Supporting information

Polyoxotungstates incorporated organophosphonate and nickel: synthesis, characterization and efficient catalysis for epoxidation of allylic alcohols

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Contains

IR

The infrared spectrum of the three POMs from 4000 to 500 cm^{-1} have shown the similar peaks. Here, the peaks of W-O_b-W, W-O_c(As) and W=O appear at 876 cm^{-1}, 705 cm^{-1} and 928 cm^{-1}, respectively. Besides, the peaks of glyphosate ligand are mainly divided into two group: 1110 cm^{-1} (the stretching vibration of P–O), 1595 cm^{-1} and 1394 cm^{-1} (the peaks of carboxyl). In addition, the strong band at 3430 cm^{-1} corresponds to the stretching vibration of O–H and the sharp peak at 1640cm^{-1} corresponds to the bend vibration of O–H in crystal water.

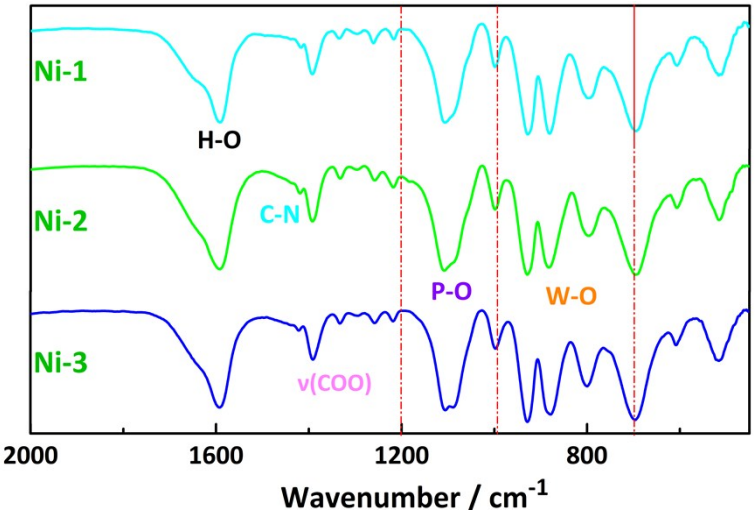


Fig. S1. The infrared spectrum of the three POMs.

XPRD

In order to detect the purity of test sample, the powder XRD analysis of three POMs has completed. In Fig. S2, the powder XRD pattern of the POMs are well in agreement with their simulated ones from X-ray single-crystal data, and peak intensity is discrepant due to the anisotropic effects of crystal. No apparent differences can be found in the patterns, implying that the sample used for all the characterization and test is pure.

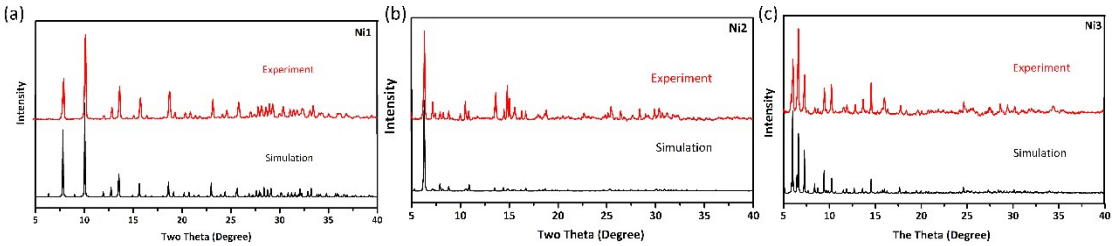


Fig. S2. The XRD of the three POMs

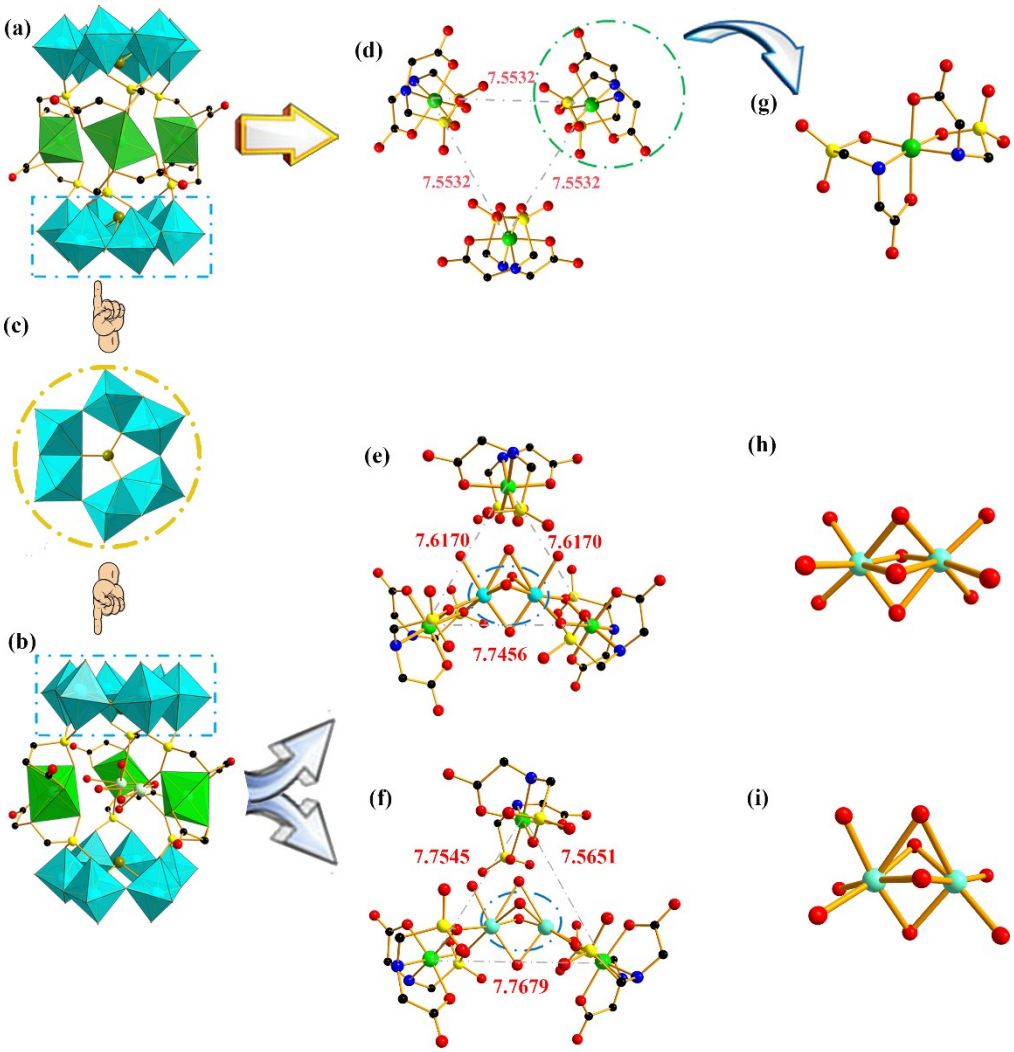
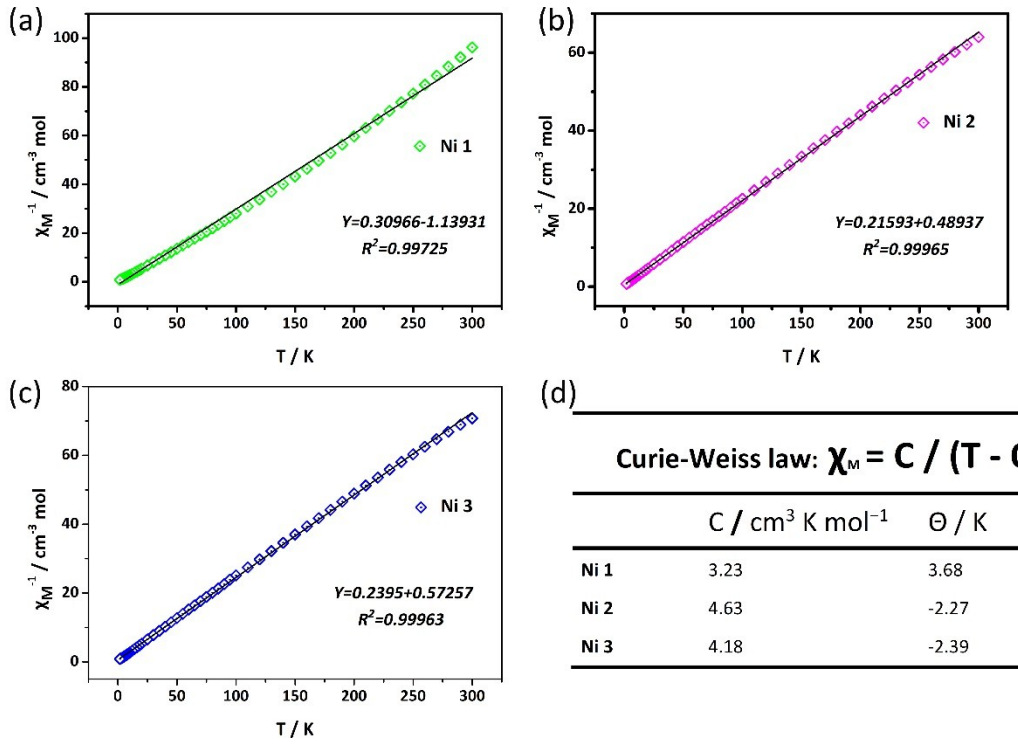


Fig. S3. (a) The polyhedral/ball-and-stick representation of the polyanionic skeleton of Ni1; (b) The ball-and-stick representation of the building blocks; (c) The planform of the three Ni atoms incorporated with glyphosate ligands; (d) the coordination mode between one Ni atom and two ligands.

Structure

Magnetic Properties



(d)

Curie-Weiss law: $\chi_M = C / (T - \Theta)$

	C / cm^3 K mol^{-1}	Θ / K
Ni 1	3.23	3.68
Ni 2	4.63	-2.27
Ni 3	4.18	-2.39

Fig. S4. The plots for and χM^{-1} vs T between 1.8 K and 300 K for Ni1 (a), Ni2 (b) and Ni3 (c); (d) The Curie-Weiss law and the Curie-Weiss constants of three POMs.

TG analysis

Thermal gravimetric analyses of the three POMs have been investigated in the flowing N_2 atmosphere with heating at a speed of 10 °C min^{-1} in the range of 25–870 °C. As it has shown in Fig. S5, all of them exhibited two steps weight loss from 25–870. For **Ni1**, the first weight loss of 13.38% (calcd. 14.19%) was from 25 to 338 °C, which was assigned to the release of 30 crystal water molecules and the sublimation of As_2O_3. The second weight loss of 10.47% (calcd. 9.93%) from 338–832 °C corresponded to the removal of six {$OOCCH_2NCH_2$} groups. As to **Ni2** and **Ni3**, there were also two weight loss steps in the temperature range of 25–870 °C, which are similar with **Ni1**: the first weight loss (Found 15.73%, calcd. 15.42% for **Ni2**; Found 14.59%, calcd. 14.60% for **Ni3**) were assigned to the liberation of 32 water molecules for **Ni2** but 30.5 water molecules for **Ni3** and As_2O_3 of **Ni2** and **Ni3**, while the temperature range was 25–347 °C and 25–322 °C, respectively. Whereafter, the six {$OOCCH_2NCH_2$} groups also left at the range of 347–870 °C for **Ni2** and 322–870 °C for **Ni3** corresponding to the weight loss of 10.30% (calcd. 10.28%) for **Ni2** and 10.12% (calad. 10.08%) for **Ni3**.

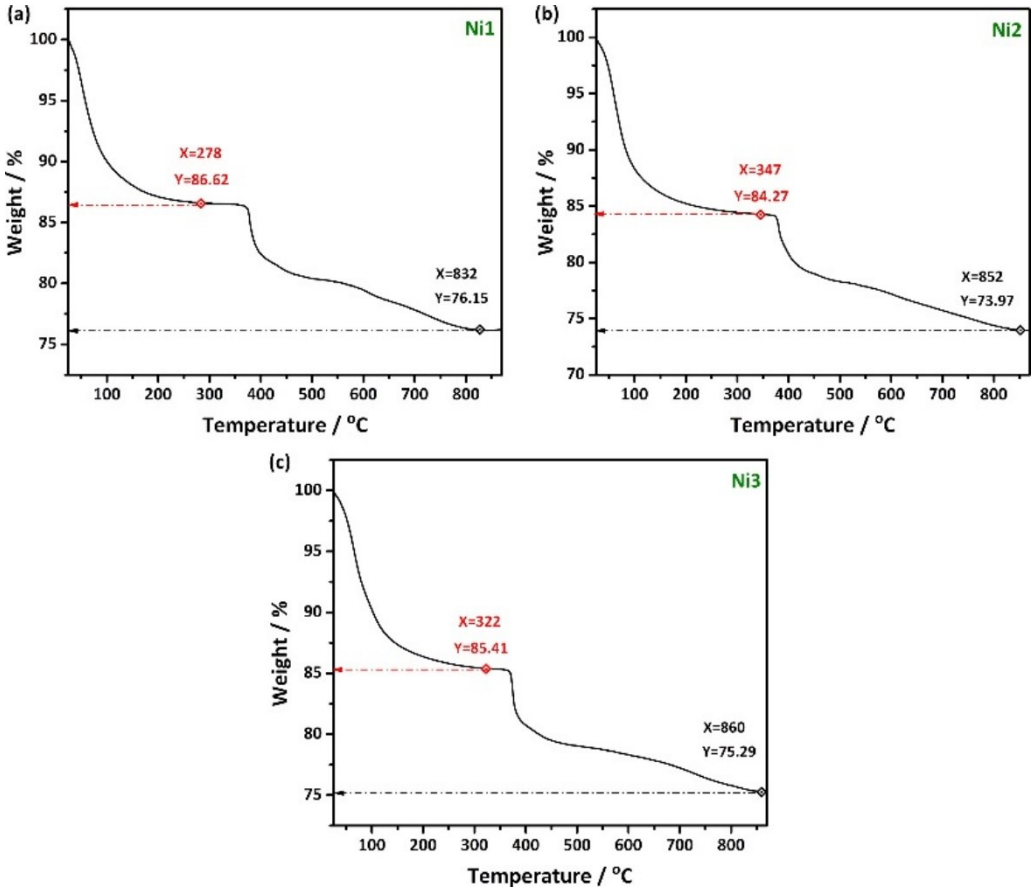


Fig. S5. The TGA curves of **Ni1** (a), **Ni2** (b) and **Ni3** (c)

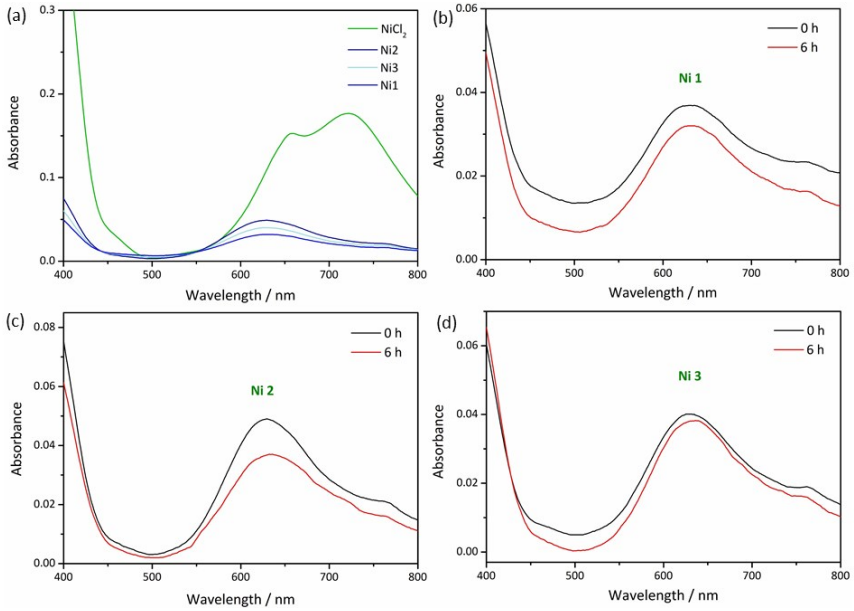


Fig. S6. (a) The Vis spectra of **Ni1**, **Ni2**, **Ni3** and $NiCl_2$; The compared Vis spectra of the POMs aqueous solutions between 0 h and 6 h: (b), **Ni1**; (c), **Ni2**; (d), **Ni3**.

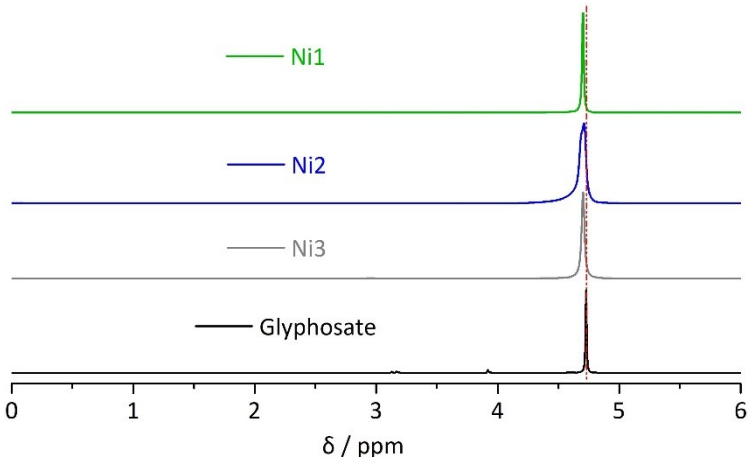


Fig. S7. the comparison of solution ^{1}H NMR spectra of the three POMs and glyphosate.