

DEVELOPMENT OF MEMBRANE REACTOR FOR EPOXIDATION OF PROPYLENE TO PROPYLENE OXIDE IN A SINGLE STEP PROCESS

Sugeng Triwahyono¹, Aishah A. Jalil², Hadi Nur¹, Halimatun Hamdan¹ and Masayoshi Kobayashi³

¹Ibnu Sina Institute for Fundamental Science Studies, ²Faculty of Chemical and Natural Resources Engineering, 81310 UTM, Skudai, Johor

³Faculty of Chemical and Environmental Engineering, Kitami Institute of Technology, 165, Koenchou, Kitamishi, 090 Japan

E-mail: sugeng@ibnusina.utm.my

ABSTRACT

The epoxidation of propylene to propylene oxide in a heterogeneous system was studied by using a Micro Porous Glass (MPG) membrane reactor immobilised 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). The selectivity of propylene oxide for DFR, CFR, and PFR were evaluated as 1-18 %, 12-14 %, and 1.5-4 % respectively at 423-523 K, and the CFR was observed to be the most suitable reactor for epoxidation of propylene to 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. At 503 K, the selectivity of propylene oxide was widely shifted from 11.2-17.5 % depending on the total reactant flow rate in the membrane pores, as flow rate is 50-150 cm³/min, indicating the convection flow in the pore to contribute to a selective growth of propylene oxide.

Keywords: CFR, Cs-Ag/MPG Membrane Reactor, Epoxidation of Propylene

1. INTRODUCTION

The utilisation of propylene oxide has been increasing in the polymer industry in recent years. Major conventional production methods of propylene oxide such as chlorohydrin and Halcon processes have many disadvantages of multi-step process, using an expensive reactant such as hydroperoxide reagents and produce large amount of low commercial values and hazardous by-products such as chlorinated organic compounds [1]. These environmentally disadvantageous processes suffer from plant complexity and production inefficiencies. Several alternative methods are being approached to overcome the deficiencies in the current industrial processes. The direct synthesis of propylene oxide by the use of molecular oxygen was reported by Haruta *et al.* in which Au was incorporated on TiO₂ or Ti/MCM-41 solid catalysts to synthesize propylene oxide from mixed gasses of propylene, O₂ and H₂ at 303-393 K with a greater than 90 % of propylene oxide selectivity and less than 4 % of propylene conversion [2,3]. Over support materials such as titania, anatase, zeolite and TS-1 and modified by K, Pd, Ag or Mo, also exhibited as effective catalysts for the epoxidation of propylene to propylene oxide, though either low selectivity or low yield was obtained [4-8]. The use of silver catalyst only gave a few order selectivity of propylene oxide because of the easiness of molecule with allylic hydrogen atoms like propylene to be perfectly combusted by surface oxygen species [4].

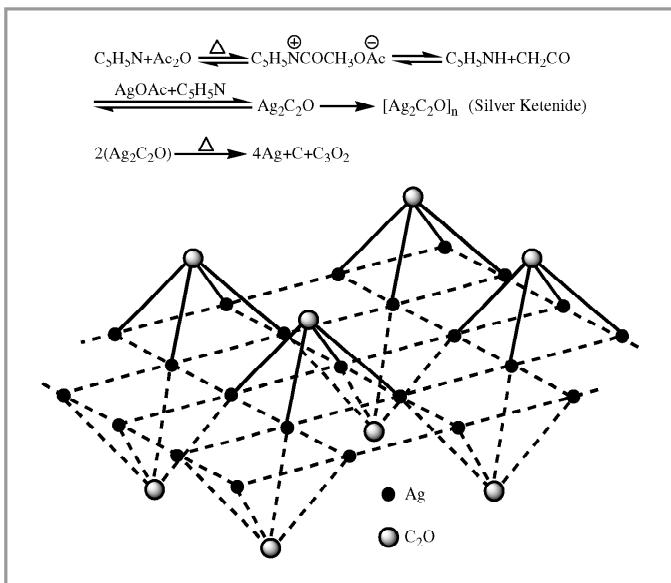
Although the epoxidation of propylene to propylene oxide in heterogeneous catalysis has been challenged by a large number of researchers, the direct synthesis of propylene oxide for industrial process is still not achieved. To solve this difficulty, a new process for the epoxidation of propylene is crucially required and a new membrane reactor system might

be considered as one possible solution. In laboratory scale application, a large number of researchers have studied to develop a new membrane system with a high yield of propylene oxide [9, 10]. Hazbun *et al.* reported that an extraordinary propylene oxide productivity at 30 % of propylene oxide selectivity and 15 % of propylene conversion at 573-773 K by using a calcia/yttria/magnesia stabilised zirconia tube externally coated with a film of Zr:Y:Ti [11]. In our previous paper [12], the transient behavior of propylene oxide and carbon dioxide was 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 %. 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 immobilised 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 gases 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 were (1) to design the most efficient reactor for the synthesis of propylene oxide focusing on the role of convection flow in the membrane pores, (2) to prepare the most active cesium immobilisation for the synthesis of propylene oxide and (3) to propose a possible reaction model for the epoxidation and complete oxidation of propylene.

2. EXPERIMENTAL

The MPG membrane used in this study was 10 mm OD, 8 mm ID and 100 mm length with an average pore diameter of 0.34 μm , total pore volume of 0.47 ml/g and BET surface area of 3.30 m^2/g . For the immobilisation of the catalyst in the membrane pores, a silver ketenide was formed in the membrane pores by the reaction of two solutions, (1) a mixed solution of silver acetate and (50 ml) pyridine and (2) a mixed solution of (50 ml) acetic anhydride and (75 ml) pyridine at room temperature for 12 h in a dark room as shown in Scheme 1 [13]. Cesium acetate was mixed in solution (1) as a co-catalyst and adjusted to be 2.5-10 wt% Cs to Ag catalyst. The cesium-silver ketenide supported membrane was dried at room temperature for 24 h followed by calcination at 573 K for 36 h.

The prepared membrane reactor obtained consisted of about 0.04 g of silver and 0.001-0.005 g of cesium depending on the percentage of cesium. Scanning Electron Microscope (SEM) and BET measurement were used to monitor the structure of the membrane. The prepared Cs-Ag/MPG membrane reactors have little change on the surface area, total pore volume and pore diameter due to the deposition of cesium-silver catalyst over the surface of the membrane. The detailed properties of the prepared Cs-Ag/MPG membrane reactors are listed in Table 1. Figure 1 shows the SEM of the MPG membrane before and after being treated by 5 wt% Cs-Ag catalyst. Based on the SEM and BET results, we concluded that the prepared membrane has no-collapse of porous structure after being modified by cesium-silver catalyst.



Scheme 1: Synthesis and structure of silver ketenide

Table 1: Properties of prepared membrane reactors

| Sample | Cs-Ag (g/g-MPG) | Pore Diam. (μm) | Pore Vol. (ml/g) | Surface Area (m^2/g) |
|------------------|--------------------|---------------------------------|---------------------|---|
| MPG | - | 0.34 | 0.47 | 3.30 |
| Ag/MPG | 0.036 | 0.25 | 0.41 | 3.32 |
| 2.5wt% Cs-Ag/MPG | 0.040 | 0.23 | 0.38 | 3.27 |
| 5.0wt% Cs-Ag/MPG | 0.038 | 0.22 | 0.37 | 3.35 |
| 7.5wt% Cs-Ag/MPG | 0.039 | 0.22 | 0.39 | 3.52 |
| 10wt% Cs-Ag/MPG | 0.045 | 0.21 | 0.35 | 3.36 |

The catalyst particles for the PFR were prepared by grounding the Cs-Ag/MPG to make 60-80 mesh granules. Prior to the reaction, the Cs-Ag/MPG membrane reactor was pretreated by a reaction gas mixture of propylene(11 vol%)-oxygen(18 vol%)-nitrogen(71 vol%) at 573 K and the total gas flow rate of 100 ml/min for 48 h.

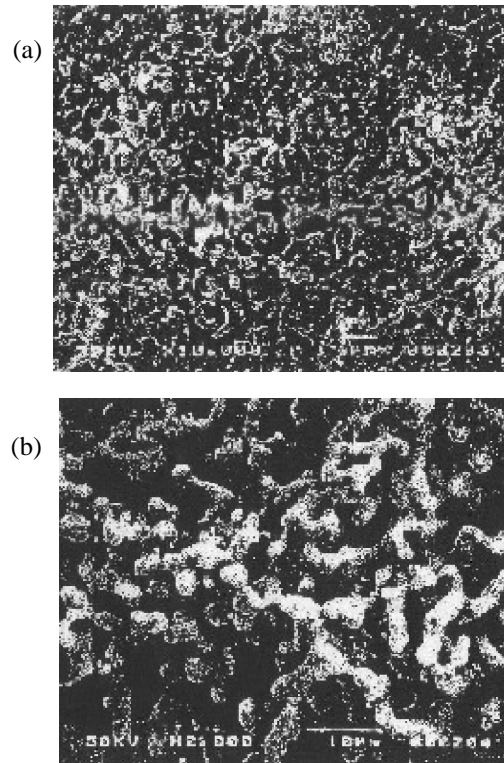


Figure 1: SEM of the MPG membrane, (A) before and (B) after being treated by 5wt% Cs-Ag catalysts

Figure 2 illustrates a schematic drawing of the DFR, CFR and PFR. An ordinal flow reactor system with 20 ml total volume of reactor was carried out. Propylene and oxygen were used as reactant gases and nitrogen was used as a carrier gas. The reaction products are propylene oxide and carbon dioxide, and no carbon monoxide was traced. The propylene oxide and carbon dioxide products were analysed using a FID gas chromatograph equipped with a column Porapak-R and a TCD gas chromatograph equipped with a column Porapak-Q, respectively. The residual reactant gases of propylene and oxygen were analysed using a FID gas chromatograph equipped with a column Porapak-R and a TCD gas chromatograph equipped with a column Molecular Sieve-5A, respectively.

3. RESULTS AND DISCUSSION

3-1. REACTOR EFFICIENCY OF PFR, CFR AND DFR

Figure 3 illustrates a reactor efficiency comparison between the three reactors depending on the reaction temperature from 423 K to 523 K. The selectivity to propylene oxide for DFR, CFR and PFR using a membrane of 5.0 wt% Cs-Ag/MPG was evaluated as 1-18 %, 12-14 % and 1.5-4 % respectively at 423-523 K, $P_{\text{Propylene}} = 0.05 \text{ atm}$, $P_{\text{Oxygen}} = 0.05 \text{ atm}$ and the total gas flow rate of 100 ml/min. DFR showed higher catalytic activity at a higher reaction

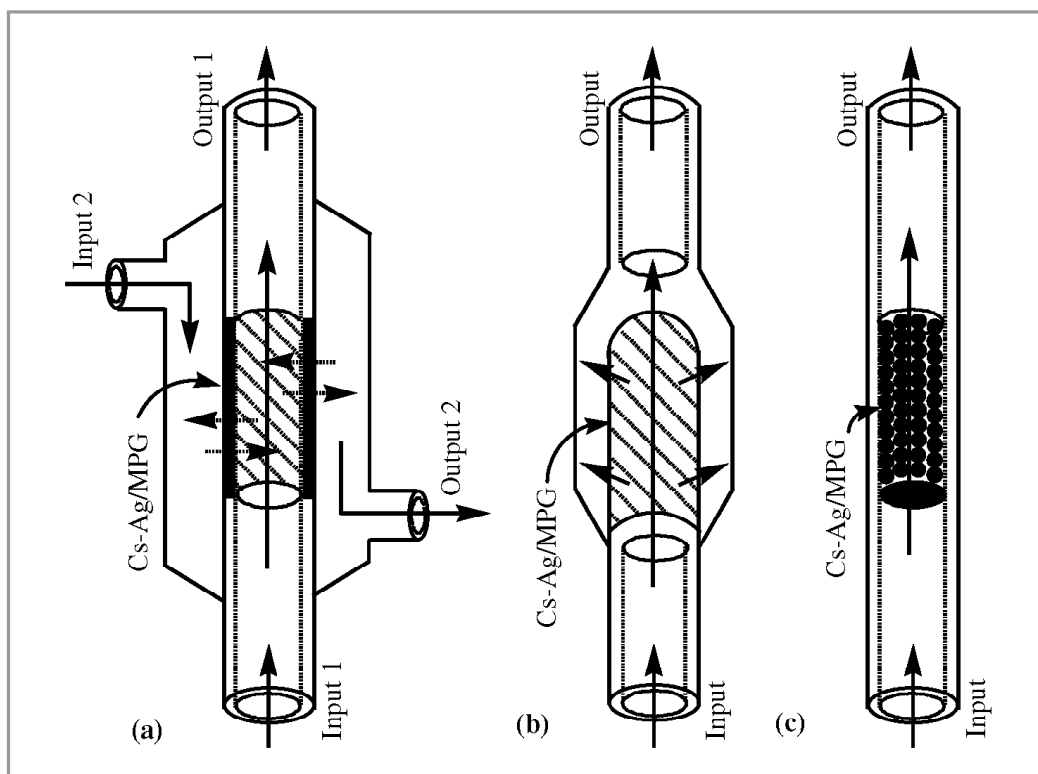


Figure 2: a) DFR, b) CFR, and c) PFR membrane reactor

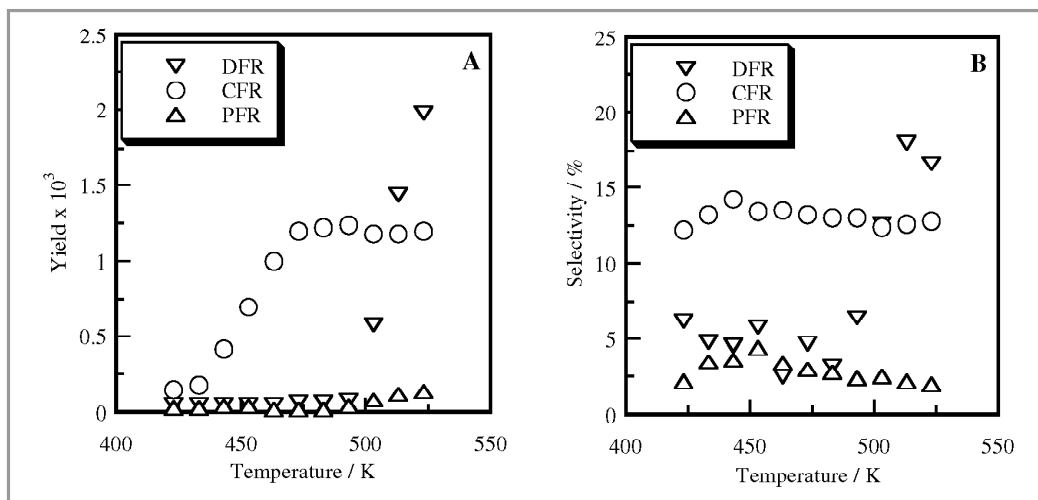


Figure 3: The yield (A) and selectivity (B) of propylene oxide as a function of temperature. Reactions were carried out by 5.0wt% Cs-Ag/MPG at $F=100\text{ml/min}$, $P_{\text{Oxygen}}=0.05\text{atm}$, $P_{\text{Propylene}}=0.05\text{atm}$

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 like DFR or CFR because it has a tendency to oxidise 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 compared to the DFR and PFR.

Figure 4 illustrates the effect of cesium on the Ag/MPG membrane reactor. It can be seen that the amount of cesium affects the catalytic property of membrane reactors. Although the role of cesium on the catalytic-reaction using Ag/MPG

which is required in the epoxidation process.

We also observed that no-catalytic performance for the synthesis of propylene oxide was detected on the MPG membrane reactor without any immobilisation of metal catalyst but the activity for synthesis of propylene oxide rose slightly by the immobilisation of silver catalyst over the MPG membrane reactor though most of the product is carbon dioxide.

Based on the above results and the comparison between 2.5, 5.0, 7.5 and 10 wt% Cs-Ag/MPG, the CFR treated with 5.0 wt% Cs-Ag gave the maximum efficiency of propylene oxide-synthesis as 14 %-selectivity and 1.2×10^{-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 the synthesis of propylene

membrane reactor is not clear yet, the change in the activity of Ag/MPG membrane reactor may not relate to the structural properties of the membrane. The Ag/MPG membrane catalysts have no significant change on the structural properties although the cesium was immobilised by up to 10 wt%. However, the change in the activity of Ag/MPG membrane reactor caused by the immobilisation of cesium may relate to the suppression effect of cesium in the formation of adsorbed oxygen in atomic state which increases the oxidation of propylene completely and/or secondary oxidation of propylene oxide to form carbon dioxide. For all reaction temperature range, the immobilisation of cesium up to 5.0 wt% increased the selectivity of propylene oxide markedly, but excessive amount of cesium decreased the selectivity of propylene oxide. It can be interpreted that the immobilisation of cesium of less than 5 wt% is not sufficient to suppress the formation of adsorbed oxygen on the Cs-Ag/MPG membrane whereas the large amount of adsorbed oxygen enhance the formation of carbon dioxide. The selectivity of propylene oxide decreased in the immobilization of cesium of more than 5 wt%, which may relate to the reducing of adsorbed oxygen extremely on the Cs-Ag/MPG membrane

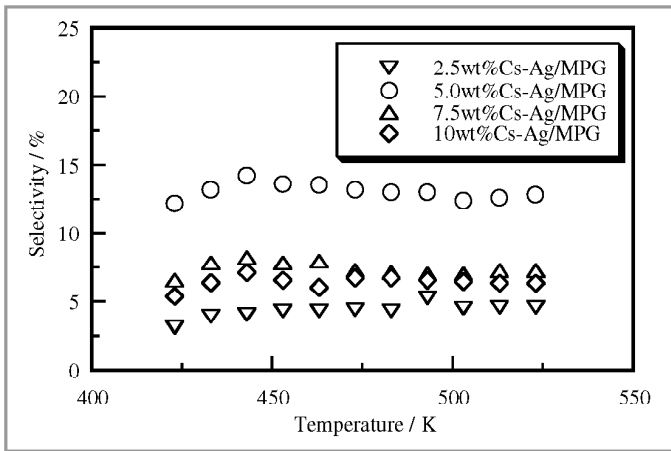
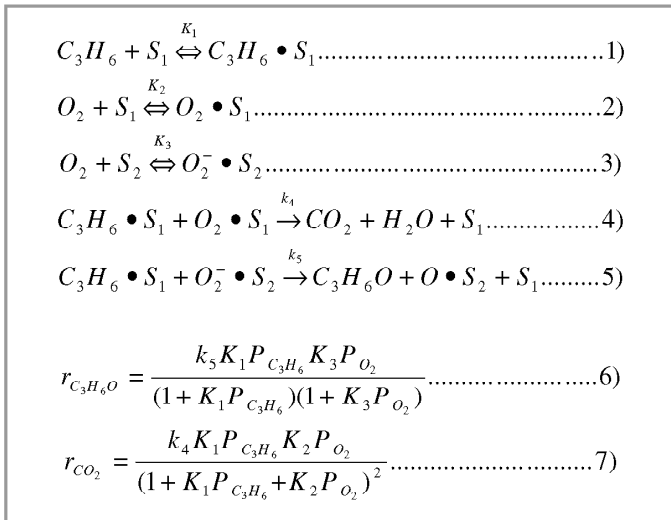


Figure 4: Selectivity of propylene oxide as a function of temperature. Reactions were carried out by CFR at $F=100\text{ml/min}$, $P_{\text{Oxygen}}=0.05\text{atm}$, $P_{\text{Propylene}}=0.05\text{atm}$

oxide and a competitive adsorption on a single active site for the synthesis of carbon dioxide as expressed in Scheme 2. The rate-determining step for the synthesis of propylene oxide was directly influenced by the reactor system and reaction temperature. The rates for the 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 characterised by Equations (6) and (7).



Scheme 2: Proposed reaction mechanisms for synthesis of propylene oxide and carbon dioxide based on the Langmuir-Hinshelwood model

Figures 5 and 6 illustrate a typical example of the linear analysis of Equations (6) and (7) for the synthesis rates of propylene oxide and carbon dioxide respectively as a function of $P_{\text{Propylene}}$ and P_{Oxygen} . From the results on Figures 5 and 6, we concluded that Equations (6) and (7) consistently explained the steady state rate data obtained.

An Arrhenius plot of the apparent rate for the synthesis of propylene oxide clearly demonstrates three different rate controlling regions as the surface reaction controlling with an activation energy (E) of 83 kJ/mol at 423-437 K, pore diffusion controlling with $E = 44$ kJ/mol at 463-473 K and the film diffusion controlling with $E = 7.7$ kJ/mol at 483-525 K, as illustrated in Figure 7. The activation energy for the formation of carbon dioxide was 75.4 kJ/mol [14].

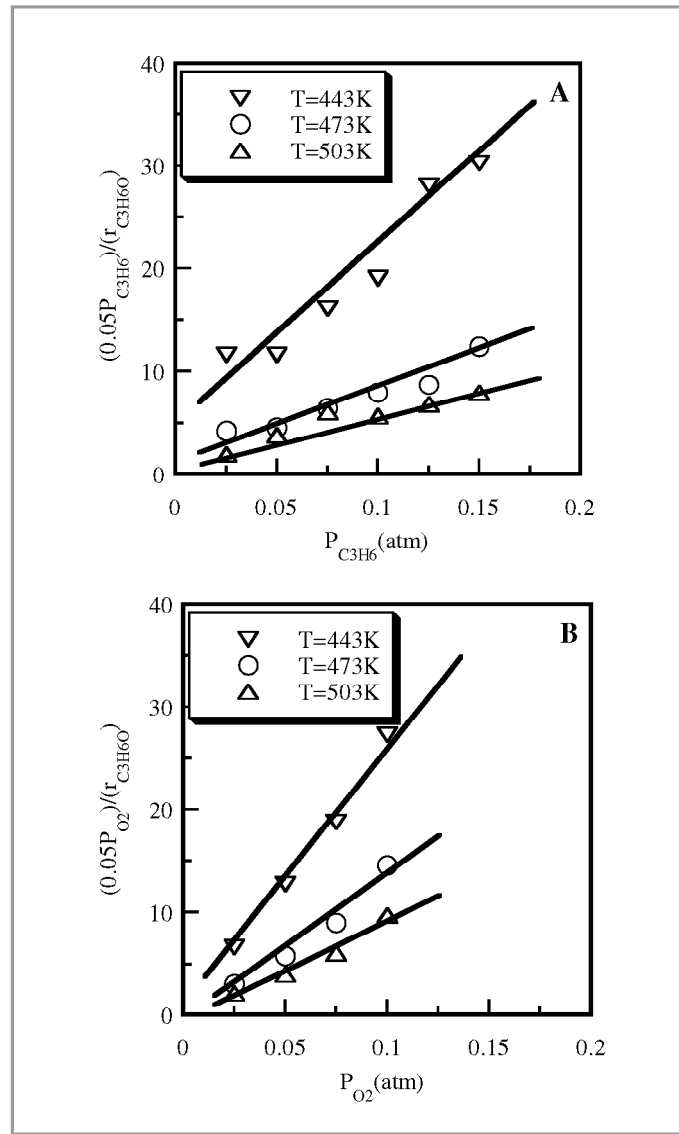


Figure 5: Synthesis rate of propylene oxide vs. partial pressure of (A) propylene and (B) oxygen. Reactions were carried out by 5.0wt% Cs-Ag/MPG with $F=100\text{ml/min}$

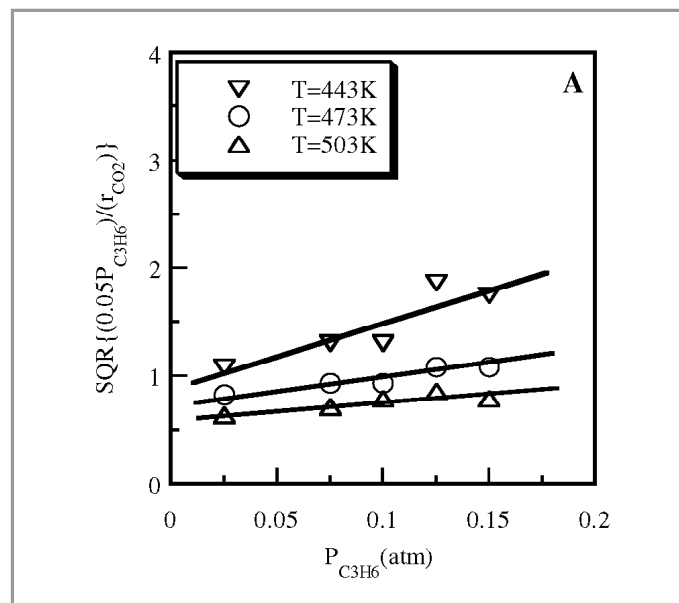


Figure 6: Synthesis rate of carbon dioxide vs. partial pressure of (A) propylene

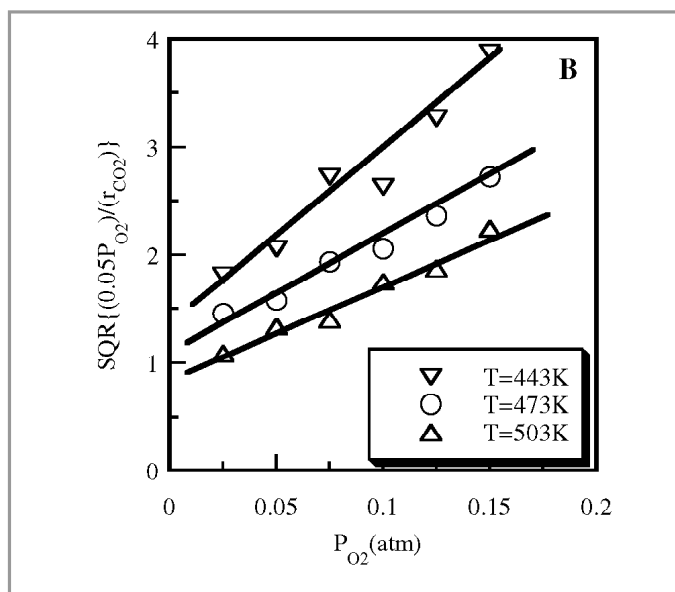


Figure 6: Synthesis rate of carbon dioxide vs. partial pressure of (B) oxygen. Reactions were carried out by 5.0wt% Cs-Ag/MPG with $F=100\text{ml/min}$

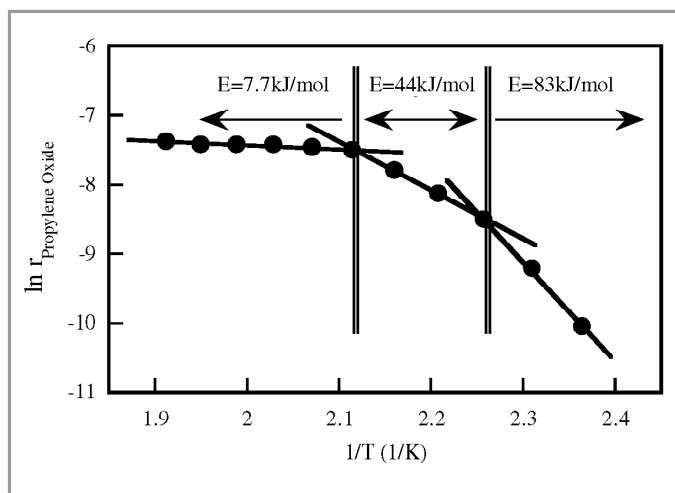


Figure 7: Arrhenius plot for synthesis of propylene oxide. Reactions were carried out by 5.0wt% Cs-Ag/MPG with $F=100\text{ml/min}$, $P_{\text{Oxygen}}=0.05\text{atm}$, $P_{\text{Propylene}}=0.05\text{atm}$

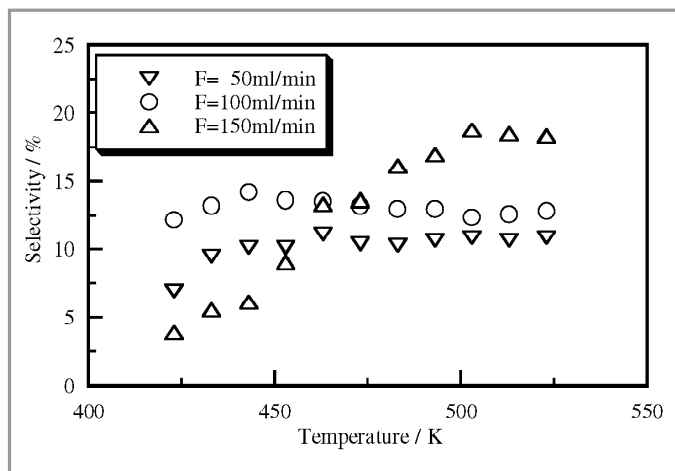


Figure 8: Selectivity of propylene oxide as a function of temperature. Reactions were carried out by 5.0wt% Cs-Ag/MPG with $P_{\text{Oxygen}}=0.05\text{atm}$, $P_{\text{Propylene}}=0.05\text{atm}$

We have also reported in a previous paper on the epoxidation of propylene over a silver-particle packed bed reactor that the activation energy for the synthesis of propylene oxide is 58.6 kJ/mol [12]. Jacquelin *et al.* reported the synthesis of propylene oxide over Ag(110) catalyst with the activation energy of 48.9 kJ/mol [15]. The lower energy activity for the synthesis of propylene oxide indicates that the Cs-Ag/MPG membrane reactor exhibits better catalytic performance than silver-particle packed bed reactor. Thus, we suggest that the MPG membrane reactor immobilised with cesium-silver catalyst be considered as a new process system for further development of direct synthesis of propylene oxide from the mixture gases of propylene and oxygen.

3-3. SELECTIVITY ENHANCEMENT CHARACTERISED BY THE CONVECTION FLOW

The selectivity of propylene oxide was increased by increasing the total reaction gas flow rate (F) passing through the membrane pores, such as 11.2-17.5 %-selectivity according to 50-150 ml/min-flow rate at 503 K as illustrated in Figure 8, 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. This experimental result also proved the validity of our previous work based on the mathematical analysis [16].

4. CONCLUSIONS

Cs-Ag/MPG membrane reactors exhibit the catalytic performance for the epoxidation of propylene to form propylene oxide in a single step process. The best results are obtained when the CFR membrane reactor is used for the synthesis of propylene oxide with the reaction condition as follows; $P_{\text{Oxygen}} = 0.05 \text{ atm}$, $P_{\text{C}_3\text{H}_6} = 0.05 \text{ atm}$, $T = 503 \text{ K}$, $F_{\text{Gas}} = 150 \text{ ml/min}$. ■

REFERENCES

- [1] R.O.Kirk, T.J. Dempsey, in : M. Grayson, D. Eckorth, H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaborg (Eds.), Kirk-Othmer, "Encyclopedia of Chemical Technology", Vol. 19, Wiley, New York, 1982, p. 246.
- [2] T. Hayashi, K. Tanaka, M. Haruta, "Selective Vapor-Phase Epoxidation of Propylene over Au/TiO₂ Catalysts in the Presence of Oxygen and Hydrogen", *J. Catal.* 178 (1998) 566.
- [3] B.S. Uphade, Y. Yamada, T. Akita, T. Nakamura, M. Haruta, "Vapor-Phase Epoxidation of Propene Using H₂ and O₂ over Au/Ti-MCM-48", *J. Appl. Catal. A: Gen.* 215 (2001) 137.
- [4] J. Lu, J.J. Bravo-Suárez, M. Haruta and S. Ted Oyama, "Direct propylene epoxidation over modified Ag/CaCO₃ catalysts", *J. Appl. Catal. A: Gen.* 302 (2006) 283.

- [5] B. S. Uphade, T. Akita, T. Nakamura and M. Haruta, "Vapor-Phase Epoxidation of Propene Using H₂ and O₂ over Au/Ti-MCM-48", *J. Catal.* 209 (2002) 331.
- [6] E.E. Stangland, K.B. Stavens, R.P. Andres, and W.N. Delgass, "Characterization of Gold-Titania Catalysts via Oxidation of Propylene to Propylene Oxide", *J. Catal.* 1991 (2000) 332.
- [7] A.M. Gaffney, A.P. Kahn, R. Pitchal, "Propylene oxide process using mixed precious metal catalyst supported on alkaline earth metal carbonate", *US Patent 5703254* (1997).
- [8] B. Cooker, A.M. Gaffney, J.D. Dewson, A.P. Kahn, R. Pitchal, "Epoxidation process using supported silver catalysts pretreated with organic chloride", *US Patent 5770746* (1998).
- [9] G. Capannelli, E. Carosini, F. Cavani, O. Monticelli and F. Trifiro, "Comparison of the catalytic performance of V₂O₅/-Al₂O₃ in the oxidehydrogenation of propane to propylene in different reactor configurations: i) packed-bed reactor, ii) monolith-like reactor and iii) Catalytic Membrane Reactor ", *Chemical Engineering Science*, 51 (1996) 1817.
- [10] V.T. Zaspalis, A.J. Burgraaf, *Inorganic Membranes Synthesis, Characterization and Application*, Van Nostrand Reinhold, New York, 1991, pp.177-207.
- [11] E.A. Hazbun, "Ceramic membrane for hydrocarbon conversion", *U.S. Patent*, 4791079 (1996).
- [12] M. Kobayashi, "Computer simulation of three dimensional visualization for dynamic behavior of complex chemical reaction processes", *Can. J. Chem. Eng.* 58 (1980) 588.
- [13] Deng Jingfa, Yang Jun, Zhang Shi, Yuan Xiahong, "Promoting effects of Re and Cs on silver catalyst in ethylene epoxidation", *J. Catal.* 138 (1992) 395.
- [14] T. Sugeng, C. Ikeda, H. Tsubo. T. Kanno, M. Kobayashi, "Epoxidation of Lower Alkane over Silver - Ceramic Porous Material", *Annual Conference of Japan Chemical Society* – Sapporo, Japan, Feb. 1994.
- [15] J. Pawelacrew and R. J. Madix, "The Effect of Subsurface Oxygen on the Desorption Kinetics of Propylene from Ag (110)", *J. Catal.* 153 (1995) 158.
- [16] M. Kobayashi, B. Golman, T. Kanno and S. Fujisaki, "Reaction pathway design and optimization in heterogeneous catalysis: I. Optimal proportion of multi-pathways designed by the transient response method", *J. Appl. Catal. A: Gen.* 151 (1997) 193.