Defective Silicotungstic acid-loaded magnetic floral N-doped carbon microspheres for ultra-fast oxidative desulfurization of high sulfur liquid fuels

Yefeng Liu a,b*, Xiaojie Yin a, Chuan Li a, Zhong Xie a, Fuyan Zhao a, Jing Li a, Jinpei Hei a, Yang Han a, nannan Wang a*, Peng Zuo a,*

a. Engineering Technology Research Center of Preparation and Application of Industrial Ceramics of Anhui Province, School of Chemistry and Material Engineering, Chaohu University, 1 Bantang Road, Chaohu, P. R. China, 238000

b. Engineering Research Center of High-frequency Soft Magnetic Materials and Ceramic Powder Materials of Anhui Province, Chaohu University, Chaohu 238000, P. R. China, 238000.

Corresponding author e-mail: lyf@chu.edu.cn (Yefeng Liu); nnw1990@126.com (nannan Wang); zp@chu.edu.cn (Peng Zuo)

1. Materials

Silicotungstic acid (H₄SiW₁₂O₄₀·xH₂O, abbreviated as SiW₁₂), H₃PW₁₂O₄₀·xH₂O (abbreviation for PW₁₂) and Phosphomolybdic acid (H₃PMo₁₂O₄₀·xH₂O, abbreviated as PMo₁₂) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Jiangsu, China); Fe₃O₄ nanoparticle particles (20 nm) and dopamine hydrochloride (DA) were obtained from Shanghai Macklin Biochemical Co., Ltd. (Jiangsu, China); tris (hydroxymethyl) aminomethane (C₄H₁₁NO₃, Tris) was obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Jiangsu, China); Dibenzothiophene (DBT), benzothiophene (BT),
and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Jiangsu, China); N-octane and acetonitrile were obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China); other drugs and reagents are commercially available analytically pure.

2. Characterization

Fourier transform infrared (FT-IR) spectra were carried out on a L1600300 Spectrum Two LITa infrared spectrometer (UK) using the KBr pellet approach. Ultraviolet-Visible spectra of the samples were obtained on a 2802 UV/Vis instrument (Youniko, Shanghai). X-ray photoelectron spectroscopy (XPS) was measured on a Thermo Fisher Scientific Escalab 250Xi X-ray photoelectron Spectrometer (American) using Al Ka radiation and the C1s peak at 284.8 eV as internal standard. The X-ray diffraction (XRD) measurements of all samples were collected with Bruker D8 Advance X-ray powder diffractometer (Germany) using a Cu Ka source to determine the chemical composition and crystalline structural properties of the samples. Scanning electronic microscopy (SEM) was determined with a Hitachi S4800 / FEI NANOSEM 450 microscope (USA). Energy-dispersive X-ray spectroscopy (EDX) analytical data were acquired on EDAX Apollo XT spectrometer (USA). Thermogravimetry analyser (TG) was conducted by a NETZSCH STA 449 F3 analyzer (Germany) in air condition from room temperature to 900 °C, with a change of 10 °C min⁻¹. The activate radicals were recorded from by EPR (MiniScope MS 5000, Magnettech, Germany) with 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) as electron capturing reagent. Tungsten content was tested by inductively-coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110, USA). The H₂ temperature-programmed reduction (H₂-TPR, MFTP3060, China) was performed with a heating rate of 10 °C/min in a 5 % H₂/Ar flow (50 cm³/min). Prior to monitoring of the TPR profiles, 100 mg of the samples were placed in a
quartz reactor and heated at 200 °C in an argon flow for 60 min. High performance liquid chromatograph (HPLC, LC98-I, Beijing Wenfen Analysis Instrument Technology Development Co., Ltd) was used to confirm the ODS reaction product.

3. The test condition of HPLC for ODS reaction

C18 reversed-phase column (200 mm×4.6 mm×5 μm ID), column temperature of 30 °C, test wavelength of 254 nm. The mobile phase was methanol/H2O (90/10, V/V) with flow rate of 1.0 mL·min⁻¹.

4. Kinetic studies of ODS, the apparent activation energy and TOF

The value of kinetic constant (k) given in Fig. 7 b can be obtained by the following equation:

\[
\frac{C_0}{C_t} = k t
\]

(1)

where \( k \) represents the rate constant, \( t \) is the reaction time, \( C_0 \) is the initial sulfur content of the model oil, and \( C_t \) is the sulfur content at time \( t \).

The plot of \( \ln k \) against \( 1/T \) is shown in Fig. 7 c according to the Arrhenius equation (2).

\[
\ln k = -\frac{E_a}{RT} + \ln A
\]

(2)

Based on the linear correlation between \( -\ln k \) and \( 1/T \) displayed in Fig. 7 c, the obtained linear equation is \( y=4665.36x-12.550 \), the estimated value of \( E_a \) is 38.79 kJ/mol.

\[ E_a \] is the apparent activation energy, kJ/mol; \( R \) is the molar gas constant, J/(mol·K); \( T \) is the thermodynamic temperature, K; \( A \) is the pre-exponential factor; and \( k \) is the reaction rate constant, min⁻¹.

\[
\text{TOF} = \frac{\text{mole number of converted DBT}}{\text{mole of active species content in catalyst} \times \text{reaction time (h)}}
\]

(3)
Fig. S1 EPR spectra of (a) $\gamma$-Fe$_2$O$_3$@NC@SiW$_{12}$-300 and Fe$_3$O$_4$@PDA@SiW$_{12}$ and (b) $\gamma$-Fe$_2$O$_3$

Fig. S2 XPS spectra of O1s of $\gamma$-Fe$_2$O$_3$@NC@SiW$_{12}$-300 and SiW$_{12}$-300

Fig. S3 Model oils containing DBT+ACN system added with $\gamma$-Fe$_2$O$_3$@NC-300 and $\gamma$-Fe$_2$O$_3$@NC@SiW$_{12}$-300, respectively.
Fig. S4 H₂-TPR spectra of γ-Fe₂O₃@NC@SiW₁₂-300, γ-Fe₂O₃@NC@PW₁₂-300 and γ-Fe₂O₃@NC@PMO₁₂-300.

Fig. S5 (a) Effects of H₂O₂ dosage on the sulfur removal rate (0.03 g catalysts; T = 60 °C); (b) Effects of catalyst dosage on the sulfur removal rate (n(H₂O₂) : n(S) = 2:1; T = 60 °C); (C) Effects of the loading amount of SiW₁₂ on the sulfur removal rate (0.03 g catalysts; n(H₂O₂) : n(S) = 2:1; T = 60 °C)

Fig. S6 HPLC chromatograms of (a) n-octane phases (b) and acetonitrile phases for ODS over γ-Fe₂O₃@NC@SiW₁₂-300 with H₂O₂ as oxidant.
Fig. S7 EPR spectra of (a) fresh and recovered $\gamma$-Fe$_2$O$_3$@NC@SiW$_{12}$-300 catalyst