W7 and W8 atoms (see Fig. 1c). The signals due to W3, W4, W5, and W6 atoms bounded to Fe_2O_5 were not observed. The disappearance of signals of W atoms bound to paramagnetic centers has been reported (31). These facts clearly show that the two iron atoms occupy the 1 and 2 positions. UV-*vis* spectrum (nm) in acetonitrile at 296 K: 275 (ε 22600 $M^{-1}cm^{-1}$), 334 (ε 10000 $M^{-1}cm^{-1}$), 470 (ε 68 M^{-1} cm^{-1}). Negative ion FAB mass spectrum: no intense peaks in the range of m/e = 4200–10000. Magnetic moment: 4.2 μ_B at 296 K. Mössbauer spectrum at 296 K: Isomer shift 0.32 mms^{-1}, quadrupole splitting 0.81 mms^{-1}). All these facts show the synthesis of the γ-$SiW_{10}Fe_2^{III,III}O_{38}^{6-}$ polyoxometalate. The preliminary characterization results have been published in Ref. (9) and the full details will be reported in due course.

Titration of hydrogen peroxide. The titration of hydrogen peroxide was carried out according to Ref. (32). One to two grams of solution were accurately weighed and quickly dissolved in 200 mL water. The solution was stirred with a magnetic stir bar at 296 K. Titration data were obtained with HM-30 pH meter (TOA Electrochemical Measuring Instruments). The potential was monitored as a solution of $Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$ in water (0.1 *M*) was added with a buret into the solution in 0.1 mL intervals.

Catalytic reaction. The oxidations of cyclohexane, cyclohexene, and *trans*-stilbene were carried out in a glass vessel. The oxidation of methane was carried out with an autoclave having a Teflon vessel. The oxidations were initiated by the addition of 30% hydrogen peroxide and substrates to acetonitrile solution containing polyoxometalates under argon and the homogeneous solution was vigorously stirred. The reaction solution was periodically sampled by the syringe and analyzed by HPLC on a CHIRALPAK AD column or by GC on TC-WAX and FFAP columns.

TABLE 1

Oxidation of Cyclohexane with Hydrogen Peroxide Catalyzed by Iron-Substituted Silicotungstates at 305 K[a]

Catalysts	Initial rate[b]	Conversion[c] /%	Catalyst turnover[d]	Selectivity/% Cyclohexanol	Selectivity/% Cyclohexanone	H_2O_2 consumed/μmol	Efficiency[e]/ percentage
γ-$SiW_{10}\{Fe(OH_2)\}_2\,O_{38}^{6-}$	5.4×10^{-1}	25.3[f]	53	32[f]	68[f]	420	99[f]
α-$SiW_9\{Fe(OH_2)\}_3\,O_{37}^{7-}$	2.5×10^{-3}	1.0	2	48	52	68	25
α-$SiW_{11}Fe(OH_2)\,O_{39}^{5-}$	2.9×10^{-3}	0.4	1	42	58	14	47
α-$SiW_{12}O_{40}^{4-}$	1.1×10^{-3}	0.1	0.3	53	47	8	28

[a] Catalyst, 8 μmol; acetonitrile, 6 mL; substrate, 1 mmol; H_2O_2, 1 mmol; reaction time, 96 h.

[b] $\text{molmin}^{-1}(\text{mol-catalyst})^{-1}$, see text.

[c] (Mol of products/mol of substrate used) $\times$ 100.

[d] Estimated by moles of oxidizing equivalent in all products/moles of catalyst.

[e] $([\text{alcohol}] + 2[\text{ketone}])/[H_2O_2]_c \times 100$ (%), where $[H_2O_2]_c$ is the concentration of H_2O_2 consumed.

[f] Conversion, selectivity, and efficiency to oxygenated products. Conversion to dicyclohexyl was <1% and no acids and oxoesters were observed.

RESULTS AND DISCUSSION

The catalytic oxidation of cyclohexane with hydrogen peroxide was carried out in the presence of γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ at 305 K. The main products were cyclohexanone and cyclohexanol. Only a trace amount of dicyclohexyl was observed, which is formed by the two cyclohexyl radicals, was observed. Neither acids nor oxoesters were observed. The same products were observed for *non-*, *mono-*, and *tri*-iron-substituted silicotungstates. The efficiency of hydrogen peroxide utilization to oxidized products was almost 100% for γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$. The results of oxidation of cyclohexane catalyzed by $SiW_{12-x}\{Fe(OH_2)\}_xO_{40-x}^{(4+x)-}$ silicotungstates are summarized in Table 1. The conversions of cyclohexane were changed considerably for the structures with iron centers and that for γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ was the highest.

The conversion for oxidation of cyclohexane was 34% under the following conditions; hydrogen peroxide, 1 mmol; cyclohexane, 2 mmol; γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$, 8 μmol; acetonitrile, 6 mL; reaction temperature, 356 K. The addition of a second increment of 1000 μmol hydrogen peroxide to a reacted cyclohexane system with γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ resulted in additional oxidation and the conversion was increased to 65%. At this stage, the turnover number for the oxidation of cyclohexane was increased up to 163, higher than 4–83 reported for various *mono-* (22, 33, 34), *di-* (21, 22, 35–37), and *tri-* (36, 38) iron complexes.

The UV-*vis* and IR spectra of γ-$SiW_{12-x}\{Fe(OH_2)\}_x O_{40-x}^{(4+x)-}$ $(x = 0$–$3)$ after use for oxidation reactions showed only the original absorption bands with almost the same intensities. The ^{183}W NMR and UV-*vis* spectra of γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ unchanged after being treated with hydrogen peroxide (9). The rate and selectivity were not changed by the repetition of the catalytic run as described. These results suggest that γ-$SiW_{12-x}\{Fe(OH_2)\}_x O_{40-x}^{(4+x)-}$ $(x = 0$–$3)$ polyoxometalates are stable under the present reaction conditions.

Oxidation of cyclohexene, *trans*-stilbene, and methane were also catalyzed by γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ in acetonitrile at 305 K. Epoxidation and allylic oxidation were observed for the oxidation of cyclohexene and epoxidation and oxidative cleavage were observed for the oxidation of *trans*-stilbene. After 96 h, the turnover numbers for the oxidation of cyclohexene and *trans*-stilbene reached 37 and 14, respectively, showing that γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ is catalytically active. Even methane was "catalytically" oxygenated into methanol (39). To our knowledge, such a high turnover number of 25 has never been reported for oxidation of methane with hydrogen peroxide by *di*-iron containing model complexes having organic ligands (22).

Figure 2 shows the effect of structures of iron sites on intrinsic catalytic activities for oxidation of not only cyclohexane but also cyclohexene and *trans*-stilbene. To compare the intrinsic catalytic activities, the rates were calculated below the conversion of 1%, where the conversions linearly increased with time. The catalytic activity of γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ for oxidation of cyclohexane, cyclohexene, and *trans*-stilbene was 10^1–10^2 times higher than those of *non-*, *mono-*, and *tri*-iron-substituted silicotungstates, showing that the *di*-iron site in γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ is an effective center for oxidation of hydrocarbons. Such a structure dependency of the catalysis is noticeable and the catalytic performance of *di*-iron-containing polyoxometalate is possibly related to the catalysis by methane monooxygenase. The rate of 5.4×10^{-1} molmin^{-1} $(\text{mol-catalyst})^{-1}$ for the oxidation of cyclohexane is higher than those (1×10^{-2}–4×10^{-1} $\text{molmin}^{-1}(\text{mol-catalyst})^{-1}$ without additives) reported for various *mono-* (22, 33, 34), *di-* (22, 34, 35), and *tri-* (36, 38) iron complexes and lower than that for $[Fe_2O(bpy)_4(OH_2)_2]ClO_4$, which was unfortunately much deactivated by hydrogen peroxide (40).

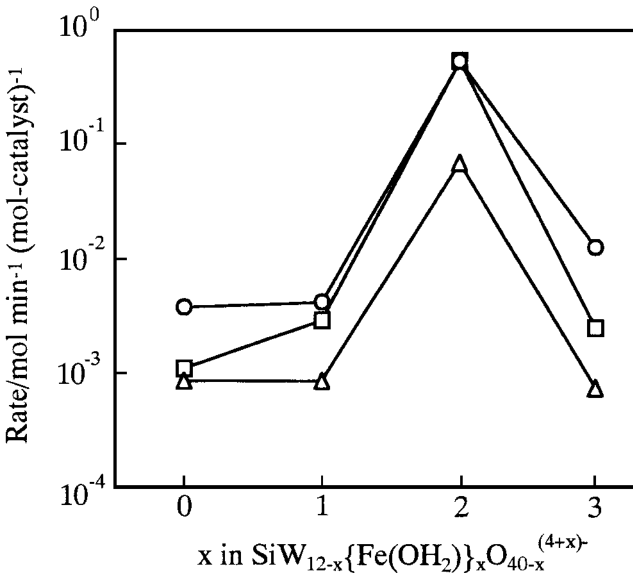

FIG. 2. Effect of Fe^{3+}-substitution for W^{6+} in $SiW_{12}O_{40}^{4-}$ on catalytic activity for oxygenation at 305 K: □, cyclohexane; ○, cyclohexene; △, *trans*-Stilbene. Reaction conditions for cyclohexane and cyclohexene (see Table 1). Reaction conditions for *trans*-stilbene; catalyst, 1.3–1.6 μmol; substrate, 0.11 mmol; H_2O_2, 0.22 mmol; acetonitrile, 3 mL. Rates evaluated below 1% conversion.

In conclusion, a remarkable dependency of catalytic activity of $SiW_{12-x}\{Fe(OH_2)\}_xO_{40-x}^{(4+x)-}$ on the iron structures was observed, γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ being the most active.

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