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Aerobic Oxidation of Sulfides to Sulfoxides Catalyzed by Gold/Manganese Oxides

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Although selective oxidation of sulfides to sulfoxides with molecular oxygen is a difficult reaction due to the overoxidation to sulfone, manganese oxides were found to catalyze the aerobic oxidation of sulfides to sulfoxides in 1,2-dichlorobenzene at 100 °C with a high selectivity above 99%. The catalytic activity depends on the preparation methods and conditions of manganese oxides but not on the valences of manganese. The deposition of Pd and Pt on manganese oxides was detrimental, whereas the deposition of Au enhanced the catalytic activity and selectivity.

Sulfoxides and sulfones are useful intermediates for the synthesis of biologically active compounds and pharmaceutical substances.^{1,2} Oxidation of sulfides can produce either sulfoxides or sulfones or both, depending on the methods and conditions.³ In general, selective oxidation to sulfoxide is difficult due to overoxidation to sulfone and requires highly selective methods, while deep oxidation to sulfones readily takes place. The conventional methods for sulfoxide synthesis use stoichiometric amounts of oxidants such as nitric acid,⁴ MnO₂,⁵ NaIO₄,⁶ and peracids.⁷ From the point of view of green chemistry, the development of a new heterogeneous catalyst using molecular oxygen as an oxidant in the absence of any other reagents is highly desired.

There are a few reports concerning the aerobic oxidation of sulfides with heterogeneous catalysts. A mixed oxide solid has been reported to be selective to sulfones but not highly active.⁸ Oxidation to sulfoxides by polyoxometallates (POM)^{9–11} is slow or/and poorly selective. Recently, oxidation by clay-supported ceric ammonium nitrate (CAN) has been reported to be highly active and selective to sulfoxides.¹²

Gold catalysts, that had long been considered to be poorly active, have gained growing attention since gold exhibits unique size- and support-dependent catalytic activity and selectivity.^{13–15} Although selective aerobic oxidation of alcohols and amines on supported gold catalysts has already been reported,^{16–19} to the best of our knowledge, there has been no report on the selective aerobic oxidation of sulfides by

using heterogeneous gold catalysts. Recently gold nanoclustercatalyzed selective oxidation of sulfide to sulfoxide has been reported, however, PhIO was used as an oxidant instead of oxygen.²⁰ In this work, we have screened a variety of metal oxide-supported gold catalysts in the aerobic oxidation of sulfide. To our surprise, manganese oxides with and even without gold nanoparticles (NPs) exhibited catalytic activity and high selectivity to sulfoxide. Manganese oxides are known as a good oxidizing reagent,^{5,21} however, it is only recently that they have been proven to be catalytically active for the aerobic oxidation of alcohols to aldehydes,^{22–25} of amines to amides,²⁶ and for the ammoxidation of alcohols to amides,^{27,28} and of methylarenes to amides.²⁹ As far as we know, the aerobic oxidation to sulfoxide with catalytic amounts of manganese oxides has not yet been reported.

Experimental

Materials. The majority of metal oxide supports used were commercially available metal oxide powders: MgO (Ube Industries, Ltd., ultra pure), Al₂O₃ (Mizusawa Industrial Chemicals, NEOBEAD300), SiO₂ (Fuji Silysia Chemical, CARiACT Q-10), TiO₂ (Nippon Aerosil, P-25), ZnO (Hakusui Tech, ZINCOX SUPER F-2), ZrO₂ (Dai-ichi Kigenso Kagaku Kogyo, RC-100), MoO₃ (Kanto Chemicals, mean particle size 1.7μ m), SnO₂ (Sigma-Aldrich, nanopowder, <100 nm), CeO₂ (Shin-etsu Chemical, 161 m² g⁻¹), and WO₃ (propriety material). Reagent grades, NH₄VO₃, MnCl₂·4H₂O, Mn(NO₃)₂·6H₂O,

KMnO₄, Fe(NO₃)₂•6H₂O, Co(NO₃)₂•6H₂O, Ni(NO₃)₂•6H₂O, Cu(NO₃)₂•6H₂O, La(NO₃)₃•6H₂O, NaClO₃, Na₂CO₃, NaOH, KOH, and HNO₃ were used as received. As gold precursors, tetrachloroauric(III) acid tetrahydrate (H[AuCl₄]•4H₂O) and acetylacetonato(dimethyl)gold(III) ([Au(acac)(CH₃)₂]) were purchased from Kishida Reagents Chemicals Co., Ltd. and Tri Chemical Laboratories Inc., respectively. Bis(ethylenediamine)gold(III) trichloride ([Au(en)₂]Cl₃) was prepared in a similar manner to the previous literature.³⁰ As noble metal precursors, palladium(II) chloride, bis(acetylacetonato)palladium(II), and bis(acetylacetonato)platinum(II) were purchased from Wako Pure Chemical Industries, Ltd. Tetraammineplatinum(II) dichloride hydrate was purchased from Kojima Chemicals Co., Ltd. 4-Bromophenyl methyl sulfide, 4-fluorophenyl methyl sulfide, 4-methoxyphenyl methyl sulfide (Tokyo Chemical Industry Co., Ltd.), 4-chlorophenyl methyl sulfide, mesitylene, methyl phenyl sulfide (thioanisole) (Wako), dibenzothiophene (Kanto Chemical Co., Inc.) and 1,2-dichlorobenzene (Aldrich) were purchased and were used without any further purification.

Metal Oxides. V_2O_5 was prepared by calcination of NH_4VO_3 in air at 300 °C for 4 h.

 MnO_{2-x} was prepared by neutralization. An aqueous solution of $Mn(NO_3)_2 \cdot 6H_2O$ (0.1 M, 400 mL) was rapidly added into an aqueous solution of Na_2CO_3 (0.1 M, 480 mL) at room temperature. After stirring for 1 h, the suspension was centrifuged and the precipitate was repeatedly washed with distilled water until the pH reached a steady value of around 8. The precipitate was filtrated, dried at 120 °C overnight, and then calcined in air at 300 °C for 4 h.

MnO2-A was prepared by reduction of KMnO4 with HCHO and KOH.³¹ MnO₂_B was prepared by oxidation of Mn(NO₃)₂ by NaClO₃ and HNO₃.³¹ For the preparation of MnO₂₋C, an aqueous solution (125 mL) of Mn(NO₃)₂·6H₂O (75 mmol) was added to an aqueous solution (125 mL) of KMnO₄ (50 mmol) and NaOH (150 mmol) at room temperature and the dispersion was stirred for 1 h.31 The precipitate was repeatedly washed with distilled water until the pH reached a steady value of around 9. The precipitate was collected by filtration, dried at 120 °C overnight, and then calcined in air at 300 °C for 4 h. For the preparation of MnO₂-D, an aqueous solution (30 mL) of MnCl₂•4H₂O (50 mmol) was added slowly to an aqueous solution (100 mL) of KMnO₄ (37 mmol) at room temperature and the dispersion was stirred for 30 min. The precipitate was repeatedly washed with distilled water until the pH reached a steady value of around 4. The precipitate was collected by filtration, dried at 120 °C overnight, and then calcined in air at 300 °C for 4 h.

Gold Catalysts. Gold on Fe₂O₃, Co₃O₄, NiO, CuO, and La₂O₃ were prepared by coprecipitation (CP) (Au/base metal = 1/19).³² Gold on acidic metal oxides such as Al₂O₃, SiO₂, V₂O₅, MoO₃, and WO₃ were prepared by solid grinding (SG) (1 wt % Au loading).³³ Gold on TiO₂, ZnO, ZrO₂, SnO₂, and CeO₂, the point of zero charge of which was above 7, were prepared by deposition–precipitation (DP) (1 wt % Au loading).³⁴ Gold on MgO was prepared by DP in the presence of Mg citrate to control the size of gold NPs (1 wt % Au loading).³⁵ Gold on manganese oxide (MnO_{2-x} and MnO₂) were prepared by SG and by DP with [Au(en)₂]Cl₃ cation complex as a precursor,

because MnO_{2-x} and MnO_2 are negatively charged in aqueous solution of pH 7 (1 wt % Au loading). Briefly, $[Au(en)_2]Cl_3$ (21.2 mg) was dissolved in 9 mL of H₂O (5.5 mmol L⁻¹ solution). The pH of the solution was adjusted to 9 by adding aqueous NaOH solution and heated to 70 °C. Subsequently, manganese oxide (1.00 g) was dispersed and stirred under the control of pH at 8 to 10 at 70 °C for 1 h. The precipitate was washed with H₂O, filtered, dried at 120 °C overnight, and then calcined in air at 300 °C for 4 h.

Palladium and platinum on manganese oxide were prepared by SG and by DP in the same procedures as gold catalysts (1 wt % loading).

Characterization. The BET specific surface area was obtained from nitrogen adsorption measurements. The samples were pretreated under vacuum at 200 °C for 2 h. Then, N₂ adsorption isotherms were measured at 77 K with a SHIMADZU Tristar. X-ray diffraction (XRD) patterns were obtained by using a Rigaku RINT-TTR III diffractometer operated at 50 kV and 300 mA with CuKa radiation. Transmission electron microscope (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) observations were carried out by using a JEOL JEM-3200FS operating at 300 kV. X-ray photoelectron spectroscopy (XPS) experiments were conducted by using a SHIMADZU ESCA-3400 spectrometer. The Mg Ka source was operated at 10 kV and 10 mA. The binding energy scale was referenced to the C 1s peak (285 eV) arising from adventitious carbon in the sample.

The amount of surface excess oxygen was measured by iodometric titration.³⁶ A mixture of weighed amount of sample (0.02-0.03 g), KI (0.02 g), and 0.1 M aqueous HCl solution (5 mL) was shaken for 5 min. The suspension was filtered and washed with ethanol and distilled water. The filtrate containing iodine was titrated with a sodium thiosulfate solution $(1.0 \times 10^{-3} \text{ M})$.

Catalytic Tests. To an autoclave was charged methyl phenyl sulfide (118 μ L, 1.0 mmol), 1,2-dichlorobenzene (5.0 mL), catalyst (40 mg), and a magnetic stirring bar. The autoclave was purged and filled with O₂ until the gauge pressure reached 0.5 MPa. The reaction mixture was stirred at 100 °C for 36 h. The mixture was extracted with chloroform and filtered. The filtrate was analyzed by ¹H NMR (JEOL 300 MHz) using mesitylene as an internal standard.

Results and Discussion

Support Screening for Gold Catalysts. Various kinds of supported gold catalysts have been screened for the oxidation of methyl phenyl sulfide (1) in 1,2-dichlorobenzene at 100 °C for 24 h under 6 atm of oxygen (Table 1). Methyl phenyl sulfoxide (2) was obtained in 38% yield with a high selectivity above 97% by using Au/MnO_{2-x} (Entry 1). The metal oxides which work as oxidation catalysts by the Mars–van Krevelen mechanism such as V₂O₅ can be a support (Entry 2).³⁷ Gold on Co₃O₄ and on CeO₂ also produce sulfoxide **2**, but the reaction is very slow (Entries 3 and 4). Only gold deposited on manganese oxides exhibited significantly high activity and high selectivity to sulfoxide **2**.

Effect of Deposition of Noble Metals on Manganese Oxides. To clarify the role of gold in this reaction, other noble metals such as Pd and Pt were deposited on MnO_{2-x} by DP and

	S Au cat., O ₂ 1,2-dichlorobenzene 100 °C, 24 h 2			
Entry	Catalyat	Conv.	Yield	d/% ^{b)}
Enuy	Catalyst	/% ^{b)}	2	3
1	Au/MnO_{2-x}	39	38	trace
2	Au/V_2O_5	6	6	trace
3	Au/Co ₃ O ₄	0.7	0.7	0
4	Au/CeO ₂	trace	trace	trace
5	Au/MgO, Au/Al ₂ O ₃ , Au/SiO ₂ , Au/TiO ₂ , Au/Fe ₂ O ₃ ,	Not detected		
	Au/NiO, Au/CuO, Au/ZnO, Au/ZrO ₂ , Au/MoO ₃ ,			
	Au/SnO ₂ , Au/La ₂ O ₃ , Au/WO ₃			

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Table 1. Selective Aerobic Oxidation of Sulfide 1 by Using a Variety of Supported Gold Catalysts^{a)}

a) Reaction conditions: 1 (1.0 mmol), catalyst (0.04 g), 1,2-dichlorobenzene (5 mL), pO₂ (0.5 MPa, gauge pressure), 100 °C, 24 h. b) Determined by ¹H NMR spectroscopy using mesitylene as an internal standard.

Table 2. Effect of Deposition of Noble Metals on Manganese Oxides in the Aerobic Oxidation of Sulfide 1^{a)}

Entry	Catalyst	Method	$S_{\rm BET}$ $/{ m m}^2{ m g}^{-1}$	Conv.	Yield/% ^{b)}	
				/% ^{b)}	2	3
1	Au/MnO_{2-x}	DP	102	54	54	0
2	Au/MnO_{2-x}	SG	91	50	49	trace
3	Pt/MnO_{2-x}	DP	100	41	40	trace
4	Pt/MnO_{2-x}	SG	98	37	37	trace
5	Pd/MnO_{2-x}	DP	92	42	41	trace
6	Pd/MnO_{2-x}	SG	101	32	31	trace
7	MnO_{2-x}	—	101	50	49	trace

a) Reaction conditions: 1 (1.0 mmol), 1.0 wt % noble metal loading catalyst (0.04 g), 1,2-dichlorobenzene (5 mL), pO₂ (0.5 MPa, gauge pressure), 100 °C, 36 h. b) Determined by ¹H NMR spectroscopy using mesitylene as an internal standard.

Table 3. Catalytic Activities of MnO_2 and MnO_{2-x} for the Aerobic Oxidation of Sulfide 1^{a}

Enter	Catalwat	$S_{\rm BET}$	Surface excess oxygen	Conv.	Yield	/% ^{c)}	Sel. of 2
Enuy	Catalyst	$/m^2 g^{-1}$	$/{ m mg}{ m g}^{-1{ m b})}$	/% ^{c)}	2	3	/%
1	MnO ₂₋ A	0.9	2.92	0.7	0.7	0	100
2	$MnO_{2-}B$	9	3.44	5	5	0	100
3	MnO ₂₋ C	71 ± 24	4.18	25 ± 9	22 ± 9	3 ± 2	88 ± 8
4	$MnO_{2}D$	142 ± 47	4.16	47 ± 5	45 ± 6	2 ± 1	95 ± 4
5	MnO_{2-x}	98 ± 10	4.40	44 ± 5	43 ± 5	trace	98 ± 0
6 ^{d)}	MnO_{2-x}	123	_	46	44	1	96
7 ^{e)}	MnO_{2-x}	123	_	11	9	0	82

a) Reaction conditions: 1 (1.0 mmol), manganese oxide (0.04 g), 1,2-dichlorobenzene (5 mL), pO₂ (0.5 MPa, gauge pressure), 100 °C, 36 h. b) Obtained by iodometric titration. c) Determined by ¹H NMR spectroscopy using mesitylene as an internal standard. d) Reaction conditions: 1 (0.5 mmol), manganese oxide (0.10 g), toluene (5 mL), 100 °C, 24 h, under O₂ atmosphere (1 atm). e) Reaction conditions: 1 (0.5 mmol), manganese oxide (0.10 g), toluene (5 mL), 100 °C, 24 h, under N₂ atmosphere (1 atm).

SG methods. The DP method was better than the SG method in all cases (Table 2). It was proven that Pd and Pt were inhibitors, whereas Au acted as a promoter. The selectivity to sulfoxide was always very high irrespective of the kind of noble metal.

Catalytic Performances of Different Types of Manganese In order to explore the most active and selective Oxides. manganese oxide, along with MnO2-x, four kinds of MnO2 samples were prepared (Table 3, Entries 1-5). MnO2-C samples were prepared four times by the same method under the same conditions (Entry 3). The specific surface areas of catalysts differed between experiments in a range of 71 \pm 24 m²g⁻¹. MnO₂₋D samples were prepared two times by the same method under the same conditions (Entry 4). The specific surface areas differed between experiments in a range of $142 \pm 47 \text{ m}^2 \text{g}^{-1}$. As shown in Figure 1, the larger surface area led to higher catalytic activity. MnO_{2-x} samples were prepared



Figure 1. Conversions of sulfide 1 on MnO₂ and MnO_{2-x}. with different specific surface areas ■: MnO₂, ○: MnO_{2-x}. Reaction conditions: 1 (1.0 mmol), manganese oxide (0.04 g), 1,2-dichlorobenzene (5 mL), pO₂ (0.5 MPa, gauge pressure), 100 °C, 36 h.



Figure 2. Rate constant for the aerobic oxidation of sulfide 1 as a function of the amount of surface excess oxygen of manganese oxides.

Table 4. Catalytic Activities of MnO_2 and MnO_{2-x} with Au Deposition for the Aerobic Oxidation of Sulfide 1^{a)}

Enters	Catalyst	$S_{\rm BET}$	Time	Conv.	Yield	/% ^{b)}	Sel. of 2
Entry	Catalyst	$/m^2 g^{-1}$	/h	/% ^{b)}	2	3	/%
1	Au/MnO ₂ _C	70 ± 6	36	50 ± 0	48 ± 0	2 ± 0	96 ± 0
2	Au/MnO ₂ _D	113	36	54	52	2	96
3	Au/MnO_{2-x}	126 ± 1	36	52 ± 1	51 ± 6	trace	98 ± 0
4	Au/MnO ₂ _C	74	24	49	48	1	98
5 ^{c)}	Au/MnO2_C (2nd run)		24	39	38	1	97
6 ^{c)}	Au/MnO2_C (3rd run)		24	37	37	trace	99
7	Au/MnO_{2-x}	144	24	46	45	trace	98
8 ^{c)}	Au/MnO_{2-x} (2nd run)		24	34	34	0	100
9 ^{c)}	Au/MnO_{2-x} (3rd run)	—	24	27	27	0	100

a) Reaction conditions: **1** (1.0 mmol), 0.7 wt % Au/MnO₂ or 1.0 wt % Au/MnO_{2-x} catalyst (0.04 g), 1,2-dichlorobenzene (5 mL), pO_2 (0.5 MPa, gauge pressure), 100 °C. b) Determined by ¹H NMR spectroscopy using mesitylene as an internal standard. c) Washed with water and ethanol before reuse.

four times by the same method under the same conditions (Entry 5). The specific surface areas of MnO_{2-x} also differed among experiments (98 ± 10 m² g⁻¹) but the range was smaller than that of MnO₂.

MnO₂₋A, MnO₂-B, and MnO₂-C exhibited much lower activity and selectivity than MnO_{2-x} which was assumed to be a mixture of γ -MnO₂ and α -Mn₂O₃ based on XRD. It was opposite to a hypothesis that higher valences of Mn might lead to higher catalytic activity. Meanwhile MnO₂-D showed similar catalytic activity to that of MnO_{2-x}. It should be noticed that the catalytic activity depends on the preparation methods of manganese oxides but not on the valences of manganese. Although the XRD patterns were very broad, MnO₂-A, MnO₂-B, MnO₂-C, and MnO₂-D were assigned to δ -MnO₂, γ -MnO₂, δ -MnO₂, and α -MnO₂, respectively.

The surface excess oxygen on manganese oxide was reported to be responsible for the catalytic activity for carbon monoxide oxidation³⁸ and for hydrogen peroxide decomposition.³⁹ The amounts of surface excess oxygen were measured by iodometric titration (Table 3). Figure 2 shows a log–log plot of reaction rate (log k (mol L⁻¹ h⁻¹)) against the amount of surface excess oxygen (log $O_{surface}$ (mg g⁻¹)). As previously reported, a straight relationship was obtained with an order of 10.^{38,39}

Effect of Deposition of Gold on Different Types of Manganese Oxides. The deposition of gold on manganese oxides by DP method promoted the reaction in all cases (Table 3, Entries 3–5 and Table 4, Entries 1–3). In particular, on Au/MnO₂-C the conversion of sulfide 1 was improved to a level similar to that of Au/MnO₂-D and Au/MnO_{2-x}. The catalytic activity was improved by twice that of original MnO₂-C (Table 3, Entry 3 and Table 4, Entry 1).

The time yield of sulfoxide based on the catalyst weight of Au/MnO_{2-x} was calculated to be 0.38 mmol_{sulfoxide} $g_{catalyst}^{-1}h^{-1}$, which was lower than that of CAN (2.0 mmol_{sulfoxide} $g_{catalyst}^{-1}h^{-1})^{12}$ but higher than that of POM (0.12 mmol_{sulfoxide} $g_{catalyst}^{-1}h^{-1})^{11}$ Since with POM the oxidation of sulfide to sulfoxide and sulfoxide to sulfone was faster than with Au/MnO_{2-x}, it exhibited much lower selectivity to sulfoxide (22%) and to sulfone (78%). Au/MnO_{2-x} achieved selectivity to sulfoxide as high as CAN did, namely 98%.

The catalytic activity of Au/MnO_{2-x} for the aerobic oxidation of various sulfides was investigated (Table 5). Although the

Entry	Substrate	Conv.	Yield/% ^{b)}		
Entry		/% ^{b)}	Sulfoxide	Sulfone	
1	4-methoxyphenyl methyl sulfide	46	45	trace	
2	methyl phenyl sulfide	50	50	trace	
3	4-fluorophenyl methyl sulfide	38	38	trace	
4	4-chlorophenyl methyl sulfide	26	25	trace	
5	4-bromophenyl methyl sulfide	22	22	trace	
6	dibenzothiophene	_	14	_	

Table 5. Selective Aerobic Oxidation of Various Sulfides by Using Au/MnO_{$2-x^{a}$}

a) Reaction conditions: sulfide (1.0 mmol), 1.0 wt % Au/MnO_{2-x} (0.04 g), 1,2-dichlorobenzene (5 mL), pO_2 (0.5 MPa, gauge pressure), 100 °C, 36 h. b) Determined by ¹H NMR spectroscopy using mesitylene as an internal standard.



Figure 3. TEM images of a) MnO₂-C, b) Au/MnO₂-C, c) HAADF-STEM image of Au/MnO₂-C, and d) distribution of the diameter of Au NPs.

reactions of methyl phenyl sulfides exchanged with electronwithdrawing groups and dibenzothiophene were slow, the corresponding sulfoxides were obtained with high selectivities, indicating that the rate of sulfone production was much slower.

Characterization of MnO₂_C with and without Au. The TEM images of MnO_2_C and Au/MnO_2_C are shown in Figure 3. The diameters of primary particles of MnO_2 are 50 to 100 nm for MnO_2 alone and 20 to 40 nm for Au/MnO_2 (Figures 3a and 3b). It is advantageous for the release of oxygen that the diameters of primary particles of MnO_2 were reduced by more than two times by gold deposition. The presence of gold was confirmed by energy-dispersive spectroscopy (EDS). Figure 3c shows a HAADF-STEM image as well as a distribution of the diameter of gold NPs in Au/MnO_2_C . It was obvious that gold NPs were highly and almost homogeneously dispersed over the surfaces of MnO_2_C . The mean diameter of gold NPs from more than 20 images observed by a HAADF-STEM.

Figure S1 shows XPS Au 4f spectrum obtained for Au/ MnO₂-C. The Au $4f_{7/2}$ main peak at 83.9 eV corresponds to metallic Au⁰, which can be correlated with small NPs observed in TEM. Since the peaks of cationic gold species are known to shift toward positive values by about 0.5 to 2.5 eV with respect to metallic gold,³⁴ the broad peaks can be partly assigned to the Au $4f_{7/2}$ signals from Au³⁺ and/or Au⁺ species which are present at the gold-support interface. Figure S2 shows the Mn $2p_{3/2}$ peak located at 642.3 eV, which is in good agreement with those reported for MnO₂.⁴⁰ Two surface oxygen species were observed in the O 1s XPS spectra (Figure S3). The binding energy of 529–530 eV is characteristic of the lattice oxygen and the binding energy of 531–532 eV was assigned to defect oxide or the surface oxygen species.⁴⁰ Intensities of surface oxygen species increased by the gold deposition. This phenomenon was in good accordance with enhancement in catalytic activities by gold deposition.

Reaction Pathway for Aerobic Oxidation to Sulfoxide. As a plausible reaction pathway, first, surface excess oxygen and lattice oxygen in MnO₂ is consumed for the oxidation of sulfide to form MnO_{2-n} (n = 1/2, 2/3, and 1). Then, MnO_{2-n} is reoxidized by molecular oxygen in the gas phase. The reaction under nitrogen atmosphere gave sulfoxide **2** in only 9% yield, whereas the same reaction under 1 atm of oxygen gave **2** in 44% yield (Table 3, Entries 6 and 7). These results indicate that molecular oxygen is involved in the catalytic reaction, in particular, catalytic regeneration of manganese oxides having higher valences.

Gold may act as a good promoter to activate molecular oxygen on MnO_{2-n} to facilitate the oxidation reaction of sulfides catalytically. The time courses of yield of sulfoxide 2 (Figure 4a) show that the yield of 2 on MnO_{2-x} and Au/ MnO_{2-x} were similar to each other up to 24 h until reaching 37%. In the case of MnO_{2-x} , the yield tends to increase very slowly from 37% to 43%, meaning that the catalytic oxidation of sulfide on MnO_{2-n} (n = 1/2, 2/3, and 1) is very slow. The reaction on Au/MnO_{2-x} proceeded continuously even after reaching 37% yield, indicating that the coexistence of gold NPs promotes the activation of oxygen molecule on MnO_{2-n} (n = 1/2, 2/3, and 1), which is formed by the reduction of manganese oxides. It is likely that the reoxidation of manganese oxides to MnO₂ and/or the oxidation of sulfide by activated oxygen are promoted by depositing gold NPs on MnO₂.

To confirm the reproducibility of experiments, similar experiments were also made at Corma's laboratory. The catalysts, MnO_{2-x} and Au/MnO_{2-x} , were prepared by using Spanish reagents and water. Reinforced glass reactors which



Figure 4. Yield-time curves obtained by a) using Haruta laboratory's autoclave reactors (50 mL) and catalysts prepared at Haruta laboratory, b) using Corma laboratory's reinforced glass semicontinuous reactors (2 mL) and catalysts prepared at the Corma laboratory. \odot : Au/MnO_{2-x}, \bigcirc : MnO_{2-x}. Reaction conditions: **1** (1.0 mmol), catalyst (0.04 g), 1,2-dichlorobenzene, pO_2 (0.5 MPa, gauge pressure), 100 °C.

enabled us to work with only 1 mL of solvent were used. As shown in Figure 4b, these catalysts showed similar activities to the Japanese catalysts, providing sufficiently high reproducibility.

In order to verify that the catalysis is derived from solid but not leached species, the reaction was carried out under the conditions described in Table 4 (Entries 4 and 7). Au/MnO₂_C and Au/MnO_{2-x} were removed from the reaction mixture by filtration. The filtrates were again heated at 100 °C for 24 h under 6 atm of oxygen. In these cases, no further production of 2 and 3 were observed, meaning that sulfoxidation by gold NPs on manganese oxides proceeds heterogeneously. In the recycling tests, the catalytic activity of Au/MnO2-C and Au/ MnO_{2-x} was decreased but maintained at 74–80% (Table 4, Entries 5, 6, 8, and 9). These results were consistent with a plausible reaction pathway mentioned above. The initial step is the consumption of surface excess oxygen and lattice oxygen of manganese oxides which work like a stoichiometric oxidant. After the consumption of active oxygen species was over, the reaction is slowed down but proceeds catalytically.

Conclusion

An explorative study has been conducted on the heterogeneous catalysts for the aerobic oxidation of sulfides and the following experimental results were obtained.

1) Among almost all base metal oxides, only manganese oxides are active and selective in the aerobic oxidation of sulfides to sulfoxides.

2) Among manganese oxides, MnO_{2-x} which was prepared by a simple neutralization method and MnO_2 which was prepared by the reaction of $MnCl_2$ with $KMnO_4$ in acidic solution exhibited the highest activity and selectivity. A linear logarithmic relationship is obtained between catalytic activity and the amount of surface excess oxygen.

3) Although the deposition of Pd and Pt NPs on manganese oxides was detrimental to the catalytic performance, the deposition of gold NPs on manganese oxides improved the catalytic activity and selectivity.

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Supporting Information

XPS spectra for MnO_2 -C and Au/MnO_2 -C. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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