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Hollow Fiber Catalytic Membranes

Authors:

Y.H. Ma
W. Moser
A. Shelekhin
S. Pien

Contractor:

Worcester Polytechnic Institute
Center for Inorganic Membrane Studies
Chemical Engineering Department
100 Institute Road
Worcester, MA 01609

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CONTRACT INFORMATION

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Contractor Worcester Polytechnic Institute,
Center for Inorganic Membrane Studies,
Chemical Engineering Department,
100 Institute Rd., Worcester, MA 01609
(508) 831-5398

Contractor Project Manager Yi Hua Ma

Principal Investigators Yi Hua Ma
William Moser
Alexander Shelekhin
Shyhing Pien

METC Project Manager Venkat K.Venkataraman

Period of Performance September 15, 1992 to May 15, 1993

Schedule and Milestones

FY93 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Permeability Study	_____											
Catalyst Study		_____										
Membrane Reactor Study			_____									
Mathematical Modeling					_____							
Comparative analysis								_____				

OBJECTIVES

The objective of the present research is to investigate the possibility of the enhancement of the H₂S thermal decomposition in the IGCC system by employing the hollow fiber catalytic membrane reactor. To accomplish the objective, the following major components in the analysis of the high temperature membrane reactor must be investigated:

- * high-temperature stability of the porous glass membrane;
- * catalytic properties of MoS₂ and of the porous glass membrane;
- * catalytic decomposition of H₂S in a packed bed reactor;
- * catalytic decomposition of 100%, 8.6%, and 1.1% H₂S gas mixtures in the membrane reactor.

BACKGROUND INFORMATION

In the past decade intensive research and development efforts were directed toward the development of a principally new class of reactors - membrane reactors. The concept of the membrane reactors is based on integration of reaction and separation processes into one technological unit operation. Such an integration enables one to increase the degree of conversion of an equilibrium controlled reaction.

In the case of H_2S , hydrogen formed as a result of the catalytic thermal decomposition, passes across the membrane and is separated from the feed stream. It has been demonstrated by Kameyama et al. [1] that increased conversion of H_2S can be achieved in the membrane reactor.

Three types of membranes were proposed for the membrane reactor design. Porous glass and porous alumina membranes were employed by Kameyama et al. [1]. The decomposition of H_2S in a membrane reactor with Pd and Pt composite membranes was studied by Edlund and Pledger [2]. Molecular-sieve glass membranes with high selectivity to H_2 separation were used to design a membrane reactor by Ma et al. [3]. In all of the reported experiments an enhancement in the thermal decomposition of H_2S in the membrane reactors was reported.

Membrane reactors for the catalytic decomposition of H_2S have the following attractive features.

- * Higher conversion of H_2S compared to the packed bed reactors at the same operation temperature.

- * Hydrogen recovery from the feed stream. If the selectivity coefficient to H_2

separation exceeds 100 the concentration of hydrogen in the permeate exceeds 95%.

- * The membrane reactor is a process unit operating continuously.

PROJECT DESCRIPTION

The thermal decomposition of H_2S was conducted in membrane reactors and packed bed reactors. For the packed bed reactors, temperature and pressure dependencies of the thermal decomposition of H_2S were obtained. The membrane reactor consisted of quartz tube of 13 mm ID and 16 mm OD. The length of the quartz tube was 30 cm. The porous glass membrane length was also 30 cm. One end of the membrane was fixed to the quartz tube with epoxy Duralco 4525 (Cotronics). The other end of the membrane was glued with the same epoxy. The membrane had ID/OD=4.5/6.0 mm. Molybdenum sulfide was acquired from Johnson-Matthey. The catalyst was packed on the shell side of the membrane reactor. The length of the packing was ~ 10 cm. The weight of the catalyst in all experiments was 11 g. An Hewlett Packard HP-5890 G.C. was used to analyze the gas mixture. The oven length of the reactor system was 15 cm. The temperature of the experiments on the catalytic decomposition of H_2S in the membrane reactor was held at 800 °C. Membrane reactor studies were carried out at 20 psig and 100 psig

RESULTS

Permeability studies

Two types of membranes were considered for the design of the high temperature membrane reactor: microporous molecular-sieve membranes provided by PPG Industries Inc. (pore size less than 20

Figure 1. Transmembrane flow versus temperature in molecular-sieve membrane.

A) and porous Vycor glass membranes with pore size ~ 80 Å. Figure 1 represents a dependence of the transmembrane gas flow versus the temperature of the membrane

Figure 2. Permeability of porous glass versus temperature of pretreatment.

module for He. The permeability of the microporous molecular-sieve glass membrane decreased at temperatures higher than 300 °C. When operating temperatures

exceeded 650 °C, the permeability of the membrane dropped so much that the membrane was no longer suitable to be used in a membrane reactor operating at 800 °C. The selectivity properties of the membrane, however, remained intact even after treatment at 800 °C.

The Vycor glass porous membrane retained its selective and permeability properties up to 950 °C. Figure 2 depicts changes in porous Vycor glass permeability with temperature. The permeability increases up to the temperature of 800 °C followed by an abrupt decrease in permeability at temperatures higher than 900 °C. The membrane melted at $T > 1200$ °C. Vycor glass porous membranes were used for the design of the membrane reactor because of their relatively good thermal and mechanical stability at high temperatures.

Catalyst activity studies

Molybdenum sulfide was used as a catalyst in the membrane reactor. The catalyst activity did not decrease during several months of operation. The temperature range of operation was 500–1000 °C in an atmosphere of H_2S . The composition of the gas mixture varied from 1.1% to 100% H_2S and the operating pressures were from 10 psig to 150 psig. It was found that due to the high activity of the catalyst external mass transfer limitations were the rate controlling step.

The catalytic activity of the Vycor glass membrane was also studied at 800 °C and at 100 psig. The conversion of H_2S at 800 °C and at 100 psig was the same for MoS_2 and the Vycor glass membrane itself. Therefore, the membrane exhibits catalytic activity equal to that of the MoS_2 catalyst under the conditions of the experiment.

Catalytic properties of MoS_2 and the

Vycor glass membrane were studied in the packed bed reactor. Due to the high catalytic activity of the MoS_2 catalyst the overall reaction rate was controlled by external mass transfer limitations. Figure 3 shows the H_2S conversion as a function of the contact time for packed beds loaded with different amounts of MoS_2 (2.41g, 1.57g, 0.85g, and 0.32g). At a constant contact time, H_2S conversion increases with an increase in the

Figure 3. Conversion in the packed bed reactor versus space time W/F [μs].

amount of the catalyst. Therefore, the rate of the conversion is limited by the external mass transfer in this case.

The external mass transfer limitations were reduced by grinding the particles of the catalyst to the size of 0.3 ± 0.05 mm. Further grinding of the catalyst particles to a smaller size was limited by excessive pressure drop along the packed bed. The optimum size of the catalyst particles was calculated based on a reasonable pressure drop along the packed bed reactor. At inlet pressures higher than 20 psig, the pressure drop along the 10 cm long bed packed with 0.3 mm particles was less than 5%.

The conversion of 1.1%, 8.6%, and 100% H_2S and nitrogen mixtures was studied in the packed bed tubular membrane reactor. The MoS_2 catalyst was packed on the shell side of the membrane. The Vycor glass membrane was placed inside the quartz tube with one side sealed and the other side fixed to the quartz tube. All of the experiments were conducted at 800 °C and at pressures of 20 psig and 100 psig. The conversion in the membrane reactor increased with stage cuts and exceeded the equilibrium conversion on the shell side. The stage cut was calculated in accordance with

$$\theta = F_T / (F_S + F_T)$$

where F_S , F_T are the flow rates on the shell

Figure 4. Concentration of H_2 at the membrane reactor outlets.

and tube sides, respectively. Figure 4 and Figure 5 represent the concentration of hydrogen at the shell and tube side outlets of the membrane reactor. For pure H_2S and 8.6% gas mixture of H_2S (with 1.6% H_2 in it) the concentration of H_2 increases on the permeate (tube) side as the pressure gradient across the membrane increases from 20 psig to 100 psig. The concentration of H_2 on the reaction (shell) side decreases with the

pressure increase. This decrease may be

Figure 5. H_2 concentrations at the outlets of the membrane reactor.

attributed to two factors. First, the H_2S conversion decreases at higher pressures.

Figure 6. Total conversion in the membrane reactor.

Simultaneously, at high pressure ratios the separation performance of the membrane increases thus providing better "stripping" of H_2 from the shell side.

Total conversion in the membrane reactor can be calculated in accordance with

$$X_{Total} = (F_S * X_S + F_T * X_T) / (F_S + F_T)$$

Figure 7. Total conversion in the membrane reactor.

where X_S, X_T are conversions on the shell and tube sides respectively. Dependencies of the conversion versus the stage cut are presented in Figure 6 and Figure 7. At low stage cuts $\theta < 0.3$ the conversion decreases. The observed decrease was attributed to the external mass transfer resistance in the packed bed. To increase the stage cut in the membrane reactor the feed flow rate have to be decreased. As the space velocity decreases the effect of the external mass transfer resistance increases. At stage cut higher than 0.3 the conversion rises and reaches its maximum value at stage cut $\theta = 1$. It appears that the conversion increases due to increased effect of the membrane separation on the reaction process. For pure H_2S the conversion at $\theta = 0.13$ equals 3.6% while at $\theta = 1$ the conversion is equal 7.3%. For 8.6% H_2S gas mixture the conversion changes from 1.4% at $\theta = 0.08$ to 8.4% at $\theta = 1$.

FUTURE WORK

Based on the obtained experimental data on the conversion of H_2S gas mixtures in the packed bed and membrane reactor a comparison between these process units will be made. Such a comparison must be performed in a wide range of operating conditions. To achieve this goal a mathematical model for process simulation will be developed. Based on this model productivity and energy efficiency of both processes will be analyzed.

CONCLUSION

It has been shown that the conversion of the H_2S can be increased in the packed bed membrane reactor compared to the equilibrium conversion on the shell side. The development of a mathematical model for the proposed process is in progress. The model will enable optimization of the process conditions of the H_2S decomposition. These conditions include selectivity factors and pressure drop across the membrane.

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