

Fig. S1 (a) Photographs of α -Fe₂O₃ dendrites with various Cr loadings of 0%, 1%, 5%, and 10%. The colour changed from reddish brown to dark brown with increasing Cr content. (b) Optical microscopy images ($\times 100$) of α -Fe₂O₃ dendrites with various Cr loadings of 0%, 1%, 5%, and 10%.

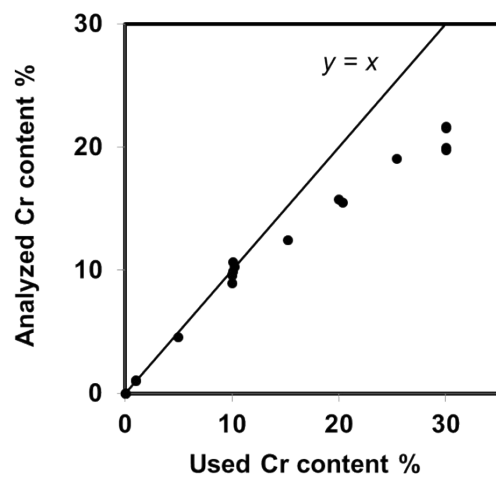


Fig. S2 Comparison of Cr contents (%) estimated by XRF spectroscopy. Horizontal axis: Cr content (% Cr/(Cr+Fe)) used in the synthesis. Vertical axis: measured Cr content (% Cr/(Cr+Fe)) in the obtained samples.

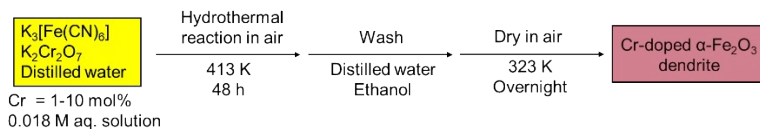
Supporting information 1: XRD-Rietveld analysis

The lattice parameters of a ($= b$) and c in the set of prepared α -Fe₂O₃ samples were analyzed by powder XRD-Rietveld analysis. The analysis was performed using HighScore software provided by PANalytical Co. The measured XRD profiles and a profile calculated from crystal structure (JCPDS: 01-072-0469) were compared to minimize the variation of parameters. The fitting index R_{wp} , which was shown in eq. S1, was set to within around 10% in this study,

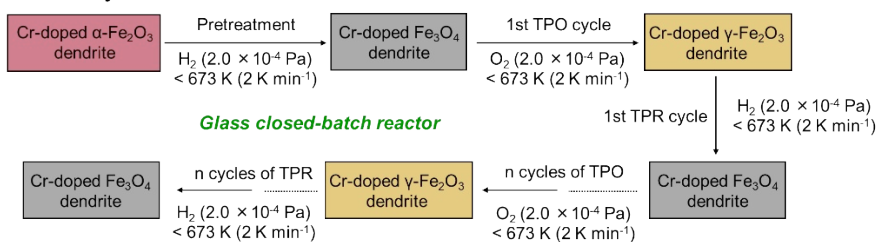
$$R_{wp} = \left\{ \frac{\sum_i w_i [y_i - f_i(x)]^2}{\sum_i w_i y_i^2} \right\}^{1/2} \quad \cdot \cdot \cdot \text{eq. (S1)}$$

where w_i is a statistical weight, y_i is observed signal intensity, and $f_i(x)$ is theoretical diffraction intensity.

Sample preparation



TPR/TPO cycles



In-situ XAFS measurement with TPO

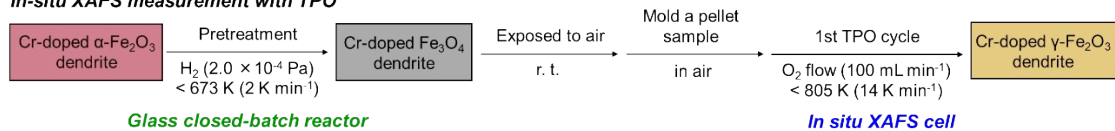


Fig. S3 Flow charts showing the experimental procedures and conditions used for the sample synthesis, TPR/TPO experiments, and *in situ* XANES measurements.

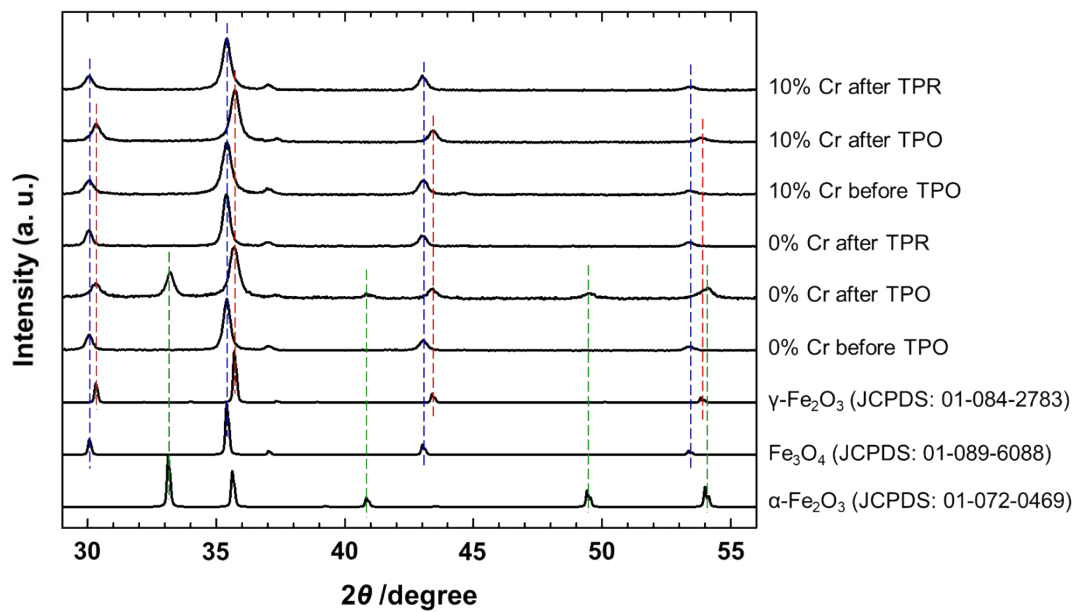


Fig. S4 Powder XRDs of the pristine (0% Cr) and 10% Cr-loaded iron oxide dendrite samples before and after TPO (room temperature to 573 K) and TPR (room temperature to 623 K), alongside reference samples (Fe₃O₄, α-Fe₂O₃, and γ-Fe₂O₃).

Supporting information 2: ICP-AES and XRD analyses of the prepared iron oxide dendrite samples

The Fe contents of the prepared Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ samples were determined by ICP-AES. Samples (100 mg) of Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ were treated with hydrochloric acid (50 mL) at 50 °C for 96 h to completely dissolve the solid. The resulting solutions were diluted to a volume of 1 L with distilled water and analysed by ICP-AES. The reliability of a standard curve calibrated using Fe standard solutions (0, 20, 40, 60, and 100 ppm) was greater than 99.9%. The ICP-AES measurements were conducted in triplicate, and their average values were shown in Table S1.

Table S1 Fe concentrations of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ samples estimated by ICP-AES,

Sample	Expected Fe concentration	Measured Fe concentration
	(A) $\times 10^{-3}$ M	(B) $\times 10^{-3}$ M
Fe_3O_4	1.27	1.22
$\gamma\text{-Fe}_2\text{O}_3$	1.24	1.20

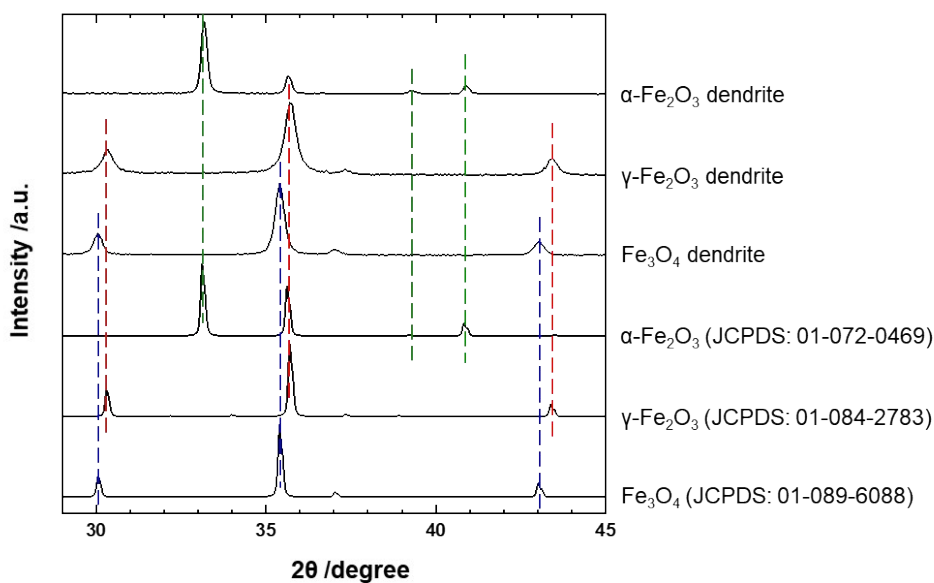


Fig. S5 Powder XRDs of the as-prepared $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 (TPR < 623 K), and $\gamma\text{-Fe}_2\text{O}_3$ samples (TPO < 550 K) for dendrites and data in the crystal database.

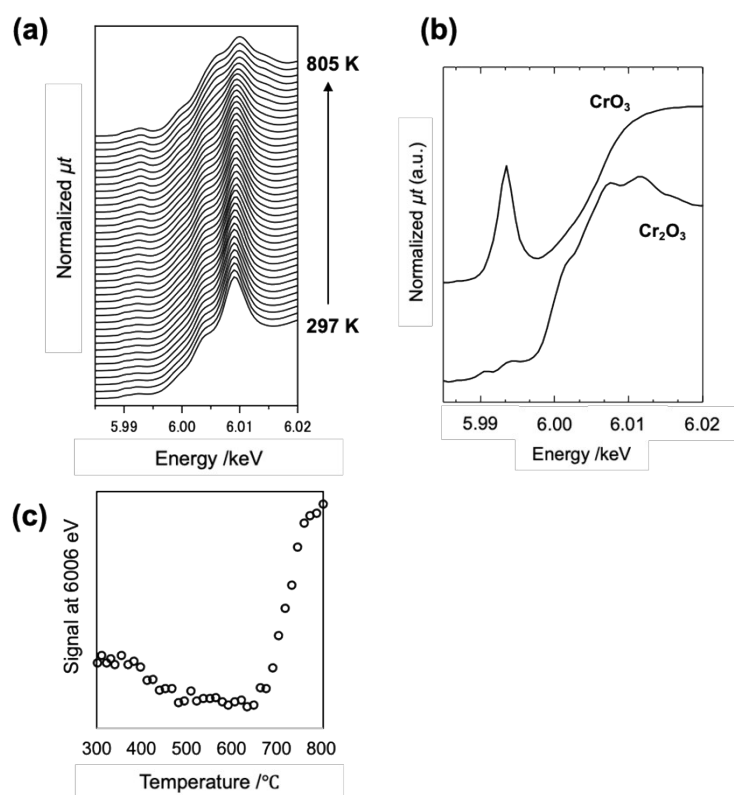


Fig. S6 (a) *In situ* Cr *K*-edge XANES spectra for 10% Cr-loaded iron oxide dendrites as the sample temperature was increased from 293 to 805 K at 14 K min⁻¹ step under O₂ flow (100 mL min⁻¹). The temperatures shown in the figure are the averages of the initial and final temperatures for each step (14 K intervals). (b) Cr *K*-edge XANES spectra for Cr₂O₃ (Cr³⁺, Wako Chemicals) and CrO₃ (Cr⁶⁺, Wako Chemicals) as standard samples. (c) The intensity at 6006 eV in (a).

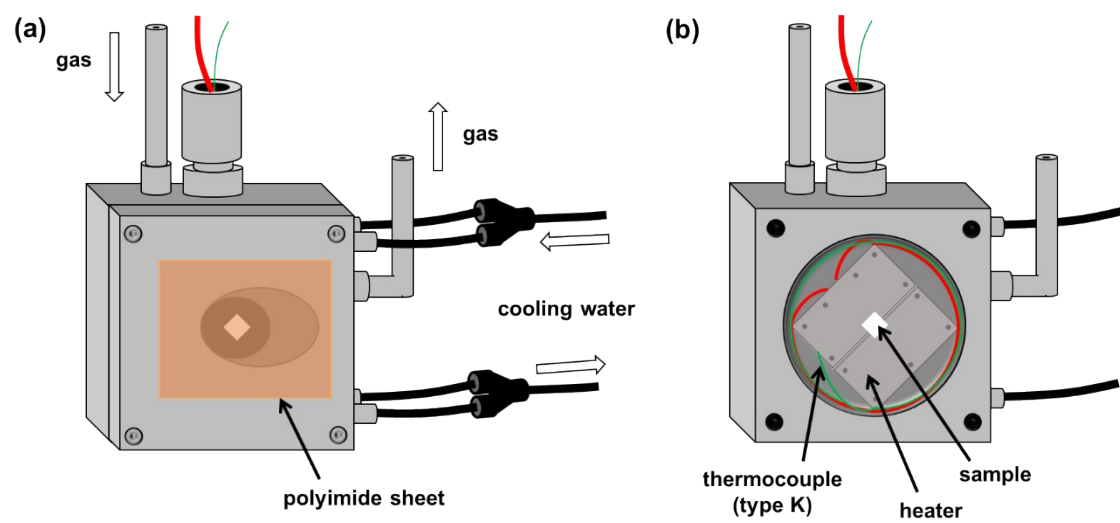


Fig. S7 Schematic depictions of the (a) exterior and (b) interior of the *in situ* XAFS cell. The sample temperature was precisely controlled using a proportional-integral-differential system.

Supporting information 3: TPO/TPR experiment in a glass closed-batch reactor

The stoichiometry and activity of the redox properties of the iron oxide samples were examined in a glass closed-batch reactor equipped with a diaphragm vacuum gauge and electromagnetic pump (Fig. S8). The reactor had a cyclic structure (shown in red), and a pair of check plates and a piston electromagnetic pump were used to feed the low-pressure reaction gas (H_2 or O_2) to the sample.

The consumption of the reaction gas during TPO or TPR was monitored against the sample temperature. For background calibration, the thermal expansion of gases was determined by an experiment under an inert He atmosphere. The stoichiometry of the oxidation or reduction reaction was estimated using eqs. (S1) and (S2).



To avoid pressure changes due to the H_2O generated during TPR, a liquid N_2 trap was placed in the circulation line.

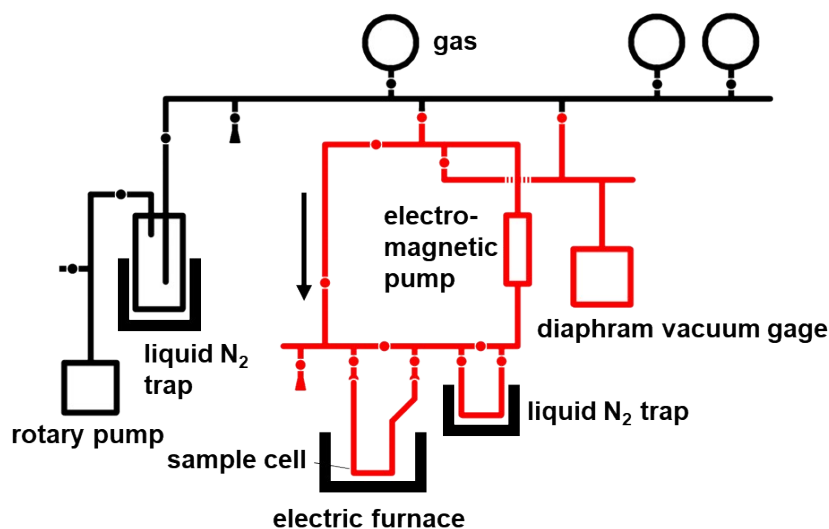


Fig. S8 Schematic depiction of the glass closed-batch reactor.