

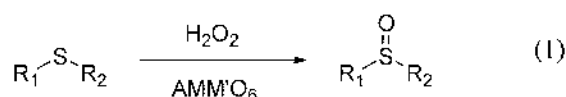
Communications

Selective Oxidation of Organic Sulfides to Sulfoxides by Hydrogen Peroxide with Trirutile-Type Solid Oxide Catalyst HNbMoO_6

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Received December 1, 2003***Key Words :** Sulfoxide, Hydrogen peroxide, Trirutile solid oxide, Heterogeneous catalyst

Selective oxidation of organic sulfides to sulfoxides has been the subject of extensive research because of their importance of sulfoxides as intermediates in various organic reactions.¹ One of the simplest methods for oxidation of sulfides to sulfoxides is the use of hydrogen peroxide as an oxidant in the presence of a catalyst. Though a number of catalysts including soluble metal complexes have been used for the reaction,^{1,2} there are a few reports employing a heterogeneous catalyst despite the advantage in separation and reuse of the catalyst.³ In this paper, we introduce a new heterogeneous catalyst, HNbMoO_6 , which shows an excellent catalytic activity in the oxidation of sulfides.

Trirutile-type solid oxide, $\text{AMM}'\text{O}_6$, was first synthesized in 1970.⁴ Since then, many applications of the solid oxide in various fields such as non-linear optics and composites have been reported.⁵ However, the catalytic activity of the oxide in organic reactions has not been well studied in spite of the potentials expected from the two different transition metals contained in the solid oxide. Recently, we reported a selective sulfoxidation of allylic sulfides catalyzed by the trirutile-type solid oxide, LiNbMoO_6 ⁶ and successfully applied the oxidation method to the synthesis of Lansoprazole.⁷ Because of the good catalytic activity shown by the LiNbMoO_6 in the sulfoxidation of sulfides, we decided to test other trirutile-type solid oxides, $\text{AMM}'\text{O}_6$ (A=H, Li, M=Nb, Ta, M'=Mo, W), as a catalyst in the hydrogen peroxide oxidation of sulfides to sulfoxides (Eq. 1).



We first examined the oxidation of thioanisole in the

presence of various trirutile-type solid oxides. Typically, the oxidation was performed by adding an equimolar amount of aqueous hydrogen peroxide to thioanisole in methanol in the presence of $\text{AMM}'\text{O}_6$ at room temperature. The amount of thioanisole sulfoxide produced was monitored by HPLC. As reported in the Table 1, HNbMoO_6 , LiNbMoO_6 and HNbWO_6 showed excellent catalytic activities. Though the oxidations were completed after 3 hr (entry 1-3), more than 90% of thioanisole was oxidized to its sulfoxide within 1hr. Among the three solid oxides, HNbMoO_6 showed the highest catalytic activity along with the selectivity for the sulfoxide. The thioanisole sulfoxide was not observed in the reaction without the catalyst within 3 hr (entry 9). Other

Table 1. Oxidation of thioanisole by hydrogen peroxide at room temperature

Entry	Catalyst ^a	Reaction time (hr)	Yield(%) ^d	
			Sulfoxide	Sulfone
1 ^a	HNbMoO_6	3	99	–
2 ^a	LiNbMoO_6	3	86	14
3 ^a	HNbWO_6	3	96	–
4 ^b	LiNbWO_6	24	65 (<10) ^c	34
5 ^b	HTaMoO_6	24	91	9
6 ^b	LiTaMoO_6	24	90	9
7 ^b	HTaWO_6	24	94	4
8 ^b	LiTaWO_6	24	80	19
9 ^b	–	24	5	–

^aThioanisole 0.5 mmol, hydrogen peroxide 0.5 mmol, catalyst 2.5 mg, MeOH 2 mL. ^bSince the reaction rate was slow, concentrations of the sulfide, hydrogen peroxide and the catalyst were increased (thioanisole 1 mmol, hydrogen peroxide 1 mmol, catalyst 5.0 mg, MeOH 2 mL). ^cParticle size, ca. 1–3 μm ^dHPLC (Genesis Silica 4 μm) yield. ^eafter 3 hr.

Table 2. Oxidation of organic sulfides with hydrogen peroxide and HNbMoO₆

Entry	Substrate	Reaction Time (hr)	Sulfoxide Yield ^a	Entry	Substrate	Reaction Time (hr)	Sulfoxide Yield ^a
1		2.5	99	7		3.5	97
2		2.5	99	8		3	95
3		3	96	9		2.5	83
4		1	97	10		18	72
5		3	90	11		18	72
6		7	88	12		1	94
				13		1	73

^aIsolated yield. Products were identified by comparison of physical data with literature values.⁹

solid oxides also catalyzed the oxidation, however, required long reaction time. The result indicated that the presence of Nb metal is critical to get a high catalytic activity of the trirutile-type solid oxide.

We also studied the oxidation of other organic sulfides employing HNbMoO₆ as the catalyst (Table 2).⁸ In the oxidation of *para*-substituted thioanisole, the substituent effect was not observed (entry 1-5). However, the oxidation of *o*-bromothioanisole was slow (entry 6). The slow reaction rate might be due to the steric interaction between *o*-bromo group and the surface of the heterogeneous solid catalyst. The oxidation of sulfides containing vinyl and benzimidazole group also required long reaction time (entry 10-11). Since the catalyst, HNbMoO₆ is slightly acidic, the acid and base equilibrium between the catalyst and the sulfide might be occurred and slow the sulfoxidation. The catalyst also showed a good catalytic activity to the oxidation of dialkylsulfides (entry 9, 12 and 13).

In conclusion, we have found that hydrogen peroxide oxidized organic sulfides to their sulfoxides efficiently in the presence of trirutile-type solid oxides.

Acknowledgement. This work was supported by grant No. R01-2003-000-10187-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

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- The following procedure is typical: To a solution of thioanisole (63 mg, 0.51 mmol) and HNbMoO₆ (2.5 mg, 8.7 × 10⁻³ mmol) in methanol (2 mL) was added a solution of commercial 34% hydrogen peroxide (0.05 mL, 0.5 mmol). The mixture was stirred at room temperature and the reaction progress was monitored by TLC. After completion of the reaction, solvent was evaporated. Isolation of pure methyl phenyl sulfoxide (69 mg, 96% yield) from the resulting residue was accomplished by flash chromatography (hexane/ethyl acetate).
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