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Article

Morphology evolution of acetic acid-modulated MIL-53(Fe) for efficient selective oxidation of H₂S

Xiaoxiao Zheng, Sihui Qi, Yanning Cao, Lijuan Shen *, Chaktong Au, Lilong Jiang #

National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou 350002, Fujian, China

ARTICLE INFO

Article history:

Received 27 March 2020

Accepted 11 May 2020

Published 5 February 2021

Keywords:

Fe-metal-organic frameworks

Hydrogen sulfide

Selective oxidation

Controllable synthesis

Acetic acid

Modulation

ABSTRACT

MIL-53(Fe) was synthesized using a “modulator approach” that utilizes acetic acid (HAc) as an additive to control the size and morphology of the resulting crystals. We demonstrate that after activation under vacuum at 100 °C, the MIL-53(Fe) functions well for H₂S selective oxidation. The introduction of acetic acid in the presence of benzene-1,4-dicarboxylic acid (H₂BDC) would result in a series of MIL-53(Fe) nanocrystals (denoted as MIL-53(Fe)-xH, x stands for the volume of added HAc with morphology evolving from irregular particles to short hexagonal columns. The vacuum treatment facilitates the removal of acetate groups, thus generating Fe³⁺ Lewis acid sites. Consequently, the resulted MIL-53(Fe)-xH exhibits good catalytic activity (98% H₂S conversion and 92% sulfur selectivity) at moderate reaction temperatures (100–190 °C). The MIL-53(Fe)-5H is superior to the traditional iron-based catalysts, showing stable performance in a test period of 55 h.

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1. Introduction

Hydrogen sulfide (H₂S), originating from industrial processes such as coal gasification and oil refining, is one of the most malodorous and toxic gases [1–3]. The gas is not only corrosive to metals pipelines, but also hazardous to health and harmful to the environment [4,5]. It is hence imperative to control the emission of H₂S. Among the various established technologies for H₂S removal, the catalytic selective oxidation of H₂S to useful sulfur looks promising. It is a green process and the capital requirement is low [6,7]. In addition, thermodynamically it is possible to achieve complete conversion of H₂S to sulfur: H₂S + (1/2)O₂ → (1/n)S_n + H₂O [8]. Nonetheless, the essential task for reaching practical application is the development of efficient and stable catalysts.

Being cheap and relatively high in activity, iron oxides have

been intensely studied for H₂S selective oxidation [9]. However, for this class of catalysts, the use of excess oxygen is required and the sulfur selectivity is usually low. With the significant generation of SO₂ as a result of H₂S deep oxidation, the sulfur yield is poor [10]. Furthermore, catalyst deactivation is common due to surface sulfidation and sulfur deposition [11]. With the goal of achieving practical application, researchers have put in tremendous efforts to modify iron oxides, in particular by metal doping (e.g., Ce, Cr, V) and fabrication of support materials (e.g., Fe/β-SiC and Fe/PILC) [12–14]. However, the systems are energy consuming because the reaction temperature is relatively high (≥250 °C). Moreover, the poor dispersion and large particle size of iron species is always a concern. Also, to design a proper support for iron catalysts is a complicate issue because a support may react with H₂S or products to form sulfate, resulting in catalyst deactivation [15]. It still remains a

* Corresponding author. Tel: +86-591-83731234; E-mail: syhgslj@fzu.edu.cn

Corresponding author. Tel: +86-591-83731234; E-mail: jll@fzu.edu.cn

This work was supported by the National Science Fund for Distinguished Young Scholars of China (21825801), the National Natural Science Foundation of China (21603034), and the Natural Science Foundation of Fujian Province (2017J05022).

DOI: 10.1016/S1872-2067(20)63625-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 2, February 2021

grand challenge to develop iron catalysts that can perform acceptably well in the selective oxidation of H₂S at temperatures below 200 °C.

Emerging as a new class of porous material, metal-organic frameworks (MOFs) have triggered keen research interest owing to their unique properties and functionalities. The advantages of deploying MOFs in heterogeneous catalysis have been highlighted in recent publications [16–23]. For example, (i) the metal content of MOFs is high, and the metal atoms are maximally dispersed with the open metal centers functioning as active sites for catalytic action; (ii) the ultrahigh specific surface area and regular pore structure of MOFs enables better contact between reactants and active sites; and (iii) the structural flexibility and tunability of MOFs provides a versatile knob for functionality adjustment to meet specific catalytic needs. For these reasons, it is envisaged that MOFs could be utilized for selective oxidation of H₂S to sulfur.

The application of MOFs for desulfurization is still in its infancy. Herein, we report the preparation of MIL-53(Fe) using a modulation approach. MIL-53(Fe) (Fe(OH)BDC·xH₂BDC) was chosen as candidate for our study because of cost and stability concerns. The resulted catalyst shows outstanding performance for the selective conversion of H₂S. It was synthesized *via* a modified solvothermal method. To control the size and morphology of the resulting crystals, acetic acid (HAc) was added as capping agent to modulate the coordination between metal ions and organic linkers. The outcome is rate regulation of framework extension and crystal growth, and a series of MIL-53(Fe) particles with morphology ranging from bulky irregular shapes to highly uniform short columns was obtained. The optimized MIL-53(Fe) is highly stable, showing H₂S conversion and sulfur selectivity close to 100%. The results of *in situ* DRIFTS characterization confirm that the addition of acetic acid can lead to the creation of extra Lewis acid sites (LAS), and the discrepancy in LAS content causes difference in catalytic activity. The results of the present work can serve as guidelines for the design of stable and efficient catalysts to circumvent the shortcomings of conventional iron-based catalysts for H₂S selective oxidation.

2. Experimental

2.1. Materials

1,4-Benzenedicarboxylic acid (H₂BDC) was purchased from Sigma-Aldrich (Shanghai, China). Acetic acid (HAc), methanol, *N,N'*-dimethylformamide (DMF), and FeCl₃·6H₂O were purchased from Sinopharm Chemical Reagent (Shanghai, China). All the chemicals were directly used without further treatment.

2.2. Synthesis of catalysts

Typically, H₂BDC (1.236 g) and FeCl₃·6H₂O (4.05 g) were dissolved in DMF (45 mL) in a Teflon autoclave and sonicated to obtain a homogeneous solution. After that, a designated volume (*x*) of acetic acid was added dropwise to the solution. Then the resulted mixture was subject to sonication for 10 min,

and heated in an oven at 170 °C for 24 h. After cooling to room temperature, the solid in the form of powder was isolated by filtration and washed with a large volume of methanol. The sample obtained before vacuum activation at 100 °C is herein denoted as MIL-53(Fe)-xH (where *x* = 3, 5 and 10 mL). For comparison, a sample of non-modulated material named herein as MIL-53(Fe) was also synthesized following the above procedures but without adding HAc.

2.3. Characterization

The morphologies and elemental distribution of catalysts were acquired on an S-4800 Hitachi scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX). X-ray diffraction (XRD) analysis was conducted on an X'Pert3 Powder diffractometer using Cu K_α radiation at 45 kV and 40 mA. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were performed on a NETZSCH STA2500 Regulus TG/DSC system under flowing air with a ramping rate of 5 °C·min⁻¹. Fourier transformed infrared (FT-IR) spectra were acquired using a Nicolet-6700 spectrometer. Raman spectra were collected on a Renishaw Raman spectrometer furnished with a laser beam of λ = 325 nm. The N₂ adsorption-desorption isotherms were obtained over an U.S. Micromeritics 3Flex analyzer at −196 °C. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo ESCALAB 250 spectrometer. The Fe contents were examined on an Optima 8000 Inductively Coupled Plasma Emission spectrometer (ICP-OES). The surface acid properties of samples were studied by *in situ* DRIFTS technique using pyridine as probe. Before the adsorption of pyridine, the MIL-53(Fe)-xH samples were heated in helium atmosphere (150 °C, 3 h) to exclude the influence of adsorbed impurities.

2.4. Desulfurization measurement

The selective oxidation of H₂S to sulfur over MIL-53(Fe)-xH was conducted in a fixed-bed reactor in the temperature range of 100–190 °C under atmospheric pressure. The catalyst (0.2 g) was loaded in the central of the reactor and a mixture gas containing 2500 ppm O₂, 5000 ppm H₂S and balance N₂ was introduced into the reactor at a total flow rate of 10 mL min⁻¹. During desulfurization, the effluent gases (containing SO₂ and/or H₂S) were on-line analyzed by GC9720 furnished with a TCD. A condenser was located under the reactor to trap sulfur in the outlet. Instantaneous H₂S conversion (%), sulfur selectivity (%) and sulfur yield (%) are defined as follows:

$$\text{H}_2\text{S conversion} = ([\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}) / [\text{H}_2\text{S}]_{\text{in}} \times 100$$

$$\text{Sulfur selectivity} =$$

$$([\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}} - [\text{SO}_2]_{\text{out}}) / ([\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}) \times 100$$

$$\text{Sulfur yield} = [\text{H}_2\text{S conversion}] \times [\text{Sulfur selectivity}] \times 100$$

3. Results and discussion

3.1. Structure characterization

The schematic of MIL-53(Fe)-xH synthesis via acetic acid

coordination modulation is displayed in Fig. 1A. The SEM image of MIL-53(Fe) displays particles of bulky irregular morphology (Fig. 1B). The addition of HAc obviously has an effect on the morphology of MIL-53(Fe). The MIL-53(Fe)-3H sample is composed of uniform hexagonal spindle-shape crystals with sharp ends, which are ca. 15 μm in length and 3 μm in width (Fig. 1C). As for MIL-53(Fe)-5H, the sharp ends disappear, and the average particle length is 12 μm (Fig. 1D). When the added amount of HAc was 10 mL, the MIL-53(Fe)-10H is in the form of short hexagonal prisms 8.5 and 5.0 μm in average size (Fig. 1E). It is apparent that the addition of HAc in the synthesis of MIL-53(Fe) could strongly modulate the growth of MIL-53(Fe) crystals, making size and morphology control feasible.

The structures of MIL-53(Fe) and MIL-53(Fe)-xH before vacuum treatment at 100 $^{\circ}\text{C}$ were studied by X-ray powder diffraction (XRD). As shown in Fig. 2, the XRD pattern of MIL-53(Fe) matches well with that of the simulated one [24]. At low HAc addition, MIL-53(Fe)-3H displays main peaks at 2θ of 9.2 $^{\circ}$, 10.6 $^{\circ}$, 12.6 $^{\circ}$, 17.6 $^{\circ}$, and 25.4 $^{\circ}$, in consistent with those of MIL-53(Fe) [25]. Compared with MIL-53(Fe), MIL-53(Fe)-3H shows no obvious shift in peak position, only that the peak at 10.6 $^{\circ}$ of the latter is slightly higher in intensity. The slight increase of peak intensity is plausibly due to a change of crystal growth direction under the influence of HAc, in agreement with the SEM results (Figs. 1B and 1C)) [26,27]. However, a higher amount of HAc would significantly interfere the crystal growth of MIL-53(Fe). The MIL-53(Fe)-5H and MIL-53(Fe)-10H samples show diffraction patterns that are distinctly different from that of MIL-53(Fe). The 10.6 $^{\circ}$ and 9.7 $^{\circ}$ peaks of MIL-53(Fe)-5H and MIL-53(Fe)-10H are relatively higher in intensity in comparison with those of MIL-53(Fe), respectively, while the 12.6 $^{\circ}$ peaks weaker. The phenomena can be related to the fact that HAc is with carboxylate group similar to that of H₂BDC, and both HAc and H₂BDC can coordinate with Fe-oxo clusters

Fig. 1. (A) Schematic of MIL-53(Fe)-xH preparation (Gray, C; Blue, O; Aqua, Fe³⁺; Light Orange, Fe³⁺ Lewis acid sites; Purple dotted line, missing linker defects); SEM images of (B) MIL-53(Fe), (C) MIL-53(Fe)-3H, (D) MIL-53(Fe)-5H, and (E) MIL-53(Fe)-10H.

Fig. 2. XRD patterns of MIL-53(Fe) and MIL-53(Fe)-xH (before vacuum treatment at 100 $^{\circ}\text{C}$).

[28–30]. The pK_a for H₂BDC and HAc linkers is 3.51 and 4.76, respectively, and the competition and exchange of the two would induce structural defects [31,32]. Similar phenomena were reported in the synthesis of other MOFs when HAc was used as modulator [29]. Due to the labile and volatile property of HAc (b.p. = 118 $^{\circ}\text{C}$), it is possible to expose the Fe sites by having the acetate groups removed during vacuum treatment [31].

The XRD patterns of MIL-53(Fe) and MIL-53(Fe)-xH after vacuum treatment at 100 $^{\circ}\text{C}$ are shown in Fig. S1. It is found that the patterns of MIL-53(Fe) recorded before and after vacuum treatment are almost the same, but those of MIL-53(Fe)-xH are significantly different in terms of relative peak intensity. After vacuum activation, the strongest peak of MIL-53(Fe) is the one at 12.6 $^{\circ}$, while that of MIL-53(Fe)-3H and MIL-53(Fe)-5H is the one at 9.7 $^{\circ}$. In the case of MIL-53(Fe)-10H, it is the peak at 10.6 $^{\circ}$ that is the strongest. Interestingly, there is near complete disappearance of the 9.2 $^{\circ}$ and 10.6 $^{\circ}$ peaks when comes to MIL-53(Fe)-5H. All these discrepancies can be attributed to the variation of acetate amount in the structure of MIL-53(Fe)-xH samples before vacuum activation.

To validate the assumption that was based on the XRD data, the samples were subject to TG-DSC analysis (Fig. 3). Two weight losses are observed over MIL-53(Fe) (Fig. 3A). The gradual loss below 343 $^{\circ}\text{C}$ is due to the desorption of guest molecules (e.g., H₂O and methanol), while the major rapid one between 343 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$ can be attributed to the decomposition of frameworks together with the departure of BDC ligand [33]. The remaining mass for MIL-53(Fe) is 30.4%, revealing that the residual is largely Fe₂O₃. Despite the TG curves (Figs. 3B–3D) of MIL-53(Fe)-xH show a trend similar to that of MIL-53(Fe), there is clear difference in the DSC profiles. It is clear that the decomposition of MIL-53(Fe)-xH occurs in two steps, suggesting that there are two linkers in the framework. The remaining mass for MIL-53(Fe)-3H, MIL-53(Fe)-5H and MIL-53(Fe)-10H is 32.8%, 27.9% and 47.1% of original, respectively. The variation could be due to difference in HAc incorporation. Moreover, the heat involved in the decomposition of the samples follows the order of MIL-53(Fe) (5.39 kJ/g) >

Fig. 3. DSC (red) and TG (black) curves of prepared samples: (A) MIL-53(Fe), (B) MIL-53(Fe)-3H, (C) MIL-53(Fe)-5H, and (D) MIL-53(Fe)-10H.

MIL-53(Fe)-3H (4.40 kJ/g) > MIL-53(Fe)-5H (3.18 kJ/g) > MIL-53(Fe)-10H (2.39 kJ/g). Putting the combustion heat of HAC (875.0 kJ/mol) and H₂BDC (3225.9 kJ/mol) into consideration, a decrease of heat exchange with the increase of HAC content confirms higher HAC participation in ligand coordination with Fe³⁺ [34]. In order to obtain a clear estimation on the extent of HAC and H₂BDC coordination in MIL-53(Fe)-xH, we normalized the weight losses with respect to the Fe₂O₃ residue after heating to 500 °C. Between 300 °C and 400 °C, the weight loss of MIL-53(Fe) is in line with a BDC/Fe ratio of 1.06, indicative of FeO₆ coordination with one terephthalate anion (BDC²⁻) (Fig. S2A). As for MIL-53(Fe)-3H, the CH₃COO⁻/Fe and BDC²⁻/Fe ratio is 1.34 and 0.43, respectively (Fig. S2B). The result indicates that the coordination is one FeO₆ octahedral linking to 1.34 CH₃COO⁻ and 0.43 BDC²⁻ plausibly with a formula of Fe(OH)(CH₃COO)_{1.34}(BDC)_{0.43}·xH₂BDC. As for MIL-53(Fe)-5H and MIL-53(Fe)-10H, the CH₃COO⁻/Fe ratio is 1.50 and 0.69, respectively (Figs. S2C and S2D). Among MIL-53(Fe)-xH, MIL-53(Fe)-5H has the highest CH₃COO⁻/Fe ratio, indicating that the amount of acetate group in MIL-53(Fe)-5H is higher than that in MIL-53(Fe)-3H and

MIL-53(Fe)-10H, which is consistent with the XRD results (Fig. S1).

The FT-IR spectra of MIL-53(Fe) and MIL-53(Fe)-xH were collected (Fig. 4A). All of the samples exhibit the characteristic stretching vibrations of carboxylate groups in the range of 1700–1400 cm⁻¹. The peak at 746 cm⁻¹ is ascribed to the C–H bending vibration of aromatic ring [35,36]. As for the peak at 545 cm⁻¹, it is related to Fe–O vibration [37]. The peaks at 1543 cm⁻¹ and 1392 cm⁻¹ detected over MIL-53(Fe) could be assigned to the symmetric and asymmetric stretching mode of COO⁻ group, respectively [38]. Over MIL-53(Fe)-3H, the peak at 1543 cm⁻¹ becomes weaker and a new peak at 1587 cm⁻¹ appears. With the amount of HAC increases from 3 to 5 or 10 mL, the band intensity at 1587 cm⁻¹ gradually enhances, while the peak at 1543 cm⁻¹ disappears. The variation of the symmetric stretching vibration band of the MIL-53(Fe)-xH samples is ascribed to the successful coordination of HAC into the framework.

In addition, the structural information of MIL-53(Fe) and MIL-53(Fe)-xH was further analyzed by Raman spectroscopy. For comparison, the organic linker H₂BDC was also tested un-

Fig. 4. (A) FT-IR spectra and (B) Raman spectra of MIL-53(Fe)-xH.

der the same conditions. As shown in Fig. 4B, five Raman bands at 1615, 1454, 1125, 635, and 832 cm⁻¹ are observed over H₂BDC. The first four are attributed to the out-of-plane and in-plane deformation modes of C–H groups, while the last to the stretching vibration modes of C=O groups [39,40]. For the MIL-53(Fe) obtained by self-assembly of H₂BDC and Fe ions, the C=O peak of H₂BDC at 832 cm⁻¹ disappears and a new peak at 864 cm⁻¹ appears, which is due to C–O–Fe stretching of FeO₆ octahedral, revealing the formation of C–O–Fe coordination. In addition, two new bands appear at 463 cm⁻¹ and 1433 cm⁻¹. The former is attributed to network binding modes and lattice vibrations, while the latter to stretching modes of carboxylate groups (–OOCCH₂COO– and/or CH₃COO–) [41]. It is worth noting that the intensity of the 1433 cm⁻¹ band increases with rising HAc content. Zhang et al. proposed that the “I₁₄₃₃/I₁₆₁₅” intensity ratios can be used to analyze the variation trend of carboxyl groups [42]. It is observed that the increase of I₁₄₃₃/I₁₆₁₅ ratios follows the order of MIL-53(Fe) (0.09) < MIL-53(Fe)-5H (0.15) < MIL-53(Fe)-3H (0.16) < MIL-53(Fe)-10H (0.22). Compared to MIL-53(Fe), all the MIL-53(Fe)-xH show higher I₁₄₃₃/I₁₆₁₅ ratio, with MIL-53(Fe)-5H being the least obvious. It is envisaged that the acetate groups could be readily removed upon vacuum activation, breaking the C–O–Fe coordination and leaving behind exposed Fe sites. These results are consistent with the deduction of XRD and TG-DSC analysis. ICP-OES results shown in Table S1 further indicate that the introduction of HAc increases the Fe content of MIL-53(Fe). In addition, the N₂ adsorption-desorption isotherms of MIL-53(Fe) and MIL-53(Fe)-xH all show a type IV curve with H3-type hysteresis loops (Fig. S3). It is worth noting that the specific surface areas of these four materials (4.1, 6.5, 5.2, and 5.3 m²/g, respectively) are much smaller than that of other reported Fe-MOFs, plausibly due to the breathing effect of MIL-53(Fe) [43].

XPS analysis was conducted to clarify the chemical state of

elements. In the XPS survey scans of MIL-53(Fe) and MIL-53(Fe)-xH, signals of Fe, C and O elements are observed (Fig. 5A). The C 1s spectra can be fitted into three peaks at ca. 288.6, 285.9 and 284.6 eV, which could be ascribed to C=O, C–H, and phenyl, respectively (Fig. 5B) [44]. It is noted that the intensity of the 285.9 eV peaks increases with the rise of HAc content, mainly because of the increased coordination of HAc with Fe. For the O 1s spectra, the two deconvoluted peaks at 530.2 eV and 531.7 eV can be ascribed to Fe–O and C=O (Fig. 5C) [45,46]. It is found that with the increase of HAc content, the Fe–O peak also shows an increasing trend, reflecting that the introduction of HAc facilitates the formation of Fe–O sites. As presented in Fig. 5D, the peaks at 712.3 eV and 725.6 eV are assigned to Fe 2p_{3/2} and Fe 2p_{1/2}, while the peak at 717.7 eV to satellite signal of Fe³⁺ peak [47,48]. These results confirm that the Fe species in MIL-53(Fe) basically exists in the form of Fe³⁺. With the increase of HAc content from 3 to 10 mL, the position of Fe 2p_{3/2} peaks slightly shifts to lower binding energies, suggesting that the presence of HAc has a slight effect on the chemical environment of iron.

3.2. Catalytic activity

The catalytic properties of the prepared samples toward H₂S oxidation were tested in a packed-bed reactor under atmospheric pressure at 100–190 °C. As shown in Fig. 6A, the H₂S conversion over MIL-53(Fe) increases with rising temperature up to 160 °C, and then remains almost constant when the temperature is further increased to 190 °C. Compared with MIL-53(Fe), MIL-53(Fe)-xH shows higher catalytic activities at lower reaction temperature. The H₂S conversion follows the order of MIL-53(Fe)-5H > MIL-53(Fe)-3H > MIL-53(Fe)-10H > MIL-53(Fe). It is noted that when the temperature is increased to 160 °C, all the prepared samples can achieve 100% H₂S conversion, which is higher than that of Fe₂O₃ (80% H₂S conver-

Fig. 5. XPS spectra of MIL-53(Fe)-xH: (A) survey; (B) C 1s; (C) O 1s; and (D) Fe 2p.

Fig. 6. Effect of reaction temperature on (A) conversion of H₂S, (B) sulfur selectivity, and (C) sulfur yield over MIL-53(Fe), MIL-53(Fe)-xH and commercial Fe₂O₃.

sion) under the same reaction condition.

Fig. 6B shows the relationship between sulfur selectivity and reaction temperature. It can be seen that sulfur selectivity for all catalysts remains at ca. 100% below 130 °C. Further increase of temperature leads to gradually decrease of sulfur selectivity. It is because side reactions are promoted at high temperatures, leading to deep oxidation of H₂S ($\text{H}_2\text{S} + 3/2\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$) or oxidation of the produced sulfur ($\text{S} + \text{O}_2 \rightarrow \text{SO}_2$) [49]. Nevertheless, the sulfur selectivity is still higher than 89% for MIL-53(Fe) and MIL-53(Fe)-xH catalysts at 190 °C. As for Fe₂O₃, sulfur selectivity decreases from a value of 97% at 100 °C to 59% at 190 °C.

The relationship between sulfur yield and reaction temperature is depicted in Fig. 6C. Over the prepared catalysts, sulfur yield initially increases with rise of reaction temperature. MIL-53(Fe) shows a maximum sulfur yield of ca. 92% at 160 °C. As for MIL-53(Fe)-xH, they show higher activity than MIL-53(Fe). Over MIL-53(Fe)-5H, maximum sulfur yield of ca. 99% is achieved at 130 °C. Further increase of reaction temperature would lead to slight decrease of sulfur yield due to side reactions. All the MIL-53(Fe)-xH catalysts are superior to Fe₂O₃ in terms of sulfur yield. As for mass balance of sulfur, we recovered sulfur from the effluent and used catalyst and the result is in good agreement with the data of H₂S conversion and sulfur selectivity.

Fig. 7 presents the durability of MIL-53(Fe), MIL-53(Fe)-5H and commercial Fe₂O₃ at 190 °C. Fe₂O₃ shows obvious deactivation, exhibiting 41% H₂S conversion and 12% sulfur selectiv-

Fig. 7. Time-on-stream behavior of Fe₂O₃, MIL-53(Fe), and MIL-53(Fe)-5H for H₂S selective oxidation at 190 °C.

ity after 13 h of reaction, plausibly due to the generation of inactive Fe-S species and the deposition of sulfur [1]. In contrast, MIL-53(Fe) exhibits higher stability for desulfurization, and H₂S conversion and sulfur selectivity stabilizes at ca. 100% and 80% after 55 h, respectively. As for MIL-53(Fe)-5H, the H₂S conversion is comparable to that of MIL-53(Fe), while sulfur selectivity (ca. 86%) is higher than that of MIL-53(Fe) in a span of 55 h. The results suggest that the addition of acetic acid as modulator has a profound positive effect on the catalytic performance of MOFs. Compared with other reported catalysts, MIL-53(Fe)-5H has a significant advantage in maintaining high desulfurization activity over a long reaction time (Table S2).

We further compare the structure and chemical condition of fresh and used MIL-53(Fe)-5H. As shown in Figs. S4 and S5, the XRD and FT-IR patterns of used MIL-53(Fe)-5H are similar to those of the fresh catalyst, indicating good structure integrity. Furthermore, the morphology of used MIL-53(Fe)-5H is basically the same as that of fresh sample, except for the presence of small particulates on the catalyst surface (Fig. S6). This is mainly because the reaction temperature (190 °C) is only slightly higher than the dew point of sulfur (180 °C), causing incomplete sublimation of deposited sulfur. In addition, the recovered sulfur, EDX spectrum, and elemental mapping confirm the presence of sulfur in the used catalyst, albeit in trace amount (Figs. S7–S9). The XPS spectra of MIL-53(Fe)-5H before and after reaction are shown in Fig. S10. The Fe 2p, O 1s, C 1s and S 2p signals detected in the survey scans (Fig. S10A) confirm the presence of iron, oxygen, carbon and sulfur elements. It is noted that the Fe 2p spectrum of fresh MIL-53(Fe)-5H is almost the same as that of used one, revealing a Fe valence state of +3 (Fig. S10B). Furthermore, S 2p signal can be detected over the used MIL-53(Fe)-5H (Fig. S10C). The peak at 169.1 eV is assignable to sulfate, whereas peaks at 164.7 eV and 163.5 eV belong to sulfur [50].

3.3. Desulfurization mechanisms

According to literatures, Fe³⁺ Lewis acid sites (LAS) are active sites for selective conversion of H₂S to sulfur [50,51]. In order to understand how acetic acid acts as a regulator to affect desulfurization, the surface acidic properties of MIL-53(Fe)-xH were characterized by DRIFTS technique (Fig. 8). As shown in Fig. 8A, three characteristic peaks at 1070, 1043, and 1012 cm⁻¹

Fig. 8. Py-FT-IR spectra of (A) MIL-53(Fe), (B) MIL-53(Fe)-3H, (C) MIL-53(Fe)-5H, and (D) MIL-53(Fe)-10H after degassing at 30, 100, and 150 °C.

can be observed over MIL-53(Fe), which are attributed to ν_{18} , ν_{12} , and ν_1 modes of pyridine coordination with Fe^{3+} , respectively [52,53]. It is worth noting that the peak intensity at 1070 cm^{-1} increases with the rise of degassing temperature, indicating higher pyridine coordination with Fe^{3+} at higher temperature. More interestingly, across the MIL-53(Fe)-xH catalysts

Fig. 9. Pyridine sorption peak area (at 1070 cm^{-1}) and H_2S conversion over MIL-53(Fe)-xH.

Fig. 10. Diagram of the selective conversion of H_2S to sulfur over MIL-53(Fe)-xH.

after degassing at 100 or 150 °C, the intensity of peaks first increases and then decreases (Figs. 8B–8D). The results confirm that the introduction of an appropriate amount of HAc facilitates the generation of Fe^{3+} LAS. According to the literatures, the strength of LAS can be estimated on the basis of the peak areas of 1070 cm^{-1} [54]. Considering that the peak intensity after degassing at 30 °C is relatively weak, we only integrate the peaks collected after degassing at 150 °C to determine the content of medium-to-strong LAS. The H_2S conversions and peak areas of pyridine sorption over MIL-53(Fe) and MIL-53(Fe)-xH are displayed in Fig. 9. It is clear that the LAS content rises first and then decreases with increasing HAc content, and highest Fe^{3+} LAS content can be achieved over MIL-53(Fe)-5H. Over the four catalysts, H_2S conversion shows a trend similar to that of LAS amount. There is a positive correlation between LAS content and H_2S conversion, confirming that the catalytic performance of MIL-53(Fe)-xH for selective oxidation of H_2S is governed by LAS content.

Based on the above discussion, a plausible mechanism for catalytic H_2S selective conversion over MIL-53(Fe)-xH is proposed. As shown in Fig. 10, H_2S molecules diffuse on the surface of catalyst and adsorb on Fe^{3+} LAS. Then, the H_2S molecules are directly oxidized to S by Fe^{3+} , accompanied with the reduction of Fe^{3+} to Fe^{2+} . The Fe^{2+} ions can be re-oxidized to Fe^{3+} by active oxygen species for the sustention of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox cycle. In addition, another possible pathway is that H_2S adsorbs and dissociates to give HS^- on Fe^{3+} LAS, and then HS^- interacts with active oxygen species to generate sulfur.

4. Conclusions

In summary, a series of MIL-53(Fe) with morphology evolution from irregular bulky particles to highly uniform short hexagonal prisms have been synthesized by means of acetic

acid coordination modulation. The as-prepared MIL-53(Fe)-xH demonstrate outstanding performance for selective oxidation of H₂S. The maximum sulfur yield over the optimal sample MIL-53(Fe)-5H at 130 °C is ca. 99%, which is superior to those of conventional catalysts that are based on inorganic metal oxides. Remarkably, MIL-53(Fe)-5H also shows excellent stability (functioning for 55 h without deactivation). We envisage that the presented results can serve as impetus for the development of efficient desulfuration catalysts suitable for industrial applications.

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Graphical Abstract

Chin. J. Catal., 2021, 42: 279–287 doi: 10.1016/S1872-2067(20)63625-7

Morphology evolution of acetic acid-modulated MIL-53(Fe) for efficient selective oxidation of H₂S

Xiaoxiao Zheng, Sihui Qi, Yanning Cao, Lijuan Shen *, Chaktong Au, Lilong Jiang *
Fuzhou University

Using acetic acid coordination modulation, a series of MIL-53(Fe) with morphology evolving from irregular bulky particles to highly uniform short hexagonal prisms were synthesized and applied for H₂S selective oxidation.

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乙酸调控MIL-53(Fe)的形貌演变及其高效选择性氧化H₂S性能

郑笑笑, 齐思慧, 曹彦宁, 沈丽娟*, 区泽棠, 江莉龙[#]

福州大学化肥催化剂国家工程研究中心, 福建福州350002

摘要: 硫化氢(H₂S)广泛存在于以煤、石油和天然气等为原料的化工生产过程中, 不仅腐蚀管道和设备, 而且还会对健康和环境造成危害. 因此, 高效脱除H₂S已成为工业废气减排的重点. 在各种方法中, H₂S选择性氧化技术(H₂S + (1/2)O₂ → (1/n)S_n + H₂O)由于具有设备需求低、反应不受热力学平衡限制、理论转化率可达100%等优点展现出了巨大的应用前景. 实现这一过程的关键在于发展高效稳定的催化剂. 作为一类新兴的多孔材料, 金属-有机骨架材料(MOFs)由于其独特的结构和性质吸引了广泛的研究兴趣. 与传统的脱硫材料相比, MOFs的优势主要体现在: 1) 高度分散的金属原子可作为催化活性中心; 2) 超高比表面积和规则的孔结构有利于反应物与活性位点之间的接触; 3) 结构可调变性高, 通过在合成过程中有目的地引入配体或调控剂可产生额外的活性位点, 满足特定催化的需求. 基于以上特点可知, MOFs是一类有潜力的催化剂, 但目前将其应用于H₂S选择性氧化领域的研究尚处于起步阶段.

本文以典型的铁基MOFs MIL-53(Fe)为研究对象, 在制备MIL-53(Fe)过程中添加乙酸(HAc)作为调控剂, 通过控制HAc的量, 得到一系列具有不同形貌的MIL-53(Fe)-xH样品, 并将其应用于H₂S选择性氧化反应. SEM结果表明, 在MIL-53(Fe)的合成过程中引入乙酸可以显著影响样品的形貌和尺寸. 活化前后样品的XRD结果表明, HAc具有与对苯二甲酸(H₂BDC)相似羧基基团, 二者均可与Fe-O团簇配位. 此外, TG-DSC结果证实, 随着HAc加入量的提高, 与Fe³⁺形成配位的HAc/H₂BDC比值随之增加. FT-IR和Raman结果进一步证明HAc成功地配位到MIL-53(Fe)的框架中, 并且参与配位的HAc可通过真空活化移除从而暴露出Fe³⁺不饱和位点. H₂S选择性氧化测试表明, MIL-53(Fe)-xH的脱硫活性随着HAc含量的提高先增加然后降低, 其中MIL-53(Fe)-5H活性最优. 此外, MIL-53(Fe)-5H催化剂在连续运行55 h后仍能保持100%H₂S转化率和86%硫选择性, 性能远优于传统的Fe₂O₃催化剂. 吡啶原位红外光谱结果表明, HAc的引入可以产生额外的Lewis酸性位点(LAS), LAS含量的不同是造成催化剂活性差异的主要原因.

关键词: 金属有机骨架材料; 硫化氢; 选择性氧化; 可控合成; 乙酸; 调控

收稿日期: 2020-03-27. 接受日期: 2020-05-11. 出版日期: 2021-02-05.

*通讯联系人. 电话/传真: (0591)83731234; 电子信箱: syhgslj@fzu.edu.cn

[#]通讯联系人. 电话/传真: (0591)83731234; 电子信箱: jll@fzu.edu.cn

基金来源: 国家杰出青年科学基金(21825801); 国家自然科学基金(21603034); 福建省自然科学基金(2017J05022).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).