



Coupling catalytic hydrolysis and oxidation for CS₂ removal

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Abstract

CS₂ removal was obtained by coupling catalytic hydration on bi-functional catalyst. On the hydrolysis active sites, CS₂ is hydrolyzed to H₂S, while on the oxidation active sites, H₂S is oxidized to elemental S or sulfuric acid deposited on the porous support. The above process can be expressed as follows: CS₂ $\xrightarrow{\text{H}_2\text{O}}$ COS $\xrightarrow{\text{H}_2\text{O}}$ H₂S $\xrightarrow{\text{O}_2}$ S/SO₄²⁻. H₂S oxidation eliminates its prohibition on CS₂ hydrolysis so that the rate of coupling removal CS₂ is 5 times higher than that of CS₂ hydrolysis. The same active energy of hydrolysis and coupling reaction also indicates that H₂S oxidation does not change the reaction mechanism of CS₂ hydrolysis. Temperature has obvious effect on the process while the mole ratio of O₂ concentration to CS₂ concentration (O/S) does not, especially in excess of 2.5. The formation of sulfuric acid on the catalyst surface poisons hydrolysis active sites and causes the decrease of left OH⁻¹ concentration on the catalysts surface. Lower temperature is suggested for this bi-functional catalyst owing to the low yield ratio of S/SO₄²⁻.

Key words: carbon disulfide; coupling process; low-temperature removal

Introduction

CS₂ is a type of organic sulfur compound that widely exists in chemical processing gases from coal, natural gas, and synthesis gas. It is of significance to remove CS₂ because even ppmv levels of CS₂ can cause the catalysts' deactivation such as in the synthesis of ammonia and methanol (Williams *et al.*, 1999). CS₂ has been classified as a hazardous gaseous pollutant and is considered to be one of the most toxic solvent, causing accelerated atherosclerosis and coronary artery disease for those exposed to it in poorly ventilated factories (Ghittori *et al.*, 1998).

One of the CS₂ removal methods is CS₂ reduction into H₂S over Co-Mo-Al catalyst (Coward and Warren, 1985). Another treatment for the CS₂ removal at high levels of SO₂ is to oxidize CS₂ into CO₂ and element S (Tone *et al.*, 1992). During the hydrogenation and oxidation reaction, adding either H₂ or SO₂ is relatively expensive and inconvenient to operate for industrial plants.

Since it is difficult to remove CS₂ completely using the traditional desulfurization process, an alternative technology based on the formation of H₂S by hydrolysis has been used in most studies, while H₂S is removed via another treatment. Therefore, the combination of two processes is required to remove CS₂ completely.

In this study, we present a new method to simultaneously remove CS₂ by single process utilizing bi-functional catalyst (Ce-K-C) at lower temperature (55–95°C). It is

reported that CeO₂ has higher hydrolysis CS₂ activity especially in the presence of O₂ (Brunelle *et al.*, 1987). In ordinary case, O₂ in gas phase will cause sulfation on the surface of the catalyst and a decrease in catalytic activity. Virgin activated carbon is widely used as adsorbent for H₂S removal. As activated carbon is impregnated with caustic materials such as Na₂CO₃, K₂CO₃, its activity for H₂S removal is increased greatly (Przepiorski *et al.*, 1999). In this article, bi-functional materials (Ce-K-C) were used as the hydrolysis catalyst of CS₂ as well as the oxidation catalyst of H₂S at lower temperature. Such novel method is more economically viable with fewer facilities and no additional catalysts.

1 Materials and methods

1.1 Catalysts

Doped catalysts (Ce-K-C) were prepared using conventional incipient impregnation method. Firstly, the commercial activated carbon was dipped in a solution of Ce(NO₃)₃, dried (100°C, 2 h) and calcined (450°C, 2 h), followed by doping K₂CO₃ on the samples in the same way.

The commercial activated carbon, the characteristics of which are presented in Table 1, is used as the support because of its developed surface area, micro porosity, higher sorption capacity, and easily modified surface properties (Adib *et al.*, 1999).

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Table 1 Properties of the activated carbon

Parameter	Value
Total surface area (N ₂ , BET method) (m ² /g)	838.8
Total pore volume (ml/g)	1.216
Micropore volume (BDB equations) (ml/g)	1.103
Apparent density (bulk density, dense packing) (g/cm ³)	0.47
Real density (He displacement) (g/cm ³)	1.8

1.2 Analysis

The total CS₂ concentration of gaseous feed and effluent from the reactor were analyzed by WC-2 sulfur Micro-coulomb analyzer (Dalian Institute of Chemical Physics, China) while the different S-components in outlet gas were determined by a gas chromatograph (Varian 3800, Varian, Inc., USA) with a pulsed flame photometric detector with the detection level as low as 0.1 mgS/m³.

The OH⁻ of the catalyst was measured by chemical titration. The sample of 0.4 g was ground to below 200 mesh. The dry carbon power was added to 20 ml of water, and the suspension was stirred for 24 h to reach equilibrium. Then, the OH⁻ of the suspension was measured.

UV/Vis spectrophotometer (JASCO-550, JASCO Co., Japan) analysis was employed to study the SO₄²⁻ in catalysts. The 0.4 g of sample below 200 mesh was added to 5 ml of 5% NaOH aqueous and the suspension was stirred for 24 h to reach equilibrium. After the aqueous was washed, 5 ml of 5% H₂O₂-C₂H₅OH was added to the collected elution. After boiling the suspension, BaCl₂-NH₃ aqueous was added to it. The aqueous mixture was separated in a centrifuge. The light aqueous was measured by a UV/Vis spectrophotometer.

1.3 Experimental procedure

CS₂ hydrolysis and catalytic hydrolysis-oxidation coupling experiments were conducted in a fixed-bed glass tube reactor at ambient pressure. CS₂ (2500 ppmv in N₂) was adjusted over a wide range of concentration (300 to 1,000 ppmv). Water was introduced using a saturator system. By adjusting the water bath temperature and CS₂ flow-rates, the feed compositions could be adjusted over a wide range. In each experiment, 1.6 g of catalyst with particle 40–60 mesh was used.

The experimental procedure was as follows: After the CS₂ hydrolysis in the absence of oxygen reached stability, predetermined oxygen was introduced by shifting the three-valves. During this shifting procedure, the inlet CS₂ concentration, the relative humidity (RH), temperature, and space velocity (SV) were kept unchanged. The concentration of each S-component was measured before and after shifting.

2 Results and discussion

2.1 Effects of temperature

The hydrolysis rate of CS₂ (without oxygen) and the coupling removal CS₂ rate (by adding oxygen) as a function of temperature with a molar O/S stoichiometric ratio of 2.5 are plotted in Fig.1. These plots indicate that the rate

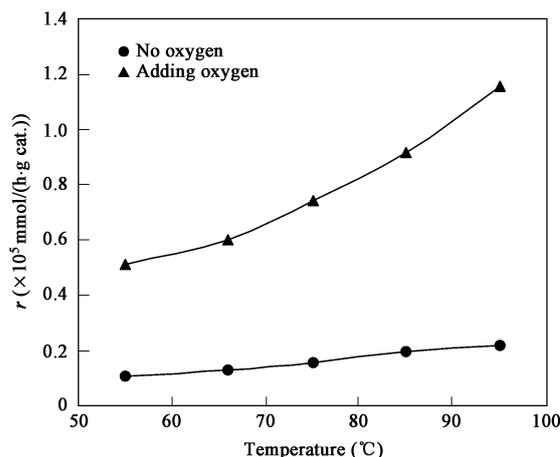


Fig. 1 Temperature effect on the rate (r) of CS₂ hydrolysis. CS₂: 750 mgS/m³; O/S=2.5; RH: 10%; SV: 1295 h⁻¹.

of CS₂ hydrolysis increased as the temperature enhanced. The rate of hydrolysis CS₂ at 95°C in the presence of O₂ was 5 times higher than that in the absence of O₂, which suggested that H₂S oxidation was beneficial to CS₂ hydrolysis. Fig.2 displays the Arrhenius relationships of CS₂ hydrolysis and coupling removal, and the activated energies of the two reactions are almost the same, namely 20.1 and 21.4 kJ/mol, respectively.

2.2 Effects of CS₂ concentration

The experiment carried out at 75°C with different inlet CS₂ concentrations is plotted in Fig.3. The result shows that the higher the level of inlet CS₂ concentration, the higher the rate of CS₂ removal. More CS₂ and H₂O molecules will be available on per volume active sites, and therefore, there is a greater probability of collisions on the surface, resulting in higher conversion. The experiment results show that the partial pressure dependency of the rate on CS₂ is unity, and it is well in accord with the literature (Tone *et al.*, 1995).

2.3 Effects of relative humidity

Relative humidity effects on CS₂ removal were investigated by introducing the feed gas through a humidifier at

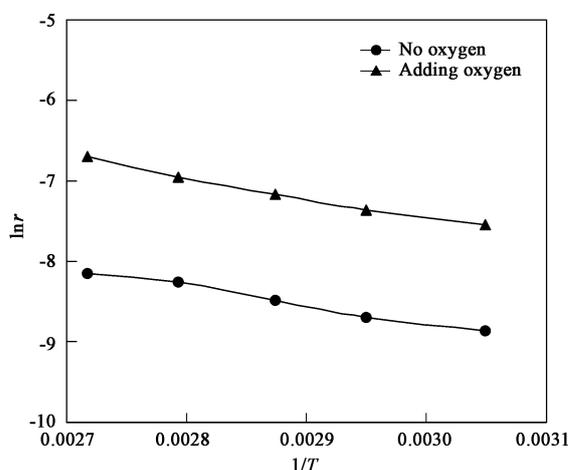


Fig. 2 Relationship between $1/T$ and $\ln r$.

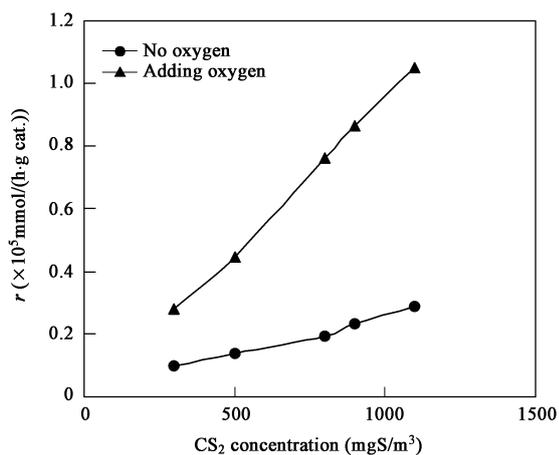


Fig. 3 CS₂ concentration effect on the rate (r) of CS₂ removal. O/S=2.5; RH: 10%; SV: 1295 h⁻¹; temperature: 75°C.

different temperatures to saturate it to a different extent. The results from these experiments are summarized in Fig.4. The results indicated that there was a critical RH of approximately 5% at which the CS₂ removal rate changed rapidly. To achieve higher CS₂ removal rate, RH at 5% was selected as an optimum RH for CS₂ removal over the catalyst.

RH plays different functions on CS₂ hydrolysis and H₂S oxidation. CS₂ hydrolysis reaction at lower temperature proceeds by the reaction of adsorbed CS₂ with surface hydroxyl species, and the wasting surface hydroxyl species will be replenished by adsorption of water on the surface (West *et al.*, 2001). However, more water will inhibit CS₂ hydrolysis for the competitive adsorption between CS₂ and water on active sites (Pechler and Emig, 1991). The adsorption capacity of CS₂ in damp gas is 60%–80% lesser than that in dry gas.

With the increase of RH in the feed, the creation of water films on activated carbon can be significantly enhanced. The presence of a water film enabled the dissociation of H₂S molecules to hydrogen sulfide ions HS⁻, which can be oxidized by oxygen radicals to elemental sulfur (Bandosz, 2002). Water played an important role in H₂S oxidation on impregnated activated carbon (Primavera *et*

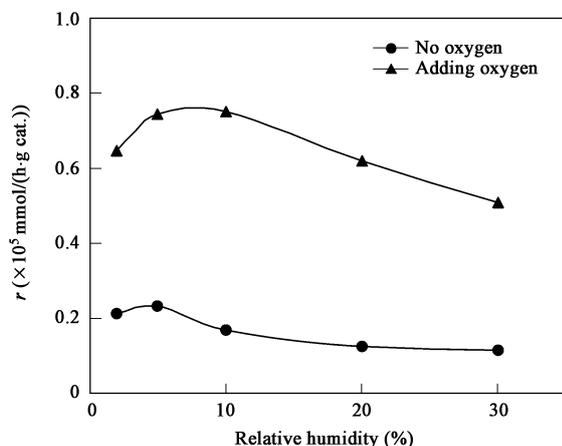


Fig. 4 Relative humidity effect on the rate (r) of CS₂ removal. CS₂: 750 mgS/m³; O/S=2.5; SV: 1295 h⁻¹; temperature: 75°C.

al., 1998). With the increase of relative humidity, the rate of H₂S oxidation will enhance greatly.

Although RH has effect on CS₂ hydrolysis and H₂S oxidation, CS₂ hydrolysis is the rate-determining step during this coupling process to remove CS₂. RH's effect on CS₂ hydrolysis is more important than that on H₂S oxidation, and then an optimal RH exist.

2.4 Effects of varying the O/S molar ratio

The curve plotted in Fig.5 provides an idea of how the CS₂ removal rate varies with the O/S ratio. In Fig.5, the dot point presents the rate of CS₂ hydrolysis in the absence of O₂, while the triangle dot presents the rate of coupling removing CS₂. The experimental results showed that O₂ addition (O/S > 2.5) made the hydrolysis rate of CS₂ improve 5 times higher than that in the case without oxygen. The reason for O₂ promotion on coupling CS₂ removal is discussed in Fig.6.

The introduced O₂ in the feed was used to oxidize CS₂ hydrolysis product—H₂S. H₂S oxidation on impregnated activated carbon occurs through an interaction between the dissociatively adsorbed H₂S and the oxygen adsorbed on impregnated activated carbon, and the reaction equation is expressed as $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S}/\text{SO}_4^{2-}$. These occurring reactions were accelerated strongly with increasing

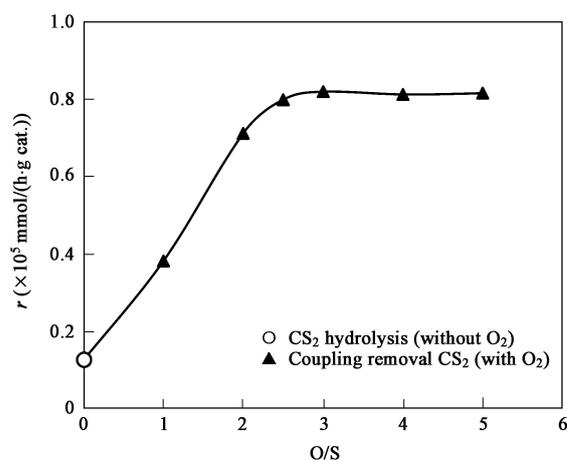


Fig. 5 O/S effect on the rate (r) of CS₂ removal. CS₂: 750 mgS/m³; RH: 10%; SV: 1295 h⁻¹; temperature: 75°C.

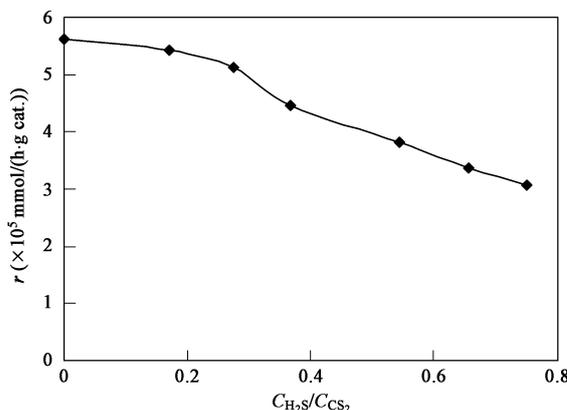


Fig. 6 Hydrolysis product—H₂S effect on CS₂ hydrolysis.

oxygen concentration to some extent. Further increasing O₂ concentration, the rate of H₂S oxidation to S does not change anymore, while the rate of H₂S oxidation to sulfuric acid increases. To guarantee the complete oxidation of H₂S and to obtain higher selectivity of sulfur/sulfate, the optimum O/S ratio is ca. 2.5 for the coupling removal of CS₂.

The effect of H₂S on CS₂ hydrolysis was testified by introducing H₂S and CS₂ mixing gas into the catalyst bed (Fig.6). With the ratio of H₂S/CS₂ in feedstock increased, CS₂ hydrolysis rate decreased greatly. Since H₂S acid is stronger than CS₂, H₂S will be more easily adsorbed on the basic hydrolysis sites, and then the CS₂ hydrolysis is restrained. H₂S oxidation eliminates its inhibition on CS₂ hydrolysis, which is confirmed by the experiment results shown in Fig.5.

The appearance of COS (carbonyl sulfide) in the effluent from CS₂ hydrolysis, via the consecutive reaction is well acknowledged as follows: CS₂ $\xrightarrow{H_2O}$ COS $\xrightarrow{H_2O}$ H₂S, COS being a proposed intermediate in the CS₂ hydrolysis reaction. During the CS₂ hydrolysis reaction (in the absence of O₂), COS about less than 1 ppmv was detected.

Compared to organic sulfur compound, H₂S is more easily removed for its active nature, and various researches have reported H₂S removal. The removal of COS is more difficult than H₂S at low temperatures in the range of room temperature to around 200°C, since COS is rather inactive compared to H₂S probably due to its neutrality and similarity to CO₂. The rate of CS₂ hydrolysis has been estimated to be 2–3 times more resistant to conversion when compared with COS under comparable conditions (Rhodes *et al.*, 2000). At lower temperature, the reaction rate of S-compounds removal follows the order: $\gamma_{H_2S} > \gamma_{COS} > \gamma_{CS_2}$. From the above analysis, it can be concluded that the CS₂ hydrolysis is the rate-determining step during this coupling process of CS₂ removal and the less difference in activation energy also confirmed that oxygen addition does not change the reaction mechanism of CS₂ hydrolysis. The whole coupling process for CS₂ removal can be expressed as follows: CS₂ $\xrightarrow{H_2O}$ COS $\xrightarrow{H_2O}$ H₂S $\xrightarrow{O_2}$ S/SO₄²⁻.

2.5 Effect of temperature on reaction production distribution

The concentrations of SO₄²⁻ and OH⁻¹ on the surface of fresh and aged catalysts were measured by chemical analysis (Figs.7 and 8). As seen in Fig.7, an increase in SO₄²⁻/S was observed with an increase of temperature. At lower temperature (< 75°C), the ratio of SO₄²⁻/S was less than 35%; when the temperature enhanced to 95°C, the ratio of SO₄²⁻/S increased to 78%.

The oxidation of H₂S, according to the reaction H₂S(g) + ½O₂ → H₂O(g) + S, is not the only reaction that may occur on impregnated activated carbon. Even at lower temperature, H₂S will also be oxidized to sulfuric acid: H₂S (g) + 2O₂ → H₂SO₄. The formations of S and sulfate on modified activated carbon are parallel-reactions, and with the increase of temperature, the yield rate of sulfuric acid will increase faster than that of element S.

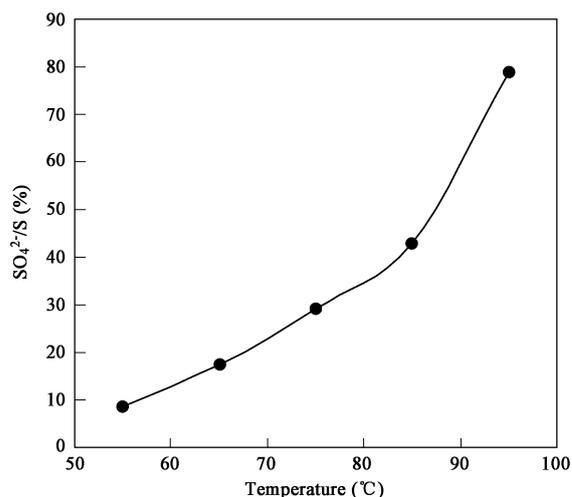


Fig. 7 Relationship between SO₄²⁻/S and temperature.

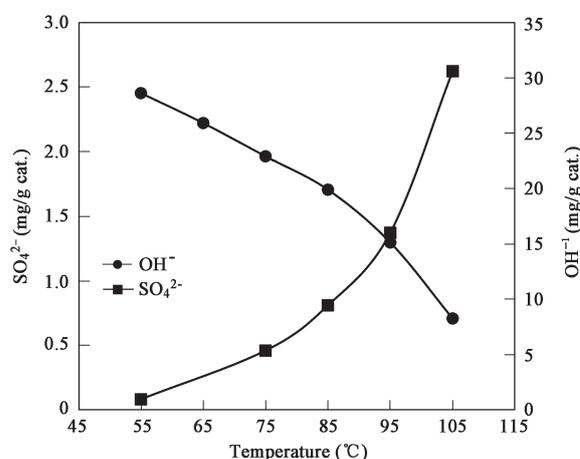


Fig. 8 Relationship of SO₄²⁻, OH⁻¹, and temperature.

At higher temperature, the selectivity of sulfur in H₂S oxidation is lower than that at lower temperature. The higher concentration of SO₄²⁻ poisons the hydrolysis active sites (Hellmut and Dalla Lana, 1984), and then deactivation of the catalyst for CS₂ hydrolysis occurs.

An increase in the yield of sulfuric acid and a decrease in OH⁻¹ concentration on the catalyst surface were observed (Fig.8). As the temperature increased, the increased sulfuric acid resulted in a decrease in the causticity of the catalyst. The predominant role of basic sites was so obvious that the activity of catalyst was in proportion to its surface basicity (Tsybulevskii *et al.*, 1998).

The chemical analysis results of fresh and aged catalysts at different temperatures show that the main production-sulfate at higher temperature was the key point for catalyst deactivation. Lower temperature was suggested to operate so as to get longer stability.

3 Conclusions

(1) Removal of carbon disulfide at lower temperature is done by coupling the hydrolysis-oxidation process that can be expressed as follows: CS₂ $\xrightarrow{H_2O}$ COS $\xrightarrow{H_2O}$ H₂S $\xrightarrow{O_2}$

S/SO₄²⁻. The faster oxidation of hydrolysis product-H₂S causes higher conversion of CS₂ with the hydrolysis reaction mechanism remaining unchanged.

(2) Temperature is the main factor that affects the coupling process. When the O/S ratio is larger than 2.5, it has no significant effect on the coupling process.

(3) With the increase of temperature, the reaction product distribution shows that sulfate was the main product. The higher concentration of sulfate on the surface of the catalysts will cause decrease of catalyst surface and CS₂ hydrolysis activity. Lower temperature is suggested to be adopted for removing CS₂ by this coupling catalytic hydrolysis-oxidation process.

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