Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

An environmentally benign multiphase solid-liquid-gas catalysis

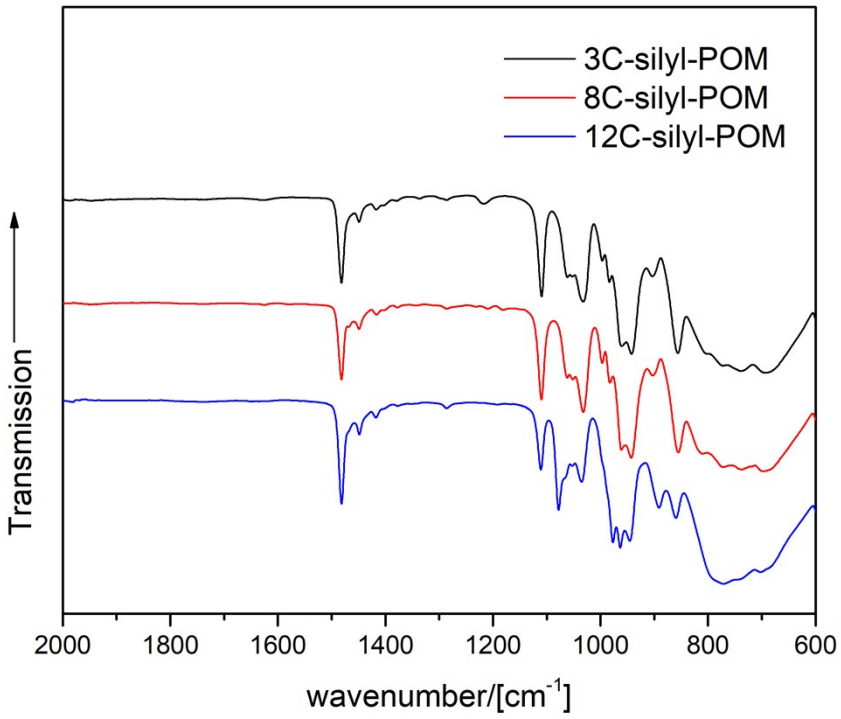
Xueli Bai,[a] Nianze Song,[a] Liang Wen,[a] Xin Huang,[a] Jian Zhang,[a] Yue Zhang,*[a] and Yongxiang Zhao*[a]

[a]Engineering Research Center of Ministry of Education for Fine Chemicals, and College of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, Shanxi 030006, China.

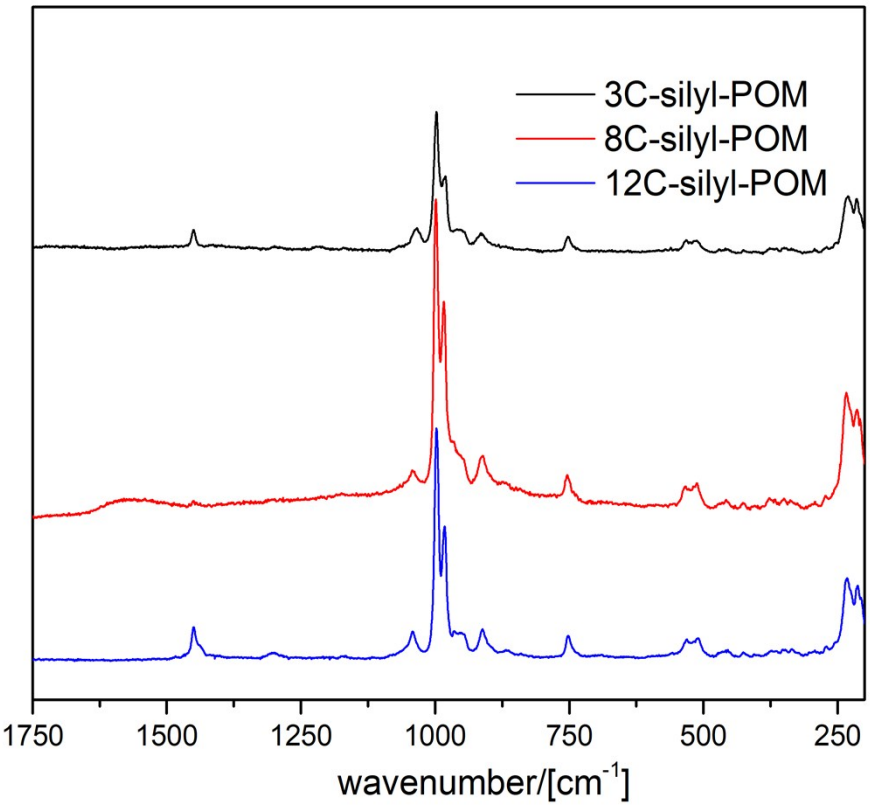
*Corresponding author (email: zyue@sxu.edu.cn and yxzhao@sxu.edu.cn)

Chemicals: All kinds of alcohols (AR) were purchased from Sinopharm. Acetonitrile (99%) was purchased from Meryer. (Octyl)-trimethoxysilane (97.0%), n-propyltrimethoxysilane (98.0%), n-dodecyltrimethoxysilane (93.0%) and tetramethylammonium chloride (99.0%) were purchased from Sinopharm. DMSO-d_6（99.9%） were purchased from Sigma-Aldrich.

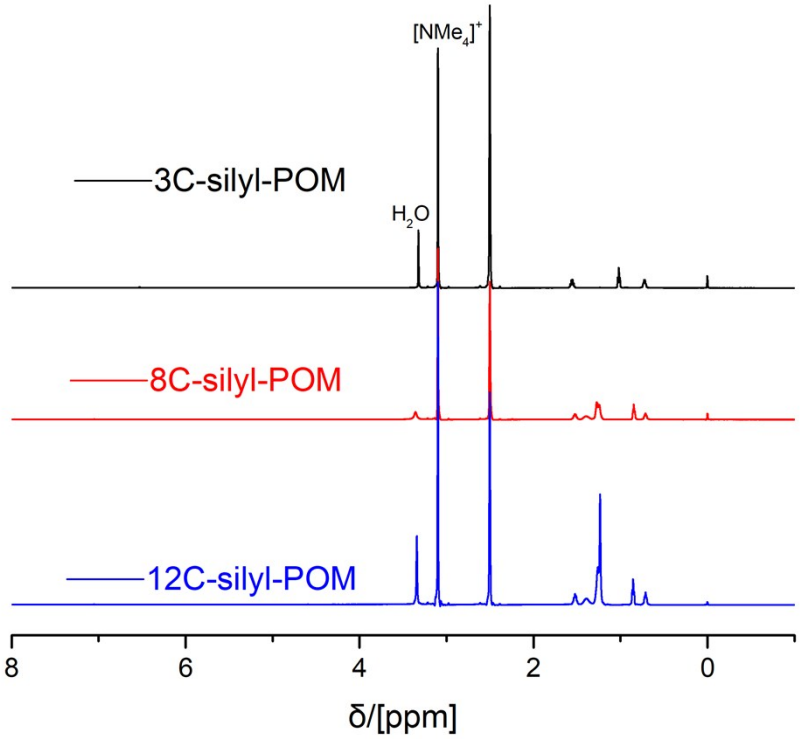
SI-1: FT-IR spectrogram of the 3C-silyl-POM, 8C-silyl-POM and 12C-silyl-POM.
SI-2: FT-Raman spectrogram of the 3C-silyl-POM, 8C-silyl-POM and 12C-silyl-POM.
SI-3: ^{1}H NMR spectrum of the 3C-silyl-POM, 8C-silyl-POM and 12C-silyl-POM.
SI-4: Tungsten content of the POM, 3C-silyl-POM, 8C-silyl-POM and 12C-silyl-POM are detected by ICP.
SI-5: ^{31}P NMR spectrum of the 3C-silyl-POM, 8C-silyl-POM and 12C-silyl-POM.
SI-6: MALDI-TOF-MS spectrum of the 8C-silyl-POM.
SI-7: ^{29}Si NMR spectrum of the 8C-silyl-POM.
SI-8: XPS spectrum of the POM, 3C-silyl-POM, 8C-silyl-POM and 12C-silyl-POM
SI-9: FT-IR spectrogram of the recycled 8C-silyl-POM and fresh 8C-silyl-POM.
SI-10: ^{1}H NMR spectrum of the recycled 8C-silyl-POM and fresh 8C-silyl-POM.
SI-11: FT-Raman spectrogram of the recycled 8C-silyl-POM and fresh 8C-silyl-POM.
SI-12: XPS spectrum of the recycled 8C-silyl-POM and fresh 8C-silyl-POM.



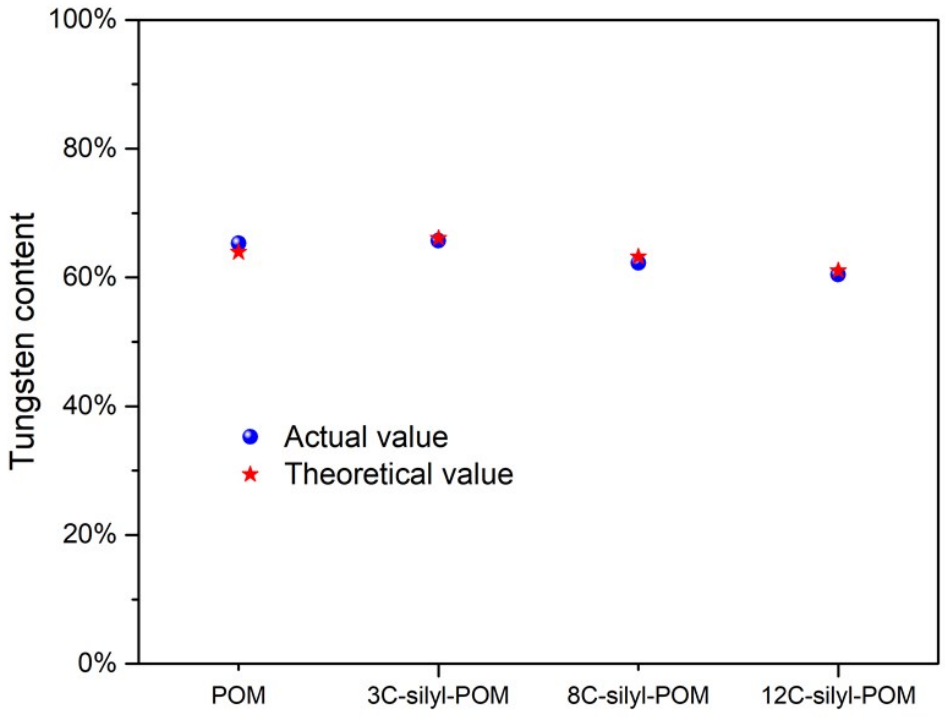
IR (ATR): 1110 (Si-O-Si), 1079~1030 (P-O), 997~940(W=O), 901~706(W-O-W)


3C-silyl-POM
8C-silyl-POM
12C-silyl-POM
1750
1500
1250
1000
750
500
250
wavenumber/[cm-1]

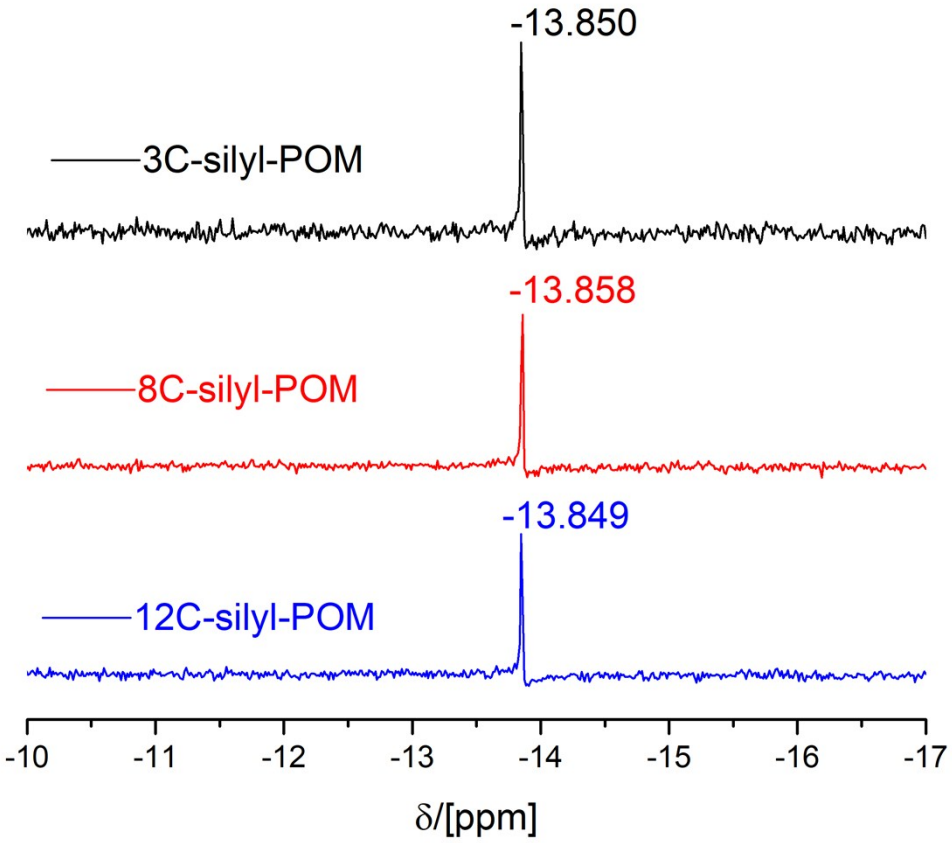
SI-2

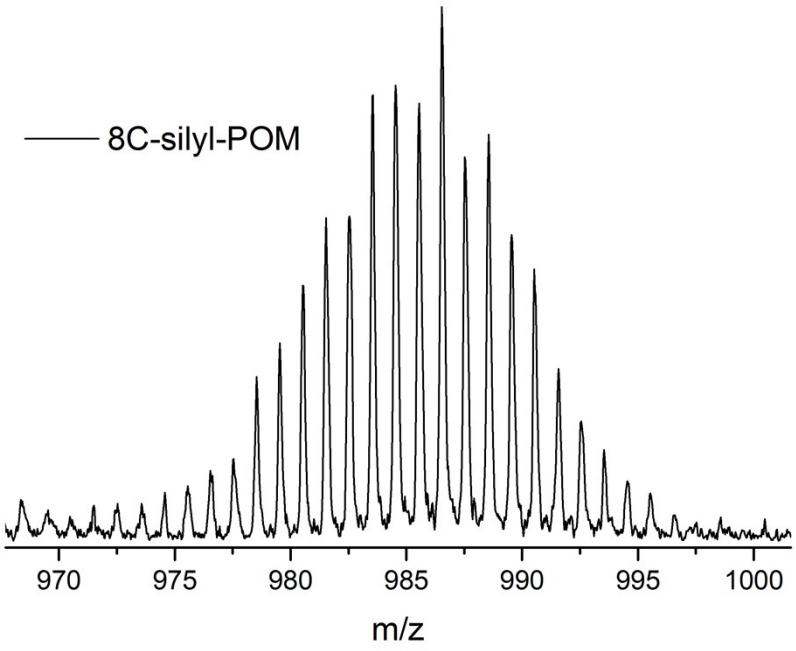


^{1}H NMR (DMSO-d_6): δ = 3.11 ($[NMe_4]^+$), 1.61~1.14 (-CH_2-), 0.85 (-CH_3), 0.71 (-CH_2-Si).

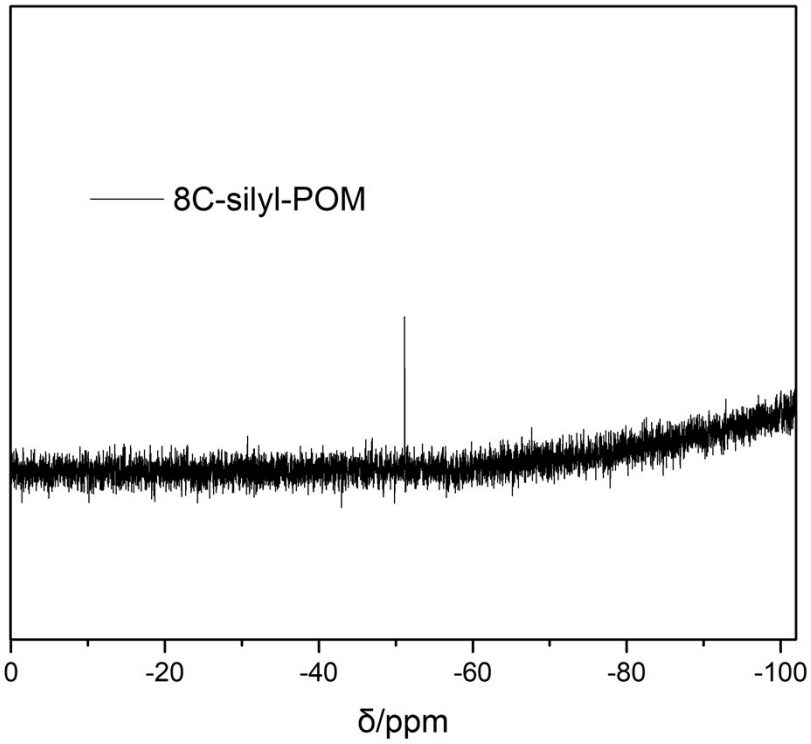

100%
80%
60%
40%
20%
0%
Tungsten content
Actual value
Theoretical value
POM
3C-silyl-POM
8C-silyl-POM
12C-silyl-POM

SI-4

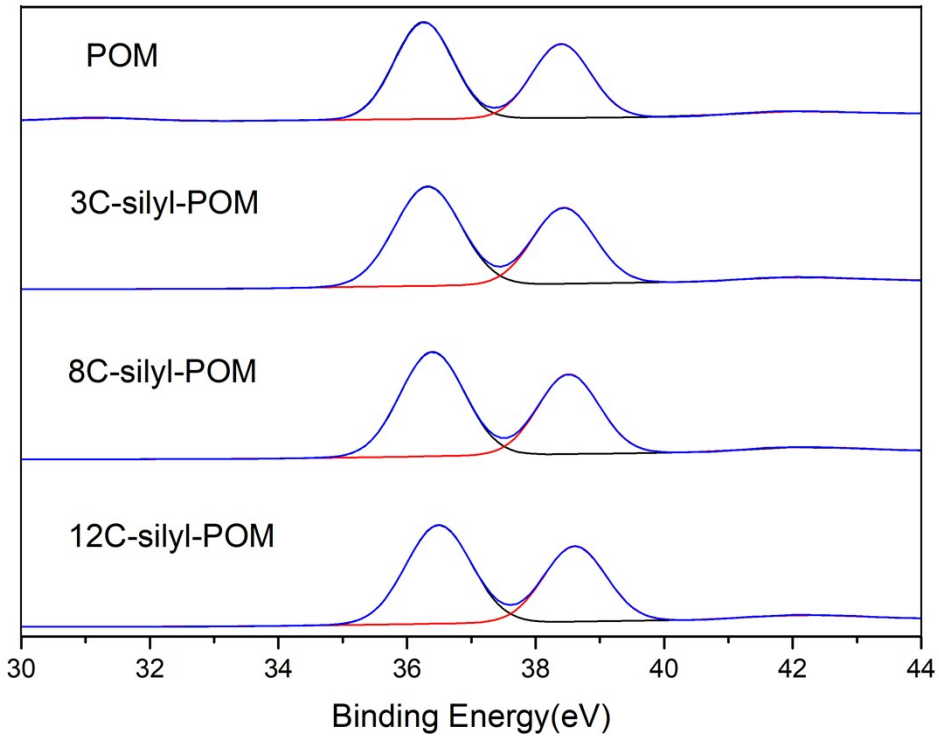

-13.850
3C-silyl-POM
-13.858
8C-silyl-POM
-13.849
12C-silyl-POM
-10
-11
-12
-13
-14
-15
-16
-17
δ/[ppm]

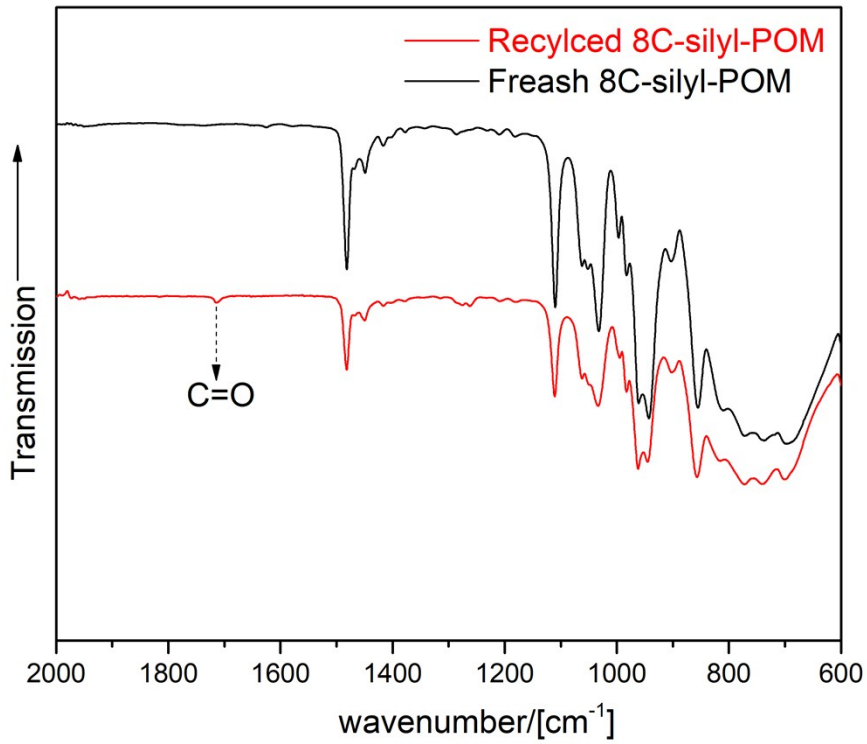


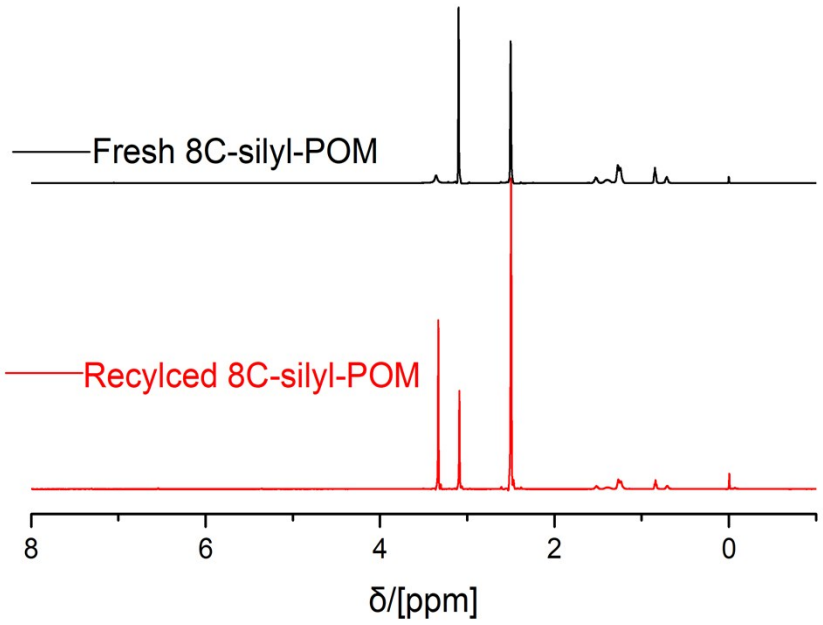
SI-6

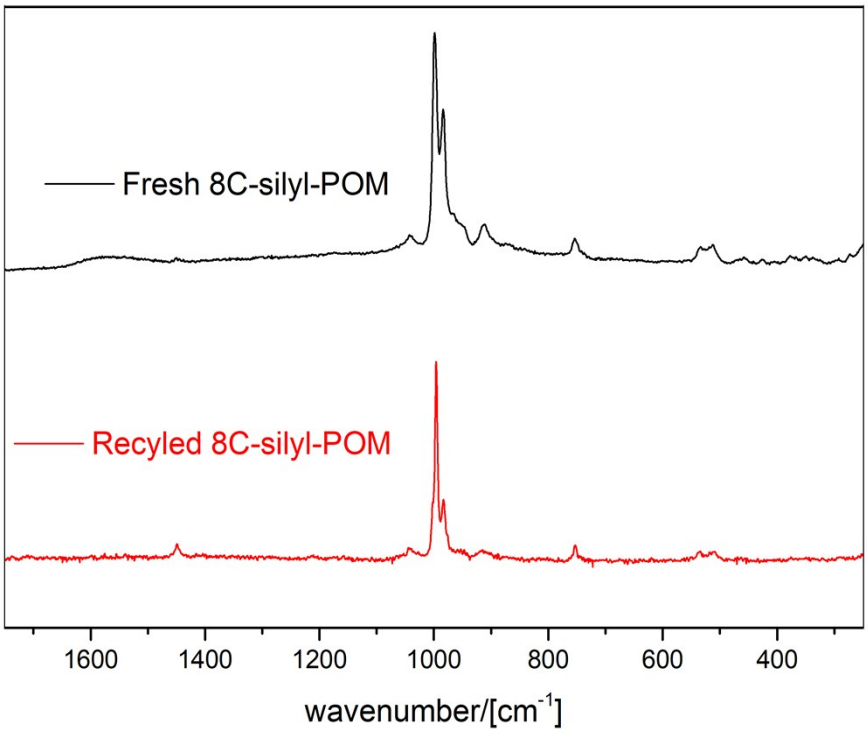


SI-7

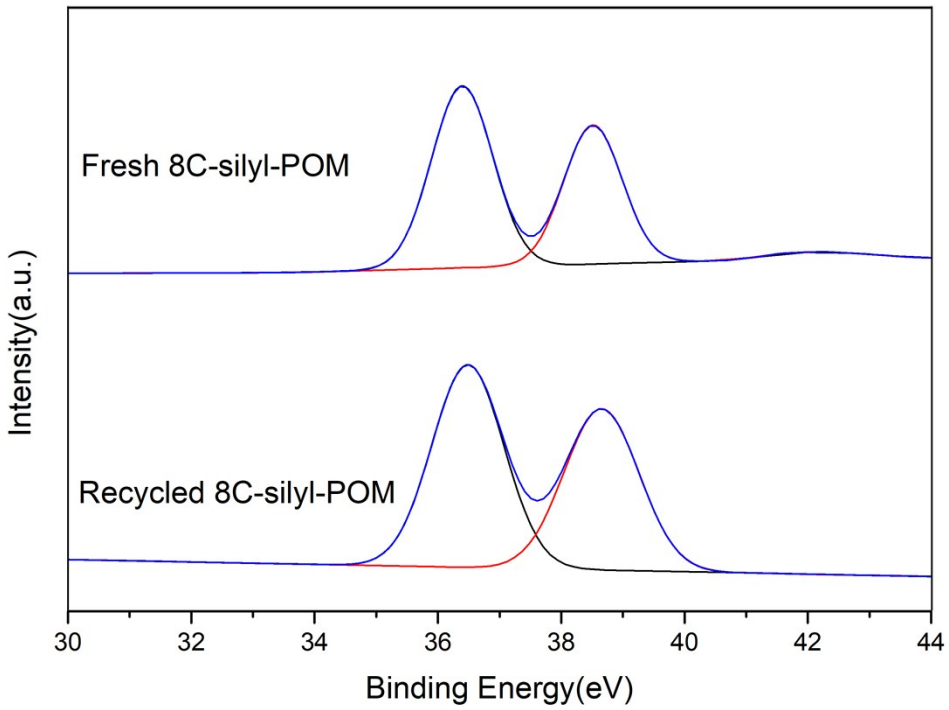

POM
3C-silyl-POM
8C-silyl-POM
12C-silyl-POM
30
32
34
36
38
40
42
44
Binding Energy(eV)

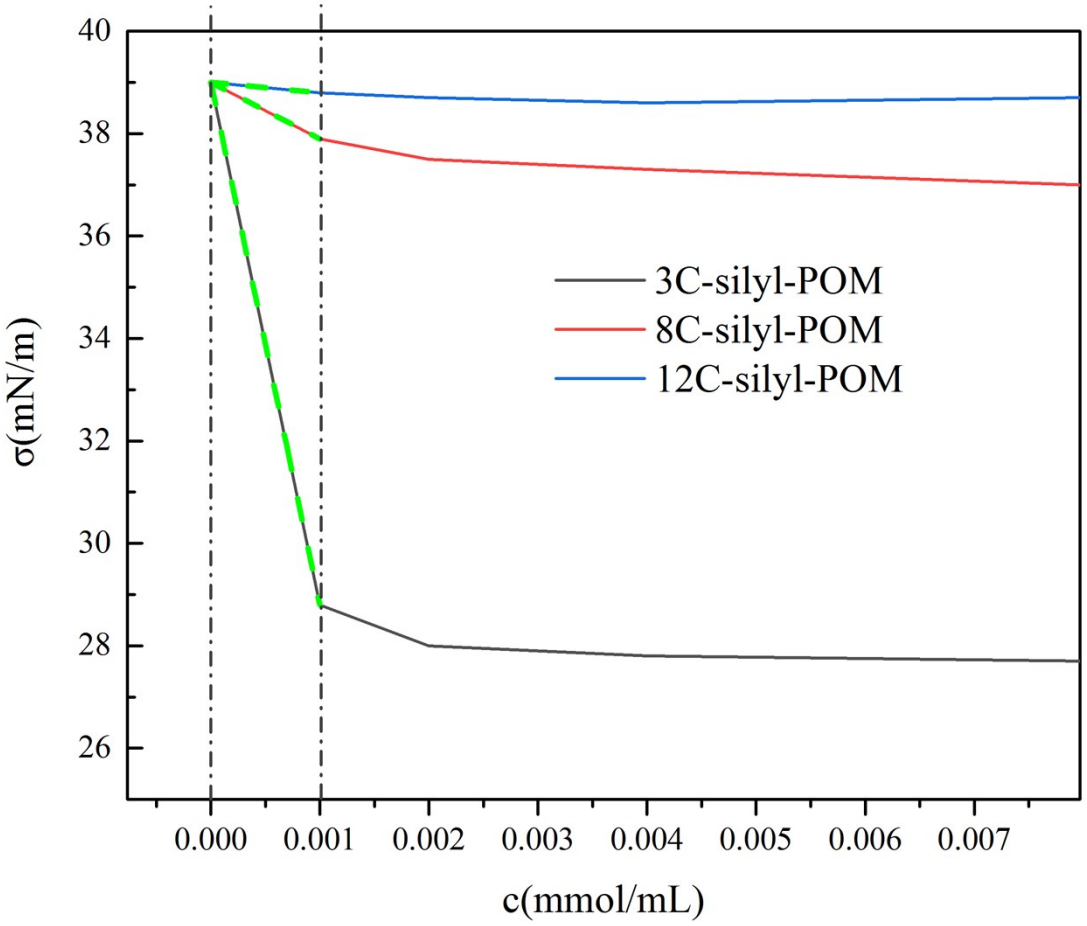

Recylced 8C-silyl-POM
Freash 8C-silyl-POM
Transmission
C=O
2000
1800
1600
1400
1200
1000
800
600
wavenumber/[cm-1]


Fresh 8C-silyl-POM
Recylced 8C-silyl-POM
8
6
4
2
0
δ/[ppm]


Fresh 8C-silyl-POM
Recyled 8C-silyl-POM
1600
1400
1200
1000
800
600
400
wavenumber/[cm-1]

SI-11

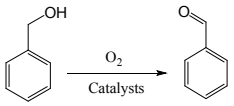
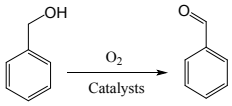

Fresh 8C-silyl-POM
Recycled 8C-silyl-POM
Intensity(a.u.)
30
32
34
36
38
40
42
44
Binding Energy(eV)



SI-13

According to the curve of surface tension and catalyst concentration (Figure 3b), the maximum slope in the interval between functions c and σ is identified (the maximum slope corresponding to 3C-silyl-POM, 8C-silyl-POM and 12C-silyl-POM is -10.2 , -1.1 and -0.2, respectively.), and the maximum adsorption capacity (Γ) of the three catalysts at the surface of benzyl alcohol can be estimated using the Gibbs adsorption equation.

Table S1. Polyoxometalates as catalysts for the oxidation of benzyl alcohol with molecular oxygen have been reported in the literatures.

Entry	catalyst	reaction	Temp. (°C)	Solvent	Coversion (%)	Selectivity (%)
1[49]	$(PW_{11})_3$/MCM-41 $(PW_{11})_3$/MCM-48		90		30 32	90 89
2[50]	$H_4PMo_{11}VO_{40}$		150	DMSO	78	90

Herein, although the catalytic conversion of the catalysts in the oxidation of alcohol is low, which is consistent with the literature (Table S1).

49. Singh, S.; Patel, A., *Catalysis Letters*, 2016, **146**, 1059-1072.
50. Qian, X.; Li, S.; Banks, M. K.; Xu, W.; Wu, R., *Catalysis Communications*, 2018, **114**, 24-27.