Supporting Information for

A new strategy for the selective oxidation of alcohol catalyzed by polyoxometalate-based hybrid surfactant at biphasic systems

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General Information

Hydrogen peroxide solution (30%) was purchased from Sinopharm. All kinds of alcohols (AR) were purchased from Sinopharm. Sodium tungstate (AR) purchased in Tianjin Kaitong Chemical Reagent Co., Ltd. Trimethoxy(octadecyl)silane (90%) and Acetonitrile (99%) were purchased from Meryer. Dibasic sodium phosphate and tetramethylammonium chloride (99%) were purchased from Sinopharm. DMSO-d6（99.9%）were purchased from Sigma-Aldrich. 18C-silyl-POM is prepared according to the literature[1]. Distilled deionized water was used in all experiments.

18C-silyl-POM: FT-IR: 981-952（W=O），857（ W–Oc–W），777-693（W–Oe–W） (c, corner sharing; e, edge sharing), 1065~1032 (P-O), 1111 (Si-O-Si). ^{1}H NMR (DMSO-d$_6$): δ=3.11 ($[NMe_4]^+$), δ=1.30~1.15 ($-CH_2-$), δ=0.85（$-CH_3$）, δ=0.71 （$-Si-CH_2-$）, δ=0.01 ($-CH_3$ was attributable to the internal standard tetramethylsilane, TMS). ^{31}P NMR (DMSO-d$_6$): δ =-13.84.

The GC analyses were performed on Agilent Technologies 7890B Network GC system (HP-5). All synthetic samples are dried using a vacuum drying chamber under vacuum conditions. The emulsion formed by different stirring speed (4000r·min^{-1}\6000r·min^{-1}\8000r·min^{-1}\10000r·min^{-1}) is stirred by the XHF-DY type high-speed disperser for 3 minutes.

Characterization methods

The ^{1}H and ^{31}P NMR spectra were recorded using an AVANCE III HD 600MHz spectrometer Using DMSO-d6 as a solvent, TMS is used as the internal standard. FT-IR analyses were performed Fourier transform infrared (FT-IR) determined by Bruker Tensor 27 spectrometer. Inductively Coupled Plasma Emission Spectrometer ICP6300 (Thermo Corporation, USA). The particle size distribution data of the droplets and the zeta potential values were measured by Malvern Zatasasizer Nano –ZS. The interfacial tension value between cyclohexanol and water was measured by the POWEREACH TX500C rotary Drop interface Tension measuring instrument. The conductivity meter uses a magnetic DDS-307. The X-ray photoelectron spectroscopy (XPS) analysis of catalysts was carried out on a Escalab 250Xi (Thermo Fisher Scientific with a monochromatic Al Kα X-ray source).

General oxidation experiments

Catalytic performance in oxidative reaction of cyclohexanol with H_2O_2: Adding 0.1g of 18C-silyl-POM (or a substantial amount of POM 0.084g) to a mixture of cyclohexanol (3mL) and 30% H_2O_2 aqueous solution (5mL). This hybrid system is stirred vigorously using a magnetic stirrer for 2h at room temperature. The reaction results are analyzed using by Agilent Technologies 7890B Network GC System (HP-5:30mm×0.32mm) with toluene as internal standard. When analyzing samples with GC system. the multiphase system is dissolved in ethanol to form a phase for analysis.

Procedures of recovery and reuse of catalyst

The multiphase system is dissolved in ethanol to form a phase after oxidation reaction. The catalyst can be readily separated from the reaction mixture by high speed centrifugation (10000 r/min). The catalyst was washed with ethanol several times until there was no organic substance in the supernatant (detected by GC system). The catalyst is then transferred to the reactor. In order to reduce the loss of samples in the transfer process, we used ethanol to wash the centrifugal tubes several times and collect all of them into the reactor. Ethanol is evaporated by vacuum distillation and then dried in a vacuum drying chamber. After the catalyst is completely dry, we apply it again to the oxidation of cyclohexanol. After the catalyst was completely dried, we applied it to the oxidation of cyclohexanol again.

Calculations of the emulsion interface area S

$$S = S_d * \frac{V_e}{\frac{4}{3}\pi(\frac{d}{2})^2}$$

S_d is the surface area of a emulsion droplet; V_e is the volume of the emulsion, d is the average particle size of the emulsion droplet under assuming the emulsion is homogeneous condition.

Calculations of TOF

TOF = (moles of substrate reacted) (moles of catalyst)$^{-1}$ (time)$^{-1}$

$TOF_{18C\text{-}silyl\text{-}POM}=146h^{-1}$; $TOF_{POM}=10h^{-1}$

References

1S. Landsmann, C. Lizandarapueyo and S. Polarz, *Journal of the American Chemical Society*, 2010, **132**, 5315-5321.

2 Knoth W H, *Journal of the American Chemical Society*, 1979, **101,** 2211-2213.

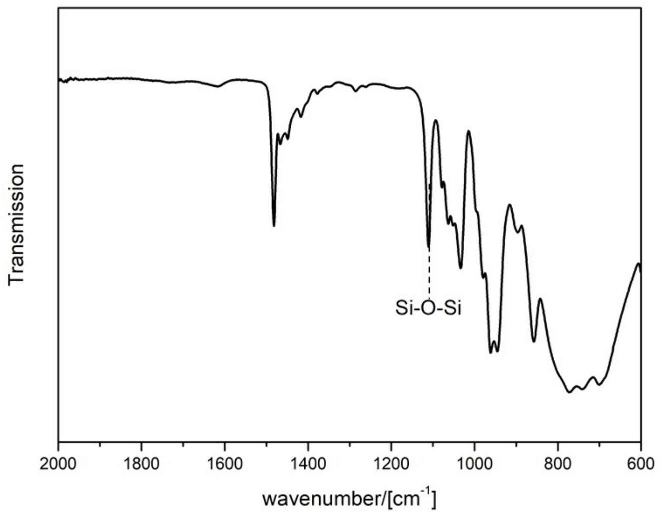


Fig. S1. FT-IR spectrum of 18C-silyl-POM

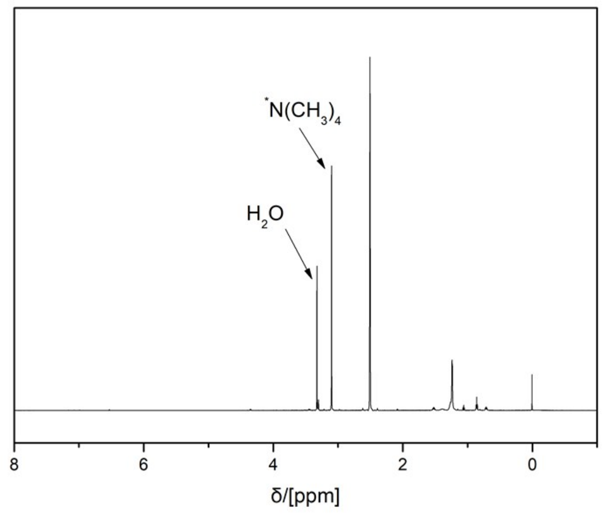


Fig. S2. ^{1}H NMR spectrum of 18C-silyl-POM

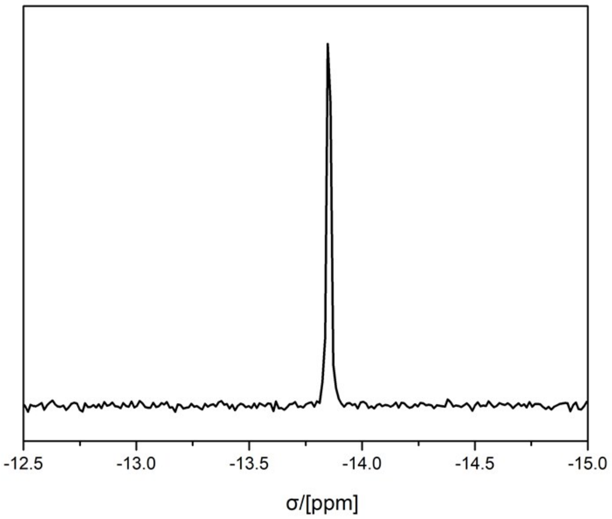


Fig. S3. ^{31}P NMR spectrum of 18C-silyl-POM

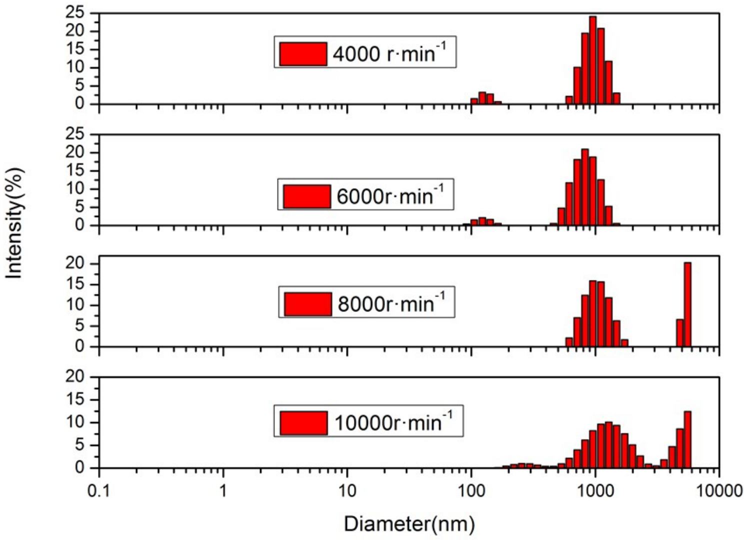


Fig. S4. Particle size distribution of emulsion formed at different stirring speeds.

Table S1. Particle size and interfacial area of emulsions formed at different rotational speeds, and yield of cyclohexanone

Stirring speed /r·min^{-1}	Particle size /nm	Interfacial area /nm^2	Selectivity of cyclohexanone/%	Yield of cyclohexanone /%	TOF /h
4000	1717	2.80×10^{19}	>99.9	53.2	267
6000	1088	4.41×10^{19}	>99.9	60.6	304
8000	2726	1.76×10^{19}	>99.9	38.5	193
10000	2037	2.36×10^{19}	>99.9	48.6	241

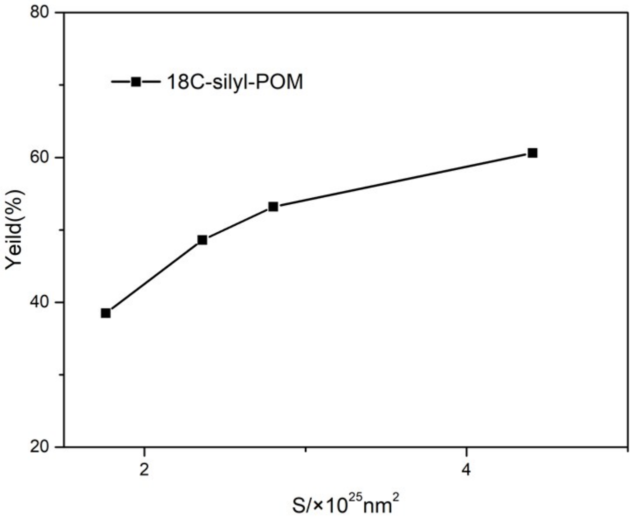


Fig. S5. Relationship curve of yield of cyclohexanone and interfacial area.

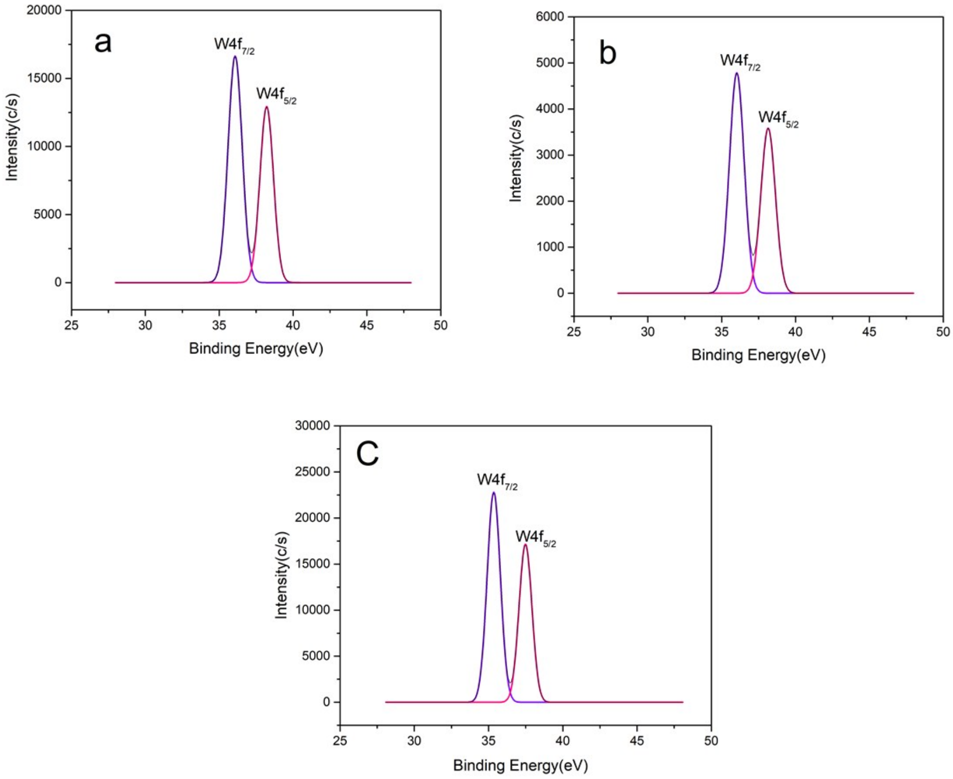


Fig. S6. W4f XPS spectra of 18C-silyl-POM after oxidation reaction(a), fresh 18C-silyl-POM(b) and POM(c).

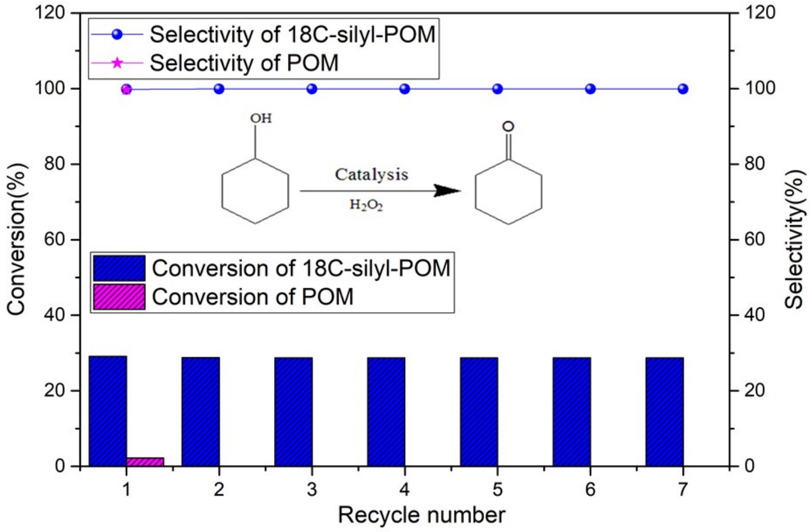


Fig. S7. Oxidation of cyclohexanol in the presence of POM and reusable 18C-silyl-POM.

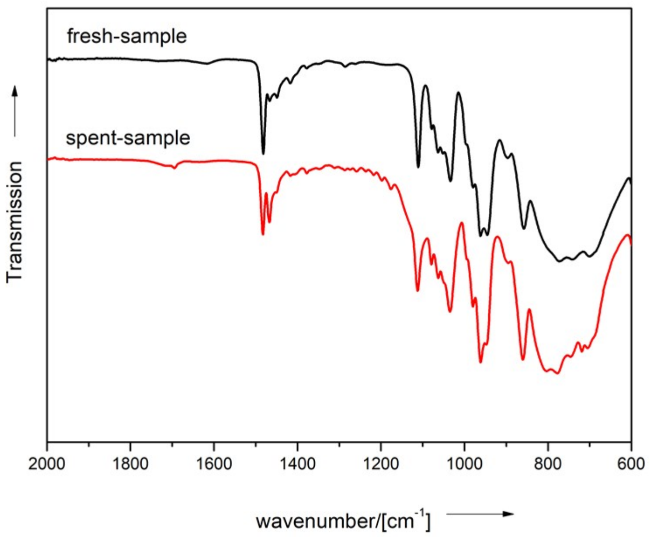


Fig. S8. FT-IR spectra of 18C-silyl-POM before(fresh-sample) and after reaction(spent-sample).

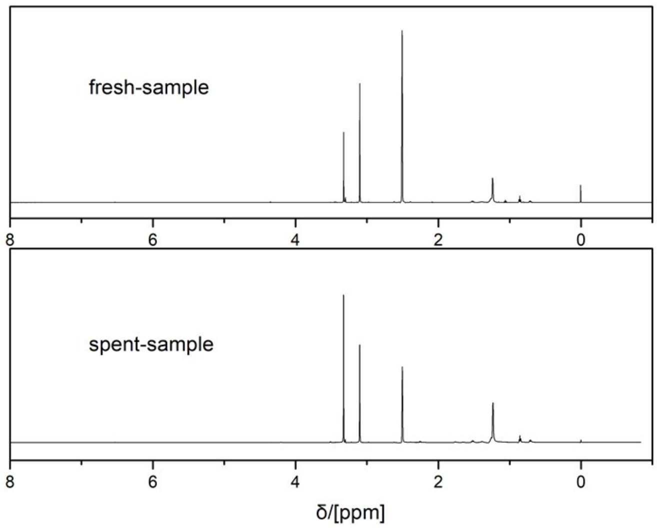


Fig. S9. ^{1}H NMR spectra of 18C-silyl-POM before(fresh-sample) and after reaction (spent-sample).

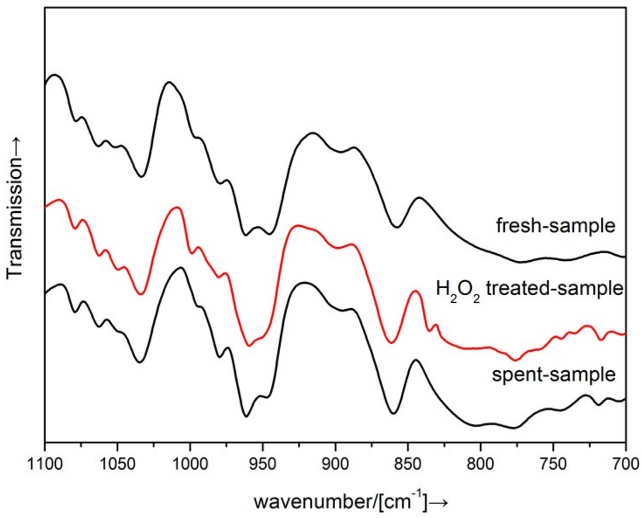
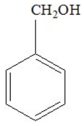
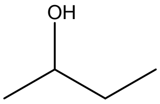


Fig. S10. FT-IR spectra of fresh 18C-silyl-POM, 18C-silyl-POM treated by H_2O_2 and 18C-silyl-POM after reaction.

Table S2. The average particle size and the interfacial area of the emulsion formed by different alcohols.

Entry	Substrate	Average particle size /nm	Interfacial area /nm^2	Selectivity /%	Yield /%
1		4812	9.98×10^{18}	>99.9	53.2
2		2160	2.22×10^{19}	>99.9	38.6
3		1173	4.09×10^{19}	>99.9	45.1
4		4918	9.76×10^{18}	>99.9	36.9

Reaction conditions: 3mL alcohol, 5mL 30% aqueous H_2O_2, 0.1g 18C-silyl-POM, 5h, room temperature.

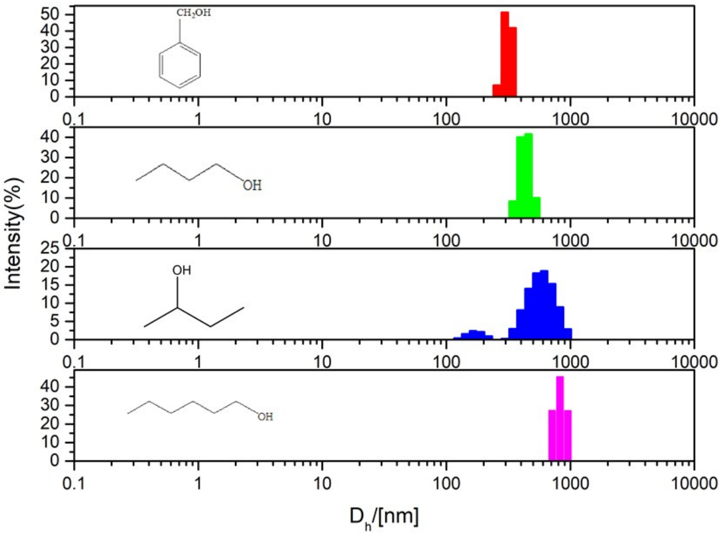


Fig. S11. Particle size distribution of emulsion formed by different alcohols and water.