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Article

A facile sulfur-assisted method to synthesize porous alveolate Fe/g-C₃N₄ catalysts with ultra-small cluster and atomically dispersed Fe sites

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ABSTRACT

Heterogeneous catalysts with ultra-small clusters and atomically dispersed (USCAD) active sites have gained increasing attention in recent years. However, developing USCAD catalysts with high-density metal sites anchored in porous nanomaterials is still challenging. Here, through the template-free S-assisted pyrolysis of low-cost Fe-salts with melamine (MA), porous alveolate Fe/g-C₃N₄ catalysts with high-density (Fe loading up to 17.7 wt%) and increased USCAD Fe sites were synthesized. The presence of a certain amount of S species in the Fe-salts/MA system plays an important role in the formation of USCAD S-Fe-salt/CN catalysts; the S species act as a “sacrificial carrier” to increase the dispersion of Fe species through Fe-S coordination and generate porous alveolate structure by escaping in the form of SO₂ during pyrolysis. The S-Fe-salt/CN catalysts exhibit greatly promoted activity and reusability for degrading various organic pollutants in advanced oxidation processes compared to the corresponding Fe-salt/CN catalysts, due to the promoted accessibility of USCAD Fe sites by the porous alveolate structure. This S-assisted method exhibits good feasibility in a large variety of S species (thiourea, S powder, and NH₄SCN) and Fe salts, providing a new avenue for the low-cost and large-scale synthesis of high-density USCAD metal/g-C₃N₄ catalysts.

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1. Introduction

The development of USCAD catalysts is a new frontier in heterogeneous catalysis. This is attributed to the excellent cat-

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alytic performance, high atom-utilization, good stability, and reusability of the catalysts in a variety of applications [1–6]. However, the synthesis of USCAD catalysts in a controlled manner has been very challenging [7,8]. Various methods have been developed, including (1) anchoring USCAD sites *via* ligands, uncapped sites, or defects [9–11]; (2) encapsulating metal clusters within cages or channels of metal-organic frameworks and zeolites [12–14]. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is emerging as an ideal support for USCAD catalysts, due to its chemical stability, low cost, and abundant N anchoring sites to stabilize USCAD sites [15–17]. Thermal condensation is commonly used to synthesize USCAD catalysts supported on $g\text{-C}_3\text{N}_4$ [18–21]. However, the obtained catalysts generally have bulky structures with a low specific surface area, and most sites are encased by $g\text{-C}_3\text{N}_4$, resulting in low catalytic efficiency. USCAD catalysts with a porous structure and increased active sites can be prepared by adding hard templates for pyrolysis [22,23]. Unfortunately, this method suffers from complex procedures, high metal leaching, and high cost during de-templating. Therefore, it is highly desirable to develop a facile, template-free approach for synthesizing USCAD catalysts with increased active sites.

Owing to their low cost and environmental advantages, heterogeneous Fe-based catalysts have been widely studied and applied in many catalysis fields, such as in the synthesis of ammonia, Fischer-Tropsch process, electrocatalysis, and advanced oxidation processes (AOPs) [24–26]. Recently, to solve the water crisis caused by human activities, AOPs, which are among the most effective strategies for dealing with contaminated water, have gained considerable attention [27]. However, most traditional heterogeneous Fe-based catalysts used in AOPs have large particles and wide particle size distribution leading to low catalytic efficiency [2,28]. Bearing these aspects in mind, and motivated by the fact that USCAD catalysts have exhibited superior performance in heterogeneous catalysis, we anticipate that the application of Fe-based USCAD catalysts should enhance the catalytic efficiency. In this regard, USCAD catalysts based on $g\text{-C}_3\text{N}_4$, with good photocatalytic properties, environmental friendliness, and low cost, were expected to be highly efficient catalysts for AOPs. For the enhancement of catalytic performance, the key is to design and synthesize porous metal/ $g\text{-C}_3\text{N}_4$ catalysts with high-density USCAD sites. Herein, we report a template-free S-assisted method to synthesize porous alveolate $g\text{-C}_3\text{N}_4$ with high-density and increased USCAD Fe sites *via* a one-step pyrolysis process. The presence of a certain amount of S species in the Fe-salts/MA system is proven to be quite important for synthesizing USCAD S-Fe-salt/CN catalysts with porous alveolate structure. The role of S is detailed by TG-MS, XPS, and IR. S acts as a “sacrificial carrier” to increase the dispersion of Fe species and produce the porous alveolate structure accompanied by escaping in the form of SO_2 during pyrolysis, thereby avoiding the complex de-templating process. Due to the high-density USCAD Fe sites and promoted accessibility, S-Fe-salt/CN catalysts exhibit excellent activity and reusability for degrading various model organic pollutants in AOPs. We have delimited commercially low-cost ingredients used in the whole synthesis. The facile and low-cost S-assisted

method shows promising potential for the synthesis of high-density USCAD catalysts and will advance the practical applications of heterogeneous Fe-based catalysts in AOPs.

2. Experimental

2.1. Materials

All chemicals are of analytical grade and were used without further purification. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferrous oxalate (FeC_2O_4), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ammonium ferric sulfate hexahydrate ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), ferric acetylacetonate ($\text{Fe}(\text{acac})_3$), ferric ammonium citrate (NH_4FeCit), methyl orange (MO), methylene blue (MB), rhodamine B (RhB), phenol, and acetophenone were purchased from Damao Chemical Reagent Factory (Tianjin, China). Ammonium nitrate (NH_4NO_3), urea, thiourea (TU), S powder, ammonium thiocyanate (NH_4SCN), and 30% hydrogen peroxide aqueous solution (H_2O_2 , 30%) were obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Melamine (MA) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were received from Aladdin (Shanghai, China).

2.2. Synthesis of catalysts

First, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and MA were fully ground in an agate mortar with an Fe:MA mole ratio of 1:10; thereafter, the mixture was calcined at 600 °C for 5 h in a tube furnace at a ramping rate of 5 °C min^{-1} in N_2 atmosphere. Prior to the calcination, the tube furnace was pre-purged by vacuuming and back-filling with N_2 twice. The resultant catalyst was named as Fe/CN, and the corresponding precursor was named as Fe/CN-pre. The catalysts synthesized by pyrolyzing the mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, MA, and TU were carried out by using the same procedure, and the catalysts were noted as S-Fe/CN-X (X represents the ratio of MA to TU), and the corresponding precursors were named as S-Fe/CN-X-pre. For comparison, TU was also replaced by S powder, NH_4SCN , urea, and NH_4NO_3 , and the samples were named as Fe/CN-S powder, Fe/CN- NH_4SCN , Fe/CN-urea, and Fe/CN- NH_4NO_3 , respectively.

2.3. Catalyst characterization

The catalysts synthesized by pyrolyzing the mixture of Fe-salts and MA and the mixture of Fe-salts, MA and TU (the ratio of MA to TU is 4) were denoted as Fe-salt/CN and S-Fe-salt/CN-4, respectively. Thermogravimetric analysis (TGA) of the samples was performed on a SDT Q600 thermal gravimetric analyzer (TA Instruments, USA) from room temperature to 800 °C at a ramping rate of 10 °C min^{-1} under air or N_2 atmosphere. The FT-IR spectra of the samples were collected on a EQUINOX55 Fourier transform infrared spectrometer with a resolution of 4 cm^{-1} . Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffractometer with a nickel-filtered $\text{Cu K}\alpha$ X-ray source at a scanning rate of

0.02° over the range of 5°–80°. High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) was carried out using a JEM-ARM200F instrument. Energy-dispersive X-ray spectroscopic (EDS) images were collected using a JED-2300T instrument. Transmission electron microscopic (TEM) images were taken on a Tecnai G2 20 S-twin instrument (FEI Company) with an acceleration voltage of 200 kV. The samples for TEM analysis were prepared by dipping the carbon-coated copper grids into ethanol solutions of the samples and drying under ambient conditions. The tube voltage and current used were 45 kV and 200 mA, respectively. Photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCA Lab250 spectrometer with a monochromatic Al K_{α} X-ray source. Binding energies were calibrated by the C 1s peak at 284.6 eV. N₂ adsorption/desorption isotherms were recorded at –196 °C on a Quantachrome QUADRASORB SI instrument. The sample (0.05–0.1 g) was degassed in a vacuum at 150 °C for 4 h prior to measurement. The Brunauer-Emmauer-Teller (BET) method was used to calculate the specific surface area. The dissolved Fe concentration was detected by an inductively coupled plasma-atomic emission spectrometer (Optima 2000DV, USA). ⁵⁷Fe Mössbauer spectra were recorded at room temperature using a Topologic 500A spectrometer with a proportional counter. The involved radical species were confirmed using Bruker Electron Paramagnetic Resonance (A200-9.5/12, Ger). XANES and EXAFS measurements at the Fe K-edge (7112 eV) were conducted on the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT, 10-BM) and sector 20 (20-BM) at the Advanced Photon Source (APS), Argonne National Laboratory. Ionization chambers were optimized at the midpoint of the Fe spectrum for the maximum current with linear response ($\sim 10^{10}$ photons detected per second) using 35% He in N₂ (15% absorption) in the incident X-ray detector and a mixture of $\sim 17\%$ Ar in N₂ (70% absorption) in the transmission X-ray detector. A third detector in the series simultaneously collected a Fe foil reference spectrum with each measurement for energy calibration. A cryogenically cooled double-crystal Si(111) monochromator was used and detuned to 50% to minimize the presence of harmonics. The X-ray beam was 0.5 mm $\times$ 1.5 mm, and the data were collected in transmission geometry in 10 min in a step scan mode, in air. All the samples were diluted, ground with BN, and pressed into pellets to obtain an approximate edge jump of 1.0. The data analysis was performed using the Demeter 0.9.26 software package.

2.4. Heterogeneous photo-Fenton reaction

The photo-Fenton catalytic activities of the catalysts were evaluated for the degradation of four model organic pollutants (MB, MO, RhB, and phenol) with the addition of H₂O₂ under visible light irradiation at neutral pH. In a typical process, 25 mg (or 20 mg) of the catalyst was added into 50 mL of organic solutions (50 or 200 mg L^{–1}). The mixture was ultra-sonicated for 10 min and subsequently stirred for 30 min in the dark to establish adsorption/desorption equilibrium. The reaction was initiated by adding 400 μ L (or 200 μ L) of H₂O₂ (30 wt%) aque-

ous solution and simultaneously turning on a 300 W Xe arc lamp (PLS-SXE 300CUV, Beijing Perfect Light Co., Ltd.) equipped with a UV-CUT filter to cut off light of wavelength <420 nm. The temperature was maintained at 35 °C using recycled water. During illumination, approximately 400 μ L of suspension was withdrawn at certain intervals after separation of the catalyst using a filter, and was analyzed using a UV-Vis spectrophotometer (JASCO V570, Japan) or an Agilent high-performance liquid chromatograph (HPLC 1200) with an Eclipse XDB-C18 (150 mm $\times$ 4.6 mm $\times$ 5 μ m) column. The photo-Fenton activities of the catalysts were calculated by the concentration of a dye (C C₀^{–1}) according to the absorbance (A A₀^{–1}), where C_0 and A_0 were the initial concentration and absorbance of the dye, respectively.

3. Results and discussion

3.1. S-assisted pyrolysis, morphology of catalysts, and dispersion of Fe species: IR, XPS, SEM, HRTEM, and HAADF-STEM

The S-assisted pyrolysis is illustrated in Fig. 1. The mixture of Fe(NO₃)₃·9H₂O, MA, and TU was firstly ground with a mortar and pestle. Interestingly, a color change from white to yellow-green to orange was observed (Fig. S1), suggesting the presence of a chemical bonding interaction between Fe cation and TU, which is further demonstrated by IR spectra (Fig. S2) and XPS results (Fig. S3). During the pyrolysis at 600 °C in a N₂ atmosphere, a large number of gases (NH₃, CO₂, and SO₂) were released, accompanied by the decomposition of Fe(NO₃)₃-MA-TU precursor and significant volume expansion (Fig. S4). Finally, the S-Fe/CN-X (X represents the mass ratio of MA over TU) catalysts were obtained with a porous alveolate structure and homogeneous distribution of Fe, N, and C. The porous alveolate structure of S-Fe/CN-2, S-Fe/CN-2-4, and S-Fe/CN-2-8 are revealed by the SEM and TEM images (Figs. 2a–2d). The holes in the materials are interlaced, as evidenced by the transverse section of the sample in Figs. 2b and 2c. However, S-Fe/CN-0 and Fe/CN (synthesized by pyrolyzing the mixture of Fe(NO₃)₃·9H₂O and MA without adding TU) only show bulk structures, as shown in Figs. S5a and S5b, respectively. Correspondingly, the S-Fe/CN-2, S-Fe/CN-2-4, and S-Fe/CN-2-8 catalysts show higher specific surface areas than those of Fe/CN and S-Fe/CN-0 (Fig. S6). This indicates that the pyrolysis in the presence of a certain amount of TU facilitates the formation of the alveolate structure in the S-Fe/CN-X catalysts. Other S species (S powder and NH₄SCN) were also tested.

Fig. 1. Illustration of S-assisted pyrolysis to synthesize S-Fe-salt/CN catalysts.

Fig. 2. SEM images and the corresponding TEM images of (a) S-Fe/CN-2 (b, c) S-Fe/CN-4, (d) S-Fe/CN-8, (e) Fe/CN-S powder, and (f) Fe/CN-NH₄SCN.

The resulting catalysts (noted as Fe/CN-S powder and Fe/CN-NH₄SCN) all exhibit the porous alveolate structure, as shown in Figs. 2e and 2f. Moreover, the FeSO₄/CN and (NH₄)₂Fe(SO₄)₂/CN catalysts show porous structures, which were synthesized by two S-containing Fe-salts (FeSO₄·7H₂O and (NH₄)₂Fe(SO₄)₂·6H₂O) and MA without adding TU (Fig. S7). For other Fe-salts (FeCl₂·4H₂O and FeC₂O₄) and MA precursors, pyrolysis in the presence of TU also leads to the porous structure of catalysts (denoted as S-FeCl₂/CN-4 and S-FeC₂O₄/CN-4), as illustrated in Fig. S8. All these demonstrate that the introduction of S species in the Fe-salts/MA system facilitates the formation of S-Fe-salt/CN catalysts with porous alveolate structures.

High-resolution transmission electron microscope (HRTEM) images reveal that no Fe nanoparticles were formed in the S-Fe/CN-4 catalyst (Fig. S9), which is consistent with the results of the XRD patterns: that no diffraction peaks are assigned to Fe species (Fig. S10). Ultra-small Fe clusters (Fig. 3a) and atomically dispersed Fe sites (Figs. 3b and 3c) are observed in the HAADF-STEM images of S-Fe/CN-4. The catalyst has high-density USCAD Fe sites, corresponding to the high Fe loading (17.7 wt%) determined by TGA. EDS images (Fig. 3d and Fig. S11) also reveal a homogeneous distribution of Fe, N, and C elements and a trace amount of residual S element in the catalyst, indicating that most of the S species escape after

Fig. 3. (a, b, c) HAADF-STEM images and (d) elemental mappings for the Fe, N, C, and S atoms of the S-Fe/CN-4 catalyst.

high-temperature pyrolysis rather than remain in the catalyst.

3.2. Chemical state information: XPS, ⁵⁷Fe Mössbauer spectra, XANES, and EXAFS

In the N 1s XPS spectra of S-Fe/CN-2, S-Fe/CN-2-4, and S-Fe/CN-2-8 (Figs. 4a, 4b and 4c), the three peaks at 398.4, 399.7, and 400.6 eV are assigned to the pyridinic N in the *sp*² C=N-C bond, *sp*³ tertiary nitrogen N-(C)₃ groups, and N-H groups in g-C₃N₄, respectively [29,30]. This indicates that the structure of g-C₃N₄ in the catalysts was consistent with the XRD results (Fig. S10b). The XPS peaks of pyridinic N in S-Fe/CN-2, S-Fe/CN-4, and S-Fe/CN-8 show a negative shift (0.1–0.3 eV) versus pure g-C₃N₄ (Fig. 4d), suggesting the presence of the chemical coordination interaction between Fe and N atoms. Meanwhile, the relatively high content of pyridinic N in S-Fe/CN-2, S-Fe/CN-4, and S-Fe/CN-8 versus g-C₃N₄ (78.2%, 77.6%, 75.8%, and 63.6% for S-Fe/CN-2, S-Fe/CN-4, S-Fe/CN-8, and g-C₃N₄, respectively) provides more anchoring sites for Fe atoms; thus, it is beneficial to increasing the Fe loadings. However, the proportion of three kinds of N atoms in Fe/CN and S-Fe/CN-0 are close to that in pure g-C₃N₄, indicating a complete skeleton structure of g-C₃N₄ on the surfaces of Fe/CN and S-Fe/CN-0 (Figs. 4e and 4f). This, combined with the weak signal for Fe species in the Fe 2p spectra of Fe/CN and S-Fe/CN-0 (Figs. S12a and S12b), leads to the conclusion that most of the Fe species are encased by g-C₃N₄ in Fe/CN and S-Fe/CN-0 and few Fe species are exposed on the surface. The porous alveolate structures of the S-Fe/CN-2, -4, and -8 catalysts are helpful to increase the number of Fe species exposed on the surface, corresponding to their sharply increased Fe content determined by XPS versus those in Fe/CN and S-Fe/CN-0 (Table S1). The dominant Fe 2p peaks at 710.2 and 723.5 eV are assigned to Fe 2p_{3/2} and Fe 2p_{1/2} of Fe(II), respectively, and the peaks at 713.7 and 727.0 eV correspond to Fe 2p_{3/2} and Fe 2p_{1/2} of Fe(III), respectively (Fig. S12) [31,32]. In the S 2p spectra of the catalysts (Fig. S13a), no significant peaks of the S species could be detected on the surfaces of S-Fe/CN-4 and FeSO₄/CN, and trace amount of S species remain in the interior of the catalysts, evidenced by Ar etching mode S 2p XPS spectra of the catalysts (Fig. S13b). However, the noticeable signal for S species could be detected in the S 2p spectrum of S-Fe/CN-0, which is consistent with the XRD result (Fig. S10) that noticeable peaks for FeS particles appear in the pattern. The results demonstrate that the synthesis of USCAD S-Fe-salt/CN catalysts with porous alveolate structures is the combined effect of Fe-salts, S species, and MA. The pyrolysis of Fe-salts with pure MA or TU only leads to the encasing of Fe species or the generation of FeS particles.

Fig. 5 illustrates the ⁵⁷Fe Mössbauer spectra of S-Fe/CN-4 and Fe/CN. All the spectra can be fitted with three doublets (D1–D3), with the analysis results given in Table S2. The fitting model of the spectra is similar to that in our previous work about FeN_x/g-C₃N₄ [16]. The minor doublet D1 with relatively small isomer shift (IS) values is assigned to Fe(III). The majority of Fe species (76.2% and 78.3% for S-Fe/CN-4 and Fe/CN, respectively) are 2 doublets (D2 and D3) of high spin Fe(II)

Fig. 4. N 1s XPS spectra of (a) S-Fe/CN-2, (b) S-Fe/CN-4, (c) S-Fe/CN-8, (d) g-C₃N₄, (e) Fe/CN, and (f) S-Fe/CN-0.

coordinated to N atoms, as expected from Fe(II)-N_x species anchored in the g-C₃N₄ matrix [33]. The different quadrupole splitting (QS) values of Fe(II) suggest that these Fe species are in different chemical environments [34]. The absence of any sextet peaks demonstrates that no Fe_xC species exist in catalysts [35]. Noteworthy, the Fe(II) content in S-Fe/CN-4 does not show noticeable decrease *versus* that in Fe/CN. Combining SEM and XPS results, it is confirmed that the S-assisted method can prepare USCAD S-Fe-salt/CN catalysts with both high-density Fe sites and high Fe(II) content.

As shown in the Fe K-edge X-ray absorption near-edge structure (XANES) spectra (Fig. 6a), all the S-Fe/CN-X samples have small pre-edge peaks at 7112.6 and 7114.7 eV, suggesting the presence of both Fe(II) and Fe(III), which is consistent with the XPS results as well as the ⁵⁷Fe Mössbauer spectra results. The S-Fe/CN-2, S-Fe/CN-4, and S-Fe/CN-8 catalysts have similar Fe K-edge XANES spectra that are quite different from the standard samples of Fe foil, Fe₂O₃, and S-Fe/CN-0 (FeS/g-C₃N₄),

as shown in Fig. 6a. The extended X-ray absorption fine structure (EXAFS) results of the catalysts are consistent with the proposed Fe-N_x configuration. As shown in Fig. 6d, there is no Fe-S contribution at about 1.94 Å and Fe-Fe contribution at about 2.20 Å for the S-Fe/CN-2, S-Fe/CN-4, S-Fe/CN-8, and Fe/CN catalysts. The EXAFS fitting results indicate that the Fe-N bonds are at ~2.06 Å, which is in the normal range of Fe-N bond distances (Table S3). The average coordination number of the catalysts is ~4.8, suggesting the presence of coordinated unsaturated Fe sites, which is desired for catalysis. The absence of a large higher shell peak (within 2–3 Å) demonstrates that all the Fe species are dispersed as USCAD sites in S-Fe/CN-2, S-Fe/CN-4, and S-Fe/CN-8, as well as in Fe/CN, which shows more smaller peak in its EXAFS.

3.3. State change of S in pyrolysis: TG-MS, IR, and XPS

The above results demonstrate that S plays a crucial role in the formation of USCAD Fe/g-C₃N₄ catalysts with porous structures. We investigated the thermal decomposition of the precursors of Fe/CN and S-Fe/CN-4 (denoted as Fe/CN-pre and S-Fe/CN-4-pre, respectively) using thermogravimetric-mass spectra (TG-MS), and the results are shown in Fig. S14 and Fig. 7a. In the pyrolysis of MA, the primary polycondensation occurs during 350–520 °C, where MA is condensed to melem and further to large extended CN-structures [36,37]. If no templates (solid and gas) participate in the polycondensation, the intermediate units (melam and melem) tend to form stacked layered structures due to the 2D characteristics of g-C₃N₄, leading to the coating of the metal species. As exemplified in the TG-MS spectra of Fe/CN-pre (Fig. S14), NH₃⁺ (*m/z* = 17), NO⁺ (*m/z* = 30), NHCNH₂⁺ (*m/z* = 43), and CO₂⁺ (*m/z* = 44) were detected before 325 °C and after 515 °C, corresponding to the initial decomposition of the Fe(NO₃)₃/MA precursor and the destruction of part of the g-C₃N₄ structure, respectively. Only small

Fig. 5. Room temperature ⁵⁷Fe Mössbauer spectra of the (a) S-Fe/CN-4 and (b) Fe/CN catalysts.

Fig. 6. (a) K-edge XANES spectra and (b) R-space EXAFS magnitude of different samples.

amounts of gas could be detected in the critical temperature range for the primary polycondensation of MA (325–518 °C). Thus, the bulk Fe/CN catalyst is generated, for which most of the Fe species are encased by g-C₃N₄, as evidenced by the XPS spectra (Figs. 4e and S12a). Interestingly, the gases were released at relatively low temperatures, and most of SO₂⁺ ($m/z = 64$) were detected at 390 °C in the TG-MS spectra of S-Fe/CN-4-pre (Fig. 7a). This indicates that the Fe-S_x complex mainly decomposed during the polycondensation of MA (325–520 °C) accompanied by the release of Fe ions and SO₂, which facilitates the in-situ capture of Fe ion by intermediate units and the generation of pores by SO₂ gas template in materials. Therefore, S-Fe/CN-X catalysts with high-density USCAD Fe sites anchored in porous alveolate g-C₃N₄ matrix are obtained.

The S 2p XPS spectra of S-Fe/CN-4-pre, pyrolytic intermediates at different temperatures (denoted as S-Fe/CN-4-330 and S-Fe/CN-4-350) and S-Fe/CN-4 give a clear state change of S during pyrolysis, as shown in Fig. 7b. The peaks at 161.6 and 162.8 eV in the S 2p spectrum of S-Fe/CN-4-pre, ascribed to the S 2p_{3/2} and S 2p_{1/2} of C=S species in TU, move toward lower binding energy in comparison with the corresponding peaks in

the S 2p spectrum of the MA/TU mixture. This suggests that the Fe cations coordinate with the S atoms in the C=S groups of TU, thereby realizing the uniform dispersion of Fe ions, which is consistent with the Fourier transform infrared spectroscopy (FT-IR) results shown in Fig. S2. The peaks at 163.6 and 168.3 eV in the S 2p spectra of S-Fe/CN-4-330 and S-Fe/CN-4-350 are assigned to Fe-S_x and oxidized Fe-SO_x species, respectively [38,39], and these S species escape in the form of SO₂ after high-temperature pyrolysis rather than remain in the catalyst, as evidenced by the lack of S 2p signal and Fe-S bonds in S-Fe/CN-4. The result is quite different from that in the literature, which reports that FeS_x nanoparticles are formed [40]. We could only detect FeS nanoparticles in S-Fe/CN-0, indicating that the MA (or melam and melem) and the trace amounts of oxygen (Fe(NO₃)₃/MA/TU) restrained the formation of FeS_x nanoparticles. This explains why S-Fe/CN-0 shows a block structure, i.e., the Fe-S_x intermediate is difficult to break down into highly dispersed Fe species and SO₂ at relatively high temperatures when MA is absent in precursors, and the initial decomposition of S-Fe/CN-0-pre at an overly early stage (before 300 °C, Fig. S15) indicates that the gas templates are released at much lower temperatures. Combined with the TG-MS results,

Fig. 7. (a) TG-DTG-MS analysis of the gases released from the thermal decomposition of S-Fe/CN-pre, and (b) S 2p XPS spectra of the precursors, pyrolytic intermediates, and catalyst.

we speculate that the Fe cations are uniformly dispersed by forming Fe-TU complex. During the pyrolysis of $\text{Fe}(\text{NO}_3)_3/\text{MA}/\text{TU}$ precursors, this complex decomposes into amorphous Fe-S_x and Fe-SO_x species, and these Fe-S species are further oxidized to release Fe species and SO_2 (during the polycondensation of condensed MA, 325–520 °C). Thus, the in-situ capture of Fe species by intermediate units (melam and melem) and the in-situ pore formation by SO_2 gas template occur simultaneously during the polycondensation of MA. Finally, a USCAD Fe catalyst with a porous alveolate structure was obtained. Herein, we demonstrate the dual role of S as a “sacrificial carrier” to disperse Fe species and form porous alveolate structures in the S-assisted pyrolysis of $\text{Fe}(\text{NO}_3)_3/\text{MA}/\text{TU}$ precursors.

3.4. Catalytic performance

The catalytic performance in AOPs was evaluated by the degradation of MB aqueous solution with the addition of H_2O_2 under visible light irradiation at neutral pH. In the blank experiments (Fig. S16), MB is very difficult to remove under visible light irradiation with H_2O_2 or catalyst (the period between 0 and 30 min represents the adsorption/desorption equilibrium between the catalyst and organics). The Fe/CN and S-Fe/CN-0 catalysts only exhibit low removal efficiency due to their bulk structures and low exposed Fe sites (Fig. 8a). Due to the

high-density USCAD Fe sites and promoted accessibility of active sites by the porous alveolate structure, S-Fe/CN-4 exhibits a high MB removal efficiency approaching 100% within 5 min. The S-Fe/CN-2 and -8 catalysts also exhibit high catalytic activity (Fig. S17). This suggests that pyrolysis in the presence of TU in $\text{Fe}(\text{NO}_3)_3/\text{MA}$ precursors could greatly improve the catalytic activity of the Fe/CN catalyst. When changing the kind of S species (S powder and NH_4SCN), the catalysts (Fe/CN-S powder and Fe/CN- NH_4SCN) also exhibit similar promoted removal efficiency of MB as S-Fe/CN-4 (Fig. 8a). Other compounds with pore-creating effects, such as urea and NH_4NO_3 , were also investigated by adding them to the $\text{Fe}(\text{NO}_3)_3/\text{MA}$ precursors. However, Fe/CN-urea and - NH_4NO_3 only exhibited slightly promoted activity; thus, they are considerably inferior to the S-Fe/CN-4, Fe/CN-S powder, and Fe/CN- NH_4SCN catalysts (Fig. 8a), demonstrating the superiority of the S-assisted strategy to synthesize highly efficient USCAD catalysts. As shown in Figs. 8b and 8c, the removal efficiencies of MB all reach 100% within 25 min over the S-Fe-salt/CN-4 catalysts (synthesized by S-assisted pyrolysis of Fe-salts/MA/TU precursors), exhibiting a significantly promoted activity compared to the corresponding Fe-salt/CN catalysts (synthesized by pyrolysis of other Fe-salts/MA precursors). The FeSO_4/CN and $\text{NH}_4\text{Fe}(\text{SO}_4)_2/\text{CN}$ catalysts also exhibited high catalytic activity (Fig. 8b). Thus, the S-assisted strategy exhibits good feasibility in a large variety of S species and Fe salts to synthesize highly efficient

Fig. 8. Removal efficiency of MB using (a) Fe/CN and Fe/CN catalysts reformed by different templates, (b) Fe-salts/CN catalysts, and (c) S-Fe-salts/CN-4 catalysts. (d) Removal efficiency of various organic pollutants using S-Fe/CN-4 catalyst. Reaction conditions: (a, b, c) 50 mg L^{-1} MB, 34 mmol L^{-1} H_2O_2 , 0.4 g L^{-1} catalyst, 35 °C, and visible light. (d) 200 mg L^{-1} organics (MB, MO, RhB, and phenol), 77 mmol L^{-1} H_2O_2 , 0.5 g L^{-1} catalyst, 35 °C, and visible light.

Table 1

Comparison of the catalytic activities of S-Fe/CN-4 with the Fe-based catalysts in the literature.

Catalyst	Organics	m_{Cat} (g L ⁻¹)	C_{Org} (ppm)	$C_{\text{H}_2\text{O}_2}$ (mmol L ⁻¹)	T (°C)	t (min)	Conversion (%)	Ref.
Fe/MnO ₂	MB	0.5	100	33	25	120	94	[41]
10%Fe-g-C ₃ N ₄	MB	0.5	50	200	25	90	100	[42]
FeOCl	MB	0.2	80	16	40	30	21	[43]
Fe ₃ O ₄ -U-rGO-1	RhB	0.2	20	192	25	50	99	[44]
Fe-g-C ₃ N ₄ /GMC	RhB	0.8	50	40	25	40	95	[18]
Fe ₃ O ₄ /MIL-101	RhB	0.5	10	20	25	30	100	[45]
FeOOH	MO	0.1	80	88	60	60	98	[46]
Fe ₂ O ₃ @ZSM-5	Phenol	2	1000	149	50	60	100	[47]
FePc/Graphene	Phenol	0.2	50	49	25	180	77	[48]
Fe-ZSM-5	Phenol	2	50	9	35	180	100	[49]
S-Fe/CN-4	MB	0.5	200	77	35	10	96	This work
	RhB	0.5	200	77	35	10	98	
	Phenol	0.5	200	77	35	10	98	
	MO	0.5	200	77	35	15	95

Fig. 9. (a) The reusability of S-Fe/CN-4 catalyst. Reaction conditions: 50 mg L⁻¹ MB, 38.5 mmol L⁻¹ H₂O₂, 0.4 g L⁻¹ catalyst, 35 °C, and visible light. (b) DMPO trapped EPR spectra of S-Fe/CN-4 reaction systems and H₂O₂-aqueous system at 1 min.

S-Fe-salt/CN catalysts.

The S-Fe/CN-4 catalyst exhibits high removal efficiency for various organic pollutants (MB, RhB, and phenol); the removal efficiency reaches 96%, 98%, and 98% within 10 min, respectively, (the removal efficiency of MO reaches 95% within 15 min), as shown in Fig. 8d, exhibiting much better catalytic properties compared with previously reported Fe-based Fenton-type catalysts listed in Table 1. The S-Fe/CN-4 catalyst exhibits good recyclability (Fig. 9a), and the removal efficiency is maintained for five cycles, which is consistent with little Fe leaching (Table S4). Fig. 9b shows the results of the electron paramagnetic resonance (EPR)/5, 5-dimethyl-1-pyrroline N-oxide (DMPO) experiment. A strong 4-fold characteristic peak with an intensity ratio of 1:2:2:1 was detected in the DMPO trapped spectra at one minute of reaction time, corresponding to the typical HO•/DMPO complex adduct [50]. This indicates that the high-density USCAD Fe sites in S-Fe/CN-4 can rapidly activate H₂O₂ to generate HO•, a powerful oxidizing agent. Compared to the dark reaction, the S-Fe/CN-4 catalyst exhibits promoted removal efficiency of MB under visible light irradiation (Fig. S18), due to the photocatalytic activity of g-C₃N₄ and promoted light-absorption by the porous alveolate structure.

4. Conclusions

In summary, the porous alveolate S-Fe-salt/CN catalysts with high-density USCAD Fe sites anchored in g-C₃N₄ matrices were successfully synthesized via a facile S-assisted pyrolysis process. S atoms acted as a “sacrificial carrier” to increase the dispersion of Fe species and produce the porous alveolate structure, thus promoting mass transfer and accessibility to the active sites. This S-assisted method showed good application potential in a variety of S species (TU, S powder, and NH₄SCN) and Fe salts to synthesize highly efficient catalysts. The S-Fe-salt/CN catalysts exhibited significantly promoted activity and good recyclability for degrading various organic pollutants in AOPs *versus* the corresponding Fe-salt/CN catalysts. The facile S-assisted method opens new avenues for the low-cost and large-scale synthesis of high-density USCAD metal/g-C₃N₄ catalysts with novel porous structures.

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Graphical Abstract

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A facile sulfur-assisted method to synthesize porous alveolate Fe/g-C₃N₄ catalysts with ultra-small cluster and atomically dispersed Fe sites

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A template-free S-assisted method to synthesize porous alveolate Fe/g-C₃N₄ catalysts with ultra-small clusters and atomically dispersed Fe sites for highly efficient catalytic advanced oxidation processes.

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一种简易的硫辅助方法制备多孔蜂窝状铁超小原子簇和单原子Fe/g-C₃N₄

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摘要: 超小原子簇和单原子分散的活性位点(USCAD)催化剂由于其高原子利用率、高活性、高稳定性等优点, 成为多相催化领域一个新兴的研究热点。USCAD通常由载体缺陷、配体和分子筛或金属有机框架的孔道和笼锚定。而制备高密度的USCAD催化剂需要载体上有足够的锚定位点。石墨相氮化碳(g-C₃N₄)具有高稳定性、高密度且均匀分散的氮原子, 是制备USCAD催化剂的理想载体。但是传统热解法制备的金属/g-C₃N₄催化剂通常为块体结构, 会导致金属物种被严重包覆, 进而导致催化活性下降。加入固体模板可以制备得到多孔金属g-C₃N₄催化剂, 但是后续复杂的除模板过程制约了其实际应用。因此, 开发一种简易的无模板方法制备USCAD金属/g-C₃N₄催化剂具有重要意义。

本工作开发了一种简易的硫辅助热解法制备得到蜂窝状结构的高密度(Fe载量为17.7 wt%)USCAD Fe/g-C₃N₄催化剂。其多孔蜂窝状结构使催化剂能够暴露更多的USCAD Fe活性位点, 增加了活性位点与反应物的可接近性。通过球差电镜和同步辐射X射线吸收技术证明了Fe物种的分散形式。硫辅助热解法只需要在热解铁盐/三聚氰胺前驱体中加入适量的硫源即可得到蜂窝状的USCAD Fe/g-C₃N₄催化剂。硫元素作为一种“牺牲载体”通过与铁离子配位促进铁物种在前驱体混合物中分散, 经过高温煅烧后以SO₂的形式释放而不残留在催化剂中, 免除了后续的除模板过程。通过TG-MS, XPS和IR等手段证明了硫元素在热解过程中的状态变化。这种硫辅助热解法表现出非常好的普适性, 改变硫源种类(硫脲、硫粉、硫氰酸铵)和铁盐种类都可以得到具有蜂窝状孔道结构的USCAD Fe/g-C₃N₄催化剂。将催化剂应用于高级氧化过程可以高效降解各种有机污染物(苯酚、亚甲基蓝、亚甲基橙、罗丹明B), 催化剂性能远远优于文献报道的其它Fe基催化剂和传统热解法制备的Fe/g-C₃N₄催化剂。该硫辅助热解法为无模板法制备纳米多孔USCAD金属/g-C₃N₄催化剂开辟了一条简易可行的途径。

关键词: 硫辅助法; 多孔蜂窝状结构; 超小原子簇和单原子; Fe/g-C₃N₄; 高级氧化技术

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