



Highly efficient N-doped carbon supported FeS_x - Fe_2O_3 catalyst for hydrogenation of nitroarenes via pyrolysis of sulfurized N,Fe-containing MOFs

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Funding information

the Reform and Development Fund Project of Local University supported by the Central Government; Heilongjiang Provincial Government Postdoctoral Science Foundation, Grant/Award Number: LBH-Z17190; Doctoral Fund of Ministry of Education of China, Grant/ Award Number: 2017M621315; Reform and Development Fund Project of Local University supported by the Central Government

Integrating MOFs as precursor, especially for employing N-containing organic linkers, with sulfides is an effective method to prepare the highly efficient N-doped carbon supported metal-based catalysts for hydrogenation of nitroarenes. In this work, a N,Fe-containing metal organic frameworks (MOFs; termed as MIL88-HMTA) with spindle-like structure was prepared via self-assembly method, in which hexamethylenetetramine (HMTA) linker was introduced as N source. Subsequently, N-doped carbon supported FeS_x-Fe₂O₃ catalyst (named FeS_x-Fe₂O₃@CN) was fabricated upon the pyrolysis of sulfurized MIL88-HMTA. Catalytic experiments reveal that the FeSx-Fe₂O₃@CN delivered excellent performance for hydrogenation of nitroarenes in comparison with those of catalyst without sulfidation process (Fe₂O₃@CN) and conventional MIL88 derived catalyst (Fe₂O₃@C). The XRD, TEM, SEM/EDX, Raman, UV, and XPS analyses have revealed that the developed FeS_x-Fe₂O₃@CN catalyst exhibited outstanding catalytic efficiency was ascribed to synergistic effect between FeS_x and Fe₂O₃ species, abundant structural defects, more Fe-N_x species, and strengthened decomposition ability of hydrazine hydrate (N₂H₄·H₂O). Furthermore, the effect of sulfidation ratio (the mass ratio between thioacetamide and MIL88-HMTA) towards preparation of the developed FeS_x-Fe₂O₃@CN on the catalytic activity of hydrogenation reaction was also systematically performed. Notably, the optimized catalyst (denoted as FeS_x-Fe₂O₃@CN-8) exhibited unexpected performance and recyclability for hydrogenation of nitroarenes under mild condition. The pyrolysis of sulfurized N-containing MOFs may present a facile approach for fabricating MOFsderived N-doped carbon supported catalysts, which provides a potential application in heterogeneous catalytic reactions.

K E Y W O R D S

 ${\rm FeS_{x}\mathchar`selent} FeS_{x}\mbox{-} Fe_2O_3$ catalysts, hydrogenation of nitroarenes, N,Fe-containing MOFs, N-doped carbon, sulfidation

1 | INTRODUCTION

Catalytic hydrogenation, one of outmost important reactions in organic synthesis, is normally employed in the preparation of commercial applications of numerous products. Among hydrogenation products, arylamines are valuable intermediates for production of dyes, pharmaceuticals, pigments, and agricultural chemicals.^[1–7] For hydrogenation process, the transition metal (Fe, Co, Ni, etc.) catalysts,^[8–17] especially for Fe-based catalysts, have been considered as ideal catalysts compared with noblemetal (such as Pd, Pt, and Ru) catalysts^[18–33] due to their low cost and availability.

To date, the performance of N doped carbon catalysts for catalytic reactions was greatly boosted due to the N dopant could alter the wettability, Lewis basicity, and electronic structure of carbon materials.^[34-42] For the hydrogenation of nitroarenes, the N dopant is favorable for strengthening the interaction between acidic nitroarenes molecules and carbon-nitrogen carrier by dipole-dipole interaction, which is apt to promote the absorption and/or activation of the nitroarenes. Until now, the direct utilization of MOFs as suitable precursors/templates for fabricating the structure-tailored carbon hybrid materials without extra synthesis has become an increase tendency.^[43-47] In previously reported studies,^[48] the Fe-MOFs (MIL88) as a subclass of material has been extensively investigated on the basis of its 3D topological structure, abundant carbon, and high Fe content. In order to broaden its potential applications in heterogeneous reactions, it is highly desirable to employ a tailored MIL88 MOFs (introducing the N-functionalized linker) as the sacrificing precursor/template to fabricate N-doped carbon supported Fe-based catalyst.

Herein, we present an N,Fe-containing MOFs (MIL88-HMTA) as precursor to prepare highly efficient FeS_x -Fe₂O₃ catalyst for hydrogenation of nitroarenes to arylamines via pyrolysis of sulfurized N,Fe-containing MOFs. The developed MIL88-HMTA with spindle-like

morphology as self-templating precursor, prepared with Fe (NO₃)₃·9H₂O, fumaric acid (FMA), and hexamethylenetetramine (HMTA), where HMTA served as the N donor, introduced into the frameworks of MIL88-HMTA without using extra N source. Subsequently, FeS_x-Fe₂O₃@CN catalyst was fabricated via pyrolysis of the sulfurized MIL88-HMTA. The developed FeS_v-Fe₂O₃@CN catalyst showed unexpected activity and selectivity for hydrogenation of nitroarenes by using N_2H_4 ·H₂O as reductant on the basis of its abundant, low cost, and relatively safe (Scheme 1).^[49,50] Extensive characterization techniques including XRD, FESEM, TEM and HAADF-STEM, SEM/EDX, Raman, and XPS were performed to investigate the origin of enhanced catalytic performance of FeSx-Fe2O3@CN catalyst for hydrogenation of nitroarenes. This pyrolysis of sulfurized N,Fecontaining MOFs may create a promising method for the rational design of effective N doped carbon supported non-noble metal-based catalysts in other heterogeneous reaction.

2 | EXPERIMENTAL

2.1 | Synthesis of MIL88-HMTA and MIL88 MOFs

The MIL88-HMTA was prepared as described previously with some modifications.^[48] In a typical procedure, 0.36 mmol fumaric acid (FMA), 0.40 mmol Fe $(NO_3)_3 \cdot 9H_2O$, and hexamethylenetetramine (HMTA) were added together into the reactor. Subsequently, the homogeneous solution stood at 110 °C by solvothermal method. After cooling down to room temperature naturally, the precipitate was collected by centrifugation and washed for several times and dried at 80 °C overnight.

The MIL88 was similar to that of MIL88-HMTA except without choosing HMTA as the N-donor linker to add into the mixed solution.



2.2 | Synthesis of FeS_x - Fe_2O_3 @CN-*n* (*n* = 3, 6, 8, and 10)

The MIL88-HMTA was formed a homogeneous suspension by ultrasonication method. Then, various dosages of thioacetamide at the different mass ratio (from 1:3 to 1:10) with MIL88-HMTA were added, followed by stirring vigorously for 1 h. Then, the solution was transferred into a Teflon-lined stainless-steel autoclave, which was subsequently heated at 130 °C. The final product was separated, washed with water three times, and dried in an oven. Then, a series of N-doped carbon supported FeS_x-Fe₂O₃ catalysts with different sulfidation ratios were fabricated by pyrolyzing the sulfurized MIL88-HMTA composites at 500 °C. The resultant samples were denoted as FeSx-Fe2O3@CN-n (n represents the mass ratios of thioacetamide and MIL88-HMTA, n = 3, 6, 8, and 10). In addition, Fe₂O₃@CN and Fe₂O₃@C catalysts were also synthesized by pyrolyzing MIL88-HMTA and MIL88 MOFs under the same condition, respectively.

2.3 | Catalytic performance tests for hydrogenation of nitrobenzene

A mixture of nitrobenzene (0.81 mmol), N_2H_4 · H_2O (3.2 mmol), catalyst (10 mg), and ethanol (10 ml) were added into a 25 ml three-necked flask; then, the whole equipment was purged three times with N_2 to remove air. The resultant solution was heated to 85 °C. After cooling the reactor to room temperature naturally, the catalyst was separated and washed with ethanol for several times. The resulting solution was analyzed by gas chromatography-mass spectrometry (GC-MS) analysis.

2.4 | Catalytic decomposition of hydrazine hydrate

The catalytic reaction was carried out in 50 ml roundbottom flask containing N_2H_4 · H_2O (3.2 mmol), catalyst (10 mg), and ethanol (3 ml) at 85 °C oil bath. Catalytic decomposition reaction of N_2H_4 · H_2O , which releases of H_2 (along with N_2), was initiated by stirring the mixture. The gaseous products during the reaction were passed through a trap containing hydrochloric acid (1.0 M) to ensure the absorption of NH₃. The gas released was analyzed by a gravimetric waterdisplacement method.

2.5 | Characterization

Powder X-ray diffraction (XRD) patterns were tested by a Rigaku D/Max-3B X-ray diffractometer equipped with a Cu K α source ($\lambda = 1.5406$ Å). Field emission scanning electron microscopy (FESEM) experiments were performed by JEOLJSM-5600LV SEM/EDX instrument. Transmission electron microscopy (TEM) and high-angle annular dark field-scanning TEM (HAADF-STEM) images were taken on JEM-F200 instrument coupled with an element energy-dispersive X-ray spectrometer (EDS) (200 kV). Fourier transform infrared (FT-IR) was carried out on a Perkin-Elmer 100 spectrometer using KBr pellets. Thermal analyses were determined in an alumina pan from 30 to 800 °C at a heating rate of 10 °C min^{-1} by STA-6000. The N₂ adsorption-desorption measurements were recorded on a quantachrome autosorb IO and ASIOwin instrument at 77 K. The Raman data were analyzed on a Thermo Scientific DXR Raman microscope by using laser light of 532 nm wavelength to characterize the graphitic nature of the carbon material. The X-ray photoelectron spectroscopy (XPS) measurements were employed by ESCALAB 250 XPS system. The magnetic property of the prepared catalyst was measured by Quantum Design SOUID MPMS-XL7 magnetometer at 293 K.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and structural characterization of MIL88-HMTA

The fabrication procedure towards N-containing MIL88-HMTA precursor is depicted in Scheme 1. The MIL88-HMTA was first successfully synthesized by a feasible solvothermal method. The XRD analyses of the resulting MIL88-HMTA and MIL88 showed high crystallinity and matched well with that of the reported MIL88 (Figure S1a). As shown in Figure S1b, it can be observed that the decreased specific surface area (309.3 $m^2 g^{-1}$) and total pore volume (0.31 $\text{cm}^3 \text{g}^{-1}$) of MIL88-HMTA in comparison with that of MIL88 (511.5 $m^2 g^{-1}$ and $0.39 \text{ cm}^3 \text{ g}^{-1}$, respectively), which may be attributed to the channel blocked by HMTA linker. The FT-IR analysis further verifies the effect of HMTA linker on the structure of MIL88-HMTA (Figure S1c). The three characteristic absorption peaks are attributable to the symmetric and asymmetric vibration modes of -COOH (1,594 and 1,386 cm⁻¹) and N–H/O–H vibration (3,355 cm⁻¹) towards MIL88, respectively. For spectrum of



MIL88-HMTA, a new peak appeared at $1,255 \text{ cm}^{-1}$ mainly originates from the C—N stretching vibration of HMTA linker. In addition, the obviously red-shift $(1,392 \rightarrow 1,386 \text{ cm}^{-1})$ for —COOH stretching and the increased intensity of the N—H/O—H in spectrum of MIL88-HMTA as compared to that of MIL88 may be formation of hydrogen bonding after introduction of HMTA.

FESEM images of MIL88 (Figure S1d) and MIL88-HMTA MOFs (Figure 1a) suggest that the pristine MIL88 exhibits rod-shaped structure with an average size of \sim 5 µm in length and \sim 2 µm in diameter. However, it can be observed that MIL88-HMTA displays uniformly distributed spindle-like morphology with a length of $\sim 2 \,\mu m$ and a diameter of $\sim 0.4 \,\mu m$. All of which indicate that the introduction of HMTA has a significant effect on the morphology and size of the MIL88-HMTA MOFs during the synthesis process. The HAADF-STEM analysis (Figure 1b) further confirms the existences of Fe, C, N, and O elements from MIL88-HMTA. The uniformly distribution of N element on the surface of MIL88-HMTA suggests that the introduction of HMTA linker is consistent with following SEM/EDX mapping analysis (Figure S2).

TG-DSC analysis (Figure S3) for MIL88-HMTA on thermal property shows that an initial weight loss below 110 °C is assigned to the loss of physically adsorbed water. And then the main weight loss above 287 °C corresponds to the decomposition of the MIL88-HMTA framework (279 °C for MIL88). Moreover, for the DSC profiles of MIL88-HMTA and MIL88, the characteristic peak shifts to higher temperature for MIL88-HMTA (312 °C) in comparison with that of MIL88 (305 °C), indicating that the introduction of HMTA promotes the thermal stability of MIL88-HMTA.

3.2 | Catalytic performance and characterizations of as-synthesized catalysts

The catalytic performance of three Fe-based catalysts for hydrogenation of nitrobenzene to aniline was investigated (Figure 2a). The developed FeS_x -Fe₂O₃@CN catalyst exhibits the higher catalytic activity (69.6%) and yield (69.5%) in comparison with those of Fe₂O₃@CN (37.3% and 37.1%) and Fe₂O₃@C (16.5% and 16.1%). On the basis of previous reports,^[51,52] the N dopant plays an



FIGURE 1 FESEM image (a), HAADF-STEM image (b) of MIL88-HMTA and the corresponding mapping images (Fe, C, N, and O elements) (b1–b4), and the EDS spectrum (c) as well as surface content (d) **FIGURE 2** The catalytic performance (a), the XRD patterns (b), N₂ adsorptiondesorption isotherms (c), and Raman spectra (d) of FeS_x-Fe₂O₃@CN, Fe₂O₃@CN and Fe₂O₃@C catalysts for hydrogenation of nitrobenzene. Reaction condition: $n_{\text{nitrobenzene}} = 0.81 \text{ mmol},$ $n_{\text{hydrazine hydrate}} = 3.2 \text{ mmol},$ $m_{\text{catalyst}} = 10 \text{ mg},$ $V_{\text{ethanol}} = 10 \text{ ml}, T = 85 °C,$ t = 1.0 h



TABLE 1 Physicochemical properties of FeS_x - Fe_2O_3 @CN, Fe_2O_3 @CN and Fe_2O_3 @C catalysts

Catalyst	${S_{\rm BET}}^{\rm a}$ (m ² g ⁻¹)	$V_{\rm P}{}^{\rm b}$ (cm ³ g ⁻¹)	D _P c (nm)	$I_{\rm D}/I_{\rm G}^{\rm d}$
FeS _x -Fe ₂ O ₃ @CN	56.8	0.35	2.4	0.89
Fe ₂ O ₃ @CN	179.7	0.32	4.4	0.72
Fe ₂ O ₃ @C	92.6	0.14	4.4	0.85

 ${}^{a}S_{BET}$ is the specific surface area.

 ${}^{b}V_{\rm P}$ is the total pore volume measured at $P/P_0 = 0.99$.

 $^{c}D_{P}$ is the most probable NLDFT pore size.

 ${}^{d}I_{\rm D}/I_{\rm G}$ is the relative intensity ratio of D to G bands.

essential role on the charge mobility and electric hydrogenation of nitroarenes, property. In the decomposition experiments of N_2H_4 ·H₂O (Figure S4a) were conducted to verify the activated H species abilities of FeS_x-Fe₂O₃@CN, Fe₂O₃@CN, and Fe₂O₃@C catalysts. The experimental results have demonstrated that FeS_x-Fe₂O₃@CN catalyst (3.9 μ mol s⁻¹) exhibits higher decomposition rate (denoted as DC_{HH}) of $N_2H_4 \cdot H_2O$ than those for Fe_2O_3 @CN (2.8 µmol s⁻¹) and Fe_2O_3 @C (2.5 μ mol s⁻¹) under the same conditions (Table 1). Furthermore, a comparative experiment was further performed to investigate the effect of sulfidation towards FeS_x-Fe₂O₃@CN catalyst on hydrogenation activity and decomposed N₂H₄·H₂O ability. As shown in Figure S4b, for fully sulfurized catalyst (denoted as FeS_x@CN), the FeS_x@CN (43.5% and 43.3%) exhibits higher conversion and yield for hydrogenation of nitrobenzene compared to Fe₂O₃@CN (37.3% and 37.1%) under the same conditions. However, the catalytic activity of developed FeS_x-Fe₂O₃@CN (69.6% and 69.5%) for hydrogenation of nitrobenzene is highest among three Fe-based catalysts. In addition, for FeS_x@CN, the decomposition rate of N₂H₄·H₂O is 3.2 µmol s⁻¹ (Figure S4a), which is lower than that of developed FeS_x-Fe₂O₃@CN catalyst (3.9 µmol·s⁻¹). All of experiment results suggest that the sulfidation could promote the catalytic performance of FeS_x-Fe₂O₃@CN catalyst, which achieves unique synergistic effect between FeS_x and Fe₂O₃ species could quickly activate N₂H₄·H₂O to release H species and further enhance the hydrogenation efficiency in reaction.

In general, the modified measurements (e.g., N modification and sulfidation) on the preparation of catalysts have promotional effects on the absorption and/or activation of acidic nitroarenes molecules on the surface of catalysts due to its unique electronic structure and Lewis basicity.^[31,37,53] Herein, UV analysis was performed to investigate the interaction between nitrobenzene and as-prepared catalysts. As shown in Figure S5, the characteristic absorption band corresponding to nitrobenzene was observed at 259 nm. The desorption rate (denoted as $DS_{\rm NB}$) of Fe₂O₃@CN ($8.8 \times 10^{-3} \mu {\rm mol min}^{-1}$) changes significantly in contract to that of Fe₂O₃@C ($1.6 \times 10^{-2} \mu {\rm mol min}^{-1}$) at regular time intervals

(Table 1). However, the FeS_x-Fe₂O₃@CN exhibits the significantly lower $DS_{\rm NB}$ rate (4.5 × 10⁻³ µmol min⁻¹) than those for other two catalysts, implying that the pyrolysis of sulfurized N,Fe-containing MOFs method could enhance the adsorption and/or activation ability of acidic nitrobenzene molecules and further accelerate the reaction rate for hydrogenation of nitrobenzene.^[43] In addition, various characterizations have been proceeded to examine the relationship between structure of FeS_x-Fe₂O₃@CN catalyst and catalytic performance for hydrogenation of nitroarenes.

Figure 2b exhibits XRD patterns of the as-prepared FeS_x-Fe₂O₃@CN, Fe₂O₃@CN and Fe₂O₃@C catalysts. As shown in Figure 2b, the characteristic diffraction peaks at 30.2 °, 35.6 °, 43.3 °, 57.1 °, and 62.9 ° can be ascribed to the (220), (311), (400), (511), and (440) planes of γ -Fe₂O₃ (JCPDS No. 39-1346), respectively. For Fe₂O₃@CN catalyst, the full width at half maximum of Fe₂O₃ species becomes broader than that of Fe₂O₃@C. This phenomenon indicates that the introduction of the HMTA may improve the dispersity of Fe₂O₃ species. For pattern of FeS_x-Fe₂O₃@CN, new peaks corresponding to FeS₂ (JCPDS No. 71-1680) and Fe₇S₈ (JCPDS No. 71-0591) emerged, which suggests that pyrolysis of sulfurized N,Fe-containing MOFs could generate the FeS_x species.

The pore characters and specific surface areas (S_{BET}) of FeSx-Fe2O3@CN, Fe2O3@CN, and Fe2O3@C catalysts were evaluated by N2 adsorption-desorption analysis.^[54,55] The pore size distribution analyses (D_P) of the resulting carbon materials, based on the NLDFT (non-local density function theory) method, are listed in Table 1. As shown in Figure 2c, Fe₂O₃@CN catalyst presents higher S_{BET} (179.7 m² g⁻¹) and larger pore volume $(V_{\rm p})$ (0.32 cm³ g⁻¹) than that of conventional Fe₂O₃@C catalyst (92.6 m² g⁻¹and 0.14 cm³ g⁻¹, respectively). For FeS_x -Fe₂O₃@CN catalyst, the S_{BET} abruptly decreases to 56.8 $m^2\ g^{-1}\!,$ while the total pore volume increases to $0.35 \text{ cm}^3 \text{ g}^{-1}$. It can be observed that FeS_x-Fe₂O₃@CN possesses the largest pore volume among these three Fe-based catalysts, which may strengthen the adsorption of nitrobenzene during the hydrogenation process. Based on above analysis, it can be observed that the S_{BET} is not the main factor on the catalytic efficiency of three catalysts for hydrogenation of nitroarenes. Therefore, the following Raman and XPS characterizations were performed to investigate the difference in catalytic performance of three catalysts for hydrogenation process.

The structural changes and defects of three assynthesized catalysts were investigated by Raman technique. As depicted in Figure 2d, two signal peaks at around \sim 1,375 and 1,587 cm⁻¹ correspond to the D and G bands, which refer to the defect degree of carbon and the in-plane vibration of sp² carbon atoms, respectively. The relative intensity ratio of D band to G band $(I_{\rm D}/I_{\rm G})$ for the Fe₂O₃@CN (0.72) is obviously lower than that of $Fe_2O_3@C$ (0.85), suggesting that the incorporated N species originated from HMTA linker could redistribute charge and promote the electron transfer between Febased species and carbon-framework. However, for FeS_x-Fe₂O₃@CN catalyst, the I_D/I_G ratio is 0.89, which is obvious higher than that of Fe₂O₃@CN (0.72) catalyst, indicating that the pyrolysis of sulfurized N,Fe-containing MOFs could increase the amounts of surface structural defects of carbon support. The generated surface structural defects could expose more active sites and enhance mass transfer in the hydrogenation process.

The surface chemical bonding states of FeS_x-Fe₂O₃@CN, Fe₂O₃@CN, and Fe₂O₃@C catalysts were elucidated by XPS analysis (Figure 3a-c). For Fe₂O₃@C, the deconvolution of Fe 2p can be divided into five characteristic peaks. The peaks at approximately 723.9 and 710.7 eV are assigned to Fe²⁺, whereas 725.3 and 712.4 eV are attributed to Fe^{3+} . The satellite peak (718.7 eV) is consistent with the characteristic of γ -Fe₂O₃^[56] In contrast to that of Fe₂O₃@C, the Fe 2p XPS spectra of FeSx-Fe2O3@CN and Fe2O3@CN catalysts display a new peak at 710.2 eV corresponding to Fe coordinated N to form Fe-N_x configuration,^[57,58] which helps immobilize the metallic Fe atoms on their original position and prevent their agglomeration and mobility. Among three catalysts, the developed FeS_x-Fe₂O₃@CN catalyst has the highest contents of Fe^{2+} and $Fe-N_x$ species, suggesting that pyrolysis of sulfurized N,Fecontaining MOFs could generate more active Fe²⁺ species and enhance the dispersity of Fe species. Moreover, from the S 2p XPS analysis (Figure 3d), it can be observed that the S_n^{2-} and S^{2-} (164.8, 163.9, 163.2, and 162 eV) as well as oxidized sulfur species (SO_x^{2-}) (168.8 and 168.3 eV) species were formed on the surface of developed FeS_x-Fe₂O₃@CN catalyst. Generally, the degree of sulfidation plays a crucial impact on the preparation of the sulfurized catalysts.^[59] Therefore, the sulfidation ratios between thioacetamide and MIL88-HMTA for synthesis of FeSx-Fe2O3@CN catalyst were optimized.

3.3 | Effect of sulfidation ratio

As shown in Figure 4a, the catalytic conversion of FeS_x - Fe_2O_3 @CN-*3* for hydrogenation of nitrobenzene is 27.3%. With the sulfidation ratio increases from 3 to 6, the catalytic conversion and yield of FeS_x - Fe_2O_3 @CN-*6* increase from 27.3% to 49.5% and 27.1% to 49.3%, respectively.

FIGURE 3 Fe 2p XPS spectra (a-c) for FeS_x-Fe₂O₃@CN, Fe₂O₃@CN and Fe₂O₃@C catalysts, and S 2p XPS spectrum (d) for FeS_x-Fe₂O₃@CN catalyst



FIGURE 4 Catalytic activity (a), XRD patterns (b), Raman spectra (c) of the FeS_x-Fe₂O₃@CN-*n* (n = 3, 6, 8,and 10) catalysts, and Fe 2p XPS spectrum for FeS_x-Fe₂O₃@CN-8. Reaction condition: $n_{\text{nitrobenzene}} = 0.8 \text{ mmol},$ $n_{\text{hydrazine hydrate}} = 3.2 \text{ mmol},$ $m_{\text{catalyst}} = 10 \text{ mg},$ $V_{\text{ethanol}} = 10 \text{ ml}, T = 85^{\circ}\text{C},$ t = 40 min

Further increasing the sulfidation ratio, the catalytic conversion and yield of FeS_x - Fe_2O_3 @CN-8 reached to 73.3% and 73.2%, respectively. Then, a decrease catalytic

conversion (40.5%) and yield (40.3%) of FeS_x-Fe₂O₃@CN-10 for hydrogenation reaction was detected when increasing the sulfidation ratio to 10. Therefore,

the differences in catalytic activities of four FeS_{x} - Fe_2O_3 @CN-*n* (*n* = 3, 6, 8, and 10) catalysts for hydrogenation of nitrobenzene to aniline have been elucidated by various techniques including the following XRD, SEM/EDX, TEM, Raman, and XPS.

The crystalline structures of the as-prepared FeS_x- Fe_2O_3 @CN-*n* (*n* = 3, 6, 8, and 10) catalysts with different sulfidation ratios were investigated by XRD analysis. As shown in Figure 4b, for FeS_x-Fe₂O₃@CN-3, the dominated γ -Fe₂O₃ phase is identified by JCPDS file (JCPDS No. 39-1346). Upon increasing the sulfidation ratio from 3 to 6, the FeS₂ (JCPDS No. 71-1680) and Fe₇S₈ (JCPDS No. 71-0591) species were generated in FeS_x-Fe₂O₃@CN-6. Then, the ratio of FeS₂ versus Fe₇S₈ was improved when the sulfidation ratio increased from 6 to 8. However, the ratio of FeS₂ versus Fe₇S₈ obviously decreased for FeS_x-Fe₂O₃@CN-10 catalyst with the sulfidation ratio is 10. Based on the above catalytic results, much more active FeS₂ species contained in FeS_x-Fe₂O₃@CN-8 may a reason for why the FeSx-Fe2O3@CN-8 delivers the highest catalytic efficiency in hydrogenation of nitrobenzene.

The structural changes and defects of the four FeS_x - $Fe_2O_3@CN$ -n (n = 3, 6, 8, and 10) catalysts were evaluated by Raman experiment (Figure 4c). It can be observed that the ratio values of I_D/I_G for the four FeS_x - $Fe_2O_3@CN$ -n (n = 3, 6, 8, and 10) catalysts with different sulfidation ratios are 1.1, 0.89, 0.86, and 1.1, respectively. Obviously, the developed FeS_x - $Fe_2O_3@CN$ -8 catalyst exhibits the lowest I_D/I_G ratio among four catalysts, which endows FeS_x - $Fe_2O_3@CN$ -8 with unique electronic configuration to facilitate the electron transfer and further accelerate the hydrogenation rate in catalytic process.

The effect of the sulfidation ratios on the surface chemical states of Fe and S elements for FeS_x-Fe₂O₃@CN-*n* (n = 6 and 8) catalysts was evaluated by XPS experiment (Figures 4d and S6). From the Fe 2p spectra, the Fe²⁺ and Sn²⁻ contents in FeS_x-Fe₂O₃@CN-8 (64.6% and 26.3%) are obviously higher than those of FeS_x-Fe₂O₃@CN-6 (55.8% and 7.6%), indicating that more active FeS₂ species were formed in FeS_x-Fe₂O₃@CN-8, which is well consistent with above XRD analysis.



FIGURE 5 The TEM (a) and HRTEM (b) images, as well as the HAADF-STEM image of (c) the FeS_x-Fe₂O₃@CN-8 catalyst and the corresponding mapping images (S, O, and Fe elements) (c1–c3) and the EDS result (d) (inset is the values of elements)

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Entry	Substrate	Product	Time (h)	Yield (%)	Selectivity (%)
1	NO ₂	NH ₂	2.0	99.1	>99.9
2		CI	2.0	97.5	>99.8
3		NH ₂ CI	2.0	95.7	>99.9
4 ^[b]	NO ₂	NH ₂	5.0	99.2	>99.7
5	NO ₂ CF ₃	NH ₂ CF ₃	2.0	99.8	>99.7
6	NO ₂ COOC ₂ H ₅	COOC ₂ H ₅	2.0	99.7	>99.9
7	NO ₂	NH ₂ CN	1.0	99.6	>99.7
8	NO ₂	NH ₂ NH ₂	5.0	99.7	>99.8
ð _[p]		NH2 NH2	7.0	98.6	>99.7
10 ^[b]		NH ₂ NO ₂	1.0	93.6	>99.5
11	OH OH	OH OH	3.0	99.8	>99.9

TABLE 2 Hydrogenation of various substituted nitroarenes over FeS_x-Fe₂O₃@CN-8 catalyst^a

(Continues)

TABLE 2 (Continued)

Entry	Substrate	Product	Time (h)	Yield (%)	Selectivity (%)
12	NO ₂ CH ₃	NH2 CH3	8.0	96.8	>99.8
13 ^[b]	NH ₂ CI NO ₂	NH2 CI NH2	4.0	99.2	>99.9

^aReaction condition: substrate (0.8 mmol), hydrazine hydrate (3.2 mmol), catalyst (10 mg), ethanol (10 ml), 85°C.

^bReaction condition: substrate (0.4 mmol), hydrazine hydrate (1.6 mmol).

The nanostructure of as-prepared FeS_x-Fe₂O₃@CN-8 catalyst was analyzed by TEM (Figure 5). As shown Figure 5a, it can be observed that the sulfidation process significantly affects the morphology of as-synthesized FeS_x-Fe₂O₃@CN-8 catalyst. From Figure 5b, the five values of d- spacings were attributed to the (200) and (111) planes of FeS₂ phases (0.274 and 0.312 nm, respectively), (203) and (200) planes of Fe_7S_8 phase (0.265 and 0.298 nm, respectively), and (220) plane of γ -Fe₂O₃ phase (0.255 nm), which is well in accordance with the above XRD analysis. Meanwhile, distributions of Fe, S, and O elements were investigated by HAADF-STEM and the corresponding energy-dispersive X-ray (EDX) elemental mapping analysis (Figure 5c). The representative HAADF-STEM analysis of FeSx-Fe2O3@CN-8 revealed that Fe, S, and O elements were uniformly distributed on the carbon-nitrogen support without any obvious aggregation. Moreover, The SEM/EDX analysis was also performed to investigate the distributions of C, N, O, S, and Fe elements on surfaces of the FeS_x - Fe_2O_3 @CN-n (n = 3, 6, 8, and 10) catalysts. As depicted in Figure S7, the SEM images of each catalyst and their corresponding EDX mappings of overlay, C, N, S, O, and Fe coupled with EDX spectra have also been conducted. From the EDX mappings of Fe, O, and S elements coupled with Fe, O, and S signals, it can be observed that FeS_x-Fe₂O₃@CN-8 catalyst exhibits the most uniform distributions of Fe, O, and S species among these four catalysts, which may endow FeS_x-Fe₂O₃@CN-8 to deliver the highest catalytic performance in hydrogenation process.

3.4 | Hydrogenation of nitroarenes to substituted arylamines over FeS_x -Fe₂O₃@CN-8 catalyst

A wide variety of substituted nitroarenes were employed as substrates for the hydrogenation to arylamines

catalyzed by FeS_x-Fe₂O₃@CN-8 under the optimized reaction condition. The catalytic results are summarized in Table 2; the FeSx-Fe2O3@CN-8 catalyst exhibits high activity (99.1%) and selectivity (>99.9%) (entry 1), which is higher than other reported catalysts (Table S1). Moreover, the catalytic performance of FeS_x-Fe₂O₃@CN for hydrogenation of nitrobenzene into aniline has also been tested with H₂ as reductant (Table S2). Meanwhile, it reveals that nitroarenes with electron-deficient groups (containing chloro-, fluoro-, trifluomethyl-, ester-, and cyano-, etc.) exhibited highly efficient yields and outstanding selectivities to their corresponding arylamines (Table 2, entries 2–10). Other substrates bearing electronrich groups including hydroxyl- and methyl- were fully hydrogenated into corresponding arylamines (Table 2, entries 11 and 12). The hydrogenation of multi-amino nitroarene was also investigated (Table 2, entry 13). Notably, all substituted nitroarenes exhibited activities (>93.0%) and selectivities (>99%) without any products. The above reaction results demonstrate that the FeS_x-Fe₂O₃@CN-8 catalyst may serve as a promising candidate for hydrogenation of diverse nitroarenes to their corresponding functionalized arylamines.

3.5 | Reusability of FeS_x-Fe₂O₃@CN-8 catalyst

Recyclability of catalysts is a significant criterion in the heterogeneous reactions.^[60–62] Therefore, the reusability of FeS_x -Fe₂O₃@CN-8 catalyst was investigated in Figure 6. The magnetic property of FeS_x -Fe₂O₃@CN-8 was measured by the Quantum Design SQUID MPMS-XL7 magnetometer. As shown in Figure 6a, the magnetic hysteresis loop for developed FeS_x -Fe₂O₃@CN-8 catalyst exhibits a saturated magnetization of 10.4 emu g⁻¹ at 5,500 Oe at 293 K.^[63,64] As shown in Figure 6a inset, the

Applied Organometallic_WILEY^{11 of 13} Chemistry (a) 10 (b) Conversion Selectivity Magnetization (emu/g) 5 0 -5 -10 0 3 Cycles -5500 Ó 5500 2 5 1 4 Magnetic Field (Oe)

FIGURE 6 Hysteresis loop (a) and recyclability tests (b) for FeS_x-Fe₂O₃@CN-8 catalyst



4 | CONCLUSIONS

The MIL88-HMTA was first synthesized by a feasible solvothermal reaction between Fe³⁺ ion, FMA, and N-containing HMTA organic linkers. A highly efficient N-doped carbon supported FeSx-Fe2O3 catalyst (FeSx-Fe₂O₃@CN) has been prepared via pyrolysis of sulfurized MIL88-HMTA. Integrating the unique properties of MOFs and sulfides yields synergistic effect between FeS_x and Fe₂O₃, high dispersion of Fe species and content of Fe^{2+} , and more structural defects in the carbon-nitrogen framework, which accelerate adsorption and/or activation of reactant molecules (nitroarenes and N_2H_4 · H_2O) during the hydrogenation process. All these unique endow the developed FeSx-Fe₂O₃@CN characters catalyst exhibits unexpected hydrogenation activity and selectivity for hydrogenation of nitroarenes in comparison with those of catalyst without sulfidation process (Fe₂O₃@CN) and conventional MIL88 derived catalyst (Fe₂O₃@C). Moreover, the optimized FeS_x-Fe₂O₃@CN-8 catalyst may be a potential candidate for other hydrogenation reactions due to its outstanding catalytic performance and recyclability.

ASSOCIATED CONTENT

Supporting Information includes XRD, N_2 adsorption– desorption analysis, SEM and TGA of MIL88-HMTA and MIL88, SEM/EDX of MIL88-HMTA, UV, XPS, SEM/EDX and TGA of Fe-based catalysts, and the possible catalytic mechanism.

ACKNOWLEDGMENTS

This work was financially supported by the Reform and Development Fund Project of Local University supported by the Central Government, Doctoral Fund of Ministry of Education of China (2017M621315), and Heilongjiang Provincial Government Postdoctoral Science Foundation (LBH-Z17190).

AUTHOR CONTRIBUTIONS

Xuewei Li: Formal analysis; investigation. Wei She: Software; validation. Jing Wang: Software; validation. Weizuo Li: Conceptualization; project administration. Guangming Li: Funding acquisition; resources.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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