Supporting information

Singlet Oxygen-Promoted One-Pot Synthesis of Highly Ordered Mesoporous Silica Materials via the Radical Route

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Fig. S15 The hydrolysis rate of TEOS in different system at identical pH value of 3.1.

Fig. S16 XRD patterns of the samples one-pot synthesized in the (NH$_4$)$_2$Ce(NO$_3$)$_6$ system and Na$_2$S$_2$O$_8$ system at identical pH value of 3.1.

Fig. S17 The TEM image and EDS mapping (Fe: red, O: yellow, Si: green) of the Fe-SBA-15 sample synthesized by the one-pot route.

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Fig. S20 The low-angle XRD pattern (A), SEM image (B), nitrogen adsorption-desorption isotherm (C) and the pore size distribution (D) of the MSU-4 materials one-pot synthesized in the (NH$_4$)$_2$Ce(NO$_3$)$_6$ system.

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Fig. S22 Gibbs free energy profile and optimized geometry of the structures involved in the incorporation of Ce and/or Fe within the mesoporous silica materials.

Table S1. Physicochemical properties of calcined samples prepared using different methods.
1. Experimental section

1.1 Reagents

Tetraethyl orthosilicate (TEOS, 98%, Tianjin Fuchen Chemical Reagents Factory)
Polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymers (P123, average Mn~5800, Sigma-Aldrich Co.)
Hydrochloric acid (HCl, AR, wt.%:36.0~38.0, Beijing Chemical Works)
Ferrous sulfate heptahydrate (99%, Sinopharm Chemical Reagent Co., Ltd.)
H₂O₂ (30% (v/v), Beijing Chemical Works)
Sodium persulfate (98%, Sinopharm Chemical Reagent Co., Ltd)
5,5-Dimethylpyrroline-N-oxide (DMPO, Sigma-Aldrich Co.)
2,2,6,6-tetramethyl-4-piperidinol-N-oxyl (TMPN, Sigma-Aldrich Co.)
Ceric ammonium nitrate (CAN, Sinopharm Chemical Reagent Co., Ltd)
L-histidine (Sinopharm Chemical Reagent Co., Ltd)
Tween 60 (Sinopharm Chemical Reagent Co., Ltd)

1.2 One-pot synthesis of samples

(NH₄)₂Ce(NO₃)₆ system:

1 g of P₁₂₃ was dissolved in 50 g of deionized water and TEOS (4.5 g) was mixed with a different amounts (0.005 g, 0.02 g, 0.08 g, 0.1 g, 0.16 g, 0.2 g) of (NH₄)₂Ce(NO₃)₆. The mixture was stirred vigorously for 24 h at 313 K (precursor) and then was transferred into an autoclave, aged for 72 h at 373 K. The resultant solid was filtered, washed, and dried at 333 K for 15 h. After calcined at 823 K for 10 h, the samples1-6 were obtained.

0.78 g of Tween 60 was dissolved in 50 g of deionized water and TEOS (1.43 g) was mixed with a trace amount (0.0125 g) of (NH₄)₂Ce(NO₃)₆. The mixture was stirred vigorously for 24 h at 318 K (precursor) and then was transferred into an autoclave, aged for 24 h at 373 K. The resultant solid was filtered, washed, and dried at 333 K for 15 h. After calcined at 823 K for 10 h, the sample 9 was obtained.

Fenton reagents system:

1 g of P₁₂₃ was dissolved in 50 g of deionized water and TEOS (4.5 g) was mixed with a trace amount (0.01 g) of FeSO₄·7H₂O and 300μL 30wt%H₂O₂. The mixture was stirred vigorously for 24 h at 313 K (precursor) and then was transferred into an autoclave, aged for 72 h at 373 K. The resultant solid was filtered, washed, and dried at 333 K for 15 h.
After calcined at 823 K for 10 h, the sample 7 (Fe-SBA-15) was obtained.

0.78 g of Tween 60 was dissolved in 50 g of deionized water and TEOS (1.43 g) was mixed with a trace amount (0.02 g) of FeSO$_4$$\cdot$7H$_2$O and 300 $\mu$L 30 wt% H$_2$O$_2$. The mixture was stirred vigorously for 24 h at 318 K (precursor) and then was transferred into an autoclave, aged for 24 h at 373 K. The resultant solid was filtered, washed, and dried at 333 K for 15 h. After calcined at 823 K for 10 h, the sample 10 was obtained.

Na$_2$S$_2$O$_8$ system:

1 g of P$_{123}$ was dissolved in 50 g of deionized water and TEOS (4.5 g) was mixed with a trace amount (0.0087 g) of Na$_2$S$_2$O$_8$. The mixture was stirred vigorously for 24 h at 313 K (precursor) and then was transferred into an autoclave, aged for 72 h at 373 K. The resultant solid was filtered, washed, and dried at 333 K for 15 h. After calcined at 823 K for 10 h, the sample 8 (disordered structure material) was obtained.

1.3 Release experiment

Ce-SBA-15: 10 ml of 20% hydrochloric acid was added to 0.2 g of Ce-SBA-15 sample and stirred at room temperature for 5 minutes. After that, the sample was centrifuged and dried. ICP and small angle XRD detection were used to compare the difference between the acquired sample and the original Ce-SBA-15 sample.

Fe-SBA-15: 10 ml of 20% hydrochloric acid was added to 0.2 g of Fe-SBA-15 sample and stirred at room temperature for 5 minutes. After that, the sample was centrifuged and dried. ICP and small angle XRD detection were used to compare the difference between the acquired sample and the original Fe-SBA-15 sample.

1.4 Calculation of samples yields

The yields were calculated by the formula below based on the SiO$_2$:

$$\text{Yield} = \frac{\text{Weight of calcined sample}}{\text{Theoretical weight of SBA-15/MSU-4}}$$

The theoretical weight of SBA-15/MSU-4 was calculated according to the mole of SiO$_2$ from TEOS.

1.5 Theoretical calculation

In this work, we used Gaussian 16 software$^{[1]}$ for all calculations within the framework of DFT. All the molecular structures were computed with the B3LYP (Becke, three-parameter, Lee-Yang-Parr) hybrid functional$^{[2]}$ to describe the exchange–
correlation energies. Basis sets were employed for high-level B3LYP calculations at 6-31+G(d,p) was adopted for atoms including C, O, Si, and H \cite{3}. Vibrational frequency calculations were performed on all minima states, and each minimum was identified to have no imaginary frequencies.

The reaction pathway is as follow: TEOS interacts with the $^{1}\text{O}_2$ leading to a Gibbs free energy of 3.35 kcal/mol. The first transition states ascribed by formation of OOH group for $^{2}\text{O}_2$ via obtaining a H atom from the CH$_2$ group. The second transition state is contributed by formation of OH and CH$_3$CHO-O-Si group (dissociation of O-O bond in the OOH). The C atom only bonded with the O atom obtains the H atom, forming CH$_3$COOH. The OH group interacts with the Si atom, leading to the final products. The rate-determining step is break of the O-O bond.

2. Characterizations

XRD patterns were recorded on a Bruker D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) (40 kV and 40 mA) over the range 0.5-5°. By means of a JEM-2100Plus (JEOL, Japan) instrument, transmission electron microscopic (TEM) images of the samples were obtained. The Scanning electron micrographs (SEM) were taken on HITACHI UHR FE-SEM SU8010 electron microscope. Nitrogen adsorption/desorption measurements were carried out on a McKesson ASAP-2460 analyzer at 77.2 K after the samples were degassed at 350 °C under vacuum. The pore size distribution curves were calculated from the analysis of desorption branch of the isotherm by the BJH (Barrett-Joyner-Halenda) method. The Fe concentration in solution was measured by an inductively coupled plasma (ICP) emission spectrometer (Prodigy).

All MS measurements were carried out on a quadrupole time-of-flight (Q-TOF) mass spectrometer (6545B, Agilent Technologies, USA). The original ESI source was removed and the interlock was overridden. A typical DC high voltage of 2.7 kV was applied between the PESI probe and the ion sampling orifice of the mass spectrometer for electrospraying. Full-scan positive ion spectra were acquired and processed using the default Mass Hunter Workstation package. The capillary temperature was maintained at 275 °C. The dry gas flow rate was set to 2 L min$^{-1}$. The fragmentor voltage, skimmer voltage and oct rf $V_{pp}$ voltage were set at 60, 10 and 400 V, respectively. The collision voltage was adjusted at 0 V to avoid the generation of in-source fragmentation products which might be misinterpreted to be degradation products of the precursor.
The EPR spectra were recorded on a Brookhaven FA300 EPR spectrometer equipped with a UV lamp (center wave length: 365nm). The detailed instrumental parameters were as follows: scanning frequency: 9.8 GHz; central field: 3510 G; scanning width: 100 G; scanning power: 6 mW; scanning temperature: 293 K.

DMPO trappings are shown in the following reaction:

\[
\text{N}^\cdot\text{O} + \text{R} \rightarrow \text{N}_\alpha\text{H}_\beta.
\]

The hyperfine coupling constants \((hfc\text{s})\) of the nitrogen and \(\beta\)-proton \((a_N\text{ and } a_{H\beta})\) were given in the main text when referred.

**Detection of \(\bullet\text{OH/DMPO}:\)**

200 \(\mu\text{L}\) of initial reaction mixture was added into 200 \(\mu\text{L}\) of aqueous DMPO solution with the concentration of 80 mM. The mixture was shaken by hand for 1 minute and transferred into a quartz cell. Then, the solution was transferred into an aqueous cell and the EPR data collection was started.

TMPN trappings are shown in the following reaction:

\[
\text{H}\text{O} + \text{N}^\cdot\text{O} \rightarrow \text{N}^\cdot\text{O}.
\]

**Detection of \(^1\text{O}_2/\text{TMPN}:\)**

200 \(\mu\text{L}\) of initial reaction mixture was added into 200 \(\mu\text{L}\) of aqueous TMPN solution with the concentration of 80 mM. The mixture was shaken by hand for 1 minute and transferred into a quartz cell. Then, the solution was transferred into an aqueous cell and the EPR data collection was started.

**Ref:**


3. Supplementary Figures and Table

![Figure S1](image1.png)  
**Fig. S1** SEM images of the samples one-pot synthesized without addition of acid by adding (NH$_4$)$_2$Ce(NO$_3$)$_6$ (A), adding the Fenton reagent (B), and adding Na$_2$S$_2$O$_8$ (C)

![Figure S2](image2.png)  
**Fig. S2** TEM image and EDS mapping (Ce: Cyan, O: red, Si: orange) of the Ce-SBA-15 sample synthesized by the one-pot route
**Fig. S3** UV-vis spectra (A) and Ce 3d XPS spectra (B) of the Ce-SBA-15 sample synthesized by the one-pot route

**Fig. S4** The Ce/Si molar ratio (A) and XRD patterns (B) of the as-synthesized Ce-SBA-15 sample and acid-treated Ce-SBA-15 sample

**Fig. S5** The images of TEOS hydrolysed by adding \((\text{NH}_4)_2\text{Ce(NO}_3\text{)}_6\) (A), Fenton reagent (B), and \(\text{Na}_2\text{S}_2\text{O}_8\) (C) at different time under the same conditions
**Fig. S6** Time-resolved PESI-MS results of the hydrolysis reaction of TEOS promoted by (NH$_4$)$_2$Ce(NO$_3$)$_6$

**Fig. S7** Time-resolved PESI-MS results of the hydrolysis reaction of TEOS promoted by 2 mol/L HCl
Fig. S8 Time-resolved PESI-MS results of the hydrolysis reaction of TEOS promoted by Na$_2$S$_2$O$_8$

Fig. S9 Time-resolved PESI-MS results of the hydrolysis reaction of TEOS promoted by the Fenton reagent
Fig. S10 Intensity of the ion at m/z 209 (black) and m/z 93 (red) as a function of time in the hydrolysis reaction promoted by (NH₄)₂Ce(NO₃)₆

Fig. S11 Intensity of the ion at m/z 209 (black) and m/z 93 (red) as a function of time in the hydrolysis reaction promoted by 2 mol/L HCl

Fig. S12 Intensity of the ion at m/z 209, m/z 231 (black) and m/z 93 (red) as a function of time in the hydrolysis reaction promoted by Na₂S₂O₈
Fig. S13 Intensity of the ion at m/z 209 (black) and m/z 93 (red) as a function of time in the hydrolysis reaction promoted by Fenton reagent.

Fig. S14 XRD patterns of the samples one-pot synthesized in the $(\text{NH}_4)_2\text{Ce(NO}_3)_6$ system (A) and Fenton reagent system (B) with the addition of H$_2$O (blue), CH$_3$OH (red), and L-histidine (black).

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Fig. S22 Gibbs free energy profile and optimized geometry of the structures involved in the incorporation of Ce and/or Fe within the mesoporous silica materials.
Table S1. Physicochemical properties of calcined samples prepared using different methods

<table>
<thead>
<tr>
<th>Sam</th>
<th>Reaction system</th>
<th>Initiator</th>
<th>Products</th>
<th>Metal /Si molar ratio(^a) (%)</th>
<th>(d^b) (nm)</th>
<th>(S_{\text{BET}}) (m(^2)g(^{-1}))</th>
<th>Pore volume (cm(^3)g(^{-1}))</th>
<th>Pore diameter (nm)</th>
<th>Wall thickness (nm)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEOS-P(_{123})-(NH(_4))(_2)Ce(NO(_3))_6(-)H(_2)O</td>
<td>(NH(_4))(_2)Ce(NO(_3))_6/ mmol</td>
<td>0.009</td>
<td>Ce-SBA-15</td>
<td>10.3</td>
<td>447</td>
<td>1.37</td>
<td>9.4</td>
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<td>0.036</td>
<td>Ce-SBA-15</td>
<td>0.15</td>
<td>9.9</td>
<td>0.98</td>
<td>6.2</td>
<td>5.2</td>
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<td>3</td>
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<td>0.144</td>
<td>Ce-SBA-15</td>
<td>0.101</td>
<td>879</td>
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<td>5.8</td>
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<td>4</td>
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<td>0.182</td>
<td>Ce-SBA-15</td>
<td>-</td>
<td>9.2</td>
<td>0.967</td>
<td>6.06</td>
<td>5.6</td>
<td>85</td>
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<td>0.29</td>
<td>Ce-SBA-15</td>
<td>0.87</td>
<td>748</td>
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<td>6</td>
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<td></td>
<td>0.36</td>
<td>Ce-SBA-15</td>
<td>9.5</td>
<td>0.967</td>
<td>6.06</td>
<td>5.6</td>
<td>60</td>
<td></td>
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<td>7</td>
<td>TEOS-P(_{123})-Fenton-H(_2)O</td>
<td>300µL 30wt%H(_2)O(_2)+FeSO(_4)-7H(_2)O/ mmol</td>
<td>0.036</td>
<td>Fe-SBA-15</td>
<td>0.13</td>
<td>10.1</td>
<td>0.967</td>
<td>6.06</td>
<td>5.6</td>
<td>95</td>
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<tr>
<td>8</td>
<td>TEOS-P(_{123})-Na(_2)S(_2)O(_4)-H(_2)O</td>
<td>Na(_2)S(_2)O(_4)/ mmol</td>
<td>0.036</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>TEOS-Tween60- (NH(_4))(_2)Ce(NO(_3))_6-H(_2)O</td>
<td>(NH(_4))(_2)Ce(NO(_3))_6/ mmol</td>
<td>0.036</td>
<td>Ce-MSU-4</td>
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<td>10</td>
<td>TEOS-Tween 60-Fenton-H(_2)O</td>
<td>300µL 30wt% H(_2)O(_2)+FeSO(_4)-7H(_2)O/ mmol</td>
<td>0.072</td>
<td>Fe-MSU-4</td>
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\(^a\)The Metal/Si ratios in the calcined materials were calculated by the ICPAES method. \(^b\)\(d_{\text{100}}\) spacing or \(d\) value of characteristic reflection of the as-synthesized products after calcination at 550 °C for 6 h. \(^c\)The pore diameters were calculated by the desorption branch of the isotherms according the BJH method. \(^d\)Calculated by \(a^d = 2d_{\text{100}} / 3^{1/2}\)