

Partial oxidation of propylene by using cesium-silver immobilized ceramic-membrane reactor

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Abstract

The epoxidation of propylene to propylene oxide in a heterogeneous system was studied by using a Micro Porous Glass (MPG) membrane reactor immobilized with cesium-silver (Cs-Ag) catalysts. For a quantitative evaluation of the membrane reactor efficiency to produce a propylene oxide, three different reactor systems were compared by using a diffusion flow reactor (DFR), convection flow reactor (CFR) and plug flow reactor (PFR). CFR was observed to be the most suitable reactor for synthesis of propylene oxide because of a reaction stability. The steady state rate analysis of CFR consistently proposed the Langmuir-Hinshelwood model equation based on two different active sites adsorption for the synthesis of propylene oxide and a competitive adsorption on a single active site for the synthesis of carbon dioxide.

Keywords: epoxidation of propylene, Cs-Ag/MPG membrane reactor, CFR

1. Introduction

Although the epoxidation of propylene to propylene oxide in heterogeneous catalysis has been challenged by a large number of researches, the direct synthesis of propylene oxide for commercial process is still not achieved [1-4]. To solve this difficulty, a new process for epoxidation of propylene is vitally required and a new membrane reactor system might be considered as one possible solution. In laboratory scale application, a large number of researches have studied to develop new membrane system with high efficiency of objective products [5,6]. Hazbun [7] reported that an extraordinary propylene oxide productivity as 30% of propylene oxide selectivity and 15% of propylene conversion at 573-773K by using a

calcium/yttria/magnesia stabilized zirconia tube externally coated with a film of Zr:Y:Ti. We also reported the propylene oxide and carbon dioxide were studied on a silver oxide containing sodium chloride and sodium hydrogen sulfate by using the transient response method, and the transient selectivity of propylene oxide gave 80% even though the steady state selectivity was less than 10% [8]. These results strongly suggested a possibility of propylene oxide selectivity enhancement to be expected on a membrane modified by silver catalyst. In our present study, the epoxidation of propylene to propylene oxide over a cesium-silver (Cs-Ag) catalyst immobilized in the pores of Micro Porous Glass (MPG) membrane was studied by using three different reactors: (1) a diffusion flow reactor (DFR) in which oxygen and propylene passed through the membrane pores by a counter current, (2) a convection flow reactor (CFR) in which reactant gasses passed through the ceramic membrane pores by convection flow, and (3) a plug flow reactor (PFR) in which the catalyst particles prepared by grinding the membranes prepared for the DFR and CFR were packed. The objectives of this study are (1) to design the most efficient reactor for the synthesis of propylene oxide, (2) to prepare the most active cesium loaded for the synthesis of propylene oxide and (3) to propose a possible reaction model for epoxidation and total oxidation of propylene.

2. Experimental

The MPG membrane used in this study was 10mm OD, 8mm ID and 100mm length with the average pore diameter of 0.34 μ m, total pore volume of 0.47ml/g and BET surface area of 3.30m²/g. For the immobilization of the catalyst in the membrane pores, a cesium-silver ketenide was formed *in situ* by the reaction of two solutions, (1) a mixed solution of silver acetate, cesium acetate and pyridine and (2) a mixed solution of acetic anhydride and pyridine at room temperature for 12h in a dark room [9]. The cesium-silver ketenide supported membrane was dried at room temperature for 24h followed by calcination at 573K for 36h. The prepared membrane reactor obtained consisted of about 0.04g of Ag and 0.001-0.005g of Cs depending on the percentage of cesium and was characterized by average pore diameter of 0.21-0.23 μ m, total pore volume of 0.35-0.39ml/g and BET surface area of 3.3-3.6m²/g. Fig. 1 shows the SEM of the MPG membrane before and after being treated by 5wt% Cs-Ag catalysts. Based on the SEM and BET results, we concluded that the prepared membrane has no-collapse of porous structure after being treated by Cs-Ag catalyst.

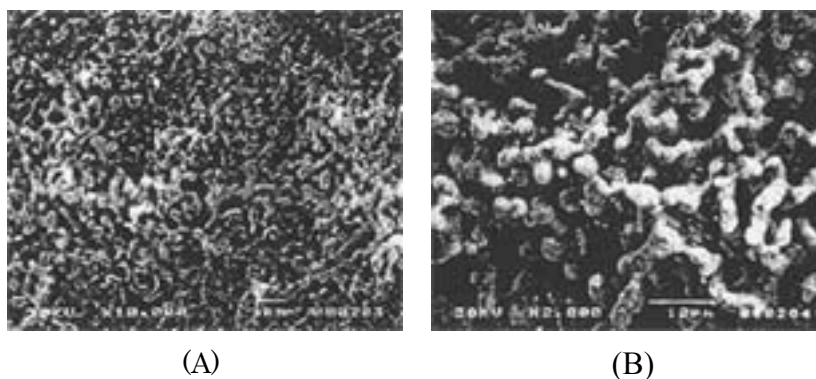


Fig. 1. SEM of the MPG membrane, (A) before and (B) after treated by 5wt% Cs-Ag catalysts

The catalyst particles for the PFR were prepared by grounding the Cs-Ag/MPG to make 60-80mesh granules. Fig. 2 illustrates a schematic drawing of the DFR, CFR and PFR. The feeds (propylene and oxygen) and products (propylene oxide and carbon dioxide) were analyzed using online GC equipped with TCD and FID detectors.

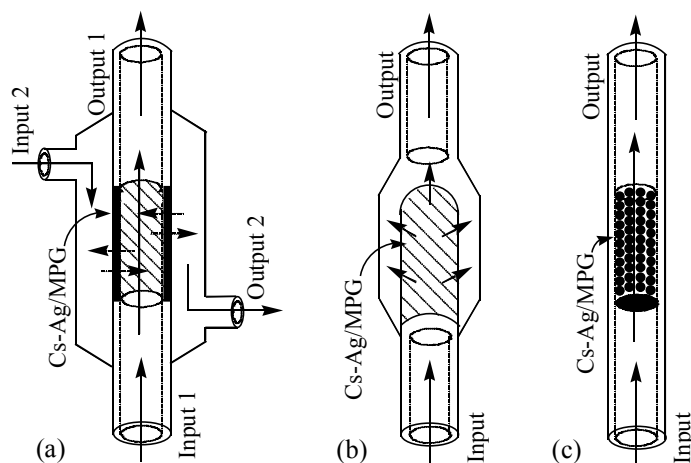


Fig. 2. a) DFR, b) CFR, and c) PFR membrane reactor

3. Results and discussion

3.1. Reactor efficiency of PFR, CFR and DFR

Fig. 3 illustrates a reactor efficiency comparison between the three membrane reactors depending on the reaction temperature from 423K to 523K.

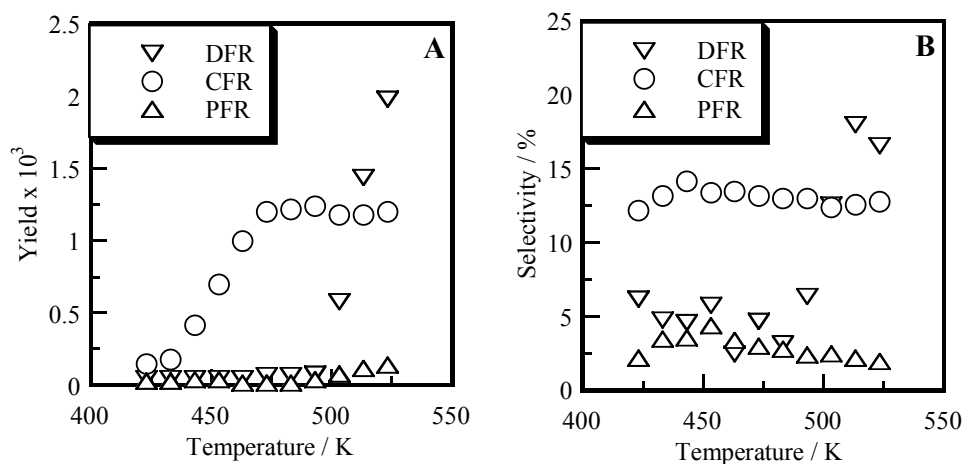


Fig. 3. The yield (A) and selectivity (B) of propylene oxide as a function of temperature. Reactions were carried out by 5.0wt% Cs-Ag/MPG at

$$F=100\text{ml/min}, P_{\text{Oxygen}}=0.05\text{atm}, P_{\text{Propylene}}=0.05\text{atm}.$$

DFR showed higher catalytic activity at a higher reaction temperature than CFR and PFR, but the reaction will be unstable due to the thermal instability of membrane at low reaction temperature. CFR resulted in high yield and selectivity of propylene oxide and showed a stable reaction for all reaction temperature range. On the contrary, PFR did not show an effective membrane reactor as DFR or CFR because it has a tendency to oxidize propylene completely to form a carbon dioxide due to the secondary oxidation of the propylene oxide product over the catalyst particles of Cs-Ag/MPG membrane. Therefore, CFR was chosen as the most suitable reactor for higher propylene oxide-selectivity and -yield and the stable operation compare to the DFR and PFR.

The addition of cesium up to 5.0wt% enhanced the catalytic activity of membrane reactor, but excessive amount of cesium lead to increase the synthesis of carbon dioxide. Thus, we concluded that CFR immobilized with 5.0wt% Cs-Ag gave the maximum efficiency of propylene oxide-synthesis as 14%-selectivity and

1.2x10⁻³-yield.

3.2. *Steady state rate kinetics for CFR*

The steady state rate analysis of CFR consistently proposed the Langmuir-Hinshelwood model equation based on two different active sites adsorption for synthesis of propylene oxide and a competitive adsorption on a single active site for synthesis of carbon dioxide as expressed in Scheme 1. The rate-determining step for synthesis of propylene oxide was directly influenced by reactor system and reaction temperature. The rates for synthesis of propylene oxide and carbon dioxide in a surface reaction controlling region obtained at a limited temperature region of the CFR was explained by two different reaction pathways characterized with equations (1) and (2).

$$r_{C_3H_6O} = \frac{k_{C_3H_6O} K_{C_3H_6} P_{C_3H_6} K_{O_2} P_{O_2}}{(1 + K_{C_3H_6} P_{C_3H_6})(1 + K_{O_2} P_{O_2})} \dots\dots\dots 1)$$

$$r_{CO_2} = \frac{k_{CO_2} K_{C_3H_6} P_{C_3H_6} K_{O_2} P_{O_2}}{(1 + K_{C_3H_6} P_{C_3H_6} + K_{O_2} P_{O_2})^2} \dots\dots\dots 2)$$

Scheme 1. Proposed reaction mechanisms for synthesis of propylene oxide and carbon dioxide based on the Langmuir-Hinshelwood model.

Fig. 4 illustrates a typical example of the linear analysis of equations (1) and (2) for the synthesis rates of propylene oxide and carbon dioxide as a function of P_{Propylene}. From the results on Fig. 4, we concluded that the equations (1) and (2) consistently explained all of the steady state rate data obtained.

An arrhenius plot of the apparent rate for synthesis of propylene oxide clearly demonstrated three different rate controlling regions as the surface reaction controlling with activation energy (E) of 83kJ/mol at 423-437K, pore diffusion controlling with E=44kJ/mol at 463-473K and the film diffusion controlling with E=7.7kJ/mol at 483-523K, as illustrated in Fig. 5. The activation energy for synthesis of propylene oxide over membrane reactor is lower than that of silver-particle packed bed reactor of 58.6kJ/mol [10] and Ag(110) catalyst of 48.9kJ/mol [11]. Thus, we suggested that the membrane catalyst exhibited better catalytic performance than silver - particle packed bed reactor and it should be considered as a new process system for further development of direct synthesis of propylene oxide from the mixture gasses of propylene and oxygen.

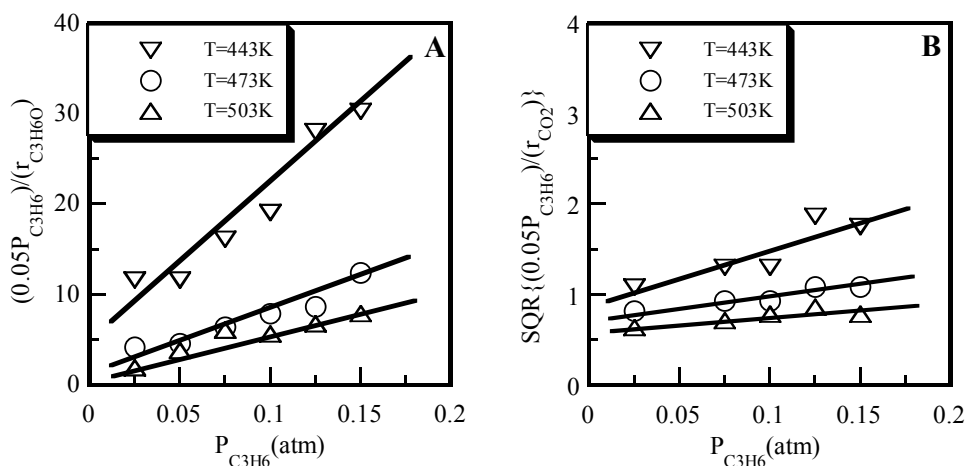


Fig. 4. Synthesis rate of (A) propylene oxide and (B) carbon dioxide vs. partial pressure of propylene and oxygen. Reactions were carried out by

5.0wt% Cs-Ag/MPG with $P_{\text{Oxygen}}=0.05\text{atm}$, $F=100\text{ml/min}$.

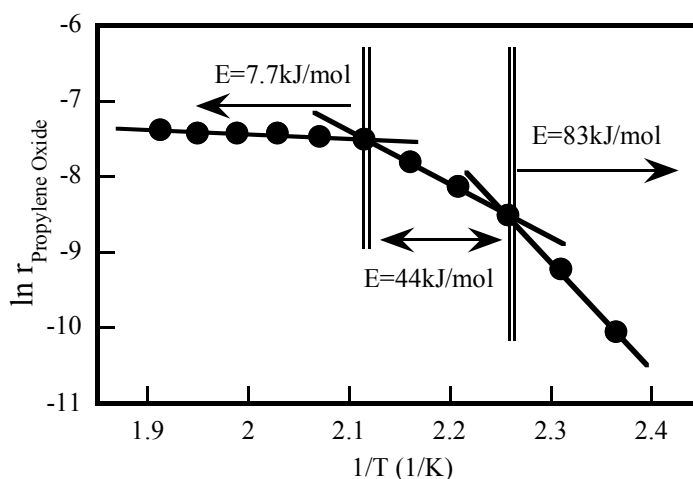


Fig. 5. Arrhenius plot for synthesis of propylene oxide.

3.3. Selectivity enhancement characterized by the convection flow

The selectivity of propylene oxide was increased with increasing the total reaction gas flow rate (F) passing through the membrane pores, such as 11.2-17.5%-selectivity according to 50-150ml/min-flow rate at 503K, indicating an effective role of the convection flow in the membrane pores for the enhancement of selectivity compared to the intraparticle diffusion in a spherical particle as a catalyst support used for the conventional packed bed reactors.

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