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Sodium dodecyl sulfate-decorated MOF-derived porous Fe₂O₃ nanoparticles: High performance, recyclable photocatalysts for fuel denitrification

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ABSTRACT

Magnetically recyclable porous sodium dodecyl sulfate (SDS)/Fe₂O₃ hybrids, which combine the porous structure of Fe₂O₃ and hydrophobicity of SDS, have been successfully synthesized for the first time. Porous Fe₂O₃ has been first pyrolyzed from MIL-100(Fe) using a simple two-step calcination route. Then, the obtained porous Fe₂O₃ nanoparticles have been self-assembled with SDS molecules and yielded hydrophobic SDS/Fe₂O₃ hybrids. The porous SDS/Fe₂O₃ hybrids have been demonstrated to be highly efficient for the denitrification of pyridine under visible light irradiation. The pyridine removal ratio has reached values as high as 100% after irradiation for 240 min. Combining the results of a series of experimental measurements, it was concluded that the superior photocatalytic performance of SDS/Fe₂O₃ hybrids could be attributed to (i) the fast electron transport owing to the unique porous structure of Fe₂O₃, (ii) the superior visible light absorption of Fe₂O₃ nanoparticles, and (iii) the “bridge molecule” role of SDS efficiently improving the separation and transfer across the interfacial domain of SDS/Fe₂O₃ of photogenerated electron-hole pairs. More significantly, after the catalytic reaction, the SDS/Fe₂O₃ hybrids could be easily recovered using magnets and reused during subsequent cycles, which indicated their stability and recyclability.

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1. Introduction

Nitrogen-containing compounds (NCCs) have been regarded as some of the most significant atmospheric pollutants nowadays [1–3]. Crude gasoline fuel naturally contains high amounts of NCCs, such as pyridine. As the world population increased recently, the removal of NCCs from crude gasoline fuel has be-

come a global research hotspot. Currently, the removal of NCCs is achieved via a conventional catalytic refining process [4]. However, this refining process usually requires exceptionally high temperature and pressure conditions, and therefore, exploring more mild and effective denitrification technologies has become one of the most attractive topics in the field of gasoline fuel purification.

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Currently, researchers have been focused their attention on using photocatalysts for one-pot removal of NCCs [5–7]. While α -Fe₂O₃ presents a narrow band gap (2.3 eV) and is a promising photocatalyst [8,9], its low photocatalytic efficiency, which is caused by the high photogenerated carrier recombination rate and low surface-to-volume ratio, limits its practical applications. The performance of catalysts is often affected by morphological features, such as size, shape, and hierarchical structure [10–18]. Considering their high specific surface area and excellent photogenerated carrier transport properties, porous nanostructures have been considered pivotal building blocks for photocatalytic materials [19–22]. Numerous methods, including sol-gel processes [23], thermal heating [24], and spray pyrolysis [25] have been explored for fabricating different α -Fe₂O₃ photocatalysts featuring high surface area, however, the reported synthetic procedures often required high temperature and expensive equipment. Thus, it is of critical importance to develop a relatively low-temperature and low-cost process to controllably synthesize porous α -Fe₂O₃.

Metal-organic frameworks (MOFs), which exhibit exceptional surface areas and high porosity would be favorable self-sacrificed templates for fabricating porous metallic oxides [26–30]. Using Fe-based MOFs as templates, porous Fe₂O₃ has been synthesized and used for the absorption of As(V) [31,32]. Cho *et al.* [33] have obtained porous Fe₂O₃ featuring spindle-like structure, which presented excellent Li⁺ storage performance and was used for lithium ion batteries. The reports published so far on preparing metal oxide nanoparticles via thermolysis of MOFs, focused on using the obtained nanoparticles for adsorption and lithium ion batteries, while studies on the utilization of porous α -Fe₂O₃ for photocatalytic denitrification have been rather scarce.

MIL-100(Fe), which is a typical iron-based MOF featuring high pore volume and specific surface area, has been selected as promising template for preparing porous α -Fe₂O₃. Herein, porous α -Fe₂O₃ has been fabricated using a novel two-step calcination route, and was then used for the photo-denitrification of NCCs. Instead of using traditional aqueous media, octane has been used as model gasoline fuel, in the photo-denitrification system in this study. This led to obvious aggregation in the traditional hydrophilic medium-photocatalyst system. The dispersibility of materials could be improved significantly using surfactant modification [34–37]. Therefore, to increase the interfacial contact between α -Fe₂O₃ and hydrophobic octane, we have used sodium dodecyl sulfate (SDS), an anionic surfactant to serve as “bridge molecule”. That is, the hydrophilic sulfonate ion heads of SDS could be adsorbed on the surface α -Fe₂O₃, while the hydrophobic dodecyl tails would point toward the outside and form “micelle-like” structures, which could efficiently increase the substrate (hydrophobic octane) contact area and promote reaction efficiency. The SDS/Fe₂O₃ nanocomposites (NCs) were synthesized via self-assembly, which occurred owing to the electrostatic attractions between the positively charged α -Fe₂O₃ and negatively charged SDS in aqueous solution. Compared with the original α -Fe₂O₃, the as-synthesized SDS/Fe₂O₃ NCs exhibited superior visible light photoactivity for the denitrification of

typical NCCs, such as pyridine. In this study, MOFs were used as template for the preparation of denitrification photocatalysts for the first time. Furthermore, herein, we also highlighted the importance and necessity of the controllable synthesis of surfactant-modified semiconductors as photocatalysts for specific applications.

2. Experimental

2.1. Materials

Iron(III) chloride hexahydrate (FeCl₃·6H₂O) was supplied by Aladdin Reagent Co., Ltd., trimethyl 1,3,5-benzenetricarboxylate (C₁₂H₁₂O₆) was supplied by J&K Scientific Co., Ltd., and SDS and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Fabrication of MIL-100(Fe)

MIL-100(Fe) was synthesized according to the procedure described by Canioni *et al.* [38].

2.3. Fabrication of porous α -Fe₂O₃

MIL-100(Fe) was placed in a ceramic crucible and was first heated to 300 °C for 2 h in a muffle furnace, at the heating rate of 5 °C/min in air. Then the temperature was increased to 400, 450, and 500 °C at the heating rate of 1 °C/min. When the target temperature was reached, the crucible was immediately removed from the furnace. The obtained reddish-brown powder was designated to be Fe₂O₃-X (Fe₂O₃-300, Fe₂O₃-400, Fe₂O₃-450 and Fe₂O₃-500, respectively), where X is the calcination temperature (°C). In addition, for comparison, direct one-step calcination was also performed: MIL-100(Fe) was heat-treated at 450 °C at the heating rate of 5 °C/min, which generated Fe₂O₃-450D samples.

2.4. Fabrication of SDS/ α -Fe₂O₃

Briefly, 100 mg Fe₂O₃-450 was dispersed in 20 mL water. Then, 10 mL SDS solution (1, 0.5, 0.25, and 0.125 g/L) was added to the above dispersion. After mixing for 30 min, the mixture was washed using deionized water and subsequently dried. The as-prepared SDS/Fe₂O₃-450 NCs featuring different percentages of added SDS will hereafter be referred to as 1%, 0.5%, 0.25%, and 0.125%SDS/Fe₂O₃-450 NCs.

2.5. Characterizations

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance X-ray diffractometer. Zeta potential (ζ) measurements were carried out using a 3000HSA Zeta sizer. Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449F3 unit at the heating rate of 5 °C/min in air. Fourier-transform infrared reflectance (FT-IR) spectra were measured using a Shimadzu IRPRESTIGE-21 spectrophotometer. Transmission electron microscopy (TEM) and

high-resolution TEM (HRTEM) images were obtained using a JEOL JEM 2010 EX instrument. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were obtained using a Shimadzu UV-2700 UV-Vis spectrophotometer. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured using an ASAP 2460 apparatus. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCA Lab 250 spectrometer. The magnetization curves were measured at room temperature using a BHV-55 vibrating sample magnetometer (VSM). Elemental analysis (EA) was performed using an Elementar vario EL cube. Temperature-programmed desorption of ammonia (NH_3 -TPD) was performed in a flow apparatus using a Micrometrics 2910 Autochem analyzer. Electron spin response (ESR) experiments were conducted using a JEOL JES-FA200 spectrometer. The ESR signals of the radicals spin-trapped using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were recorded at visible light wavelengths longer than 420 nm. High-performance liquid chromatography-mass spectrometry (HPLC-MS) experiments were performed using an Agilent 1200 series system, equipped with an Agilent Zorbax Eclipse XDB-C18 column (2.1 mm $\times$ 100 mm $\times$ 3.5 μm). The HPLC-MS measurements for pyridine were performed using an isocratic elution program, where methanol/acetone = 70:30 (v/v) was utilized as mobile phase. The flow rate was maintained at 0.2 mL/min and the injection volume was 10 μL . Mott-Schottky measurements were performed using a Zahner Zennium electrochemical workstation. For the Mott-Schottky experiment, the potential ranged from 0.4 to 0.8 V (vs. Ag/AgCl, pH 6.8), the perturbation signal was 20 mV and the frequency was 1000 and 1500 Hz. Photocurrent measurements were conducted using a BAS Epsilon workstation. Electrochemical impedance spectroscopy (EIS) experiments were conducted using a Precision PARC workstation. Photoluminescence (PL) spectra were obtained using a Cary Eclipse spectrofluorometer at the excitation wavelength of 335 nm. Time-resolved PL spectra were recorded using a FLS980 spectrometer. The obtained decay profile could be reasonably fitted to a double exponential model:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (1)$$

where $I(t)$ is the transient PL intensity, τ_1 and τ_2 are the decay time constants, and A_1 and A_2 are the corresponding magnitudes.

2.6. Activity testing

First, 100 $\mu\text{g/g}$ simulated NCCs-containing gasoline fuel was prepared by dissolving 70 mg pyridine in 1.0 L octane. Then, 40 mg photocatalyst and 40 mL pyridine/octane solution (100 $\mu\text{g/g}$) were added into a quartz reactor. The suspension was stirred in the dark for 1 h to ensure the adsorption-desorption equilibrium was reached. Afterward, the suspensions were irradiated using a 300 W Xe lamp (PLS-SXE 300) equipped with a UV-cut filter to cut off light of wavelength shorter than 420 nm. At selected time intervals, aliquots of the suspension were removed and centrifuged. The residual concentration of pyri-

dine in the supernatant was monitored using a Varian Cary 50 spectrometer.

3. Results and discussion

3.1. Characterizations

Thermogravimetric analysis of MIL-100(Fe) has been performed to determine its optimum calcination temperature (Fig. 1). MIL-100(Fe) degraded in successive steps, and the initial loss of free/bound water molecules occurred at approximately 100–200 $^{\circ}\text{C}$. The second-stage weight loss started at 300 $^{\circ}\text{C}$, which indicated the breakdown of trimesic acid. Lastly, the TGA curve began to stabilize at approximately 450 $^{\circ}\text{C}$ when 32% of the initial mass of MIL-100(Fe) remained. Therefore, to protect the structure of the MOF template and remove the organic ligands completely, the temperature of the first calcination step should be 300 $^{\circ}\text{C}$. Then, the temperature of the second calcination step should be in the 400–500 $^{\circ}\text{C}$ range to convert FeO_x into $\alpha\text{-Fe}_2\text{O}_3$. By contrast, as displayed in Fig. 1, almost no weight loss occurred for the Fe_2O_3 -450 sample, which suggested that carbon has been completely removed from Fe_2O_3 . This was further confirmed using EA which revealed that the carbon content of Fe_2O_3 -450 was lower than 100 ppm.

As illustrated in Fig. 2(a), when increasing the temperature of the second calcination step, the intensities of the XRD peaks of MIL-100(Fe) gradually decreased, which suggested the collapsing of the framework. When the calcination temperature reached 450 $^{\circ}\text{C}$, the diffraction peaks specific to MIL-100(Fe) were barely visible, while the diffraction peaks of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 89-8103) appeared. Fig. 2(b) presents the typical FT-IR spectra of MIL-100(Fe) and porous $\alpha\text{-Fe}_2\text{O}_3$. As the calcination temperature increased, the carboxylate bands of MIL-100(Fe) at approximately 1456, 1376, 759, and 711 cm^{-1} gradually disappeared, which was consistent with the XRD results. The ξ values of porous $\alpha\text{-Fe}_2\text{O}_3$ (Fe_2O_3 -450) are displayed in Fig. 3. When dispersed in water (pH = 6), the ξ value of Fe_2O_3 -450 was +19.2 mV, which suggested that the surface of Fe_2O_3 -450 was positively charged. The chemical formula of SDS, which is an anionic surfactant, is $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$. Thus, the negatively charged $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-$ ions could interact with the positively

Fig. 1. Thermogravimetric analysis curves of MIL-100(Fe) and Fe_2O_3 -450.

Fig. 2. (a) X-ray diffraction patterns and (b) Fourier-transform infrared reflectance spectra of MIL-100(Fe) and Fe₂O₃ prepared at different calcination temperatures.

Fig. 3. Zeta potential (ξ) of Fe₂O₃-450 and 0.25%SDS/Fe₂O₃-450 as function of pH.

charged Fe₂O₃-450 via electrostatic attraction to form SDS/Fe₂O₃. We also determined that the ξ value of 0.25%SDS/Fe₂O₃-450 decreased gradually, which further corroborated the occurrence of electrostatic attractions.

Fig. 4(a) illustrates the XRD patterns of α-Fe₂O₃ and SDS/Fe₂O₃ NCs. The diffraction peaks of SDS/Fe₂O₃ NCs have

not been affected by the addition of SDS. Moreover, no characteristic peaks of SDS were observed in the XRD spectra of the SDS/Fe₂O₃ samples. This could be ascribed to the low amount of SDS present in the SDS/Fe₂O₃ NCs (<1 wt%). To further determine the successful combination of porous α-Fe₂O₃ and SDS via electrostatic self-assembly, FT-IR spectra have been obtained (Fig. 4(b)). The absorption bands at approximately 1500–1000 cm⁻¹ in the spectrum of SDS could be attributed to the C–H bonds of the hydrocarbon tail [39]. That is, the band at 1461 cm⁻¹ was attributed to the bending vibration of methylene, whereas the weak band at 1377 cm⁻¹ was assigned to the bending vibration of methyl. The bands specific to SDS and MIL-100(Fe) were observed in the FT-IR spectrum of 0.25%SDS/Fe₂O₃-450, which confirmed the presence of SDS in the 0.25%SDS/Fe₂O₃-450 composite. The BET surface areas and pore volumes of the SDS/Fe₂O₃ samples (Fig. 5 and Table 1) decreased significantly as the calcination temperature increased, which was in agreement with the decomposition of organic ligands in the framework. The BET surface area and pore volume of Fe₂O₃-450 were determined to be approximately 134.5 m²/g and 0.159 cm³/g, respectively (see Table 1), which were twice as large as those of Fe₂O₃-450D. The results also implied that after the introduction of SDS, the BET surface

Fig. 4. (a) X-ray diffraction patterns and (b) Fourier-transform infrared reflectance spectra of samples.

Fig. 5. Nitrogen adsorption isotherms at -196 °C of (a) porous Fe₂O₃ nanoparticles obtained by annealing MIL-100(Fe) at different calcination temperatures and (b) products prepared under different conditions.

Table 1

BET surface areas and pore volumes of MIL-100(Fe), Fe₂O₃ and SDS/Fe₂O₃-450 nanocomposites.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)
MIL-100(Fe)	1906.4	0.906
Fe ₂ O ₃ -300	726.5	0.594
Fe ₂ O ₃ -400	480.8	0.324
Fe ₂ O ₃ -450	134.5	0.159
Fe ₂ O ₃ -500	32.1	0.031
0.25%SDS/Fe ₂ O ₃ -450	117.1	0.143
Fe ₂ O ₃ -450D	68.4	0.077

area of SDS/Fe₂O₃-450 was still as high as 217.1 m²/g, which was very similar to that of Fe₂O₃-450.

The TEM images of porous α -Fe₂O₃ and MIL-100(Fe) are presented in Fig. 6. MIL-100(Fe) consisted of smooth polyhedrons 100–200 nm in size (Figs. 6(a) and (b)). As illustrated in Figs. 6(c) and (d), the morphology of the sample obtained at the lowest calcination temperature (Fe₂O₃-300) was similar to that of MIL-100(Fe), but FeO_x nanoparticles began to decorate its surface, which was attributed to the thermal decomposition of MOF in air [33]. As the calcination temperature increased (Fe₂O₃-400, Figs. 6(e) and (f)), the FeO_x nanoparticles decorat-

Fig. 6. Transmission electron microscopy images of (a, b) MIL-100(Fe), (c, d) Fe₂O₃-300, (e, f) Fe₂O₃-400, (g, h) Fe₂O₃-450, (i, j) Fe₂O₃-500, and (k, l) Fe₂O₃-450D.

ing the surface of MIL-100(Fe) changed from slightly scattered into thickly dotted. As suggested by the images in Figs. 6(g) and (h) crystallization was accelerated as the calcination temperature increased to 450 °C, and the Fe₂O₃-450 samples presented uniform particle size distribution (~20 nm). The porosity of Fe₂O₃-450 was attributed primarily to the structure of the organic ligand support, which was completely broken down during the preparation of these iron oxide nanoparticles. The average size of the Fe₂O₃-500 particles (Figs. 6(i) and (j)) increased, which was due to the growth of the crystals. Moreover, individual Fe₂O₃-450D particles can be observed in Figs. 6(k) and (l), and their mean size was 50 nm. Therefore, direct, fast heating was unfavorable for maintaining the pore structure of MOFs. Based on these results, the morphology and structure of the products are illustrated in Scheme 1. As illustrated in Figs. 7(a)–(c), the inter planar spacing of 0.25%SDS/Fe₂O₃-450 was measured to be 0.36 nm, which corresponded to the (104) plane of α -Fe₂O₃. The addition of SDS did not affect the structure of Fe₂O₃-450 (Fig. 7(d)). Moreover, no characteristic structure of SDS clusters could be observed for 0.25%SDS/Fe₂O₃-450, which could be attributed to the small molecular size or relatively low content of SDS. Furthermore, the EDS elemental mapping results indicated that Fe, O, and S were uniformly spread throughout the SDS/Fe₂O₃-450 sample (Figs. 7(e)–(g)), which further confirmed that a robust SDS/Fe₂O₃-450 architecture has been obtained via the electrostatic self-assembly process.

Scheme 1. Schematic illustration of morphology and structure of products. I: 300 °C; II: 400 °C; III: 450 °C; IV: 500 °C.

Fig. 7. (a) Transmission electron microscopy (TEM), (b, c) high-resolution TEM and (d–g) energy dispersive spectroscopy element mapping images of 0.25%SDS/Fe₂O₃-450.

The UV-Vis DRS spectra suggested that all Fe₂O₃-based samples exhibited strong visible light absorption (Fig. 8(a)). Moreover, the absorption edge of Fe₂O₃-450 was measured to be 625 nm, which corresponded to the band gap of 1.98 eV. Compared with Fe₂O₃-450, the absorption edge of Fe₂O₃-450D displayed a blue shift. This was reasonable because of the synergistic effect of the surface microstructure and morphology on band gap narrowing, which could originate from the different atomic configurations on each crystal surface [40,41]. The band gap of 0.25%SDS/Fe₂O₃-450 was 1.97 eV, and was based on the absorption edge of approximately 628 nm. The absorption band of SDS could not be observed in the spectrum of 0.25%SDS/Fe₂O₃-450. This could be attributed to the low light harvest capability of SDS in the SDS/Fe₂O₃-450 NCs. The results of the NH₃-TPD measurements are presented in Fig. 8(b). The appearance of the peak at 200 °C was associated with the desorption of the physisorbed NH₃ from surface of Fe³⁺, which suggested the presence of Lewis acid centers on the surfaces of the samples [42]. In addition, the peak at 330 °C could be attributed to the desorption of chemisorbed NH₃, which implied the presence of strong Brønsted acid sites on the surfaces of the samples. In the above referenced temperature range, the amounts of NH₃ adsorbed by Fe₂O₃-450 and SDS/Fe₂O₃-450 were larger than that adsorbed by Fe₂O₃-450D. Furthermore, the desorption temperatures of Fe₂O₃-450 and SDS/Fe₂O₃-450 were relatively higher than that of Fe₂O₃-450D. Therefore, it

Fig. 9. Blank pyridine denitrogenation experiments under different conditions.

was concluded that the strong surface acidity of Fe₂O₃-450 and SDS/Fe₂O₃-450 led to the superior photoactivity of pyridine, the adsorbing Lewis base [43].

3.2. Photocatalytic performance

The photoactivities of Fe₂O₃-X for the denitrogenation of NCCs (e.g., pyridine) have been evaluated using visible light ($\lambda \geq 420$ nm). As illustrated in Fig. 9, Fe₂O₃-450 exhibited much higher photocatalytic activity within 240 min compared with TiO₂ (~8%) and commercial α -Fe₂O₃ (~12%). Fig. 10(a) displays the comparison of the pyridine denitrogenation efficiencies of Fe₂O₃-X and Fe₂O₃-450D. Of the four samples prepared using the two-step calcination method, sample Fe₂O₃-450 presented the highest photoactivity (~69.2%). The reaction kinetics data for the pyridine photo-denitrogenation reaction are displayed in Fig. 10(b). The rate constants of Fe₂O₃-300, Fe₂O₃-400, Fe₂O₃-450, Fe₂O₃-500, and Fe₂O₃-450D were calculated to be 0.097, 0.221, 0.256, 0.072, and 0.107 h⁻¹, respectively. The quantitative analysis data suggested that the photocatalytic activity of Fe₂O₃-450 was approximately 2.4 times higher than that of Fe₂O₃-450D. The higher photoactivity of Fe₂O₃-450 could be attributed to: (i) the larger specific surface areas of porous Fe₂O₃ nanoparticles, which benefited the ad-

Fig. 8. (a) Ultraviolet-visible absorption spectra and (b) temperature-programmed desorption of ammonia profiles of samples.

Fig. 10. (a) Photocatalytic denitrogenation of pyridine, (b) kinetics of photocatalytic denitrogenation of pyridine over Fe_2O_3 prepared at different calcination temperatures, (c) photocatalytic denitrogenation of pyridine, and (d) kinetics of photocatalytic denitrogenation of pyridine over SDS/ Fe_2O_3 -450 under visible light irradiation.

sorption of pyridine molecules onto the Fe_2O_3 surface; (ii) the shorter distance for carriers that transferred to surface active sites in such a unique porous structure; (iii) the superior optical light absorption properties, which contributed to the relatively efficient carrier separation. Herein, it was concluded that the porous structure of Fe_2O_3 was beneficial for increasing its photocatalytic denitrogenation ability for pyridine.

To understand the advantages of SDS modification on increasing the photoactivity of SDS/ Fe_2O_3 in the hydrophobic pyridine/octane system in this study, we selected the photocatalytic denitrogenation of pyridine as model reaction. Using SDS/ Fe_2O_3 -450 as an example (Fig. 10(c)), the photo-denitrogenation efficiencies of all samples decreased as follows: 0.25%SDS/ Fe_2O_3 -450 > 0.125%SDS/ Fe_2O_3 -450 > 0.5%SDS/ Fe_2O_3 -450 > pure Fe_2O_3 -450 > 1%SDS/ Fe_2O_3 -450. When an excess amount of SDS was added to Fe_2O_3 , the photo-

catalytic denitrogenation activity of the SDS/ Fe_2O_3 NCs was inhibited. This was reasonable because as the concentration of SDS further increased, SDS multilayered clusters tended to coat the surface of Fe_2O_3 [44]. This could lead to shielding the active sites and hindering the reaction of the photogenerated carriers with pyridine molecules, which could be considered to be a “shielding effect”. The rate constants for the photocatalytic denitrogenation reaction in the presence of above catalysts were obtained. As illustrated in Fig. 10(d), 0.25%SDS/ Fe_2O_3 -450 exhibited the highest pyridine denitrogenation rate constant (0.988 h^{-1}), which was 2.86, 1.64, 2.38, and 3.70 times higher than those of Fe_2O_3 -450 (0.256 h^{-1}), 0.125%SDS/ Fe_2O_3 -450 (0.374 h^{-1}), 0.5%SDS/ Fe_2O_3 -450 (0.292 h^{-1}), and 1%SDS/ Fe_2O_3 -450 (0.210 h^{-1}), respectively. The photocatalytic activities of 0.25%SDS/ Fe_2O_3 -450 and those of other catalysts reported in the literature are compared in Table 2.

Table 2

Comparison of catalytic activities of 0.25%SDS/ Fe_2O_3 -450 and other reported catalysts for denitrogenation of pyridine under visible light irradiation.

Photocatalyst	C_{pyridine} ($\mu\text{g/g}$)	C_{cat} (mg/mL)	Light source	Time (h)	Denitrogenation efficiency (%)	Ref.
0.25%SDS/ Fe_2O_3 -450	100	1.0	300 W ($\lambda > 420 \text{ nm}$)	4.0	99	This study
$\text{TiO}_2/\text{Fe}_2\text{O}_3$	100	1.0	300 W ($\lambda > 420 \text{ nm}$)	4.0	92	[45]
$\text{Bi}_{20}\text{TiO}_{32}$	100	1.0	400 W ($\lambda > 400 \text{ nm}$)	2.5	81	[46]
$\text{Bi}_{20}\text{TiO}_{32}$ nanosheets	100	1.0	400 W ($\lambda > 400 \text{ nm}$)	2.5	86	[47]
$\text{CuO}/\text{ZnO}/3\text{A}$	100	1.5	400 W ($\lambda > 400 \text{ nm}$)	2.5	69	[48]
$\text{CeO}_2/\text{TiO}_2$	100	1.0	400 W ($\lambda > 400 \text{ nm}$)	2.5	76	[49]
$\text{Na}(0.3)\text{-C}_3\text{N}_4$	400	5.0	500 W ($\lambda > 400 \text{ nm}$)	6.0	90	[50]
g- C_3N_4	130	5.0	500 W ($\lambda > 400 \text{ nm}$)	6.0	91	[50]

Fig. 11. (a) Reusability of 0.25%SDS/Fe₂O₃-450 for photocatalytic denitrogenation of pyridine. (b) Room temperature magnetization curves of samples; digital photographs in inset demonstrate the facile catalyst recovery using a magnet.

Compared with other photocatalysts, 0.25%SDS/Fe₂O₃-450 exhibited better or comparable photocatalytic activity for pyridine denitrogenation under visible light irradiation [45–50]. The superior photocatalytic activity of 0.25%SDS/Fe₂O₃-450 could be explained as follows: (i) the addition of SDS inhibited the self-assembly of α -Fe₂O₃ in the pyridine-octane solution; (ii) the hydrophobic tails of SDS facilitated the adsorption of pyridine molecules.

The durability of 0.25%SDS/Fe₂O₃-450 toward the denitrogenation of pyridine has been tested (Fig. 11(a)), and it was concluded that 0.25%SDS/Fe₂O₃-450 exhibited good stability after recycling tests. Detailed magnetic measurements revealed that both 0.25%SDS/Fe₂O₃-450 and Fe₂O₃-450 presented characteristic ferromagnetic hysteresis curves (Fig. 11(b)). The saturation magnetization values of 0.25%SDS/Fe₂O₃-450 and

Fe₂O₃-450 were 9.2 and 23.7 emu/g, respectively. These differences could be attributed to the addition of non-magnetic SDS component to Fe₂O₃. The inset in Fig. 11(b) illustrates that the 0.25%SDS/Fe₂O₃-450 hybrids could be easily separated from the pyridine denitrogenation medium using an external magnet.

3.3. Photocatalytic mechanism

Mott-Schottky experiments have been performed to determine the flat-band potential of the 0.25%SDS/Fe₂O₃-450 sample in this study (Fig. 12(a)). The results of the Mott-Schottky measurements revealed that the flat-band potential of the 0.25%SDS/Fe₂O₃-450 sample was approximately 0.17 V vs. Ag/AgCl at pH 6.8. Therefore, the band structure of

Fig. 12. (a) Mott-Schottky plots and band structure (inset) of 0.25%SDS/Fe₂O₃-450. (b) Transient photocurrent responses of α -Fe₂O₃, Fe₂O₃-450, and Fe₂O₃-450. (c) Nyquist impedance plots of α -Fe₂O₃, Fe₂O₃-450, and Fe₂O₃-450. (d) Transient photocurrent responses of SDS/Fe₂O₃-450 samples. (e) Nyquist impedance plots of Fe₂O₃-450 and SDS/Fe₂O₃-450 samples.

Fig. 13. (a) Dispersion experiment, (b) photoluminescence spectra, and (c) time-resolved photoluminescence decay spectra of Fe_2O_3 -450 and 0.25%SDS/ Fe_2O_3 -450.

0.25%SDS/ Fe_2O_3 -450 was investigated based on the combination of the flat-band potential and band gap (see inset of Fig. 12(a)). As displayed in Fig. 12(b), the photocurrent intensity of Fe_2O_3 -450 was much higher than those of Fe_2O_3 -450D and commercial α - Fe_2O_3 when the light was turned on, which suggested that the lifetime of photogenerated electron-hole pairs of Fe_2O_3 -450 was higher than those of Fe_2O_3 -450D and commercial α - Fe_2O_3 . Moreover, to better understand the excellent charge carrier transmission performance of Fe_2O_3 -450, EIS Nyquist plots have been obtained. Compared with α - Fe_2O_3 and Fe_2O_3 -450D, the semicircle of Fe_2O_3 -450 was smaller, which indicated the significantly increased charge-carrier transfer of Fe_2O_3 -450 compared with those of α - Fe_2O_3 and Fe_2O_3 -450D (Fig. 12(c)). We also determined that during photocurrent and EIS measurements, the signals of SDS/ Fe_2O_3 -450 almost coincided with those of Fe_2O_3 -450 (Figs. 12(d) and (e)), however, the photocatalytic performance of SDS/ Fe_2O_3 -450 was superior to that of Fe_2O_3 -450.

It could be speculated that the main role of SDS in the 0.25%SDS/ Fe_2O_3 -450 NC was not to act as co-catalyst to improve charge carriers transport, but serve as “bridge molecule” between the hydrophilic surface of Fe_2O_3 -450 and hydrophobic octane molecules. This could be intuitively demonstrated using a dispersion experiment (5 mg sample was dissolved in 5 mL pyridine/octane solution, Fig. 13(a)). The dispersion experiment indicated that the addition of SDS improved the dispersibility of SDS/ Fe_2O_3 -450 hybrids in octane. In addition, the important role of SDS in promoting the separation of photoexcited electron-hole pairs of the hybrids in this study has been confirmed using steady-state PL and time-resolved PL spectroscopy data (transferring the above solution to a quartz cuvette, then recording the steady-state PL and time-resolved PL spectra). According to the PL data, as displayed in Fig. 13(b), under

the excitation wavelength of 335 nm, the PL intensity of 0.25%SDS/ Fe_2O_3 -450 was much weaker than that of Fe_2O_3 -450, and thus, suggested the longer lifetime of photo-generated charge carriers of 0.25%SDS/ Fe_2O_3 -450. As illustrated in Fig. 13(c), the PL decay spectra of the 0.25%SDS/ Fe_2O_3 -450 NC and Fe_2O_3 -450 samples can be well fitted to the double exponential model (Eq. (1)). The average fluorescence lifetime of the 0.25%SDS/ Fe_2O_3 -450 NC was calculated to be 3.6 ns, which was longer than that of Fe_2O_3 -450 (3.3 ns). Owing to this long-lived charge-separated state, 0.25%SDS/ Fe_2O_3 -450 would be more efficient for photocatalytic applications.

To date, detailed mechanistic studies on the denitrogenation pathway of pyridine have been very limited. Indirect and ESR spectroscopy studies have been carried out to determine the photocatalytic reaction mechanism in this study. The HPLC-MS spectrometry results are displayed in Fig. 14. Upon irradiation for 240 min, the peak intensity of pyridine at approximately $m/z = 81.5$ was greatly decreased, which implied the successful denitrogenation of pyridine. At the same time, two new peaks at $m/z = 85.0$ and 46.1 gradually appeared, which suggested that pyridine has been transformed into $\text{C}_4\text{H}_4\text{O}_2$ and CH_3NH_2 , which are protonated intermediate products. The most reliable and direct method for investigating reactive species is ESR. In the presence of SDS/ Fe_2O_3 -450, even after 10 min of irradiation, the signal of $\text{DMPO} \cdot \text{O}_2^-$ was still relatively weak, which implied that $\cdot \text{O}_2^-$ was not the main active species during this reaction (Fig. 15(a)). The characteristic quartet peaks of the $\text{DMPO} \cdot \text{OH}$ adduct can be easily detected after visible light irradiation for 10 min (see Fig. 15(b)), which demonstrated that $\cdot \text{OH}$ radicals have also been generated. The valence band potential of 0.25%SDS/ Fe_2O_3 -450 was more positive than $E(\cdot \text{OH}/\text{H}_2\text{O})$ (2.27 V vs. NHE), and thus producing $\cdot \text{OH}$ radicals via

Fig. 14. High-performance liquid chromatography profiles of pyridine after different irradiation times: (a) 0 and (b) 4 h.

Fig. 15. (a–c) Electron spin response spectra of various radical adducts and (d) possible denitrogenation pathway of pyridine.

the oxidation of H_2O (the trace H_2O molecules in octane) was thermodynamically possible. Other active species, holes, have also been detected. The TEMPO molecules have been regarded to be a hole probes during the photocatalytic reaction [51,52], because their free radicals can be oxidized by holes. As illustrated in Fig. 15(c), the ESR signal of TEMPO decreased, which confirmed the production of photogenerated holes. Furthermore, the possible denitrogenation pathway of pyridine is illustrated in Fig. 15(d), and is in agreement with the information reported in one of our previously published papers [45].

Based on the above results, a photocatalytic mechanism for the denitrogenation of pyridine over SDS/ Fe_2O_3 -450 NCs was proposed (Fig. 16). Under visible light exposure, Fe_2O_3 nanoparticles in the SDS/ Fe_2O_3 -450 NCs became photoexcited and produced photogenerated carriers. Owing to the specific porous structure of Fe_2O_3 -450, the electron-hole pairs could easily transfer from the bulk to the surface of Fe_2O_3 -450. Subsequently, the introduction of SDS as “bridge molecule” between the hydrophilic surface of Fe_2O_3 -450 and hydrophobic octane conferred SDS/ Fe_2O_3 -450 NCs superior dispersibility. Moreover, such a hydrophobic interface also helped improve the adsorbability of SDS/ Fe_2O_3 -450 toward pyridine.

4. Conclusions

In summary, SDS/ Fe_2O_3 -450 NCs have been obtained using a simple two-step calcination strategy, followed by efficient electrostatic self-assembly. The photocatalytic denitration of pyridine has been selected as probe reaction to investigate the

activity of the as-prepared photocatalysts. The SDS/ Fe_2O_3 -450 NCs exhibited significantly increased photoactivity compared with commercial α - Fe_2O_3 and Fe_2O_3 -450D, which was attributed to the improved visible light absorption properties and efficient photogenerated-carrier separation as well as the abundance of active sites owing to the unique porous matrix structure of Fe_2O_3 -450. Specifically, the addition of SDS also boosted the dispersion capability of Fe_2O_3 -450 toward pyridine molecules. These factors synergistically led to the overall significant activity improvement of SDS/ Fe_2O_3 -450 NCs for pyridine denitration. This study offered specific examples of using surfactant decorated photocatalysts for the denitration of gasoline fuel. It would be expected that this study could not only offer key information for the fabrication of porous metal oxide

Fig. 16. Possible mechanism of photocatalytic denitrogenation of pyridine.

Graphical Abstract

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Sodium dodecyl sulfate-decorated MOF-derived porous Fe_2O_3 nanoparticles: High performance, recyclable photocatalysts for fuel denitrification

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SDS/ Fe_2O_3 nanocomposites have been fabricated using a simple two-step calcination strategy, followed by efficient electrostatic self-assembly. The obtained SDS/ Fe_2O_3 photocatalysts have exhibited outstanding photoactivities for the denitrification of pyridine.

materials but would provide a general method to rapidly tune the surface structure of photocatalysts for the denitrification of NCCs.

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经由MOFs煅烧制得多孔Fe₂O₃表面修饰十二烷基磺酸钠：一种高活性且易回收的燃油脱氮光催化剂

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摘要:化石燃料燃烧的排放物是目前最严重的环境污染源, 其中含氮有机物燃烧产生的NO_x等是污染大气和形成雾霾的主要污染物。伴随石油存量的不断减少、重质石油的更多利用以及机动车的大规模增加, 由此引起的污染问题日趋严重, 因此发展高效的燃油脱氮技术对保护环境意义重大。光催化氧化是近几十年发展起来的新型高级氧化还原技术, 由于其可以利用太阳光且在室温下进行, 成本低易于进行, 是一类理想的燃油脱氮技术。在众多光催化材料中, α-Fe₂O₃无毒、廉价且具有合适的带隙(2.3 eV), 是目前公认较好的光催化材料。然而, 在光催化过程中α-Fe₂O₃较快的电子-空穴复合速度以及过低的比表面积大降低了其效率。通常, 选择性地设计高比表面的多孔半导体金属氧化物被认为是一种简单且实效的提高光催化反应效率的方法。近年来, 以金属有机框架结构(MOFs)为硬模板制备多孔金属氧化物的方法逐渐获得了科学家们的关注, 这主要得益于热稳定性差的MOFs本身可以通过调控金属离子以及配体种类从而实现原位均匀的调节和修饰半导体金属氧化物, 而且可以作为获得多孔性材料的基底。

本文通过水热法合成了一种典型的MOFs即MIL-100(Fe)。利用MIL-100(Fe)材料自身多孔性及热不稳定性, 采用自模板法煅烧制备成多孔Fe₂O₃。制得的多孔Fe₂O₃亲油性较差, 进行模拟燃油脱氮光催化反应时相互之间容易聚集成团, 无法均匀分散于燃油体系中, 导致光催化脱氮效率较低。因此, 若能对所得多孔Fe₂O₃进行表面修饰使其亲油性增强并可均匀分散于燃油体系中, 无疑将促进底物的吸附, 从而提高光催化燃油脱氮效果。Fe₂O₃表面带有正电荷, 因此我们巧妙地选用一种阴离子表面活性剂十二烷基磺酸钠(SDS)作为修饰剂, 采用简单的静电自组装方法制备了SDS/Fe₂O₃光催化剂。选用吡啶脱氮作为探针反应, 考察了SDS/Fe₂O₃复合光催化剂的可见光光催化性能。结果表明, 与未使用修饰剂的Fe₂O₃相比, SDS/Fe₂O₃中长链烷基的存在使其表面亲油性增强, 能够在模拟燃油溶液中更加均匀地分散进而提高了脱氮效率。其中煅烧温度为450 °C且修饰0.25%SDS的样品活性最佳, 可见光(λ ≥ 420 nm)照射240 min后吡啶的脱氮率接近100%。

关键词: MIL-100(Fe); Fe₂O₃; 表面活性剂; 光催化脱氮; 吡啶

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