

Remarkable Effect of Manganese Center on Catalytic Activity for Decomposition of Hydrogen Peroxide

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The structures of manganese centers remarkably influenced the catalytic activities for the decomposition of hydrogen peroxide and tri-manganese-substituted silicotungstate, $[\alpha\text{-SiW}_9\{\text{Mn}^{\text{III}}(\text{H}_2\text{O})\}_3\text{O}_{37}]^{7-}$, was the most active among the polyoxometalates tested and other inorganic manganese compounds.

Hydrogen peroxide has been used in a variety of applications throughout many industries such as wastewater treatment and bleaching for its oxidizing properties and environmentally benign end products of water and oxygen.¹⁻⁶ Residual hydrogen peroxide from industries may cause biological harm upon its radical chain degradation.³ In addition, oxygen from decomposed hydrogen peroxide has recently been used as a source for enhanced bioremediation of soil.⁷⁻¹⁰ Therefore, the decomposition of hydrogen peroxide is important and has been extensively studied with manganese- or iron-containing catalysts.

It has been reported that bacteria of *Lactobacillus plantarum*, *Thermus thermophilus*, and *Thermoleophilium album* possess non-heme catalases with dinuclear manganese site, which efficiently decomposes hydrogen peroxide.¹¹⁻¹⁴

The oxidation catalysis and the decomposition of hydrogen peroxide by mono-transition-metal-substituted polyoxometalates have been extensively studied,¹⁴⁻¹⁹ and the decomposition activity of mono-manganese-substituted silicotungstate is less than $0.2 \text{ M}^{-1}\text{s}^{-1}$ and low.^{15,16} However, nothing is known of the decomposition of hydrogen peroxide catalyzed by di-, tri-, and tetra-manganese-substituted polyoxometalates.

Here, we compare the catalytic activity of non-, mono-, di-, tri-, and tetra-manganese-substituted polyoxometalates for decomposition of hydrogen peroxide and find that trinuclear manganese center shows the highest activity.

The following polyoxometalates, $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$, $[\alpha\text{-SiW}_{11}\{\text{Mn}^{\text{III}}(\text{H}_2\text{O})\}\text{O}_{39}]^{5-}$, $[\gamma\text{-SiW}_{10}\{\text{Mn}^{\text{III}}(\text{H}_2\text{O})\}_2\text{O}_{38}]^{6-}$, $[\alpha\text{-SiW}_9\{\text{Mn}^{\text{III}}(\text{H}_2\text{O})\}_3\text{O}_{37}]^{7-}$, and $[\text{P}_2\text{W}_{18}\text{Mn}^{\text{II}}_4\{\text{H}_2\text{O}\}_2\text{O}_{68}]^{10-}$ were synthesized according to references 20-25,²⁶ The polyoxometalates were abbreviated by $\text{SiW}_{12-x}\text{Mn}^{\text{III}}_x$ ($x = 0-3$) and $\text{P}_2\text{W}_{18}\text{Mn}^{\text{II}}_4$, respectively, and the structures are shown in Figure 1. The decomposition reaction of hydrogen peroxide was carried out in a thermostated 30 mL round-bottomed flask. To an acetonitrile (6 mL) solution of catalyst, hydrogen peroxide was introduced using a microsyringe ([catalyst] = 0-1.3 mM; $[\text{H}_2\text{O}_2] = 0-0.25 \text{ M}$). The amounts of oxygen evolved were measured with a gas burette. The amount of unreacted hydrogen peroxide was obtained with the Ce^{4+} titration.

Figure 2 shows the time courses of the decomposition of hydrogen peroxide catalyzed by $\text{SiW}_{12-x}\text{Mn}^{\text{III}}_x$ ($x = 0-3$). It was confirmed that the amount of hydrogen peroxide reacted after 60 min was two times that of gaseous oxygen evolved for each reaction. The kinetic studies for $\text{SiW}_{12-x}\text{Mn}^{\text{III}}_x$ ($x = 0-3$) showed reasonable first-order plots for the decrease in the con-

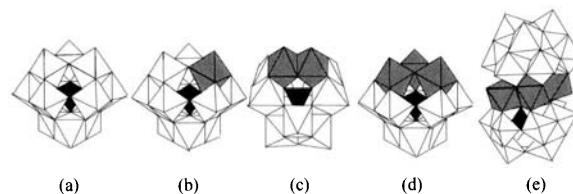


Figure 1. Polyhedral representation of (a) SiW_{12} , (b) $\text{SiW}_{11}\text{Mn}^{\text{III}}_1$, (c) $\text{SiW}_{10}\text{Mn}^{\text{II}}_2$, (d) $\text{SiW}_9\text{Mn}^{\text{III}}_3$, and (e) $\text{P}_2\text{W}_{18}\text{Mn}^{\text{II}}_4$. Manganese atoms are represented by shaded octahedra. WO_6 octahedra occupy the white octahedra, and SiO_4 and PO_4 groups are shown as the internal black tetrahedra.

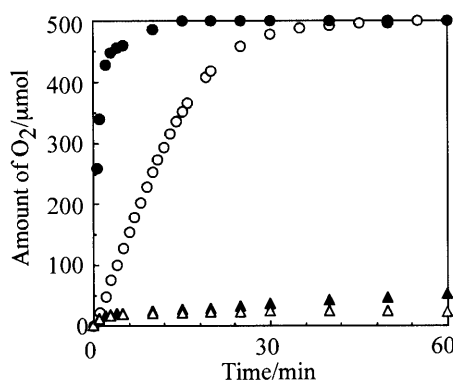


Figure 2. Time course of decomposition of hydrogen peroxide catalyzed by $\text{SiW}_{12-x}\text{Mn}^{\text{III}}_x$ ($x = 0-3$). Reaction conditions; catalyst, $8 \mu\text{mol}$; H_2O_2 , $1000 \mu\text{mol}$; CH_3CN , 6 mL ; at 305 K ; under Ar. ●, $\text{SiW}_9\text{Mn}^{\text{III}}_3$; ○, $\text{SiW}_{10}\text{Mn}^{\text{II}}_2$; ▲, $\text{SiW}_{11}\text{Mn}^{\text{III}}_1$; △, SiW_{12} .

centration of hydrogen peroxide; e.g., the rates for $\text{SiW}_9\text{Mn}^{\text{III}}_3$ were $0, 0.05, 0.13, \text{ and } 0.20 \text{ M min}^{-1}$ at [hydrogen peroxide] of $0, 0.042, 0.083, \text{ and } 0.17 \text{ M}$, respectively. Similar first-order dependences on the concentrations of $\text{SiW}_{12-x}\text{Mn}^{\text{III}}_x$ ($x = 0-3$) were observed; e.g., the rates for $\text{SiW}_9\text{Mn}^{\text{III}}_3$ were $0, 0.016, 0.077, \text{ and } 0.20 \text{ M min}^{-1}$ at [catalyst] of $0, 0.11, 0.53, \text{ and } 1.3 \text{ mM}$, respectively. These results indicate that the rate of decrease in [hydrogen peroxide] is expressed by $-\text{d}[\text{H}_2\text{O}_2]/\text{dt} = k[\text{catalyst}]^1[\text{H}_2\text{O}_2]^1$, and therefore the catalytic activities were evaluated by the k values.

The k values are summarized in Table 1. Non- and mono-manganese substituted silicotungstates showed very low activity, and the catalytic activity of $\text{SiW}_{12-x}\text{Mn}^{\text{III}}_x$ increased monotonically with x ; $\text{SiW}_9\text{Mn}^{\text{III}}_3 \gg \text{SiW}_{10}\text{Mn}^{\text{II}}_2 \gg \text{SiW}_{11}\text{Mn}^{\text{III}}_1 > \text{SiW}_{12}$ with the ratios of $1.0:0.05:0.005:0.003$, respectively. The higher catalytic activities of $\text{SiW}_{10}\text{Mn}^{\text{II}}_2$ and $\text{SiW}_9\text{Mn}^{\text{III}}_3$ may be related to the fact that the decomposition of hydrogen peroxide is a two-electron transfer reaction. Tetra-

Table 1. Apparent rate constants for the decomposition of H₂O₂ catalyzed by SiW_{12-x}Mn^{III}_x and P₂W₁₈Mn^{II}₄ in CH₃CN at 305 K

Catalysts	k/M ⁻¹ s ⁻¹
SiW ₁₂	0.05
SiW ₁₁ Mn ^{III} ₁	0.07
SiW ₁₀ Mn ^{III} ₂	0.71
SiW ₉ Mn ^{III} ₃	15.1
P ₂ W ₁₈ Mn ^{II} ₄	0.15

Reaction conditions; catalyst, 8 μmol; H₂O₂, 1000 μmol; CH₃CN, 6 mL; under Ar.

manganese-substituted sandwich-type P₂W₁₈Mn^{II}₄ was less active than SiW₉Mn^{III}₃. These facts show that the structures of manganese centers remarkably influenced the catalytic activities for the decomposition of hydrogen peroxide and that the oxo-bridged tri-manganese site was the most effective. The activity of SiW₉Mn^{III}₃ was much higher than 0.2 M⁻¹s⁻¹ of MnO₂. Taking into account the report that MnO₂ is much more active than MnCl₂, Mn(OAc)₂, and Mn(H₂O)₆(ClO₄)₂,^{27,28} the result shows that SiW₉Mn^{III}₃ is one of the most active catalysts among Mn-containing inorganic compounds. The activity of SiW₁₀Mn^{III}₂ was higher than those of [γ-SiW₁₀{Fe^{III}(H₂O)}₂O₃₈]⁶⁻ and [γ-SiW₁₀{Cu^{II}(H₂O)}₂O₃₈]⁸⁻, showing that manganese is an active transition metal for the decomposition of hydrogen peroxide.

The Keggin-type polyoxometalates show characteristic UV-vis bands in the range of 250–300 nm. The UV-vis spectrum of SiW_{12-x}Mn^{III}_x (x = 1–3) after use for the decomposition of hydrogen peroxide showed the characteristic absorption bands with almost the same intensities as those of fresh polyoxometalates. After 60 min, further addition of hydrogen peroxide to SiW₉Mn^{III}₃ gave identical catalytic activity. These facts suggest the catalyst stability. A similar stability in the presence of hydrogen peroxide has been reported for manganese-containing polyoxometalates.^{29,30} This is in contrast with the decomposition of organic ligands by hydrogen peroxide.

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References and Notes

- W. T. Hess, "Hydrogen peroxide," in "Kirk-Othmer Encyclopedia of Chemical Technology," Wiley, New York (1993), vol. 13, p. 961.
- K. Rajeshwar, *Chem. Ind.*, **1996**, 454.
- B. C. Larisch and S. J. B. Duff, *Wat. Res.*, **31**, 1694 (1997).
- M. A. Robitaille, *Pulp Paper Can.*, **89**, 167 (1988).
- D. M. Knotter, S. de Gendt, M. Baeyens, P. W. Merten, and M. M. Heyns, *J. Electrochem. Soc.*, **146**, 3476 (1999).
- J. J. Rusek, *J. Propul. Power*, **12**, 574 (1996).
- C. M. Miller and R. L. Valentine, *Wat. Res.*, **33**, 2805 (1999).
- R. J. Watts, M. K. Foget, S.-H. Kong, and A. L. Teel, *J. Hazard. Mater.*, **69**, 229 (1999).
- R. E. Hinchee, D. C. Downey, and P. K. Aggarwal, *J. Hazard. Mater.*, **27**, 287 (1991).
- J. C. Spain, J. D. Milligan, D. C. Downey, and J. K. Slaughter, *Ground Water*, **27**, 163 (1989).
- Y. Kono and I. Fridovich, *J. Biol. Chem.*, **258**, 6015 (1983).
- M. Shank, V. Barynin, and G. C. Dismukes, *Biochem.*, **33**, 15433 (1994).
- G. S. Allgood and J. J. Perry, *J. Bacteriol.*, **168**, 563 (1986).
- C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, **143**, 407 (1995).
- Y. Wu, S.-H. Qu, H.-M. Ma, and S.-K. Ye, *Catal. Lett.*, **23**, 195 (1994).
- N. I. Kuznetsova, L. I. Kuznetsova, and V. A. Likhobolov, *J. Mol. Catal.*, **108**, 135 (1996).
- X. Lu, N. Mizuno, and M. Misono, *Nippon Kagaku Kaishi*, **1998**, 23.
- S. Dong and M. Liu, *J. Electroanal. Chem.*, **372**, 95 (1994).
- J. E. Toth, J. D. Melton, D. Cabelli, B. H. J. Bielski, and F. C. Anson, *Inorg. Chem.*, **29**, 1952 (1990).
- A. Tézé, G. Hervé, and M. T. Pope, *Inorg. Synth.*, **27**, 85 (1990).
- C. M. Tourné, G. F. Tourné, S. A. Malik, and T. J. R. Weakly, *J. Inorg. Nucl. Chem.*, **32**, 3875 (1970).
- X.-Y. Zhang, C. J. O'Conner, G. B. Jameson, and M. T. Pope, *Inorg. Chem.*, **35**, 30 (1996).
- J. Liu, F. Ortéga, P. Sethuraman, D. E. Katsoulis, C. E. Costello, and M. T. Pope, *J. Chem. Soc., Dalton Trans.*, **1992**, 1901.
- X.-Y. Zhang and M. T. Pope, *J. Mol. Catal.*, **114**, 201 (1996).
- R. G. Finke, M. W. Droege, and P. J. Dommille, *Inorg. Chem.*, **26**, 3886 (1987).
- [(n-C₄H₉)₄N]₄[α-SiW₁₂O₄₀]. Anal. Found: C, 20.15; H, 3.55; N, 1.54%. Calcd: C, 20.00; H, 3.78; N, 1.46%. IR spectrum (cm⁻¹): 967(s), 920(s), 884(s), and 801(s, br). UV-vis spectrum in acetonitrile at 296 K: λ_{max} = 264 nm (ε 37,200 M⁻¹cm⁻¹). Both spectra were characteristic of α-Keggin structure. [(n-C₅H₁₁)₄N]₄H[α-SiW₁₁{Mn^{III}(H₂O)}₃O₃₉]. Anal. Found: C, 24.00; H, 4.19; N, 1.44%. Calcd: C, 23.89; H, 4.46; N, 1.39%. IR spectrum (cm⁻¹): 966(s), 919(s), 883(m), and 798(s, br) in agreement with those of K₆[α-SiW₁₁{Mn^{II}(H₂O)}₃O₃₉].2H₂O. UV-vis spectrum in acetonitrile at 296 K: λ = 262 nm (ε 44,000 M⁻¹cm⁻¹) and 483 nm (ε 300 M⁻¹cm⁻¹). [(n-C₄H₉)₄N]₄H₂[γ-SiW₁₀{Mn^{III}(H₂O)}₂O₃₈].1.5CH₃CN.2H₂O. Anal. Found: C, 20.96; H, 3.97; N, 2.18%. Calcd: C, 21.13; H, 4.06; N, 2.02%. IR spectrum (cm⁻¹): 958(s), 911(s), 897(s), and 792(s, br). UV-vis spectrum in acetonitrile at 296 K: λ = 284 nm (ε 15,800 M⁻¹cm⁻¹), 348 nm (ε 3125 M⁻¹cm⁻¹), 460 nm (ε 1150 M⁻¹cm⁻¹), and 580 nm (ε 280 M⁻¹cm⁻¹). [(n-C₆H₁₃)₄N]_{7-x}H_x[α-SiW₉{Mn^{III}(H₂O)}₃O₃₇]. Anal. Found: C, 31.48; H, 5.80; N, 1.67%. Calcd: C, 31.67; H, 6.00; N, 1.54%. IR spectrum (cm⁻¹): 956(s), 916(s), and 795(s, br). UV-vis spectrum in acetonitrile at 296 K: λ = 258 nm (ε 38,000 M⁻¹cm⁻¹). [(n-C₄H₉)₄N]₈H₂[P₂W₁₈Mn^{II}₄(H₂O)₂O₆₈]. Anal. Found: P, 1.13; Mn, 3.66; W, 50.53%. Calcd for K_{10-x}H_x[P₂W₁₈Mn₄(H₂O)₂O₆₈]: P, 1.13; Mn, 4.02; W, 51.64%. Found: C, 19.12; H, 3.64; N, 1.44%. Calcd for [(n-C₄H₉)₄N]₈H₂[P₂W₁₈Mn₄(H₂O)₂O₆₈]: C, 18.92; H, 3.68; N, 1.58%.
- R. T. Stibrany and S. M. Gorun, *Angew. Chem., Int. Ed. Engl.*, **29**, 1156 (1990).
- A. Gelasco, A. Askenas, and V. L. Pecoraro, *Inorg. Chem.*, **35**, 1419 (1996).
- M. Bösing, A. Nöh, I. Loose, and B. Krebs, *J. Am. Chem. Soc.*, **120**, 7252 (1998).
- R. Neumann and M. Gara, *J. Am. Chem. Soc.*, **117**, 5066 (1995).