Contents lists available at ScienceDirect



## Arabian Journal of Chemistry



journal homepage: www.ksu.edu.sa

## Original article

# Simultaneous removal of $SO_2$ and $NO_x$ by potassium-modified carbide slag



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#### ARTICLE INFO

## ABSTRACT

Keywords: Carbide slag Potassium Simultaneous desulfurization and denitrification Activation energy The treatment of solid waste carbide slag (CS) poses an urgent challenge in terms of its resolution. This study presented an efficient and cost-effective method for simultaneous desulfurization and denitrification at low temperatures using different modified potassium compounds (KOH, K<sub>2</sub>CO<sub>3</sub>, and KHCO<sub>3</sub>) as adsorbents. The experimental results revealed the significant impact of potassium modification on the performance of the CS, leading to a significant improvement in its denitrification activity while maintaining the same desulfurization effect. The denitrification rates of the modified CS demonstrated increases by 30 % (KOH), 25 % (K<sub>2</sub>CO<sub>3</sub>), and 40 % (KHCO<sub>3</sub>), respectively, compared to the unmodified CS at 200 °C. The NO adsorption capacities were 2.48 (KOH), 2.24 (K<sub>2</sub>CO<sub>3</sub>), and 3.05 (KHCO<sub>3</sub>) times that of CS, respectively. Subsequent investigations suggested that the potassium modification process induced changes in the microstructure of CS, augmenting the abundance of oxygen vacancies,  $KO_x$ , C = O, and  $O_{ads}$ , thereby enhancing the intensity and quantity of basic sites. This reduced the activation energy of the CS during simultaneous desulfurization and denitrification. In addition, it was observed that certain byproducts formed during the desulfurization and denitrification processes, such as sulfate, sulfite, and nitrate, accumulated on the surface and within the inner pores of the adsorbents, ultimately resulting in a decline in catalytic activity. This study aims to embrace the "treat waste with waste" approach and is expected to provide guidance for the advancement of simultaneous desulfurization and denitrification technologies targeting solid waste CS.

#### 1. Introduction

Carbide slag (CS) represents a solid waste generated within the chloralkali industry, that can produce calcium carbide slag and acetylene following the hydrolysis of calcium carbide. This byproduct is referred to as poor-quality  $Ca(OH)_2$  and manifests as a white powder, with slight solubility in water and alkaline. China currently holds the position of the world's leading CS producer, which annually discharges large quantities of CS from both the polyvinyl chloride (PVC) and chloralkali industries. In 2020, China's CS production reached 27.58 million tons, accounting for over 90 % of the global production, signifying a year-on-year increase of 6.8 % (Gong et al., 2022). The high alkalinity of CS renders conventional disposal methods, such as landfills, inadequate due to their potential to generate severe environmental issues, including soil alkalization and contamination of surface and groundwater(Ma et al., 2016). Moreover, CS is characterized by an elevated Ca(OH)<sub>2</sub> content, pronounced particle dispersion, expansive specific surface area, and substantial pore structure. Following appropriate treatment, CS can serve as an outstanding secondary calciumbased resource, capable of substituting limestone in flue gas desulfurization processes, consequently presenting a broad range of applications (Mathieu et al., 2013, Huang et al., 2019). The utilization of CS as an adsorbent exhibits the remarkable advantage of diminishing both raw materials and processing costs, reducing the treatment load and pollution associated with CS, and ultimately realizing the comprehensive utilization of secondary resources.

Among the available desulfurization options, CS is regarded as a costeffective desulfurization agent. Gong et al. (2022) and Wu et al. (2016) explored the adsorption performance of CS for SO<sub>2</sub>, revealing a superior adsorption capacity compared to limestone with larger particle sizes. Furthermore, using a fixed bed reactor, Cheng et al. (2009) investigated the desulfurization capacity of three industrial wastes containing

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https://doi.org/10.1016/j.arabjc.2023.105363 Received 3 July 2023; Accepted 11 October 2023

Available online 16 October 2023

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Peer review under responsibility of King Saud University. Production and hosting by Elsevier.

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sodium calcium, namely white lime mud, CS, and salt cement. Compared to the other two industrial wastes, CS-derived CaO demonstrated the highest number of SO<sub>2</sub> diffusion channels and largest specific surface area, which facilitated the effective removal of SO<sub>2</sub>. Bian et al. (2020) investigated the performance of Al-Mg-modified CS for SO<sub>2</sub> removal at high temperatures with the utilization of a double fixed bed reactor. The Al- and Mg-modified CS exhibited significantly higher SO<sub>2</sub> removal capacity and cycling stability than CS due to the presence of beneficial compounds, such as Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and MgO. In addition, the field has progressed beyond simple desulfurization, and now seeks to achieve simultaneous desulfurization and denitrification. Wang et al. (2018, 2020) developed a method for producing pellets from CS, bagasse pellets, CS, and coal coke via an extrusion rounding process. The prepared pellets demonstrated 100 % efficiency in the removal of SO<sub>2</sub>/NO within the optimum reaction temperature range of 850-875 °C. Meng et al. (2022) conducted research on the synergistic preparation of hybrid pellets with the application of CS and sludge, evaluating the SO<sub>2</sub>/NO removal capacity in depth. The addition of sludge to the CS pellets vielded a satisfactory denitrification efficiency of up to 70 % at 550 °C. Furthermore, Wang et al. (2020) prepared a composite adsorbent using modified rice husk ash and CS. The results revealed that the synthetic adsorbent exhibited an increase in the removal of NO and SO<sub>2</sub> by 44 % and 2 %, respectively, at 700 °C. However, these methods require high temperature and complex material preparation techniques. It is imperative to propose strategies that can further reduce the reaction temperature while achieving cost-effective and highly efficient desulfurization and denitrification.

Numerous studies have demonstrated the superior efficacy of alkali metal-modified materials for the removal of gaseous  $SO_2/NO$ . In particular, the utilization of potassium for  $SO_2/NO$  removal has garnered considerable research attention (Fortier et al., 2007, Gao et al., 2018, Severa et al., 2018, Yang et al., 2019). Impregnating the material

surface with potassium creates a robust interaction effect, significantly enhancing the adsorption capacity of the material (Lee et al., 1998). Tang et al. (2015) introduced potassium into manganese cobalt oxides to augment their low-temperature NO oxidation activity. Qie et al. (2020) employed potassium-assisted catalytic activation to prepare activated coke with a high specific surface area and stratified pore structure, which exhibited outstanding SO<sub>2</sub> and NO adsorption capacities. Furthermore, adsorbents containing potassium exhibited the best performance in terms of NO adsorption and played a crucial role in preserving surface oxygen, thus increasing the occurrence of oxygen vacancies, which can be an essential factor for catalytic performance (Cheng et al., 2018).

This study focused on the modification of CS using different potassium sources to investigate its performance in desulfurization and denitrification. Additionally, the activation energy of different modified CS samples was calculated. The materials were thoroughly characterized using several techniques including X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), CO<sub>2</sub>-temperature programmed desorption (CO<sub>2</sub>-TPD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Building on these findings, a possible mechanism was proposed, which provides a promising strategy for the future utilization of waste resources.

## 2. Experimental

## 2.1. Adsorbent preparation

In this experiment, the modified CS was prepared by ultrasonic impregnation, and its visual preparation flowchart is shown in Fig. 1(a). The CS samples were immersed in the solutions of KOH,  $K_2CO_3$ , and KHCO<sub>3</sub>, each at a concentration of 1.0 mol·L<sup>-1</sup>, respectively, and



**Fig. 1.** (a) Preparation process of adsorbents; (b) schematics of the experimental setup: (1) Gas cylinder; (2) mass flowmeter; (3) gas mixing tank; (4) control valve; (5) resistance tube furnace; (6) quartz tube; (7) temperature controller; (8) flue gas analyzer; (9)  $K_2$ MnO<sub>4</sub> solution; (10) NaOH solution.

sonicated at 100 W and 59 Hz for 15 min. Subsequently, the resulting solution was dried in a blast drying oven at 100 °C for 12 h. Finally, the prepared modified CS was sieved using a particle size range of 40–60 mesh. The initial carbide slag was recorded as CS, the potassium-modified calcium carbide slag was recorded as KCS, and the different potassium-modified carbide slags were recorded as CS-KOH, CS-K<sub>2</sub>CO<sub>3</sub>, and CS-KHCO<sub>3</sub>. Following the reaction, the modified carbide slags were further recorded as UCS-KOH, UCS-K<sub>2</sub>CO<sub>3</sub>, and UCS-KHCO<sub>3</sub>.

#### 2.2. Activity evaluation

Desulfurization and denitrification reactions were conducted in a fixed bed using 1.0 g of modified CS within a quartz tube reactor with an inner diameter of 6 mm. The performance of the modified CS in terms of SO<sub>2</sub>/NO removal was assessed using the experimental setup illustrated in Fig. 1(b). To simulate real conditions, a dynamic gas distribution was adopted, setting the flow rate of the simulated flue gas was 200 mL·min<sup>-1</sup>, and the gas hour space velocity (GHSV) at 8488 h<sup>-1</sup>. The flue gas composition consisted of 1500 mg $\cdot$ m<sup>-3</sup> of SO<sub>2</sub>, 700 mg $\cdot$ m<sup>-3</sup> of NO, and 5 % of O<sub>2</sub>, with N<sub>2</sub> serving as the equilibrium gas. To monitor the SO2/NO concentration in the flue gas, an online MRU infrared flue gas analyzer was employed. Any escaping SO<sub>2</sub>/NO from the experiment was subsequently oxidized and absorbed by an absorption solution comprising NaOH and K<sub>2</sub>MnO<sub>2</sub> before discharge. Eqs. (1) and (2) represent the removal efficiency and adsorption capacity of SO<sub>2</sub>/NO, respectively. In accordance with the national standard (Emission standard, 2014), a denitrification rate of 45 % and desulfurization rate of 75 % were employed as benchmarks for measuring effective removal. Denitrification efficiency was evaluated using  $T_{NO}45\%$ , indicating the duration of denitrification with a denitrification rate exceeding 45 %. Similarly, T<sub>SO2</sub>75% was utilized to evaluate the desulfurization efficiency signifying the duration of desulfurization with a desulfurization rate above 75 %.

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$
<sup>(1)</sup>

$$q_e = \frac{Q \int_{t_0}^{t_b} (C_{\rm in} - C_{\rm out}) dt}{m} \times 10^{-6}$$
(2)

where  $\eta$  denotes the SO<sub>2</sub>/NO removal rate (%),  $C_{in}$  denotes the SO<sub>2</sub>/

NO concentration before the reaction (mg·m<sup>-3</sup>),  $C_{out}$  denotes the SO<sub>2</sub>/ NO concentration after the reaction (mg·m<sup>-3</sup>),  $q_e$  denotes the adsorption capacity of SO<sub>2</sub>/NO (mg·g<sup>-1</sup>), Q is the gas flow rate (mL·min<sup>-1</sup>),  $t_0$  and  $t_b$ denotes the onset and end time of adsorption (min), respectively, and mdenotes the material mass (g).

## 2.3. Characterization methods

The detailed characterization methods are shown in Supplementary Text.

#### 3. Results and discussion

#### 3.1. Results of adsorbent activity evaluation

In the conducted experiment, the reaction temperature emerged as a critical factor affecting the activity of the modified CS. The impact of different reaction temperatures on the simultaneous desulfurization and denitrification activities of the modified CS is presented in Fig. 2. The adsorption capacities of potassium-modified CS for SO<sub>2</sub>/NO at different temperatures are shown in Fig. 3. As shown in Figs. 2 and 3, the SO<sub>2</sub>/NO removal activity and adsorption capacity of different modified CS exhibited temperature dependent variations. Notably, the denitrification efficiency of the modified CS was significantly higher than that of CS alone. The highest denitrification rate of CS-KHCO3 was 62 %, whereas the denitrification performance of CS-KOH and CS-K<sub>2</sub>CO<sub>3</sub> was improved to 50 % and 48 %, respectively. From the data in Fig. 2(a), the effect of the reaction temperature on the NO removal rate of the CS exhibited relatively minor fluctuations. In the temperature range of 100-250 °C, the NO removal rate remained below 45 %, and the NO adsorption capacity was limited. As the reaction temperature increased from 100°C to 200 °C, the value of  $T_{NO}$ 45 % increased with increasing temperature at 120 min for CS-KOH, 75 min for CS-K<sub>2</sub>CO<sub>3</sub>, and 120 min for CS-KHCO<sub>3</sub>. During this period, the NO adsorption capacities of CS-KOH, CS-K<sub>2</sub>CO<sub>3</sub>, and CS-KHCO<sub>3</sub> were 2.48, 2.24, and 3.05 times higher than those of CS. However, as time progressed, NO removal decreased, possibly due to the coverage of active sites by the products after SO<sub>2</sub>/NO adsorption (Guo et al., 2022). However, when the reaction temperature reached 250 °C, the NO removal rate of different modified CS decreased. This is because SO<sub>2</sub> has a higher boiling point than NO,



**Fig. 2.** Efficiency of SO<sub>2</sub>/NO removal at different temperatures: (a)(b) CS; (c)(d) CS-KOH; (e)(f) CS-K<sub>2</sub>CO<sub>3</sub>; (g)(h) CS-KHCO<sub>3</sub>. Reaction conditions: gas flow rate of 200 mL·min<sup>-1</sup>; initial concentrations of SO<sub>2</sub> at 1500 mg·m<sup>-3</sup>, NO at 700 mg·m<sup>-3</sup>, and O<sub>2</sub> at 5 %.



Fig. 3. Adsorption capacity of potassium-modified CS for SO2/NO at various temperatures.

making NO more prone to diffusion than SO<sub>2</sub> at lower temperatures (100 °C) (Silas et al., 2018). Molecules with higher boiling points have stronger van der Waals forces, whereas those with lower boiling points exhibit weaker intermolecular interactions. Consequently, NO can be readily displaced and desorbed by SO<sub>2</sub> at higher temperatures. Therefore, the feasible denitrification temperature of the modified CS was 200 °C.

As illustrated in Fig. 2(b) and 3(a), the desulfurization rate of CS exhibited relatively minor fluctuations within the range of 100–250 °C, which proved that the effect of reaction temperature on the performance of CS for SO<sub>2</sub> removal was not predominantly evident. The optimal performance of CS in terms of SO<sub>2</sub> removal remained consistent with a 100 % desulfurization rate within 120 min, and its SO<sub>2</sub> adsorption capacity reached 36 mg·g<sup>-1</sup>. From Fig. 2(d), (f), (h), and 3(a), the removal performance of the modified CS for SO<sub>2</sub> decreased slightly at temperatures below 200 °C. However, the T<sub>SO2</sub>75 % values for all three modified CS continued to increase with increasing in temperature. At 200 °C, the SO<sub>2</sub> adsorption capacities of the three materials are essentially equal. This can be attributed to the gradual increase in temperature, which reduced the mass transfer resistance and accelerated the reaction rate, leading to an enhanced SO<sub>2</sub> adsorption capacity (Li et al., 2021).

Table 1 summarizes the optimal reaction temperatures, removal efficiencies, and durations of the potassium-modified calcium carbide slag. It is evident that potassium-modified cs at 200 °C showed the most efficient and stable SO<sub>2</sub>/NO removal. In summary, based on the desulfurization and denitrification rates, the removal capacity of the modified CS can be derived as follows: CS-KHCO<sub>3</sub> > CS-KOH > CS-K<sub>2</sub>CO<sub>3</sub> > CS.

## 3.2. Activation energy of adsorbents

From the above experimental results, the desulfurization performance of the different modified CS exhibited slight variations. However, the denitrification performance was significantly different. Therefore, the reaction activation energy of the modified CS for  $SO_2/NO$  removal was determined. The reaction rate constant *k* in the rate equation of the

#### Table 1

Optimal reaction temperature and efficiency of the modified CS.

Sample	Temperature (°C)	$\eta_{\mathrm{SO2}}(\%)$	T <sub>SO2</sub> 75 % (min)	η <sub>NO</sub> (%)	T <sub>NO</sub> 45 % (min)
CS	100	100	120	30 %	0
CS-KOH	200	100	80	50	120
CS-	200	100	120	48	45
K <sub>2</sub> CO <sub>3</sub> CS- KHCO <sub>3</sub>	200	100	90	62	120

catalytic oxidation can be expressed using the Arrhenius equation (Dou et al., 2020).

as follows:

$$k = A e^{-\frac{Ea}{RT}} \tag{3}$$

where *k* denotes the reaction rate constant (mol·s<sup>-1</sup>·g<sup>-1</sup>); *A* is denotes the pre-exponential factor; *R* denotes the gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>); *T* denotes the reaction temperature (K); and Ea denotes the activation energy (kJ·mol<sup>-1</sup>).

The rate equation of the NO catalytic oxidation of the modified CS is represented by Equation (4). Subsequently, Equation (4) is incorporated into Equation (3), resulting in Equation (5). Simultaneously, the logarithm of both sides of Equation (5) is taken, yielding Equation (6). The conversion rate of NO at different temperatures was measured while maintaining the inlet concentration constant, and the reaction rate *r* was calculated using Equation (7) (Lei et al., 2020). Using Equation (6), a plot can be constructed with  $T^{-1}$  as the x-axis and ln*r* as the y-axis. This plot facilitates the derivation of a linear regression equation. The reaction activation energy (*Ea*) was determined by multiplying the slope of the fitted regression equation by with gas constant *R* (Zheng et al., 2018).

$$r = k[NO]^{\alpha}[O_2]^{\beta} \tag{4}$$

$$r = A e^{-\frac{Ea}{RT}} [NO]^{\alpha} [O_2]^{\beta}$$
(5)

$$\ln r = -\frac{Ea}{RT}\ln A + \alpha \ln[NO] + \beta \ln[O_2]$$
(6)

$$r = \frac{\eta_{NO} C_{NO} Q}{V_m m} \tag{7}$$

where *r* denotes the reaction rate (mol·s<sup>-1</sup>·g<sup>-1</sup>);  $\eta_{NO}$  denotes the NO conversion rate (%);  $C_{NO}$  denotes the NO inlet concentration (mg·m<sup>-3</sup>); *Q* denotes the total gas flow (L·s<sup>-1</sup>); *m*denotes the mass of the adsorbents (g); and  $V_m$  denotes the molar volume of the gas.

As shown in Fig. 4(a)–(d), the correlation coefficients  $R^2$  of the linear regression equations for the NO activation energies of CS, CS-K<sub>2</sub>CO<sub>3</sub>, CS-KOH, and CS-KHCO<sub>3</sub> were 0.9692, 0.9385, 0.9429, and 0.9554, respectively. The calculated activation energies of NO for CS, CS-K<sub>2</sub>CO<sub>3</sub>, CS-KOH, and CS-KHCO<sub>3</sub> were  $-7.2446 \text{ kJ} \cdot \text{mol}^{-1}$ , 15.9048 kJ·mol<sup>-1</sup>, 8.7301 kJ·mol<sup>-1</sup>, and 6.7838 kJ·mol<sup>-1</sup>, respectively. These results demonstrated a significant reduction in the activation energy of the modified CS, indicating higher reaction rates and enhanced catalytic oxidation of NO (Lei et al., 2020). In addition, the negative activation energy of CS suggested a decrease in the reaction rate *r* with increasing temperature, leading to a weakening of the catalytic oxidation of NO



Fig. 4. Linear regression diagram of SO<sub>2</sub>/NO surface activation energy for different materials: (a) (e) CS; (b) (f) CS-K<sub>2</sub>CO<sub>3</sub>; (c) (g) CS-KOH; (d) (h) CS-KHCO<sub>3</sub>.

(Valverde 2015, Jayakumar et al., 2017, Joshi et al., 2018). These findings suggest that modified CS materials promote favorable reactions by effectively reducing energy barriers. Hence, the catalytic mechanism of the modified CS was further changed to improve the catalytic efficiency of NO. As shown in Fig. 4(e)–(h), the activation energy for the SO<sub>2</sub> reaction in CS-  $K_2CO_3$  was 10.10 kJ·mol<sup>-1</sup>, and it remained at 0 kJ·mol<sup>-1</sup> for all other materials. This indicates that  $K_2CO_3$  modification slightly increased the activation energy for CS desulfurization, leading

to a reduced reaction rate. Combined with Fig. 2, it became evident that the lower activation energy of the modified CS reaction promoted easier occurrence of the catalytic process and improved desulfurization and denitrification. The catalytic activities of the different modified CS materials can be ranked as follows: CS-KHCO<sub>3</sub> > CS-KOH > CS-K<sub>2</sub>CO<sub>3</sub>, which is consistent with their respective SO<sub>2</sub>/NO removal performance.



Fig. 5. (a-d) SEM, (e) XRD, (f) FTIR spectra, (g) O 1 s, (h) C 1 s, and (i) K 2p spectra of CS, CS-K<sub>2</sub>CO<sub>3</sub>, CS-KOH, and CS-KHCO<sub>3</sub>.

#### 3.3. Characterization of materials

According to the XRF characterization results, the main compositions of CS are shown in Table S1 (as oxides, wt %), such as CaO (96.96 %), K<sub>2</sub>O (0.05 %), SiO<sub>2</sub> (1.20 %), Fe<sub>2</sub>O<sub>3</sub> (0.80 %), and Al<sub>2</sub>O<sub>3</sub> (0.44 %). To facilitate the comparison, the K2O content was used to express the total potassium oxide (KO<sub>x</sub>) content. Loading potassium onto the CS surface increased its potassium content, with K<sub>2</sub>O reaching 22.92 %, 10.34 %, and 12.20 % for CS-K<sub>2</sub>CO<sub>3</sub>, CS-KOH, and CS-KHCO<sub>3</sub>, respectively, whereas SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> experienced slight decreases. Combining these findings with Fig. 2, the addition of potassium can promote the oxidation efficiency observed in NO, which likely explained the increased denitrification efficiency observed in the modified CS. However, CS-K<sub>2</sub>CO<sub>3</sub> exhibited poor effectiveness in desulfurization and denitrification, which can be attributed to the excessive blockage of pore channels and surface adsorption sites on the surface caused by excessive KO<sub>x</sub> concentration resulting from K<sub>2</sub>CO<sub>3</sub> addition(Yang et al., 2019). The SEM images in Fig. 5(a-d) illustrated the significant changes in the microstructure of CS before and after modification. Ultrasonic impregnation disrupted the CS structure, facilitating accelerated potassium loading on the CS surface. In addition, different potassium modifications vielded distinct microstructures. Fig. 5(a) displayed layered bulk particles of CS with a rough surface, few cracks, and no noticeable pore structure. Fig. 5(b) and 5(c) indicated irregular porous layered surfaces and bulk structures of CS-KOH and CS-K<sub>2</sub>CO<sub>3</sub>, respectively, after ultrasonic impregnation and potassium modification. The CS-KOH particles exhibited small honeycomb pores on the surface and a significant number of channels within the particles. In contrast, CS-K<sub>2</sub>CO<sub>3</sub> displayed fewer small surface pores than CS-KOH, potentially due to pore channel blockage caused by excess KO<sub>x</sub> (Yang et al., 2019). The microstructure of CS-KHCO3 shown in Fig. 5(d) revealed a unique flower cluster-like ordered structure at high resolution, characterized by a loose and uniform appearance. This flower cluster-like microstructure could provide abundant volume and active sites to facilitate the mass transfer of desulfurization and denitrification reaction intermediates (Peng et al., 2021). These microstructural observations were closely linked to CS composition modifications and adherence of potassium to the adsorbent surface (Ding and Liu 2020).

In Fig. 5(e), the XRD spectra of different potassium-modified CS exhibited characteristic peaks of Ca(OH)<sub>2</sub> and some CaCO<sub>3</sub>. The modified CS also indicated certain diffraction peaks corresponding to K2Ca (CO<sub>3</sub>)<sub>2</sub>, K<sub>2</sub>O, and KO<sub>2</sub>. From Fig. 5(e), the intensity of the Ca(OH)<sub>2</sub> diffraction peaks in CS-KHCO<sub>3</sub> and CS-K<sub>2</sub>CO<sub>3</sub> was significantly reduced, whereas the intensity of the Ca(OH)2 diffraction peaks in CS-KOH was higher than that in CS. This observation confirmed that the addition of KHCO3 and K2CO3 reduced the crystallinity of CS, resulting in a more dispersed Ca(OH)<sub>2</sub> in the modified CS (Tang et al., 2015). Moreover, Ca (OH)2 in CS played a crucial role in the reaction process and promoted the formation of desulfurization and denitrification products (Guo et al., 2022). However, the doping of KOH improved the crystallinity of CS. Notably, the XRD spectra in Fig. 5(e) revealed that the characteristic peaks of KO<sub>x</sub> in CS-KHCO<sub>3</sub> were significantly more than those of CS-K<sub>2</sub>CO<sub>3</sub> and CS-KOH, indicating that doped KHCO<sub>3</sub> can facilitate the formation of more KO<sub>x</sub>, which played a critical role in the denitrification process of desulfurization (Li et al., 2022). However, in the modified CS, CaCO<sub>3</sub> easily combined with KO<sub>x</sub>, to form a stable potassium phase containing calcium carbonate and K<sup>+</sup>. This interaction affected the activity of KO<sub>x</sub>, thereby reducing the catalytic capacity of KO<sub>x</sub> and the adsorption capacity of Ca(OH)2 on sulfur oxides (Li et al., 2022). In Fig. 5(e), CS-K<sub>2</sub>CO<sub>3</sub> exhibited numerous characteristic peaks of K<sub>2</sub>Ca  $(CO_3)_2$ , resulting in a reduction in  $KO_x$  content, which may explain the poor desulfurization and denitrification performance of CS-K<sub>2</sub>CO<sub>3</sub>. As shown in Fig. 5(f), the FTIR spectra were employed to investigate the surface functional groups of CS before and after modification(CS, CS-KOH, CS-K<sub>2</sub>CO<sub>3</sub>, and CS-KHCO<sub>3</sub>). The FTIR absorption peaks of the modified CS did not exhibit new appearances or disappearances

compared to CS; instead, only the intensity of the modified CS peaks changed in the infrared spectrum, without the formation of new functional groups. A strong narrow peak at 3643 cm<sup>-1</sup> was observed, representing the O-H bond created by the vibrational pulse. This peak is attributable to the stretching vibration of O-H caused by surface hydroxyl groups and chemically adsorbed potassium water on the adsorbent surface (Cong and Mei 2021). The stretching vibration of the carbonyl C=O surface functional group was represented by an absorption peak at 1430 cm<sup>-1</sup> (Tang et al., 2013, Ding and Liu 2020). The O-CO- band in  $CO_3^2$ , demonstrated peaks at 710 cm<sup>-1</sup> and 869 cm<sup>-1</sup>, corresponding to its in-plane and out-of-plane bending vibrations, respectively (Li and Yi 2020, Ma et al., 2021). After potassium modification, the intensity of the C = O peaks increased due to the activation and oxidation properties of potassium, resulting in the generation of numerous oxygen-containing functional groups (Ding and Liu 2020). Zhao et al. (1994), demonstrated that an increase in oxygen-containing functional groups improved the adsorption capacity of SO<sub>2</sub> and NO. Interestingly, although CS and modified CS shared similar characteristics, CS-KOH and CS-KHCO<sub>3</sub> exhibited a stronger C=O stretching pattern than CS and CS-K<sub>2</sub>CO<sub>3</sub>, which indicated a higher concentration of oxygen functional groups in CS-KOH and CS-KHCO<sub>3</sub>. In summary, the adsorption capacity of modified CS was closely related to the concentration of its surface organic functional groups.

The high-resolution XPS spectra of O 1 s, C 1 s, and K 2p for CS, CS-KOH, CS-K<sub>2</sub>CO<sub>3</sub>, and CS-KHCO<sub>3</sub> are shown in Fig. 5(g)-5(i). Table S2 lists the corresponding binding energies and their relative contents. In Fig. 5(g), the O 1 s spectra of the modified CS and the corresponding fitted curves were illustrated, which can be deconvoluted into two peaks. A unique peak at a binding energy of 531 eV corresponds to the formation of lattice oxygen (denoted as O<sub>lat</sub>, such as O<sup>2-</sup>) by the defective oxides present in the modified CS. Surface adsorbed oxygen (denoted as  $O_{ads}$ , such as  $O_2^2$ , O<sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) in modified CS exhibited a characteristic peak in the range of 531.20 eV-532.90 eV (Panov et al., 2006, Liu and He 2010). It is widely recognized that Oads possesses higher mobility and activity than Olat, thereby accelerating the oxidation process through redox reactions (Liu et al., 2021). In addition, low coordination O<sub>ads</sub> greatly facilitated the formation of surface oxygen groups, such as carbonyl (-COOH), surface-active chemisorbed oxygen (O2, O, etc.), and surface hydroxyl groups (-OH). Table S2 illustrates that the  $O_{ads}$  content of CS was 14.93 %, and the loading of potassium resulted in higher peak area ratios of Oads than CS for CS-KOH and CS-KHCO<sub>3</sub>, which reached 18.54 % and 47.47 %, respectively. In contrast, the O<sub>ads</sub> content of CS-K<sub>2</sub>CO<sub>3</sub> was only 2.69 %, which could be attributed to the fact that K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> covered the CS surface and blocked the pore channels, consistent with the SEM results of CS-K2CO3. The content of O<sub>ads</sub> followed the order: CS-KHCO<sub>3</sub> > CS-KOH > CS > CS-K<sub>2</sub>CO<sub>3</sub>, with CS-KHCO<sub>3</sub> showing the highest percentage of O<sub>ads</sub>. This indicated that CS-KOH and CS-KHCO3 possessed a higher content of surface hydroxyl and/or surface active chemisorbed oxygen. The increased Oads content enhanced the oxidation ability of the modified CS at low temperatures, which aligned with the previous analysis (Ding and Liu 2020). Tiwari et al. (2018) concluded that Oads indicated alkaline properties; thus, high levels of  $\boldsymbol{O}_{ads}$  can be more favorable for the adsorption of acidic gases. The measured C1 s spectra of the modified CS are shown in Fig. 5 (h). The C 1 s peak was deconvoluted into three functional groups, including graphitic carbon (C–C,  $284.8 \pm 0.1$  eV), carbonyl (C=O, 287.7 $\pm$  0.2 eV), and carboxyl and/or ester groups (–COO, 289.6  $\pm$  0.2 eV) (Li et al., 2021, Li et al., 2022). As shown in Table S2, CS- KHCO<sub>3</sub>, CS-KOH, and CS-K<sub>2</sub>CO<sub>3</sub> demonstrated lower C-O contents than CS, but higher C=O contents. The C=O content of CS was 11.17 %, and after modification, the C=O contents of CS-KOH, CS-K<sub>2</sub>CO<sub>3</sub>, and CS-KHCO<sub>3</sub> increased to 23.46 %, 14.41 %, and 21.35 %, respectively. This increase may be attributed to the basicity of potassium, which introduces defective or unpaired electrons on the CS surface. These electrons promote the formation of surface functional groups via the absorption of oxygen from the environment (Liu et al., 2014). This was particularly

evident on the CS-KOH surface. Combining these observations with Fig. 2, it was evident that the adsorption capacities of CS-KHCO<sub>3</sub>, CS-KOH, and CS-K<sub>2</sub>CO<sub>3</sub> for SO<sub>2</sub>/NO were superior to that of CS. This can be attributed to the higher C = O content in CS-KHCO<sub>3</sub>, CS-KOH, and CS-K<sub>2</sub>CO<sub>3</sub>, which was favorable to improve the adsorption capacity of SO<sub>2</sub>/ NO. According to the literature(Zhang et al., 2017), the essential property of C = O Brønsted is the active center of SO<sub>2</sub>/NO oxidation. As shown in Fig. 5(i), the K 2p spectrum presented two components at 292.72 eV and 295.42 eV, confirming the presence of K ions. The peaks of K 2p1/2 were observed at 295.40 eV and 295.71 eV, while the peaks of K 2p3/2 appeared at 292.47 eV and 293.14 eV, respectively, with evident differences in the relative intensities. The binding energies of the different valence states of K cations (K<sup>4+</sup> and K<sup>+</sup>) with K 2p electrons were different. As observed in Fig. 5(d) and Table S2, the relative  $K^{4+}$ content on the surface of CS-KOH and CS-KHCO3 was higher than that of CS-K<sub>2</sub>CO<sub>3</sub>. This is in accordance with the XRD results, indicating that CS-KOH doped with KHCO<sub>3</sub> promoted the formation of more KO<sub>2</sub>. KHCO<sub>3</sub> loading led to the generation of oxygen vacancies on the modified CS surface and increased the O<sub>ads</sub> content by absorbing oxygen from the environment, which was consistent with the Oads content in the O 1 s spectrum. This may account for the higher effectiveness of CS-KHCO<sub>3</sub> in desulfurization and denitrification. It can be inferred that a certain amount of K<sup>4+</sup> can potentiate the oxidation of NO and SO<sub>2</sub> during the redox process, thereby promoting the redox reaction and increasing the adsorption activity of CS. These results are consistent with those presented in Figs. 2 and 3.

#### 3.4. Mechanism analysis

To gain deeper understanding of the mechanisms underlying desulfurization and denitrification, the reaction materials were examined by XRD, CO<sub>2</sub>-TPD, and XPS. The obtained results are presented in Fig. 6. Fig. 6(a) displayed the XRD patterns of several modified CS samples after desulfurization and denitrification. Following these processes, multiple distinctive diffraction peaks corresponding to K<sub>2</sub>SO<sub>4</sub>, KNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, CaSO<sub>4</sub>, and CaSO<sub>3</sub> were observed (Guo et al., 2022). The production of Ca(NO<sub>3</sub>)<sub>2</sub>, CaSO<sub>4</sub>, and CaSO<sub>3</sub> suggested the participation of Ca(OH)<sub>2</sub> in the denitrification reaction during desulfurization. In comparison with Fig. 4(e), the intensity of the diffraction peaks related to  $KO_x$  decreased after desulfurization and denitrification, accompanied by  $K_2SO_4$  and  $KNO_3$  diffraction peaks, indicating the involvement of  $KO_2$  in the reaction. Meanwhile, a new  $K_2Ca(CO_3)_2$  diffraction peak was detected, indicating the formation of stable  $K_2Ca(CO_3)_2$  during the desulfurization and denitrification. This formation can lead to a decline in the activity of CS after modification. Especially, the intensity of the diffraction peak of  $K_2Ca(CO_3)_2$  followed the CS- $K_2CO_3$  reaction, which generated a substantial amount of  $K_2Ca(CO_3)_2$ . The combined analysis in Fig. 2 further demonstrated that  $K_2Ca(CO_3)_2$  hindered the denitrification and desulfurization.

To observe the variation in the alkaline sites on the surfaces of the materials, CO2-TPD experiments were conducted on both the premodified and post-modified materials. The experimental results, according to the experimental findings illustrated in Fig. 6(b), revealed the presence of distinct desorption peaks at weak basic sites (0-200 °C), medium basic sites (200-400 °C), and strong basic sites (>400 °C) (de Oliveira et al., 2022). Compared with CS, the modified CS exhibited the following changes: (i) a slight reduction in the intensity of weakly basic sites, (ii) relatively unchanged medium basic sites, and (iii) a significant increase in the intensity of strongly basic sites for CS-KOH and CS-KHCO<sub>3</sub>. This further indicated that potassium addition had a substantial impact on the distribution of the basic sites in the CS. From Fig. 6(b) and 2, CS exhibited a larger peak area in the weakly basic site, implying a greater number of basic sites and enhanced desulfurization efficiency. This indicated that the removal of SO<sub>2</sub> occurred mainly through chemisorption and an acid-base neutralization reaction. However, the weak base sites of the modified CS were reduced, whereas the denitrification effect of the modified adsorbents was significantly enhanced, which can be attributed to the promotion of denitrification by KO<sub>x</sub>.

The C 1 s spectrum of modified CS obtained after the reaction is shown in Fig. 6(c). Upon comparison with Fig. 4(h), it was evident that the surface functional groups underwent significant changes following the utilization of the modified CS in the desulfurization and denitrification processes. The contents of C = O in UCS-KOH, UCS-K<sub>2</sub>CO<sub>3</sub>, and UCS-KHCO<sub>3</sub> were reduced by 23.46 %, 14.41 %, and 11.09 %,



Fig. 6. (a) XRD patterns, (b) CO<sub>2</sub>-TPD profiles, (c) C 1 s, (d) O 1 s, (e) S 2p, and (f) N 1 s spectra of UCS-KHCO<sub>3</sub>, UCS-KOH, and UCS-K<sub>2</sub>CO<sub>3</sub>.

respectively. Conversely, the C-O content in UCS-KOH increased to 45.5 %, and typical C-O (285.0  $\pm$  0.5 eV) peaks were observed for UCS-K<sub>2</sub>CO<sub>3</sub> and UCS-KHCO3 with 55.13 % and 33.89 %, respectively. This indicated the involvement of C = O in the oxidation of  $SO_2/NO$  and its consumption in the  $SO_2/NO$  removal process. The presence of C = O, influenced the adsorption capacity of the modified CS surface by facilitating electron transfer to the adsorbed oxygen species (Fang et al., 2017). Considering the analysis in Figs. 2 and 4(h), C = O, serving as the main active site for acid gas chemisorption (Li et al., 2003, Wang et al., 2020), may play a crucial role in the effective simultaneous desulfurization and denitrification achieved by the modified CS. The O 1 s spectra of UCS-KOH, UCS-K2CO3, and UCS-KHCO3, and their fitted curves are presented in Fig. 6(d). Comparing Tables S2 and S3, a significant decline of the Oads content on UCS-KHCO3 was observed, dropping from 47.47 % to 38.34 %. Only Olat characteristic peaks existed for UCS-KOH and UCS-K2CO3, with the disappearance of the characteristic peaks of Oads. The results indicated a significant decrease in the value of  $O_{ads}$  after the reaction, which further determined the involvement of adsorbed oxygen in the reaction and possibly played a key role in the oxidation reaction of the modified CS. Fig. 6(d) illustrated the XPS results of S 2p after desulfurization and denitrification of different modified CS. The S 2p in the XPS spectrum demonstrated two peaks at 168.67 eV and 169.81 eV for sulfate  $SO_4^2$  and sulfite  $SO_3^2$  2-3 (Li et al., 2016, Lian et al., 2017, Arfaoui et al., 2018, Li et al., 2018), respectively. This suggested that Ca<sup>2+</sup> readily formed sulfur-containing substances with  $SO_4^2$  and  $SO_3^2$  on the surface of the modified CS. These sulfates and sulfites adhered to the material surface, obstructing the pore channels and covering the active sites, which ultimately led to the deactivation of the modified CS due to SO<sub>2</sub> poisoning(Wu et al., 2016, Silas et al., 2018). The formation of NO<sub>3</sub> was responsible for the peak in the N 1 s XPS spectrum of UCS-KHCO3 at 407 eV (Hao et al., 2017), as shown in Fig. 6(f). In contrast, UCS-KOH and UCS-K<sub>2</sub>CO<sub>3</sub> failed to form characteristic peaks, probably due to the partial occupation of surfaceactive sites by the formation of sulfate, resulting in a low level of surface-bound N. The XPS data further confirmed the production of sulfate, sulfite, and nitrate during the reaction, which is consistent with Fig. 6(a).

Based on the above process, the successive steps involved in the desulfurization of the modified CS can be postulated through the following equations (Eq. (8) to Eq. (13)) (Li et al., 2022). Firstly, SO<sub>2</sub> in the flue gas was converted to the adsorbed state SO<sub>2</sub>(ads). The Brønsted basic sites on the Ca(OH)<sub>2</sub> surface react with SO<sub>2</sub>(ads) to form CaSO<sub>3</sub>. Furthermore, the modified CS containing KO<sub>2</sub>, which has potent oxidizing properties, supplied active oxygen (O\*) and facilitated the desulfurization process. As a result, O\* originating from the modified CS and O<sub>2</sub> in the flue gas oxidized SO<sub>2</sub>(ads) into SO<sub>3</sub>(ads). Finally, the formed SO<sub>3</sub>(ads) was combined with Ca(OH)<sub>2</sub> and K<sub>2</sub>O on the modified CS to form CaSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>. Meanwhile, the reaction mechanism of the denitrification process was speculated and summarized as the following equations (Eq. (14) to Eq. (18)). In the process of denitrification, NO was converted to the adsorbed state and subsequently oxidized by O\* to generate NO<sub>2</sub>(ads), and NO<sub>2</sub>(ads) dimerizes to N<sub>2</sub>O<sub>4</sub>(ads). In addition, the formation of N<sub>2</sub>O<sub>4</sub> was also promoted by O<sub>2</sub>. N<sub>2</sub>O<sub>4</sub> isomerizes to NO<sup>+</sup>NO<sub>3</sub><sup>-</sup> at low temperatures (Wu et al., 2012) and then reacts with Ca (OH)<sub>2</sub> in the presence of O\* to form Ca(NO<sub>3</sub>)<sub>2</sub> according to an acid-base reaction (Liu et al., 2011). The reaction intermediate products NO<sub>2</sub>(ads) and K<sub>2</sub>O combine to form KNO<sub>3</sub>. Deactivation of the modified CS after the reaction was due to the production of sulphate, sulphite, and nitrate. These substances covered the surface of the modified CS, obstructing the access of SO<sub>2</sub>/NO to the active sites, thus resulting in a decrease in the adsorption activity of the modified CS(Li et al., 2022).

$$SO_2(g) \rightarrow SO_2(ads)$$
 (8)

$$2KO_2 \rightarrow K_2O + 3O^* \tag{9}$$

$$SO_2(ads) + O^* \rightarrow SO_3(ads)$$
 (11)

$$Ca(OH)_2 + SO_3(ads) \rightarrow CaSO_4 + H_2O \tag{12}$$

$$K_2O + SO_3(ads) \rightarrow K_2SO_4 \tag{13}$$

$$NO(g) \rightarrow NO(ads)$$
 (14)

$$NO(ads) + O^*/O_2 \rightarrow NO_2(ads) + NO_2(ads) \rightarrow N_2O_4(ads)$$
(15)

$$N_2O_4(ads) \rightarrow NO^+ NO_3^- \tag{16}$$

$$Ca(OH)_{2} + NO^{+}NO_{3}^{-} + O^{*} \rightarrow Ca(NO_{3})_{2} + H_{2}O$$
(17)

$$K_2O + 2NO_2(ads) + O^* \rightarrow 2KNO_3 \tag{18}$$

#### 4. Conclusions

In this study, potassium modification of CS significantly improved its desulfurization and denitrification performance. At 200 °C, T<sub>SO2</sub>75% of CS-KOH, CS-K<sub>2</sub>CO<sub>3</sub> and CS-KHCO<sub>3</sub> were maintained at 120 min, and T<sub>NO</sub>45 % of denitrification rates were for 120 min, 75 min, and 120 min, respectively. The surface characteristics of the modified CS particles varied after potassium modification: CS-KOH displayed small honeycomb-like pores on the surface, CS-K<sub>2</sub>CO<sub>3</sub> exhibited a laminar surface, and CS-KHCO<sub>3</sub> formed a unique flower cluster-like structure. The results indicated that the NO catalytic activation energy of the modified CS was reduced, which lowered the reaction barriers of CS. The contents of  $KO_x$ , C = O, and  $O_{ads}$  in different modified CS were responsible for the variations in the activity effects, while the doping of KOH and  $KHCO_3$  could effectively increase the contents of C = O and Oads. The presence of Ca(OH)2 in the modified CS presented excellent  $\mathrm{SO}_2$  trapping ability, and the presence of  $\mathrm{K}^{4+}$  facilitated the conversion of NO to NO<sub>3</sub> and SO<sub>2</sub> to SO<sub>4</sub><sup>2</sup>. Desulfurization and denitrification reactions are hampered by  $K_2Ca(CO_3)_2$ , which can be generated during the modification process. Moreover, sulfates, sulfites, and nitrates produced by the reactions can potentially deactivate the activation sites in the modified CS, which can further result in reduced adsorption activity.

#### CRediT authorship contribution statement

Fang Wang: Conceptualization, Supervision, Funding acquisition. Shaojun Luo: Investigation, Visualization, Writing – original draft. Hui Li: Data curation. Jiyun Gao: Data curation, Methodology. Futing Xia: Data curation, Formal analysis. Shuo Cui: Project administration, Resources. Lijuan Jia: Supervision, Project administration, Funding acquisition. Jiayu Feng: Project administration, Validation. Mingwu Xiang: Conceptualization, Formal analysis.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51968075).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2023.105363.

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