Heterogeneous Conversion of $\text{SO}_2$ on Nano $\alpha$-$\text{Fe}_2\text{O}_3$: the Effect of Morphology, Light Illumination and Relative Humidity

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Preparation of α-Fe₂O₃ samples

Synthesis of nanocapsule-like α-Fe₂O₃ (α-Fe₂O₃-A): according to the reported procedure, 0.2 mmol SDS was added into 40 mL deionized water under magnetic stirring. Then 2.0 mmol FeCl₃·6H₂O and 2.0 mmol CH₃COONa were added to the SDS solution orderly under stirring. The colorless transparent SDS solution transferred to turbid solution immediately after the FeCl₃·6H₂O and CH₃COONa were added. After being stirred for 20 min, the slurry was treated at 140 °C for 24 h in 50-mL Teflon-lined autoclave, and then cooled to room temperature naturally. The precipitate was centrifuged for 5 min under 4000 rpm. The obtained product was washed with deionized water and ethanol for 3 times, and then dried at 80 °C for 12 h. The obtained powders were finely ground and collected for experiments.

Synthesis of hollow nanoring-like α-Fe₂O₃ (α-Fe₂O₃-B): in a typical procedure, 1.62 g FeCl₃·6H₂O was added into 300 mL deionized water with stirring to form a transparent solution. Then 0.0062 g NH₄H₂PO₄ and 0.023 g Na₂SO₄ were added respectively under stirring. After being stirred for 10 min, the solution was transferred into three 100-mL Teflon-lined autoclaves and maintained at 220 °C for 48 h. After the autoclave cooled to room temperature, the precipitate was separated by centrifugation, washed with deionized water and ethanol for 3 times. The product was dried at 80 °C for 12 h and finely ground for following experiments.

Synthesis of hexagonal nanoplate-like α-Fe₂O₃ (α-Fe₂O₃-C): according to previous work, 4 mmol FeCl₃·6H₂O was dissolved in 40.0 mL ethanol with a trace addition of deionized water (2.8 mL) under magnetic stirring. After dissolution, 3.2 g of CH₃COONa was added while stirring. The solution was transferred into 50-mL Teflon-lined autoclave and maintained at 180 °C for 12 h. Following natural cooling to room temperature, the products were centrifuged and washed with
distilled water and ethanol for 3 times. Then the product was dried at 80 °C for 12 h and finely ground.

Synthesis of agglomerated nanoparticle-like $\alpha$-Fe$_2$O$_3$ ($\alpha$-Fe$_2$O$_3$-D): according to the previously reported procedure,$^4$ 40.4 g Fe(NO$_3$)$_3$$\cdot$9H$_2$O, 4.2 g NaHCO$_3$, 33.6 g KOH were added into 500, 50, 300 mL deionized water under stirring, respectively, and then the three solutions were heated to 363 K with water bath. Then mixed them together in a polyethylene bottle and the pH is adjusted to 8.0–8.5 before aging at 363 K for 48 h. After cooling to room temperature, the precipitate was centrifuged and washed with distilled water and ethanol for 3 times. Then the product was dried at 80 °C for 12 h and finely ground.
Table S1. Parameters for uptake coefficient calculation

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate formation rate: $\frac{d[SO_4^{2-}]}{dt}$ (ion·s$^{-1}$)</td>
<td>According to reactions</td>
</tr>
<tr>
<td>$A_{\text{HET}}$ (m$^2$/g)</td>
<td></td>
</tr>
<tr>
<td>$A_{\text{geo}}$ (m$^2$)</td>
<td>$7.85 \times 10^{-5}$</td>
</tr>
<tr>
<td>Reactant concentration: $c_{SO_2}$ (molecule·m$^{-3}$)</td>
<td>$7.37 \times 10^{19}$</td>
</tr>
<tr>
<td>Gas constant: $R$ (J·mol$^{-1}·K^{-1}$)</td>
<td>8.314</td>
</tr>
<tr>
<td>Temperature: $T$ (K)</td>
<td>298</td>
</tr>
<tr>
<td>Molar mass: $M_{SO_2}$ (Kg·mol$^{-1}$)</td>
<td>$6.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\pi$ (dimensionless)</td>
<td>3.14</td>
</tr>
</tbody>
</table>
Figure S1. In situ DRIFTS spectra of different samples (1400–900 cm$^{-1}$) under light illumination. a, α-Fe$_2$O$_3$-A. b, α-Fe$_2$O$_3$-B. c, α-Fe$_2$O$_3$-C. d, α-Fe$_2$O$_3$-D.
Figure S2. In situ DRIFTS spectra of collected α-Fe₂O₃ samples (3720-3560 cm⁻¹) under light illumination.

a, α-Fe₂O₃-A. b, α-Fe₂O₃-B. c, α-Fe₂O₃-C. d, α-Fe₂O₃-D.
Figure S3. Calculated ions of sulfates on different $\alpha$-Fe$_2$O$_3$ samples under light illumination.
Figure S4. The spectrum of the Xe lamp with optical fiber (model CEL-TCX250, Beijing Jin Yuan Science and Technology Co., Ltd.).
Figure S5. In-situ DRIFTS spectra collected at 120 min on α-Fe₂O₃-C under different 68% RH saturation time.
Supplementary References


