



Desulfurization matching with coal poly-generation system based on dual gas resources

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ABSTRACT

The coal poly-generation system for the production of alcohol and ether fuels as well as power is one of advanced coal utilization techniques. The team led by Professor Xie Kechang is carrying out the research on the poly-generation system to produce the syngas from the combination of gasified and pyrolyzed coal gas (dual gas resources) for the alcohol ether synthesis. Gas desulfurization is one of the key technologies for this system. The desulfurization matching with dual gas resources based poly-generation system for the production of alcohol and ether fuels as well as power is presented according to gas components, sulfur content, sulfur species and desulfurization accuracy in this technology. This matching desulfurization is classified into hot gas desulfurization, normal gas desulfurization, warm gas desulfurization and organic sulfur catalytic conversion. The preparation of H₂S removal sorbents, organic sulfur hydrolysis catalyst and the evaluation of their activities involved in the system were investigated. The H₂S removal efficiencies of the crude and fine desulfurization sorbents prepared for hot gas desulfurization are 90% and 99% at 500 °C in simulating coal gas, and their sulfur capacities are 21.85 wt.% and 24.91 wt.%, respectively. The organic sulfur catalyst shows the high hydrolysis activity, and the hydrolysis conversion of COS is more than that of CS₂ on the same catalyst. The research will provide necessary information for the matching desulfurization technology in the demonstration project on dual gas resources coal poly-generation system.

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1. Introduction

Development of alternative clean fuel from other than petroleum has become an important research subject to meet the progressive increase in the energy needs in the world. Coal has been the main primary energy since quite a long term in China, sharing as much as about 67% of total energy supply in the country. However, the traditional utilization of coal has brought about deteriorating environment problems. To protect our environment, the recent development of clean and efficient advanced coal utilization technology is changing into the focus of the production of power, chemical products and clean synthetic fuels. Integrated gasification combined cycle (IGCC) power system and integrated gasification with molten carbonate fuel cells (IGFC) are being advanced worldwide to produce power from coal due to their potential for superior environmental performance, economics and efficiency [1–5]. Increasing attention is being paid to the production of alcohol and ether fuels from coal gas as one of the most promising energy instead of gasoline or diesel fuels [6–8]. The poly-generation sys-

tem for the production of alcohol and ether fuels as well as power also comes to the research focus [9–11].

The coke-making industry based upon pyrolysis as main process is rapidly developing in China. A lot of coke-oven gas co-products had not been effectively utilized leading to pollute environment and consume energy resource in China. The research on coke-oven gas as feedstock for IGCC process and chemical fuel synthesis will result in both environmental and economic benefits. The team led by Professor Xie Kechang proposed a poly-generation system to produce the syngas from the combination of gasified and pyrolyzed coal gas (dual gas resources) for the alcohol ether synthesis [10,11]. An advantage of this proposal is that the CO₂ from gasified coal gas and the CH₄ from pyrolyzed coal gas can undergo dry reforming, or CO₂ reforming of CH₄, to produce syngas, CO and H₂; thus CO₂ emission from coal gas can be suppressed. Nevertheless, one of the challenges that have to overcome is the purification of the coal gas, because there are many gaseous contaminants such as sulfur, nitrogen and chlorine pollutants, alkali metal, heavy metal and tar vapor in dual gas resources, which may damage or poison the downstream pipelines, instrument and catalysts. The high temperature purification of these gaseous contaminants plays an important role in the dual gas resources poly-generation system. The removal of nitrogen and chlorine

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pollutants, alkali metal, heavy metal and tar vapor in high temperature has been studied by many researchers [12–14]. Removing H_2S and organic sulfur from coal gas is focused in this poly-generation system. There are obvious differences for sulfur species, sulfur content in coal gas, so the optimization of operation parameters for desulfurization are very important to meet the demand of sulfur removal precision and sorbent stability according to the different units in the coal poly-generation system using dual gas resources. The desulfurization process marching with coal gas based poly-generation system with the production of alcohol and ether fuels as well as power is presented according to gas components, sulfur content, sulfur species and desulfurization accuracy in this paper. The different H_2S removal sorbents and organic sulfur catalyst were developed and their performances were test under simulated conditions in poly-generation process.

2. Proposal of coal poly-generation system

2.1. Description of coal poly-generation system

A new coal poly-generation system where both gasification coal gas and pyrolysis coal gas are used as feedstock to produce alcohol and ether fuels as well as power has been put forward based on China characteristics for the present coal utilization status such as low utilization efficiency, high environmental pollution and poor economic performance [9–11]. The flow diagram of this coal poly-generation system is shown in Fig. 1.

In comparison with traditional coal utilization processes, the coal poly-generation system can improve significantly the utilization efficiency of source and energy. In terms of the CO_2 mitigation specialty equation of dual gas resources poly-generation system compared to the case of coal to methanol conventionally, the dual gas resources poly-generation system may reduce CO_2 emission for 879.22 kg/1000 m^3 syngas and the efficiency of calorific value for producing syngas by this system may improve 19.7% more than traditional production process [15].

This coal poly-generation system consists of five sections: (i) coal gas production from coal gasification and pyrolysis. This section includes an air separation unit, an ash agglomerating fluidized bed coal gasifier, a coal carbonization oven. (ii) Coal gas cleanup,

which includes H_2S crude removal, H_2S fine removal and organic sulfur conversion. (iii) Power generation including a gas turbine and a steam turbine. (iv) Syngas (H_2 and CO) production from CO_2 to CH_4 reforming reaction. (v) Synthesis of alcohol and ether using slurry catalysis reactors and chemical separation units.

Adopting dual gas resources is the feature for this coal poly-generation system. In China, there are many coke-oven plants and abundant coke-oven gas which contains 55–60 vol.% H_2 , 23–27 vol.% CH_4 , 5–8 vol.% CO . Gasification coal gas mainly is composed of 45–54 vol.% CO , 32–38 vol.% H_2 , 10–18 vol.% CO_2 . The gasification gas with rich carbon such as carbon dioxide and the coke-oven gas with rich hydrogen such as methane are catalytically reformed to produce the syngas, which will be used to produce alcohol and ether fuels. In accord with the characteristics of gasification coal gas and pyrolysis coal gas, CH_4 – CO_2 catalytic reforming reaction was presented to obtain synthesis gas CO and H_2 from CH_4 in coke-oven gas and CO_2 in gasification gas [16]. The reforming process decreases the emission of CO_2 by the reaction of CO_2 with CH_4 to form CO and H_2 , which is free from the water–gas shift to get more H_2 prior to synthesis in traditional process. In this reforming process, coke was used as reforming catalyst and it possess good anti-sulfur peculiarity. The synthesis gas reformed with proper H/C ratio is used to produce alcohol and ether fuels by slurry catalyst, which CuO/ZrO_2 can directly synthesize dimethyl ether from CO hydrogenation without adding any methanol dehydration component, and the highest DME selectivity reaches 92.12% [17]. The prominent features in this coal poly-generation system are that water–gas shift reaction is not demand and CO_2 emission is reduced adopting gasification and pyrolysis dual gas resources.

2.2. Matching desulfurization process

The desulfurization matching with the coal poly-generation system using dual gas resources is presented according to gas components, sulfur content, sulfur species and desulfurization accuracy in this technology. The flow diagram of the matching desulfurization process is shown in Fig. 2.

From Fig. 2, it is seen that the matching desulfurization process consists of three sections. Desulfurization unit number one (DS-1)

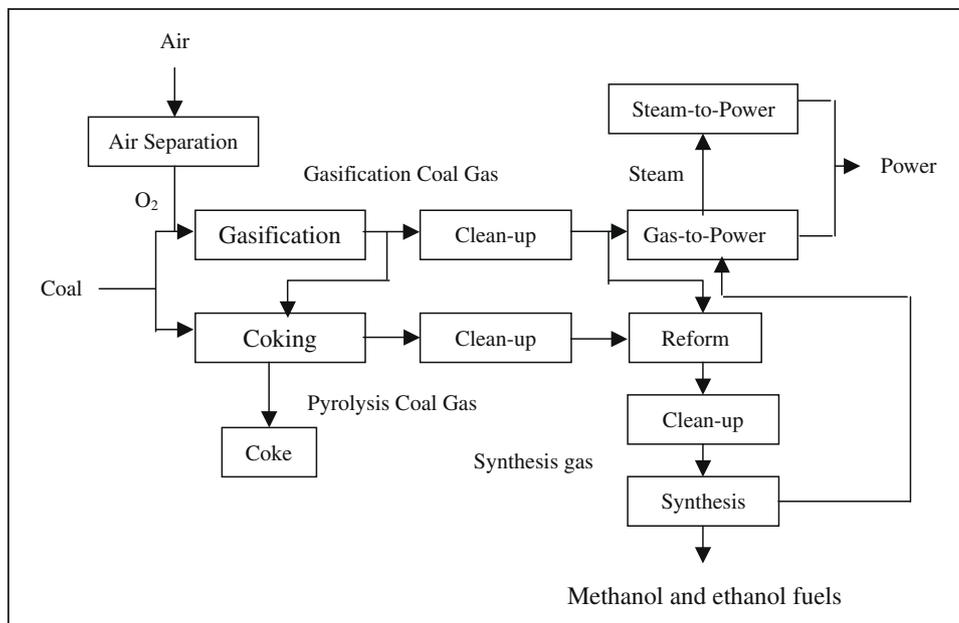


Fig. 1. Flow diagram of the dual gas resources based poly-generation system.

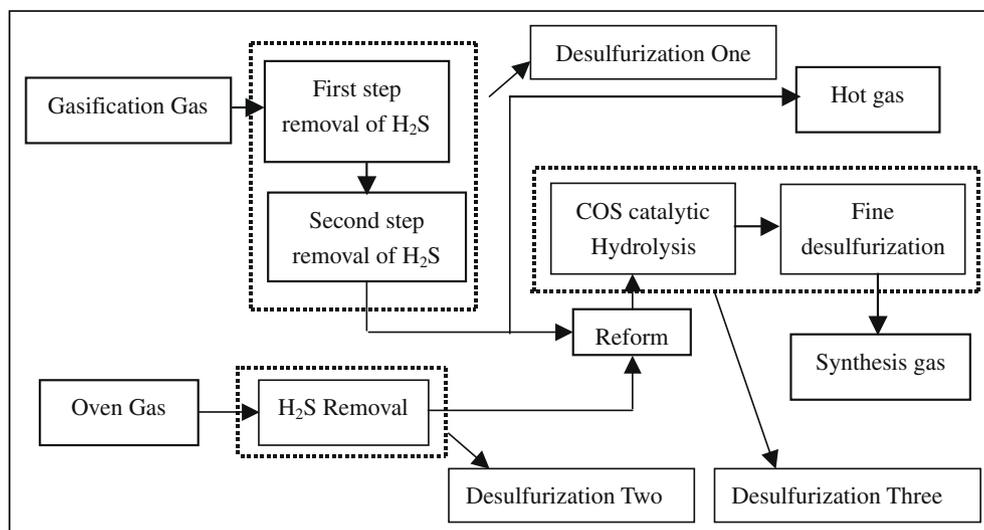


Fig. 2. Flow diagram of the desulfurization processes matching with the poly-generation system.

is a two-step H₂S removal unit working at high temperature (hot desulfurization). Desulfurization unit number two (DS-2) is a single H₂S removal unit working at atmospheric temperature (normal desulfurization). And desulfurization unit number three (DS-3) includes COS and CS₂ catalytic hydrolysis followed by a fine H₂S removal step operating at 200–400 °C (warm desulfurization).

The purpose of DS-1 is removing H₂S to below 20 ppm in gasification coal gas at above 500 °C, then the gas goes to generate power in gas-turbine engine or takes part in the reaction of CO₂–CH₄ reforming. H₂S in gasification coal gas will be removed by 70% in step one (crude desulfurization) and continuously removed to below 20 ppm in step two (fine desulfurization) in DS-1 unit. The crude desulfurization sorbent should possess high H₂S removal capacity and low run cost, and the fine desulfurization sorbent must have high efficiency for H₂S removal.

DS-2 unit is applied to remove H₂S in coke-oven gas to below 20 ppm at atmospheric temperature, and desulfurization sorbent is required to have both high efficiency and capacity for H₂S removal. Then the cleaned gas goes to CH₄–CO₂ reforming process. Coke is used as catalyst, which is also active in the gas below 20 ppm H₂S, for reform reaction between CH₄ with CO₂. Therefore, a fine desulfurization is not installed before reforming step.

DS-3 unit is mainly used in removing total sulfur to 0.1 ppm in coal gas at 200–400 °C, then the cleanup gas is sent to alcohol and ether fuels synthesis step. COS and CS₂ are converted into H₂S during organic sulfur catalytic conversion. Then H₂S formed is removed to 0.1 ppm by the fine desulfurization sorbent. The COS and CS₂ hydrolysis catalyst should hold the performances in higher conversion and anti-poisoning. The high accuracy of H₂S removal for the fine desulfurization sorbent is required.

3. Experimental

3.1. Preparation of desulfurization sorbent

Two kinds of H₂S removal sorbents for DS-1 unit were prepared for this study. The crude desulfurization sorbent employs iron oxide as main active component. The red mud, mixed clay, organic blinder and extrusion were mixed mechanically with water. The mixture was blended and extruded into cylindrical pellet. Then, the cylindrical pellets were dried at 120 °C and calcinated at 550 °C to form the crude desulfurization sorbents.

The fine desulfurization sorbent uses the mixed zinc oxide based as primary active component. The active components were obtained by co-precipitation method from Fe(NO₃)₃ and Zn(NO₃)₂. The clay was mixed with the co-precipitation powder and water was added to the powder mixture. The mixture was blended and extruded into cylindrical pellet. Then, the cylindrical pellets were dried at 120 °C and calcinated at 550 °C to form the fine desulfurization sorbents.

3.2. Preparation of organic sulfur hydrolysis catalyst

The hydrolysis catalyst for COS and CS₂ conversion is Al₂O₃-based loaded with K₂O, TiO₂ and V₂O₅. Pseudo diaspore, TiO₂, V₂O₅ and K₂CO₃ of a certain ratio were mixed to form a solid mixture. The mixture was wetted by an organic blind and water and then was extruded. The cylindrical pellets from the extruder were dried at 120 °C and calcinated at 550 °C to form COS and CS₂ hydrolysis catalyst.

3.3. Performance test

Desulfurization sorbent performances in successive sulfidation-regeneration were conducted in a quartz upflow fixed-bed reactor. The sorbents were located in the isothermal region of the reactor and the temperature was monitored using a thermocouple located approximately at the center of the sample. Analysis of the outlet and inlet gas from the reactor was carried out using a gas chromatograph with a flame photometric detector (FPD).

The same procedure was used to test the activities of COS and CS₂ hydrolysis catalyst.

4. Results and discussion

4.1. Activity of desulfurization sorbent

The activities of the crude and fine desulfurization sorbent were test in a fixed bed under atmospheric pressure, 500 °C and space velocity of 2000 h⁻¹ (STP). The composition of reactant gas (simulated coal gas) was 39.86 vol.% H₂, 32.69 vol.% CO, 19.5 vol.% CO₂, 5 vol.% H₂O, 2000–3500 mg/m³ H₂S, N₂ as balance gas. When the H₂S concentration in the outlet gas stream reached 200 mg/m³, or the efficiency of H₂S removal low 90%, the test was terminated and the spent sorbent was removed out from the reactor bed.

The spent sorbent was regenerated at 700 °C using a gas composed of 5 vol.% O₂, 30 vol.% H₂O, N₂ as the balance gas. The desulfurization sorbent regenerated was used to removal H₂S again.

The crude desulfurization sorbent was used in a sulfidation-regeneration cycle for five times and the breakthrough curves are shown in Fig. 3. So was the fine desulfurization sorbent for three times and the breakthrough curves are shown in Fig. 4.

From Fig. 3, it can be seen the breakthrough curve for the crude desulfurization sorbent maintains also the same in sulfidation in the five sulfidation-regeneration cycles. With the efficiencies of H₂S removal no less than 90% from the simulated coal gas, the average sulfur capacity for every sulfidation at 500 °C in the five sulfidation-regeneration cycles was 21.85 wt.%. The mechanical strength of desulfurization sorbent after five sulfidation-regeneration cycles was 236 N/cm, which is good for reuse. Although the thermodynamics for FeO–H₂S are less favorable than that for ZnO–H₂S, the preparation cost for iron oxide desulfurization sorbent is low and elemental sulfur can be directly obtain by the regeneration of iron oxide desulfurization sorbent. Therefore, the iron oxide desulfurization sorbent was taken as the crude desulfurization sorbent to remove heavy load of H₂S in coal-derived gas.

From Fig. 4, it can be seen the breakthrough curve for the fine desulfurization sorbent is similar in three sulfidation-regeneration cycles. When the efficiencies of H₂S removal were no below 99.9%, the average sulfur capacity in three sulfidation-regeneration cycles was 24.91 wt.% in simulated coal gas at 500 °C. The mechanical

strength of desulfurization sorbent after three sulfidation-regeneration cycles is 103 N/cm, which is also strong enough for reuse. Although the thermodynamics of ZnO–H₂S reaction is more favorable than that of FeO–H₂S, the run cost for zinc oxide desulfurization sorbent is high and the regeneration process is complex. Therefore the mixed zinc oxide desulfurization absorbent was taken as the fine desulfurization sorbent to remove small part of H₂S in coal-derived gas and reduce H₂S to 0.1 ppm in synthesis gas.

4.2. Catalytic activity of organic sulfur hydrolysis catalyst

The catalytic activities of organic sulfur hydrolysis catalyst were tested using a fixed bed under atmospheric pressure, 300 °C and space velocity of 2000–14,000 h⁻¹ (STP). The composition of reactant gas was 1–5 vol.% H₂O, 200–300 mg/m³ of COS or CS₂ and N₂ as balance gas.

The hydrolysis conversion of COS and CS₂ at the different space velocity for catalyst prepared under study are given in Figs. 5 and 7, respectively. The rate constants of COS and CS₂ hydrolysis over catalysts prepared are shown in Figs. 6 and 8, respectively.

From Figs. 5 and 6, it can be seen that the COS hydrolysis conversions are 99% at 300 °C, atmospheric pressure, space velocity 4000–13,000 h⁻¹. The COS hydrolysis rate constant promotes with the increase of space velocity from 4000 to 10,000 h⁻¹ and approaches a stable value of 17.11 s⁻¹ above 10,000 h⁻¹. This is

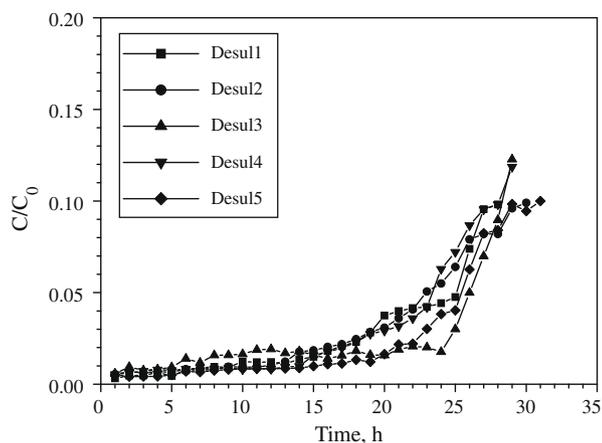


Fig. 3. Breakthrough curve of the crude desulfurization sorbent.

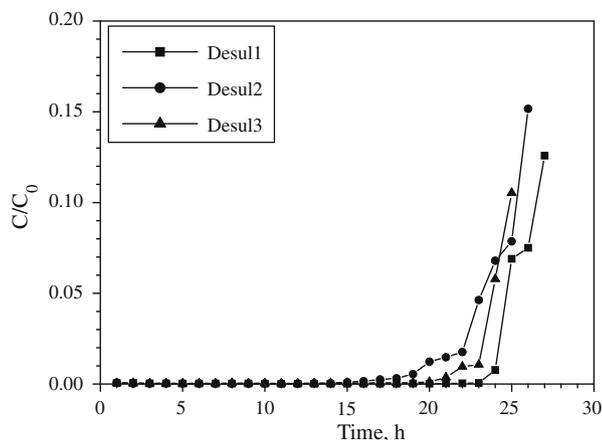


Fig. 4. Breakthrough curve of the fine desulfurization sorbent.

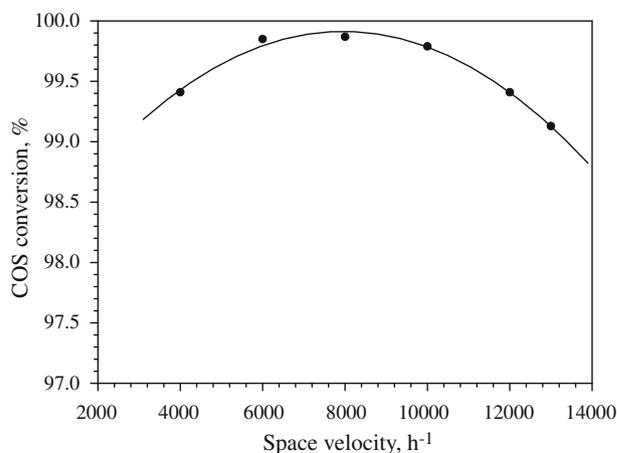


Fig. 5. COS hydrolysis conversion over the prepared catalyst at different space velocity.

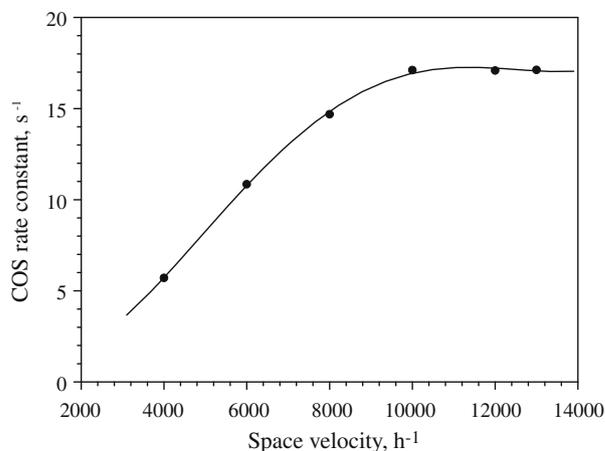


Fig. 6. Rate constant for COS hydrolysis over the prepared catalyst at different space velocity.

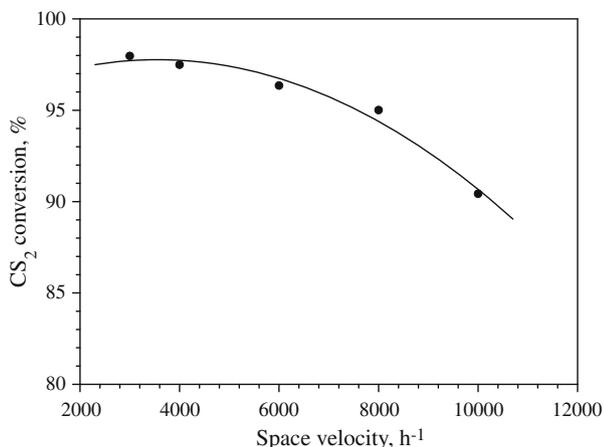


Fig. 7. CS₂ hydrolysis conversions over the prepared catalyst at different space velocity.

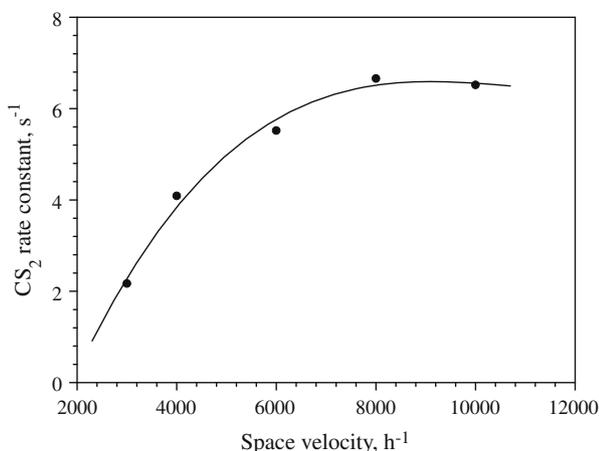


Fig. 8. Rate constant for CS₂ hydrolysis over the prepared catalyst at different space velocity.

caused by the external diffusion at lower line speed. When the external diffusion was eliminated with the increase of line speed, the catalyst exhibited the real catalytic activity of COS and has high catalytic activity.

From Figs. 7 and 8, it can be seen that the CS₂ hydrolysis conversions are 90% at 300 °C, atmospheric pressure, space velocity 3000–10,000 h⁻¹ and CS₂ hydrolysis rate constants approach 6.59 s⁻¹. As shown above, the catalytic activity for CS₂ increase with space velocity, the catalytic activity for CS₂ is controlled by the external diffusion under the condition of lower space velocity.

Comparison between the catalytic activity for COS with CS₂ conversion, it can be seen that the catalytic activity for CS₂ is less than that for COS. This is due to the interaction between CO₂ and CS₂, as well as COS being a proposed intermediate in the CS₂ hydrolysis reaction. Furthermore, the low reactivity of CS₂ is also a severe problem as CS₂ is present in similar concentrations to COS in acid gas streams but contains twice the number of sulfur atoms. Since CS₂ is non-polar, a reduced interaction between the polar hydroxyl groups/H₂O on the catalyst surface and CS₂ is considered to occur. CS₂ has been estimated to be 2–3 times more resistant to conversion when compared with COS under comparable conditions [18].

5. Conclusion

The desulfurization process, which matches with coal based poly-generation system using gasification and pyrolysis coal gas to produce alcohol and ether fuels as well as power, consists of H₂S removal at high temperature, H₂S removal at normal temperature, organic sulfur catalytic conversion and H₂S fine removal at warm temperature. The removal efficiencies for the crude and fine desulfurization sorbent prepared for hot coal gas are 90% and 99% at 500 °C in simulating coal gas, and their sulfur capacities are 21.85 wt.% and 24.91 wt.%, respectively. The organic sulfur catalyst shows the high hydrolysis activity, the hydrolysis conversion of COS is more than that of CS₂ on the same catalyst. The matching desulfurization technology in this work will provide necessary information for demonstration project on dual gas resources coal poly-generation system.

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