Electronic Supplementary Information (ESI)

Double-shelled hollow iron-encapsulated zeolite for enhanced mass transfer and reusability in persulfate activation

Qibo Liu,[ac] Wei Pang,[b] Xiaohan Chen,[c] Pinli Diao,[c] Wen Tian,[ab] Feng Cui,[a] Yide Han,*[a] Huanying Zhou,*[b] and Sibudjing Kawi,*[c]

[a]Department of Chemistry, College of Sciences, Northeastern University, Shenyang, 110819, P. R. China

[b]Tianjin Key Laboratory of Risk Assessment and Control Technology for Environment and Food Safety, Military Medical Sciences Academy, Academy of Military Sciences, Tianjin 300050, China

[c]Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, 117585, Singapore

* Corresponding authors.

E-mail addresses: hanyide@mail.neu.edu.cn (Y. Han), houhytj@163.com (H. Zhou), chekawis@nus.edu.sg (S. Kawi).

Chemicals and reagents

Tetracycline (TC), methylene blue (MB), rhodamine B (RhB), levofloxacin (LEV), sulfamethoxazole (SMX), tetraethyl orthosilicate (TEOS), peroxydisulfate (PDS), 1, 10-phenanthroline ($C_{12}H_8N_2$), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), methanol (MeOH), p-benzoquinone (p-BQ), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were obtained from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Aluminum isopropoxide ($Al[OCH(CH_3)_2]_3$), tetrapropylammonium hydroxide (TPAOH), iron(III) chloride ($FeCl_3$), 2, 2, 6, 6-tetramethylpiperidine N-oxide (TEMP), tert-butanol (TBA), furfuryl alcohol (FFA), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), sodium phosphate dibasic (Na_2HPO_4), sodium bicarbonate ($NaHCO_3$) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Deionized (DI) water was used in the all experiments. The environmental water samples were collected from Nanhu Park, Hun River and Yellow Sea.

Synthesis of catalysts

Synthesis of ZSM-5: ZSM-5 was synthesized by dissolving 15.4 mL tetraethyl orthosilicate (TEOS), 16.5 mL of 25 wt% tetrapropylammonium hydroxide (TPAOH), and 0.55 g aluminum isopropoxide in 33 mL deionized water under stirring at 35 °C for 3 h. The resulting homogeneous mixture was transferred into a Teflon-lined autoclave and crystallized at 170 °C for 72 h. The solid product was calcined at 550 °C for 6 h to obtain 4.5 g of ZSM-5.

Synthesis of Fe_2O_3/ZSM-5: Fe_2O_3/ZSM-5 was prepared by impregnating 1 g of ZSM-5 with 0.5 mL of 0.18 mol/L $FeCl_3$ solution. After stirring for 12 h, the material was calcined at 500 °C for 4 h.

Synthesis of Fe_2O_3@H-ZSM-5: 0.5 g of Fe_2O_3/ZSM-5 was mixed with 10 mL of 0.3 mol/L TPAOH solution and transferred into a Teflon-lined autoclave. The mixture was treated at 170 °C in a rotating oven (60 r/min) for 72 h. The obtained solid was calcined at 500 °C for 4 h to yield 0.3 g of Fe_2O_3@H-ZSM-5.

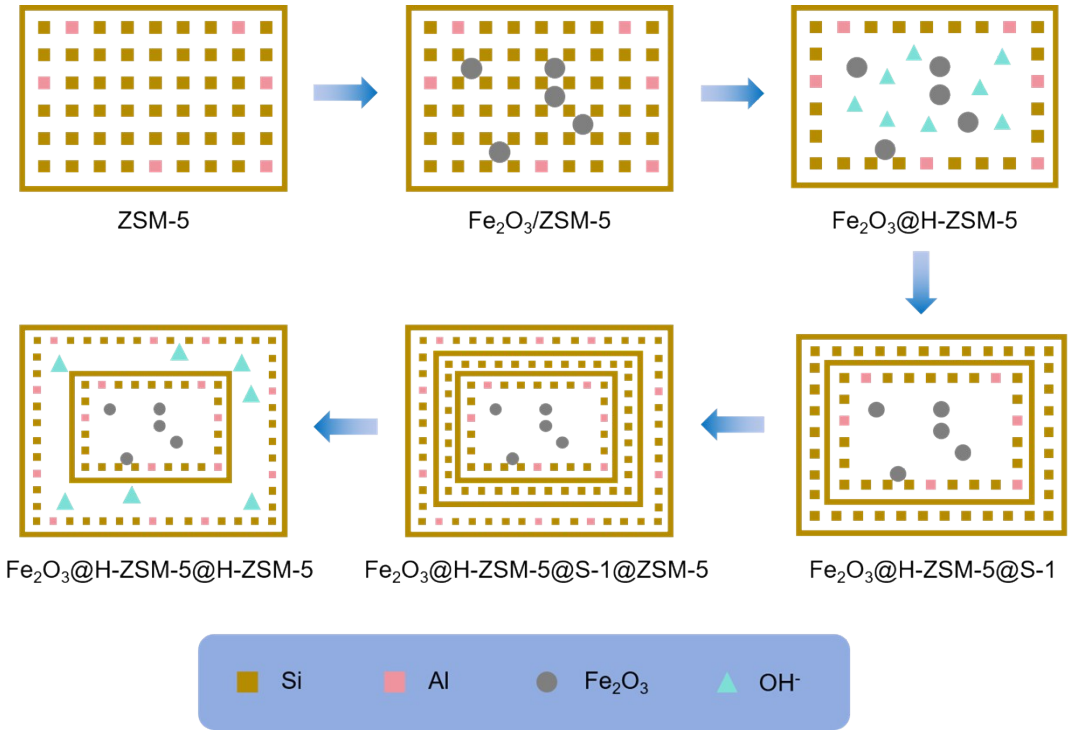
Synthesis of Fe_2O_3@H-ZSM-5@S-1: 4 g of Fe_2O_3@H-ZSM-5, 15.4 mL TEOS, and 16.5 mL of 25 wt% TPAOH were mixed in 33 mL deionized water and stirred at 35 °C for 3 h. The mixture was crystallized at 170 °C for 72 h to obtain 8 g of Fe_2O_3@H-ZSM-5@S-1.

Synthesis of Fe_2O_3@H-ZSM-5@S-1@ZSM-5: 6 g of Fe_2O_3@H-ZSM-5@S-1, 15.4 mL TEOS, 16.5 mL of 25 wt% TPAOH, and 0.55 g aluminum isopropoxide were mixed in 33 mL deionized water and stirred at 35 °C for 3 h. The mixture was crystallized at 170 °C for 72 h, followed by calcination at 550 °C for 6 h to obtain 10 g of Fe_2O_3@H-ZSM-5@S-1@ZSM-5.

Synthesis of Fe_2O_3@H-ZSM-5@H-ZSM-5: 0.55 g of Fe_2O_3@H-ZSM-5@S-1@ZSM-5 was mixed with 10 mL of 0.3 mol/L TPAOH solution and treated at 170 °C in a rotating oven (60 r/min) for 72 h. The final product was calcined at 500 °C for 4 h to obtain 0.4 g of Fe_2O_3@H-ZSM-5@H-ZSM-5.

To more clearly illustrate the necessity of each synthetic step, a schematic illustration of the structural evolution during the synthesis process has shown in

Schematic S1.



Schematic S1. Schematic illustration of the stepwise structural evolution during the synthesis of Fe_2O_3@H-ZSM-5@H-ZSM-5.

Characterization

The phase identifications of all samples were measured on a X'Pert Pro MRDDY2094 powder X-ray diffractometer (XRD) using Cu-Kα radiation (λ = 1.5418 Å) in the 2θ range of 4-40°. The morphology and sizes of all as-prepared samples were observed by a Hitachi SU-8010 scanning electron microscopy (SEM). The size of iron-oxide species and main elements mapping of Fe_2O_3@H-ZSM-5@H-ZSM-5 were measured on a FEI Tecnai F20 transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS), respectively. The proportion of main elements in samples were measured on a Perkin Elmer 8300 Inductively Coupled Plasma (ICP). The valence state proportions of iron-oxide species in samples were

analyzed on a Thermo Scientific K-Alpha X-ray photoelectron spectroscopy (XPS).

Experimental procedures

The TC degradation experiments were conducted in a 100 mL beaker at 25℃ with a stirring speed of 600 rpm for 120 min. The effects of different operation parameters on the TC degradation are investigated, including pH value (2, 3, 5, 7, 9, 11), catalysts dosage (5 mg, 15 mg, 30 mg, 45 mg, 60 mg, 75 mg), and PDS dosage (10 mg, 20 mg, 30 mg, 40 mg, 50 mg, 60 mg). The quenching experiments were carried out by adding various quenchers (MeOH, TBA, p-BQ and FFA) to investigate the contribution rates of each ROS. The different concentrations (5 mM, 10 mM, 20 mM) of NO_3^-, Cl^-, SO_4^{2-}, HPO_4^{2-}, HCO_3^- were added into the degradation system to explore anti-interference capability. The calculation formula for removal rate (eq. (1)) and the pseudo first order kinetic model (eq. (2)) are as follows:

$$\eta = \frac{(C_0 - C)}{C_0} \times 100\% \quad (1)$$

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

where η (%) is removal rate, C_0 (mg L^{-1}) is initial concentration of the organic pollutant, C (mg L^{-1}) is the concentration of the organic pollutant after the reaction, t (min) is the reaction time, and k (min^{-1}) represents the pseudo first order rate constant.

Analytical methods

The TC, RhB, MB, SMX and LEV concentration were tested on a 5500PC UV-visible spectrophotometer through a 0.45 μm water filter. The leaching concentration of iron species was determined by the modified 1,10-phenanthroline method[1] on a

5500PC UV-visible spectrophotometer. The ROS was detected on a Bruker a300 electron paramagnetic resonance (EPR) employing DMPO and TEMP as capture agents.

Table S1. The proportion of the main elements in different catalysts.

Sample	Si/Al ratio	Fe loading (wt. %)
ZSM-5	42.95	-
Fe_2O_3/ZSM-5	48.73	4.49
Fe_2O_3@H-ZSM-5@H-ZSM-5	67.51	0.90

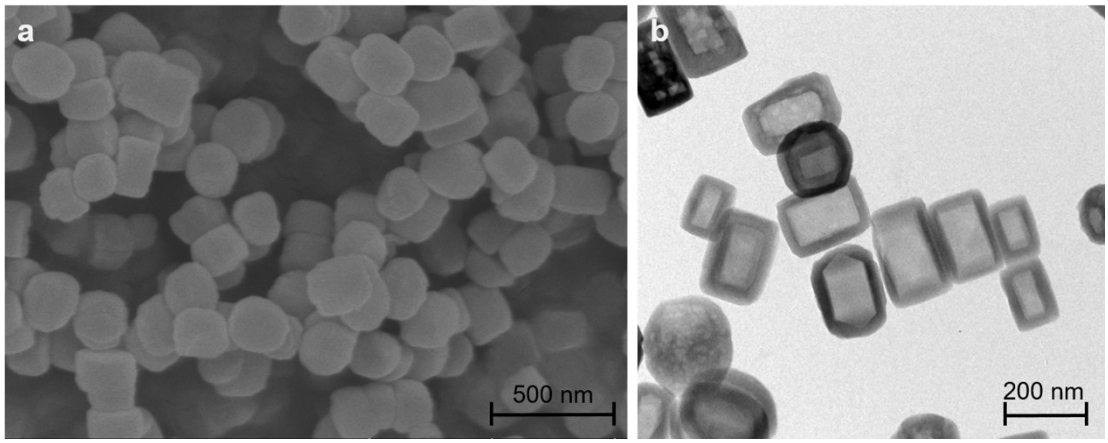


Fig. S1. SEM (a) and TEM (b) images of Fe_2O_3@H-ZSM-5.

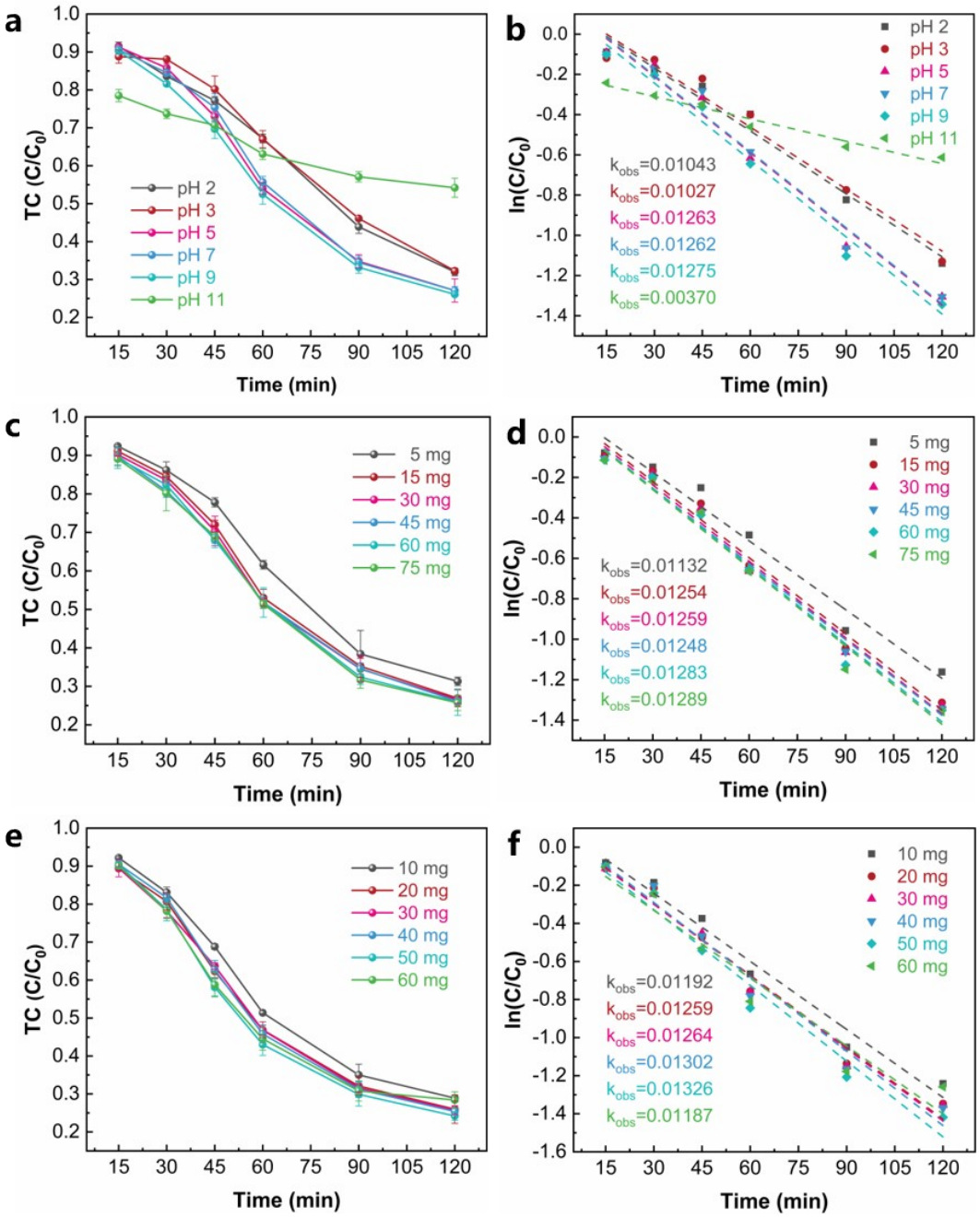


Fig. S2. Effects of (a) initial pH, (c) Fe_2O_3@H-ZSM-5@H-ZSM-5 dosage, (e) PDS dosage on TC degradation efficiency. Effects of (b) initial pH, (d) Fe_2O_3@H-ZSM-5@H-ZSM-5 dosage, (f) PDS dosage on the value of k_{obs}.

Table S2. Comparison of leaching concentrations of iron species in the reported catalysts.

Catalyst	Dosage ($g\ L^{-1}$)	Fe leaching concentration ($mg\ L^{-1}$)	Ref.
Fe_2O_3/S-1	2	1.86	(Dai et al., 2017)[2]
Fe_2O_3@Hol S-1	2	0.44	(Dai et al., 2017)[2]
Fe_2O_3-CuO/S-1	2	1.67	(Dai et al., 2017)[2]
Fe_2O_3-CuO@Hol S-1	2	0.28	(Dai et al., 2017)[2]
Fe_3O_4@ZSM-5	0.25	0.64	(Yu et al., 2010)[3]
ZSM-5(C@Fe)	0.5	0.065	(Chi et al., 2020)[4]
Fe_2O_3@H-ZSM-5@H-ZSM-5	0.3	0.011	This work

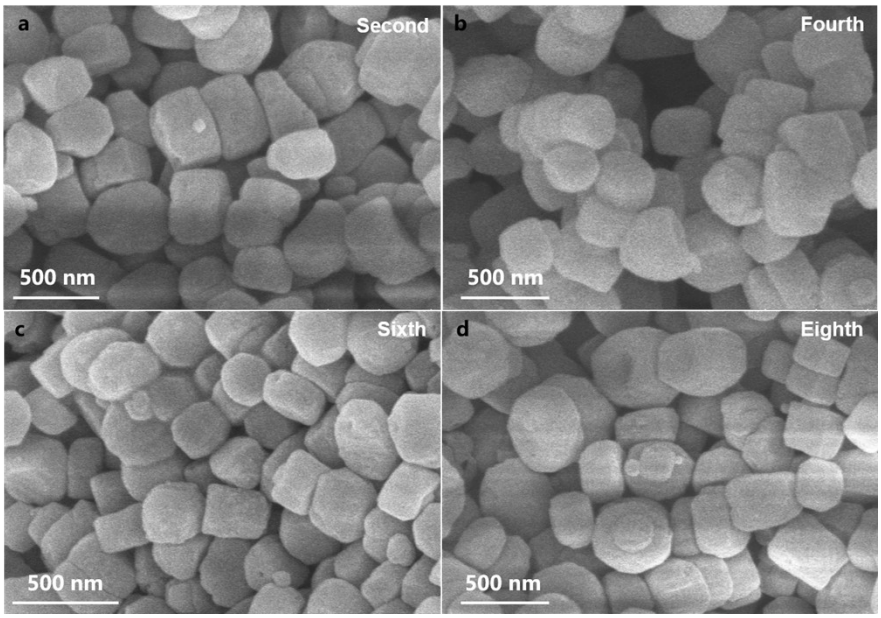


Fig. S3. SEM images of Fe_2O_3@H-ZSM-5@H-ZSM-5 after the (a) second, (b) fourth, (c) sixth, and (d) eighth catalytic cycles.

References

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