

Fabrication of TS-1 Catalytic Membrane Reactor for the Selective Oxidation Reaction

Xiaoming Zhang, Xiangshu Chen, Hidetoshi Kita and Kenichi Okamoto

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai
2-16-1, Ube, Yamaguchi 755-8611

Fax: 81-836-85-9601, e-mail: kita@yamaguchi-u.ac.jp

TS-1 membranes have been prepared on the outer surface of porous mullite tubes by in situ hydrothermal crystallization, and a novel pervaporation catalytic membrane reactor was fabricated based on the TS-1 membrane. The catalytic performance of the pervaporation catalytic membrane reactor was tested for the epoxidation of allyl chloride with aqueous H_2O_2 as the oxidants and CH_3OH as the solvent. The allyl chloride was selectively epoxidized to the epichlorohydrin during it permeate through the TS-1 membrane together with the H_2O_2 and solvents under pervaporation conditions. The crystal structure and membrane morphology were characterized by XRD and FE-SEM analysis. The catalytic membrane reactor overcame the catalyst recovery and recycle problems existed in the conventional catalytic process and enabled the continuously production of important intermediate chemicals from the selective oxidation of organic substrates.

Key words: TS-1 membrane, pervaporation, catalytic membrane reactor, allyl chloride, epoxidation

1. INTRODUCTION

TS-1 is a well-known selective oxidation catalyst for several scientific and industrial important catalytic processes such as the epoxidation of alkenes [1,2], hydroxylation of aromatics [3], oxidation of alkanes and alcohols [4], and ammoximation of cyclohexanone [5]. In these processes, aqueous hydrogen peroxide is used as the oxidant, and the reaction is usually performed under mild conditions (low temperature and ambient pressure). These processes are environmentally benign and have the advantages of high product selectivity and yield [6,7]. In most of the liquid phase reactions, the TS-1 catalyst is employed in suspension, and the recovery and recycle of the catalyst are serious problem since the TS-1 powder is very fine and it must be separated from the reaction mixture by high speed centrifugation. Furthermore, in this suspension model, the reaction can only be performed batch by batch, and cannot produce the product continuously. To overcome these drawbacks, a catalytic membrane reactor that integrates the catalytic and separation functions will be a very powerful choice.

In the last decade, intensive research activities have been performed in the field of zeolite membranes [8-11]. Based on the different hydrophilic and hydrophobic nature of zeolites, the zeolite membranes have been widely studied for the dehydration of organic solvents and removal of organics from the water solution. They are also potential in gas separation, organic/organic separation, and catalysis [12]. The zeolite membranes have been used in catalytic membrane reactors to improve the conversions of the reactions that are limited by equilibrium by selective removing one of the products. The typical reactions included removal of H_2 in the dehydrogenation reactions [13] and removal of H_2O in the esterification reaction [14]. Furthermore, the MFI and V-MFI zeolite membranes have also been used

as oxygen distributors for propane oxidative dehydrogenation [15]. In the conventional zeolite membrane reactors, the zeolite membrane was catalytic inactive and its role was only separation. Since the zeolites are excellent catalysts for various reactions, it is desirable to fabricate a zeolite membrane reactor in which the zeolite membrane exhibited both catalytic and separation functions. Bernal et al [16] used a catalytically active H-ZSM-5 membrane to carried out the esterification of acetic acid with ethanol. The reaction and separation function were coupled efficiently and conversion was greater than in conventional fixed bed reactors. TS-1 powders have been embedded in a polydimethylsiloxane (PDMS) matrix to prepare a composite membrane [17]. This composite membrane (TS-1/PDMS) was used as interphase contactor for the oxyfunctionalization of n-hexane by aq. H_2O_2 . TS-1 membrane has also been prepared on the porous stainless steel support by hydrothermal method [18]. However, most of studies were focused on the gas or liquid separation application, and there is no report about its catalytic application while the most outstanding characteristic of TS-1 molecular sieve is the excellent selective oxidation catalytic activity. Recently, Wan et al [19] reported the fabrication of a TS-1 microreactor. The TS-1 films were grown within the channels of microstructured silicon reactors, and the deposited TS-1 films were active for catalyzing 1-pentene epoxidation.

Here, we described the fabrication of a novel TS-1 pervaporation catalytic membrane reactor for the epoxidation of allyl chloride. In this membrane reactor, the allyl chloride was epoxidized to epichlorohydrin with high selectivity and activity during it permeated through the TS-1 membrane together with the hydrogen peroxide under pervaporation conditions.

2. EXPERIMENTAL

TS-1 membranes with different titanium contents were prepared on the outer surface of porous mullite tubes (Nikkato Corp., 12 mm outer diameter, 1.5 mm thickness, 1.3 μm average pore size, 10 cm in length) by in situ crystallization. Tetraethylorthosilicate (TEOS), tetrabutylorthotitanate (TBOT), tetrapropylammonium hydroxide (TPAOH), and hydrogen peroxide (H_2O_2 , 30 wt%) were used as the raw materials. Firstly, a clear precursor solution was prepared by mixing TEOS, TPAOH, H_2O , TBOT, and H_2O_2 under vigorously stirring. The molar composition was SiO_2 : $x\text{TiO}_2$: 0.35TPAOH : $0.12\text{H}_2\text{O}_2$: $28\text{H}_2\text{O}$, where $x=0.01$, 0.02 , and 0.03 , respectively. After stirring for about 2 h at room temperature, the clear solution was transferred into a PTFE-lined autoclave in which two mullite tubes were set vertically. The hydrothermal crystallization was carried out at 150 $^\circ\text{C}$ for 72 h. After crystallization, the membrane was taken out, washed carefully with hot distilled water, dried at 100 $^\circ\text{C}$ overnight, and finally calcined at 500 $^\circ\text{C}$ for 15 h with a heating and cooling rate of 0.5 $^\circ\text{C}/\text{min}$. The accompanying powders in the bottom of autoclave were collected by centrifugation, thoroughly washed with water, and calcinated.

XRD patterns of the powders and membranes were recorded on a Rigaku RINT 2200YS X-ray diffractometer (Cu K α radiation at 40 kV and 20 mA). FT-IR characterization of the TS-1 powders was measured by a JASCO FT/IR-610 spectrometer, and the titanium contents were determined by ICP-AES (Perkin-Elmer Optima 4300DV spectrometer). The surface and cross sectional morphologies of TS-1 membranes were observed on a field emission scanning electron microscopy (FE-SEM, JEOL 6335F).

The catalytic reaction experiment was carried out on a batch-type pervaporation apparatus equipped with a condenser (Fig. 1). One end of the membrane was connected to a non-porous glass tube, and another end was connected to a vacuum system, both end were sealed with silicon tube and thermoplastic tube. The inside of the membrane was continuously evacuated while the outside was in contact with the feed solution.

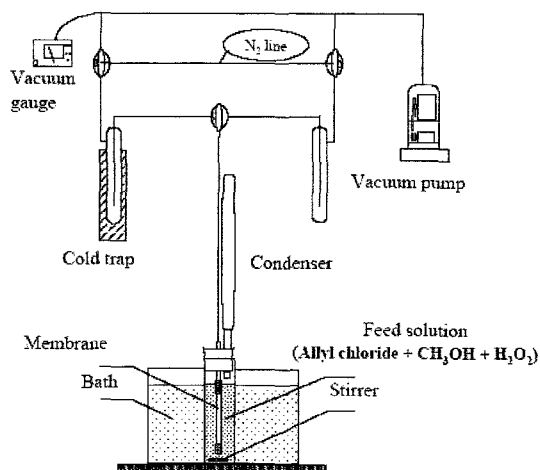


Fig. 1. Scheme of batch-type pervaporation catalytic membrane reactor for the epoxidation of allyl chloride with H_2O_2 over TS-1 membrane

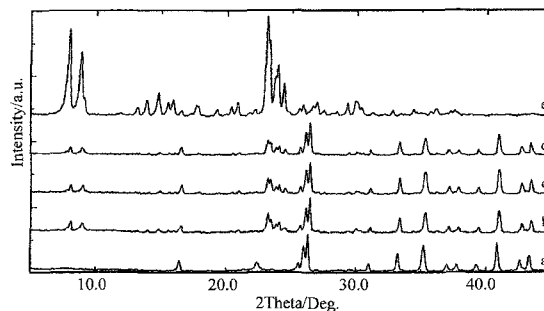


Fig. 2. XRD patterns of TS-1 membranes with different titanium contents.(precursor composition: SiO_2 : $x\text{TiO}_2$: 0.35TPAOH : $28\text{H}_2\text{O}$, $x=0.01$ (b), 0.02 (c), 0.03 (d), a. mullite support, e. TS-1($x=0.03$) powders)

The permeate vapor was collected by a cold trap cooled with liquid nitrogen. The effective membrane areas were about 20 cm^2 . The feed solution was composed of CH_3OH , allyl chloride (AC), and aqueous H_2O_2 (30 wt%). The total volume of the feed solution was about 1000 mL. The concentration AC was 5 wt%, and the molar ratio of H_2O_2 to AC was adjusted to 1. The reaction was performed at 40 $^\circ\text{C}$. Both the feed and permeate were quantitatively analyzed with a GC. In order to evaluate and compare the catalytic performance of different membranes, two parameters were defined. The rate referred to the production rate of the epichlorohydrin (ECH), that is the amount of ECH (in moles) obtained per square meter of membrane area per hour, and the conversion was the relative molar concentration of ECH in the total related organics in permeates (ECH and AC).

3. RESULTS AND DISCUSSION

The XRD patterns of the accompanying powders collected from the bottom of autoclave after hydrothermal preparation were consistent with those reported in the literatures [20], and the titanium contents determined by ICP-AES were close to those added in the precursor solutions. The isomorphous substitution of titanium in the tetrahedral framework position was confirmed by the FT-IR spectroscopy, which showed a characteristic band at ca. 960 cm^{-1} .

Fig. 2 shows the XRD patterns of the mullite support, TS-1 membranes with different titanium contents, and the corresponding TS-1 powder. The XRD patterns of the TS-1 membranes are composed of the diffraction peaks of TS-1 molecular sieve and mullite support. There is no obviously difference among the TS-1 membranes with different titanium contents. The relative intensities of the peaks corresponding to the TS-1 zeolite are lower than those of mullite support's peaks, indicating that the zeolite layer was not too thick. This can be further confirmed by the FE-SEM observation of the surface and cross section of the TS-1 membrane (Fig. 3). The surface of the mullite support was covered with randomly and loosely arranged TS-1 crystals with the size of ca. $1 \times 2 \mu\text{m}$. Since the pore size of the mullite support is rather large (1.3 μm), and the crystallization was carried out from a clear precursor solution at relative low temperature, the TS-1 zeolite crystals were formed in the pores of the support as well as on the sur-

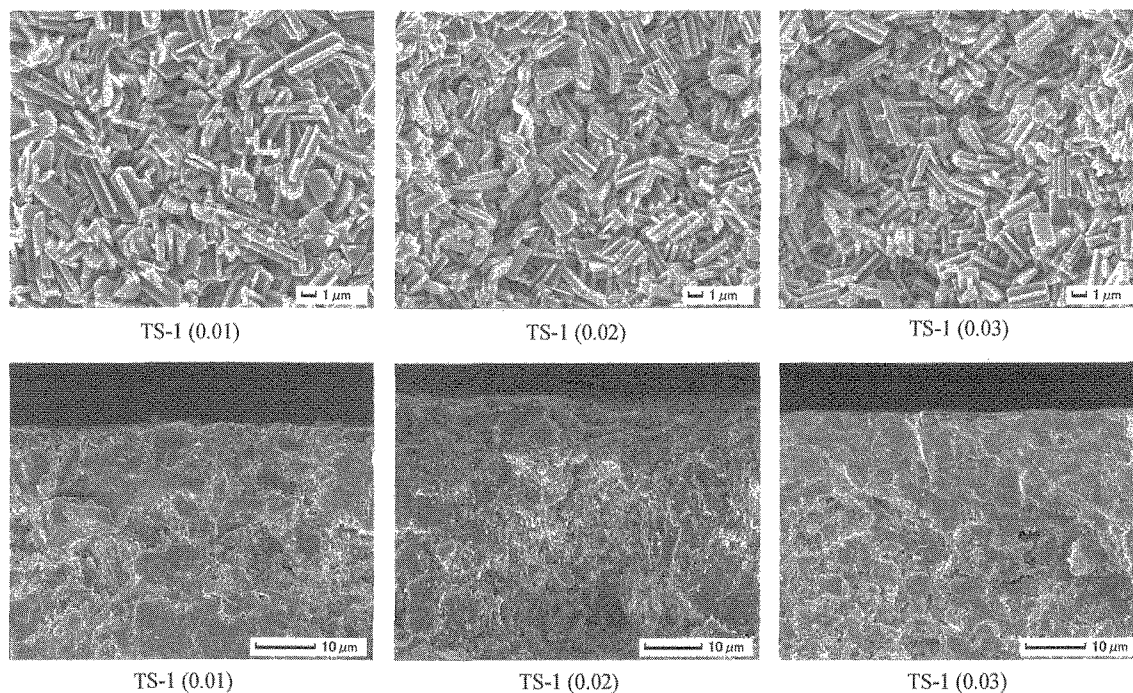


Fig. 3. FE-SEM images of TS-1 membranes with different titanium contents (Upper . Surface section ($\times 5000$); Bottom. Cross section ($\times 2000$))

face. The intergrowth between the crystals at surface was not obvious and no clear intermediate layer can be observed. In this study, we found that this kind of membrane exhibited high catalytic performance for the epoxidation of allyl chloride with aqueous hydrogen peroxide.

Figure 4 shows the pervaporation catalytic reaction results over the membranes with different titanium contents. The production rate of ECH and conversion of AC increased linearly upon the increase of titanium

contents in the precursor solutions. For the membrane with high titanium content (TS-1 (0.03)), the concentration of allyl chloride in permeate side was very low (<1 wt%), it was oxidized to epoxide with high conversion. This is a rational result since the catalytic activity of TS-1 zeolite is closely related with the titanium contents.

In order to test the long-term stability of TS-1 membrane for the pervaporation catalytic epoxidation of allyl chloride, a TS-1 ($x=0.03$) membrane was

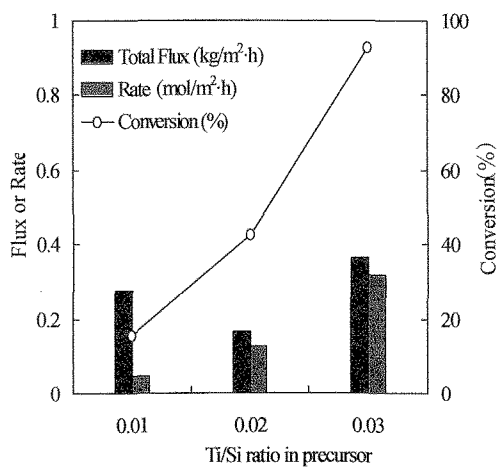


Fig. 4. Effects of titanium contents in the precursor solution on the pervaporation catalytic epoxidation of allyl chloride with H_2O_2 over TS-1 membranes

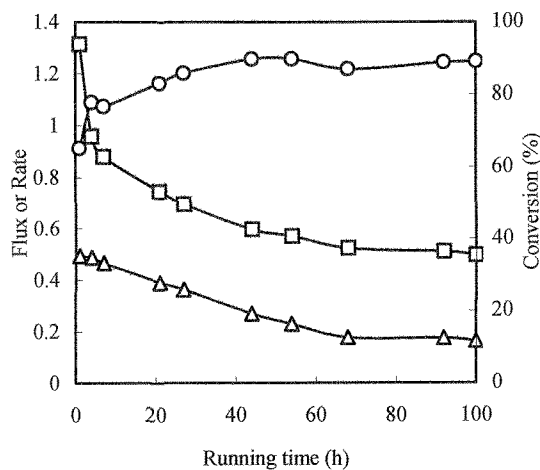


Fig. 5. Long-term stability of TS-1 ($x=0.03$) membrane for the pervaporation catalytic epoxidation of allyl chloride. (\circ conversion (%), \square flux (kg/m²·h), Δ rate (mol/m²·h))

Table I. Preparation reproducibility of TS-1 ($x=0.03$) membranes for the catalytic epoxidation of allyl chloride

Membr.	AC wt% in feed	Total flux (kg/m ² ·h)	AC wt% in permeate	ECH wt% in permeate	Rate (mol/m ² ·h)	Conv. (%)
TS-101	6.564	0.260	0.931	7.289	0.2048	86.62
TS-107	5.472	0.363	0.517	8.068	0.3165	92.81
TS-108	5.917	0.195	2.953	16.326	0.3441	82.05
TS-109	5.785	0.504	1.456	5.095	0.2775	74.32

continuously measured for 100 h. The starting concentration of allyl chloride in the feed was 5 wt%, the molar ratio of H₂O₂ to allyl chloride was 1, and the permeate was collected and analyzed intermittently. Figure 5 shows the changes of total flux, ECH production rate and AC conversion during the long-term running. For the new calcinated membrane, the total flux initially decreased largely in the first 20 h and smoothly in the following 40 h, and then almost leveled off. The steady state total flux was about 40% of the initially value. The production rate of ECH decreased smoothly at the first 60 h and then slightly changed. Correspondingly, the conversion of allyl chloride increased firstly and then kept at 85-90%. The concentration of H₂O₂ in the permeate solution was always lower than 0.01 %wt, indicating the conversion of H₂O₂ was almost completely. After continuously running for 60 h, the pervaporation catalytic reaction almost reached steady state, and the allyl chloride in the feed solution was continuously oxidized to the epichlorohydrin with H₂O₂ through the TS-1 membrane. No epichlorohydrin was detected in the feed solution after 100 h continuously running, confirming that the reaction only occurred when the reactants permeated through the TS-1 membranes under pervaporation conditions. Of course, the concentration of epichlorohydrin and allyl chloride in the permeate was lower than the initially values after 100 h continuously running because the concentration of allyl chloride and H₂O₂ in the feed solution decreased for long time running.

Table I lists the pervaporation catalytic performances of TS-1 membranes prepared at 150 °C for 72 h in different batches. Although the concentration of allyl chloride in permeate varied relative largely from one to another, the total flux, production rate of epichlorohydrin and conversion of allyl chloride maintained in a high level. This indicated the reproducibility of the membrane preparation was satisfactory.

4. CONCLUSION

In situ prepared TS-1 membranes have been employed for the direct epoxidation of allyl chloride to epichlorohydrin under pervaporation conditions. The integration of excellent selective oxidation catalytic activity of TS-1 molecular sieve and the separation function of zeolite membrane made it possible to carry out the reaction continuously and avoided the difficulties in recovery and recycle of catalyst in conventional suspension reaction model. Furthermore, the activity of the TS-1 membrane can be easily recovered by simple calcination. This pervaporation catalytic membrane reactor is potential in various selective oxidation

reactions in which the TS-1 molecular sieve has been proved to be highly active.

ACKNOWLEDGMENT

The present work was partially supported by a grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science and VBL project of Yamaguchi University in Japan.

REFERENCES

- [1] M. G. Clerici, P. Ingallina, *J. Catal.*, 140, 71 (1993).
- [2] I. Schmidt, A. Krogh, K. Wienberg, A. Carlsson, M. Brorson, C. J. H. Jacobsen, *Chem. Commun.*, 2157 (2000)
- [3] T. Atoguchi, S. Yao, *J. Mol. Catal. A: Chem.*, 176, 173 (2001).
- [4] P. Ingallina, M. G. Clerici, L. Rossi, G. Bellussi, *Stud. Surf. Sci. Catal.*, 92, 31 (1995).
- [5] A. Thangaraj, *J. Catal.*, 173, 252 (1992).
- [6] B. Notari, *Adv. Catal.*, 41, 353 (1996).
- [7] C. Perego, A. Carati, P. Ingallina, M. A. Mantegazza, G. Bellussi, *Appl. Catal. A: General*, 221, 63 (2001).
- [8] A. Tavoraro, E. Drioli, *Adv. Mater.*, 11, 975 (1999).
- [9] J. Caro, M. Noack, P. Kolsch, R. Schafer, *Micropor. Mesopor. Mater.*, 38, 3 (2000).
- [10] A.S.T. Chiang, K. -J. Chao, *J. Phys. Chem. Solids*, 62, 1899 (2001).
- [11] T. C. Bowen, R. D. Noble, J. L. Falconer, *J. Membr. Sci.*, 245, 1 (2004).
- [12] J. Coronas, J. Santamaria, *Topics in Catal.*, 29, 29 (2004).
- [13] P. Ciavarella, D. Casanave, H. Moueddeb, S. Miachon, K. Fiaty and J.A. Dalmon, *Catal. Today*, 67, 177 (2001).
- [14] K. Tanaka, R. Yoshikawa, C. Ying, H. Kita and H.-I. Okamoto, *Catal. Today*, 67, 121 (2001).
- [15] A. Julbe, D. Farrusseng, J.C. Jalibert, C. Mirodatos and C. Guizard, *Catal. Today*, 56, 199 (2000).
- [16] M. P. Bernal, J. Coronas, M. Menendez, J. Santamaria, *Chem. Eng. Sci.*, 57, 1557 (2002).
- [17] S. Wu, J.-E. Gallot, M. Bousmina, C. Bouchard, S. Kaliaguine, *Catal. Today*, 56, 113 (2000).
- [18] L. T. Y. Au, J. L. H. Chau, C. T. Ariso, K. L. Yeung, *J. Membr. Sci.*, 183, 269 (2001).
- [19] Y. S. S. Wan, J. L. H. Chau, K. L. Yueng, A. Gavriilidis, *J. Catal.*, 223, 241 (2004).
- [20] M. Taramasso, G. Perego and B. Notari, US Patent 4410501 (1983).