Supplementary Information

Fe- and Mn-modified SO_4^{2-}/ZrO_2 conjoined O_2-Ac_2O as composite catalytic system for highly selective nitration of 1-nitronaphthalene with NO_2 to valuable 1,5-dinitronaphthalene

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1. Materials and instruments

1-NN (AR, 99%), $ZrOCl_2 \cdot 8H_2O$ (AR, 98%), and $Mn(NO_3)_2$ (AR, 50 wt% in H_2O), $Fe(NO_3)_3 \cdot 9H_2O$ (AR, 98.5%), $Ca[CH_3COO]_2$ (AR, 98%) and $La(NO_3)_3 \cdot 6H_2O$ (AR) were purchased from the Macklin Reagent Corporation. The liquid nitrogen dioxide (NO_2 purity>99.9%) was obtained from the Gas Company of Chengdu Keyuan Gas Co., Ltd. Zeolites (Hβ, HY, HZSM-5, Mordenite and MCM-41) and other solvents were obtained from commercial sources and were of the highest purity available. The quantitative analysis of nitration products was performed on gas chromatograph (GC) (Agilent 7890B), and nitrobenzene was used as the internal standard substance. The qualitative analysis of nitration products was performed on GC-MS (Shimadzu, GCMS-QP2010Plus).

2. Catalysts preparation

The metal-modified SZ containing Fe-Mn metals were prepared by coprecipitation-immersion process. The typical preparation procedures were as follows: 10.0 g $ZrOCl_2 \cdot 8H_2O$ and a certain amount of nitrates were dissolved in 150 mL of deionized water to form a precursor solution, and the solution was titrated dropwise concentrated ammonia water with vigorous agitation until the pH value of solution was reached to 9-10. After overnight aging at room temperature, the obtained precipitate was separated by filtration, and washed with deionized water until no detection of chloride. The washed precipitate was dried at 110 °C for 24 h,

and followed by immersing in a 1.0 mol/L H_2SO_4 (1 g solid/15 ml H_2SO_4) aqueous solution for 6 h. Finally, the resulted solid was dried, and calcined at 600 °C for 3 h. The obtained catalysts were abbreviated as M_mN_n-SZ, where "m and n" were the nominal contents of metals. Besides, tetragonal phases ZrO_2 was prepared by adding additional precipitate of $Ca[CH_3COO]_2$ to the precursor hydroxide suspension, then washed with ethylenediamine aqueous solution and calcined at 600 °C for 1 h. All zeolites catalysts were calcined at 600 °C for 3 h.

Preparation of treated $Fe_{1.5}Mn_{0.5}$-SZ. To further investigate the possible mechanism and catalyst interface changes during 1-NN nitration in NO_2-O_2-Ac_2O system, the $Fe_{1.5}Mn_{0.5}$-SZ was treated over NO_2-O_2-Ac_2O system. The treated process is the same as that of the following typical experimental procedure without 1-NN. The resulted suspension was centrifugation and the catalyst was dried at 60 °C for 6 h. The sample was marked as "Treated $Fe_{1.5}Mn_{0.5}$-SZ".

3. Catalysts characterizations

X-ray diffraction (XRD) patterns of samples were collected on a Japan Rigaku D/Max-2550V$^+$ diffractometer with Cu Kα radiation (λ=1.5418 Å) at 40 kV voltage and 300 mA electric current. The crystallite size D (nm) of samples was calculated by using Debye-Scherrer's equation.[1, 2] Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrometer in the wavenumber range of 400-

4000 cm^{-1}. The laser Raman spectra of samples were recorded with a Renishaw RM2000 spectrometer using the 325 nm line of Ar$^+$ laser emission, and the scan time was 60-180 s for a single spectrum. The total surface areas and the textural properties of samples were measured by the Brumaire-Emmer-Teller (BET) method on the NOVA-2200e nitrogen adsorption/desorption analyzer at 77 K. High-resolution transmission electron microscopy (HRTEM) images of samples were obtained on a FEI TALOS F200 instrument, equipped with a capable of energy dispersive X-ray (EDX) spectrometer. The thermal characterizations of samples were performed on Mettler TGA/DSC1/ 1600HT under 40 mL/min of nitrogen flow and 10 ^{o}C/min of heating rate room-temperature to 800 ^{o}C. The pyridine adsorption infrared spectra (Py-FT-IR) of samples were examined using a Thermo Nicolet 380 FT-IR spectrometer in the range of 1400-1650 cm^{-1}. The NH$_3$-TPD was performed on a Micromeritics AutoChem Ⅱ 2920 instrument from 50 to 600 ^{o}C. The element content of samples was determined by the inductively coupled plasma-optical emission spectrometer (ICP-OES) technique on an Agilent ICPOES730 instrument. The X-ray photoelectron spectroscopy (XPS) spectra of samples were collected on Thermo ESCALAB 250xi spectrometer with Al Kα radiation, and the binding energy referred to the C 1s peak (284.8 eV).

4. Catalytic test

The catalytic nitration of 1-NN with NO_2 was carried out in a 100 mL stainless reaction kettle with a magnetic stirring apparatus and temperature controller. Firstly, 1-NN (1.73 g), cold liquid NO_2 (1.84 g), solvent (10.0 g, acetic anhydride (Ac_2O) or acetonitrile (AN)) and catalyst (0.5 g) were added in the autoclave. Then, oxygen maintained at 0.5 MPa pressure was continuously input into the reactor through the inlet pipe until the reaction was finished. Finally, the resulted mixture was dissolved in the solvents of dichloroethane and AN (v/v=1:3). The products were quantified and identified by GC and GC-MS, respectively. The nitration products involved 1,5-, 1,8-, 1,3-, 1,4-, 1,6-, and 1,7-dinitronaphthalene with trace amounts of phthalandione and trinitronaphthalene (1,4,5-, and 1,3,8-trinitronaphthalene).
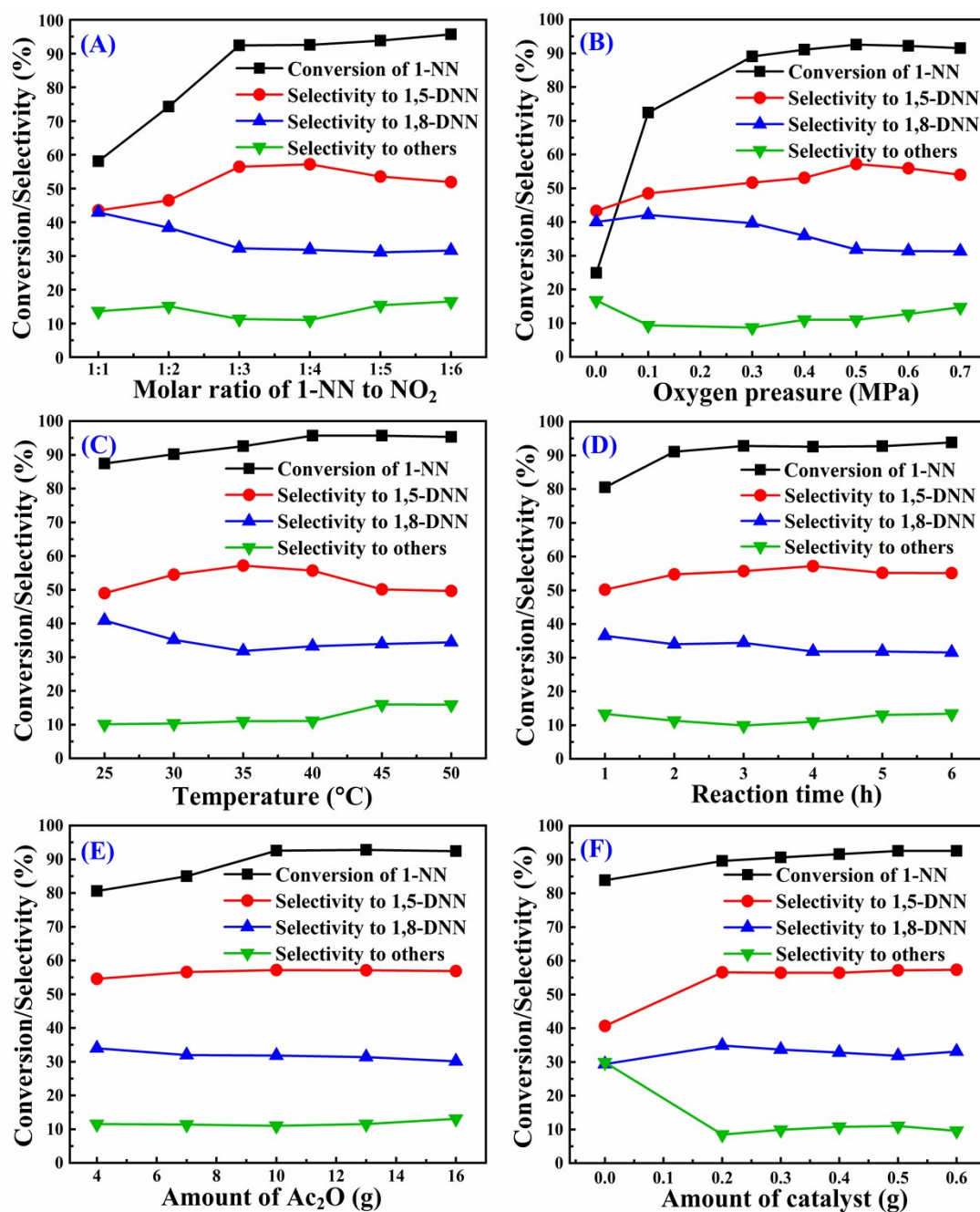
Fig. S1. The optimization of reaction parameters. Reaction conditions: (A) catalyst ($Fe_{1.5}Mn_{0.5}$-SZ) amount 0.5 g; Ac_2O 10.0 g; 35 °C; 4 h; and 0.5 MPa O_2; (B) molar ratio (1-NN/NO_2) 1:4; catalyst amount 0.5 g; Ac_2O 10.0 g; 35 °C; and 4 h; (C) molar ratio (1-NN/NO_2) 1:4; catalyst amount 0.5 g; Ac_2O 10.0 g; 4 h; and 0.5 MPa O_2; (D) molar ratio (1-NN/NO_2) 1:4; catalyst amount 0.5 g; Ac_2O 10.0 g; 35 °C; and 0.5 MPa O_2; (E) molar

ratio (1-NN/NO_2) 1:4; catalyst amount 0.5 g; 35 °C; 4 h; and 0.5 MPa O_2;

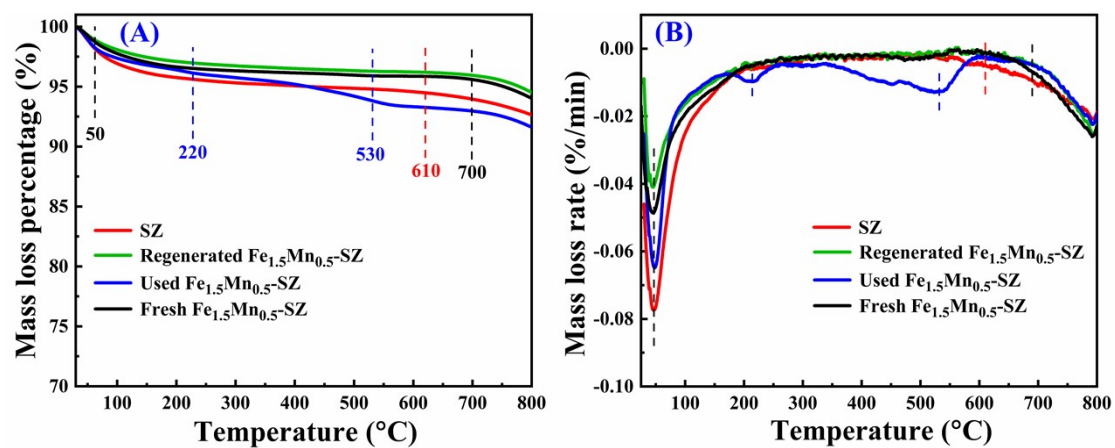(F) molar ratio (1-NN/NO_2) 1:4; Ac_2O 10.0 g; 35 °C; 4 h; and 0.5 MPa O_2.
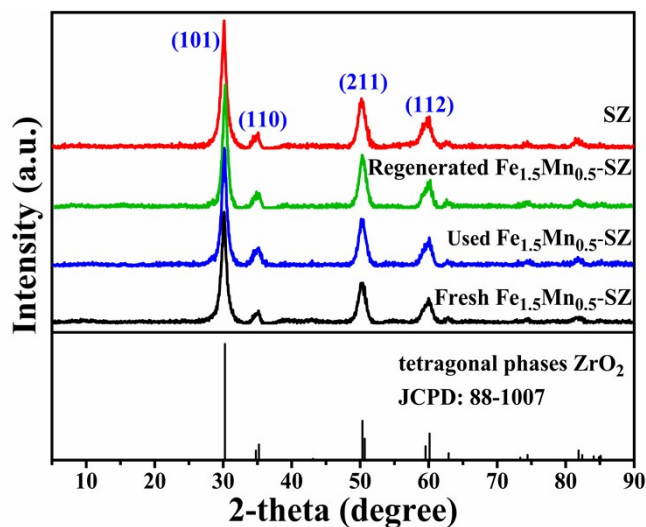
Fig. S2. XRD patterns of SZ, fresh, used and regenerated $Fe_{1.5}Mn_{0.5}$-SZ catalysts.
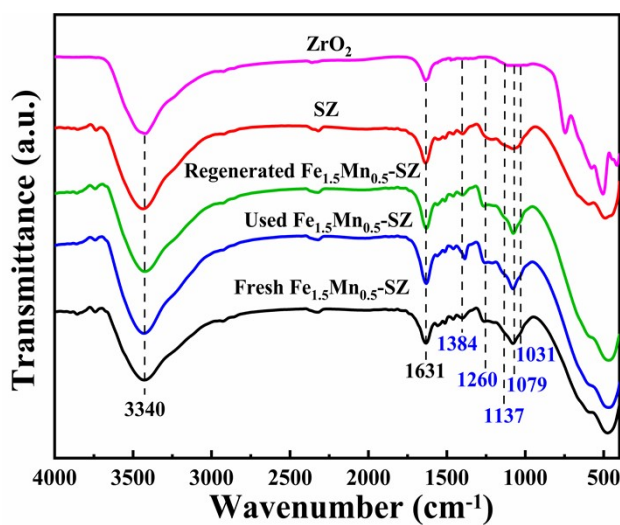
Fig. S3 FT-IR spectra of ZrO_2, SZ, fresh, used and regenerated $Fe_{1.5}Mn_{0.5}$-SZ catalysts.

Fig. S4 TG/DTG curves of SZ, fresh, used and regenerated $Fe_{1.5}Mn_{0.5}$-SZ catalysts.

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