

High resistance SO₂ adsorbent of Fe-Ce-La oxides @ Si-Al carrier for arsenic capture from middle-low-temperature flue gas

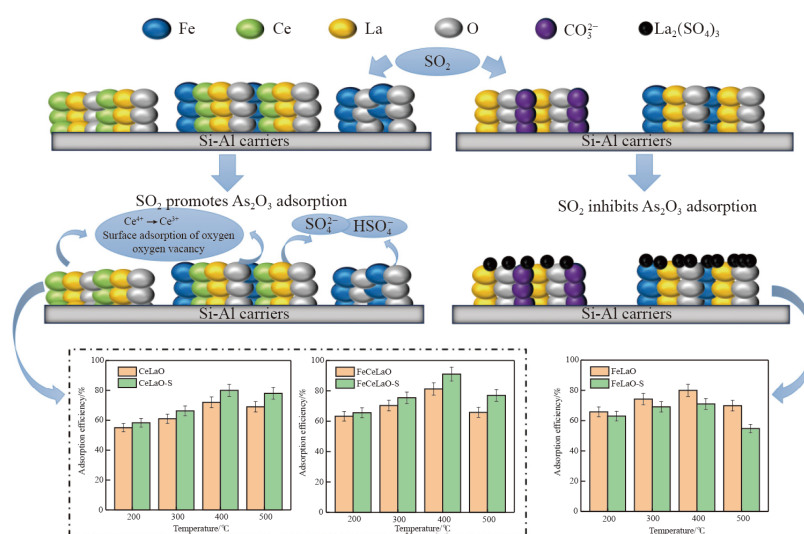
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Abstract: It is crucial to develop arsenic removal adsorbents with strong sulfur resistance under middle-low-temperature flue gas conditions (<400 °C). In this work, five Fe-Ce-La oxides were prepared by co-precipitation method, and FeCeLaO/SiO₂-Al₂O₃ composite adsorbents were prepared by coupling fly ash-based Si-Al carriers. The active components Fe-Ce-La oxides and Si-Al carriers were characterized by TPD, TG, XRF, BET and XPS, respectively. The effects of temperature, Si/Al ratio and FeCeLaO loading rate on the sulfur

resistance were investigated. Results show that the SO₂ promotes the arsenic removal of Fe₂O₃, CeLaO and FeCeLaO. At 400 °C, the arsenic removal efficiencies of the three oxides increase from 45.3%, 72.5% and 81.3% without SO₂ to 62.6%, 80.5% and 91.0%, respectively. The SO₂ inhibits the arsenic removal of La₂O₂CO₃ and FeLaO, and the inhibition effect is pronounced at high temperatures. The sulfur poisoning resistance of Si-Al carriers increases with the increase of Si/Al ratio. When the Si/Al ratio is increased to 9.74, the arsenic removal efficiency in the SO₂ environment is 13.9% higher than that in the absence of SO₂. Introducing FeCeLaO active components is beneficial for enhancing the SO₂ poisoning resistance of Si-Al carriers. The strong sulfur resistance of the FeCeLaO/SiO₂-Al₂O₃ composite adsorbent results from multiple factors: protective effects of Ce on Fe, La and Al; sulfation-induced generation of Ce³⁺ and surface-adsorbed oxygen; and strong surface acidity of SiO₂.

Key words: arsenic removal; sulfur resistance; flue gas; Fe-Ce-La oxides; fly ash



China is the world's largest coal producer and consumer. Conventional pollutants such as NO_x, SO_x and particulate matter generated by coal combustion, as well as heavy metal pollutants such as As, Se, Pb and Hg, seriously harm human health and natural environment^[1-2]. Arsenic, as a heavy metal pollutant, is now attracting more and more attention due to its strong volatility, bio-accumulation in ecosystems, carcinogenicity and teratogenicity to

humans^[3-4]. It can also cause arsenic poisoning in selective catalytic reduction (SCR) catalyst of coal-fired power plants, which is reported to be one of the most common causes of SCR catalysts deactivation^[5]. Therefore, it is urgent to strengthen the control of arsenic pollution from coal combustion process. Especially in recent years, the "dual-carbon" goal requires coal-fired power units with high carbon emissions to operate at medium-to-low loads or

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perform deep peak-shaving^[6-7], which results in a significant decrease in the tail flue gas temperature. For example, the denitrification device's inlet temperature will drop below 300 °C. Therefore, it is significantly important to develop arsenic pollution control technology under middle-low-temperature flue gas conditions (<400 °C).

Adsorption is currently a mature method for arsenic removal from flue gas^[8-10]. To reduce arsenic poisoning of SCR catalysts, arsenic removal adsorbents are generally added to the flue before the denitrification unit. In this case, the adsorbent can be easily deactivated or its service life can be reduced due to poisoning by high concentration of SO_2 and other substances in the flue gas. Therefore, developing sulfur resistant adsorbents for arsenic removal from middle-low-temperature flue gas is exceedingly desired.

In previous work, the authors developed Fe-rare earth composite oxide adsorbents, including FeLaO, CeLaO and FeCeLaO^[11], which can efficiently remove arsenic from middle-low-temperature flue gas (<400 °C) and can meet the current needs of low load operation or deep peak shaving of coal-fired power units. Especially for the FeCeLaO, the total adsorbed arsenic reaches 583.7 µg/g at 400 °C, and the arsenic removal efficiency is as high as 89%. Therefore, this work uses Fe-Ce-La oxides as the active component and further couples it with a sulfur resistant carrier to prepare a composite adsorbent, aiming to achieve both low-temperature arsenic removal and high-efficiency sulfur resistance in coal-fired flue gas.

Up to date, only a few studies on the sulfur resistance of arsenic removal adsorbents have been reported. Hu et al.^[12] used the DFT method to study the effect of the SO_2 on the adsorption of As_2O_3 on $\gamma\text{-Al}_2\text{O}_3$ by calculating the adsorption structure, adsorption energy, electron transfer and other characteristics. They found that the SO_2 mainly changed the electron distribution around O atom of the first layer of $\gamma\text{-Al}_2\text{O}_3$ and caused almost all previous As_2O_3 adsorption structures on $\gamma\text{-Al}_2\text{O}_3$ surface to become or stay in chemisorption. Therefore, the SO_2 generally favors the adsorption of As_2O_3 on the $\gamma\text{-Al}_2\text{O}_3$ surface. Li et al.^[13] concluded that the SO_2 has no significant effect on arsenic adsorption on the CaO. Firstly, the reaction rate constant between CaO and gaseous arsenic was greater than that between CaO and SO_2 . These indicate that in the initial stage, the SO_2 cannot compete with As_2O_3 for active sites on the CaO surface. Secondly, they demonstrated that calcium sulfate also can adsorb gaseous arsenic. Therefore, even if the CaO surface was fully sulfated, it still had a certain adsorption capacity for gaseous arsenic. However, Chen et al.^[14] showed that the SO_2 inhibited the adsorption process of arsenic on CaO between 300 and 800 °C. This is attributed to the fact that the generated $\text{CaSO}_3/\text{CaSO}_4$ occupies the free surface available for arsenic capture, and reduces the arsenic capture ability of the CaO. Zhao et al.^[15] investigated the effect of the SO_2 on the removal of As_2O_3 by $\text{Fe}_3\text{Mn}_x\text{O}_y$. Results showed that the SO_2 occupied the active sites for As_2O_3 adsorption, consumed lattice oxygen in the adsorbent, and converted it into SO_4^{2-} , thus inhibiting

the adsorbent's ability to remove As_2O_3 . These previous studies have well illustrated sulfur resistance in common metal oxide adsorbents for arsenic removal. However, the sulfur resistance and synergistic mechanisms of multi-metal oxide composite adsorbents require further investigation.

Fly ash is a by-product of coal-fired power plants. After alkali fusion^[16], acid washing^[17] and other modification, the silica-alumina glass with high degree of polymerization, quartz, and mullite are depolymerized or destroyed^[18]. The SiO_2 and Al_2O_3 are dissolved in the amorphous matters^[19]. After drying and calcination, the active Si-Al carrier can be obtained, which has the advantages of porosity, large specific surface area and high thermal stability^[20]. Compared with some common carriers such as activated carbon and TiO_2 , it has strong surface acidity and can inhibit the adsorption of acid SO_2 in flue gas. Therefore, it may have good SO_2 poisoning resistance.

In this work, a series of Fe-Ce-La oxides were prepared by co-precipitation method, and active Si-Al carriers were obtained by modifying fly ash. Then the FeCeLaO/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ composite adsorbents were prepared. To investigate the effects of Fe, Ce, La and Si/Al ratio on surface properties, the Fe-Ce-La oxides and carriers were characterized using temperature programmed desorption (TPD), thermogravimetry (TG), X-ray fluorescence spectroscopy (XRF), specific surface area analysis (BET), and X-ray photoelectron spectroscopy (XPS). The effects of temperature, SO_2 concentration and Si/Al ratio on the arsenic adsorption performance and sulfur poisoning resistance were also investigated in depth.

1 Experimental procedures and methods

1.1 Preparation of Fe-Ce-La oxides

Five adsorbents, pure Fe_2O_3 , pure $\text{La}_2\text{O}_2\text{CO}_3$, FeLaO, CeLaO and FeCeLaO, were prepared by co-precipitation method.

1.1.1 Preparation of precursor solution

0.1 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water, respectively, and then polyethylene glycol with a mass ratio of 1:1 to the theoretical yield of the product Fe_2O_3 or $\text{La}_2\text{O}_2\text{CO}_3$ was added to obtain pure Fe_2O_3 and $\text{La}_2\text{O}_2\text{CO}_3$ precursor solutions.

0.05 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water, and then 0.05 mol H_2O_2 was added. The mixed solution was stirred for 30 min. Polyethylene glycol with the theoretical yield/mass ratio of the product 1:1 was added. After stirring and dissolving, 0.05 mol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to obtain the precursor solution of CeLaO. 0.1 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.05 mol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to obtain the precursor solution of FeCeLaO.

0.05 mol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized

water. Polyethylene glycol with a mass ratio of 1:1 to the theoretical yield of the product was mixed. 0.05 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added after stirring and dissolving to obtain a precursor solution of FeLaO .

1.1.2 Preparation of Fe-Ce-La oxides by co-precipitation method

The molar ratio of $(\text{NH}_4)_2\text{CO}_3$ to ammonia was ensured to be 1:1, and diluted with deionized water to prepare a mixed alkaline precipitant with an ammonia concentration of 10%. Then it was added drop by drop to the above five precursor solutions until the pH value was 9.5. Aging at room temperature for 24 h, centrifugal separation, the filter cake was washed sufficiently with deionized water until the pH of the cleaning solution was neutral, after which it was dried at 105 °C. The dried powder was calcined at 500 °C for 5 h, and then was ground for further use.

1.2 Preparation of Si-Al carrier by fly ash activation

A certain amount of fly ash was taken. The particles of equal mass of NaOH or Na_2CO_3 were added and then ground thoroughly (among which samples 1#–5# were NaOH particles and sample 6# was Na_2CO_3 particle). The samples were roasted in muffle furnace at 800 °C for 2 h, and were cooled to room temperature.

A hydrochloric acid solution with a volume concentration of 11% was prepared. Its amount was determined based on the molar ratios of $n(\text{HCl})/n(\text{NaOH})$ at 1:2, 1:1, 3:2 and 3:1, respectively, to perform acid washing for alkali-fused ash. The reaction was conducted at 60 °C with stirring for 80 min. After 10 h settling, the cake was filtered and washed until the supernatant reached neutral pH. The filter cake was dried at 105 °C for 10 h, grounded and labeled as samples 1#–4#.

In order to obtain the Si-Al carrier with great difference in Si/Al ratio, 30% and 60% hydrochloric acid solutions were further prepared. The dosage of hydrochloric acid solution was determined according to the ratio of $n(\text{HCl})/n(\text{NaOH or Na}_2\text{CO}_3)$ as 2:1 and 4:1, respectively. Then the above steps were repeated to obtain 5#–6# samples.

1.3 Preparation of $\text{FeCeLaO}/\text{SiO}_2\text{-Al}_2\text{O}_3$ composite adsorbents

Using the 3# Si-Al carrier with a Si/Al ratio of 1.85 as an example, composite adsorbents with different loading ratios (active component/carrier) were prepared. 25, 10, 5, 2.5 and 1.7 g of the 3# Si-Al sample were weighed and separately added to the FeCeLaO precursor solution. The alkaline precipitant was then added dropwise until pH value = 9.0–10.0. The steps described in Section 1.1 were subsequently repeated to obtain composite adsorbent

samples with loading ratios of 1:5, 1:2, 1:1, 2:1 and 3:1, respectively.

1.4 Adsorbents characterization

The chemical composition of the active Si-Al carrier was determined by X-ray fluorescence spectrometer (XRF, BRUKER PUMA Series 2, Germany), and its Si/Al ratio was calculated.

The specific surface area of the activated Si-Al carriers was determined using a Micromeritics ASAP 2020 analyzer. The samples were degassed at 300 °C for 1 h before testing in order to remove impurities from the pores. Specific surface area information was obtained from the measured N_2 adsorption isotherms and Brunauer-Emmett-Teller (BET) results.

SO_2 -TPD analysis was performed on the Fe-Ce-La oxides and Si-Al carriers using a chemical adsorption analyzer (ChemBET Pulsar TPD/TPR, Quantachrome, USA). The sample was first heated to 400 °C under high-purity N_2 purge and held for 20 min, then exposed to a gas stream containing 2.0×10^{-3} SO_2 and 5% O_2 at 400 °C for 2.5 h to achieve saturation adsorption. Subsequently, the sample was purged with high-purity N_2 for about 40 min until the SO_2 signal disappeared in order to remove reversibly adsorbed SO_2 gas, and then cooled to 50 °C; Finally, temperature-programmed desorption (TPD) was conducted by heating the sample from 50 to 1000 °C at a rate of 10 °C/min, and the data was recorded simultaneously to obtain the TPD curve.

Thermogravimetric (TG) analysis was performed in N_2 atmosphere using Netzsch STA 449 F3 analyzer (Germany), with a nitrogen flow rate of 60 mL/min. The heating rate was 10 °C/min and the sample was heated up to 1200 °C until it no longer lost weight to obtain a TG-DTG curve. The surface atomic states of the adsorbents were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALab 250 Xi, Thermo Fisher, USA) with Al $K\alpha$ radiation ($h\nu=1486.6$ eV). The binding energies were calibrated using the C 1s peak at 284.6 eV as a reference.

1.5 Experimental device and method of SO_2 resistance

The experimental setup for evaluating the sulfur poisoning resistance of the adsorbent during arsenic removal from flue gas was shown in Figure 1. It consists of four parts: a simulated flue gas supply unit, an arsenic source generation unit, an anti- SO_2 poisoning reaction unit, and an exhaust gas treatment unit. The simulated flue gas supply unit provided a mixture of N_2 , O_2 and SO_2 . The total gas flow rate was maintained at 200 mL/min. The arsenic source generator and adsorbent fixed bed were integrated into the same quartz tube reactor. This reactor was installed inside two small electric furnaces which could be heated separately.

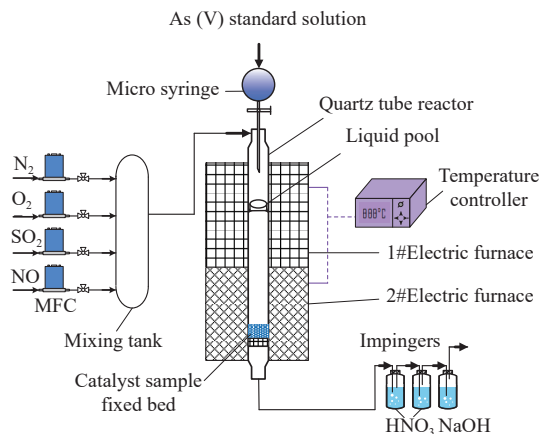


Fig. 1 The schematic of the fixed bed reaction system

The arsenic source was obtained through the vaporization and decomposition of the $\text{As}_2\text{O}_5/\text{H}_2\text{O}$ standard solution (Inorganic Ventures, USA, As (V) concentration $999 \pm 5 \mu\text{g/mL}$). It was evenly dropped into the small liquid pool through a micro-syringe and then heated to 400°C . It is reported that As_2O_5 can lose O and convert to As_2O_3 because of instability near 300°C ^[21], so heating at 400°C in this study will completely produce As_2O_3 gas. The As_2O_3 vapor was carried by the simulated flue gas through the fixed adsorbent bed located at the bottom of the reactor. Different reaction temperatures could be achieved by adjusting the temperature of the 2# furnace. The simulated flue after adsorption reaction enters the tail gas treatment unit, the escaped arsenic and SO_2 were captured in impingers containing HNO_3 (0.5 mol/L) and NaOH (0.5 mol/L), respectively.

Detailed experimental methods for resistance to sulfur poisoning are as follows:

Firstly, the Fe-Ce-La oxides, activated Si-Al carriers and composite adsorbents were pre-sulfurized so that sulfur poisoning occurred sufficiently in advance. The pre-sulfurization conditions were as follows: the adsorbent dosage was 0.3 g, which was placed in the quartz tube adsorption bed. The quartz tube was put into an electric furnace. The carrier gas composition, flow rate and temperature were adjusted for pre-sulfurization to match the corresponding anti- SO_2 poisoning experimental conditions. After the gas path and temperature stabilized, the pre-sulfurization treatment commenced and lasted for 1.5 h.

Secondly, the $\text{As}_2\text{O}_3(\text{g})$ removal performance of fresh and sulfur poisoned adsorbents was compared. The flow rates of SO_2 , O_2 and N_2 were each adjusted to obtain different component concentrations and the total flow rate was kept at 200 mL/min. Then the furnace 1 was set to 400°C and the furnace 2 was set to the different target temperatures. approximately 0.3 g of fresh or sulfur poisoned adsorbent was uniformly placed on the quartz tube bed, and all pipes were connected. After gas flow stabilization, the arsenic source was added dropwise to initiate the reaction. The dosage of arsenic source was 0.4 mL and the reaction time was 90 min.

In order to reduce the experimental error, the above

experiments were repeated more than three times under the same conditions.

1.6 Arsenic analysis method

Total arsenic contents of the samples were determined using hydrochloric acid digestion and hydride generation atomic fluorescence spectrometry. The specific procedure was as follows: 0.1 g of sample was digested in 100 mL of 10% hydrochloric acid at 80°C for 12 h. The total arsenic content in the resulting solution was then measured by AFS-933 Hydride Generation Atomic Fluorescence Spectrometer (Beijing Jitian Instrument Co, Ltd).

The total arsenic removal efficiency (η) was defined as follows:

$$\eta = \frac{As_{\text{ad}}}{[As_0(1-\alpha)]} \times 100\% \quad (1)$$

where As_{ad} is the total arsenic content in the adsorbent, μg ; As_0 is the total amount of added arsenic, μg ; α is the ratio of the sum of arsenic adhered to the reactor wall and non-volatilized arsenic to the total arsenic input, %.

2 Results and discussion

2.1 XRF and BET analysis

The composition of Si-Al carriers obtained from fly ash activation is shown in Table 1. The total contents of SiO_2 and Al_2O_3 in the raw ash are approximately 85.51%, and the Si/Al ratio is 1.43. With the increase of acid concentration and $n(\text{HCl})/n(\text{NaOH}$ or $\text{Na}_2\text{CO}_3)$ molar ratio during the activation treatment, the Al_2O_3 content is gradually reduced, the Si/Al ratio is significantly increased, and the concentration of impurities such as SO_3 is significantly reduced. When the hydrochloric acid concentration is 60% and the $n(\text{HCl})/n(\text{Na}_2\text{CO}_3)$ molar ratio is 4:1, the Si/Al ratio of the obtained 6# Si-Al carrier is 9.74, which is approximately 7 times the Si/Al ratio of the original ash, and the sum of the impurity contents such as SO_3 is only 2.83%. These indicate that high-concentration acid washing significantly enhances the Si/Al ratio while effectively removing most impurities from fly ash, including Fe and Ca components that possess adsorption activity toward As_2O_3 . The increase of Si/Al ratio is favorable to enhance the surface acidity, thereby inhibiting competitive SO_2 adsorption in flue gas and reducing pore blockage induced by sulfate precipitation. These combined effects potentially enhance the adsorbent's sulfur poisoning resistance.

Table 2 shows the variation of specific surface area of raw fly ash and activated Si-Al carrier. As the concentration and dosage of acid increase during the acid-washing process, the specific surface area of the Si-Al carriers significantly increases. Among them, the 6# Si-Al carrier exhibits the largest specific surface area, reaching $568.04 \text{ m}^2/\text{g}$. This fully meets the requirements for use as an adsorbent or carrier to enhance adsorption capacity.

Table 1 Mineral composition of Si-Al carriers under different activation conditions

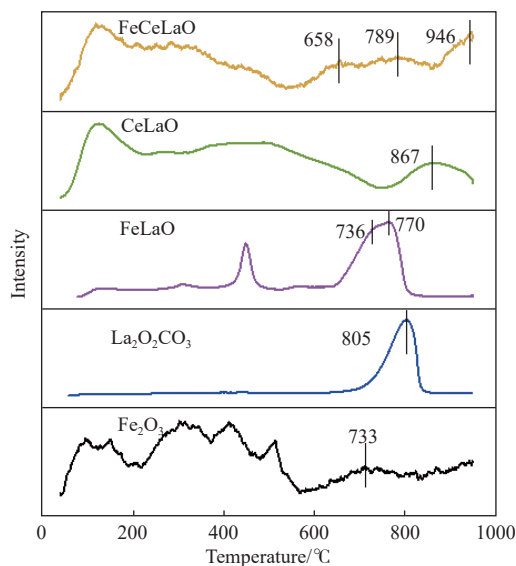
Chemical composition	w/%						
	raw ash	1# sample	2# sample	3# sample	4# sample	5# sample	6# sample
SiO ₂	50.35	52.96	54.73	55.13	55.96	60.84	87.45
Al ₂ O ₃	35.16	31.02	30.07	29.98	22.55	21.96	8.98
Fe ₂ O ₃	5.25	7.64	6.17	6.08	4.48	4.77	0.07
CaO	3.83	3.45	3.16	3.12	1.20	1.19	0.67
SO ₃	1.66	1.17	0.96	0.66	0.59	0.42	0.60
K ₂ O	1.60	1.35	1.22	1.09	0.43	0.34	0.11
TiO ₂	1.52	1.93	1.88	1.74	1.67	1.83	1.15
P ₂ O ₅	0.18	—	0.05	0.72	0.22	0.245	0.08
Other	0.47	0.48	0.56	0.40	0.98	0.33	0.79
Si/Al ratio	1.43	1.71	1.82	1.85	2.48	2.77	9.74

Table 2 BET results of Si-Al carriers under different activation conditions

Sample	Raw ash	3# Si-Al carrier	5# Si-Al carrier	6# Si-Al carrier
Specific surface area /(m ² ·g ⁻¹)	2.16	100.48	286.93	568.04

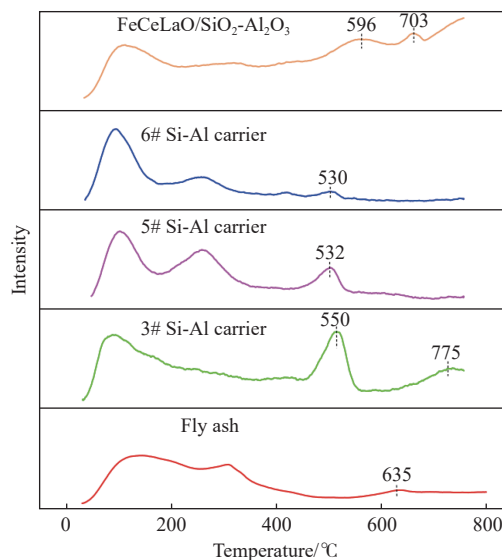
2.2 SO₂-TPD analysis

SO₂-TPD measurements were carried out on oxides FeLaO, CeLaO and FeCeLaO, as well as pure oxides Fe₂O₃, La₂O₂CO₃ as comparison. As is shown in Figure 2, the five adsorbents exhibit different desorption peaks. Desorption peaks between 50–500 °C correspond to SO₂ release from adsorbent surfaces or pores^[22]. FeLaO and pure La₂O₂CO₃ exhibit minimal low-temperature SO₂ adsorption, likely due to their limited specific surface area and poor sulfur affinity^[11]. The 600–800 °C desorption peak for Fe₂O₃ is attributed to iron sulfate decomposition^[23], while La₂O₂CO₃ shows a peak at 805 °C from lanthanum sulfate decomposition. FeLaO displays dual peaks at 736 and 770 °C, which are attributed to the decomposition of lanthanum sulfate or iron sulfate, suggesting that both Fe and La elements in FeLaO may have been sulfated.

Fig. 2 SO₂-TPD curves of the five Fe-Ce-La oxides adsorbents

CeLaO exhibits a characteristic peak at 867 °C assigned to cerium sulfate decomposition. No desorption peak corresponding to lanthanum sulfate is detected, indicating that Ce in CeLaO preferentially reacts with SO₂, thereby protecting La from sulfation. For FeCeLaO, peaks at 658, 789 and 946 °C correspond to decomposition of Fe₂(SO₄)₃, La₂(SO₄)₃ and Ce(SO₄)₂, respectively^[24]. The dominant cerium sulfate peak indicates severe sulfation of Ce, while small iron/lanthanum sulfate peaks suggest mild sulfation of Fe and La. This confirms Ce's protective role in CeLaO and FeCeLaO systems, shielding Fe and La active sites from sulfur poisoning.

SO₂-TPD tests were also carried out on Si-Al carriers and composite adsorbents as shown in Figure 3. Desorption peaks between 50–500 °C belong to the desorption of SO₂. Peaks between 500–600 °C for 3#, 5# and 6# carriers are attributed to iron sulfate decomposition^[25–26].

Fig. 3 SO₂-TPD curves of Si-Al carriers and FeCeLaO/SiO₂-Al₂O₃ composite adsorbent

These peaks diminish with increasing Si/Al ratios due to decreasing Fe content and increasing surface acidity, and thereby weaken sulfation. The 775 °C peak for 3# carrier originates from decomposition of $\text{Al}_2(\text{SO}_4)_3$, while these peaks disappear at high Si/Al ratios. For composite adsorbents, desorption peaks at or above 703 °C stem from decomposition of $\text{Ce}(\text{SO}_4)_2$.

2.3 TG analysis

TG analysis was employed to identify the sulfate species formed on the SO_2 poisoned adsorbents and the variation of sulfation degree with temperature or Si/Al ratio.

Figure 4 shows the weight loss peaks of fresh Fe_2O_3 and pre-sulfurized Fe_2O_3 at different temperatures. Fresh Fe_2O_3 has almost no weight loss peaks, while SO_2 poisoned Fe_2O_3 exhibits three weight loss peaks. The peak below 200 °C is attributed to the evaporation of surface adsorbed water. The peak around 430 °C may be attributed to the decomposition of the hydrogen sulfate. The peak between 500 and 800 °C is ascribed to the decomposition of the iron sulfate^[23,27]. The degree of SO_2 poisoning in Fe_2O_3 initially increases and then decreases with the increasing of the pre-sulfidation temperature. At 300 °C, the mass loss of the iron sulfate reaches 3.17%, indicating the maximum degree of sulfation. As the temperature continues to rise (>300 °C), the degree of sulfur poisoning is weakened. Possible reasons for this are as follows: (1) a weakening of SO_2 adsorption on the Fe_2O_3 surface, and (2) the decomposition of the formed iron sulfate^[28].

Figure 5 shows the weight loss peaks of fresh $\text{La}_2\text{O}_2\text{CO}_3$ and pre-sulfurized $\text{La}_2\text{O}_2\text{CO}_3$ at different temperatures. The weight loss peak between 650 and 800 °C is attributed to the decomposition of $\text{La}_2\text{O}_2\text{CO}_3$ into La_2O_3 and CO_2 . The weight loss peak around 1200 °C is ascribed to the decomposition of $\text{La}_2(\text{SO}_4)_3$ ^[29]. When the pre-sulfidation temperatures are 300, 400 and 500 °C, the mass losses of $\text{La}_2(\text{SO}_4)_3$ decomposition are 2.12%, 3.56%, and 7.04%, respectively. These indicate that the higher the temperature, the more severe the sulfur poisoning of $\text{La}_2\text{O}_2\text{CO}_3$.

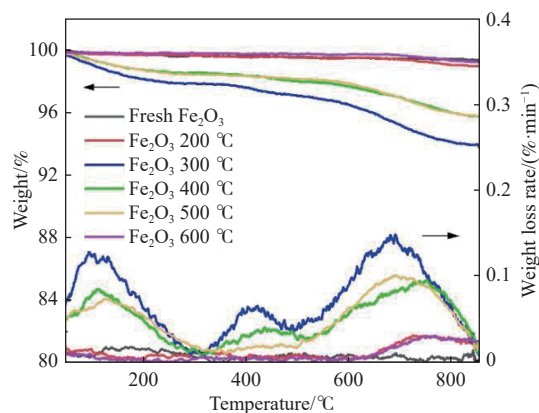


Fig. 4 TG-DTG curves of fresh Fe_2O_3 and sulfur poisoned samples at different temperatures

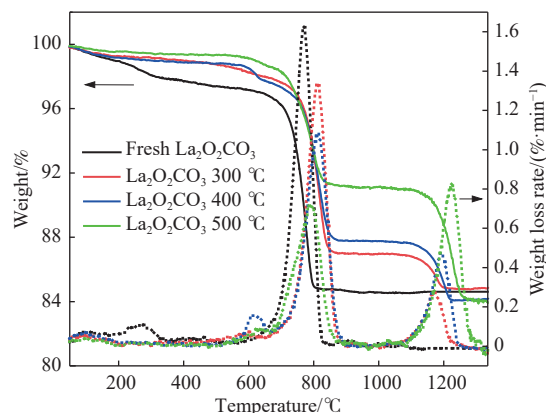


Fig. 5 TG-DTG curves of fresh $\text{La}_2\text{O}_2\text{CO}_3$ and sulfur poisoned samples at different temperatures

Figure 6 shows the TG-DTG curves of FeLaO. The weight loss peak at 460 °C is attributed to the decomposition of LaCO_3OH into $\text{La}_2\text{O}_2\text{CO}_3$, H_2O and CO_2 ^[30]. The weight loss peaks at 600–1000 °C may be due to the decomposition of $\text{La}_2\text{O}_2\text{CO}_3$ or $\text{Fe}_2(\text{SO}_4)_3$, as their decomposition temperatures are similar. The weight loss peak at 1200 °C is attributed to the decomposition of $\text{La}_2(\text{SO}_4)_3$. With increasing presulfidation temperature, the weight loss corresponding to the former peak gradually decreases, while that corresponding to the latter peak gradually increases. The mass loss of $\text{La}_2(\text{SO}_4)_3$ is 3.38%, 4.63% and 9.67% when the temperatures were 300, 400 and 500 °C, respectively. It indicates that the sulfur poisoning of FeLaO becomes more severe overall with increasing temperature.

Figure 7 shows the TG-DTG curves of CeLaO. The weight loss peaks below 200 °C are attributed to the evaporation of adsorbed water. The weight loss peaks around 500–750 °C are caused by the decomposition of LaCO_3OH or $\text{La}_2\text{O}_2\text{CO}_3$. The weight loss peaks around 850 and 1200 °C are ascribed to the decomposition of $\text{Ce}_2(\text{SO}_4)_3$ and $\text{La}_2(\text{SO}_4)_3$, respectively. When the pre-sulfidation temperature are 300, 400 and 500 °C, the mass loss of cerium sulfate increases gradually, with values of 1.91%, 2.11% and 4.98%, respectively. The mass loss of $\text{La}_2(\text{SO}_4)_3$ also gradually increases, with values of 2.96%, 3.51% and 5.05%, respectively.

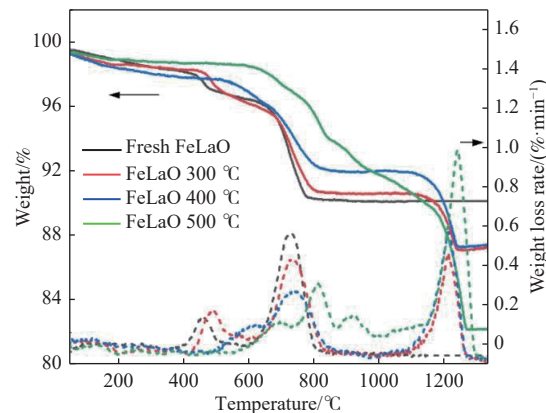


Fig. 6 TG-DTG curves of fresh FeLaO and sulfur poisoned samples at different temperatures

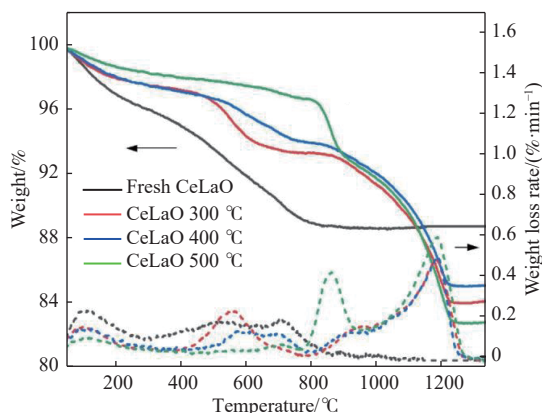


Fig. 7 TG-DTG curves of fresh CeLaO and sulfur poisoned samples at different temperatures

These indicate that both Ce and La undergo sulfation simultaneously. However, compared with FeLaO, the sulfation degree of La in CeLaO is less severe. This is attributed to the presence of Ce, which inhibits the sulfation of La to some extent.

Figure 8 shows the TG-DTG curves of FeCeLaO. Compared with the fresh adsorbent, the sulfur poisoned adsorbents exhibits three weight loss peaks around 800, 920 and 1200 °C, which are attributed to the decomposition of $\text{Ce}(\text{SO}_4)_2$, $\text{Ce}_2(\text{SO}_4)_3$ and $\text{La}_2(\text{SO}_4)_3$, respectively^[31–32]. When the pre-sulfation temperatures are 300, 400 and 500 °C, the mass loss of cerium sulfate increases sequentially, reaching 1.42%, 4.11% and 6.19%, respectively. In contrast, the weight loss of lanthanum sulfate is relatively small, and the weight loss of iron sulfate is almost not observed. These indicate that Ce element preferentially reacts with SO_2 , inhibiting the sulfation of Fe and La components. Therefore, Ce plays a protective role by preventing the active sites of Fe and La from sulfur poisoning.

Figure 9 shows the TG-DTG curves of fresh Si-Al carriers. For all samples with different Si/Al ratios, the weight loss peaks below 200 °C are attributed to the evaporation of surface-adsorbed water and internal bound water.

The weight loss peaks around 1200 °C are attributed to the slow decomposition of residual crystalline phases such as anhydrite.

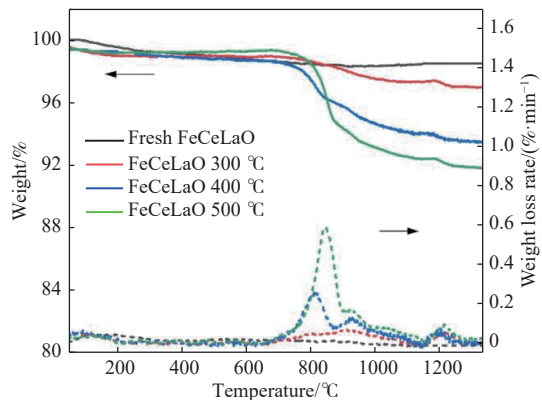


Fig. 8 TG-DTG curves of fresh FeCeLaO and sulfur poisoned samples at different temperatures

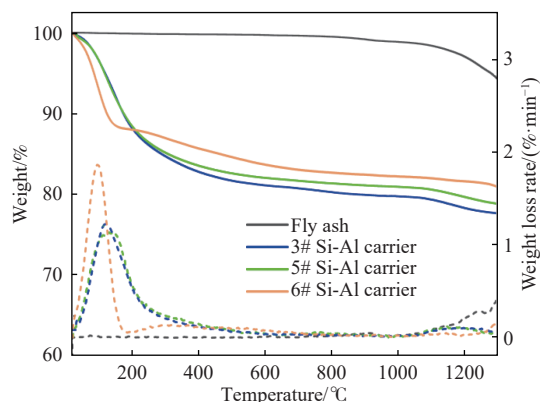


Fig. 9 TG-DTG curves of fresh Si-Al carriers

Figure 10 shows the TG-DTG curves of sulfur poisoned Si-Al carriers. Compared with the fresh samples, the weight loss curve of SO_2 -poisoned raw ash remains basically unchanged, indicating that it is difficult for the raw fly ash to adsorb SO_2 gas or undergo sulfation reaction. For the 3#, 5# and 6# carriers, the weight loss peaks at 500–800 °C are ascribed to the decomposition of iron sulfate. Peaks at around 1000 °C are attributed to the decomposition of CaSO_3 or $\text{Al}_2(\text{SO}_4)_3$. As the Si/Al ratio increases, the weight loss of each carrier gradually decreases. This indicate that the acid washing treatment removes the alkaline metal oxides in the fly ash, leading to increasing surface acidity and reducing sulfation degree.

2.4 XPS analysis

X-ray photoelectron spectroscopy (XPS) was performed to determine the surface element chemical states of the fresh and SO_2 poisoned Fe-Ce-La oxides, and the results were shown in Table 3.

Figure 11 shows the XPS spectra of Fe 2p before and after sulfation of each adsorbent. Two peaks are detected around 710.2 and 723.8 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. The Fe in all three adsorbents is Fe³⁺, and the valence state of Fe remains unchanged before and after sulfur poisoning. The Fe 2p_{3/2} orbital of FeLaO splits into three peaks, with the peaks centered at 710.1 and 712.5 eV are attributed to Fe³⁺.

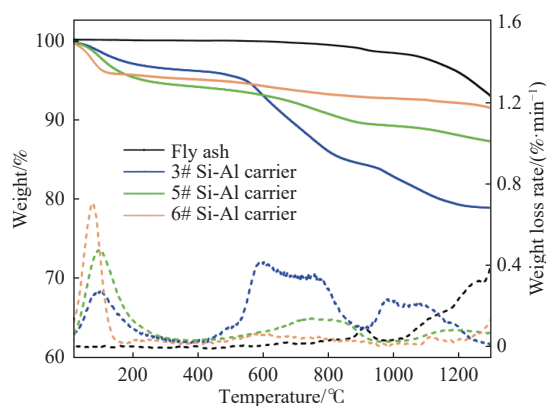


Fig. 10 TG-DTG curves of sulfur poisoned Si-Al carriers

Table 3 Surface atomic concentrations of adsorbents before and after sulfur poisoning

Sample	Surface atomic concentration/%					Proportion of surface atoms/%	
	Fe ³⁺	Ce ³⁺ +Ce ⁴⁺	La ³⁺	O	S ⁶⁺	Ce ³⁺ /Ce ³⁺ +Ce ⁴⁺	O _a /O _a +O _β
Fe ₂ O ₃ (fresh)	32.55	—	—	67.44	—	—	44.7
Fe ₂ O ₃ (-S)	20.08	—	—	72.39	7.52	—	69.31
La ₂ O ₂ CO ₃ (fresh)	—	—	14.8	85.2	—	—	91.25
La ₂ O ₂ CO ₃ (-S)	—	—	12.14	78.42	9.45	—	88.63
FeLaO(fresh)	5.47	—	11.06	83.47	—	—	76.84
FeLaO(-S)	3.39	—	4.77	80.49	11.35	—	53.20
CeLaO(fresh)	—	9.94	9.28	80.77	—	22.57	73.87
CeLaO(-S)	—	6.42	4.08	76.01	13.49	28.04	85.21
FeCeLaO(fresh)	5.64	7.04	7.3	80.01	—	23.98	61.05
FeCeLaO(-S)	2.89	3.76	4.83	72.58	15.95	30.05	92.83

Note: the proportion of surface oxygen atoms in the pre-sulfurized FeLaO sample is O_a/O_a+O_β+O_γ.

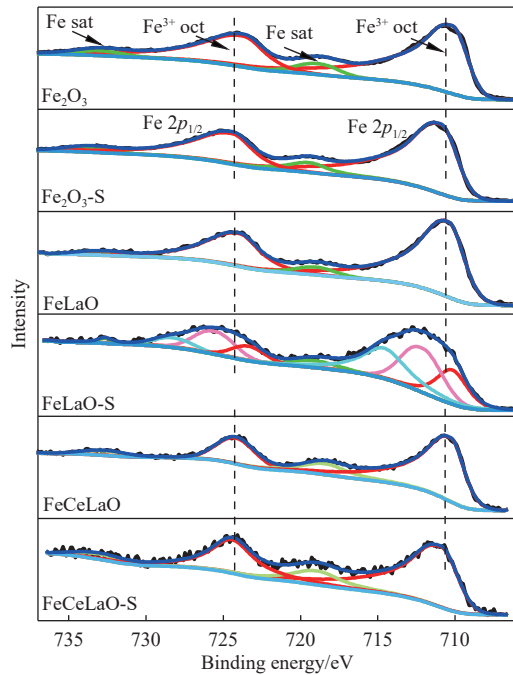


Fig. 11 Fe 2p spectra of Fe₂O₃, FeLaO and FeCeLaO before and after sulfur poisoning

The peak centered at 714.7 eV is attributed to Fe³⁺ bound to -OH^[33–34]. Compared to fresh adsorbents, both Fe 2p_{3/2} and Fe 2p_{1/2} peaks of the sulfur poisoned adsorbent shifts to high binding energies, which is attributed to the inductive effect of SO₄²⁻. The strong electronegativity of SO₄²⁻ has a strong attraction for electrons, resulting in a decrease in the electron density around Fe³⁺ ions.

Figure 12 shows the O 1s XPS spectra before and after sulfur poisoning. The peaks at 531.3–532.3 eV are attributed to the surface chemisorbed oxygen (O_a), while the peaks at 529.2–530.3 eV are ascribed to lattice oxygen species (O_β)^[35]. The O 1s of FeLaO is split into three peaks, with the peak centered at 535.0 eV identified as O_γ, attributed to oxygen in -OH or SO₄²⁻^[36–37].

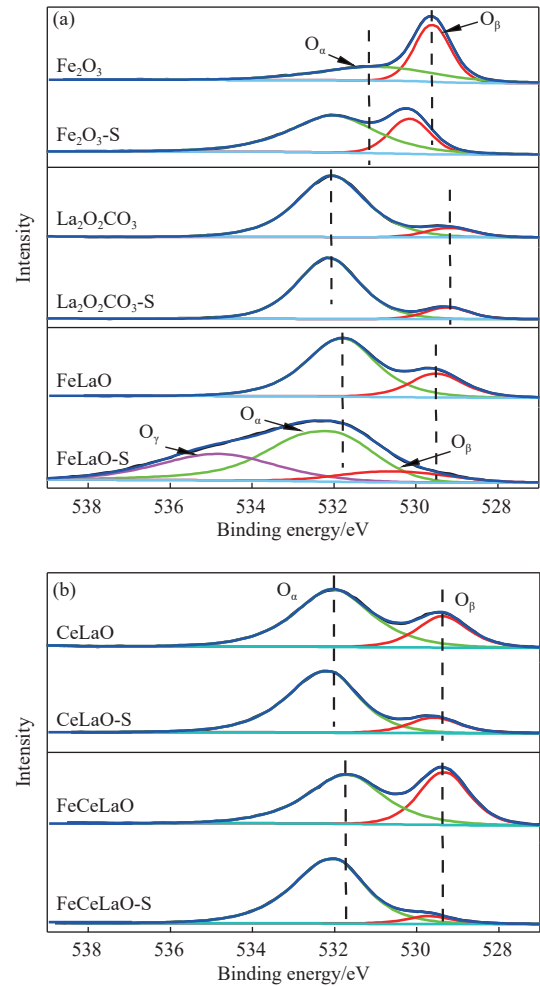


Fig. 12 O 1s spectra of adsorbents before and after sulfur poisoning

As shown in Table 3, the O_a/O_a+O_β ratios for Fe₂O₃, CeLaO and FeCeLaO are 44.7%, 73.87% and 61.05% respectively. After SO₂ poisoned, 69.31%, 85.21% and 92.83%, indicating a significant rise in surface-adsorbed

oxygen content, with FeCeLaO exhibiting the greatest increase. The added surface oxygen species are mainly derived from S–OH generated by SO₄^{2−} hydrolysis^[38] and oxygen vacancies provided by the formed Ce³⁺^[39]. Surface oxygen exhibits greater mobility than lattice oxygen, thereby enhancing the oxidative adsorption reactivity toward As₂O₃. In contrast, the surface oxygen ratios of La₂O₂CO₃ and FeLaO decrease by 2.62% and 23.64%, respectively, after sulfur poisoning, suggesting a reduction in their oxidative adsorption activity for As₂O₃.

The XPS curves of La in La₂O₂CO₃ (a), FeLaO (b), CeLaO (c) and FeCeLaO (d) before and after pre-sulfuration are shown in Figure 13. The La 3d_{3/2} peak appears at 835.1 eV and the La 3d_{5/2} peak appears at 852.1 eV, with an energy separation of about 16.8 eV between the two peaks. Each main La 3d peak corresponds to a satellite peak. These results regarding the binding energy and multiple splitting peak are consistent with existing reports on La³⁺^[40–41]. Compared to fresh adsorbents, four sulfur poisoned adsorbents exhibit various degrees of blue shift in their La 3d peaks, indicating the formation of S–O–La bond^[42–43], namely the generation of La₂(SO₄)₃.

Figure 14 shows the Ce 3d spectral curves for CeLaO and FeCeLaO. Eight characteristic peaks are fitted: v, v', v'', v''' are attributed to Ce 3d_{5/2} spin orbitals, u, u', u'', u''' are ascribed to Ce 3d_{3/2} spin orbitals. Among them v, v'', v''', u, u'', u''' correspond to Ce⁴⁺, v', u' correspond to Ce³⁺. Before SO₂ poisoned, the Ce³⁺/Ce³⁺+Ce⁴⁺ ratios in CeLaO and FeCeLaO are 22.57% and 23.98%. After SO₂ poisoned the ratios increase to 28.04% and 30.05%. Sulfation significantly increases the proportion of Ce³⁺, which

facilitates the generation of oxygen vacancies and enhances surface chemisorbed oxygen^[11,44], thereby promoting the oxidative adsorption of As₂O₃.

Figure 15 shows the S 2p XPS spectra of the adsorbents after sulfur poisoning. Distinct S 2p curves are detected on all adsorbents, indicating that sulfation occurs on them. The characteristic peaks located near 170 and 168.8 eV belong to S 2p_{1/2} and S 2p_{3/2} in SO₄^{2−} (or HSO₄[−])^[37,45]. No spectral signatures of S⁴⁺ compounds such as SO₃^{2−} or HSO₃[−] are observed.

2.5 Sulfur poisoning resistance of active component Fe-Ce-La oxides

Figure 16 shows the arsenic removal efficiency of sulfur poisoned Fe₂O₃ in the temperatures of 200–600 °C and under SO₂ concentration of 1000. The arsenic removal efficiency of fresh Fe₂O₃ is also represented in the figure for comparison. The arsenic removal efficiency of Fe₂O₃ is significantly higher with SO₂ than that without SO₂. At temperatures of 200, 300, 400, 500 and 600 °C, the arsenic removal efficiency increases by 8.2%, 23.9%, 17.4%, 17.3% and 7.6%, respectively. This can be attributed to the sulfation of Fe₂O₃ in the SO₂ atmosphere, which generates abundant SO₄^{2−}/HSO₄[−] species on the surface. These species also possess effective capabilities for oxidizing and adsorbing As₂O₃^[46–47]. The most significant improvement in arsenic removal efficiency occurs between 300 and 500 °C. This indicates that the Fe₂O₃ exhibits the strongest resistance to sulfur poisoning at this temperature range.

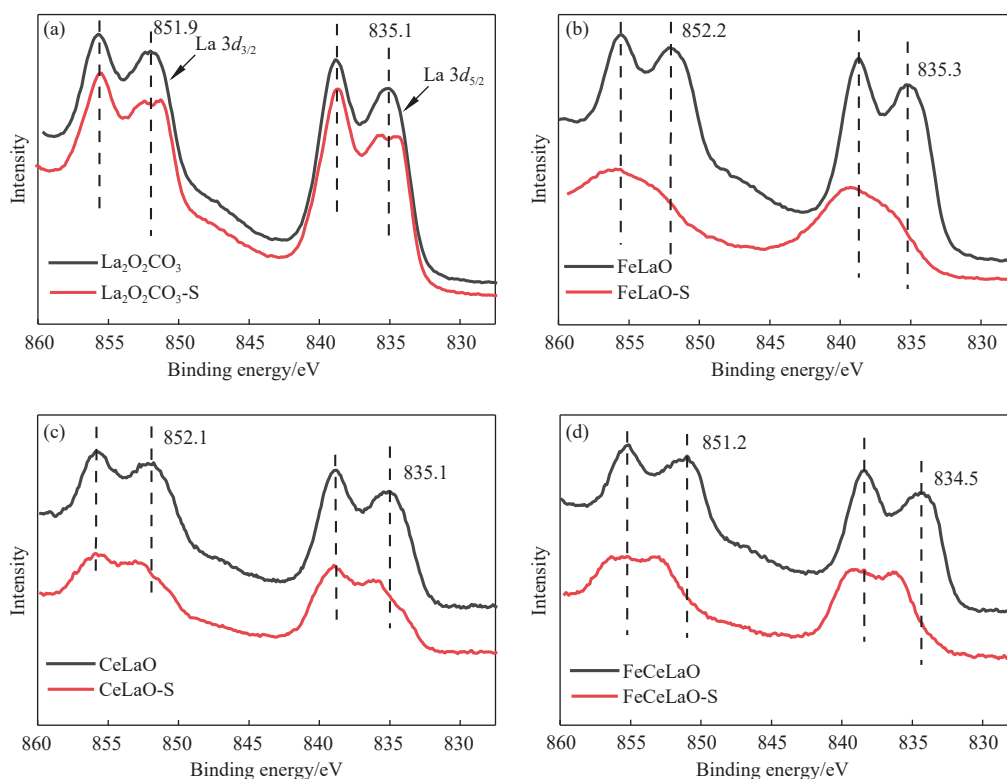


Fig. 13 La 3d spectra of adsorbents before and after sulfur poisoning

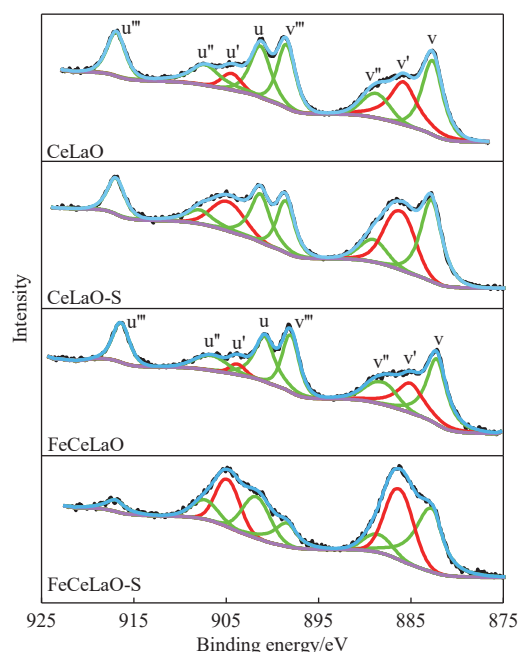


Fig. 14 Ce 3d spectra of adsorbents before and after sulfur poisoning

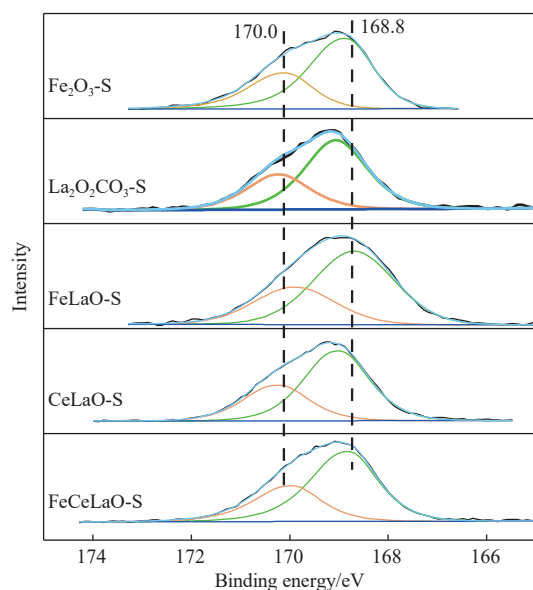


Fig. 15 S 2p spectra of adsorbents after sulfur poisoning

However, excessively high temperature ($>500\text{ }^{\circ}\text{C}$) causes the decomposition of the iron sulfate salt active sites, weakening their promoting effect on arsenic removal. These findings are in agreement with the TG results of Fe_2O_3 before and after pre-sulfation.

Figure 17 and Figure 18 show the arsenic removal efficiency of pre-sulfurized $\text{La}_2\text{O}_2\text{CO}_3$ and FeLaO. Their arsenic removal efficiency in the presence of SO_2 is significantly reduced compared with that in the absence of SO_2 . At 200, 300, 400 and $500\text{ }^{\circ}\text{C}$, the arsenic removal efficiency of pre-sulfurized $\text{La}_2\text{O}_2\text{CO}_3$ decreases by 2.1%, 4.6%, 10.2% and 18.8%, respectively, while pre-sulfurized FeLaO decreases by 2.8%, 5.1%, 9.0% and 15.1%. It shows that $\text{La}_2\text{O}_2\text{CO}_3$ and FeLaO exhibit poor sulfur poisoning resistance. The higher the temperature, the worse the

resistance to sulfur poisoning.

Based on the TG and SO_2 -TPD analyses, La reacts with SO_2 to form $\text{La}_2(\text{SO}_4)_3$, and the newly generated $\text{La}_2(\text{SO}_4)_3$ exhibits no activity for adsorbing As_2O_3 . XPS results further indicate that the sulfation of La leads to a reduction in the surface adsorbed oxygen ratio ($\text{O}_\alpha/\text{O}_\alpha+\text{O}_\beta$), suppressing oxidation and adsorption activity.

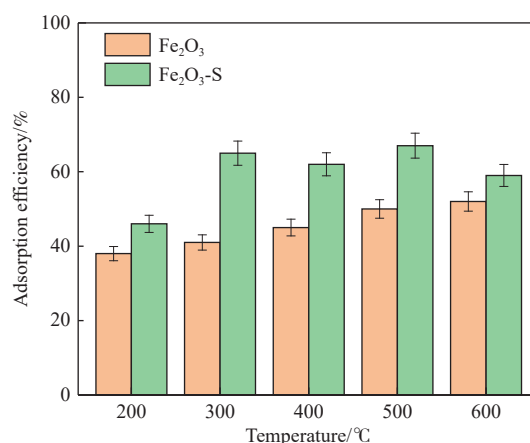


Fig. 16 Effect of SO_2 on arsenic removal efficiency of Fe_2O_3 at different temperatures

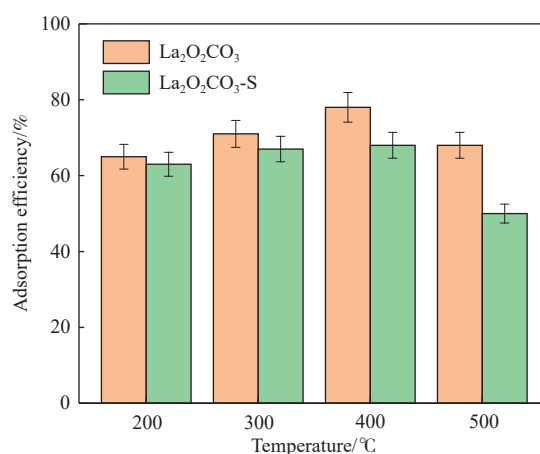


Fig. 17 Effect of SO_2 on arsenic removal efficiency of $\text{La}_2\text{O}_2\text{CO}_3$ at different temperatures

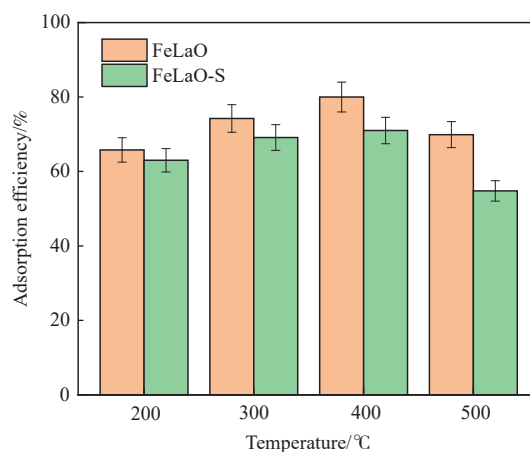


Fig. 18 Effect of SO_2 on the arsenic removal efficiency of FeLaO at different temperatures

Consequently, the arsenic removal efficiency decreases. This is in agreement with the findings of Peralta et al.^[48]: $\text{K/La}_2\text{O}_3$ catalyst undergoes sulfation and forms inactive $\text{La}_2(\text{SO}_4)_3$ at 400 °C in flue gas containing $1.0 \times 10^{-3} \text{ SO}_2$, which results in complete catalyst deactivation.

Figure 19 and Figure 20 show the arsenic removal efficiency of pre-sulfurized CeLaO and FeCeLaO. The arsenic removal efficiencies of both CeLaO and FeCeLaO are significantly enhanced with SO_2 than those without SO_2 . At adsorption temperatures of 200, 300, 400 and 500 °C, pre-sulfurized CeLaO shows efficiency improvements of 3.3%, 5.3%, 8.0% and 9.8%, respectively, and pre-sulfurized FeCeLaO indicates increases of 2.3%, 5.1%, 9.7% and 11.2%, respectively. At 400 °C, the efficiency reaches 80.5% for CeLaO and 91.0% for FeCeLaO. These findings align with the TPD and XPS results.

TPD analysis reveals that Ce preferentially reacts with SO_2 in flue gas, thereby protecting Fe and La active sites. XPS results show that after sulfation, both Ce^{3+} ratio ($\text{Ce}^{3+}/\text{Ce}^{3+}+\text{Ce}^{4+}$) and surface adsorbed oxygen content ($\text{O}_a/\text{O}_a+\text{O}_b$) increase significantly. These synergistic effects collectively enhance arsenic removal efficiency.

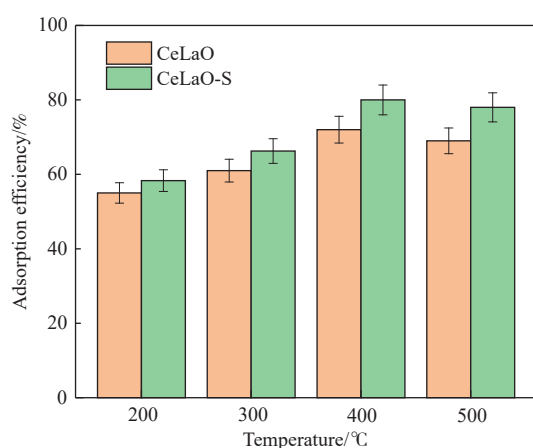


Fig. 19 Effect of SO_2 on arsenic removal efficiency of CeLaO at different temperatures

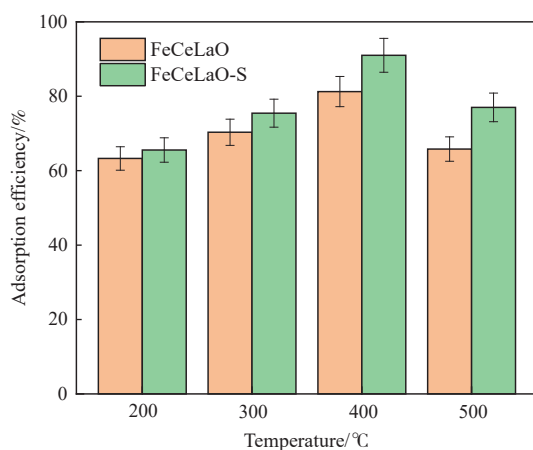


Fig. 20 Effect of SO_2 on arsenic removal efficiency of FeCeLaO at different temperatures

2.6 Sulfur poisoning resistance of Si-Al carrier

In order to investigate the resistance of active Si-Al carriers with different Si/Al ratios to SO_2 in flue gas, the experiments were carried out at 400 °C and $5.0 \times 10^{-4} \text{ SO}_2$, and the results are shown in Figure 21. Compared with the fresh adsorbent, the pre-sulfurized Si-Al carriers exhibit progressively enhanced resistance to sulfur poisoning as the Si/Al ratio increases. The arsenic removal efficiency of original fly ash after SO_2 poisoning is 30.7%, which is basically the same as that of fresh fly ash. When the Si/Al ratio is 1.85, the arsenic removal efficiency of SO_2 poisoned Si-Al carrier is 54.5%, which decrease by 24.2% compared with the fresh carrier. As the Si/Al ratio further increases, the difference in arsenic removal efficiency between them progressively narrows. At a Si/Al ratio of 2.77, the difference is only approximately 3%. When the Si/Al ratio is 9.7, the arsenic adsorption efficiency of the pre-sulfurized carrier reaches the maximum value of 74.6%, which is 13.9% higher than the arsenic removal efficiency of the fresh carrier. Therefore, increasing Si/Al ratio in the carrier promotes enhancing sulfur resistance in the adsorbent.

The possible reason is that as the Si/Al ratio increases, the content of alkali metal oxide in active Si-Al carrier decreases, both the content of SiO_2 and the surface acidity increase. This inhibits the adsorption of SO_2 from flue gas and weakens the competitive adsorption between SO_2 and gaseous As_2O_3 , thereby preventing the formation of metal sulfates that would otherwise cause active site depletion or pore blockage. At the same time, the increase in the Si/Al ratio can obtain a large specific surface area. Therefore, the ability to resist sulfur poisoning is enhanced.

2.7 Sulfur poisoning resistance of FeCeLaO/ $\text{SiO}_2\text{-Al}_2\text{O}_3$

The 3# Si-Al oxide with Si/Al ratio of 1.85 was used as the carrier to prepare the composite adsorbents with different loading ratios. The effect of FeCeLaO loading ratio on sulfur resistance was investigated at 400 °C and under $5.0 \times 10^{-4} \text{ SO}_2$. The results are shown in Figure 22.

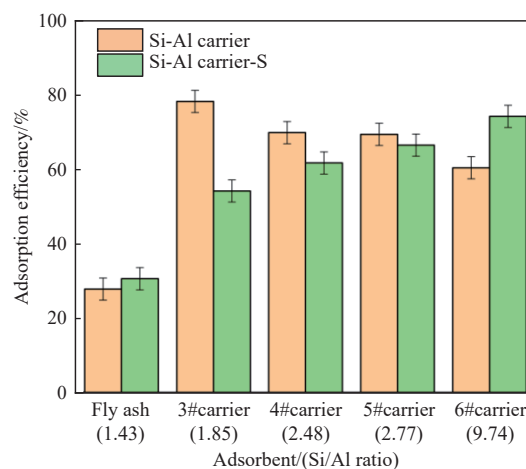


Fig. 21 Anti-sulphur toxicity of activated Si-Al carriers at different Si/Al ratios

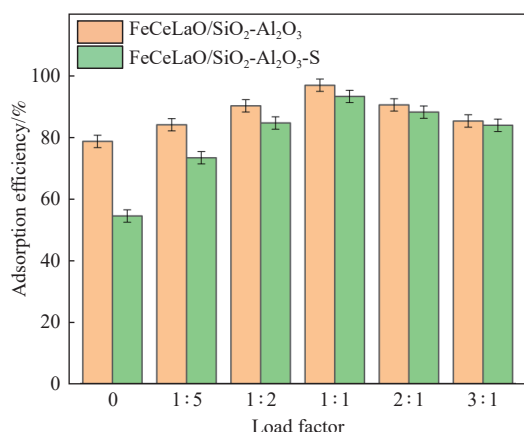


Fig. 22 Anti-sulphur toxicity of composite adsorbents at different loading rates

For the pure Si-Al carrier (0 loading ratio), the arsenic removal efficiency decreases by 24.2% after sulfur poisoning. As the loading ratio increases to 1:5, 1:2, 1:1, 2:1 and 3:1, the arsenic removal efficiency of SO₂ poisoned adsorbents is 73.3%, 84.7%, 93.2%, 88.2% and 83.9%, respectively. Compared with the corresponding fresh adsorbents, these efficiencies still decline, decreasing by 10.8%, 5.5%, 3.6%, 2.3% and 1.4%, respectively. However, the degree of the decline in arsenic removal efficiency has gradually narrowed. This demonstrates that incorporating FeCeLaO active components is beneficial to enhance the sulfur poisoning resistance of the adsorbent. Furthermore, as the loading ratio increases, the degree of sulfur resistance improvement becomes more pronounced. Especially when the loading ratio exceeds 1:2, the decrease in arsenic removal efficiency of the pre-sulfurized adsorbent is less than 5%; When the loading ratio is 1:1, the removal efficiency of sulfur poisoned adsorbent is still as high as 93.2%. Therefore, the FeCeLaO/SiO₂-Al₂O₃ composite adsorbent is undoubtedly a low-cost adsorbent with superior sulfur resistance for arsenic removal.

The reason for this phenomenon is as follows: after introducing the FeCeLaO active component, as its loading ratio increases, the content of Ce component increases. The Ce element preferentially reacts with SO₂, thereby protecting the Fe and La active components as well as the Al component in the carrier from sulfur poisoning. This prevents the loss of active sites and thus enhances the resistance to sulfur poisoning. It is precisely due to the protective effect of Ce components and the surface acidity of SiO₂ that the composite adsorbent FeCeLaO/SiO₂-Al₂O₃ retains high adsorption efficiency and demonstrates excellent SO₂ resistance in SO₂-containing environments.

3 Conclusions

This study aims to develop superior arsenic removal adsorbents in the middle-low-temperature region which could be applied efficiently even in the presence of SO₂. The as-prepared CeLaO, FeCeLaO and FeCeLaO/fly ash

derived SiO₂-Al₂O₃ can exhibit arsenic removal efficiencies of 80.5%, 91.0% and 93.2% respectively at 400 °C in the SO₂ atmosphere, which not only have a low arsenic removal temperature window (≤ 400 °C), but also have a strong resistance to sulfur toxicity.

The Si-Al carrier with a specific surface area as high as 568.04 m²/g used in this study is derived from coal fly ash. Notably, it does not require additional silicon-aluminum sources, and has advantages of strong sulfur resistance and low-cost. This approach provides a pathway for the resource utilization of coal fly ash.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] SIGNES-PASTOR A J, VIOQUE J, NAVARRETE-MUNOZ E M, et al. Inorganic arsenic exposure and neuropsychological development of children of 4-5 years of age living in Spain[J]. *Environ Res*, 2019, 174: 135–142.
- [2] NACHMAN K E, GINSBERG G L, MILLER M D, et al. Mitigating dietary arsenic exposure: Current status in the United States and recommendations for an improved path forward[J]. *Sci Total Environ*, 2017, 581–582: 221–236.
- [3] MUKHERJEE S, SRIVASTAVA S K. Trace elements in high-sulfur Assam coals from the Makum coalfield in the northeastern region of India[J]. *Energy Fuels*, 2005, 19(3): 882–891.
- [4] CHENG K, WANG Y, TIAN H, et al. Atmospheric emission characteristics and control policies of five precedent-controlled toxic heavy metals from anthropogenic sources in China[J]. *Environ Sci Technol*, 2015, 49(2): 1206–1214.
- [5] LI X, LI J, HE X, PENG Y, CHANG H. Poisoning mechanism and regeneration process of the denitration catalyst[J]. *Chem Ind Eng Prog*, 2015, 34: 4129–4138.
- [6] BURKE M J, STEPHENS J C. Political power and renewable energy futures: A critical review[J]. *Energy Res Social Sci*, 2018, 35(7/8): 78–93.
- [7] BIRD L, LEW D, MILLIGAN M, et al. Wind and solar energy curtailment: A review of international experience[J]. *Renewable Sustainable Energy Rev*, 2016, 65: 577–586.
- [8] WINTER R M, MALLEPALLI R R, HELLEM K P, et al. Determination of As, Cd, Cr, and Pb species formed in a combustion environment[J]. *Combust Sci Technol*, 1994, 101: 45–58.
- [9] MERCEDES D A-S, M ROSA M N-T. Retention of trace elements using fly ash in a coal gasification flue gas[J]. *J Chem Technol Biotechnol*, 2002, 77: 396–402.
- [10] RAJA A, JADHAV R A, HIMANSHU G, et al. Mechanism of selenium sorption by activated carbon[J]. *Can J Chem Eng*, 2000, 78: 168–174.
- [11] ZHANG K, HU L, WANG C, et al. Middle-low-temperature oxidation and adsorption of arsenic from flue gas by Fe-Ce-based composite catalyst[J]. *Chemosphere*, 2022, 288(1): 132425.

- [12] HU P, WENG Q, LI D, et al. Effects of O₂, SO₂, H₂O and CO₂ on As₂O₃ adsorption by gamma-Al₂O₃ based on DFT analysis[J]. *J Hazard Mater*, 2021, 403: 123866.
- [13] LI Y, TONG H, ZHUO Y. Simultaneous removal of SO₂ and trace As₂O₃ from flue gas: Mechanism, kinetics study, and effect of main gases on arsenic capture[J]. *Environ Sci Technol*, 2007, 41(8): 2894–2900.
- [14] CHEN D, HU H, XU Z, et al. Findings of proper temperatures for arsenic capture by CaO in the simulated flue gas with and without SO₂[J]. *Chem Eng J*, 2015, 267: 201–206.
- [15] ZHAO S, WANG Y, XIE X, et al. Arsenic removal from Coal-fired flue gas by MnO₂ coated magnetic flower-like Fe₃O₄ composites: Experimental and DFT study[J]. *Chem Eng J*, 478 (2023) 147481.
- [16] QU P, GAO X, WANG Q, et al. Study on alkali hydrothermal treatment of fly ash and its adsorption properties[J]. *Shanxi Chem Ind*, 2021, 41(6): 1–2,9.
- [17] SOMERSET V S, PETRIK L F, WHITE R A, et al. Alkaline hydrothermal zeolites synthesized from high SiO₂ and Al₂O₃ co-disposal fly ash filtrates[J]. *Fuel*, 2005, 84(18): 2324–2329.
- [18] ZHAO Y, ZHANG J, LIU J, et al. Experimental study on fly ash capture mercury in flue gas[J]. *Sci China Tech Sci*, 2010, 40(4): 385–391.
- [19] ZHAO Y, ZHANG J, WANG Z, et al. Study on mineralogy and micro-structure of high-calcium fly ash[J]. *J Eng Thermophysics*, 2008, (8): 1427–1430.
- [20] QI L, WANG X, WANG W, et al. Mercury removal from coal combustion flue gas by pyrite-modified fly ash adsorbent[J]. *Environ Sci Pollut Res Int*, 2022, 29(26): 39228–39238.
- [21] ZHANG Y, WANG C, LIU H. Experiment and mechanism research on gas-phase As₂O₃ adsorption of Fe₂O₃/γ-Al₂O₃[J]. *Fuel*, 2016, 181: 1034–1040.
- [22] DONG W K, KWANG H P, HEON P H, et al. The role of molybdenum on the enhanced performance and SO₂ resistance of V/Mo-Ti catalysts for NH₃-SCR[J]. *Appl Surf Sci*, 2019, 481: 1167–1177.
- [23] YA Y, WEI T, DONG Q, et al. Insight into the SO₂ resistance mechanism on γ-Fe₂O₃ catalyst in NH₃-SCR reaction: A collaborated experimental and DFT study[J]. *Appl Catal B: Environ*, 2021, 281: 119544.
- [24] CHEN Y, JIANG Y, LI W, et al. Adsorption and interaction of H₂S/SO₂ on TiO₂[J]. *Catal Today*, 1999, 50: 39–47.
- [25] WEI Y, CHEN P, HOU X, et al. SO₂ poisoning mechanism of Fe-Mn/TiO₂ catalyst for low-temperature NH₃ denitration[J]. *J Funct Mater*, 2021, 52(4): 4132–4139+4146.
- [26] YU Y, CHEN C, MA M, et al. SO₂ promoted in situ recovery of thermally deactivated Fe₂(SO₄)₃/TiO₂ NH₃-SCR catalysts: From experimental work to theoretical study[J]. *Chem Eng J*, 2019, 361: 820–829.
- [27] LEE T, BAI H. Metal sulfate poisoning effects over MnFe/TiO₂ for selective catalytic reduction of NO by NH₃ at low temperature[J]. *Ind Eng Chem Res*, 2018, 57(14): 4848–4858.
- [28] KWON D W, NAM K B, HONG S C. The role of ceria on the activity and SO₂ resistance of catalysts for the selective catalytic reduction of NO_x by NH₃[J]. *Appl Catal B: Environ*, 2015, 166–167: 37–44.
- [29] LIU R, YANG Y, ZHU T, et al. Role of NO and SO₂ in mercury oxidation over a La₂O₃/Fe₂O₃ catalyst with high thermal stability[J]. *J Environ Sci China*, 2021, 109: 36–44.
- [30] LEE M H, JUNG W S. Hydrothermal synthesis of LaCO₃OH and Ln³⁺-doped LaCO₃OH powders under ambient pressure and their transformation to La₂O₂CO₃ and La₂O₃[J]. *Bull Korean Chem Soc*, 2013, 34(12): 3609–3614.
- [31] ZHOU Y, SU B, REN S, et al. Nb₂O₅-modified Mn-Ce/AC catalyst with high ZnCl₂ and SO₂ tolerance for low-temperature NH₃-SCR of NO[J]. *J Environ Chem Eng*, 2021, 9(5): 106323.
- [32] CHANG H, CHEN X, LI J, et al. Improvement of activity and SO₂ tolerance of Sn-modified MnO_x-CeO₂ catalysts for NH₃-SCR at low temperatures[J]. *Environ Sci Technol*, 2013, 47(10): 5294–5301.
- [33] SHWAN S, JANSSON J, OLSSON L, et al. Chemical deactivation of H-BEA and Fe-BEA as NH₃-SCR catalysts—effect of potassium[J]. *Appl Catal B: Environ*, 2015, 166–167: 277–286.
- [34] THOMAS J E, JONES C F, SKINNER W M. The role of surface sulfur species in the inhibition of pyrrhotite dissolution in acid conditions[J]. *Geochimica et Cosmochimica Acta*, 1998, 62(9): 1555–1565.
- [35] ZHAO L, LI C, LI S, et al. Simultaneous removal of elemental mercury and NO in simulated flue gas over V₂O₅/ZrO₂-CeO₂ catalyst[J]. *Appl Catal B: Environ*, 2016, 198: 420–430.
- [36] LIU J, DU Y, LIU J, et al. Design of MoFe/Beta@CeO₂ catalysts with a core-shell structure and their catalytic performances for the selective catalytic reduction of NO with NH₃[J]. *Appl Catal B: Environ*, 2017, 203: 704–714.
- [37] YANG S, GUO Y, YAN N, et al. Nanosized cation-deficient Fe-Ti spinel: A novel magnetic sorbent for elemental mercury capture from flue gas[J]. *ACS Appl Mater Interfaces*, 2011, 3(2): 209–217.
- [38] WEI L, CUI S, GUO H, et al. DRIFT and DFT study of cerium addition on SO₂ of manganese-based catalysts for low temperature SCR[J]. *J Mol Catal A: Chem*, 2016, 421: 102–108.
- [39] ZHANG L, QU H, DU T, et al. H₂O and SO₂ tolerance, activity and reaction mechanism of sulfated Ni-Ce-La composite oxide nanocrystals in NH₃-SCR[J]. *Chem Eng J*, 2016, 296: 122–131.
- [40] WU Q, LIU M, JAEGERMANN W. X-ray photoelectron spectroscopy of La_{0.5}Sr_{0.5}MnO₃[J]. *ACS Mater Lett*, 2005, 59(12): 1480–1483.
- [41] PAWLAK D A, ITO M, OKU M, et al. Interpretation of XPS O (1s) in mixed oxides proved on mixed perovskite crystals[J]. *J Phys Chem B*, 2002, 106: 504–507.
- [42] SU J, LYU T, YI H, et al. Superior arsenate adsorption and comprehensive investigation of adsorption mechanism on novel Mn-doped La₂O₂CO₃ composites[J]. *Chem Eng J*, 2020, 391: 123623.
- [43] LIU X, ZONG E, HU W, et al. Lignin-derived porous carbon loaded with La(OH)₃ nanorods for highly efficient removal of phosphate[J]. *ACS Sustainable Chem Eng*, 2018, 7(1):

758–768.

- [44] WANG H, QU Z, XIE H, et al. Insight into the mesoporous $\text{Fe}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ catalysts for selective catalytic reduction of NO with NH_3 : Regulable structure and activity[J]. J Catal, 2016, 338: 56–67.
- [45] FERRIZZ R M, GORTE R J, VOHS J M. TPD and XPS investigation of the interaction of SO_2 with model ceria catalysts[J]. Catal Lett, 2002, 82(1/2): 123–129.
- [46] XINGS J, WANG C, HUANG Y, et al. A comprehensive exploration about the effects of O_2 , SO_2 and NO on As_2O_3 adsorption over Cu/ γ - Al_2O_3 SCR catalyst: A DFT study[J]. Chem Eng Sci, 2022, 248: 117260.
- [47] XING J, WANG C, HUANG Y, et al. Mechanism of the arsenic adsorption over Cu/ γ - Al_2O_3 SCR catalyst: An experimental combined theoretical analysis[J]. Chem Eng Sci, 2022, 254: 117610.
- [48] PERALTA M A, ULLA M A, QUERINI C A. SO_2 influence on the K/ La_2O_3 soot combustion catalyst deactivation[J]. Catal Today, 2008, 133–135: 461–466.

高耐硫硅铝负载 Fe-Ce-La 复合吸附剂用于中低温烟气砷捕集

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摘 要: 开发中低温烟气条件下 (<400 °C) 抗硫性强的烟气脱砷吸附剂, 实现燃煤烟气低温脱砷和高效抗硫至关重要。本工作采用共沉淀法制备了五种铁-铈-镧氧化物, 并耦合粉煤灰基 Si-Al 载体制备 $\text{FeCeLaO}/\text{SiO}_2\text{-Al}_2\text{O}_3$ 复合吸附剂。通过 TPD、TG、XRF、BET 和 XPS 等对活性组分铁-铈-镧氧化物和 Si-Al 载体进行表征, 进而研究温度、Si/Al 比和 FeCeLaO 负载率对抗硫性的影响。结果表明, SO_2 对 Fe_2O_3 、 CeLaO 和 FeCeLaO 脱砷具有促进作用, 在 400 °C 时, 三者的脱砷效率分别从无 SO_2 时的 45.3%、72.5% 和 81.3% 增大到 62.6%、80.5% 和 91.0%。 SO_2 对 La_2O_3 和 FeLaO 脱砷具有抑制作用, 且温度越高, 抑制作用越强。Si-Al 载体的抗硫中毒能力随 Si/Al 比的增大而增强, 当 Si/Al 比增大为 9.74 时, SO_2 环境中的脱砷效率比无 SO_2 时升高了 13.9%。引入 FeCeLaO 活性组分, 有利于增强 Si-Al 载体的抗硫中毒能力。 $\text{FeCeLaO}/\text{SiO}_2\text{-Al}_2\text{O}_3$ 复合吸附剂的强抗硫性来自于活性组分和载体的多重作用: Ce 元素对 Fe、La、Al 等活性组分的保护效应, 硫酸化诱导产生了 Ce^{3+} 和表面吸附氧, 以及 SiO_2 较强的表面酸性。

关键词: 脱砷; 抗硫; 烟气; Fe-Ce-La 氧化物; 飞灰

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