doi:10.1246/cl.2012.591
Published on the web May 19, 2012

Sol–Gel-derived Bridged Polysilsesquioxane as a Hydrogen Peroxide Decomposition Catalyst: Immobilization of a Dimanganese Complex and Its Improved Thermal Stability

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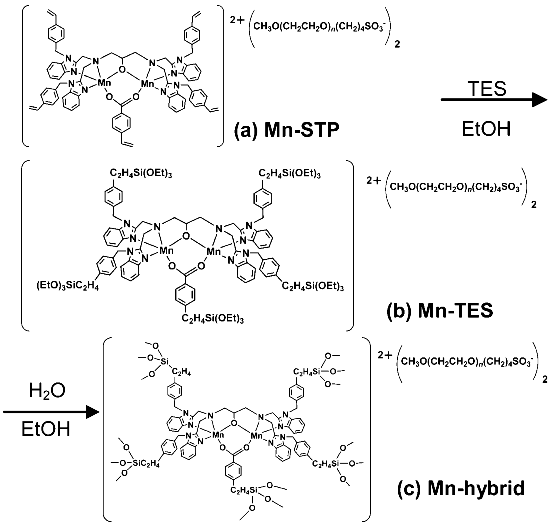
Bridged polysilsesquioxane possessing dimanganese complex moiety, a model complex for catalase, exhibited catalytic activity for the hydrogen peroxide decomposition reaction without any deactivation. The catalytic activity was mostly retained, even after 24-h acid treatment at 80 °C, improving thermal stability after immobilization.

Fuel cells are expected to become a new source of clean energy. Among fuel cells, the polymer electrolyte fuel cell (PEFC) is an excellent candidate for batteries for use in portable electric apparatuses and electric vehicles.[1–3] In the operation of PEFCs, hydrogen peroxide is formed by the crossleak and gradually degrades ionomer membranes such as acidic Nafion mediums.[4–6] Decreasing the volume of hydrogen peroxide is thus a problem to be solved. One effective method of removing the hydrogen peroxide formed is to employ catalysts to decompose it. Since PEFCs generally operate at 80–100 °C under acid conditions, sufficient thermal stability is required of such catalysts.

Catalase enzymes decompose hydrogen peroxide in nature by a dismutation reaction ($2H_2O_2 \rightarrow 2H_2O + O_2$).[7] Since catalase possesses two manganese ions, bioinspired binuclear-manganese complexes have been extensively designed.[8–14] Immobilization in matrices is important for application of these complexes, and inorganic matrices are superior to organic matrices in terms of durability and thermal stability. The sol–gel process is a common method for the formation of inorganic networks, such as siloxane (Si–O–Si) networks, and metal complexes can be immobilized into siloxane networks through covalent bonds by using appropriate precursors possessing trialkoxysilyl groups.[15] The introduction of multiple trialkoxysilyl groups is advantageous for gel formation, and the resulting hybrids are called bridged polysilsesquioxanes.[16–29] Various bridged polysilsesquioxanes bearing metal complexes have thus been reported to date. A polysilsesquioxanes bearing binuclear-manganese complex moiety is thus an attractive catalyst for the reduction of hydrogen peroxide in PEFCs.

Here we report preparation of a new bridged polysilsesquioxane possessing a dimanganese complex moiety and its ability to achieve decomposition reactions. The dimanganese complex $[Mn_2(L)(\mu\text{-}X)]Y_2$, where μ-X: $p\text{-}CH_2{=}CHC_6H_4CO_2$, Y: $CH_3O(CH_2CH_2O)_n(CH_2)_4SO_3^-$ (n = ca. 45), L: *N*,*N*,*N*′,*N*′-tetrakis{[1-(4-styrylmethyl)benzimidazol-2-yl]methyl}propane-1,3-diamin-2-olato,[8] (abbreviated as Mn–STP, Scheme 1a), was synthesized from a precursor possessing *p*-vinylbenzoate anion (Y: $CH_2{=}CHC_6H_4COO^-$), which was identified by ESI-MS (*m*/*z* 1477.4), via an ion-exchange reaction. Mn–STP was modified with triethoxysilane (TES) via hydrosilylation, and the resultant product *N*,*N*,*N*′,*N*′-tetrakis[(1-{4-[2-(triethoxysilyl)ethyl]benzyl}-benzimidazol-2-yl)methyl]propane-1,3-diamin-2-olato (abbreviated as Mn–TES, Scheme 1b), was hydrolyzed to obtain a bridged silsesquioxane (Mn–hybrid, Scheme 1c). The catalytic activity of hydrogen peroxide decomposition was assessed at 80 °C under acid conditions, in which PEFCs in electric vehicles typically operate.[4]



Scheme 1. The scheme of Mn–hybrid preparation.

The hydrosilylation reaction of Mn–STP was manipulated under an inert atmosphere using standard Schlenk techniques. TES was used after vacuum distillation, and a 0.1 mol L^{-1} xylene solution of 1,3-di(η^2-vinyl)-1,1,3,3-tetramethyldisiloxane platinum(0) (Karstedt's catalyst) was used as received. Mn–STP (600 mg) was dissolved in dry ethanol (18 mL), and TES (0.37 mL) and Karstedt's catalyst solution (0.33 mL) were then added to the solution. The mixture was allowed to react at 60 °C for four days with stirring. After cooling to room temperature and drying under vacuum, 920 mg of Mn–TES was obtained. The dark brown color of Mn–STP was retained after hydrosilylation. The completion of hydrosilylation was confirmed by Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectrum of Mn–TES showed the disappearance of δ(C=C) (950–1000 cm^{-1}) and ω(C=C) (545–555 cm^{-1}) bands originat-

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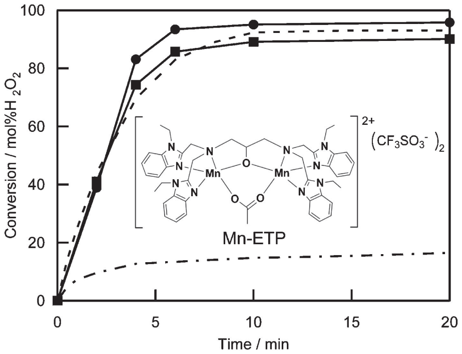

Figure 1. The time–conversion plot for hydrogen peroxide decomposition catalysis of Mn–hybrid and Mn–ETP after 5-min and 24-h treatments under acid conditions at 80 °C: black circle: Mn–hybrid after 5-min treatment; black square: Mn–hybrid after 24-h treatment; dotted line: Mn–ETP after 5-min treatment; dashed line: Mn–ETP after 24-h treatment.

ing from Mn–STP, as well as ν(Si–H) (ca. 2100 cm^{-1}) and δ(Si–H) (800–950 cm^{-1}) bands which were observed in the spectrum of TES. New adsorption bands due to ν(C–H) at ca. 2950 cm^{-1}, ν(C–O) at 1050–1100 cm^{-1}, and ν(Si–C) at ca. 780 cm^{-1}, all of them originating from TES, were also observed in Mn–TES.[29,30]

A hybrid gel was prepared by the sol–gel process under acid conditions. A mixture of ethanol (1.9 mL), water (240 µL), and 0.10 mol L^{-1} HCl (66 µL) was added dropwise to Mn–TES (200 mg) diluted in ethanol (5.0 mL) with stirring at room temperature, and the solution was then allowed to stand to form a wet gel via the formation of a siloxane (Si–O–Si) network. The wet gel was then dried under vacuum to yield Mn–hybrid. As apparent from its FT-IR spectrum, a ν(C–O) band (1050–1100 cm^{-1}) due to the ethoxy group was decreased and a ν(Si–O–Si) band (1030–1090 cm^{-1}) caused by the formation of a siloxane network appeared. A very weak ν(SiO–H) band was observed at 3200–3700 cm^{-1}, indicating that the degree of condensation should be sufficient.

The catalytic activity of Mn–hybrid was measured after 5-min and 24-h treatments of Mn–hybrid (4.3 µmol/Mn) in pH 4 tartaric acid buffer/ethylene glycol (1 mL/1 mL) at 80 °C (Figure 1). The pH and temperature were selected for its possible use at cathodes of PEFCs.[4] The measurement was performed by quantification of the oxygen evolving via decomposition of hydrogen peroxide (2.3 mmol). A similar heterogeneous catalytic decomposition was also performed with the corresponding unimmobilized dimanganese complex, $[Mn_2(L)(\mu\text{-}OAc)](CF_3SO_3)_2$, L: *N*,*N*,*N*′,*N*′-tetrakis[(1-ethylbenzimidazol-2-yl)methyl]propane-1,3-diamin-2-olato,[8,31] (abbreviated as Mn–ETP) (8.4 µmol/Mn). The initial slope of the time–conversion plot at 5-min treatment for Mn–hybrid was almost equal to that of Mn–ETP, although the amount of catalyst employed for Mn–hybrid was less than that for Mn–ETP. These results indicate that the present immobilization does cause no deactivation of the dimanganese catalyst. The catalytic activity of Mn–hybrid was mostly retained, even after 24-h treatment, while that of Mn–ETP decreased significantly after 24 h. This clearly demonstrates the high thermal stability of Mn–hybrid upon immobilization.

In conclusion, a bridged polysilsesquioxane possessing a dimanganese complex moiety was successfully prepared via the sol–gel process. The thermal stability of hydrogen peroxide decomposition catalysis of a dimanganese complex under acid conditions at 80 °C was drastically improved by immobilization in siloxane networks with no deactivation. The present results strongly suggest that bridged silsesquioxanes bearing catalase moieties have potential for hydrogen peroxide decomposition catalysis in PEFCs.

This work was financially supported in part by the Global COE Program "Center for Practical Chemical Wisdom" by MEXT, Japan.

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