

## Chemoselective Oxidation of Sulfides Promoted by a Tightly Convoluted Polypyridinium Phosphotungstate Catalyst with H<sub>2</sub>O<sub>2</sub><sup>†</sup>

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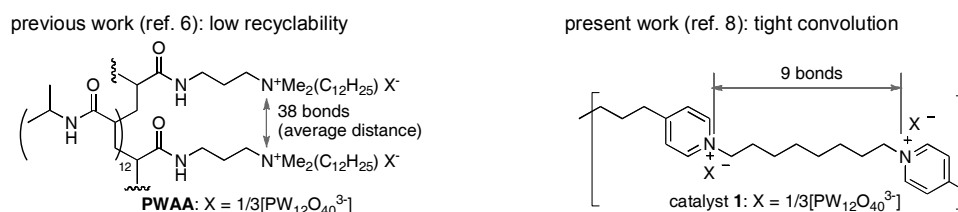
**Key Words:** Polymer-supported catalyst, Tungsten, Oxidation, Sulfide, Sulfone

Sulfones have generated considerable interest due to their presence in a number of biologically active compounds and also to their utility in organic synthesis.<sup>1</sup> Sulfide oxidation is one of the standard approaches to sulfones, where a stoichiometric or larger amount of hazardous oxidants such as KMnO<sub>4</sub>, MCPBA, and MMPP is often required.<sup>2</sup> If sulfides could be efficiently oxidized with hydrogen peroxide by using a recyclable catalyst, the catalytic oxidation system would provide a viable, safe, clean, and environmentally benign alternative to the conventional stoichiometric oxidations.<sup>3</sup> While there has been no lack of pioneering work on sulfide oxidation with aq. H<sub>2</sub>O<sub>2</sub> promoted by a homogeneous catalyst,<sup>4</sup> the heterogeneous-switching of the catalytic oxidation to meet green chemical requirements still remains a major challenge. We have previously developed a novel concept for catalyst-immobilization, also known as molecular convolution,<sup>5-8</sup> where a soluble linear polymer having multiple ligand groups was convoluted (non-covalently cross-linked) with transition metals *via* coordinative or ionic complexation to achieve the one-step preparation of the insoluble polymeric metal composite, combining heterogeneity and catalytic activity in one system. This author (YMA) and his coworkers designed and prepared an ionically convoluted polymeric phosphotungstate catalyst, PWAA, *via* salt formation of PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> with poly(*N*-isopropyl-acrylamide) bearing branched ammonium cation units (Figure 1, left). Although PWAA was found to promote the sulfide oxidation with H<sub>2</sub>O<sub>2</sub>, it could not be readily recycled, presumably because of its physical fragility.<sup>6,7</sup> To overcome this problem, we recently developed a tightly convoluted polymeric catalyst **1** of main-chain polypyridinium and phosphotungstate (Figure 1, right) that exhibits high catalytic activity and recyclability for the oxidative cyclization of alkenols and alkenoic acids.<sup>8</sup> Here, we report the oxidation of a variety of sulfides with aq. H<sub>2</sub>O<sub>2</sub> in the presence of **1** that was efficiently reused without loss of catalytic activity to afford the

corresponding sulfones in quantitative yield.

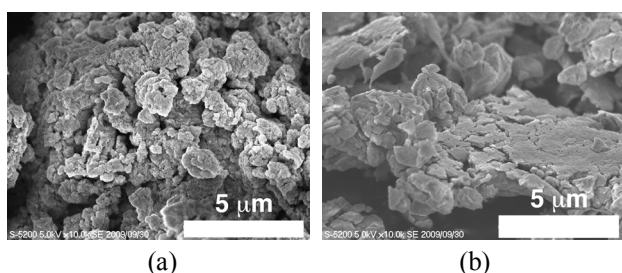
When the oxidation of thioanisole (**2a**) was examined with 30% aq. H<sub>2</sub>O<sub>2</sub> (4 mol equiv) in the presence of the convoluted polypyridinium phosphotungstate catalyst **1** (1 mol %) in *t*-BuOH at 50 °C for 3 h, we were pleased to find that the oxidation proceeded smoothly to give methyl phenyl sulfone (**3a**) in 99% isolated yield (Table 1, entry 1). In contrast, as a control experiment, the reaction without a catalyst under otherwise similar conditions gave **3a** in 5% yield. Ethylthiobenzene (**2b**) was converted to ethylsulfonylbenzene (**3b**) in 97% yield (entry 6). The sterically hindered diphenyl sulfide (**2c**) was efficiently oxidized to afford diphenyl sulfone (**3c**) in 99% yield (entry 7). The chemoselective oxidation of bromo- and formyl-substituted thioanisoles **2d** and **2e** afforded the corresponding sulfones **3d** and **3e** in 99% and 94% yield, respectively, where the bromo and formyl groups remained intact under the oxidation conditions (entries 8 and 9). Likewise, the chemoselective reaction of the phenyl sulfides **2f** and **2g** bearing an olefin and a hydroxy group proceeded smoothly to give the corresponding sulfones **3f** and **3g** each in 99% yield (entries 10 and 11). 2-(Methanesulfonyl)benzothiazole (**3h**), a useful synthon for the Julia olefination, was readily prepared in 93% yield from 2-(methylthio)benzothiazole (**2h**) under similar conditions in which the benzothiazole ring survived (entry 12). The catalytic system was applied to the oxidation of the benzothiophenes **2i** and **2j** affording the corresponding benzothiophene dioxides **3i** and **3j** in 94% and 99% yield (entries 13 and 14). A dialkyl sulfide **2k** underwent the oxidation under similar conditions to give dibutyl sulfone (**3k**) in 99% yield (entry 15).

Recycling experiments of the catalyst **1** were carried out for the oxidation of **2a**. Thus, the reaction of **2a** with aq. H<sub>2</sub>O<sub>2</sub> was effected with 1 mol % of **1** under the above-mentioned conditions to give **3a** in 99% yield (Table 1, entry 1). The catalyst was recovered by filtration and reused four times to afford **3a** in



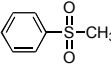
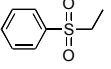
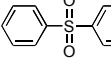
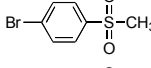
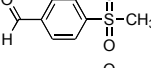
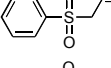
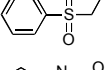
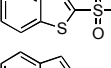
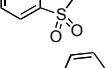
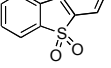
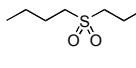
**Figure 1.** A tightly convoluted polypyridinium phosphotungstate **1**.

<sup>†</sup>This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.



**Figure 2.** SEM images of the catalyst **1** before and after use (bar: 5 μm).

**Table 1.** Oxidation of sulfides **2** to sulfones **3** catalyzed by **1** with H<sub>2</sub>O<sub>2</sub><sup>a</sup>

entry	time (h)	sulfone <b>3</b>	yield (%) <sup>b</sup>
		$\text{R}^1\text{-S-R}^2 \xrightarrow[\text{t-BuOH, 50 }^\circ\text{C}]{\text{1 (1 mol \%), 30\% aq H}_2\text{O}_2 \text{ (4 mol equiv)}} \text{R}^1\text{-S(=O)}_2\text{-R}^2$	
1	3		99
2	3	<b>3a</b> ( <b>1</b> ; 2nd use)	99
3	3	<b>3a</b> ( <b>1</b> ; 3rd use)	99
4	3	<b>3a</b> ( <b>1</b> ; 4th use)	99
5	3	<b>3a</b> ( <b>1</b> ; 5th use)	99
6	3		97
7	3		99
8	3		99
9	3		94
10	1		99
11	3		99
12	8		93
13	3		94
14	8		99
15	3		99

<sup>a</sup>Conditions: sulfide **2** (1 mmol), 30% aq H<sub>2</sub>O<sub>2</sub> (4 mmol), catalyst (1 mol %), 50 °C; <sup>b</sup>Isolated yield.

stable chemical yield (2nd use: 99%, 3rd use: 99%, 4th use: 99%, and 5th use: 99%; entries 2-5) during which no significant change of the morphology of the catalyst was observed by SEM (Figure 2).

In conclusion, we have found that the tightly convoluted polypyridinium phosphotungstate catalyst **1** efficiently promoted the chemoselective oxidation of sulfides to sulfones with hydrogen peroxide. The catalyst was reused four times without loss of catalytic activity.

**Supporting Information.** General information, procedure for oxidation of sulfides, NMR & GC-MS data of the products are available. This material is available on line via the internet at <http://journal.kcsnet.or.kr>.

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