Phosphorus-doped macroporous carbon spheres for high

efficiency selective oxidation of cyclooctene by air

Supplementary Information

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Experiment Details

1. Catalysts preparation

1.1 Materials

Tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), aqueous ammonia solution (NH₃·H₂O, 28 wt %), glucose, ethanol, silicone oil, hydrofluoric acid, hydrazine hydrate and hexane were all purchased from Aladdin Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Phytic acid, cyclooctene (95 %), p-benzoquinone (BZQ) and tert-butyl hydroperoxide (TBHP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Deionized water was prepared in our laboratory and applied in all treatment processes needed.

1.2 Preparation of colloidal silica beads

Monodispersed silica colloidal crystal particles with a diameter of about 150 nm were prepared via the Stöber sol-gel method,¹ and washed by deionized water for three times. Colloidal silica beads were prepared from silica colloidal crystal particles by using adeveloped stirring-assembly technique.² Typically, the colloidal silica crystal particles (3 mL, concentration of 30 % in water) and silicone oil (10 mL) were stirred at constant angular velocity (ca. 500 rpm) using a stirrer at room temperature for 2 h, and the uniform emulsion droplets were formed in the suspension liquid. Then colloidal crystallization of the emulsion droplets gradually occurred when water in the droplets was evaporated at 333 K. After about 72 h, colloidal silica crystal beads were formed. Finally after solidification, the colloidal silica crystal beads were washed by hexane thoroughly to remove the silicone oil and finally calcined at 1173 K before use. **1.3 Synthesis of macroporous carbon spheres with different contents of phosphorus (PMCS, PMCS-4, PMCS-2 and NPMCS)**

The macroporous carbon spheres with different content of phosphorus were prepared by loading different contents of phytic acid and glucose into the colloidal silica crystal beads, followed by removal of the silica templates.

1.3.1 Synthesis of PMCS

Typically, 0.2 g of colloidal silica beads was immerged into 5 mL of phytic acid. The mixture was kept at 373 K for 6 h and then heated to 433 K and kept for 6 h. The mixture was treated again at 373 and 433 K after adding another 5 mL of phytic acid. Further carbonization was carried out by heating the resulting material to 1173 K with

a ramping rate of 10 K/min and kept for 6 h under nitrogen atmosphere. The composite was washed with hydrofluoric acid at room temperature to remove the silica templates. The obtained phosphorus-doped macroporous carbon spheres were washed by ethanol and deionized water, respectively, and finally dried at 333 K for further use.

1.3.2 Synthesis of PMCS-4

0.2 g of colloidal silica beads was immerged into a solution composed of 5 mL phytic acid, 0.15 g glucose and 5 mL H₂O. The mixture was kept at 373 K for 6 h and then heated to 433 K and kept for 6 h. The following synthesis condition and process were the same as PMCS.

1.3.3 Synthesis of PMCS-2

0.2 g of colloidal silica beads was immerged into a solution composed of 5 mL phytic acid, 0.25 g glucose and 10 mL H₂O. The mixture was kept at 373 K for 6 h and then heated to 433 K and kept for 6 h. The next synthesis condition and process were the same as PMCS.

1.3.4 Synthesis of NPMCS

We immersed 0.2 g of colloidal silica beads into the solution of 0.2 g glucose and 10 mL H₂O. The mixture was kept at 373 K for 6 h and then heated to 433 K and kept for 6 h. The mixture was treated again at 373 and 433 K after adding another 0.2 g glucose and 10 mL H₂O. The next synthesis condition and process were the same as PMCS.

1.4 Synthesis of non-porous structural carbon material with 6 % content of phosphorus (NPC)

NPC was prepared by carbonizing 10 mL phytic acid without the silica templates. 5 mL phytic acid was kept at 373 K for 6 h and then heated to 433 K and kept for 6 h. It was kept at 373 and 433 K again after adding another 5 mL of phytic acid. The next synthesis condition and process were the same as PMCS.

2. Catalytic selective oxidation of cyclooctene

The catalytic selective oxidation of cyclooctene using phosphorus-doped macroporous carbon spheres (PMCS) was carried out in a 50 mL round-bottom flask with condenser pipe and continuous magnetic stirrering. 50 mg PMCS and 0.12 g tert-butyl hydroperoxide (TBHP) were put into 10 mL cyclooctene (95 %). The mixture was stirred for 48 h at 353 K. The samples were collected every 6 h before 24 h and every 12 h after 24 h. After filtering off the catalyst, the filtrate was analyzed by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS).

The control experiments used PMCS-4, PMCS-2, NPMCS and NPC, the experiment conditions of which were the same as the process above.

3. Characterization

The scanning electron microscopy (SEM) images were taken on a FEI-quanta 200 scanning electron microscope with the acceleration voltage of 20 kV with EDS analyses. The transmission electron microscopy (TEM) images were obtained with a FEI/Philips Tecnai 12 BioTWIN transmission electron microscope operated at 200 kV. The TEM samples were prepared by dropping the solution onto a copper grid covered with carbon film and dried in air. Raman spectrum was collected on an HR 800

Raman spectroscope (J Y, France) equipped with a synapse CCD detector and a confocal Olympus microscope. The spectrograph uses 600 g mm⁻¹ gratings and a 633 nm He-Ne laser. The Fourier Transform Infrared (FT-IR) spectrum was obtained with a Nicolet 360 spectrometer. Brunauer-Emmett-Teller (BET) specific surface areas and pore size distributions were calculated by plotting the adsorption isotherm of N₂ at liquid N₂ temperature (77 K). These measurements were made on a Micromeritics ASAP 2050 porosimeter. The X-ray diffraction (XRD) patterns were obtained on an X'Pert-ProMPD (Holand) D/max-γAX-ray diffractometer using Cu Kα radiation $(\lambda=0.154178 \text{ nm})$. For XRD observations, the samples were dispersed in ethanol and then dried on a quartz film. The X-ray photoelectron spectroscopy (XPS) was obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatized Mg Ka X-ray. The gas chromatography measurements (GC-MS) were performed in a Varian 3400 GC column with a cross-linked 5 % PhMe silicone column (25 m \times 0.20 mm \times 0.33 µm) and a FID detector under the following conditions: carrier gas (N₂) at 140 K; temperature program 333 K, 1 min, 15 K/min, 453 K, 15 min; split ratio, 10 : 1; injector, 573 K; detector, 573 K.



Fig. S1 (a) SEM image of monodispersed silica colloidal crystal particles. (b) SEM image of colloidal silica crystal bead.



Fig. S2 EDS spectra of (a) NPMCS, (b) PMCS-2, (c) PMCS-4 and (d) NPC, respectively.



Fig. S3 Fourier transform infrared (FT-IR) spectra of NPMCS, PMCS-4, PMCS-2 and NPC.



Fig. S4 Raman spectra of NPMCS, PMCS-4, PMCS-2 and NPC.

	Product sele	ectivity (%)						
Reaction time (h)		o	Conversion (%)	$\Sigma_{sel}C_{8\S}$				
0	0	0	0	0				
6	65.57	32.60	5.89	98.17				
12	68.64	29.19	12.26	97.83				
18	71.47	25.95	17.65	97.42				
24	74.02	23.29	24.68	97.31				
36	80.76	16.22	38.16	96.98				
48	88.47	8.37	50.69	96.84				
^a Reaction conditions: PMCS (0.05 g), cyclooctene (10 mL), TBHP (0.12 g), 353 K. § Total selectivity to C ₈ partial oxidation products.								

Table S1. Effect of reaction time on selective oxidation of cyclooctene using PMCS as catalysts.^a

Table S2. Elemental compositions of NPMCS, PMCS-2, PMCS-4, PMCS and NPC,

respectively.

Samples	C (wt %)	O (wt %)	P (wt %)
NPMCS	75.40	24.60	0
PMCS-2	77.66	20.17	2.17
PMCS-4	75.61	20.49	3.90
PMCS	70.43	23.52	6.05
NPC	69.77	24.21	6.02

Table S3. Effect of the amount of phosphorus among macroporous carbon spheres on selective oxidation of cyclooctene.^a

		Product selec			
Catalysts	COP (%)		o	Conversion (%)	$\Sigma_{sel}C_{8\S}$
NPMCS	0	77.43	16.19	25.01	93.62
PMCS-2	2	79.24	14.79	31.73	94.03
PMCS-4	4	81.76	14.14	37.56	95.90
PMCS	6	88.47	8.37	50.69	96.84

^aReaction conditions: macroporous carbon spheres with different amount of phosphorus (0.05 g), cyclooctene (10 mL), TBHP (0.12 g), 353 K.

§ Total selectivity to C₈ partial oxidation products.

Table S4	1. Effect	of the	macroporou	s structure	on sel	lective	oxidation	of cvc	clooctene.ª	ι

		Product se	lectivity (%)		
Catalysts	Macroporous structure	\bigwedge^{\bullet}	0	Conversion (%)	$\Sigma_{sel}C_{8\S}$
PMCS	Yes	88.47	8.37	50.69	96.84
NPC	No	81.31	11.49	20.14	92.80

^aReaction conditions: as-synthesized catalysts (0.05 g), cyclooctene (10 mL), TBHP (0.12 g), 353 K.

 $\$ Total selectivity to C_8 partial oxidation products.

Table	S5.	Effect	of	PMCS	processed	by	hydrazine	hydrate	as	catalyst	on	selective
oxidati	on c	of cyclo	oct	tene. ^a								

	Product sele	ectivity (%)							
Reaction conditions	\bigcirc	O	Conversion (%)	$\Sigma_{sel}C_{8\$}$					
PMCS without	88.47	8.37	50.69	96.84					
hydrazine hydrate									
PMCS with hydrazine	80.14	14.33	18.70	94.47					
hydrate									
^a Reaction conditions: ca	^a Reaction conditions: catalysts (0.05 g) or without catalysts, cyclooctene (10 mL),								
ТВНР (0.12 g), 353 К.									

§ Total selectivity to C₈ partial oxidation products.

Table S	S6.	Effect	of	with	or	without	catalysts	on	selective	oxidation	of	cyclooctene
(blank r	eac	tions). ^a	ı									

	Product sel	ectivity (%)						
Reaction conditions	\bigwedge^{\bullet}	o	Conversion (%)	$\Sigma_{sel}C_{8\S}$				
With catalysts (PMCS)	88.47	8.37	50.69	96.84				
Without catalysts (PMCS)	Trace	Trace	Trace	0				
^a Reaction conditions: catalysts (0.05 g) or without catalysts, cyclooctene (10 mL),								
TBHP (0.12 g), 353 K.§ Total selectivity to C_8 partial oxidation products.								

Notes and references

W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci., 1968, 26, 62.
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