Supporting Information

Stabilisation of high-valent Cu$^{3+}$ in a Keggin-type polyoxometalate

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The characterisation details, ESI-MS results, IR spectra and TG curve of 1-Cs, XPS spectra of 1-Cs and 2-Cs are provided here.

General characterisation methods

XRD patterns were recorded on a Bruker D2 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) operated at 10 mA and 30 kV. The scanning rate was 3°·min$^{-1}$ from 5 to 90°. The FT-IR spectra were recorded in the range of 4000-500 cm$^{-1}$ with a Nicolet Nexus 470 FTIR spectrometer using KBr pellets. Elemental analysis was performed on a Thermo Elemental IRIS Intrepid ICP atomic emission spectrometer. XPS measurements were conducted in the range of 0-1100 eV under a pressure of $1.0 \times 10^{-6}$ Pa on a PerkinElmer PHI 5000C ESCA X-ray photoelectron spectrometer using Mg $K\alpha$ radiation (1253.6 eV). Calibration was conducted with the contaminant carbon (C 1s = 284.6 eV). UV-Vis diffuse reflectance spectra were recorded with a Lambda 650S UV-Vis spectrometer. Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC 3+ thermogravimetric analyser in a range of 40~700 ºC with a temperature rising rate of 10 ºC/min.

Magic angle spinning solid-state nuclear magnetic resonance spectroscopy (MAS NMR)

The $^{31}$P MAS NMR spectra were recorded on a Bruker AVANCE III 400WB spectrometer at 162.1 MHz with a spinning rate of 12 kHz and 85% H$_3$PO$_4$ as the standard. The pulse width was 1.1 μs and the relaxation delay was 15 s. The sample was dried in vacuo and then transferred into a Bruker 4 mm zirconia rotor under nitrogen atmosphere.

Electrospray ionisation mass spectrometry

The mass spectrometry was conducted on a Bruker MicrOTOF II mass spectrometry in the m/z range of 1200-6000 with a capillary voltage of 4000 V and an electrospray ionisation (ESI) source. The mode was negative ion. The nebuliser pressure was 1.0 bar and the dry heater temperature was 180 ºC with a dry gas flow of 4.0 L·min$^{-1}$.
Fig. S1 XPS survey spectrum and the corresponding quantitative result of I-Cs.
Fig. S2 XPS survey spectrum and the corresponding quantitative result of 2-Cs.
Fig. S3 TG curve of 1-Cs.

Fig. S4 Crystal structure of 3-Cs.\textsuperscript{A1,A2} The structure of 1-Cs is very similar to that of 3-Cs with the only difference of partial (1/12) substitution of W by Cu and partial (11/12) occupancy of terminal O. W, O, P and Cs atoms are shown in grey, red, purple and green spheres, respectively.
Fig. S5 Simulated powder XRD pattern of 3-Cs (a), experimental powder XRD patterns of 3-Cs (b) and 1-Cs (c).

Fig. S6 The experimental (above) and simulated (below) ESI-MS peak of [Cs₂HCuPW₁₁O₃₉]⁻.

Fig. S7 IR spectra of 1-Cs (a), 2-Cs (b) and 3-Cs (c) in the range of 1150~500 cm⁻¹.
Fig. S8 UV-Vis diffuse reflectance spectra of 1-Cs (a), 2-Cs (b) and 3-Cs (c).

Fig. S9 UV-Vis diffuse reflectance spectra of 1-Cs after 0 (a), 4 (b) and 9 (c) day(s).
Fig. S10 Cu 2p XPS spectra of 1-Cs (a) and 2-Cs (b). Peaks marked with asterisks represent satellite peaks of Cu$^{2+}$.

Fig. S11 Solution of Na$\text{sub}_5$[Mn$^{IV}$PW$\text{sub}_{11}$O$_{39}$(OH$_2$)]:15H$_2$O after mixed with 2-Cs (left) and 1-Cs (right) followed with filtering.
Reference:
