

Green catalysis for selective oxidation of sulfides with high turnover numbers in water at room temperature

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1. Experimental

1.1 Reagents

All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

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 zessis sigma 500 field emission scanning electron microscopy. Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (Vario EL Cube). 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 a Thermo Trace DSQ II Gas Chromatography Mass spectrometer. The weight of catalyst used in the reaction was measured on Mettler Toledo XP6 Micro Balance.

1.3 Synthesis of catalyst (S₁₈-HPV₂W₁₀)

N-Octyldecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (Sulfobetaine18) was purchased from J&K Scientific company. The polyoxometalate anion (monoprofonated [γ -HPV₂W₁₀O₄₀]⁴⁻) was prepared from Cs₅[γ -PV₂W₁₀O₄₀] according to reference [23]. Firstly, NaVO₃ (1.2 mmol) was dissolved in 120 mL of hot water, the pH of the solution after cooling was adjusted to 2.0 by 3M HCl. Cs₅[γ -PV₂W₁₀O₄₀] (1.1 mmol) was dissolved in the previous solution. After 20 min with stirring, a clear solution was obtained by filtration, and then Sulfobetaine18 (4.5 mmol) was added with vigorous stirring. The mixture was stirred for 5 h, and then the precipitate was formed after ethyl alcohol adding subsequently into the system. The mixture was stirred for 0.5 h, the solid was obtained by filtration, washed with ethyl alcohol and dried in air finally (denoted as S₁₈-HPV₂W₁₀).

Calcd for $[C_{23}H_{50}NO_3S]_4[HPV_2W_{10}O_{40}]$: C, 25.73; H, 4.72; N, 1.30. Found: C, 25.26; H, 4.39; N, 1.33. IR spectrum (KBr, cm^{-1}): 2920, 2850, 2357, 1636, 1470, 1196, 1097, 1049, 961, 875, 805, 530.

1.4 Catalytic reaction

Catalytic oxidation of sulfides to sulfoxides: catalyst (0.58 μ mol, 2.5 mg, measured on Mettler Toledo XP6 Micro Balance), sulfide (20 mmol), H_2O_2 (30% aq., 20 mmol) and water (1-5 mL) were charged in a 10 mL reaction flask. The mixture was then stirred by a magnetic stirrer at room temperature (298 K) for several hours. The reaction progress was detected by GC. After completion of the reaction, 3×3 mL of ethyl acetate was added and the organic phase was separated from the aqueous phase by extraction. The organic phase was dried by anhydrous sodium sulfate and determined by GC analysis using toluene as the internal standard. The conversion and selectivity were calculated from the peak areas by GC analysis. The identification of products was identified by GC-MS or standard compound.

Catalytic oxidation of sulfides to sulfones: catalyst (0.58 μ mol, 2.5 mg, measured on Mettler Toledo XP6 Micro Balance), sulfide (20 mmol) and H_2O_2 (30% aq., 100 mmol) were charged in a 10 mL reaction flask for 6 h. The mixture was then stirred by a magnetic stirrer at room temperature (298 K). The reaction progress was detected by GC. After completion of the reaction, 3×3 mL of ethyl acetate was added and the organic phase was separated from the aqueous phase by extraction. The organic phase was dried by anhydrous sodium sulfate and determined by GC analysis using toluene as the internal standard. The conversion and selectivity were calculated from the peak areas by GC analysis. The identification of products was identified by GC-MS or standard compound.

1.5 Catalyst recycling

The catalyst of $S_{18}-HPV_2W_{10}$ has a special hydrophilic property in reaction process. A clear solution was obtained when the catalyst was treated in water and hydrogen peroxide. After reaction, the organic phase was separated by extraction to analysis by GC, whereas the clear aqueous solution on the below layer was collected after extraction. The catalyst was still remained in the aqueous solution because the good hydrophilic. So the recovered catalyst can be used with the aqueous phase for the next reaction without isolated reuse. The new reaction was carried out just adding new substrate and hydrogen peroxide to the recovered aqueous solution.

2. IR spectra

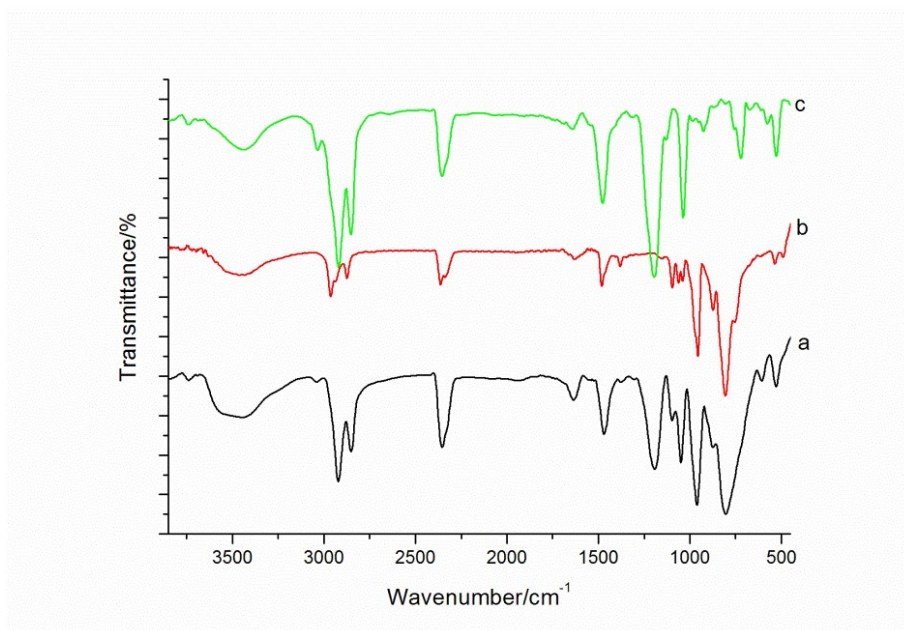


Figure S1 IR spectra: (a) the catalyst of S_{18} -HPV₂W₁₀; (b) TBA₄[γ -HPV₂W₁₀O₄₀]; (c) Sulfobetaine 18

3. UV-Vis spectra

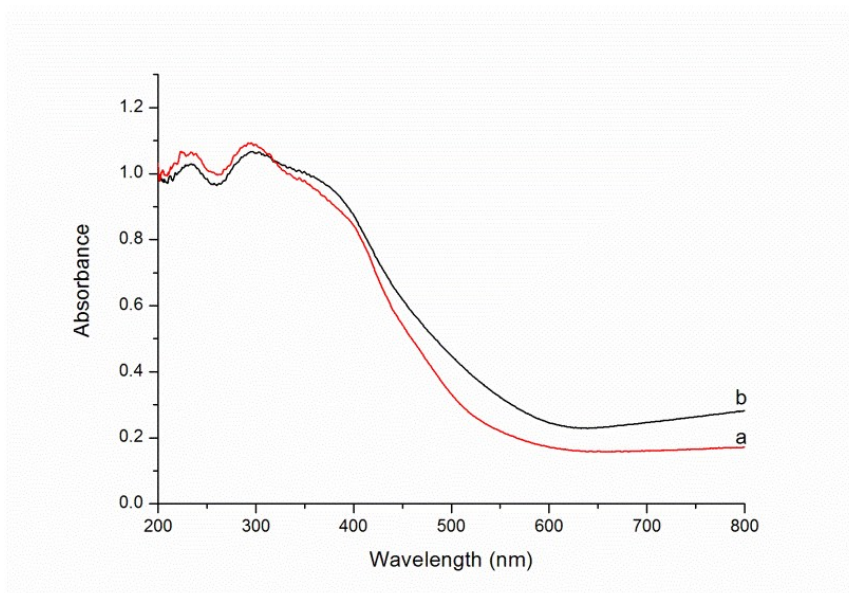


Figure S2 UV-Vis spectrum: (a) TBA₄[γ -HPV₂W₁₀O₄₀]; (b) the catalyst of S_{18} -HPV₂W₁₀

4. SEM images of prepared catalyst

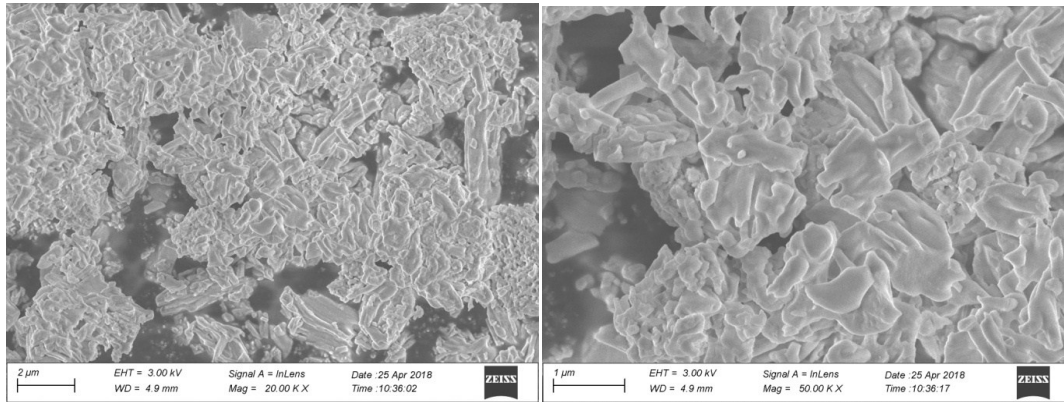


Figure S3 SEM images of prepared catalyst