Electronic Supplementary Information (ESI) for

Metal-free mesoporous SiO$_2$ nanorods as a highly efficient catalyst for the Baeyer–Villiger oxidation under mild conditions

Xueyao Zhang, Honglei Yang, Guangxue Yang, Shuwen Li, Xiang Wang and Jiantai Ma*

State Key Laboratory of Applied Organic Chemistry (SKLAOC), Gansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Tianshui South Road 222, Lanzhou 730000, PR China.

E-mail: majiantai@lzu.edu.cn; Fax: +86-931-8912582; Tel: +86-931-8912577

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Experimental Section

Materials

Hexadecyl trimethyl Ammonium Bromide (CTAB), ammonia ($NH_3 \cdot H_2O$) were purchased from Tianjin Guangfu Fine Chemical Research Institute. TEMPO and PBN were purchased from J&K Chemical Co. Ltd. Cyclohexanone, Benzaldehyde and 1,2-Dichloroethane were purchased from Tianjin Kaixin Chemical Co. Ltd. Tetraethoxysilane (TEOS) ethanol and other solvents, which were analytical grade and used without further purification, were obtained from Tianjinshi Baishi Chemical Co. Ltd. Deionized water was used throughout the experiments.

Synthesis of $mSiO_2$ rods

Mesoporous SiO_2 rods was prepared through the method given in previous reports. H_2O, EtOH and $NH_3 \cdot H_2O$ were mixed, and then CTAB was dissolved in above solution. After stiring for 15 minutes, TEOS was added dropwise to the solution along with the clear solution turning opaque quickly. The solution was magnetically stirred for 2 h and the white precipitate was collected by filtration, washing with large amount of deionized water. The white powders were dried in air at 60 ^{o}C. The templates were removed by calcining the products at 550 ^{o}C for 10 h; thus the mesoporous silica material was obtained. The molar ratios of reactants in the resulted material were 1 TEOS: x H_2O: 20 EtOH: 10.3

NH$_3$·H$_2$O: 0.3 CTAB. x ranged from 248 to 1486.

Characterization of the catalyst mSiO$_2$ rods

The synthesized catalyst was confirmed by corresponding characterization means.

Powder X-ray diffraction (XRD) patterns were carried out at room temperature and performed on a Rigaku D/max-2400 diffractometer using Cu-Ka radiation as the X-ray source in the 2θ range of 0.5-4 for small angle. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer with a DTGS detector, and samples were measured with KBr pellets. FT-IR spectra of pyridine adsorption were carried out on a Nicolet Nexus 670 FT-IR spectrometer with a spectral resolution of 4 cm^{-1} in absorbance mode. The pyridine adsorption was realized by exposing the wafer to the corresponding vapors at room temperature for 1 h after the specimen was dehydrated at 723 K for 2 h to remove any water in the material. The FT-IR spectra of adsorbed pyridine were collected for 1 h as the desorption temperature was increased from 323 to 473 K. The morphology and microstructure of mSiO$_2$ rods were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images was recorded on a Hitachi S-4800 (Chiyoda-ku, Tokyo, Japan) operated under high vacuum with an accelerating voltage of 7 kV. The TEM images were

obtained through Tecnai G2 F30 electron microscope operating at 300 kV, and the samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporating the solvent in air at room temperature. N_2 physical sorption was carried out on micromeritics ASAP2020 volumetric adsorption analyzer (before the measurements, samples were out gassed at 200 ℃ for 6 h). The Brunauer–Emmett–Teller (BET) surface area was evaluated from data in the relative pressure range from 0.05 to1.0. The total pore volume of each sample was estimated from the amount adsorbed at the highest P/P_0 (above 0.99). Pore diameters were determined from the adsorption branch using Barrett–Joyner–Halenda (BJH) method and Density Functional Theory (DFT) method. The conversion was estimated by GC-MS (Agilent 6,890N/5,973N). EPR spectra were obtained by Bruker A300 electron paramagnetic resonance spectroscopy.

Table S1 Optimization conditions of the B-V reaction with EtOAc
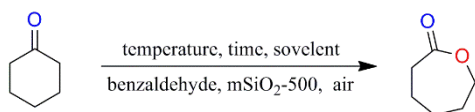
Entry	Amount of catalyst (mg)	Temperature (℃)	Time (h)	solvent	Yield [a] (Sel.) (%)
1	10	50	5	EtOAc	72 (>99)
2	15	50	5	EtOAc	77 (>99)
3	20	50	5	EtOAc	92 (>99)
4	25	50	5	EtOAc	82 (>99)
5	30	50	5	EtOAc	79 (>99)
6	35	50	5	EtOAc	75 (>99)
7	40	50	5	EtOAc	67 (>99)
8	25	20	5	EtOAc	54 (>99)
9	25	30	5	EtOAc	61 (>99)
10	25	40	5	EtOAc	74 (>99)
11	25	60	5	EtOAc	72 (>99)
12	20	50	1	EtOAc	40 (>99)
13	20	50	2	EtOAc	53 (>99)
14	20	50	3	EtOAc	72 (>99)
15	20	50	4	EtOAc	86 (>99)
17	20	50	6	EtOAc	91 (>99)

[a] The yield and selectivity were determined by GC–MS based on the internal standard method (dodecane)

Table S2 The source of oxygen for the B-V oxidation reaction [a]

Entry	The source of oxygen	Yield [b] (Sel.) (%)
1	O_2 balloon	>99 (>99)
2	Open air	74 (>99)
3	Pumping air	>99 (>99)
4	N_2 balloon	— (—)
5 [c]	H_2O_2	9% (26%)

[a] Reaction conditions: cyclohexanone (2mmol), benzaldehyde (2.0 equiv.), dodecane (1 mmol), mSiO$_2$-500 25 mg, in DCE (5mL), 50℃, 5 h

[b] The yield and selectivity were determined by GC–MS based on the internal standard method (dodecane) [c] Reaction conditions: cyclohexanone (2mmol), H_2O_2 (12 mmol (approx.)), 25 mg mSiO$_2$ nanorods, 50 ^{o}C for 5 h under argon atmosphere.

Table S3. The B-V oxidation reaction of various aldehydes [a]

Entry	aldehyde	Amount of aldehyde	Yield of Ɛ-Caprolactone [b] (Sel.) (%)
1	bezaldehyde	1 equiv	61 (>99)
2	bezaldehyde	1.5 equiv	94 (>99)
3	bezaldehyde	2 equiv	>99 (>99)
4	bezaldehyde	2.5 equiv	>99 (>99)
5	bezaldehyde	3 equiv	>99 (>99)
6	Formaldehyde solution	2 equiv	trace
7	Paraformaldehyde [c]	2 equiv	trace
8	glyoxal	2 equiv	trace
9	chloroacetaldehyde	2 equiv	trace
10	propenal	2 equiv	trace
11	propionaldehyde	2 equiv	trace
12	n-butanal	2 equiv	21 (>99)
13	n-heptanal	2 equiv	45 (>99)
14	p-phthalaldehyde	2 equiv	60 (>99)
15	p-nitrobenzaldehyde	2 equiv	57 (>99)
16	p- bromobenzaldehyde	2 equiv	81 (>99)
17	p-chlorobenzaldehyde	2 equiv	86 (>99)

[a] Reaction conditions: cyclohexanone (2mmol), mSiO$_2$-500 25 mg, in

DCE (5mL), 50℃, 5 h, pumping air [b] The yield and selectivity were determined by GC–MS [c] the reaction temperature was 120℃

Table S4 Oxidation of Cyclohexanone by m-Chloroperoxybenzoic Acid [a]

catalyst	Conversion (%)	Yield (%)	Selectivity (%)
mSiO$_2$ nanorods	99	99	>99
no catalyst	93	93	>99

[a] reaction conditions: cyclohexanone, 1.0 mmol, m-CPBA, 1.0 mmol, mSiO$_2$ nanorods 12 mg; 1,2-dichloroethane, 5 mL; O$_2$; 50 °C.
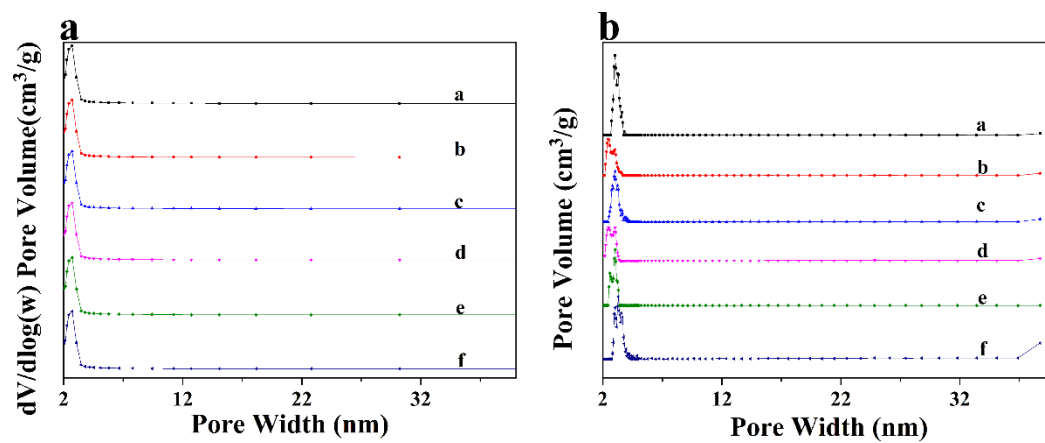
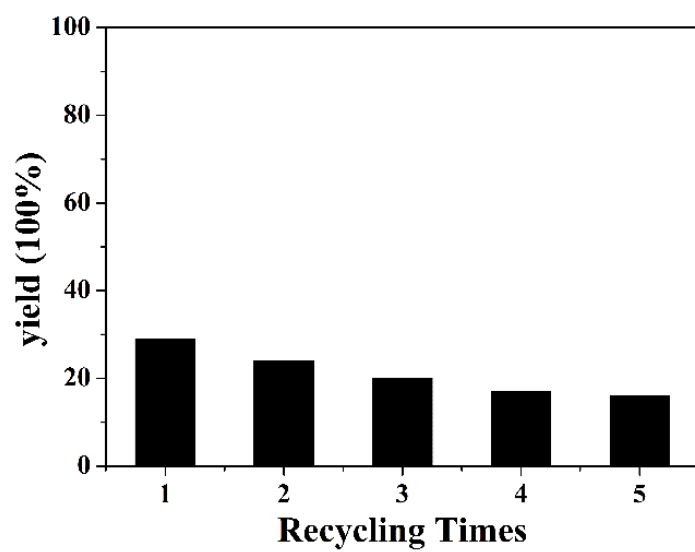Fig. S1 The pore size distribution of mSiO$_2$ nanoparticles measured by (a) BJH method and (b) DFT method

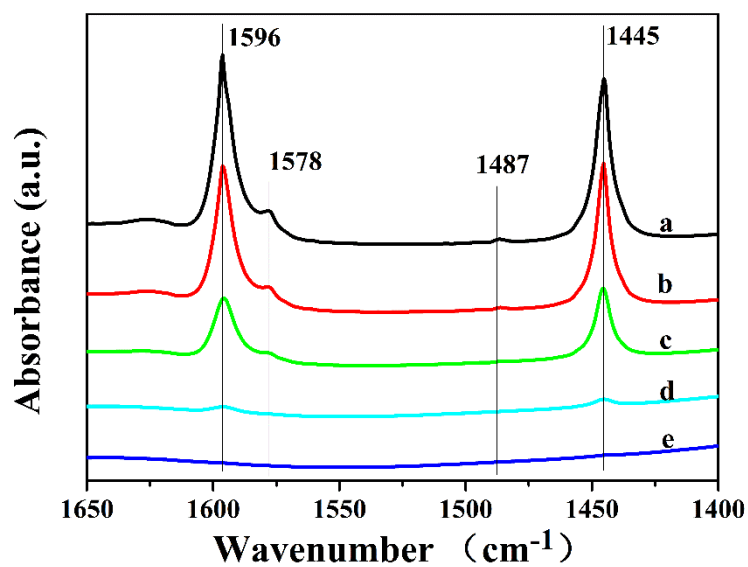Fig. S2 Recycling experiments of the mSiO$_2$ nanorods catalyst

Fig. S3 FT-IR spectra of mSiO$_2$ nanorods after pyridine adsorption at room temperature for 1 h and desorption at (a) 50 ^{o}C (b), 85 ^{o}C (c) 100 ^{o}C (d) 150 ^{o}C and (e) 200 ^{o}C for 1 h, respectively.