Photooxygenation of Hydrocarbons over Efficient and Reusable Decatungstate Heterogenized on Hydrophobically Modified Mesoporous Silica

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Electronic Supplementary Information

1. Experimental details

1.1. Catalysts preparation

Mesoporous silica (SBA-15) was prepared following a literature procedure [Ref. S1] (pore diameter 6.7 nm, S_{BET} 757 $m^2 \cdot g^{-1}$). 2 g Pluronic P123 triblock polymer ($EO_{20}PO_{70}EO_{20}$, M_{av} =5800, Aldrich) was dissolved in 65 mL deionized H_2O at room temperature stirred until fully dissolved, followed by adding 10 mL concentrated HCl (36.5%) solution and heated to 40 °C in a water bath. Then 4.5 mL TEOS was added dropwise in the homogeneous solution with stirring. This gel mixture was continuously stirred at 40 °C for 20 h, and finally hydrothermally treated in a Teflon-lined autoclave at 96 °C for 24 h in an oven. The solid product was separated by centrifuge, filtered, washed with deionized water, and dried in air at room temperature and calcined at 550 °C for 5 h.

The organo-grafting procedure was as follows [Ref. S2]: typically 1 g of the calcined SBA-15 powder refluxed with an excess amount of $C_nH_{2n+1}Si(OC_2H_5)_3$ (1.3 mmol) in anhydrous toluene (50 mL) at 120 °C for 12 h. After refluxing, the reaction mixture was filtered off, washed with hot anhydrous toluene and dried in vacuum at 40 °C over night to obtain "C_n-SBA". Then 3-aminopropyl (AP) groups were grafted on "C_n-SBA" by refluxing 0.35 g (1.3 mmol) of 3-aminopropyl-triethoxysilane (APTES) in 50 mL anhydrous toluene to obtain "C_n-AP-SBA".

A series of catalysts having different alkyl-chain length was prepared by acidification of C_n-AP-SBA using trifluoromethanesulfonic acid and ion exchange by decatungstate [Ref. S3]. Typically, 0.75 g of C_n-AP-SBA was mixed with 0.35 g (2.3 mmol) of CF_3SO_3H and stirred in 10 mL CH_2Cl_2 for 8 h, and then filtered off, washed with EtOH (15 mL), Ether (15 mL) respectively and dried in vacuum at room temperature for 3 h. The obtained powder was mixed with 0.78 g (0.3 mmol) of $(n\text{-}Bu_4N)_4W_{10}O_{32}$ in CH_3CN(15 mL) and stirred for 24 h. A straw yellow powder was filtered off, washed with CH_3CN until lacking of the typical UV-vis spectrum of the decatungstate (λ_{max}=323 nm) for the washing filtrate, then washed with water (15 mL) and acetone (15 mL) respectively. Then the powder was dried in vacuum at room temperature over night to obtain W_{10}/ C_n-AP-SBA. The most active catalyst was W_{10}/ C_8-AP-SBA, and the final loading amount of $W_{10}O_{32}^{4-}$ was 12 % (determined by ICP analysis).

1.2. Characterization of the catalysts

The textural structures were measured by N_2 adsorption at -196 °C in a Micromeritics TriStar ASAP 3000 system, and specific surface areas of samples were calculated using Brunauer–Emmett–Teller (BET) method. The pore size distributions (average pore diameter and mean pore volume) were measured from the N_2 desorption isotherm using the cylindrical pore model (BJH method). Transmission electron micrographs were obtained using a JEOL 2011 microscope operating at accelerating voltage of 200 kV. The samples for electron microscopy were prepared by dispersing the powder in ethanol and applying a drop of very dilute suspension on copper grids. The suspensions were dried by slow evaporation at ambient temperature. The FT-IR spectra were recorded at 25 °C with a Bruker Vector33 spectrophotometer (instrument) by mixing the catalyst and KBr. UV-vis diffuse reflectance spectra (UV-vis) were obtained with a UV-vis spectrophotometer (Shimadzu UV-2450) using $BaSO_4$ as the reference sample.

1.3. Catalytic procedure

1.3.1 Experiment apparatuses

The photoreactor was designed with a cylindrical quartz cell configuration (50 mL) and the suspension which in the photoreactor was surrounded by an external light source. The temperature of the suspension was maintained at 5-10 ^{o}C by water circulation through an external cooling coil. The optical path-length was calculated 15 cm. The light source used was a 400 W high-pressure mercury lamp with a cutoff filter, cutting off wavelengths lower than 320 nm.

1.3.2 A typical procedure for photooxidation of alkanes

The heterocatalyst, substrate (1.7 mmol) and solvent (13 mL) were mixed and the suspension was stirred in the dark for 30 min with a 3 $mL \cdot min^{-1}$ flow of O_2 to obtain a good dispersion, adsorption and a pure O_2 atmosphere (101.3 KPa). After irradiation, the sample was centrifuged, the products that remained absorbed on the irradiated powders were extracted three times with CH_2Cl_2 (3×2 mL); the filtrate was then analyzed by GC using a Agilent 6890 series instrument equipped with a flame ionization detector (FID) and a HP-5MS capillary column. The determination of hydroperoxides was performed by a spectrophotometric standard method reported in the literature [Ref. S4]. The loss of substrate during the reaction and analysis was <5 % for all experiments performed. The identification of the products was done in a GC-MS spectrometer comparing with commercially pure products.

1.3.3 Recovery and reuse of the hetero-catalysts

The catalyst was collected after filtration washed with acetone and heated at 80 ^{o}C for 12 h. Then the catalyst was used for next reaction.

[Ref. S1]: (a) D.Y. Zhao, Q.S. Huo, J.L. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* 1998, ***120***, 6024; (b) D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* 1998, **279**, 548.

[Ref. S2]: (a) B. Karimi, M. Ghoreishi-Nezhad, J.H. Clark, *Org. Lett*, 2005, **7**, 625; (b) R.Y. Zhang, W. Ding, B. Tu, D.Y. Zhao, *Chem. Mater*, 2007, **19**, 4379;

[Ref. S3]: A. Molinari, G. Varani, E. Polo, S. Vaccari, A. Maldotti, *J. Mol. Catal. A: Chem*. 2007, **262**, 156.

[Ref. S4]: (a) A. Molinari, R. Amadelli, V. Carassiti, and A. Maldotti, *Eur. J. Inorg. Chem*, 2000, 91; (b) R.D. Malr and A.J. Graupner, *Analy. Chem*, 1964, **36**, 194.

2 Characterization results

2.1 UV-vis spectra of (A) $(Bu_4N)_4W_{10}O_{32}$; (B) C_8-AP-SBA; (C) W_{10}/C_8-AP-SBA

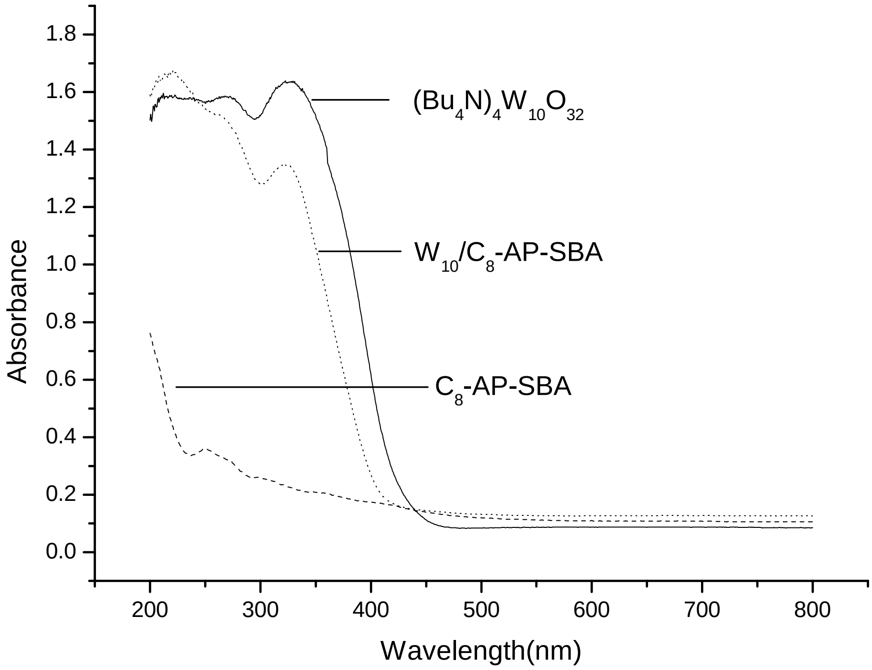

Fig S1

2.2 Physicochemical properties of the various functionalized catalysts and the SBA-15

Table S1

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
SBA-15	757	1.26	6.7
AP-SBA	613	0.98	6.4
C_8-AP-SBA	461	0.68	5.9
W_{10}/AP-SBA	498	0.76	6.1
W_{10}/C_2-AP-SBA	439	0.65	5.9
W_{10}/C_4-AP-SBA	415	0.6	5.8
W_{10}/C_8-AP-SBA	376	0.53	5.6
W_{10}/C_{16}-AP-SBA	327	0.43	5.3

2.3 TEM image of catalyst W_{10}/C_8-AP-SBA (A, B) before and (C, D) after reaction.

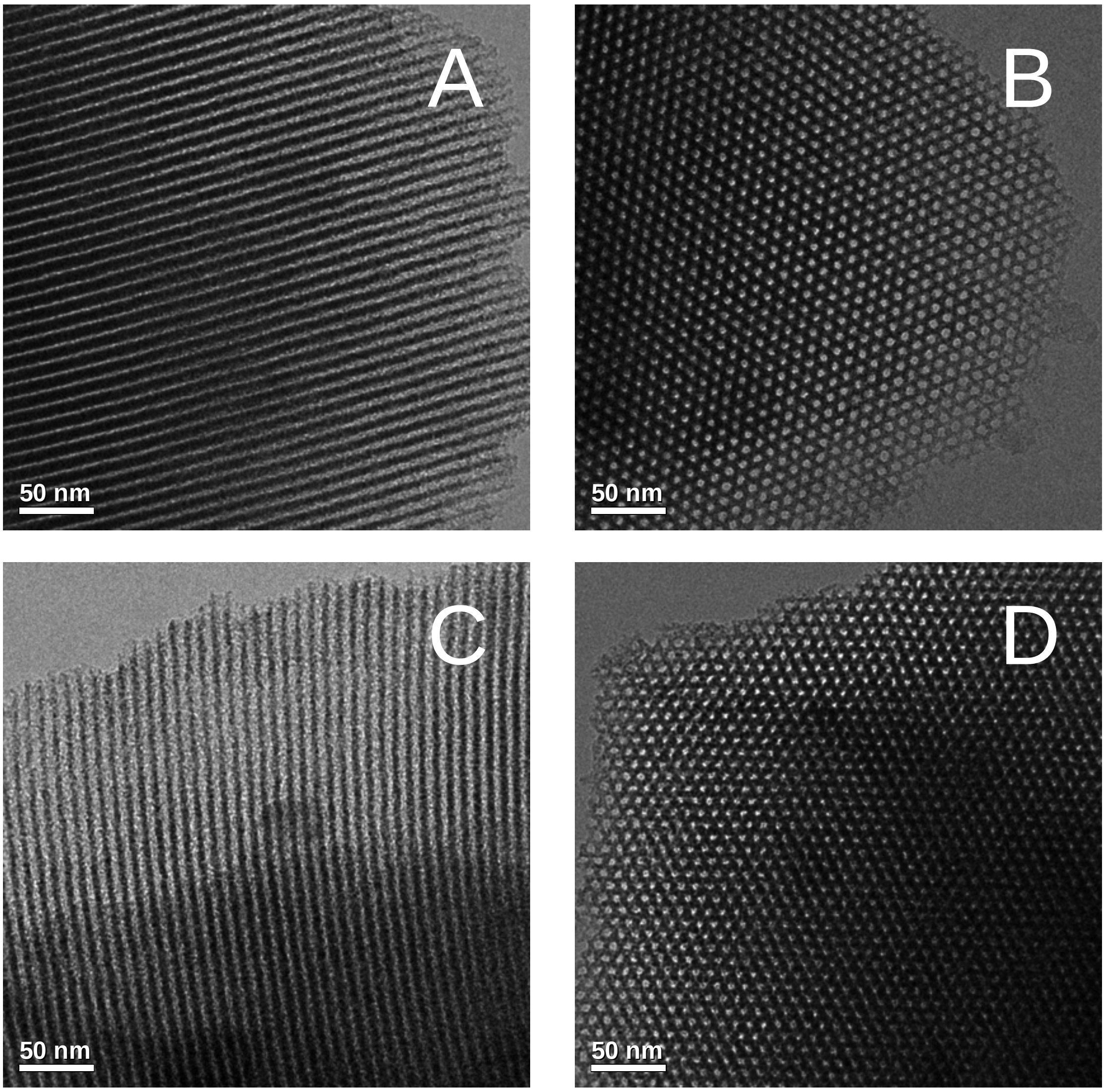

Fig S2

2.4 FT-IR spectra of (A) $(Bu_4N)_4W_{10}O_{32}$; (B) SBA-15; (C) C_8-AP-SBA; (D) W_{10}/C_8-AP-SBA before reaction; (E) W_{10}/C_8-AP-SBA after reaction for 6 times

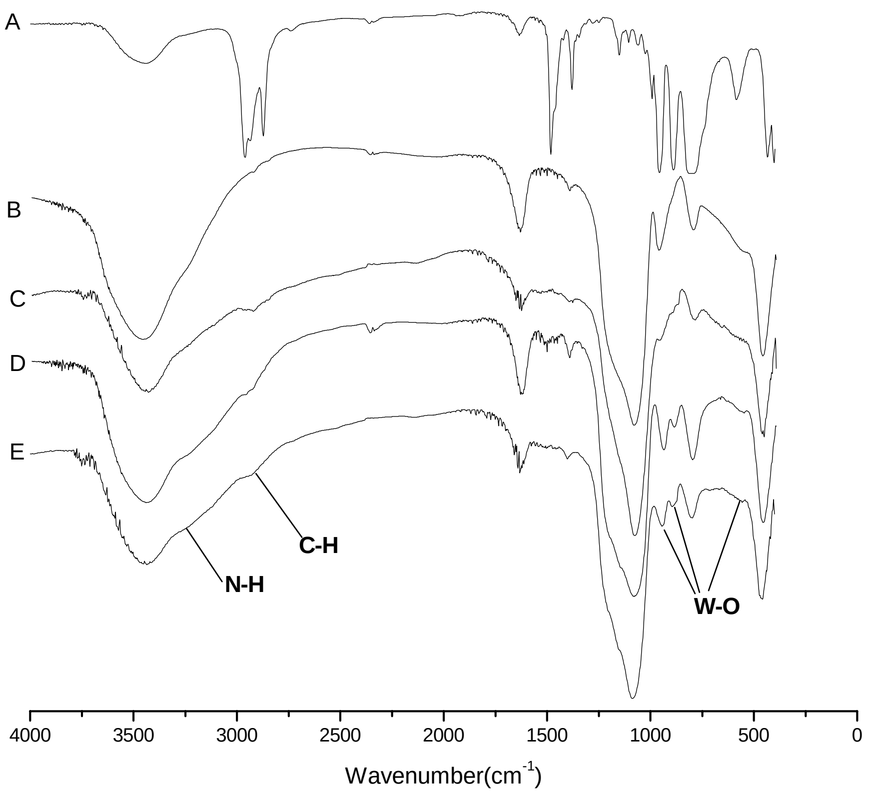

Fig S3

3 Photooxidation Reactions

3.1 O_2 photooxidation of ethylbenzene to acetophenone by (A) $(Bu_4N)_4W_{10}O_{32}$ in homogeneous and (B) W_{10}/C_8-AP-SBA in heterogeneous system using CH_3CN as solvent [black bars- mole fraction of 1-phenyl-ethylhydroperoxide in the photooxygenated products of ethylbenzene), grey bars- conversion (mol% ethylbenzene reacted)]

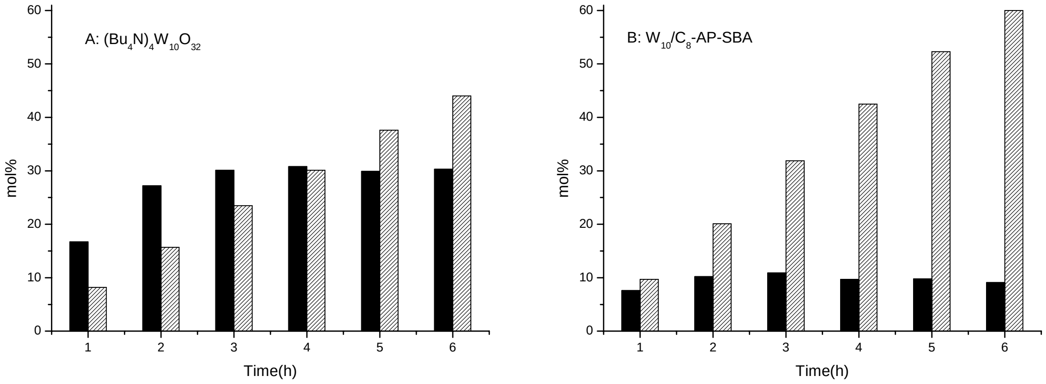

Fig S4

3.2 Comparison of photocatalytic activity and selectivity of decatungstate for ethylbenzene (Table S2) and cyclohexane (Table S3) oxygenation with different conditions used by different authors

Table S2.

Catalyst	Solvent	Reaction Time(h)	Major Product (Selectivity, mol%)	TOF(h^{-1})	Ref.
W_{10}/C_8-AP-SBA	CH_3CN/H_2O (1:1 v/v)	6	Acetophenone(96.5)	44	This work
$(Bu_4N)_4W_{10}O_{32}$	CH_3CN	24	Acetophenone(76)	5	1
$(Bu_4N)_4W_{10}O_{32}$-Et_3SiH	CH_3CN	4	Acetophenone(84)	13	2
$TBAW_{10}$-HF	neat	4	Acetophenone(20) 1-Phenylethanol(66)	110	3
R_fNW10-HF	neat	4	Acetophenone(38) 1-Phenylethanol(46)	861	3

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2. I.N. Lykakis, M. Orfanopoulos, *Tetrahedron. Lett.*, 2004, **45**, 7645.
3. M. Carraro, M. Gardan, G. Scorrano, E. Orioli, E. Fontananova and M. Bonchio, *Chem. Commun.*, 2006, 4533.

Table S3.

Catalyst	**Solvent**	**Reaction Time(h)**	**Major Product (Selectivity, mol%)**	**TOF(h^{-1})**	**Ref.**
W_{10}/C_8-AP-SBA	CH_3CN/H_2O (1:1 v/v)	6	Cyclohexanone(97.5)	48	This work
$(Bu_4N)_4W_{10}O_{32}/SiO_2$	CH_2Cl_2	1.5	Cyclohexanone(50) Cyclohexanol(50)	16.5	1
$(Et_4N)_4W_{10}O_{32}/SiO_2$	neat	4	Cyclohexanone(50) Cyclohexanol(50)	8.4	2
$(Et_3NH)_4W_{10}O_{32}/SiO_2$	neat	4	Cyclohexanone(56.5) Cyclohexanol(43.5)	9.9	2
$(Me_4N)_4W_{10}O_{32}/SiO_2$	neat	4	Cyclohexanone(54) Cyclohexanol(46)	9.6	2
$(NH_4)_4W_{10}O_{32}/SiO_2$	neat	4	Cyclohexanone(60) Cyclohexanol(40)	3	2
$Na_4W_{10}O_{32}/SiO_2$	neat	4	Cyclohexanone(76) Cyclohexanol(24)	1.5	2
W30%/MCM-41	CH_2Cl_2	2	Cyclohexanone(70) Cyclohexanol(30)	0.62	3

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2. A.Molinari, R. Amadelli, A. Mazzacani, G. Sartori, A. Maldotti, *Langmuir.*, 2002, **18**, 5400.
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