Research into the reaction process and the effect of reaction conditions on the simultaneous removal of H$_2$S, COS and CS$_2$ at low temperature

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In this work, tobacco stem active carbon (TSAC) catalysts loaded on to CuO and Fe$_2$O$_3$ were prepared by a sol–gel method and used for the simultaneous removal of hydrogen sulfide (H$_2$S), carbonyl sulfide (COS) and carbon disulfide (CS$_2$). The influences of the operating conditions such as reaction temperature, relative humidity (RH), O$_2$ concentration, and gas hourly space velocity (GHSV) were discussed. DRIFTS results showed that the deactivation was attributed to the generation of S and sulfates. H$_2$O promoted the generation of sulfate. The enhancement of the hydrolysis of COS/CS$_2$ was due to the promotion of H$_2$S oxidation by O$_2$. A high GHSV decreased the contact time between the gases and the catalyst. Meanwhile, a high GHSV was not conducive to the adsorption of gases on the surface of the catalyst. XPS results indicated that the deactivation of the catalyst was attributable to the formation of S containing components, such as thiol/thioether, S, –SO$^-_{\text{aq}}$ and sulfate. BET results indicated that the adsorptive ability of the catalyst was related to the microporous volume and surface area.

1. Introduction

H$_2$S, COS and CS$_2$ are major sulfur-containing compounds produced from industrial tail gas, such as closed carbide furnace tail gas.$^{3-5}$ H$_2$S, COS and CS$_2$ not only pollute the natural environment but also cause corrosion to reactors, and poison catalysts.$^{6,7}$ Meanwhile, there is a small amount of vapor and oxygen in the closed carbide furnace tail gas. A catalytic hydrolysis method has been widely developed to remove COS and CS$_2$ from industrial tail gas.$^{3,8,9}$ The hydrolysis product H$_2$S can be removed by a catalytic oxidation method. Raw materials that have undergone desulfurization are less hazardous and corrosive, and thus can be used to produce other products. Therefore, it is of great significance to remove H$_2$S, COS and CS$_2$.

In previous studies, many researchers focused on the influence of catalyst characterization on the removal of H$_2$S, COS and CS$_2$. However, the influence of reaction conditions is also important for the removal of H$_2$S, COS and CS$_2$. Song et al. investigated the influence of reaction conditions on the hydrolysis of COS and CS$_2$. The results showed that reaction conditions affected the reaction rate and the reaction product species. Furthermore, the reaction conditions directly affected the reaction process, such as the change of surface functional groups. In our previous studies, it could be found that –OH, –COO, and –C=O groups played important roles in the desulfurization process.$^{17-19}$ –OH promoted the hydrolysis of COS and CS$_2$, and –COO and –C=O groups promoted the oxidation of H$_2$S.$^{20-22}$ Furthermore, CO$_2$ could be converted into –COO and –C=O groups during this process, which enhanced the removal of H$_2$S. However, there are few studies on the simultaneous removal of H$_2$S, COS and CS$_2$, and the detailed changes in surface functional groups during the desulfurization process under different reaction conditions were unknown. Therefore, this study is important and valuable.

Yunnan province is the main area that produces tobacco. However, a large number of tobacco stems are discarded every year. Previous studies showed that tobacco stems could be used for the preparation of biochar, and this showed a high adsorption ability.$^{23,24}$ Therefore, the preparation of tobacco stem biochar could solve the disposal problems of waste tobacco stems. In this work, the influence of reaction conditions (reaction temperature, relative humidity (RH), O$_2$ content, and gas hourly space velocity (GHSV)) on the removal of H$_2$S, COS and CS$_2$ was investigated. Meanwhile, the influence of reaction conditions on the change of surface functional groups was analyzed by DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy), BET (surface area and pore structure analysis) and XPS (X-ray photoelectron spectroscopy).
2. Materials and methods

2.1 Catalyst preparation

The raw material of walnut shell biochar was from Yunnan province. The main preparation parameters were firstly that the tobacco stem was washed twice with water and smashed to 4 mesh size for use in this study. Then, the walnut shell was calcined at 700 °C for 1 h under nitrogen (N2) conditions, and sieved to 40–60 mesh size. After that, the carbonized material and the activator (CO2) were mixed together, and calcined at 800 °C for 1 h.

Secondly, a colloidal solution was made with certain amounts of Cu(NO3)2·3H2O solution, Fe(NO3)3·6H2O solution and K2CO3 solution. The activated carbon catalysts were supported by the desired proportions (mass fraction of CuO was 10% and Cu/Fe = 10/1). Then, the samples were dipped into ultrasonic conditions for 30 min, dried at 100 °C in the drying oven and calcined at 400 °C at a heating rate of 5 °C min⁻¹ for 4 h under nitrogen (N2) conditions. Lastly, the catalysts were impregnated by 5% (mass fraction) KOH, and kept under ultrasonic conditions for 10 min, then dried for 6 h at 100 °C in the drying oven to get the catalyst (Cu–Fe/TSAC) needed for the experiments. Cu–Fe/TSAC showed a high desulfurization efficiency, and the sulfur capacity was 231.28 mgS g⁻¹.

2.2 Catalytic activity measurements

Desulfurization tests were performed in a fixed-bed quartz reactor (3 mm inside diameter, 140 mm length) under atmospheric pressure (Fig. 1). H2S, COS and CS2 from gas cylinders (1% H2S in N2; 1% COS in N2; 0.3% CS2 in N2) were diluted with N2 (99.99%) to the required concentrations (H2S: 500 ppm; COS: 400 ppm; CS2: 60 ppm). The gas hourly space velocity (GHSV) of the reaction mixture was standardized at 10 000–20 000 h⁻¹. The water comes from a saturator system, and the relative humidity (RH) was 0–60%. The reaction temperature of this reactor was controlled at 50–70 °C by a water-bath with a circulating pump, with an accuracy of ±0.1 °C. FULI 9790II gas chromatography was used to analyze the total H2S, COS and CS2 concentrations of the gaseous feed and effluent from the reactor. The conversion rates of H2S, COS and CS2 are achieved according to eqn (1).

\[
\text{H}_2\text{S(COS, CS}_2) \text{ conversion (\%)} = \frac{\text{H}_2\text{S(COS, CS}_2)_{\text{inlet}} - \text{H}_2\text{S(COS, CS}_2)_{\text{outlet}}}{\text{H}_2\text{S(COS, CS}_2)_{\text{inlet}}} \times 100
\]

The sulfur capacity (mgS g⁻¹ catalyst) is defined as the sulfur deposition per unit mass of desulfurizer agent in H2S, COS and CS2 between time points (ending at 85% conversion).

2.3 Characterization

DRIFTS spectra were collected using a Nicolet iS50 FTIR spectrometer equipped with a smart collector. Mass flow controllers were used to control the volume flow of different gases to the required concentrations. The heating cable controlled the temperature (70 °C) of mixed gas until it entered the reactor. A reactor heater controlled the temperature (70 °C) of the reactor in the DRIFTS experiments. In this case, it ensured that the reaction temperature of the gas phase and the solid phase were the same. IR spectra were recorded by accumulating 100 scans at a resolution of 4 cm⁻¹. Nitrogen adsorption–desorption isotherms were obtained by a Quantachrome surface area analyzer instrument. Before the measurement, the samples were outgassed under vacuum at 393 K for 24 h. Specific surface areas, and mesoporous and micropore adsorption–desorption isotherms were calculated by Brunauer–Emmett–Teller (BET), Barret–Joyner–Halenda (BJH) and Horvath–Kawazoe (HK) methods, respectively. XPS (ESCALAB 250) analysis was performed using Al Kα radiation, where the energy of the Al target powered was 200 W.

3. Results and discussion

3.1 Effect of reaction temperatures on the simultaneous removal of H2S, COS and CS2

The influence of reaction temperatures on the catalytic performance of the Cu–Fe/TSAC catalyst is illustrated in Fig. 2. The conversion of H2S, COS and CS2 first increased and then decreased with increasing temperature, and was highest at 60 °C. The H2S, COS and CS2 conversion was 100% in the initial 600, 150 and 180 min respectively. As shown in Fig. 2(d), the sulfur capacity first increased and then decreased with increasing reaction temperatures. The highest sulfur capacity (231.28 mgS g⁻¹) was achieved at 60 °C.

The reaction rates of simultaneous catalytic hydrolysis of COS and CS2 and catalytic oxidation of H2S were poor at low temperatures. Therefore, with increasing reaction temperature, the sulfur capacity was increased and the reaction rate of catalytic hydrolysis can be increased, and the hydrolysis reaction could occur more easily. However, the conversion of H2S to S or
sulfate on Cu–Fe/TSAC involves parallel reactions. With increasing reaction temperatures, the yield rate of sulfuric acid increases faster than that of sulfur. At higher temperatures, H₂S can be oxidized to sulfate more easily, and the higher concentration of SO₄²⁻ poisons the hydrolysis activity.²⁵ The majority of the products on the exhausted Cu–Fe/TSAC were S/SO₄²⁻ species which accumulated on the active carbon’s surface and had a negative effect on the hydrolysis activity. Thus, the removal efficiency of H₂S, COS and CS₂ declined sharply at 70 °C.

DRIFTS results were used to further study the catalytic reaction of Cu–Fe/TSAC at different temperatures. As shown in Fig. 3, the Cu–Fe/TSAC surface generates CO₂ (2363 cm⁻¹), C=O groups (1604 cm⁻¹), C–S groups (2080 cm⁻¹) and S–O groups (1140 cm⁻¹ and 1307 cm⁻¹) as the reaction proceeds.¹,²⁶,²⁷ Furthermore, CO₂ was produced as the reaction time progressed, which can prove that the reaction is indeed the hydrolysis of COS and CS₂. The formation of S–O groups can prove that the H₂S was oxidized. Compared with reactions at 60 °C and 70 °C, fewer S–O groups were generated at 50 °C. This indicated that a temperature of 50 °C was not conducive to the oxidation of H₂S. Compared with reactions at 50 °C and 60 °C, more S–O groups and fewer C–S groups were generated at 70 °C. This indicated that a temperature of 70 °C enhanced the
hydrolysis of COS/CS₂ and the oxidation of H₂S. However, excessive oxidation of H₂S could generate more sulfate, which could lead to the deactivation of the catalyst. At the temperature of 60 °C, the number of C=O groups increased and the amount of CO₂ decreased, which indicated that CO₂ could be converted into C=O groups in the reaction. As a result, the catalyst has a good adsorptive ability for COS/CS₂/H₂S and a good oxidation ability for H₂S over time. Therefore, a temperature of 60 °C is conducive to the hydrolysis of COS/CS₂ and the oxidation of H₂S. The result was in accordance with the activity experiment.

3.2 Effects of RH on the simultaneous removal of H₂S, COS and CS₂

The effects of RH on H₂S, COS and CS₂ removal were studied by introducing feed gas through a humidifier. Influences of different RHs on the catalytic performance are plotted in Fig. 4. Removal efficiency for H₂S, COS and CS₂ first increased and then decreased with increasing RH. Low RH should benefit the hydrolysis and oxidation activities. When the RH was 49%, the catalyst showed the best activity, as 100% H₂S, COS and CS₂ conversion was maintained for about 600 min, 150 min and 180 min respectively. As shown in Fig. 4(d), the sulfur capacity first increased and then decreased with increasing RH. The sulfur capacity was highest (231.28 mgS g⁻¹) when the RH was 49%. The sulfur capacity decreased to 176.50 mgS g⁻¹ at the RH of 60%. The selective catalytic oxidation of H₂S to S or HS⁻ will be easier in the presence of less vapor. The fact that excessive water could restrain catalytic activity might be due to competition between H₂S (COS or CS₂) and vapor for the same active sites of the catalyst. Another reason is that the pores of the catalyst's surface will form water films when the RH reaches a certain amount. Although the formation of water films would provide more accommodating spaces for the product, excessive water films may stop H₂S, COS and CS₂ diffusing on the hydrolysis center and inhibit the catalytic hydrolysis reaction.

In order to further investigate the effect of different RHs on the conversion of H₂S, COS and CS₂ over Cu–Fe/TSAC, DRIFTS measurements of the catalytic reactions over Cu–Fe/TSAC were taken. As shown in Fig. 5, there was no obvious CO₂ peak when the reaction was performed at 0% RH. This indicated that the removal of COS/CS₂ was an adsorption process without H₂O. After introducing H₂O (49% RH), a peak due to CO₂ appeared over time. This proved that the removal of COS/CS₂ with H₂O was due to a hydrolysis process. Furthermore, more S-O groups were generated when the RH was 49%, which indicated that H₂O promoted the generation of sulfate. Meanwhile, the decrease in CO₂ and the increase in C=O groups indicated that H₂O promoted the conversion of CO₂. It can be deduced that the catalytic hydrolysis reaction occurs on the surface of Cu–Fe/TSAC, where the hydrolysis of COS and CS₂ produces CO₂ and H₂S.

3.3 Effect of O₂ content on the simultaneous removal of H₂S, COS and CS₂

The curves plotted in Fig. 6 show the effect of O₂ content on the removal efficiency of H₂S, COS and CS₂. It is very difficult to control the oxygen content below 0.5%, although we wanted to
investigate the lower O2 content. So the non-oxygen conditions were investigated. What is more, the O2 content is extremely low, even close to zero, in closed carbide furnace tail gas which is a reductive atmosphere. The catalytic removal efficiency initially increased and then decreased with increasing O2 content. When the O2 content was 0.5%, the removal efficiency of H2S, COS and CS2 was highest. 100% H2S, COS and CS2 conversion was maintained for about 600 min, 150 min, 180 min respectively. As shown in Fig. 6(d), the sulfur capacity first increased and then decreased with the increase in O2 content. The sulfur capacity was 231.28 mgS g\textsuperscript{-1}/C0\textsubscript{0} when the O2 content was 0%. When the O2 content was 0.5%, the sulfur capacity increased to 239.18 mgS g\textsuperscript{-1}. With a further increase in O2 content, the sulfur capacity decreased. The sulfur capacity was only 133.98 mgS g\textsuperscript{-1}/C0\textsubscript{0} when the O2 content was 5%.

It is clear that the addition of a little O2 enhanced the catalytic activity in the COS and CS2 hydrolysis. The reason may be that sufficient oxygen can increase the oxidation of H2S and promote the catalytic hydrolysis of COS and CS2. The oxidation rate of H2S speeds up with the increasing oxygen content. This will lead to the generation of more sulfate, with the inhibition effect greater than the promotion effect.

In order to further investigate the effect of different amounts of O2 on the conversion of H2S, COS and CS2 from Cu–Fe/TSAC, DRIFTS measurements of the catalytic reaction over Cu–Fe/TSAC were taken. As shown in Fig. 7, more S–O groups (related to C=O groups) appeared when the reaction was performed below 5% O2. This indicated that O2 was conducive to the removal of H2S due to the oxidation of H2S.\textsuperscript{27} Meanwhile, fewer C=O groups appeared when the O2 content was 5%, which indicated that O2 mainly promoted the oxidation of H2S but not the conversion of C=O groups.

Fig. 5 DRIFTS spectra of reactions at different RHs (reaction conditions: 500 ppm H2S; 400 ppm COS; 60 ppm CS2; reaction temperature = 60 °C; GHSV = 10 000 h\textsuperscript{-1}; O2 = 0%).

Fig. 6 Effect of O2 content on the simultaneous removal of (a) H2S, (b) COS, and (c) CS2, and (d) sulfur capacity (reaction conditions: 500 ppm H2S; 400 ppm COS; 60 ppm CS2; reaction temperature = 60 °C; RH = 49%; GHSV = 10 000 h\textsuperscript{-1}).
3.4 Effect of the gas hourly space velocity on the simultaneous removal of H$_2$S, COS and CS$_2$

As shown in Fig. 8, the removal efficiency for H$_2$S, COS and CS$_2$ decreases with increasing GHSV. 100% H$_2$S, COS and CS$_2$ conversion was maintained for about 600 min, 150 min and 180 min respectively when the GHSV was 10 000 h$^{-1}$. As shown in Fig. 8(d), the sulfur capacity was 231.28 mgS g$^{-1}$ when the GHSV was 10 000 h$^{-1}$. The sulfur capacity decreased with increasing GHSV, and the capacity was 165.55 mgS g$^{-1}$ when the GHSV was 20 000 h$^{-1}$. At low GHSV, more gases could be adsorbed on the surface of the catalyst. As a result, the catalytic hydrolysis and catalytic oxidation reactions could occur fully. However, a high GHSV decreased the contact time between the gases and the catalyst. This led to the decrease of reaction time and conversion efficiency. Meanwhile, a high GHSV was not conducive to the adsorption of gases on the surface of the catalyst. This further decreased the catalytic efficiency.

3.5 BET results and reaction process analysis

Nitrogen adsorption isotherms and microporous size distribution for fresh and deactivated Cu–Fe/TSAC are shown in Fig. 9 and Table 1. As shown in Fig. 9 and Table 1, Cu–Fe/TSAC had the characteristics of surface area (554 m$^2$ g$^{-1}$), microporous volume (0.21 cm$^3$ g$^{-1}$) and total pore volume (0.29 cm$^3$ g$^{-1}$). The N$_2$ adsorption quantity, microporous volume and surface area in the deactivated catalyst obviously decreased, which indicated that the adsorptive ability of the catalyst decreased over time. This affected the desulfurization ability of the catalyst. The XPS characterization results and the data of fresh and deactivated Cu–Fe/TSAC (S2p) are shown in Fig. 10 and Table 2. From the XPS results, it could be found that the thiol/thioether, S, –SO$^-$, and sulfate amounts increased from 0% to 1.92%, 2.90%, 0.83% and 1.25% respectively. This indicated that the deactivation of...
the catalyst was attributed to the formation of S containing components, such as thiol/thioether, S, \(-\text{SO}^-\) and sulfate. Combined with the BET results, the formation of CuO led to the decrease of the microporous volume and surface area.

According to previous experimental results, the removal processes of COS, CS\(_2\) and H\(_2\)S could be divided into two parts: the catalytic hydrolysis reaction and the catalytic oxidation reaction. In the removal processes, COS and CS\(_2\) were first hydrolyzed into H\(_2\)S, and then H\(_2\)S was oxidized into S/sulfates. Combined with previous DRIFTS results, the removal processes of COS and CS\(_2\) were different. For the removal of CS\(_2\), CS\(_2\) and H\(_2\)O were first adsorbed on the surface of the catalyst, and then the hydrolysis reaction occurred under the effect of surface functional groups and CuO. However, COS had not been found on the deactivated catalyst, which indicated that gaseous COS directly reacted with adsorbed H\(_2\)O under the effect of surface functional groups and CuO. Furthermore, the conversion process for H\(_2\)S could be regarded as H\(_2\)S \(\rightarrow\) S \(\rightarrow\) SO\(_2\) \(\rightarrow\) SO\(_4^{2-}\).

As mentioned above, the possible reaction process diagram is shown in Fig. 11. As shown in Fig. 11, the main reactions on the surface of the catalyst were as follows.

\[
\begin{align*}
    \text{H}_2\text{O} + * & \rightarrow \text{H}_2\text{O}^* \\
    \text{CS}_2 + * & \rightarrow \text{CS}_2^* \\
    \text{CS}_2 + \text{CuO} & \rightarrow \text{CuO}-\text{CS}_2^* \\
    \text{COS} + * & \rightarrow \text{COS}^* \\
    \text{COS} + \text{CuO} & \rightarrow \text{CuO}-\text{COS}^* \\
    2\text{H}_2\text{O} + \text{CuO}-\text{CS}_2^* & \rightarrow \text{CuO}-2\text{H}_2\text{S} + \text{CO}_2^* \\
    \text{H}_2\text{O}^* + \text{CuO}-\text{CS}_2 & \rightarrow \text{CuO}-\text{COS} + \text{H}_2\text{S}^* \\
    \text{H}_2\text{O}^* + \text{CuO}-\text{COS} & \rightarrow \text{CuO}-\text{H}_2\text{S} + \text{CO}_2^* \\
    \text{O}_2 + 2\text{CuO} & \rightarrow 2\text{CuO}_2 + 2\text{H}_2\text{O}^* \\
    \text{O}_2^* + \text{CuO}_2 & \rightarrow 2\text{CuO}_2\text{O}_2 + * 
\end{align*}
\]

Table 1 Porosity parameters for fresh and deactivated Cu–Fe/TSAC

| Samples               | Surface area (m\(^2\) g\(^{-1}\)) | Total pore volume (cm\(^3\) g\(^{-1}\)) | Micropore volume (cm\(^3\) g\(^{-1}\)) |
|-----------------------|-----------------------------------|---------------------------------------|--------------------------------------|
| Fresh catalyst        | 554                               | 0.29                                  | 0.21                                 |
| Deactivated catalyst  | 98                                | 0.07                                  | 0.04                                 |
In these reactions, * represents the hydrolysis activity center and Θ represents the oxidation activity center. Eqn (2)–(9) are the catalytic hydrolysis processes and eqn (10)–(12) are the catalytic oxidation processes.

4. Conclusions

Modified tobacco stem active carbon (Cu–Fe/TSAC) was prepared by a sol–gel method, and tested for the simultaneous removal efficiency of H$_2$S, COS and CS$_2$. The influences of reaction conditions for the removal of H$_2$S, COS and CS$_2$ were investigated. A high reaction temperature improved the hydrolysis and oxidation efficiency, but accelerated the deactivation of the catalyst. DRIFTS results indicated that the deactivation of the catalyst was attributed to the formation of S containing components, such as thiol/thioether, S, –SO–, and sulfate. BET results indicated that the adsorptive ability of the catalyst was related to the microporous volume and surface area.

Table 2 XPS data for fresh and deactivated Cu–Fe/TSAC

| Sample          | Elements | Binding energy (eV) | Amount (%) | Chemical speciation     |
|-----------------|----------|--------------------|------------|-------------------------|
| Fresh catalyst  | S2p      | —                  | —          | —                       |
| Deactivated catalyst | S2p    | 162.41             | 1.92       | Thiol/thioether         |
|                 | S2p      | 164.09             | 2.90       | S                       |
|                 | S2p      | 165.22             | 0.83       | –SO–                    |
|                 | S2p      | 168.83             | 1.25       | Sulfate                 |

Fig. 11 Reaction process diagram.

\[
O_2^* + 2H_2O^* + 2CuO\Theta SO_2 = 2CuO\Theta H_2SO_4 + 2^* \quad (12)
\]

Hydrolysis of COS/CS$_2$ was attributable to the promotion effect of O$_2$ for H$_2$S oxidation. A high GHSV decreased the contact time between the gases and the catalyst. Meanwhile, a high GHSV was not conducive to the adsorption of gases on the surface of the catalyst. XPS results indicated that the deactivation of the catalyst was attributed to the formation of S containing components, such as thiol/thioether, S, –SO–, and sulfate. BET results indicated that the adsorptive ability of the catalyst was related to the microporous volume and surface area.

Conflicts of interest

There are no conflicts to declare.

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