Journal of Catalysis **184,** 550–552 (1999)
Article ID jcat.1999.2455, available online at http://www.idealibrary.com on IDEAL®

## RESEARCH NOTE

# Aqueous Phase Oxidation of Methane with Hydrogen Peroxide Catalyzed by Di-iron-Substituted Silicotungstate

Noritaka Mizuno,[1] Yasuhiro Seki, Yoshiyuki Nishiyama, Ikuro Kiyoto, and Makoto Misono

*Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Received November 25, 1998; revised February 16, 1999; accepted February 18, 1999

**The title reaction was catalyzed by a water-soluble potassium salt of di-iron-substituted silicotungstate, $\gamma$-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$, mono- and tri-iron-substituted silicotungstates being much less active and nonselective for the oxidation.**

## INTRODUCTION

Strong acidity or oxidizing properties of polyoxometalates induce a lot of studies on the heterogeneous and homogeneous catalysis (1). 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, 2). For example, a high stability to hydrogen peroxide has been reported for iron- or manganese-substituted polyoxometalates (2). We have very recently reported that di-iron-substituted silicotungstate was stable in the presence of hydrogen peroxide (3).

The active site of methane monooxygenase has been shown to have a $\mu$-hydroxo di-iron structure (4). Among alkanes, the activation and functionalisation of methane have attracted much attention because of its abundance and low reactivity (5). Recently, there has been a renewed interest in the direct conversion of methane into oxygenates with environmentally clean oxidants such as molecular oxygen and hydrogen peroxide (5–7). The use of water as a solvent in homogeneous transition-metal catalysis has been of growing importance because of its environmentally friendly nature (8). In these aspects, catalytic oxygenation of methane with hydrogen peroxide in water by model complex catalysts with di-iron centers is of great interest but has been unsuccessful due to the catalyst instability (particularly organic ligands) towards hydrogen peroxide and insolubility in water. In this paper, we attempt to demonstrate catalytic oxidation of methane with hydrogen peroxide in water by di-iron-substituted silicotungstate.

## EXPERIMENTAL

### *Catalysts*

Potassium salt of $\gamma$-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ (abbreviated by **I**, see Fig. 1) was synthesized by the modification of the method reported for the $\gamma$-$SiW_{10}Mn_2O_{38}^{6-}$ polyoxometalate (9). The characterization results for the potassium salt of $\gamma$-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ polyoxometalate were as follows. Elemental analysis: found (calcd for $K_6SiW_{10}\{Fe(OH_2)\}_2O_{38} \cdot 14H_2O$): Si, 0.90 (0.92); Fe, 1.82 (1.83). TG/DTA: weight loss of 9.04% between 300 and 677 K. Calcd for $K_6SiW_{10}\{Fe(OH_2)\}_2O_{38} \cdot 14H_2O$, 9.30% ($16H_2O$). Infrared spectrum ($cm^{-1}$): 1030 (w), 1000 (w), 955 (s), 904 (s), 881 (s), 799 (s, br), 755 (s), 538 (w) in agreement with those of $[(C_4H_9)_4N]_4H_2[\gamma\text{-}SiW_{10}Mn_2^{III,III}O_{38}] \cdot 2H_2O$. The UV–vis spectrum in water at 296 K showed two $O \rightarrow W$ charge transfer bands at 270 ($\varepsilon$ 24,400 $M^{-1}\,cm^{-1}$) and 324 nm ($\varepsilon$ 4400 $M^{-1}\,cm^{-1}$) characteristic of $\gamma$-type Keggin structure.

Potassium salts of the other polyoxometalates used for reactions were synthesized according to Refs. (10–12).

### *Reactions*

The reaction was carried out with an autoclave having a Teflon vessel. The catalyst (5 $\mu$mol) was dissolved in a Teflon vessel containing 1.8 mL of water, and then aqueous hydrogen peroxide (30%, 2.4 mmol) was added. Next, this Teflon vessel was quickly attached inside an autoclave. The gas phase above the liquid was removed by evacuation, and then the autoclave was pressurized with methane (purity $\geq$ 99.9%) to 50 atm. The autoclave was heated up to the reaction temperature in an oil bath. After the reaction, the gas phase was sampled with a sampler directly connected to a gas chromatograph with Porapak QS and Molecular Sieve 5A columns. The liquid was sampled with a microsyringe and analyzed on a gas chromatography with Porapak QS and HayeSep DB columns. Product yields in the liquid and gas phases were reproducibly

0021-9517/99 $30.00

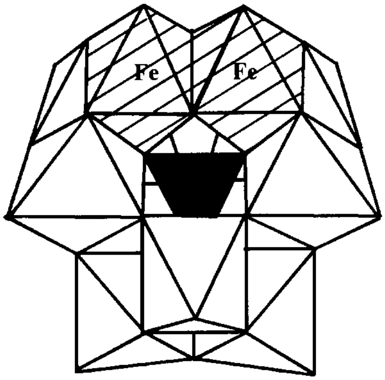

**FIG. 1.** Polyhedral representation of **I**. Iron atoms are represented by hatched octahedra. $WO_6$ octahedra occupy the white octahedra, and an $SiO_4$ group is shown by the internal black tetrahedron.

obtained within experimental errors of ±0.2 and ±2 μmol, respectively. The turnover number (TON) was estimated by moles of oxidizing equivalent in all products/moles of catalyst. The efficiency of hydrogen peroxide utilization was calculated by ([methanol] + 3[formic acid] + 4[methyl formate] + 4[carbon dioxide])/$[H_2O_2]_c$, where $[H_2O_2]_c$ was the concentration of hydrogen peroxide consumed. It was confirmed that no oxidation of methane proceeded with molecular oxygen (2 atm) at 353 K in the presence of **I**.

### *Titration of Hydrogen Peroxide*

The titration of hydrogen peroxide was carried out according to Ref. (13); 1–2 g of solution was 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.

## RESULTS AND DISCUSSION

The catalytic oxidation of methane with hydrogen peroxide was carried out in the presence of **I** for 48 h at 353 K. After 24 h, hydrogen peroxide was completely consumed and the amounts of respective products were little changed. The efficiency of the utilization of hydrogen peroxide was 4.5%. The resulting hydrogen peroxide decomposed into molecular oxygen, of which the amount was also quantitatively confirmed. The main products were methylformate (yield, 10.3 μmol) and carbon dioxide (17.8 μmol) (14). The total turnover number reached to 23 (8.4 to selective oxidation products) after 48 h, showing that **I** is catalytically active. The value was much higher than those (<1) reported for oxidation of methane catalyzed by $Fe_2O(OAc)_2(bpy)_2Cl_2$ (bpy = 2,2′-bipyridine) and $Fe_4O_2(OAc)_7(bpy)_2ClO_4$ in acetonitrile (15). To our knowledge, such catalytic oxidation of methane by iron salts and di-iron containing model complex catalysts under environmentally friendly conditions (i.e., with hydrogen peroxide in water) has never been reported (15–17). In addition, $H_4PVMo_{11}O_{40}$, which was the most active for the oxidation of methane with hydrogen peroxide in $(CF_3CO)_2O$ among vanadium-substituted polyoxometalates (6b), was inactive under the present conditions. The UV–vis spectrum of **I** after use for oxidation reaction showed only the original absorption bands with the same intensities and UV–vis spectrum of **I** unchanged after being treated with hydrogen peroxide, suggesting that **I** is stable under reaction conditions (18).

The temperature dependence of product yields and TON is shown in Fig. 2. Here the reaction time was kept for 24 h. The amount of each product significantly increased with the increase in the reaction temperature from 303 to 353 K. The amount of each product decreased by further increase in the reaction temperature to 403 K. The decomposition of hydrogen peroxide to form dioxygen and water was dominant at 403 K. This may have resulted in the decrease of the amounts of products. The catalytic activity of **I** was greatly increased by the change of solvent to acetonitrile, and the turnover number and efficiency increased to 25 and 20, respectively, even at 303 K (19).

Next, the catalytic activities and products for the oxidation of methane with hydrogen peroxide in water catalyzed by iron-substituted silicotungstates are compared in Table 1. The conversions of methane at 353 K

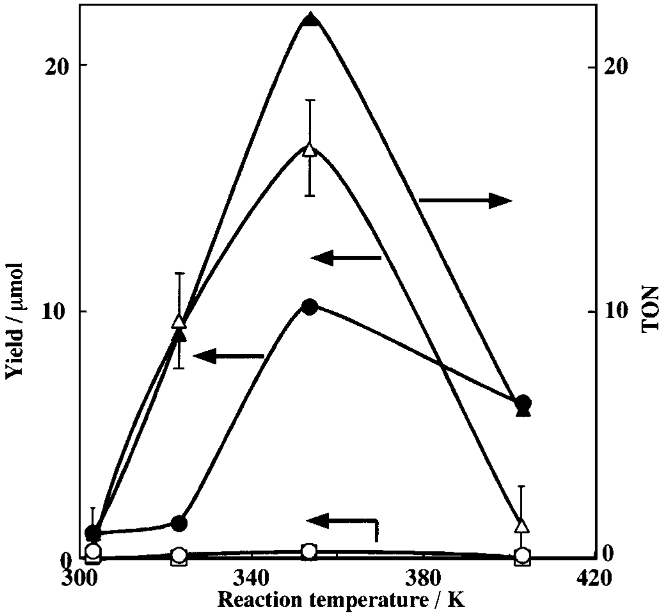

**FIG. 2.** Temperature dependence of product yields and TON: (●) methylformate; (○) methanol; (□) formic acid; (△) carbon dioxide; (▲) TON; catalyst, **I**. Error bars for selective oxidation products are included in respective symbols.

**TABLE 1**

**Oxidation of Methane with Hydrogen Peroxide Catalyzed by $SiW_{12-x}\{Fe(OH_2)\}_xO_{40-x}^{(4+x)-}$ ($x = 1$–$3$) at 353 K**

| | | Yield/$\mu$mol (selectivity/%) | | | |
|---|---|---|---|---|---|
| Catalyst | TON[a] | $CH_3OH$ | $HCO_2CH_3$ | HCOOH | $CO_2$ |
| $\alpha$-$SiW_{11}\{Fe(OH_2)\}O_{39}^{5-}$ | 11.0 ± 1.6 (0) | 0 | 0 | 0 | 13.7 ± 2.0 (100) |
| $\gamma$-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ (**I**) | 21.6 ± 1.8 (8.3) | 0.3 ± 0.2 (1) | 10.2 ± 0.1 (54) | 0.2 ± 0.2 (1) | 16.6 ± 2.0 (44) |
| $\alpha$-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$ | 3.5 ± 1.0 (0) | 0 | 0 | 0 | 4.0 ± 1.0 (57[b]) |

[a] See text. Numbers in parentheses are turnover numbers to selective oxidation products.

[b] 3.0 $\mu$mol $C_2H_6$ (selectivity, 43%) was formed.

decreased in the order of $\gamma$-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ (**I**) $>$ $\alpha$-$SiW_{11}Fe(OH_2)O_{39}^{5-} \geq \alpha$-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$ with the relative ratios of 1.0 : 0.4 : 0.3, respectively. Selective oxidation products were observed only for **I**. These facts show that the di-iron site in **I** is the effective center for the selective oxidation of methane with hydrogen peroxide.

In conclusion, it was found under the present environmentally friendly conditions that **I** catalyzed the selective oxidation of methane to methylformate, methanol, and formic acid.

## ACKNOWLEDGMENTS

We acknowledge Dr. C. Nozaki for the synthesis of **I**. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

## REFERENCES

1. Kozhevnikov, I. V., *Chem. Rev.* **98**, 171 (1998); Mizuno, N., and Misono, M., *Chem. Rev.* **98**, 199 (1998); Neumann, R., *Prog. Inorg. Chem.* **47**, 317 (1998); Okuhara, T., Mizuno, N., and Misono, M., *Adv. Catal.* **41**, 113 (1996); Hill, C. L., and Prosser-McCartha, C. M., *Coord. Chem. Rev.* **143**, 407 (1995).
2. Bösing, M., Nöh, A., Loose, I., and Krebs, B., *J. Am. Chem. Soc.* **120**, 7252 (1998); Zhang, X., Chen, Q., Duncan, D. C., Campana, C. F., and Hill, C. L., *Inorg. Chem.* **36**, 4208 (1997); Neumann, R., and Gara, M., *J. Am. Chem. Soc.* **116**, 5509 (1994).
3. Mizuno, N., Nozaki, C., Kiyoto, I., and Misono, M., *J. Am. Chem. Soc.* **120**, 9267 (1998).
4. Rozenzweig, A. C., Frederick, C. A., Lippard, S. J., and Nordlund, P., *Nature* **366**, 537 (1993).
5. Pitchai, R., and Klier, K., *Catal. Rev.-Sci. Eng.* **28**, 13 (1986); Gesser, H. D., Hunter, N. R., and Prakash, C. B., *Chem. Rev.* **85**, 235 (1985); Hutchings, G. J., Scrrell, M. S., and Woodhouse, J. R., *Chem. Soc. Rev.* **18**, 251 (1989); Crabtree, R. H., *Chem. Rev.* **95**, 987 (1995); Srivastava, R. D., Gollakota, S. V., Stiegel, G. J., and Bose, A. C., "Methane and Alkane Conversion Chemistry," p. 291. Plenum, New York, 1995.
6. (a) Suss-Fink, G., Nizova, G. V., Stanislas, S., and Shul'pin, G. B., *J. Mol. Catal. A: Chem.* **130**, 163 (1998). (b) Seki, Y., Mizuno, N., and Misono, M., *Appl. Catal. A: Gen.* **157**, L47 (1997). (c) Basickes, N., Hogan, T. E., and Sen, A., *J. Am. Chem. Soc.* **118**, 4574 (1996). (d) Fujiwara, Y., Takaki, K., and Taniguchi, Y., *Synlett* 591 (1996). (e) Yamanaka, I., Soma, M., and Otsuka, K., *Chem. Lett.* 565 (1996).
7. Moiseev, I. I., *J. Mol. Catal. A: Chem.* **127**, 1 (1997); Sheldon, R. A., *Top. Curr. Chem.* **164**, 22 (1993); Sobkowiak, A., Tung, H., and Sawyer, D. T., *Prog. Inorg. Chem.* **40**, 291 (1992).
8. Joó, F., and Kathó, Á., *J. Mol. Catal. A: Chem.* **116**, 3 (1997) and Refs. (7–11) therein; Horváth, I. T., *J. Mol. Catal. A: Chem.* **116**, 1 (1997); Horváth, I. T., and Joó, F., *NATOASI Ser.* 35 (1995); Sheldon, R. A., *CHEMTECH* 38 (1994); Kuntz, E. G., *CHEMTECH* 570 (1987).
9. Zhang, X., O'Connor, C. J., Jameson, G. B., and Pope, M. T., *Inorg. Chem.* **35**, 30 (1996).
10. Tézé, A., Hervé, G., and Pope, M. T., *Inorg. Synth.* **27**, 85 (1990).
11. Zonnevijlle, F., Tourné, C. M., and Tourné, G. F., *Inorg. Chem.* **21**, 2751 (1982).
12. Liu, J., Ortéga, F., Sethuraman, P., Katsoulis, D. E., Costello, C. E., and Pope, M. T., *J. Chem. Soc., Dalton Trans.* 1901 (1992).
13. Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis." Longman, New York, 1978.
14. The yield could be increased by a factor of 6 by increasing the volume of the reaction solution. No products were observed in blank experiments without hydrogen peroxide or without catalysts.
15. Khenkin, A. M., and Shilov, A. E., *New J. Chem.* **13**, 659 (1989).
16. Fish, R. H., Konings, M. S., Oberhausen, K. J., Fong, R. H., Yu, W. M., Christou, G., Vincent, J. B., Coggin, D. K., and Buchanan, R. M., *Inorg. Chem.* **30**, 3002 (1991).
17. (a) Rabion, A., Buchanan, R. M., Seris, J.-L., and Fish, R. H., *J. Mol. Catal.* **116**, 43 (1997). (b) Duboc-Toia, C., Ménage, S., Lambeaux, C., and Fontecave, M., *Tetrahedron Lett.* **38**, 3727 (1997). (c) Itoh, S., Okuno, T., Matsushima, H., Tokii, T., and Nishida, Y., *J. Chem. Soc., Dalton Trans.* 4479 (1996). (d) Dong, Y., Yan, S., Yong, V. G., Jr., and Que, L., Jr., *Angew. Chem., Int. Ed. Engl.* **35**, 618 (1996). (e) Ménage, S., Galey, J.-B., Hussler, G., Seité, M., and Fontecave, M., *Angew. Chem., Int. Ed. Engl.* **35**, 2353 (1996). (f) Rabion, A., Chen, S., Wang, J., Buchanan, R. M., Seris, J.-L., and Fish, R. H., *J. Am. Chem. Soc.* **117**, 12356 (1995). (g) Ménage, S., Vincent, J. M., Lambeaux, C., and Fontecave, M., *J. Chem. Soc., Dalton Trans.* 2081 (1994). (h) Leising, R. A., Kim, J., Perez, M. A., and Que, L., Jr., *J. Am. Chem. Soc.* **115**, 9524 (1993). (i) Anderson, K. K., Froland, W. A., Lee, S. K., and Lipscomb, J. D., *New J. Chem.* **15**, 411 (1991). (j) Kitajima, N., Ito, M., Fukui, H., and Moro-oka, Y., *J. Chem. Soc., Chem. Commun.* 102 (1991). (k) Fontecave, M., Roy, B., and Lambeaux, C., *J. Chem. Soc., Chem. Commun.* 939 (1991). (l) Barton, D. H. R., Csubai, E., Doller, D., Ozbalik, N., and Balavoine, G., *Proc. Natl. Acad. Sci. U.S.A.* **87**, 3401 (1990). (m) Sheu, C., Richert, S. A., Cofre, P., Ross, B., Jr., Sobkowiak, A., Sawyer, D. T., and Kanofsky, J. R., *J. Am. Chem. Soc.* **112**, 1936 (1990). (n) Nam, W., and Valentine, J. S., *New J. Chem.* **13**, 677 (1989). (o) Vincent, J. B., Huffman, J. C., Christou, G., Li, Q., Nanny, M. A., Hendrickson, D. N., Fong, R. H., and Fish, R. H., *J. Am. Chem. Soc.* **110**, 6898 (1988). (p) Barton, D. H. R., Boivin, J., Gastiger, M., Morzycki, J., Hay-Motherwell, R. S., Motherwell, W. B., Ozbalik, N., and Schwartzentruber, K. M., *J. Chem. Soc., Perkin Trans. 1* 947 (1986).
18. Studies to elucidate the nature of active species and to examine the stability of **I** under reaction conditions in more detail are in progress.
19. It was confirmed that no oxidation of the solvent, acetonitrile, proceeded at 303 K.