

Supplementary Information

A facile synthesis of iron functionalized hierarchically porous ZSM-5 and its visible-light photocatalytic degradation for organic pollutants

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Experimental Details

Materials

Indigoid dye C.I. Acid Blue 74 (high purity analysis dye), methyl orange (MO), aluminum isopropoxide $\text{Al}(\text{iPrO})_3$, tetrapropyl ammonium hydroxide (TPAOH), cetyltrimethyl ammonium chloride (CTAB) and H_2O_2 (35%, w/w) were obtained from shanghai J&K, China.

Preparation of catalysts

The hierarchically meso/microporous zeolite ZSM-5 was synthesized using a conventional process. Firstly, an oil (tetraethoxysilane TEOS, 50 mmol)-in-water (aqueous solution containing [aluminum isopropoxide $\text{Al}(\text{iPrO})_3$], 1mmol) emulsion was created at 288 K. Secondly, tetrapropyl ammonium hydroxide (TPAOH, 31mmol) was added into the emulsion dropwise and let hydrolyzing of TEOS at 288 K. Then, the mixture was stirred and aged for 24 h at 288 K. Finally, the emulsion was added into an aqueous solution of cetyltrimethyl ammonium chloride (CTAB, 2.8 mmol), and the reaction medium was stirred and aged for a period of time at room temperature. Afterward the hierarchically meso/microporous ZSM-5 (H-ZSM-5) was synthesized by hydrothermal treatment at 423 K and templates were removed at 823 K. Therein, the typical molar composition of the mixture was: $100\text{SiO}_2:1\text{Al}_2\text{O}_3:62\text{TPAOH}:16600\text{H}_2\text{O}:5.6\text{CTAB}$. The product finally was named as H-ZSM-5.

The hierarchically meso/microporous zeolite ZSM-5 functionalized with transition metal iron was synthesized by a simple direct ion exchange method, and described briefly as follows: ferric nitrate was dissolved in 20 mL distilled water to form a homogeneous solution, and then 0.5 g H-ZSM-5 sample was added into the solution for exchanging 5 h and ion-exchanged three times at 353 K. After that, the sample was washed with deionized water by centrifugation and then dried at 373 K overnight. The product finally was calcined at 823 K in air for 8 h and named as H-FeZSM-5. The Fe_2O_3 content of H-FeZSM-5 samples was adjusted by changing the concentration of the homogeneous solution of ferric nitrate (0.05M, 0.2M, 0.4 M and 0.8M).

A commercial Degussa P25 TiO_2 was used for comparison.

Catalytic procedure and analysis

Typically, 100 mg catalyst and 100 mL water solution containing organic compounds with the desired concentration were stirred magnetically at 298 K. Then 20 mM H_2O_2 was added into the mixture and initiated the reaction under the visible light irradiation (Xe-arc Osram 500 W). Representative aqueous-phase samples were withdrawn at periodic intervals and temporal concentration of organics in withdrawn samples was determined by means of UV-vis spectrophotometer. All the measurements were performed at 298 K.

Characterization

The metal contents were measured using inductively coupled plasma atomic emission

spectroscopy (ICP-AES) analyzer on a Vista AX. Powder X-ray diffraction (XRD) patterns were recorded using Cu K α radiation in the 2θ interval 5-50° on a Rigaku D/Max 2200PC diffractometer. The N₂ adsorption and desorption measurements were performed using Micromeritics Tristar 3000 at 77K. The total surface area and pore volume were calculated using the BET and BJH method. The field emission scanning electron microscopic (FE-SEM) images were obtained on a Hitachi S-4800. Transmission electron microscopic (TEM) images and energy disperse spectroscopy (EDS) were obtained on a JEOL-2010F electron microscope operated at 200 KV. UV-vis absorption spectra were recorded using a UV-3101PC Shimadzu spectroscope. X-ray photoelectron spectroscopy (XPS) signals were collected on an ESCALab250 instrument. TOC results were obtained on a TOC-CPH analyzer.

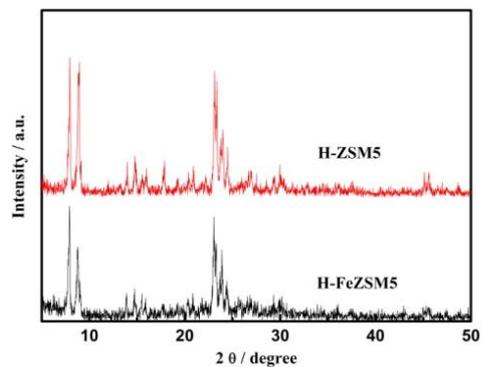


Figure S1. Wide angle XRD patterns of the prepared catalysts.

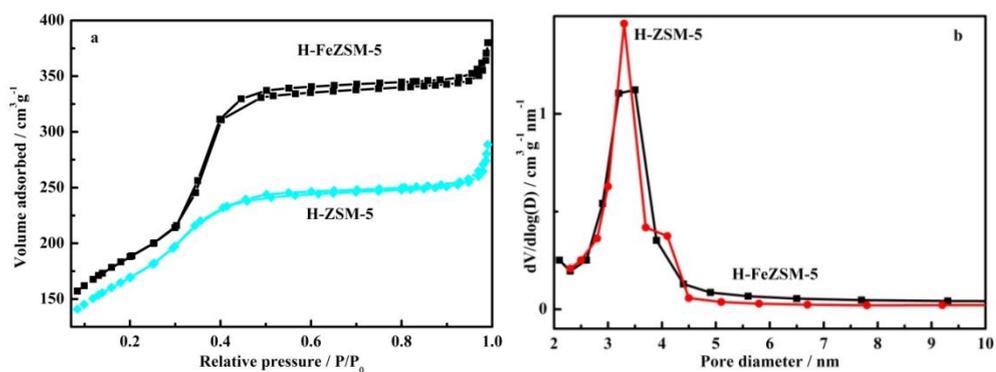


Figure S2. a-b) N₂ adsorption/desorption isotherms and corresponding BJH pore diameter

distribution curves of samples H-FeZSM-5 and H-ZSM-5.

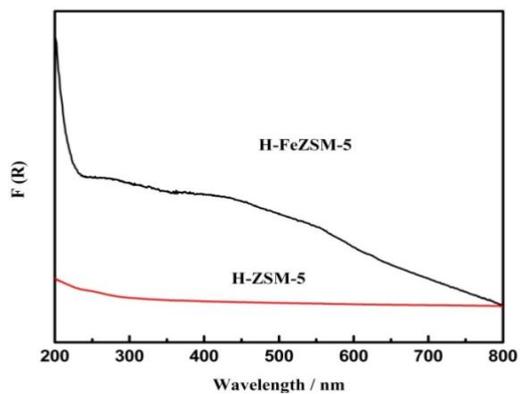


Figure S3. UV-vis spectra of samples H-FeZSM-5 and H-ZSM-5 in aqueous solution.

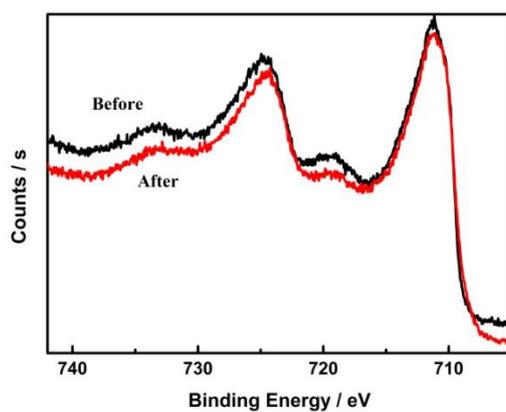


Figure S4. Fe_{2p} XPS spectra of the H-FeZSM-5 samples before and after catalytic reaction.

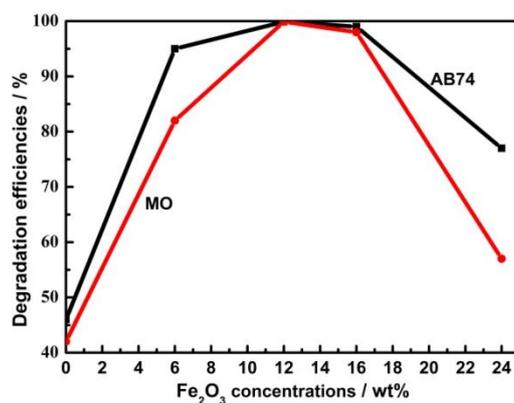


Figure S5. The variation of degradation efficiencies for MO and AB74 organic molecules with different Fe₂O₃ concentrations under visible light irradiation. (Operating conditions: catalyst: 1 g L⁻¹; Acid Blue 74 concentration: 400 mg L⁻¹; methyl orange, concentration: 200 mg L⁻¹ reaction temperature: 298 K; H₂O₂ concentration: 20 mM; natural pH (pH = 5.8); adsorption time: 720 min; degradation time of AB74 organics: 3 min. degradation time of MO organics: 30 min.)