Supporting Information for:

Hydrophilic phase transfer catalyst based on sulfoacid group and polyoxometalate for selective oxidation of sulfides in water with hydrogen peroxide

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1. Experimental

1.1 General remarks

All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated. Infrared spectra were recorded on a Nicolet 5700 FT-IR instrument using KBr pellets. UV-vis spectrum was recorded on a HITACHI UH4150 spectrophotometer. XRD data were collected on a Bruker D8 ADVANCE with Cu-Kα radiation. TEM images were obtained by TEM instrumentation (JEOL JEM-2100F). Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (Vario EL Cube).

1.2 synthesis of n-CeMe$_2$N-PS

The 3-(N,N-dimethylcetylammonium) propanesulfonate (n-CeMe$_2$N-PS) was prepared according to the literature procedure [42]. N,N-dimethylhexadecylamine (10.2 mL, 0.03 mol) was added slowly to the solution of 1, 3-propanesultone (2.5 mL, 0.03 mol) in ethyl acetate (10 mL). After 3 h at 60 °C with stirring, a white precipitate was obtained by filtration, washed by ethyl acetate and diethyl ether, and finally dried at 60 °C under vacuum. ^{1}H NMR (400 MHz, DMSO-d): δ 0.85 (t, 3H), 1.24 (s, 26H), 1.64 (s, 2H), 1.92-1.97 (m, 2H), 2.45 (t, 2H), 2.98 (s, 6H), 3.20-3.24 (m, 2H), 3.35-3.40 (m, 2H).

1.3 synthesis of CeMe$_2$N-PS-SiV$_2$W$_{10}$

The bifunctional catalyst was prepared by the assembling of n-CeMe$_2$N-PS with [γ-1,2-H$_2$SiV$_2$W$_{10}$O$_{40}$]$^{4-}$ solution. The polyoxometalate anion ([γ-1,2-H$_2$SiV$_2$W$_{10}$O$_{40}$]$^{4-}$) was prepared from K$_8$[SiW$_{10}$O$_{36}$]·12H$_2$O according to reference [40]: firstly, K$_8$[SiW$_{10}$O$_{36}$]·12H$_2$O [44] (0.8 g, 0.27 mmol) was quickly dissolved in 2.8 mL of HCl solution (1 M), then 1.1 mL of NaVO$_3$ solution (0.5 M, 0.55 mmol) was added into the previous solution. After 5 min with stirring, a clear solution was obtained by filtration, and then n-CeMe$_2$N-PS (1.08 mmol) was added. The yellow precipitate was formed after absolute ethyl alcohol (20 mL) adding subsequently into the system. The mixture was stirred for 0.5 h, a solid was obtained by filtration, washed with absolute ethyl alcohol and dried in air finally (denoted as CeMe$_2$N-PS-SiV$_2$W$_{10}$). IR spectrum (KBr, cm^{-1}): 2924, 2852, 1629, 1465, 1378, 1191, 1049, 969, 910, 870, 787, 707, 610, 537. Calcd for [C$_{21}$H$_{46}$NO$_3$S]$_4$[H$_2$SiV$_2$W$_{10}$O$_{40}$]: C, 24.13; H, 4.48; N, 1.34. Found: C, 24.81; H, 4.72; N, 1.54.

1.4 Catalytic reaction

Catalytic oxidation of sulfides to sulfones (Procedure A): catalyst (4.8 μmol), sulfide (2 mmol), H_2O_2 (30% aq., 6 mmol) and H_2O (2 mL) were charged in the reaction flask. The mixture was stirred by a magnetic stirrer at room temperature (298 K) for 1-3 h. The reaction progress was detected by TLC or GC. After completion, the products were separated from the aqueous phase by extraction with ethyl acetate. The conversion and selectivity were determined by GC and calculated from the peak areas by using an internal standard method. The products were identified by GC-MS or NMR. The aqueous phase with $CeMe_2N$-PS-SiV_2W_{10} after extraction was used for the next run.

Catalytic oxidation of sulfides to sulfoxides (Procedure B): catalyst (1.2 μmol), sulfide (2 mmol), H_2O_2 (30% aq., 2 mmol) and H_2O (3 mL) were charged in the reaction flask. The mixture was then stirred by a magnetic stirrer at room temperature (298 K) for 6 h. The reaction progress was detected by TLC or GC. After completion, the products were separated from the aqueous phase by extraction with ethyl acetate. The conversion and selectivity were determined by GC and calculated from the peak areas by using an internal standard method. The products were identified by GC-MS or NMR. The aqueous phase with $CeMe_2N$-PS-SiV_2W_{10} after extraction was used for the next run.
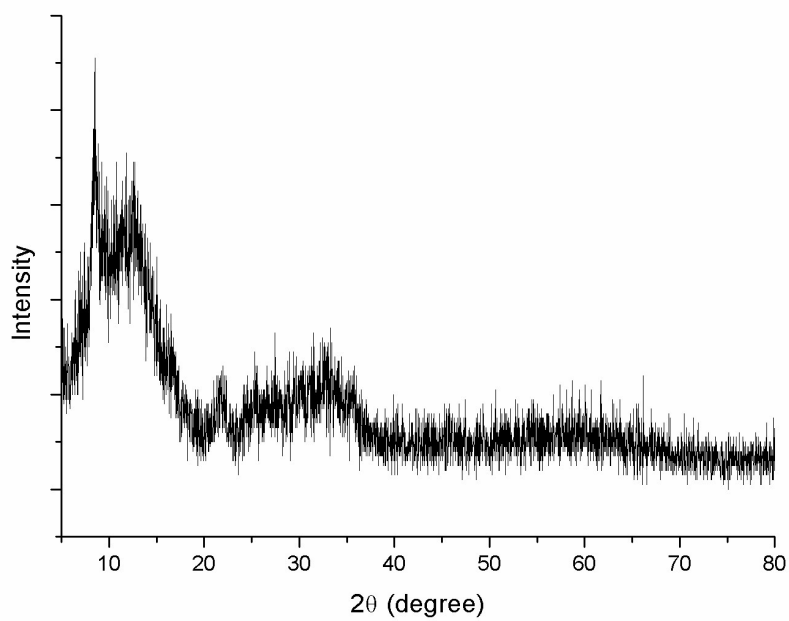
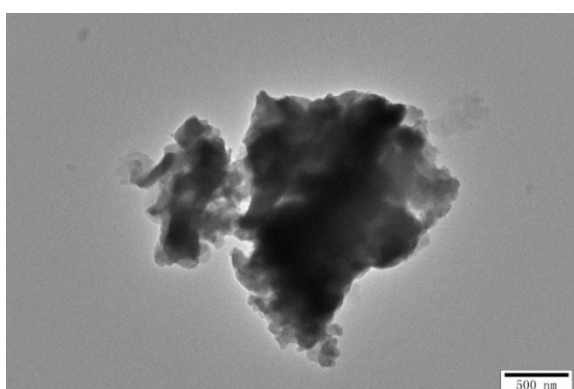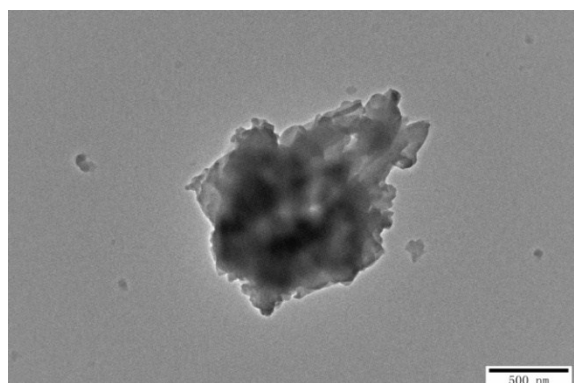## 2. IR spectrum of the catalyst
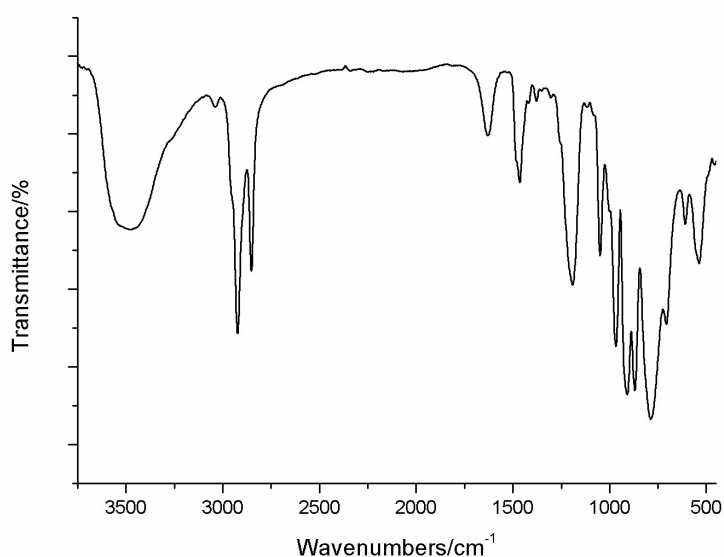
3. UV-Vis spectrum of prepared catalyst
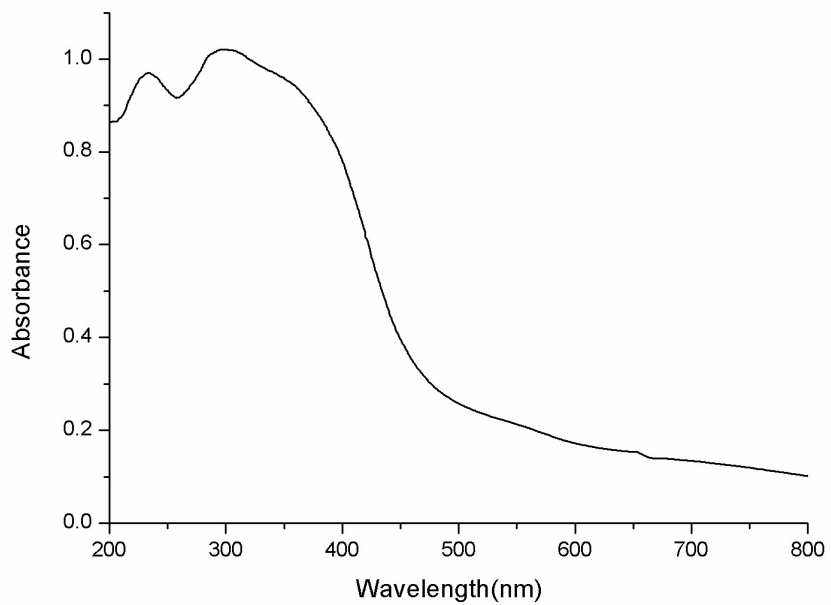
4. XRD analysis of prepared catalyst

5. TEM images of prepared catalyst in ethanol

6. Proposed mechanism of the catalytic oxidation