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# Simultaneous catalytic hydrolysis of carbonyl sulfide and carbon disulfide over $Al_2O_3$-K/CAC catalyst at low temperature

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**Abstract**

In this work, a series of coal-based active carbon (CAC) catalysts loaded by $Al_2O_3$ were prepared by sol-gel method and used for the simultaneous catalytic hydrolysis of carbonyl sulfide (COS) and carbon disulfide ($CS_2$) at relatively low temperatures of 30−70 °C. The influences of calcinations temperatures and operation conditions such as: reaction temperature, $O_2$ concentration, gas hourly space velocity (GHSV) and relative humidity (RH) were also discussed respectively. The results showed that catalysts with 5.0 wt% $Al_2O_3$ calcined at 300 °C had superior activity for the simultaneous catalytic hydrolysis of COS and $CS_2$. When the reaction temperature was above 50 °C, catalytic hydrolysis activity of COS could be enhanced but that of $CS_2$ was inhibited. Too high RH could make the catalytic hydrolysis activities of COS and $CS_2$ decrease. A small amount of $O_2$ introduction could enhance the simultaneous catalytic hydrolysis activities of COS and $CS_2$.

**Key words**

carbonyl sulfide; carbon disulfide; simultaneous catalytic hydrolysis; $Al_2O_3$-K/CAC catalysts

## 1. Introduction

COS and $CS_2$ are the major components of organic sulfur compounds from chemical gas produced from natural gas, petroleum, crude oil, industrial streams and coal [1,2]. Many methods have been developed to remove COS and $CS_2$ from Claus tail gas and other processed gas streams, since COS and $CS_2$ can not only pollute the environment but also poison the catalysts [3,4]. The main technologies for removing of COS and $CS_2$ include reduction, adsorption, photolysis, oxidation, catalytic hydrolysis, etc. [5−8] and the catalytic hydrolysis was recognized as the most promising process because of avoidance of the feed gas cracking, methanation, etc. [9]. Meanwhile, the reaction temperature of catalytic hydrolysis is lower than 300 °C, so the energy consumption is lower. And most of feed gases have $H_2O$ (one of the reactants for catalytic hydrolysis process). Recently, most studies pay attention to separately catalytic hydrolysis of COS and $CS_2$ in excess of 200 °C. There are a great variety of studies on COS and $CS_2$ separate hydrolysis especially concentrating on the development of new catalysts, particularly on $\gamma$-$Al_2O_3$, $TiO_2$, hydrotalcite-like compounds, etc. [10−13]. But poisoning resistances of $\gamma$-$Al_2O_3$ and $TiO_2$ are poorer and the industrial application prospect of hydrotalcite is not good [14,15].

The application of active carbon (AC) becomes more popular for various field, such as conductive material, adsorbent and catalyst support because of its stable structure, well-developed porous structure, large specific surface area and potential biocompatibility [16]. The pores sizes and volumes are important for physical adsorption and surface property also plays a significant role for surface reaction and chemisorptions [17,18]. Many people have attempted to modify the surface properties of AC to improve its functions so that it can suit the growing needs of purifying air [8].

In the present study, there are a large number of investigations about the separately catalytic hydrolysis of COS or $CS_2$ using AC-supported catalysts at the low temperatures (<100 °C) [19,20]. What's more, the catalytic properties of AC surfaces are also modified by adding metal oxides, especially Fe, Cu, Ni, Ce and their mixed oxides [21−24]. However, little research focuses on simultaneous catalytic hydrolysis of COS and $CS_2$ at the low temperature (<100 °C). There-

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fore, in this study, the efficiency of $Al_2O_3$-K/CAC catalysts for COS and $CS_2$ simultaneous removal in the low temperature range (30−70 °C) was investigated, included the effects of calcinations temperatures and operation conditions.

## 2. Experimental

### 2.1. Catalysts preparation

The market CAC were crushed and sieved to 40−60 mesh size. The catalysts were prepared with sol-gel method. The AC were washed four times by distilled water, and then boiled in 1mol/L KOH for 1.5 h, then washed by distilled water till no further change in pH, and finally dried at 120 °C for 3−4 h. Secondly, colloid solution was made with a certain amount of $Al(NO_3)_3 \cdot 6H_2O$ solution and $Na_2CO_3$ solution. The activated carbon catalysts were supported by desired proportion (mass fraction of $Al_2O_3$ was 5%). Then, the samples were dipped under the ultrasonic for 30 min, dried at 120 °C in the drying oven and calcined at 200−600 °C for 3 h under atmospheric conditions (82.4 kPa). At last, the catalysts were impregnated by 10% (mass fraction) KOH, and kept under the ultrasonic for 30 min, then dried for 3 h at 120 °C in the drying oven to get the catalyst ($Al_2O_3$-K/CAC) needed for the experiments.

### 2.2. Catalytic activity measurement

Desulfurization tests were performed in a fixed-bed quartz reactor (3 mm inside diameter × 100 mm length) under atmospheric pressure. The catalysts were loaded into the fixed bed and a wad of cotton wool was inserted into the reactor so that the catalyst could not escape from the vessel during the operation. COS and $CS_2$ from gas cylinder (1% COS in $N_2$; 0.3% $CS_2$ in $N_2$) were diluted with $N_2$ (99.99%) to the required concentration (COS: 350−400 ppm; $CS_2$: 10−20 ppm). The gas hourly space velocity (GHSV) of the reaction mixture was standardized at 5000−15000 $h^{-1}$. The water was introduced using a saturator system. The temperature of this reactor was controlled to 30−70 °C by water-bath with circulating pump, with accuracy of ±0.1 °C, and relative humidity (RH) was 15%–60%. The total COS and $CS_2$ concentrations of gaseous feed and effluent were analyzed by an online HC-6 sulfur phosphorus microscale analyzer with a FPD detector. The conversion of COS or $CS_2$ was determined by analyzing the inlet and outlet concentration of COS or $CS_2$:

$$\text{COS }(\text{CS}_2)\text{ conversion }(\%) = \frac{\text{COS}(\text{CS}_2)_{\text{inlet}} - \text{COS}(\text{CS}_2)_{\text{outlet}}}{\text{COS}(\text{CS}_2)_{\text{inlet}}} \times 100 \tag{1}$$

## 3. Results and discussion

### 3.1. Effect of calcination temperatures on simultaneous catalytic hydrolysis of COS and $CS_2$

The calcinations temperatures can affect the surface oxidation of metals. Figure 1 shows the effect of calcination temperatures on simultaneous catalytic hydrolysis of COS and $CS_2$ over the $Al_2O_3$-K/CAC catalyst. The results indicated that the best calcination temperature was 300 °C for simultaneous catalytic hydrolysis of COS and $CS_2$. The COS and $CS_2$ conversions were decreased sharply when the calcination temperature was over 400 °C. When calcination temperature is 200 °C, the catalytic hydrolysis activity is equal to that of 400 °C for COS, but the $CS_2$ conversion is better than that of 400 °C. The reason may be that the oxidizing nature of peroxy radicals can make the final hydrolysis product of $H_2S$ oxidize into sulfate and sulfur species which damage hydrolysis active sites at low temperatures (below 300 °C in this work). Moreover, when the calcination temperature was over 400 °C, the CAC could be oxidized to CO and $CO_2$. The decomposition rates can be enhanced with increasing of temperature. It also can be conjectured that there may be certain relationship between the crystallinity of the oxidation state and the calcination temperatures.

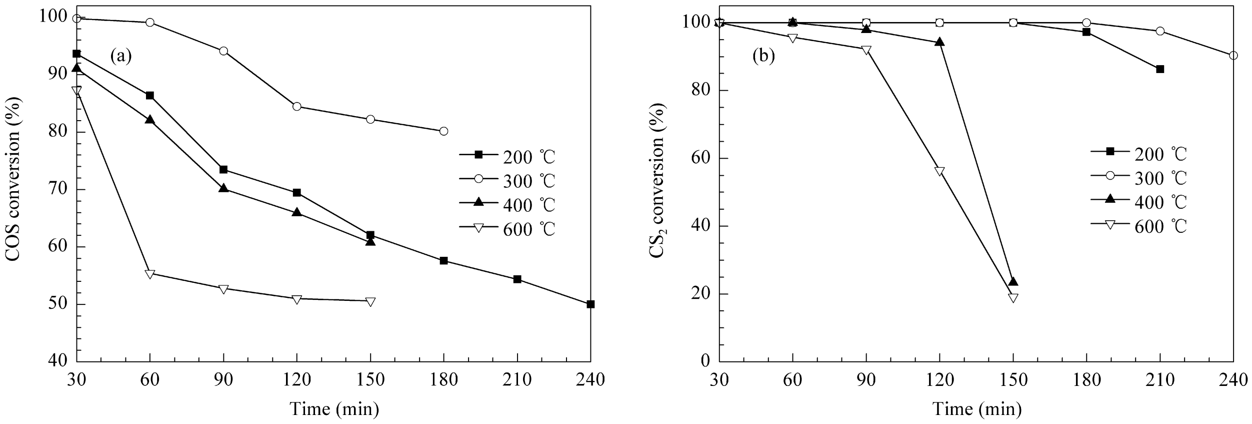

**Figure 1.** Effect of calcination temperature on simultaneous catalytic hydrolysis of COS (a) and $CS_2$ (b). Reaction condition: 400 ppm COS, 10 ppm $CS_2$, GHSV = 10000 $h^{-1}$, RH = 49%, reaction temperature = 50 °C, $O_2$ content = 0

The phase and crystalline orientation of $Al_2O_3$-K/CAC with different calcination temperatures are exhibited in Figure 2. It can be found that comparatively weak changes were detected at lower calcination temperatures. The reason is that carbon is non-crystalline, and its background peak is obvious. And the amount of metal oxide is far less than carbon. However, the diffraction peaks could be enhanced with increasing calcination temperatures (from 300 °C to 600 °C). As shown in Figure 2, strong peaks appear at $2\theta = 30.5^o$, $31.58^o$ and $44.4^o$(300 °C and 400 °C). While the more stronger peaks appear at $2\theta = 21.86^o$, $30.5^o$, $31.58^o$ and $44.4^o$ for 600 °C calcination. These diffraction peaks are matched to $Al_2O_3$ through comparing to the standard of spectral library, and the amount of $Al_2O_3$ increased with increasing calcination temperature form 300 °C to 600 °C. $Al(NO_3)_3$, $Al(OH)_3$ and $Al_2(CO_3)_3$ could turn into $Al_2O_3$ with calcination temperature increasing. Moreover, $Al_2O_3$ could enhance the hydrolytic activity. A small quantity of $Al_2O_3$ can generate at 200 °C because of only water evaporation at lower temperature. For instance, the weak peaks appear for 200 °C. Although the content of $Al_2O_3$ was highest at 600 °C (the complete decomposition temperature of $Al(NO_3)_3$ is about 500−600 °C), the active site would be occluded by overfull metal oxides, and so the hydrolytic activity was lower [25].

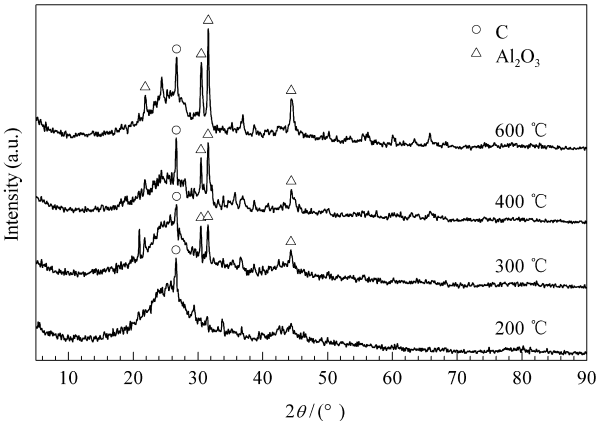

**Figure 2.** XRD patterns of $Al_2O_3$-K/CAC catalysts calcined at different temperatures

### 3.2. *Effect of reaction temperatures on simultaneous catalytic hydrolysis of COS and $CS_2$*

The influence of reaction temperatures on the catalytic performance over $Al_2O_3$-K/CAC catalyst is presented in Figure 3. With the increasing temperature from 30 to 70 °C, the variations of COS and $CS_2$ are different. The conversion of COS was increased with increasing of reaction temperatures and reached the highest conversion at 70 °C, and the COS conversion was above 90% in the initial 120 min. The $CS_2$ hydrolysis activities initially increase and then decreased with the increase of reaction temperatures. It is interesting to note that when the reaction temperature was 50 °C, the catalyst shows the best catalytic performance of $CS_2$ and no better effect occurs with the increase of reaction temperatures.

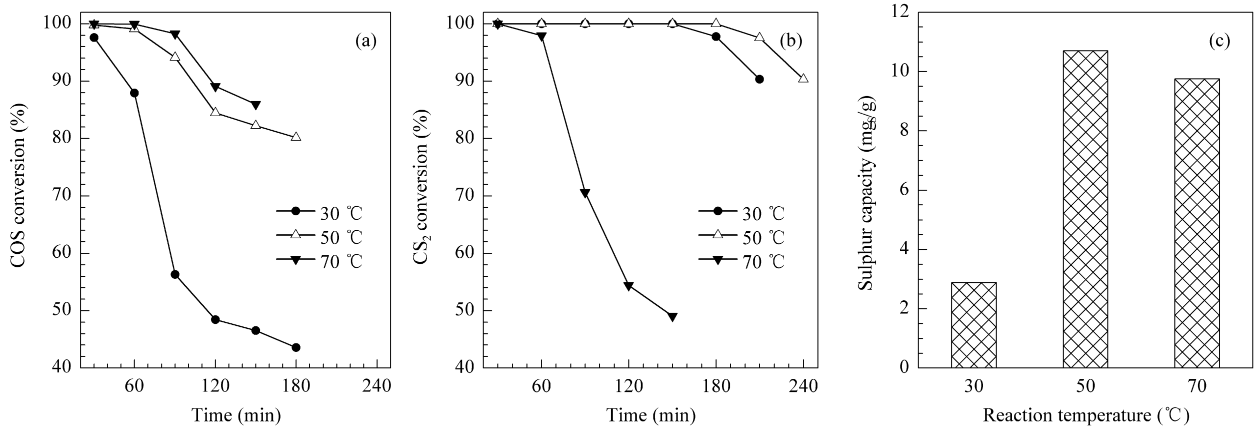

**Figure 3.** Effect of reaction temperatures on simultaneous catalytic hydrolysis of COS (a), $CS_2$ (b) and sulfur capacity (c). Reaction condition: 400 ppm COS, 10 ppm $CS_2$, GHSV = 10000 $h^{-1}$, RH = 49%, $O_2$ content = 0, calcination temperature = 300 °C

As shown in Figure 3(c), when the conversions of COS and $CS_2$ were 80% and 90% respectively, the sulfur capacity was defined as the breakthrough sulfur capacity. The sulfur capacity was 2.88 $mg_S$/g at 30 °C. The sulfur capacity was increased with increase of reaction temperatures. But the sulfur capacity increased slowly while reaction temperature was above 50 °C. Because when the reaction temperature was above 50 °C, the increasing of COS conversion was not obvious, but the $CS_2$ conversion was decreased obviously.

The reaction rates of simultaneous catalytic hydrolysis COS and $CS_2$ are poor at low temperatures. Therefore, with increasing of temperature, the reaction rate of catalytic hydrolysis can be increased and the hydrolysis reaction can be occurred more easily. The conversion of hydrolysis product ($H_2S$) to S or sulfate on modified AC is parallel-reactions, and with the increase of reaction temperatures, the yield rate of sulfuric acid will increase faster than that of element S. At higher temperature, $H_2S$ can be oxidized to sulfate more easily, and the higher concentration of $SO_4^{2-}$ poisons the hydrolysis activity. Thus, the $CS_2$ removal efficiency declines sharply above 50 °C. Although COS removal efficiency can be enhanced above 50 °C, the enhancement scope is limited and sulfur capacity is increased slowly.

### *3.3. Effect of RH on simultaneous catalytic hydrolysis of COS and $CS_2$*

The effects of RH on COS and $CS_2$ removal were studied by introducing feed gas through a humidifier at different temperatures. The influences of different RH on the catalytic performance have been plotted in Figure 4. The results clearly indicate that the RH plays an important role on the catalytic performance. The low volume fraction of water ($H_2O$) should be benefit to the hydrolysis activity. When the RH was 15% (the humidifier temperature is 0 °C), the catalyst showed the best activity, the 100% COS and $CS_2$ conversions were maintained about 90 and 270 min respectively. However, the presence of excess water could restrain the chemisorption of COS ($CS_2$), leading the hydrolysis activity decrease by the competitive adsorption between COS ($CS_2$) and $H_2O$. Moreover, the catalyst manifested the best activity when the RH was 15%. Then the hydrolysis activity was decreased with the increase of RH. For the above phenomenon, the reason may be that: the negative impact of competitive adsorption of $H_2O$ with COS/$CS_2$ on the catalyst surface is more important than the positive impact of water supplying more hydroxyl species. With the influences of RH, one reason is that the surface of catalysts pores will form water films, when RH reaches some extents. Although the formation of water films will provide more accommodating space for the product of the reaction, excess water films may stop COS or $CS_2$ diffusing into the hydrolysis center and inhibit the catalytic hydrolysis reaction [26]. As shown in Figure 4(c), when the conversions of COS and $CS_2$ were 80%, the sulfur capacity was defined as the breakthrough sulfur capacity. The sulfur capacity decreases with the increase of RH. The sulfur capacity was highest (24.55 $mg_S/g$) when the RH was 15%. Then, when the RH was 60%, the sulfur capacity decreased to 4.54 $mg_S/g$.

### *3.4. Effect of $O_2$ content on simultaneous catalytic hydrolysis of COS and $CS_2$*

The curves plotted in Figure 5 show the effect of $O_2$ content on the COS and $CS_2$ removal efficiency. The catalytic

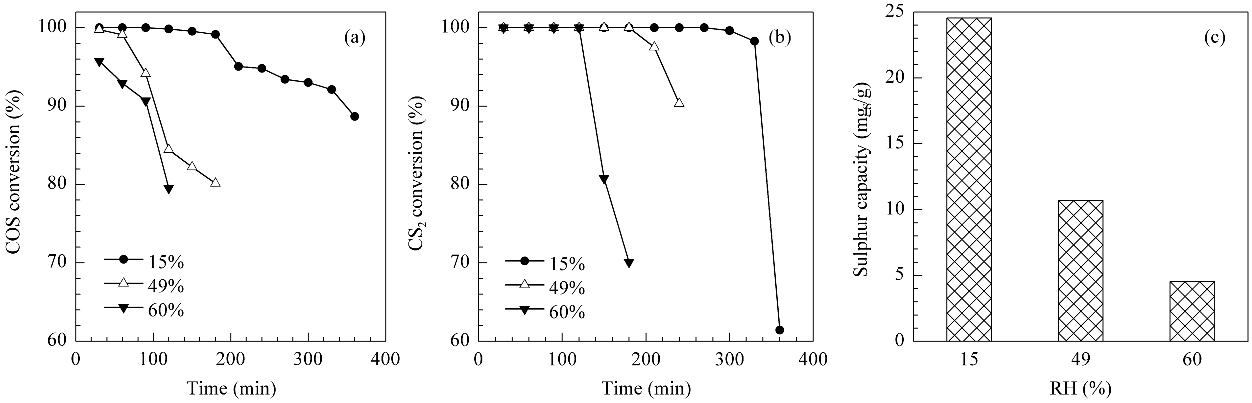

**Figure 4.** Effect of RH on simultaneous catalytic hydrolysis of COS (a), $CS_2$ (b) and sulfur capacity (c). Reaction condition: 400 ppm COS, 10 ppm $CS_2$, GHSV = 10000 $h^{-1}$, reaction temperature = 50 °C, $O_2$ content = 0, calcination temperature = 300 °C

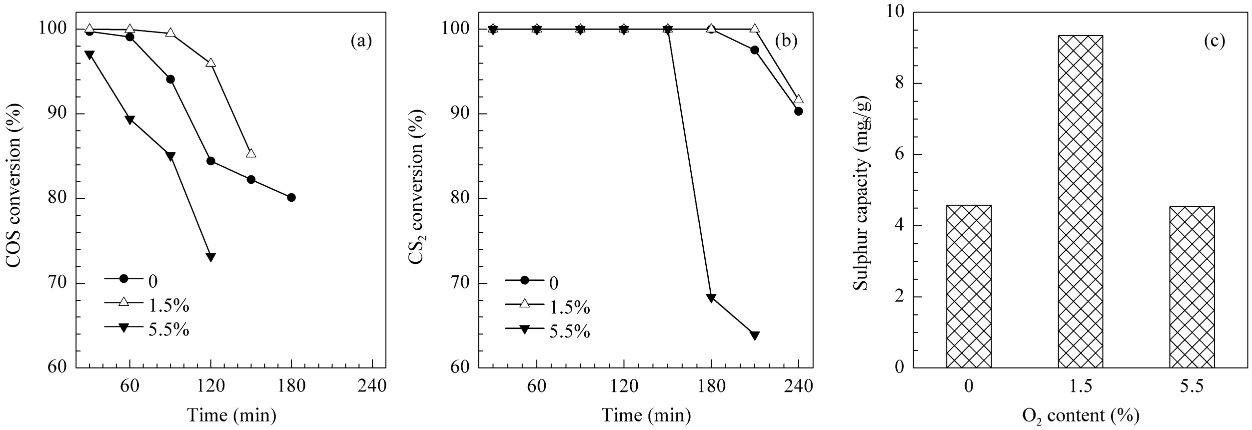

**Figure 5.** Effect of $O_2$ content on simultaneous catalytic hydrolysis of COS (a), $CS_2$ (b) and sulfur capacity (c). Reaction condition: 400 ppm COS, 10 ppm $CS_2$, GHSV = 10000 $h^{-1}$, RH = 49%, reaction temperature = 50 °C, calcination temperature = 300 °C

hydrolysis capacity initially increases and then decreases with the increasing of $O_2$ content. When the $O_2$ content is 1.5 vol%, the removal efficiencies of COS and $CS_2$ are highest. The COS conversion was 85% in initial 150 min and the 100% $CS_2$ conversion was maintained 210 min. However, the conversion of COS and $CS_2$ decreases with sequential addition of $O_2$ when $O_2$ content is 1.5 vol%. As shown in Figure 5(c), when the conversions of COS and $CS_2$ were 80% and 90% respectively, the sulfur capacity was defined as the breakthrough sulfur capacity. The sulfur capacity initially increases and then decreases with the increase of $O_2$ content. The sulfur capacity was highest (9.34 $mg_S/g$) when the $O_2$ content was 1.5 vol%.

It is clear that the addition of less $O_2$ enhances the catalytic activity in the COS and $CS_2$ hydrolysis. The reason may be that: the appropriate oxygen can increase the rate of $H_2S$ oxidization and promote the catalytic hydrolysis of COS and $CS_2$. Instead, the oxidation rate of $H_2S$ quickens with the increase of oxygen content. It will generate more sulfates and the promotion action is less than the inhibition effect. Moreover, $H_2S$ oxidation on impregnated CAC occurs through an interaction between the adsorbed $H_2S$ and oxygen on impregnated CAC, and the reaction equation is $H_2S + O_2 \rightarrow H_2O + S/SO_4^{2-}$. The generated sulfate increased with the increasing of $O_2$ content. As an important factor of catalyst poisoning, the sulfate/S can be attached on the surface of catalyst, and most micropores of catalyst would be blocked. Meanwhile, S can be oxided to more sulfate on the condition of higher $O_2$ contents. Therefore, excessively high $O_2$ content could lead to the production of more sulfates, which deactivated the catalytic hydrolysis active sites of COS and $CS_2$. So, the hydrolysis activities of COS and $CS_2$ were decreased with increasing of $O_2$ content. Another reason may be that the oxidation reaction of COS and $CS_2$ can be occurred at the high $O_2$ content. $SO_2$ and $CO_2$ can be generated (Equations 2 and 3) which restrain the catalysis hydrolysis reaction.

$$2COS + 3O_2 \longrightarrow 2SO_2 + 2CO_2 \tag{2}$$

$$CS_2 + 3O_2 \longrightarrow 2SO_2 + CO_2 \tag{3}$$

The characterization analysis related to influence of $O_2$ content was estimated by XPS. The results were listed in Tables 1 and 2. The surface concentration of S species was 3.9% on exhausted catalyst surface when the $O_2$ content was 1.5%. Moreover, the surface concentration of S species of exhausted catalyst surface was increased to 6.88% when the $O_2$ content was increased to 5.5%. The results indicated that the surface concentration of S species on exhausted catalyst surface was increased with increasing of $O_2$ content. Another results showed that the surface of C was covered by lots of reaction productions. Deconvolution of the S 2*p* spectra gives two individual component groups that represent the sulfur (164.23 eV) and the sulfate/$SO_4^{2-}$ (168.76 eV). It can be observed that S and sulfate were descended and increased respectively with increasing $O_2$ content on exhausted catalysts surface. Therefore, the increasing of $O_2$ can expedite the transformation of sulfate from S, which resulted in the deactivation of catalysts.

**Table 1. Surface elemental analysis of exhausted catalysts using XPS**

| Element | 1.5% $O_2$ (at%) | 5.5% $O_2$ (at%) |
|---|---|---|
| S | 3.9 | 6.88 |
| C | 64.4 | 52.3 |
| N | 0.38 | 1.07 |
| Al | 3.64 | 2.5 |
| O | 27.06 | 36.87 |
| K | 0.62 | 0.38 |

**Table 2. Surface content of S species on exhausted catalysts by the S 2*p* XPS peaks**

| Sample | S 2*p* (at%) | |
|---|---|---|
| | 164.23 (eV) | 168.76 (eV) |
| 1.5% $O_2$ | 1.24 | 2.66 |
| 5.5% $O_2$ | 0.45 | 6.43 |

### *3.5. Effect of gas hourly space velocity on simultaneous catalytic hydrolysis of COS and $CS_2$*

As shown in Figure 6, the removal efficiencies of COS and $CS_2$ decrease obviously with the increase of GHSV. 100% COS and $CS_2$ conversions were maintained about 450 min and 510 min respectively when the GHSV was 5000 $h^{-1}$. When

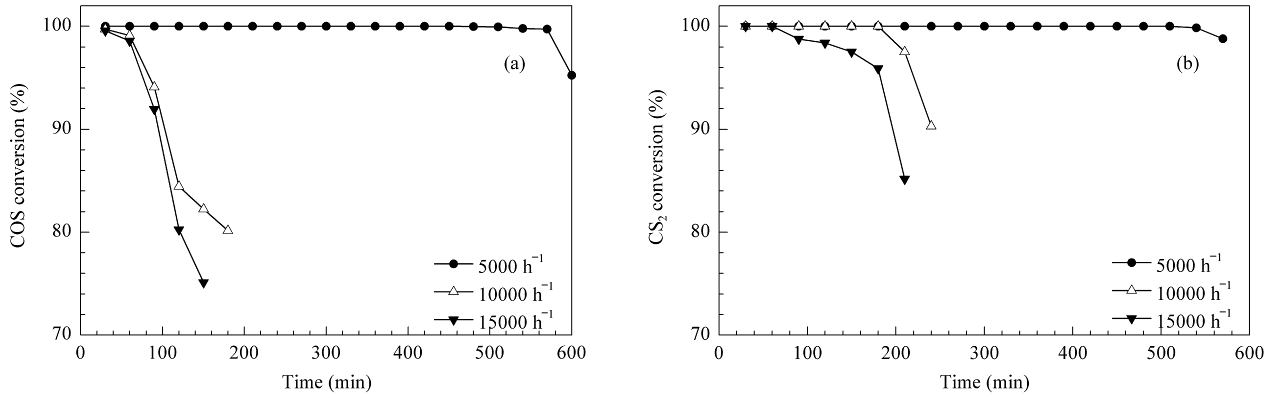

**Figure 6.** Effect of GHSV on simultaneous catalytic hydrolysis of COS (a) and $CS_2$ (b). Reaction condition: 400 ppm COS, 10 ppm $CS_2$, reaction temperature = 50 °C, RH = 49%, $O_2$ content = 0, calcination temperature = 300 °C

the GHSV was 10000 $h^{-1}$, the 100% COS and $CS_2$ conversion were maintained about 60 and 180 min respectively. However, when the GHSV was increased to 15000 $h^{-1}$, the COS conversion decreased more obviously and was only 75% in initial 150 min, and the $CS_2$ conversion was 85% in initial 210 min. The reserve time of COS, $CS_2$ and $H_2O$ in catalytic surface is long enough in low GHSV. It is beneficial for the adsorption and diffusion on catalytic surface. So the hydrolysis activity is high in low GHSV.

## 4. Conclusions

Modified coal-based active carbon ($Al_2O_3$-K/CAC) was prepared by sol-gel method, and tested for the simultaneous catalytic hydrolysis of COS and $CS_2$ at 30−70 °C. The results showed that the 5.0 wt%$Al_2O_3$-K/CAC catalyst after calcined at 300 °C has superior activity for the simultaneous catalytic hydrolysis of COS and $CS_2$. The influences of reaction conditions were also investigated. Excessively high reaction temperature (>50 °C) could enhance the catalytic hydrolysis of COS but inhibit catalytic hydrolysis of $CS_2$. Excessively high RH and $O_2$ content could lead to more sulfates formation, and make the catalytic hydrolysis activities of COS and $CS_2$ decrease.

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