

Electronic Supplementary Information for
**MOF-derived porous Fe₂O₃ with controllable shapes and
improved catalytic activities in H₂S selective oxidation**

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Experimental section

Preparation

Materials

All reagents obtained from commercial sources were used without any further purification unless otherwise stated. FeCl₃·6H₂O, N,N-dimethylformamide (DMF), acetic acid (HAc) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received without further purification. Terephthalic acid (H₂BDC) was supplied by Alfa Aesar China Co., Ltd. (Tianjin, China). Deionized (DI) water used in the synthesis was from local sources. Commercial Fe₂O₃ was supplied by Fucheng. China Co., Ltd (Tianjin, China).

Synthesis of MIL-53(Fe)-xH

MIL-53(Fe) was synthesized with minor modifications according to the reported procedures¹: First 0.618 g of H₂BDC and 2.025 g of FeCl₃·6H₂O were separately dissolved in 22.5 mL of DMF. Afterward, both solutions were mixed in a beaker and stirred for 10 min. The mixture was transferred to a Teflon-lined stainless-steel bomb and heated at 170 °C for 24 h. The product, MIL-53(Fe), was collected, washed with methanol for four times, and then heated at 80 °C for 6 h. After cooling to room temperature, the MIL-53(Fe) product was heated at 100 °C for 12 h under vacuum to remove solvent molecules in the pores. In the modulated synthesis, 0–10 mL of 95% HAc was also added to the mixture. According to the content of HAc, the synthesized samples are herein labeled as MIL-53(Fe)-xH (*x* represents the volume of introduced HAc; *x*=0, 3, 5, 10).

Synthesis of Fe₂O₃-xH

The obtained MIL-53 (Fe)-xH samples were thermally treated in 50 % N₂/O₂ at 500 °C for 3 h. The pyrolyzed products are herein denoted as Fe₂O₃-xH (x represent the added content of HAc in precursors; x=0, 3, 5, 10)

Catalyst characterization

Thermogravimetric measurements (TGA) were carried out using a TGA7 (Perkin-Elmer) thermal analyzer. The experiments were performed under an air stream from 50 to 800 °C, with a heating rate of 5 °C min⁻¹. The catalysts were characterized by a powder X-ray diffractometer (Panalytical X' Pert PRO) using Cu K α ($\lambda=0.15406\text{nm}$) radiation operating at 40 kV and 40 mA. The FT-IR spectra were measured on Nicolet NEXUS 670. Scanning electron microscopy (SEM) images were collected on an S-4800 (Hitachi, Japan) scanning electron microscope at an accelerating voltage of 5 kV. Texture parameters of samples were measured by N₂ adsorption-desorption using an ASAP2020 instrument (Micromeritics, American). Transmission electron microscopic (TEM) investigation was performed on an FEI Tecnai G2 F20 transmission microscope. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface region of catalysts (Phi Quantum 2000).

Evaluation of catalytic activity

All tests were performed in a continuous flow fixed-bed quartz reactor at atmospheric pressure with 0.2 g of catalyst (20–40 mesh) placed in the central section of the reactor. A mixture gas containing 5000 ppm of H₂S, 2500 ppm of O₂ and balance gas (N₂) was fed into the reactor at a total gas flow rate of 10 mL/min (GHSV = 3000 h⁻¹), and the reaction was conducted in the temperature range of 60–180 °C. During reaction, the effluent stream was analyzed by a gas chromatograph (GC9790 II) equipped with a FPD and TCD. A condenser was located at the bottom of the reactor to trap sulfur in the effluent stream. Instantaneous fractional conversion of H₂S, sulfur selectivity, and sulfur yield are defined as follows:

$$\text{H}_2\text{S conversion} = \frac{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}}}$$

$$\text{Sulfur selectivity} = \frac{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}} - [\text{SO}_2]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}}$$

$$\text{Sulfur yield} = [\text{H}_2\text{S conversion}] \times [\text{sulfur selectivity}]$$

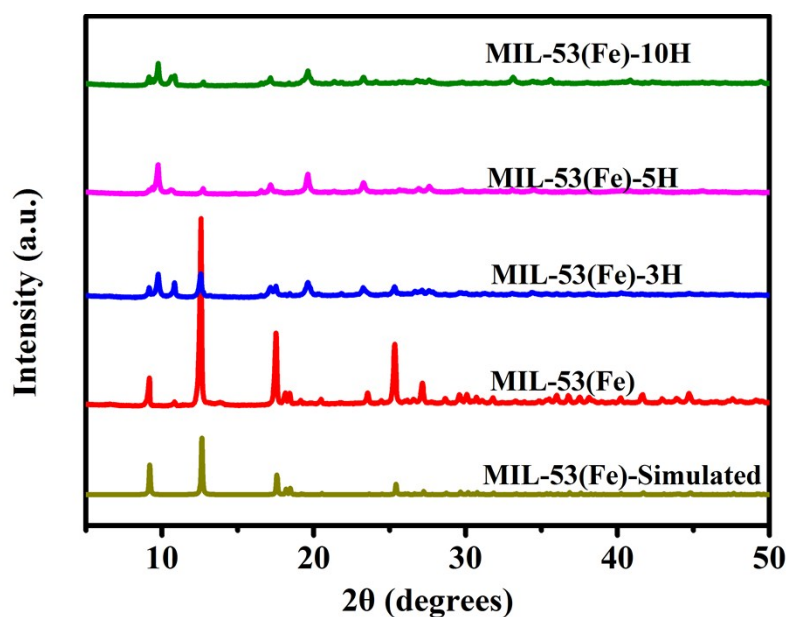


Fig. S1 XRD patterns of MIL-53(Fe)-*x*H.

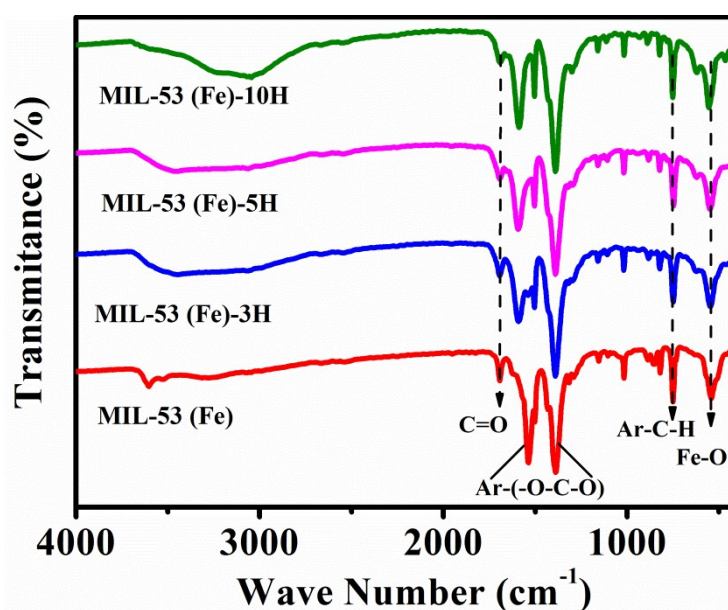


Fig.S2 FTIR spectrum of MIL-53(Fe)-*x*H.

To identify the functional groups of the MIL-53(Fe)-*x*H samples, FTIR spectroscopic studies were performed in the wavelength range of 400–4000 cm^{-1} and the results are shown in Fig. S2. The characteristic absorption peaks of the MIL-53(Fe)-*x*H samples appeared at 1680, 1543, 1396, 1020, and 750 cm^{-1} , which could be ascribed to the carboxylate groups vibrations as reported in literature.^{2,3} The two sharp peaks around 1543 and 1396 cm^{-1} are assigned to asymmetric and symmetric

vibrations of carboxyl groups, respectively, confirming the presence of dicarboxylate linker in these samples. Two strong bands at 750 cm^{-1} and 540 cm^{-1} are attributed to Ar–C–H and Fe–O vibrations respectively.

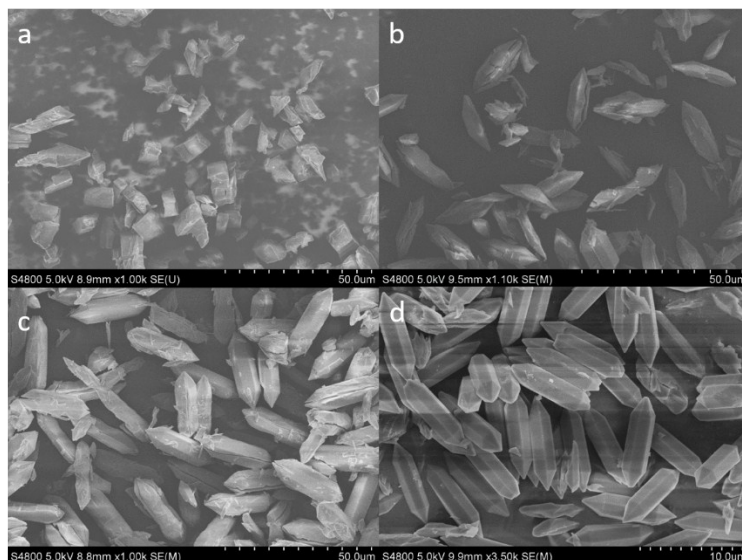


Fig. S3 (a) SEM images of MIL-53(Fe), and MIL-53(Fe)-3H prepared with different reaction periods (b) 10 h; (c) 15 h; (d) 24 h.

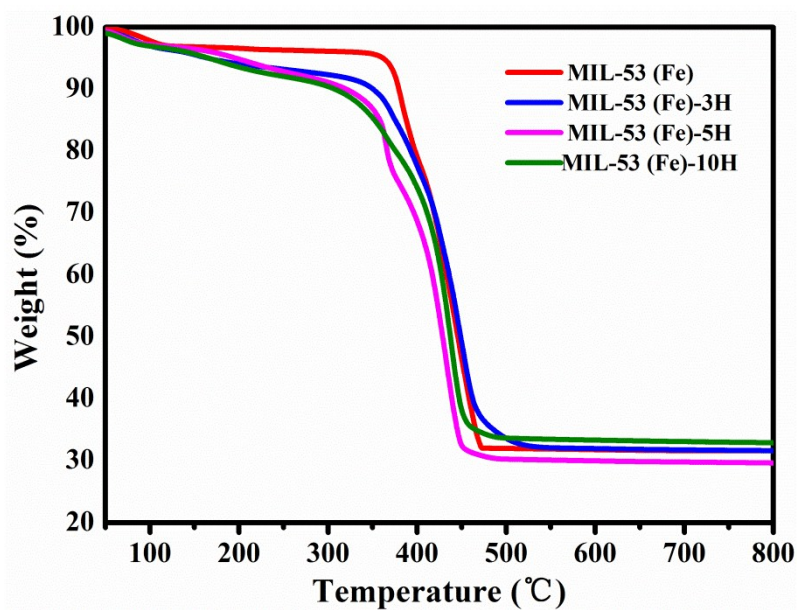


Fig. S4 TGA curves of MIL-53(Fe)-xH in air.

The thermal stabilities of the as-synthesized MIL-53(Fe)-*x*H were investigated by thermogravimetric (TGA) analysis in synthetic air from 50 to 800 °C. As shown in **Fig. S4**, the samples undergo two clear weight-loss steps between 100 °C and 500 °C. The first weight-loss at 120 °C corresponds to the evacuation of guest molecules; while the second one around 500 °C is ascribed to the decomposition of the MIL-53(Fe)-*x*H framework. Thus, a calcination temperature of 500 °C is the most suitable to obtain iron oxides with the original MOFs morphologies.

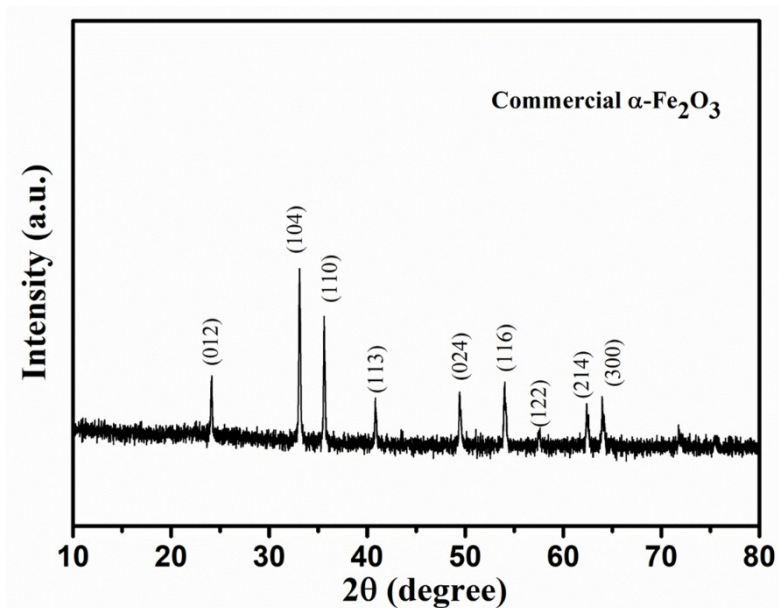


Fig. S5 XRD pattern of commercial α - Fe_2O_3 .

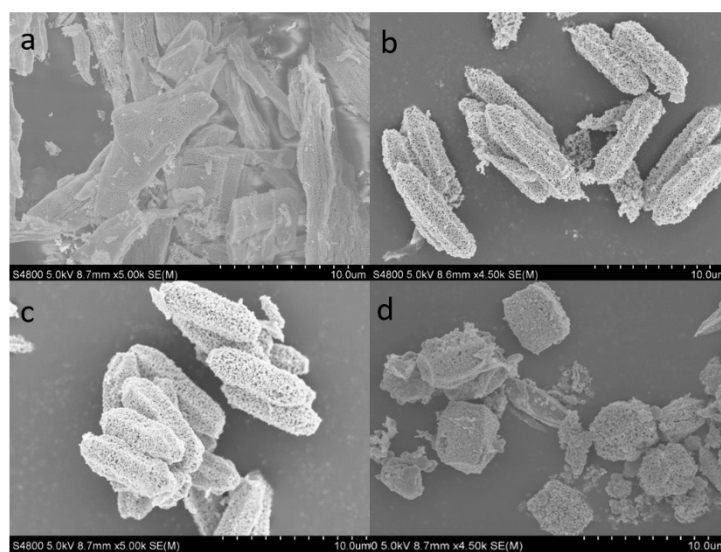


Fig. S6 SEM images of Fe_2O_3 -*x*H samples: (a) Fe_2O_3 ; (b) Fe_2O_3 -3H; (c) Fe_2O_3 -5H; (d) Fe_2O_3 -10H.

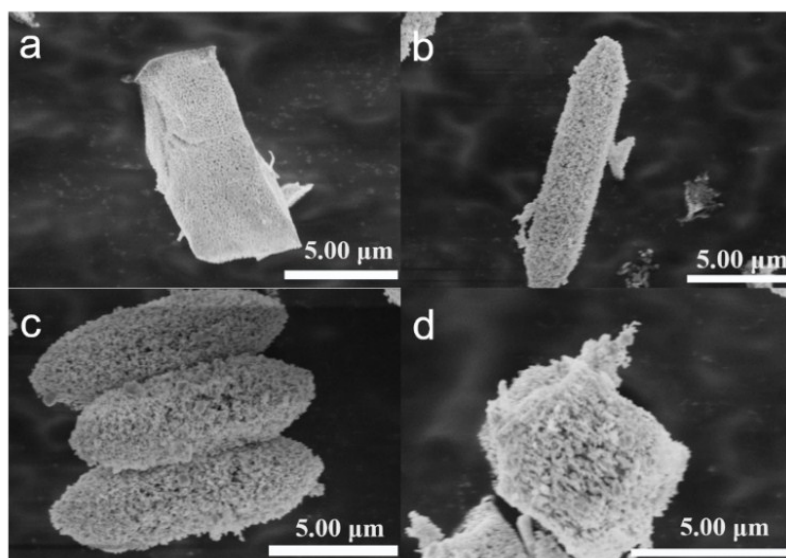


Fig. S7 SEM images of Fe₂O₃-xH samples: (a) Fe₂O₃; (b) Fe₂O₃-3H; (c) Fe₂O₃-5H; (d) Fe₂O₃-10H.

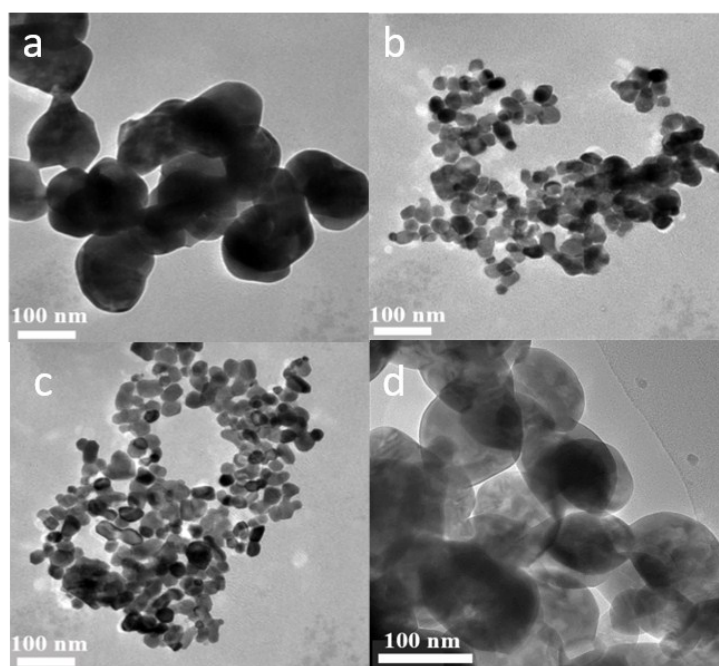


Fig. S8 TEM images of Fe₂O₃-xH samples: (a) Fe₂O₃; (b) Fe₂O₃-3H; (c) Fe₂O₃-5H; (d) Fe₂O₃-10H.

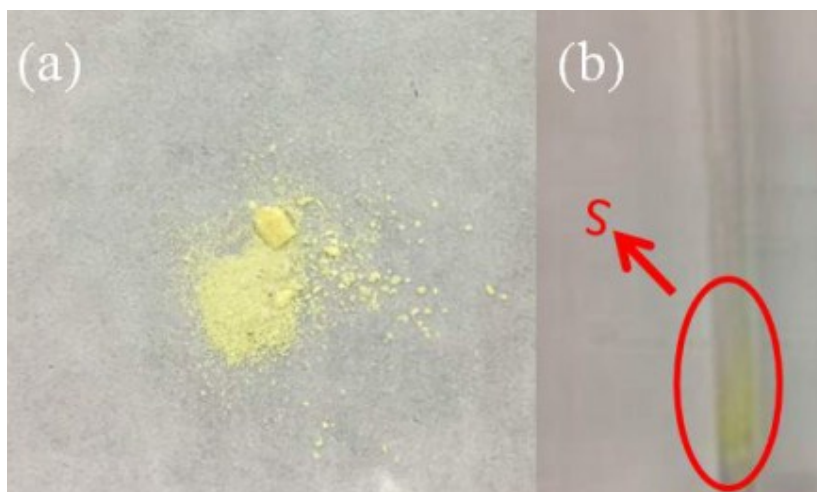


Fig. S9 Recovered sulfur.

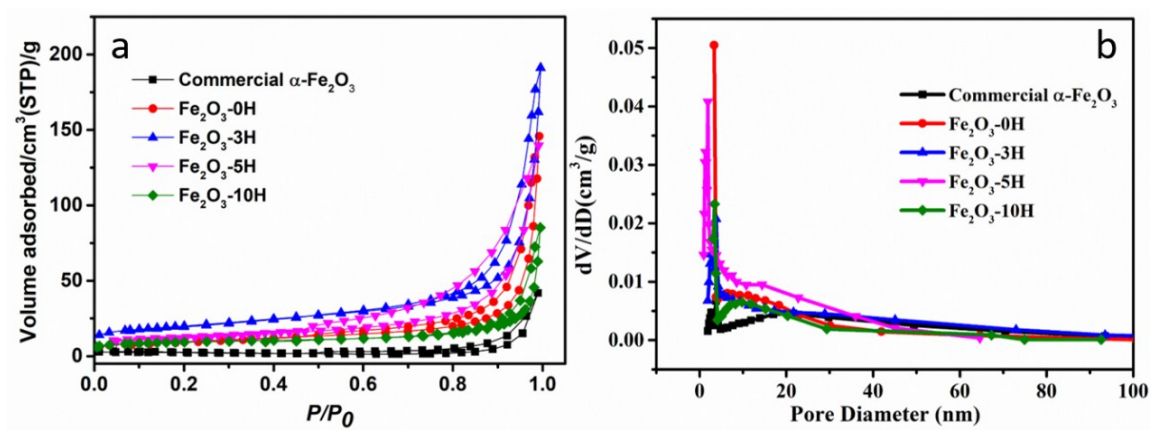


Fig. S10 (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of Fe_2O_3 -xH and commercial α - Fe_2O_3 samples.

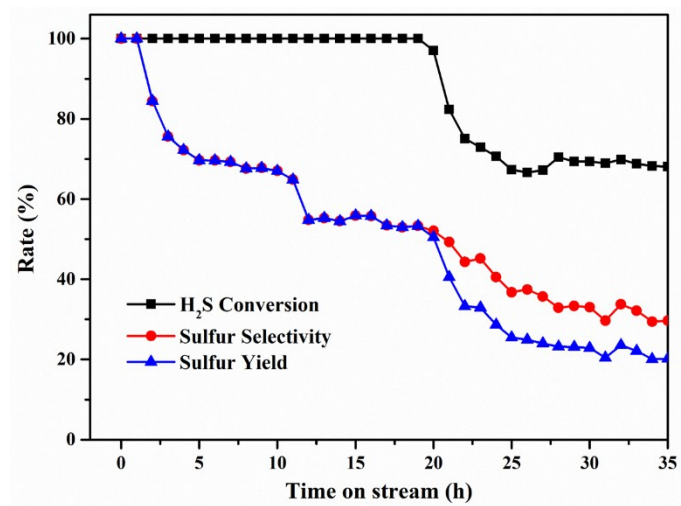


Fig. S11 Long-term stability of commercial Fe₂O₃ catalysts at 180 °C.

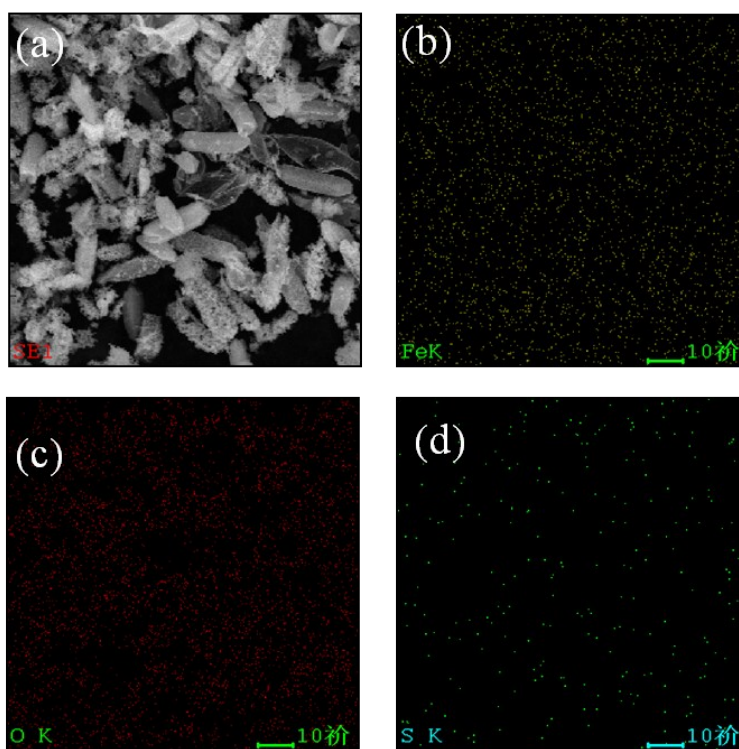
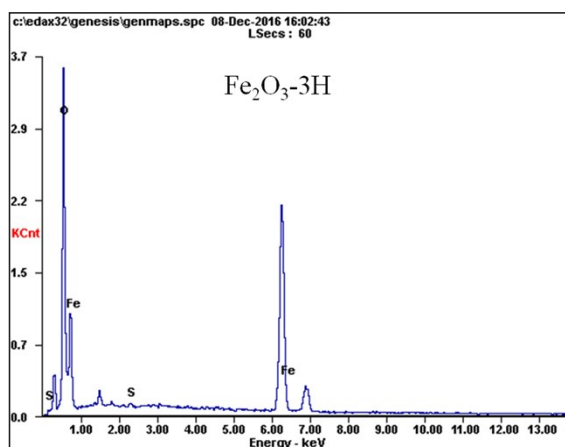


Fig.S12 SEM image and EDX mapping of the used Fe₂O₃-3H catalyst.



Element	Wt%	At%
OK	29.90	59.78
SK	00.15	00.15
FeK	69.95	40.07
Matrix	Correction	ZAF

Fig.S13 EDX results of the used Fe₂O₃-3H catalyst.

Table S1 Textural parameters of Fe₂O₃-xH and commercial α-Fe₂O₃ samples.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
Fe ₂ O ₃ -0H	29.8	0.107	15.9
Fe ₂ O ₃ -3H	40.6	0.218	7.07
Fe ₂ O ₃ -5H	35.3	0.185	14.1
Fe ₂ O ₃ -10H	30.9	0.171	13.7
Commercial α-Fe ₂ O ₃	5.72	0.019	9.5

References

1. P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774–6780.
2. T. A. Vu, G. H. Le, C. D. Dao, L. Q. Dang, K. T. Nguyen, Q. K. Nguyen, P. T. Dang, H.T.K. Tran, Q. T. Duong, T. V. Nguyen and G. D. Lee, *RSC Adv.*, 2015, **5**, 5261–5268.
3. L. Ai, L. Li, C. Zhang, J. Fu and J. Jiang, *Chem-Eur. J.*, 2013, **19**, 15105–15108.