

Selective Aerobic Oxidation of Sulfides to Sulfoxides in Water under Blue Light Irradiation over Bi₄O₅Br₂

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1. Experimental section

1.1 Reagents

All chemicals were analytical grade without further purification, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KBr, glycerol, TiO_2 and different kinds of sulfides were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. or J&K Scientific Ltd.

1.2 Characterization techniques

Infrared spectra were recorded on a Shimadzu IR Tracer-100 fourier transform infrared spectrophotometer using KBr pellets. UV-vis spectrum was recorded on a HITACHI UH4150 spectrophotometer. SEM images were obtained by ZEISS sigma 500 field emission scanning electron microscopy. TEM images were obtained by JEM-2100F field emission transmission electron microscope. GC analyses were performed on Fuli instrument GC-9720 with a flame ionization detector equipped with SE-54 capillary column. GC-MS was recorded on Aglient Technologies 5975C Gas Chromatography Mass spectrometer. X-ray diffraction patterns (XRD) were recorded by D8 DISCOVER WITH TXS. X-ray photoelectron spectroscopy (XPS) data were obtained by Thermo Scientific Escalab 250Xi.

1.3 Synthesis

$\text{Bi}_4\text{O}_5\text{Br}_2$:

The catalyst of $\text{Bi}_4\text{O}_5\text{Br}_2$ was prepared according to reference via a simple hydrolytic process of complex precursor. 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 20 mL of glycerol at 40 °C with vigorous stirring for 30 min. 2 mmol of KBr was also dissolved in another 20 mL of glycerol at 40 °C with vigorous stirring for 30 min. Then, the above two solution was mixed by dropwise under continuously stirring for 1 h. After heating treatment at 160 °C for 16 h in a 50 mL teflon-lined stainless steel autoclave, the mixture was cooled to room temperature and centrifuged to get the black compound. The solid was washed by water and ethyl alcohol for several times

to remove glycerol, and dried in oven at 80 °C for 12 h (precursor).

0.15 g of above precursor was dispersed in 150 mL of deionized water at 160 °C for 24 h. The color of solution changed from brown to yellowish green. The solid was separated from water phase, and washed by water. The final catalyst of $\text{Bi}_4\text{O}_5\text{Br}_2$ was obtained after dried at 80 °C for 12 h.

BiOBr:

0.002 mol KBr was dissolved into 20 mL ethanol and 0.002 mol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ also was dissolved into 20 mL ethanol. Then, KBr solution was added into the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution drop by drop with continuously stirring. The suspension was transferred into Teflon-lined stainless steel autoclaves (50 mL), and then the autoclaves were kept at 160 °C for 16 h. After reaction, the precipitate was obtained by centrifugation, and then washed with ethanol. Finally, it was dried at 80 °C in air.

1.4 Photocatalytic oxidation

In a typical oxidation process, a 10 mL round-bottom flask with two necks was used as reaction vessel. Firstly, 20 mg of photocatalyst and 0.2 mmol of sulfide were placed in 1 mL of water with a magnetic stirrer. The system was firstly furnished with O_2 balloon with stirring for 0.5 h, then the bottom was sealed under O_2 protection and irradiated for 12 h with a blue LED light strip (30 W, Kessil PR160-456 nm), which was placed on one side of reaction flask with 2 cm apart. After reaction, the system was centrifuged and separated from the aqueous phase by extraction with ethyl acetate. The organic phase was examined by gas chromatography (GC) by using an internal standard method for determining the conversion and selectivity. The identification of products was identified by GC-MS. The catalyst after reaction was obtained by centrifuged and washed three times by ethyl acetate and ethyl alcohol, which could be used for the next cycle after drying.

1.5 In-situ Fourier transform infrared spectrometer (FT-IR) analysis

In-situ Fourier transform infrared spectrometry was performed on a Nicolet IS-

50 instrument. The sample was filled into an in-situ IR cell, and O₂ and H₂O-methyl phenyl sulfide vapors were introduced into the cell and fiber source (FX300, Beijing Perfect Light Technology Co., Ltd., Beijing, China) through the CaF₂ window of the cell. Before the measurement, the samples were degassed at 423 K for 4 h. The baseline was obtained before the sample reached methyl phenyl sulfide adsorption equilibrium within 30 min.

2. Characterizations

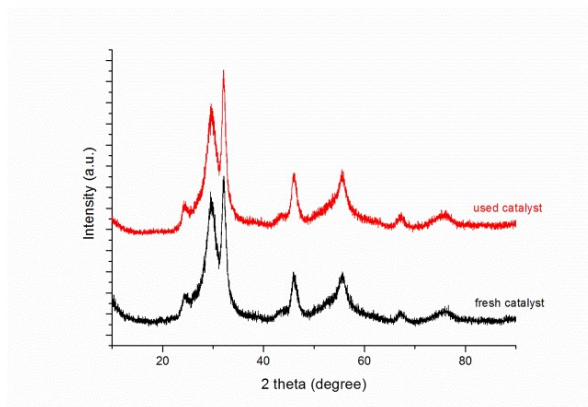


Figure S1 XRD patterns of fresh catalyst and used catalyst.

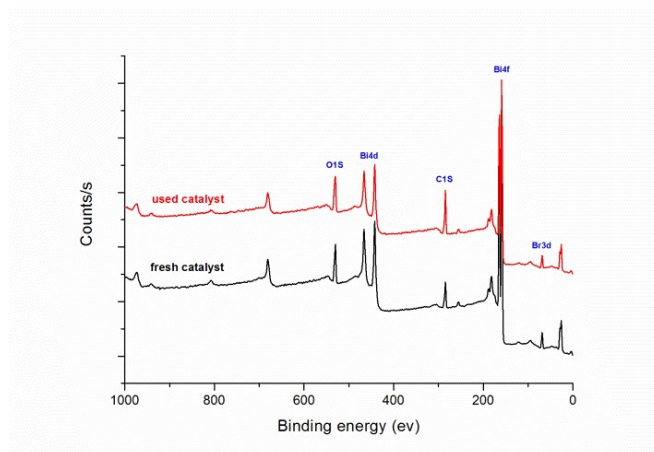


Figure S2 XPS spectra of fresh and used catalyst.

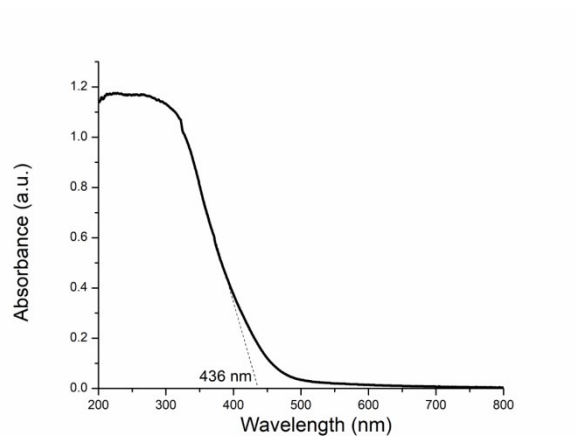


Figure S3 UV-Vis spectrum of $\text{Bi}_4\text{O}_5\text{Br}_2$ sample.

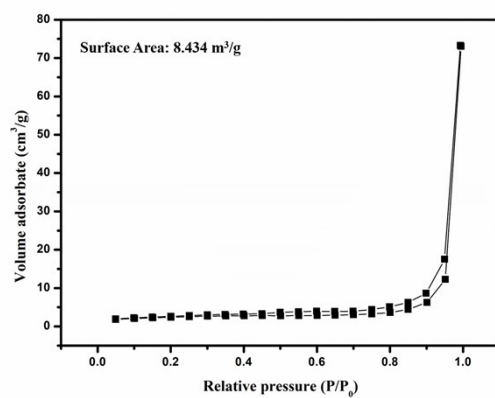


Figure S4 BET of $\text{Bi}_4\text{O}_5\text{Br}_2$ sample.

3. Solvent effect

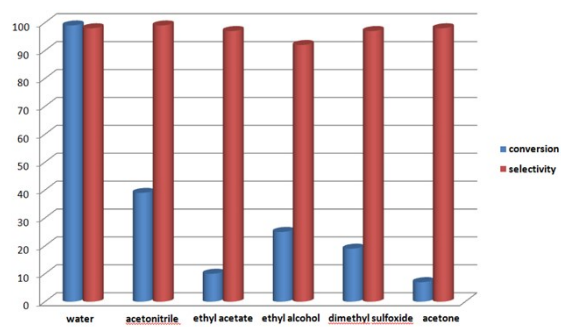


Figure S5 Solvent effect on photooxidation of methyl phenyl sulfide over $\text{Bi}_4\text{O}_5\text{Br}_2$.

4. Catalyst recycling

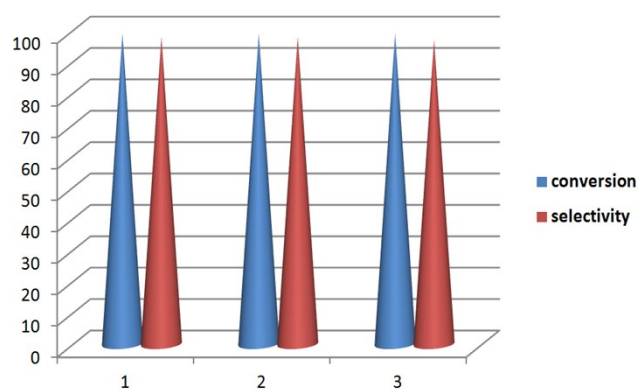


Figure S6 Recycling of photooxidation of methyl phenyl sulfide in water based on $\text{Bi}_4\text{O}_5\text{Br}_2$.

5. AQE calculation

AQE was calculated by the following equation:

$$\begin{aligned} \text{AQE} &= \frac{N_{\text{sulfoxide}}}{N_p} = \frac{2 \times \text{the number of evolved sulfoxide molecules}}{\text{the number of incident photons}} \times 100\% \\ &= \frac{2 \times N_a \times M_{\text{sulfoxide}}}{\frac{PSt\lambda}{hc}} = \frac{2 \times 6.02 \times 10^{23} \times M_{\text{sulfoxide}}}{PS \times 6 \times 3600 \times 455 \times 10^{-9}} \\ &\quad \frac{1}{6.6626 \times 10^{-34} \times 3 \times 10^8} \end{aligned}$$

LED lamp (4.5 W): $\lambda = 455 \text{ nm}$

Experimental conditions: 20 mg $\text{Bi}_4\text{O}_5\text{Br}_2$; 1 mL H_2O ; 6 h irradiation.

Power of 455 nm of Xenon lamp (P): 0.6 mW/cm²; Active area (S): 14 cm²

$M_{\text{sulfoxide}}$: 198 μmol

$$N_p = (0.6 \times 10^{-3} \times 14 \times 6 \times 3600 \times 455 \times 10^{-9}) / (6.626 \times 10^{-34} \times 3 \times 10^8) = 4.153 \times 10^{20}$$

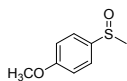
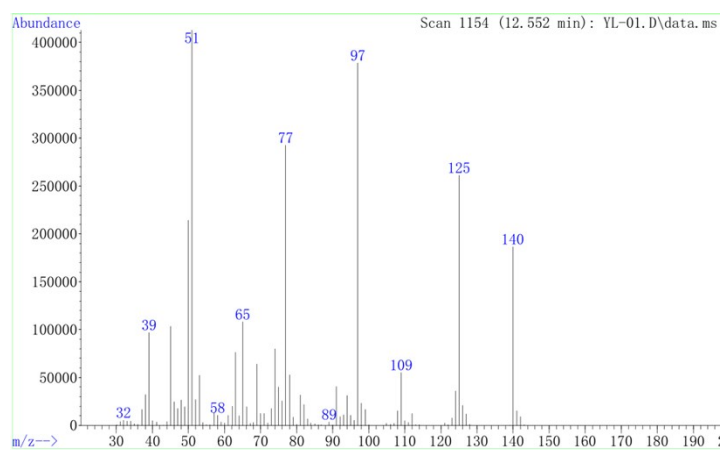
$$N_{\text{sulfoxide}} = 2 \times 6.02 \times 10^{23} \times 198 \times 10^{-6} = 2.384 \times 10^{20}$$

$$\text{AQE} = (2.384 \times 10^{20}) / (4.153 \times 10^{20}) = 57.4\%$$

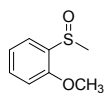
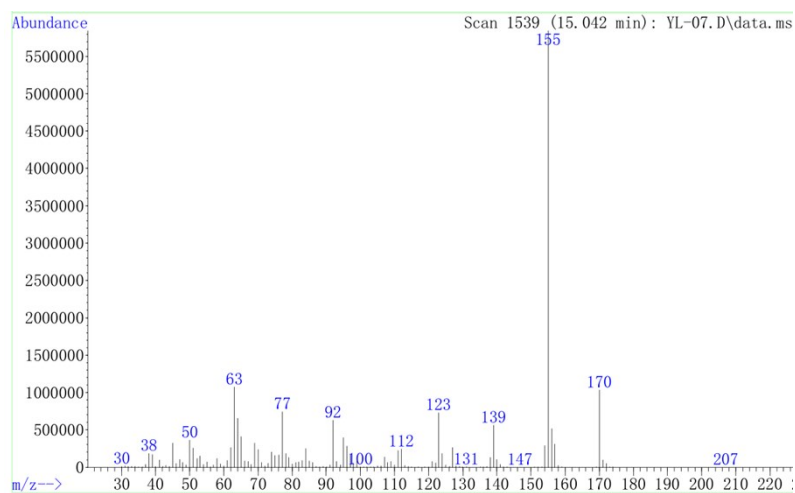
6. Compound data



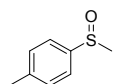
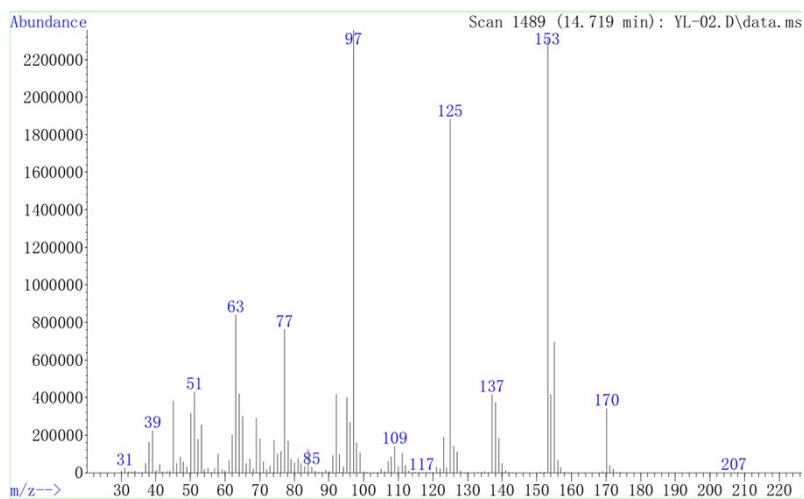
Methyl phenyl sulfoxide: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), initial column temperature (150 °C, 2 min), progress rate (20 °C /min), final column temperature (200 °C, 3 min), injection temperature (250 °C), detection temperature (280 °C), retention time of sulfoxide (4.53 min). MS (EI) m/z (%): 140 [M+].



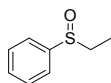
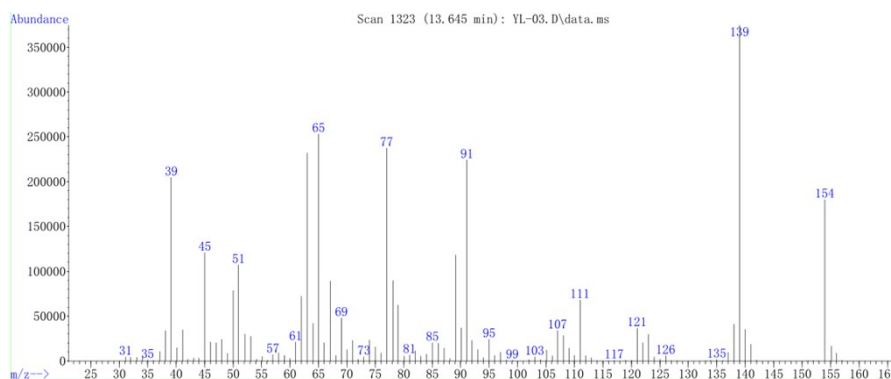
1-Methylsulfinyl-4-methoxybenzene: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), column temperature (constant, 200 °C), retention time of sulfoxide (4.67 min). MS (EI) m/z (%): 170 [M+].



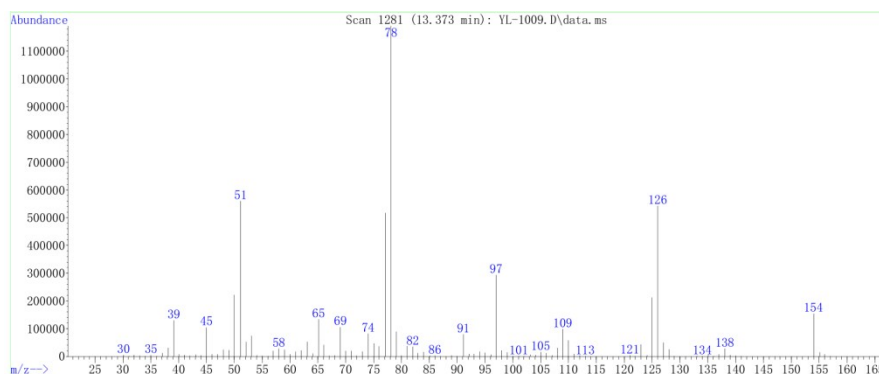
1-Methylsulfinyl-2-methoxybenzene: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), column temperature (constant, 200 °C), retention time of sulfoxide (4.17 min). MS (EI) m/z (%): 170 [M+].



Methyl p-tolyl sulfoxide: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), initial column temperature (150 °C, 2 min), progress rate (20 °C /min), final column temperature (200 °C, 3 min), injection temperature (250 °C), detection temperature (280 °C), retention time of sulfoxide (5.48 min). MS (EI) m/z (%): 154 [M+].

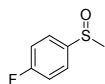
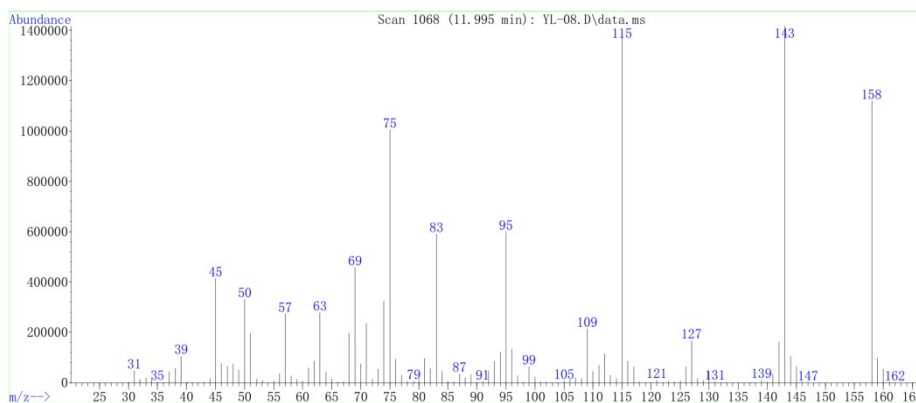


Ethyl phenyl sulfoxide: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), initial column temperature (150 °C, 2 min), progress rate (20 °C /min), final column temperature (200 °C, 3 min), injection temperature (250 °C), detection temperature (280 °C), retention time of sulfoxide (5.15 min). MS (EI) m/z (%): 154 [M+].

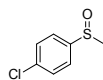
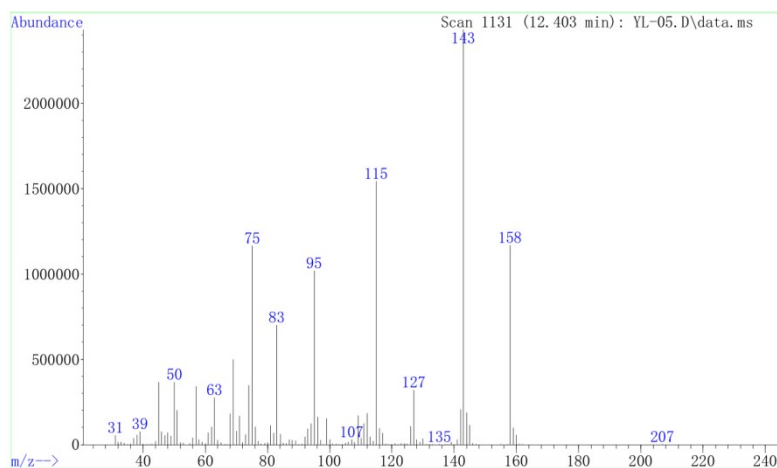




1-Fluoro-2-(methylsulfinyl)benzene: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), initial column temperature (150 °C, 2 min), progress rate (20 °C /min), final column temperature (200 °C, 3 min), injection temperature (250 °C), detection temperature (280 °C), retention time of sulfoxide (4.08 min). MS (EI) m/z (%): 158 [M+].



1-Fluoro-4-(methylsulfinyl)benzene: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), initial column temperature (150 °C, 2 min), progress rate (20 °C /min), final column temperature (200 °C, 3 min), injection temperature (250 °C), detection temperature (280 °C), retention time of sulfoxide (4.34 min). MS (EI) m/z (%): 158 [M+].



1-Chloro-4-(methylsulfinyl)benzene: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N₂), initial column temperature (150 °C, 2 min), progress rate (20 °C /min), final column temperature (200 °C, 3 min), injection temperature (250 °C), detection temperature (280 °C), retention time of sulfoxide (5.98 min). MS (EI) m/z (%): 174 [M+].

