Supporting Information

Selective catalytic oxidation of 2-chloroethyl ethyl sulfide by Keplerate-type molybdenum-oxygen cluster {Mo_{132}}

Jianbo Yin,[a,b] liming Sun, [a] Yunshan Zhou [a*] and Lijuan Zhang [a*]

[a]State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology.Beijing,100029, China.

[b]School of Environment and Health, Yanching Institute of Technology, Langfang 065201, China.

Contents

1. Synthesis of the catalysts

1.1 {Mo_{132}-Ac^-} was synthesized according to reference [1]: $N_2H_4 \cdot H_2SO_4$(0.8 g, 6.1 mmol) was added to a solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (5.6 g, 4.5 mmol) and CH_3COONH_4(12.5 g, 162.2 mmol) in H_2O(250 mL). The solution was then stirred for 10 min (color change to blue-

green) and 50% CH_3COOH (83 mL) was subsequently added. Thereaction solution, now green, was stored in an open 500 mL Erlenmeyer flask at 20 °Cwithout further stirring (fumehood; slow color change to dark brown). After 4 d the precipitated red-brown crystals were filtered off over a glass fritt(D2), washed with 90% ethanol, ethanol, and diethyl ether, and finally dried in air. Yield: 3.3 g (52% based on molybdate).

1.2 {Mo_{132}-SO_4^{2-}}was synthesized according to reference [2]: A solution of {Mo_{132}-Ac^-} (5.0 g, 0.17 mmol) and $(NH_4)_2SO_4$(20.0 g,151 mmol) in H_2O (400 mL) was adjusted with 16% HCl (about 20 mL) to pH ≈ 1 and heated under reflux for 2 h in an oil bath (ca.125°C) without stirring. The hot solution was purified by filtration and the dark-brown filtrate stored at 20°C in an open 600 mL beaker(wide necked) for crystallization. After one week the dark-brown crystals were collected by filtration, washed quickly with ice-cold 2-propanol and dried in air. Yield: 4.3 g (89% based on Mo).

2. PXRD characterization of the catalysts {Mo_{132}-Ac^-} and {Mo_{132}-SO_4^{2-}}

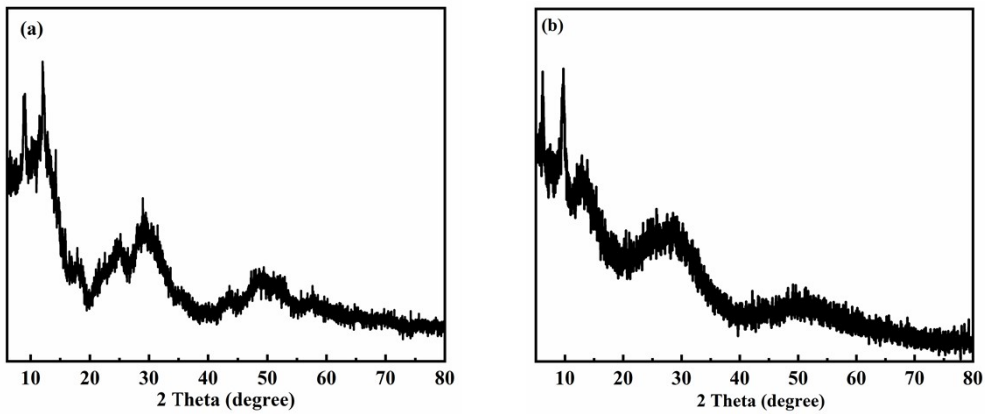


Figure S1 PXRD patterns of {Mo_{132}-Ac^-} (a) and {Mo_{132}-SO_4^{2-}} (b).

3. GC-FID analysis of reactants and products

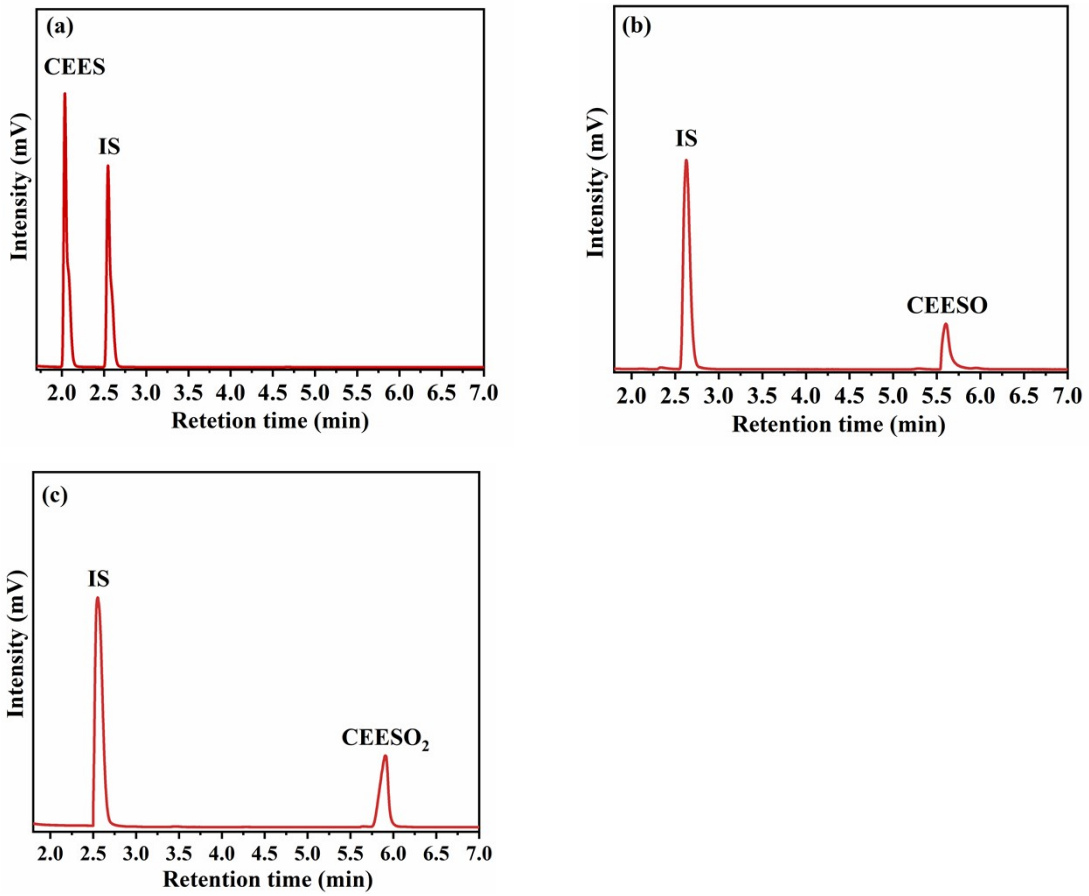
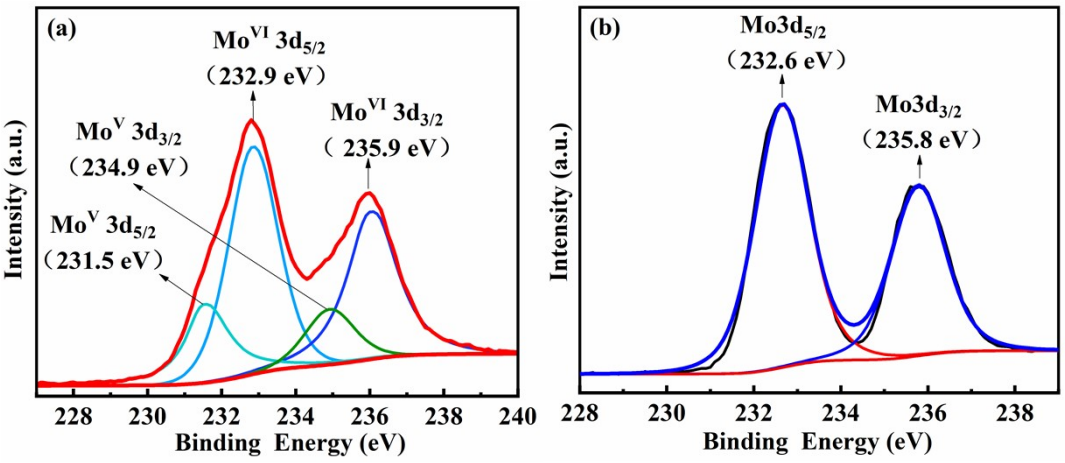


Figure S2 GC-FID signals of CEES and 1,3-dichlorobenzene as internal standard (a), of CEESO and 1,3-dichlorobenzene as internal standard (b), and of $CEESO_2$ and 1,3-dichlorobenzene as internal standard (c).

4. XPS characterization of {Mo132-SO2- 4}



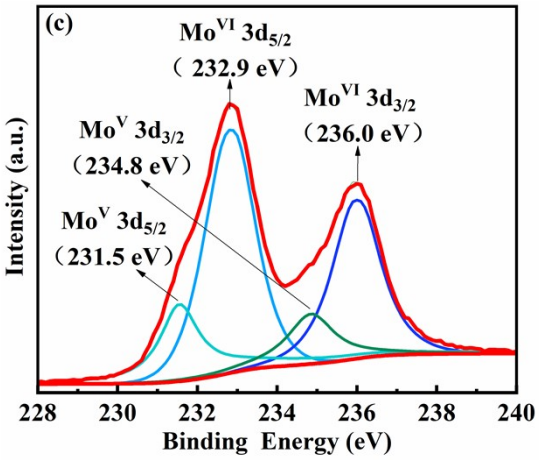


Figure S3 XPS of Mo3d of {Mo_{132}-SO2- 4}(a), Mo3d of {Mo_{132}-SO2- 4} after adding H_2O_2 (b), Mo3d of {Mo_{132}-SO2- 4} after adding H_2O_2 and substrate CEES (c)

Reference

1 Müller A, Krickemeyer E, Bögge H, Schmidtmann M and Peters F, Organizational forms of matter: an inorganic super fullerene and keplerate based on molybdenum oxide, *Angew. Chem. Int. Ed.*, 1998, 37, 3359-3363

2 Müller A, Krickemeyer E, Bögge H, Schmidtmann B B and Talismanova M O, Drawing small cations into highly charged porous nanocontainers reveals “water” assembly and related interaction problems, *Angew. Chem. Int. Ed.*, 2003, 42, 2085-2090