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Catalytic behaviors of combined oxides derived from Mg/Al_xFe_{1-x}-Cl layered double hydroxides for H₂S selective oxidation†

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A series of Mg₂Al_xFe_{1-x} LDH compounds was synthesized by a one-step method. The structural and chemical properties were studied by various methods and the derived oxides were tested for H₂S selective oxidation. It was observed that the iron species existed mainly in the form of isolated Fe³⁺ species, α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄. Moreover, the nature of the iron oxides was varied with the rise in the iron content. Significantly, the catalysts exhibited high catalytic activity and reasonable durability at a relatively lower temperature and higher GHSV. The catalysts obeyed the step-wise mechanism for H₂S selective catalytic oxidation. And the chemically adsorbed oxygen on the oxygen vacancies participated in the H₂S selective oxidation reaction and played a key role in the H₂S selective oxidation into elemental sulfur. The catalyst deactivation was due mainly to the deposit of elemental sulfur. Additionally, the small amount of the formed less active Fe₂(SO₄)₃ species also led to catalyst deactivation.

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1. Introduction

Since the environmental regulations concerning the release of sulfur-containing gases have become more stringent, H₂S contained in acidic gases needs to be carefully treated prior to emission to the atmosphere. Nowadays, the most well-known technique is the Claus process.¹ However, almost 1% H₂S is left in the Claus tail gas due to the thermodynamic limitations.²⁻⁴ Fortunately, various additional purification processes have been used such as absorption, adsorption and the selective catalytic oxidation technique.⁵ Among them, the selective catalytic oxidation technique has been of great research interest in the past decades, as it can directly catalytically oxidize H₂S into elemental sulfur. The irreversible reaction equations are as follows (eqn (1) as the main reaction, eqn (2) and (3) as the side reactions):⁶

In the reaction, SO₂ could be formed *via* deep oxidation of H₂S or further oxidation of elemental sulfur, causing a decrease in sulfur yield. Therefore, the sulfur yield strongly depends on the catalytic performance of the catalyst.

Iron oxide, one of the oldest catalysts, has been widely used as a catalyst in the process of H₂S selective oxidation. However, its sulfur selectivity is quite low due to the excess oxygen requirement. Recently, a number of methods have been established to modify iron oxide catalysts to obtain more selective and stable catalysts, particularly by incorporating a second metal element into the iron oxide structure⁷⁻¹¹ (Ce, Sb, *etc.*) and preparing supported catalysts (Fe/SiO₂, Fe/PILC, *etc.*). However, the reaction temperature is relatively high (≥250 °C) in terms of energy requirements, and the GHSV is relatively low. Moreover, for the supported catalysts, the dispersion and particle size of the iron species cannot be tuned readily. Additionally, the choice of an optimal support is absolutely a complicated problem,¹² as the support can react with H₂S or with the products to form sulfate, which can cause a decrease in the catalytic activities or even the destruction of the catalyst. Therefore, it is essential to further modify iron oxide to obtain a catalyst with high selectivity,

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activity and stability at a relatively higher GHSV and a lower reaction temperature.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are anionic clay materials.¹³ The chemical composition of LDHs can be expressed by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A_{x/n}^{n-}yH_2O]^{x-}$,¹⁴ wherein M^{II} and M^{III} are divalent and trivalent metal cations,¹⁵ A^{n-} is an n -valent anion, and x usually has values between 0.25 and 0.33. In particular, LDHs and their derivatives have been intensively investigated in recent years as catalysts and catalyst supports in many aspects. Because their acidic/basic properties can be easily tuned¹⁶ and their composition can be varied,¹⁵ which leave vast flexibility for better selection of various cations in these materials for H_2S selective oxidation. The corresponding composite oxides can be obtained after calcination, wherein, the iron species can be well-dispersed in the atomic level and incorporated into the catalyst steadily. Thus, layered double hydroxides are considered as a kind of attractive and suitable material to disperse and modify iron species.

In the present work, a facile method was provided to synthesize $Mg_2Al_xFe_{1-x}$ LDH. As expected, the catalytic activity can be enhanced due to the outstanding acidic/basic properties and reasonable thermal stability. Moreover, the physicochemical properties of the catalysts were characterized by various methods. Besides, the catalytic and catalyst deactivation mechanisms for H_2S selective oxidation over these catalysts were explored. To the best of our knowledge, it is the first time that $Mg_2Al_xFe_{1-x}$ LDH-derived oxides were used and studied for H_2S selective oxidation.

2. Experimental

2.1 Catalyst preparation

The synthesis of $Mg_2Al_xFe_{1-x}$ LDH was carried out using a modified version of Xu's method.¹⁷ $MgCl_2$, $AlCl_3 \cdot 6H_2O$, $NaOH$ and $FeCl_3$ were used as the starting materials. In a typical synthesis process, 60 mmol of $MgCl_2$, X mmol of $AlCl_3$ and $(30-X)$ mmol of $FeCl_3$ ($Mg^{2+}/(Al^{3+} + Fe^{3+}) = 2$, $Fe^{3+}/(Al^{3+} + Fe^{3+}) = 0.2, 0.4, 0.6, \text{ and } 0.8$) were dissolved in 200 ml of decarbonated water previously purged with nitrogen. Then, the solution was quickly (within 5 s) added to 800 ml of $NaOH$ solution (0.15 M) under vigorous stirring, followed by 15 min stirring in nitrogen atmosphere. $Mg_2Al_xFe_{1-x}$ LDH was obtained after centrifuging 3 times and was dried overnight at 40 °C. Finally, the derived oxide catalysts were obtained by calcining the LDH materials at 550 °C for 4 h. These catalysts were denoted as $Mg_2Al_xFe_{1-x}O$.

2.2 Characterization of the catalysts

The X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO powder diffraction system with $Cu K\alpha$ radiation ($\lambda = 0.15418$ nm) in the 2θ range of 10–80° (scanning rate of 0.5 min⁻¹).

UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded in air against $BaSO_4$ in the region of 12 500–24 000 cm⁻¹ on a Hitachi UV-3000 spectrometer.

Thermal stability was investigated by thermogravimetry (TG, Setaram, Labsys). Typically, around 30 mg of the sample was heated in an Al_2O_3 crucible at a constant heating rate of 10 °C min⁻¹ from 25 to 1000 °C, with air purging at a flow rate of 30 mL min⁻¹.

The X-ray photoelectron spectra (XPS) were recorded using a Thermo Electron Escalab250 instrument with $Al K\alpha$ radiation. The base pressure was 5×10^{-8} Pa. The binding energies were calibrated using the C 1s peak of the contaminant carbon (BE = 285 eV) as the standard, and quoted with a precision of ± 0.2 eV.

The BET surface areas and textural properties of the catalysts were determined by nitrogen adsorption-desorption isotherms using a gas sorption analyzer NOVA1200. Prior to N_2 adsorption measurement, the samples were degassed at 300 °C for 3 h.

The electron paramagnetic resonance (EPR) spectra were recorded on a JES FA200 spectrometer at room temperature.

H_2 temperature-programmed reduction (H_2 -TPR) experiments were conducted on a Micromeritics Chemisorb 2720 apparatus. The TPR profiles were obtained by passing a 5% H_2/He flow (50 ml min⁻¹) through the pretreated catalyst (about 100 mg). The temperature was increased from room temperature to 900 °C at a rate of 10 °C min⁻¹. The hydrogen concentration in the effluent was continuously monitored by using a thermal conductivity detector. Prior to each TPR run, the catalyst was pre-heated in He flow from room temperature to 300 °C and held for 30 min.

CO_2 temperature-programmed desorption (CO_2 -TPD) was carried out on the same apparatus as that in H_2 -TPR. In the process, the sample was heated from room temperature to 900 °C at a rate of 10 °C min⁻¹ in pure He . Before each TPD test, 100 mg of the sample was pre-heated in He flow from room temperature to 300 °C and held for 30 min. After cooling to room temperature, 20% CO_2/He was fed into the reactor at 50 ml min⁻¹ for 30 min, then, pure He was fed into the reactor at 50 ml min⁻¹ for 30 min to purge any residual CO_2 .

2.3 Catalytic performance tests

All tests were performed in a continuous flow fixed-bed quartz reactor at atmospheric pressure. 0.5 mL (about 0.7 g) of the catalyst (20–40 mesh) was placed in the central section of the reactor. The mixed gas containing 5000 ppm H_2S , 2500 ppm O_2 and balance gas (N_2) was fed into the reactor at a total gas flow rate of 200 ml min⁻¹ (GHSV = 24 000 h⁻¹) and reacted in the temperature range of 100 °C–200 °C. After reaction, the effluent stream was detected using a gas chromatograph (GC126) equipped with a FPD and a TCD. A condenser was located at the bottom of the reactor to trap the sulfur gas in the effluent stream. The instantaneous

fractional conversion of H_2S , sulfur selectivity and sulfur yield were defined as:

$$\text{H}_2\text{S conversion} = \frac{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}}}{(\text{H}_2\text{S})_{\text{in}}}$$

$$\text{Sulfur selectivity} = \frac{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}} - (\text{SO}_2)_{\text{out}}}{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}}}$$

$$\text{Sulfur yield} = \text{H}_2\text{S conversion} \times \text{sulfur selectivity}$$

3. Results and discussion

3.1 Characterization of $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{-Cl}$ LDHs

The XRD patterns of the $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{-Cl}$ LDHs are illustrated in Fig. 1. It can be observed that all the samples are dominated by the peaks appearing around 10° , 20° , 35° , 39° , 45° , 60° , and 61° , attributed to the (003), (006), (012), (015), (018), (110), and (113) planes, respectively, which are typical diffraction patterns of LDH materials.¹⁸ Moreover, it is significant to observe that the diffraction intensities of all the planes gradually decreased with the rise in the iron content. As is known, the diffraction intensities of the planes are contributed by the brucite-like layer and the anion interlayer. However, the LDH materials in this study have the same anion layer. Thus, the lower diffraction intensity gradually observed results from the higher atomic scattering factor with the rise in the iron content.^{19,20} Hence, it indicates that the iron species are successfully incorporated into the LDH brucite-like layer. On the other hand, the (110) plane can be used to determine the lattice parameter a , corresponding to the average cation–cation distance in a brucite layer. The (003) and (006) planes can be used to calculate the parameter c , which is related to the total thickness of the brucite-like layer and the interlayer distance.^{21,22} The detailed information is

collected in Table 1. The parameter a gradually increases with the rise in the iron content. This can be explained by the fact that the ionic radius of Fe^{3+} ($0.65 \text{ \AA}$) is larger than Al^{3+} ($0.53 \text{ \AA}$).²³ Thus, it also indicates that Fe^{3+} has successfully replaced the Al^{3+} ion in the brucite-like layers. Moreover, the decrease in the parameter c with the increase in the iron content can be attributed to the modified electrostatic interactions between the brucite-like layer and the interlayer when another metal is introduced into the LDH layer structure.²⁴ Furthermore, the highly defined peak for the (110) plane reveals quite good dispersion of the metal ions in the hydroxide layers.¹⁸

The thermal behaviors of the LDH materials during heating in air are illustrated in Fig. S1.† Three highly differentiated weight loss steps are recorded in all the cases, which are the typical characteristics of LDH materials.²⁵ The first step which occurred at $100\text{--}300^\circ\text{C}$ can be ascribed to the removal of the interlayer water molecules.²⁶ The second step which occurred at $300\text{--}500^\circ\text{C}$ is probably associated with the dehydroxylation of the layers.²⁷ Finally, the slight weight loss recorded above 500°C is ascribed to the crystallization of the new phases.²⁶ Thus, the thermal analysis indicates that the thermally stable phases are formed at *ca.* 550°C (after the second weight loss and the collapse of the layer structures). Additionally, the total weight loss decreases with the increase in the iron content, assigned to the more iron oxides formed with the rise in the iron content.

The nitrogen adsorption–desorption isotherms and the BJH pore size distribution calculated from the desorption branch of all the samples (calcined catalyst) are displayed in Fig. S2.† and the textural properties are also listed in Table 1. The catalysts exhibit type IV isotherms with clear hysteresis loops, a typical characteristic of mesoporous materials.²⁸ Simultaneously, the step of the hysteresis loops firstly shifted towards a relatively lower pressure with the rise in the iron content to 0.4. It implies that the pore diameter firstly decreased with the addition of the iron species.²⁹ Moreover, when the iron content is increased to 0.6 and 0.8, the hysteresis loops gradually shifted towards a relatively higher pressure, indicating that the pore diameter increased with the further incorporation of the iron species. It also can be

Fig. 1 XRD patterns of $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}$ LDH.

Table 1 Textural properties of the $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{O}$ catalysts

Sample	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	V_p^b ($\text{cm}^3 \text{g}^{-1}$)	D_p^c (nm)	Lattice parameter of LDH precursor	
				a	c
Mg_2AlO	172.35	0.31	6.30	—	—
$\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O}$	197.37	0.29	5.20	3.04	24.62
$\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$	176.54	0.26	5.19	3.05	24.49
$\text{Mg}_2\text{Al}_{0.4}\text{Fe}_{0.6}\text{O}$	93.80	0.23	6.97	3.07	24.33
$\text{Mg}_2\text{Al}_{0.2}\text{Fe}_{0.8}\text{O}$	123.72	0.31	6.99	3.09	24.17

^a BET specific surface area calculated at $P/P_0 = 0.05\text{--}0.25$. ^b Total pore volume estimated at $P/P_0 = 0.99$. ^c BJH pore diameter calculated from the desorption branch.

observed in Table 1 that the $\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O}$ and $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalysts present similar specific surface areas and pore structures. However, the specific surface areas and pore diameters decrease and increase with the further rise in the iron content to 0.6 and 0.8, respectively. It demonstrated that a larger particle was formed with the rise in the iron content to 0.6 and 0.8.

3.2 Catalytic performance of the $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{O}$ catalysts

3.2.1 Effect of reaction temperature. Fig. 2 demonstrates the effect of reaction temperature on the catalytic performance of the $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{O}$ catalysts for H_2S selective catalytic oxidation. As shown in Fig. 2(A), the H_2S conversion initially increased with the rise in temperature, up to 180 °C, and then remained almost constant when the temperature was increased further to 200 °C. The variation trend of H_2S conversion with respect to the iron content was different when the reaction temperature was below or exceeded 160 °C. Apparently, the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalyst showed the best H_2S conversion when the temperature was below 160 °C. However, all the catalysts showed almost the same H_2S conversion when the temperature exceeded 160 °C, with the $\text{Mg}_2\text{Al}_{0.4}\text{Fe}_{0.6}\text{O}$ catalyst showing a slightly higher H_2S conversion.

Fig. 2(B) shows the relationship between sulfur selectivity and reaction temperature. It can be seen that the sulfur selectivity was constant, at 100%, for all the catalysts when the temperature was ≤ 140 °C, and then, sulfur selectivity decreased gradually with the increase in the reaction temperature and the iron content. Sulfur selectivity decreased in the order: $\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O} > \text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O} > \text{Mg}_2\text{Al}_{0.4}\text{Fe}_{0.6}\text{O} > \text{Mg}_2\text{Al}_{0.2}\text{Fe}_{0.8}\text{O}$ when the temperature exceeded 140 °C. Nevertheless, sulfur selectivity was still $>90\%$ for all the catalysts.

Fig. 2(C) presents the influence of reaction temperature on sulfur yield. The figure shows a unique variation trend with respect to the rise in the reaction temperature and iron content, because of the distinctly different variation trends of H_2S conversion and sulfur selectivity. The sulfur yield first increased with the increase in the temperature, and then decreased with further increase in the temperature to 200 °C. The $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalyst showed the highest sulfur yield at 160 °C, as high as 97%. Thus, compared to the other metal oxide catalysts,^{5,28,30–32} the reaction temperature was effectively decreased, and the catalytic activity significantly improved.

3.2.2 Effect of GHSV. The effect of GHSV on catalytic performance was evaluated with the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalyst at 160 °C (the GHSV was gradually increased from 5000–35 000 h^{-1} by raising the mixed gas flow. Each specific point was kept for 20 min. The catalyst was purged with N_2 for 20 min before the GHSV was adjusted to the next point). As shown in Fig. 3, the sulfur selectivity was constant, at 100%, in the GHSV range of 5000–35 000 h^{-1} . However, 100% H_2S conversion can be attained even the GHSV was as high as 20 000 h^{-1} , which is better than the vanadium-containing LDH-derived oxide catalysts.³³ Subsequently, it decreased with a further rise in the GHSV, although the H_2S conversion and

Fig. 2 Effect of temperature on (A) conversion of H_2S , (B) sulfur selectivity and (C) sulfur yield for $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{O}$ catalysts.

sulfur yield were still higher than 90%. Most metal oxides present their highest catalytic activities in the GHSV range of 3000–10 000 h^{-1} .^{4,5,11,29} Here, the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalysts exhibited excellent catalytic activities at a higher GHSV.

Fig. 3 Effect of GHSV on catalytic performance for the Mg₂Al_{0.6}Fe_{0.4}O catalyst at 160 °C.

3.2.3 Durability of the Mg₂Al_xFe_{1-x}O catalysts. Fig. 4 shows the durability behavior of the Mg₂Al_{0.6}Fe_{0.4}O catalyst at 160 °C with a reactant composition of H₂S/O₂/N₂ = 5/2.5/92.5 at GHSV = 24 000 h⁻¹. It can be observed clearly that the sulfur selectivity was constant at 100% after 20 h of reaction. However, the H₂S conversion and sulfur yield gradually decreased with time, which decreased to 80% after 20 h of reaction. Therefore, the Mg₂Al_{0.6}Fe_{0.4}O catalyst exhibits reasonable durability.

In brief, the Mg₂Al_xFe_{1-x}O catalyst can present high catalytic activity and reasonable durability at a relatively low temperature and high GHSV. However, there are still several crucial issues that need to be explored in detail in order to further apply the catalyst in practice, such as, why does the Mg₂Al_{0.6}Fe_{0.4}O catalyst exhibit the best H₂S conversion below 160 °C? Why does the sulfur selectivity decrease with the rise in the temperature and iron content? Hence, it is essential to investigate the existence form of the iron active phase and

Fig. 4 Time-on-stream behavior of the Mg₂Al_{0.6}Fe_{0.4}O catalyst for H₂S selective oxidation at 160 °C.

the catalytic and deactivation mechanisms of the reaction in order to clarify the above issues.

3.3 Chemical status of the iron active phase in the Mg₂Al_xFe_{1-x}O catalyst

The nature of the iron species is important to determine the properties of the catalyst as well as the catalytic performance. The XRD patterns of the derived oxides (Fig. 5) apparently show the complete transformation from LDH to the oxide phase. In all the cases, similar features were observed. The patterns were dominated by peaks occurring at about 37°, 45°, and 62°, likely attributable to the diffractions by the (111), (200), and (220) planes, respectively, of the periclase (MgO) structure.^{34–36} However, the peaks shift towards relatively higher angles, compared to pure MgO, which is indicative of the formation of a MgO structure with defects.³⁷ Significantly, a peak which appeared at 10° was observed for the Mg₂Al_{0.2}Fe_{0.8}O catalyst, indicating that the layer-layer structure partially remained. Moreover, no peak corresponding to the iron species was observed. This suggests that the iron species are highly dispersed within the catalyst. Moreover, the surface concentration of Mg, Al, and Fe is collected in Table S1.† It is worth mentioning that a small amount of Cl remained in the catalyst even if calcined at 550 °C for 4 h.

The UV-vis DRS spectra of all the catalysts are shown in Fig. S3.† The curves present remarkable different features with the rise in the iron content. For the Mg₂Al_{0.8}Fe_{0.2}O catalyst, the spectrum was dominated by the peaks that appeared at 300 nm and 480 nm. However, the peak which appeared at 300 nm disappeared with the further rise in the iron content. Simultaneously, a new peak located at 560 nm gradually appeared with the rise in the iron content. According to the literature,^{38,39} the peak at 300 nm can be ascribed to the presence of the isolated Fe³⁺ species. Meanwhile, it is known that both the Fe₃O₄ and Fe₂O₃ species present a wide peak in the region of 400–600 nm. Thus, it can be concluded that the peaks at 480 nm and 560 nm reveal the co-existence of the

Fig. 5 XRD patterns of the Mg₂Al_xFe_{1-x}O catalysts.

Fe_3O_4 and Fe_2O_3 species. Nevertheless, it is difficult to distinguish them. Therefore, the UV spectra illustrate that the partial iron species existed in the form of isolated Fe^{3+} species when the iron content is low. And the iron species existed mainly in the form of the iron oxide species (Fe_3O_4 and Fe_2O_3) with the further rise in the iron content. It can be tentatively concluded that the formation of the different iron species can be attributed to the fact that the iron species in the inner layer of the catalyst cannot react with oxygen sufficiently and uniformly compared to that in the catalyst surface.

The Raman spectra are collected in Fig. S4† to further identify the iron oxides. It can be observed in Fig. S4(A)† that the spectrum is dominated by the peaks at 220 nm, 540 nm and 700 nm for the $\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O}$ catalyst. However, the intensities of the peaks at 220 nm and 700 nm strengthened with the rise in the iron content. Meanwhile, the peak at 540 nm gradually disappeared. Significantly, two new peaks located at 330 nm and 500 nm appeared for the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ and $\text{Mg}_2\text{Al}_{0.4}\text{Fe}_{0.6}\text{O}$ catalysts. Simultaneously, the latter peak shifted to 470 nm for the $\text{Mg}_2\text{Al}_{0.2}\text{Fe}_{0.8}\text{O}$ catalyst. In Fig. S4(B),† the neat spectra are dominated by two peaks which occurred at 1380 nm and 1570 nm for all catalysts except the $\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O}$ catalyst. Moreover, the intensity decreased with the rise in the iron content. On the other hand, only a single peak occurred at 1320 nm for the $\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O}$ catalyst. It is known that^{40–43} the peaks which appeared at 220 nm, 470 nm and 1320 nm can be assigned to the $\alpha\text{-Fe}_2\text{O}_3$ species. The peaks at 330 nm, 500 nm, 700 nm, 1380 nm and 1570 nm are related to the $\gamma\text{-Fe}_2\text{O}_3$ species, while the peak which occurred at 540 nm can be attributed to the Fe_3O_4 species. Therefore, in the case of the $\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O}$, $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ and $\text{Mg}_2\text{Al}_{0.4}\text{Fe}_{0.6}\text{O}$ catalysts, the Raman spectra demonstrate that the iron oxides existed mainly in the form of $\gamma\text{-Fe}_2\text{O}_3$ species, and only a small amount of the oxides exists in the form of the $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 species. However, in the case of the $\text{Mg}_2\text{Al}_{0.2}\text{Fe}_{0.8}\text{O}$ catalyst, the iron oxides mainly existed in the form of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ species.

In order to further investigate the nature of the iron species, the EPR spectra are presented in Fig. 6. The spectra present a rather different signal characteristic with the rise in the iron content. It indicates that different iron species were formed with the rise in the iron content. For the $\text{Mg}_2\text{Al}_{0.8}\text{Fe}_{0.2}\text{O}$ catalyst, an intense signal occurred at $g = 4.3$ and two weak signals which occurred at 2.2 and 2.0 dominate the spectrum. However, for the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ and $\text{Mg}_2\text{Al}_{0.4}\text{Fe}_{0.6}\text{O}$ catalysts, the spectrum consisted of a single intense and a broad signal at $g = 2.2$ and 2.0, respectively, even though a close observation reveals that both consisted of a very weak signal at $g = 4.3$. For the $\text{Mg}_2\text{Al}_{0.2}\text{Fe}_{0.8}\text{O}$ catalyst, the spectrum was dominated by the signal at $g = 2.8$. Meanwhile, an extremely weak signal appeared at $g = 2.0$. On the basis of earlier assignments,⁴⁴ the signal at $g = 4.3$ corresponds to the Fe^{3+} species located in the sites of less distorted octahedral/tetrahedral fields and interacts by

Fig. 6 EPR patterns of the $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{O}$ catalysts.

dipole-dipole and/or super exchange interactions, while the signal at $g = 2.0$ can be assigned to the isolated Fe^{3+} ions located in the octahedrally and/or tetrahedrally coordinated sites with a strong rhombic distortion. The signal at $g = 2.2$ is related to the 3-coordinated species in the framework that are very sensitive to sorbate molecules such as H_2O .⁴⁵ The signal at $g = 2.5\text{--}3$ is ascribed to the ferric ions in mutual magnetic interaction in minute oxide particles that exhibit superparamagnetic or even ferromagnetic behaviors.⁴⁶ Therefore, the EPR spectra illustrate that the content isolated Fe^{3+} species decreases with the rise in the iron content and the iron oxides exhibit rather different features.

3.4 Catalytic and deactivation mechanisms of the $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{O}$ catalyst

3.4.1 Catalytic mechanism. Our previous work revealed that vanadium-containing LDH-based catalysts obey step-wise mechanisms.³³ More importantly, the moderated basic sites ($\text{Mg}\text{--}\text{O}$ band) in the catalyst surface play a key role in the H_2S oxidation process, where H_2S is first adsorbed on the basic sites and then oxidized into elemental sulfur by the vanadium species. Given this process, the basic properties of the $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}\text{O}$ catalysts were also assessed by $\text{CO}_2\text{--TPD}$; the profiles are shown in Fig. 7. It is worth mentioning that the weak basicity increased gradually with the rise in the iron content. However, the moderated basicity initially increased with the rise in the iron content to 0.4, and then it decreased with the further rise in the iron content. Therefore, the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalyst possesses the largest amount of moderated basic sites. It is known that the weak basic sites were due mainly to the --OH group arising from the Al_2O_3 species.⁴⁷ The gradual increase in the amount of weak basic sites can be ascribed to the fact that more Al_2O_3 was formed with the rise in the iron content. However, more Mg species existed in the form of MgO for the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalyst. Therefore, it possesses the largest amount of moderated basic sites.

Fig. 7 CO₂-TPD patterns of the Mg₂Al_xFe_{1-x}O catalysts.

Fig. 8 O₂-TPD patterns of the Mg₂Al_xFe_{1-x}O catalysts.

Based on these analyses and the catalytic performance, the H₂S conversion process can be proposed tentatively and explained reasonably as follows. The active iron phase is not sufficiently active at lower temperature. Therefore, the active iron species linked to the moderated basic sites account for the H₂S selective oxidation. However, the catalytic activity of the Mg₂Al_{0.8}Fe_{0.2}O catalyst was limited by the low content of the iron species, where the H₂S cannot be transformed to elemental sulfur efficiently. Meanwhile, the catalytic activities of the Mg₂Al_{0.4}Fe_{0.6}O and Mg₂Al_{0.2}Fe_{0.8}O catalysts were restricted by the small amount of moderated basic sites. Consequently, the H₂S cannot be adsorbed on the catalyst surface abundantly. Significantly, the Mg₂Al_{0.6}Fe_{0.4}O catalyst presented the highest H₂S conversion below 160 °C due to the appropriate amount of moderated basic sites and the active iron content. Furthermore, the iron species are sufficiently active when the temperature was higher than 160 °C. Thus, the active iron species can transform the adsorbed H₂S to elemental sulfur effectively and immediately. Hence, the catalysts display almost constant H₂S conversion when the temperature was higher than 160 °C.

On the other hand, it is known that the adsorption oxygen vacancy also facilitates the H₂S selective oxidation. Thus, the O₂-TPD profiles are depicted in Fig. 8. The neat spectra were dominated by two peaks, which occurred at 180 °C corresponding to the removal of ordinarily chemically adsorbed oxygen and at 400 °C corresponding to the desorption of oxygen chemically adsorbed on the oxygen vacancies, respectively.³ Furthermore, the intensity of the former peak increased with the rise in the iron content. Meanwhile, the latter peak decreased with the rise in the iron content. It is particularly important to observe that the variation trend of the sulfur selectivity is extraordinarily consistent with that of the chemically adsorbed oxygen on the oxygen vacancies. Besides, the O-XPS spectra of the fresh and used (reaction for 20 h) Mg₂Al_{0.6}Fe_{0.4}O catalysts are collected in Fig. S5.† The spectra were dominated by the peak at 531.5 eV, which is

attributed to the chemically adsorbed oxygen on the oxygen vacancies.^{48,49} Simultaneously, a small shoulder peak appeared at 529.6 eV, which is assigned to the lattice oxygen. Apparently, the peaks related to the chemically adsorbed oxygen on the oxygen vacancies decreased sharply after 20 h of reaction. Therefore, the above analysis strongly suggests that the chemically adsorbed oxygen on the oxygen vacancies participates in the H₂S selective oxidation reaction and plays a key role in the H₂S selective oxidation into elemental sulfur. According to the literature,⁵⁰ the chemically adsorbed oxygen can react with the dissociatively adsorbed H₂S to yield elemental sulfur and water. And then, partial elemental sulfur can react with molecular oxygen to produce SO₂, which leads to the decrease in sulfur selectivity.

3.4.2 Deactivation mechanism. In order to further develop the catalyst catalytic activity and durability, it is necessary to clarify the catalyst deactivation mechanism. The Fe-XPS spectra of the fresh and used (reaction for 20 h) Mg₂Al_{0.6}Fe_{0.4}O catalysts are presented in Fig. 9. The spectrum of the fresh and used catalysts is almost the same. It reveals the spin-orbit splitting of the Fe 2p_{3/2} ground state at 711.9 eV and the Fe 2p_{1/2} excited state at 725.4 eV. The peak position and energy difference between Fe 2p_{3/2} and Fe 2p_{1/2} (13.5 eV) are typical of the Fe³⁺ state in an oxidic environment.² However, no peaks corresponding to the Fe²⁺ species were observed due to the small content of Fe²⁺. It means that no more Fe²⁺ species were formed during the reaction. It is also evidenced by the Raman and EPR spectra of the used catalyst exhibited in Fig. S6 and S7.† It reveals that the isolated Fe³⁺ species were retained and the iron oxides (α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄) were highly crystallized. Meanwhile, more information is supplied by the FTIR spectra (Fig. S8.†). It is particularly important to observe that a new intense and sharp peak appeared at 1190 cm⁻¹ for the used catalyst compared to the fresh catalyst, which is related to the existence of the sulfate species.³³ Thus, it indicates that some sulfate species were formed during the reaction. Furthermore, the S-XPS spectrum

Fig. 9 Fe-XPS patterns of the $\text{Mg}_2\text{Al}_{0.6}\text{Fe}_{0.4}\text{O}$ catalysts.

of the used catalyst is displayed in Fig. S9†. Two peaks around 164 eV and 169 eV were detected, which can be ascribed to the presence of the sulfate species and S_n , respectively.³³ Thus, it implies the formation of $\text{Fe}_2(\text{SO}_4)_3$ species and the deposit of elemental sulfur. Moreover, the spectrum was dominated by the peak attributed to elemental sulfur. Hence, the catalyst deactivation is mainly due to the deposit of elemental sulfur. And the small amount of the formed less active $\text{Fe}_2(\text{SO}_4)_3$ species also led to catalyst deactivation. Simultaneously, the calculation of sulfur selectivity should be reconsidered due to the presence of the sulfate species. However, the surface accumulated sulfur content is rather lower even after 20 h of reaction (the sulfur content is 1.3 wt% and the sulfate content is 0.2 wt% according to the XPS analysis and area percentage). Therefore, the formation of the sulfate species can be ignored in the calculation of sulfur selectivity with time.

Based on the above analysis, the main difference between vanadium-containing catalysts and iron-containing catalysts is the deactivation mechanism. As is known, the main reason for the deactivation of vanadium contained in a brucite-like layer catalyst is the loss of moderated basic sites due to the damage of the MgO structure by the VO^{2+} species.³³ Therefore, H_2S cannot be adsorbed on the catalyst surface sufficiently. However, when the vanadium species were exchanged into the anion layer, the moderated basic sites were retained, and the formed VOSO_4 species was favorable for the redox of the V^{5+} species.⁵¹ And the catalyst durability was improved significantly. However, for the iron-containing catalysts, the catalyst deactivation was due mainly to the deposit of elemental sulfur, which caused the decrease in the amount of active sites.

4. Conclusions

A series of $\text{Mg}_2\text{Al}_x\text{Fe}_{1-x}$ LDH compounds was synthesized by a one-step method, and the derived oxides were tested for

H_2S selective oxidation. It was observed that the iron species existed mainly in the form of isolated Fe^{3+} species, $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . Moreover, the nature of the iron oxides was varied with the rise in the iron content. Significantly, the catalysts exhibited high catalytic activity and reasonable durability at a relatively low temperature and high GHSV. The catalyst obeyed a step-wise mechanism for H_2S selective catalytic oxidation. And the chemically adsorbed oxygen on the oxygen vacancies participated in the H_2S selective oxidation reaction and played a key role in the H_2S selective oxidation into elemental sulfur. The catalyst deactivation was mainly due to the deposit of elemental sulfur. Additionally, the small amount of the formed less active $\text{Fe}_2(\text{SO}_4)_3$ species also led to catalyst deactivation.

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