Investigation into the mechanism of polyoxotungstates-catalyzed cyclooctene epoxidation by ESI-MS

LinYuan Fan, YaYu Hong, Jie Cao* and ChangWen Hu*

Key Laboratory of Cluster Science, Ministry of Education of China; Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials; School of Chemistry, Beijing Institute of Technology, Beijing 100081, P.R. China.

E-mail: jcao@not.edi.cn, cwhu@bit.edu.cn

Supporting Information

Contents

* Corresponding author.
E-mail address: jcao@bit.edu.cn
E-mail address: cwhu@bit.edu.cn

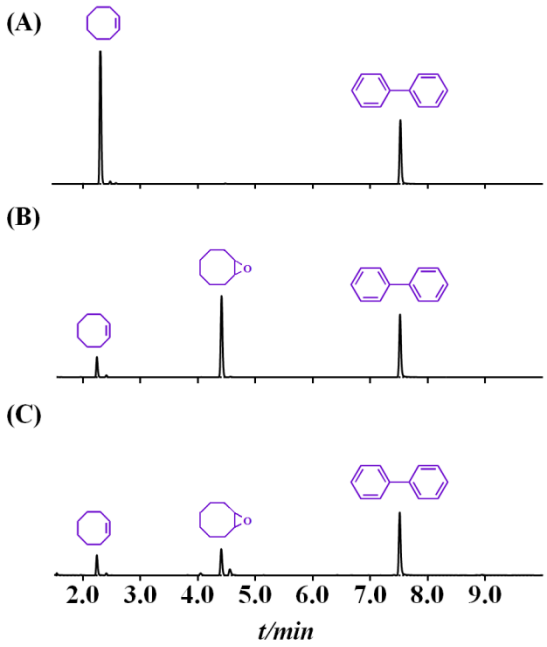

Fig. S1 GC spectra of the epoxidation reaction of cyclooctene by adding different amount of catalyst **1** ($H_3PW_{12}O_{40}$). Reaction conditions: cyclooctene (1 mmol), H_2O_2 (1 mmol), CH_3CN solvent (2 mL), 50 ℃, 4 h. (A) without catalyst **1**; (B) 0.005 mmol catalyst **1**; (C) 0.1 mmol catalyst **1**.

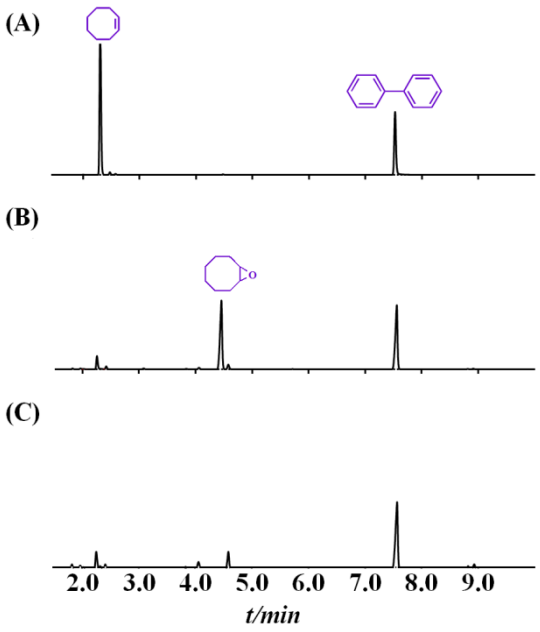

Fig. S2 GC spectra of the epoxidation reaction of cyclooctene by adding different amount of catalyst **2** (H_2WO_4). Reaction conditions: cyclooctene (1 mmol), H_2O_2 (1 mmol), CH_3CN solvent (2 mL), 50 ℃. (A) without catalyst **2**; (B) 0.06 mmol catalyst **2**; (C) 1.2 mmol catalyst **2**.

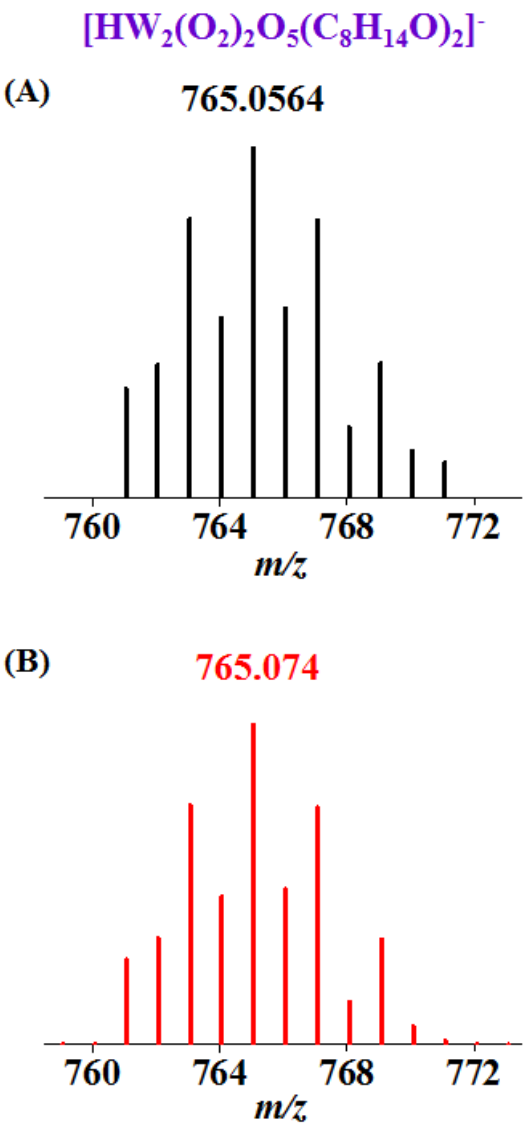

Fig. S3 The comparison of MS spectra of $[HW_2(O_2)_2O_5(C_8H_{14}O)_2]^-$ (m/z 765.1). (A) Observed; (B) Calculated.

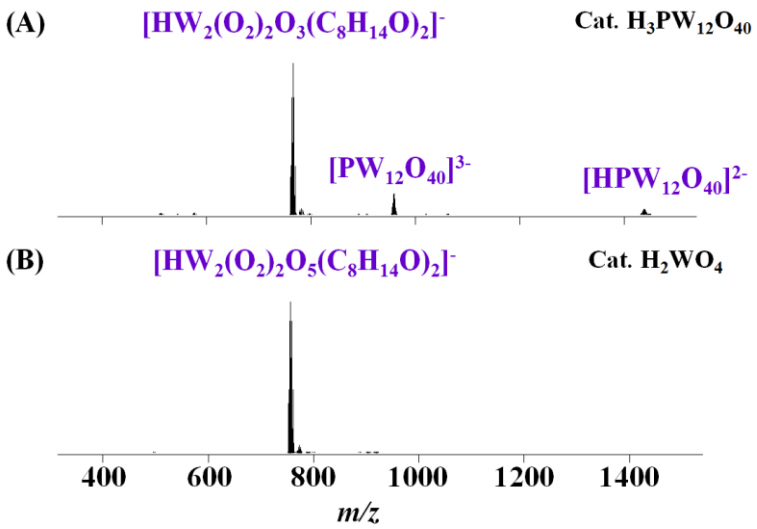

Fig. S4 MS spectra of catalytic solution of 1,2-epoxycyclooctane after the reaction with H_2O_2 and catalysts. Reaction conditions: 1,2-epoxycyclooctane (1 mmol), H_2O_2 (1 mmol), CH_3CN solvent (2 mL), 50 ℃, 4h. (A) $H_3PW_{12}O_{40}$ (0.005 mmol) as catalyst; (B) H_2WO_4 (0.06 mmol) as catalyst.

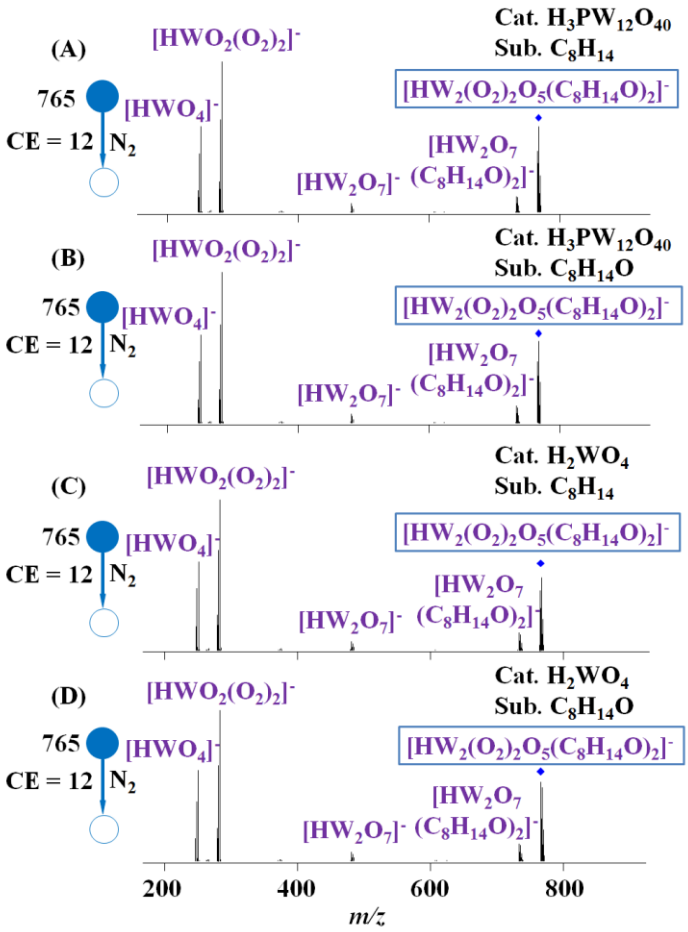

Fig. S5 CID mass spectra of $[HW_2(O_2)_2O_5(C_8H_{14}O)_2]^-$ generated from different reaction solution. (A) $H_3PW_{12}O_{40}$ (0.005 mmol) as catalyst, cyclooctene (1 mmol) as substrate, H_2O_2 (1 mmol); (B) $H_3PW_{12}O_{40}$ (0.005 mmol) as catalyst, 1,2-epoxycyclooctane (1 mmol) as substrate, H_2O_2 (1 mmol); (C) H_2WO_4 (0.06 mmol) as catalyst, cyclooctene (1 mmol) as substrate, H_2O_2 (1 mmol); (B) H_2WO_4 (0.06 mmol) as catalyst, 1,2-epoxycyclooctane (1 mmol) as substrate, H_2O_2 (1 mmol). Collision energy = 12 eV, Isolation width = 9. The parent ion (denoted by a diamond) is shown in a blue square box in each spectrum.

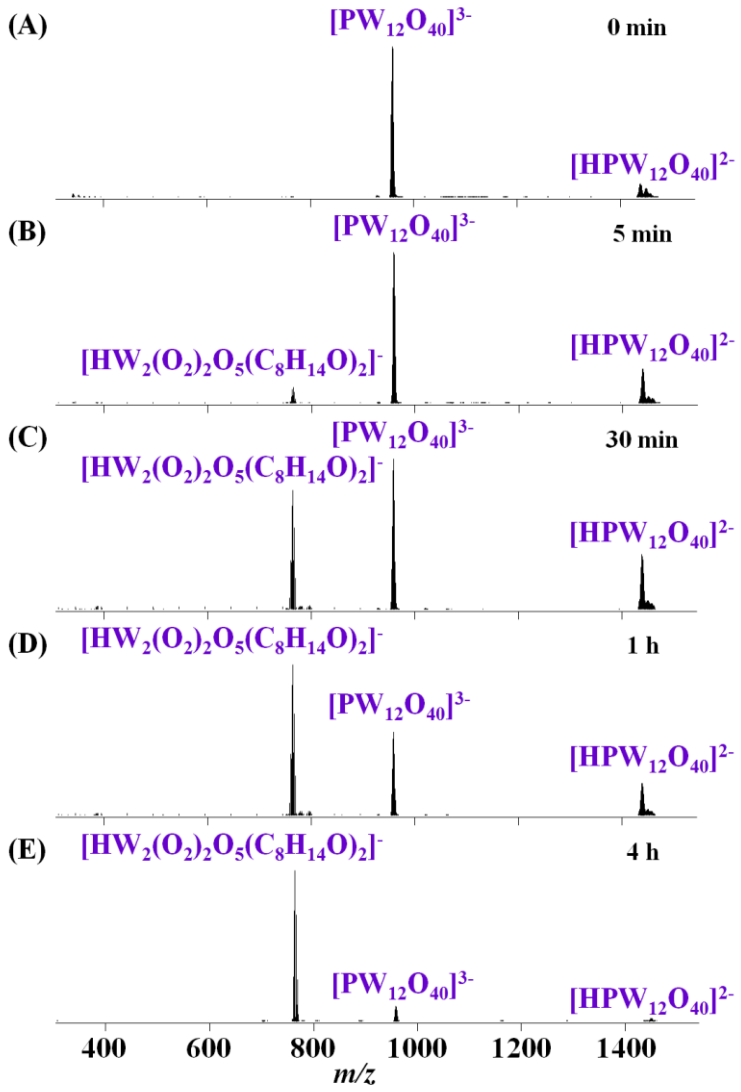

Fig. S6 Real-time monitoring on the cyclooctene epoxidation by one-step for catalyst **1**. (A) $H_3PW_{12}O_{40}$ (0.005 mmol), H_2O_2 (1 mmol) and cyclooctene (1 mmol) dissolved in CH_3CN; (B) stirring 5 min at 50 ℃; (C) stirring 30 min; (D) stirring 1 h; (E) stirrig 4 h.

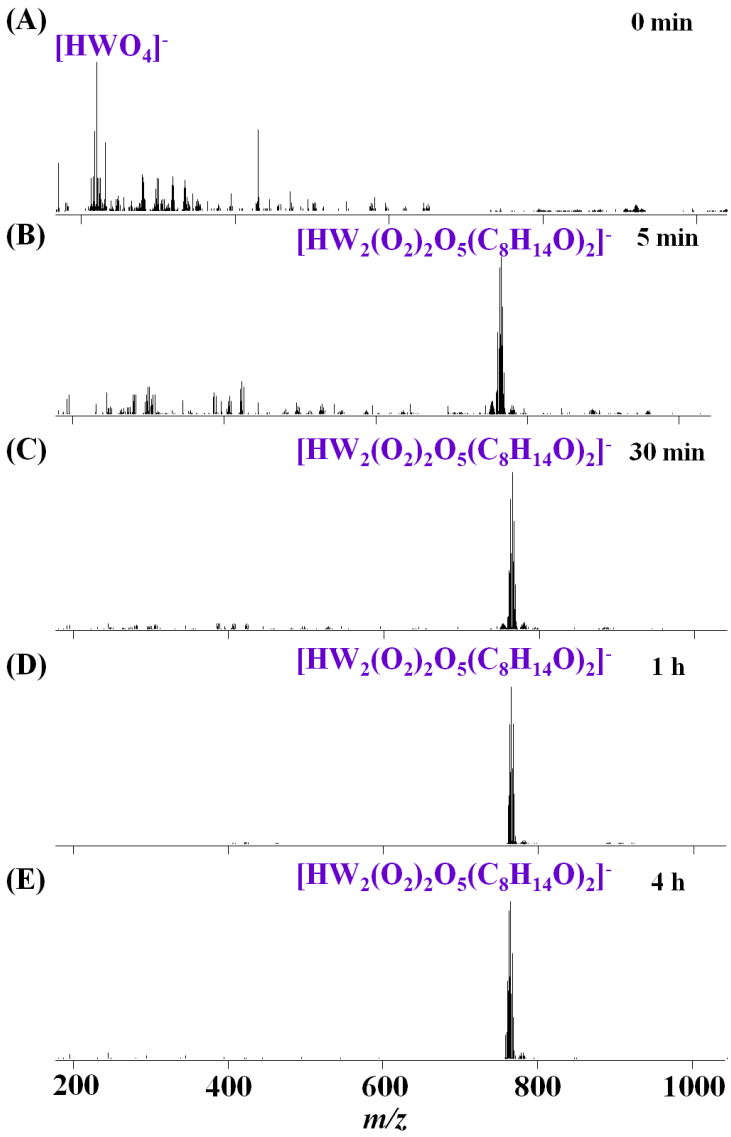

Fig. S7 Real-time monitoring on the cyclooctene epoxidation by one-step for catalyst **2**. (A) H_2WO_4 (0.06 mmol), H_2O_2 (1 mmol) and cyclooctene (1 mmol) dissolved in CH_3CN; (B) stirring 5 min at 50 ℃; (C) stirring 30 min; (D) stirring 1 h; (E) stirrig 4 h.

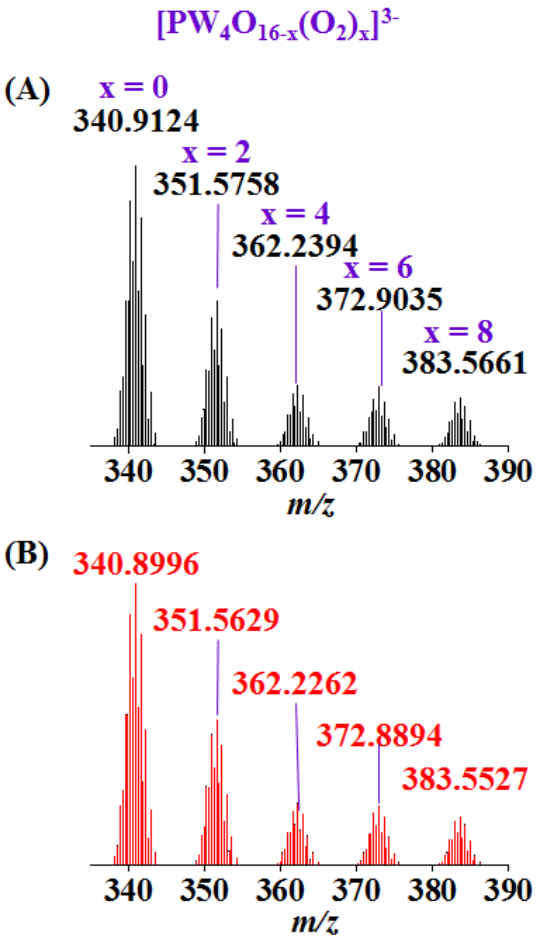

Fig. S8 The comparison of MS spectra of $[PW_4O_{16-x}(O_2)_x]^-$ (x = 0, m/z 340.9; x = 2, m/z 351.6; x = 4, m/z 362.2; x = 6, m/z 372.9; x = 8, m/z 383.6). (A) Observed; (B) Calculated.

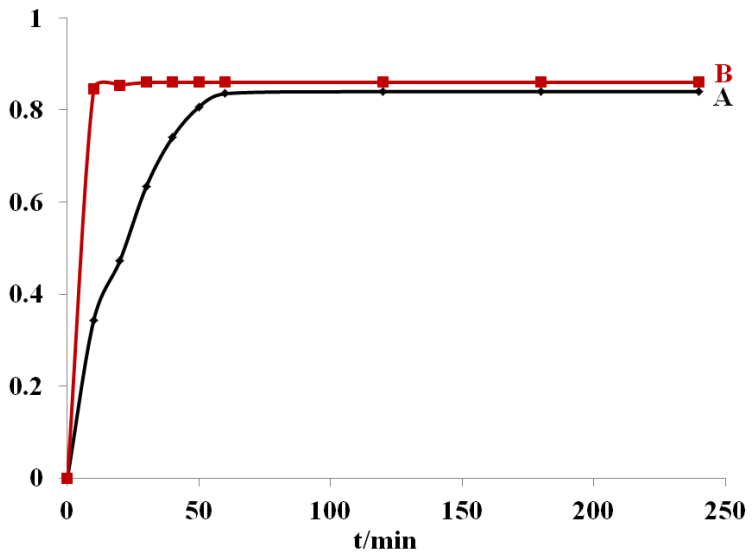

Fig. S9 The conversion-time curve of cyclooctene in system **1**. (A) cyclooctene, H_2O_2 and $H_3PW_{12}O_{40}$ was added into CH_3CN at the same time. (B) After H_2O_2 and $H_3PW_{12}O_{40}$ was added into CH_3CN and mixed at 50 ℃ for 4 h, cyclooctene was added to the mixture.

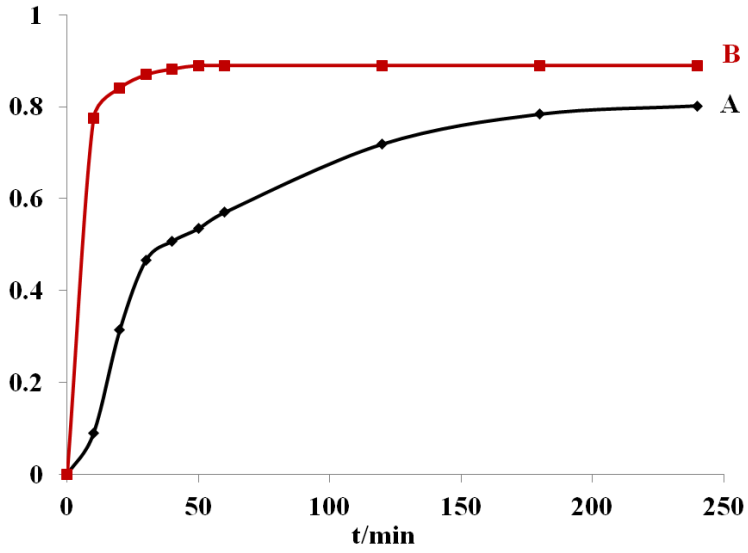

Fig. S10 The conversion-time curve of cyclooctene in system **2**. (A) cyclooctene, H_2O_2 and H_2WO_4 was added into CH_3CN at the same time. (B) After H_2O_2 and H_2WO_4 was added into CH_3CN and mixed at 50 ℃ for 4 h, cyclooctene was added to the mixture.