Synthesis of nanoscale surfactant-encapsulated silica-supported polyoxometalate [Si/AlO_2]@[PWZn]@CTAB and its catalytic application in the oxidation of alcohols

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Supporting Information

1. Experimental Section

1.1. Materials, instruments, and synthetic methods

All reagents and row materials were purchased from reputable chemical companies and used without further purification. Bindzil CAT 80 colloidal silica ([Si/AlO_2]Cl) with particular specifications (surface area: 85 m^2/g, particle size: 40 nm, SiO_2: 40 %, pH: 3-5, positive surface charge, bulk density: 1050-1400 kg/m^3) was purchased from Akzo Nobel. All products were identified by comparing their physical and spectral data with those of authentic samples, and yields refer to gas chromatography (GC) yields.

Thermogravimetric (TG-DTG) analysis was performed on a TG-50 thermogravimetric analyzer from 25-800 °C with a temperature rate of 10 °C/min. Fourier transform infrared spectra (FT-IR) were obtained from 400-4000 cm^{-1} on a Perkin-Elmer spectrophotometer (Spectrum 65) using KBr pellets. GC experiments were performed on a Varian CP-3800 gas chromatograph using CP-Wax 52 CB (30 m, 0.25 mm ID, df 0.25 µm) and CP-Sil 8 CB capillary column (30 m, 0.32

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mm ID, df 0.25 μm). Scanning electron microscopy (SEM) images of the catalyst were taken on SEM Philips XL 30. Transmission electron microscopy (TEM) images were obtained with a Hitachi H8100 electron microscope with an accelerating voltage of 200 KV without staining. X-ray powder diffraction (XRD) data were obtained on a D8 Advance Bruker using Cu Kα radiation (λ = 1.54 Å).

1.2. Preparation of [Si/AlO_2]@[PWZn]

The transition metal substituted POMs, $[PW_{11}M(H_2O)O_{39}]^{(7-m)-}.nH_2O$ (M^{m+}= Cr^{3+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}), were prepared according to the literature [1]. For example, an aqueous solution of $[PW_{11}ZnO_{39}]^{5-}$ was prepared by mixing Na_2HPO_4 (9.1 mmol) and $Na_2WO_4{\cdot}2H_2O$ (100 mmol) in water (200 mL), adjusting the pH to 4.8, and then adding the nitrate salt of Zn^{2+} (12 mmol). The aqueous colloidal suspension of Bindzil CAT 80 (100 g) was placed in an ultrasonic bath for 10 min to break up aggregates and then added dropwise to the solution of $[PW_{11}ZnO_{39}]^{5-}$ at 80 °C. The mixture was stirred for 3 h at 25 °C, and the resulting solid was filtered and washed several times with 10 mL portions of acetonitrile. Drying at 120 °C for 2 h gave the product. Infrared spectra of [Si/AlO_2]@[PWZn] (cm^{-1}): (P-O), overlapped with silica vibration frequencies; (W-O_d), 952; (W-O_b-W), 901; (W-O_c-W), 822 (Figure 1b, Table 1). Infrared spectra (cm^{-1}) of $K_5[PW_{11}Zn(H_2O)O_{39}]$: (P-O), 1072; (W-$O_d$), 957; (W-$O_b$-W), 897; (W-$O_c$-W), 823.

1.3. Synthesis of [Si/AlO_2]@[PWZn]@CTAB (SSPOM-Zn)

[Si/AlO_2]@[PWZn] (200 mg) was stirred in a solution of CTAB (100 mg) and chloroform (10 mL) for 3 h. The product was filtered and washed several times with 5 mL portions of chloroform. Drying at 120 °C for 2 h yielded SSPOM-Zn. Infrared spectra (cm^{-1}): (P-O), overlapped with silica vibration frequencies; (W-O_d), 959; (W-O_b-W), 899; (W-O_c-W), 820.

1.4. Typical procedure for oxidation of alcohols

In a typical catalytic oxidation reaction, benzyl alcohol (1 mmol), H_2O_2 (30%; 1 mL) and acetonitrile (3 mL) in the presence of SSPOM-Zn (150 mg) as a catalyst were stirred at reflux in a 25 mL round bottom flask equipped with a reflux condenser. Progress of the reaction was monitored by GC. After completion of the reaction, the catalyst was self-precipitated, and $NaHCO_3$ (10%; 10 mL) was added to the separated liquid phase. The organic phase was extracted with chloroform and dried over anhydrous $CaCl_2$. The pure product was obtained after flash chromatography on a short silica gel column with a 3:7 ethyl acetate: *n*-hexane eluent.

To study catalyst reusability, the catalyst was filtered out after each reaction run, washed several times with acetonitrile, and dried at 120 °C for 3 h. This catalyst was used for the next run following the above procedure.

2. Figures

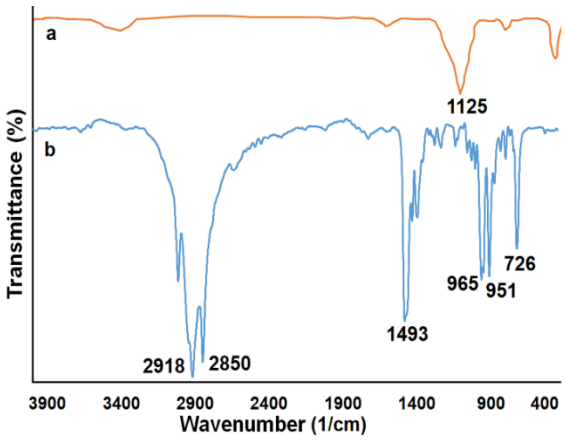

Figure S1. The FT-IR spectra of silica Bindzil CAT 80 (a) and CTAB (b)

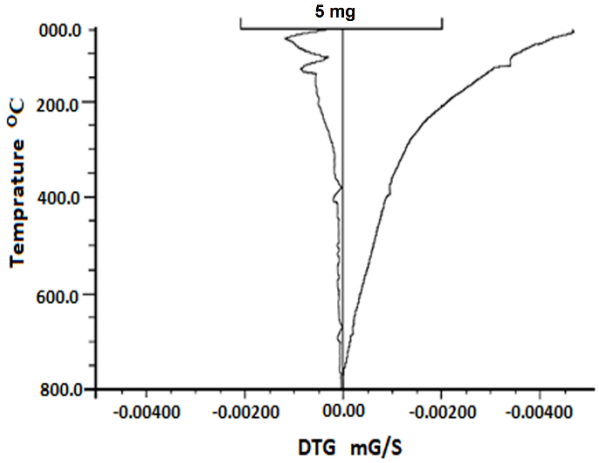

Figure S2. The TG-DTG diagram of [Si/AlO_2]Cl

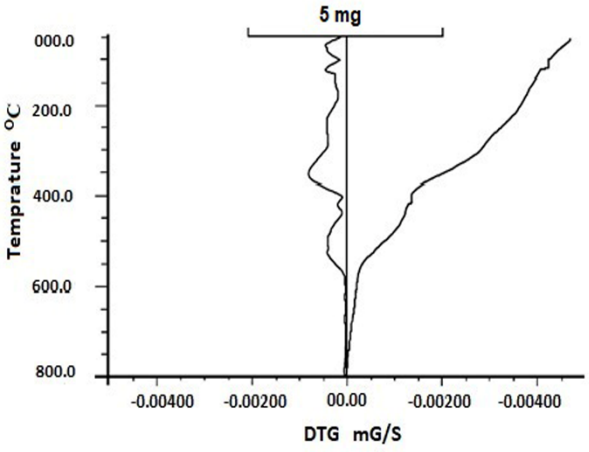

Figure S3. The TG-DTG diagram [Si/AlO_2]@[PWZn]

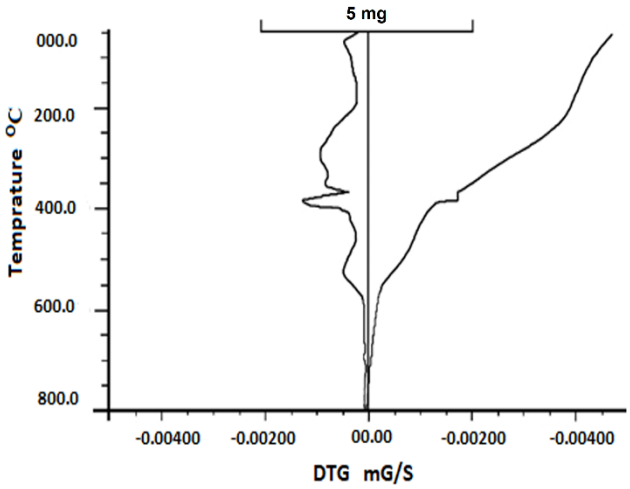

Figure S4. The TG-DTG diagram of SSPOM-Zn

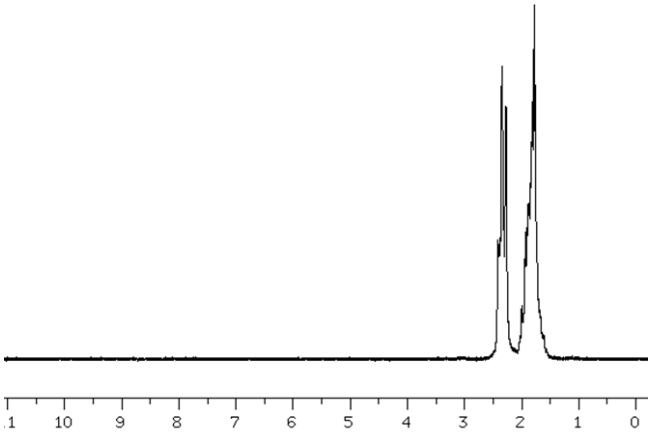

Figure S5. ^{1}H-NMR Spectra of cyclohexanone ($CDCl_3$)

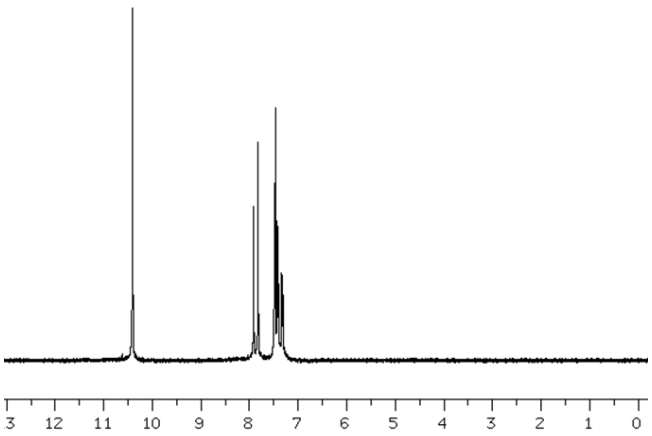

Figure S6. ^{1}H-NMR Spectra of 2,4-dichlorobenzaldehyde ($CDCl_3$)

References

[1] M. Simões, C. Conceição, J. Gamelas, P. Domingues, A. Cavaleiro, J. Cavaleiro, A. Ferrer-Correia, R. Johnstone, Keggin-type polyoxotungstates as catalysts in the oxidation of cyclohexane by dilute aqueous hydrogen peroxide, J. Mol. Catal. A: Chem. 144 (1999) 461-468. https://doi.org/10.1016/S1381-1169(99)00025-4