Transactions of the Materials Research Society of Japan 29[7] 3307-3310 (2004)

A photocatalytic membrane reactor for liquid-phase reactions using porous titanium oxide membranes

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Nanoporous TiO_2 membranes (1cm in diameter, 9cm in length) which were prepared by coating colloidal TiO_2 sol solutions on the outer surface of cylindrical porous membranes (average pore diameter 1μm) and firing at 450°C, were applied to a photocatalytic membrane reactor. A photocatalytic membrane reactor is a system where feed stream is forced to permeate through the membrane and organic pollutants can be degraded by photocatalytic reaction on the permeate side. The molecular sieving and the photocatalytic reaction can be combined to improve the selectivity. Methylene Blue (MB) was used as a model solute under the irradiation of blacklight lamps (BL) for a photocatalytic reaction. TiO_2 membranes, having an average pore diameter of 10nm, showed 60% rejection of MB based on the molecular sieving effect without BL irradiation. The rejection of MB increased under BL irradiation, depending on experimental conditions such as feed concentration and applied pressure. Permeate volume flux without BL irradiation decreased with an increase in feed concentration of MB because of pore blocking by MB. On the other hand, the permeate flux increased with BL irradiation and showed approximately constant values irrespective of MB concentration. It was suggested that the permeate flux was recovered by photocatalytic degradation of MB which fouled the membranes.

Key words: photocatalytic membrane reactor, titania, porous membranes, methylene blue,

1. INTRODUCTION

Titanium oxide (titania, TiO_2) shows excellent resistance and stability in most chemicals, and can be used in both acidic and basic pHs; therefore, TiO_2 could be one of the potential materials for nanoporous ceramic membranes. Another interesting feature of TiO_2 is the photocatalytic activity, which has been extensively investigated either in the form of powders or pellets such as packed-bed or fluidized-bed reactors [1, 2].

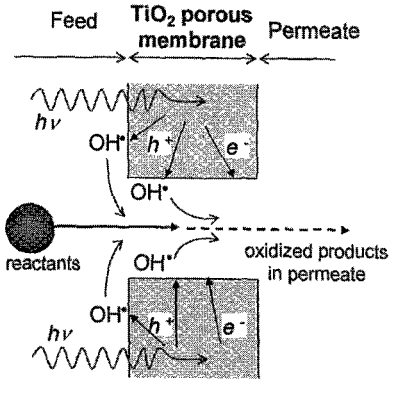

Fig. 1 Schematic of the photocatalytic membrane reactor.

We have proposed photocatalytic membrane reactors [3-6]; that is, porous TiO_2 membranes having pores of several nm, which is capable of not only filtration but also photocatalytic reaction. The photocatalytic membrane reactor can be expected in gas phase as well as liquid phase for the decomposition of organic compounds. As shown in Fig. 1, the oxidation reaction occurs both on the surface and inside the porous TiO_2 membranes. The advantages of the system are (1) the forced transport of reactants by convection to TiO_2 membranes; this would be quite effective for dilute-solution systems where the diffusion of reactants limits the total reaction rate, (2) an oxidation reaction on the outer and inner surface of the porous TiO_2 membranes where high concentrations of OH radicals would be expected, and (3) the potential for obtaining permeate stream oxidized with OH radicals after a one-pass permeation through the TiO_2 membranes.

Moreover, it is possible to combine selectivity for reactants and products by appropriate control of the pore sizes of the TiO_2 membranes, based on the molecular sieving effect. In this study, photocatalytic membrane reactors, the selectivity of which is contributed by both molecular sieving and photocatalysis, was proposed and investigated experimentally.

2. EXPERIMENTAL

Porous TiO_2 membranes were prepared by a sol-gel method. Colloidal TiO_2 sol solutions were prepared by hydrolysis and condensation of titanium *iso*-propoxide in isopropyl alcohol using hydrochloric acid as a catalyst at 30 and 50 °C. A commercial TiO_2 colloidal sol (STS01, kindly supplied by Ishihara Sangyo Kaisha, LTD, Japan), which is reported to show anatase crystals, was also utilized for the membrane preparation. Porous TiO_2 membranes (1 cm in diameter, 9 cm in length) were prepared by coating the colloidal sol solutions on the outer surface of cylindrical α-alumina supports (average pore diameter 1 μm), followed by firing at 450 °C as described previously [3].

Figure 2 shows a schematic diagram of the experimental apparatus used for a photocatalytic reaction where a porous TiO_2 membrane was placed inside a filtration cell; the outer housing of the cell was made of quartz glass tube (inner diameter of 4 cm, inner volume of 250×10^{-6} m^3). Eight blacklight lamps (4 W, main wavelength 350 nm, Sankyo Denki Co., Ltd.) were mounted outside the quartz glass tube. The feed solution was magnetically stirred and pressurized with a plunger pump in a range of 0.01 to 0.5 MPa, while the permeate stream was maintained at atmospheric pressure. Methylene blue (M.W 320) was used a model solute and the concentration was determined using UV/VIS absorbance at 664 nm.

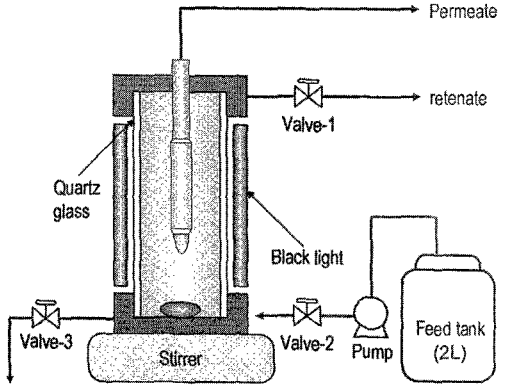

Fig. 2 Experimental apparatus for the photocatalytic membrane reactor.

3. RESULTS AND DISCUSSION

3.1 Membrane characterization

The pore size distributions of porous TiO_2 membranes were estimated, using water vapor as a condensable gas, based on nanopermporometry, as shown in Fig. 3. Average pore sizes, defined at 50 % dimensionless permeability of nitrogen, were approximately 3 nm (type-A) and 10 nm (type-B), for membranes prepared using home-made and commercial sol solutions, respectively. SEM cross-section of a photocatalytic membrane revealed that an intermediate layer was observed on the outer surface of the substrate with a thickness of approximately 1~2 μm. The top layer, which functions for molecular sieving, appears to be less than 1 μm.

Figure 4 shows molecular weight-cut off (MWCO) curves; solutes used were polyethylene glycols of various molecular weights. The MWCOs of type-A and type-B membranes were approximately 1000 and more than 10,000, respectively.

3.2 Photocatalytic decomposition of methylene blue

Figure 5 shows the time course of concentrations in feed and permeate with and without blacklight (BL) irradiation. Feed concentration was maintained approximately at 6 ppm. Without BL irradiation, initial

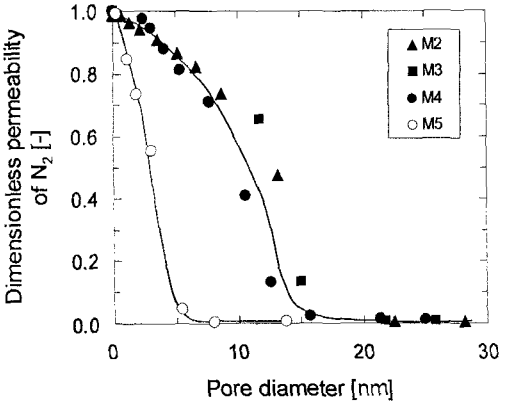

Fig. 3 Dimensionless nitrogen permeability as a function of Kelvin diameter based on nanopermporometry.

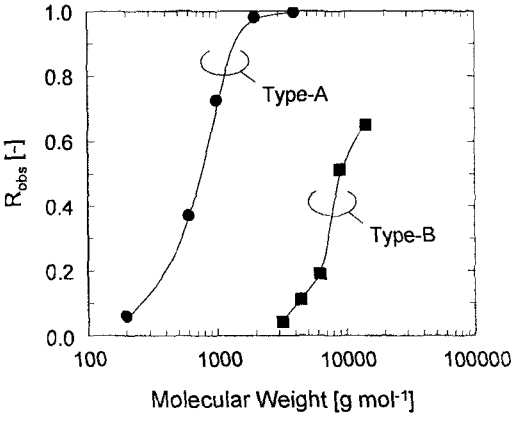

Fig. 4 Molecular weight cut-off curves of type-A and type-B TiO_2 membranes.

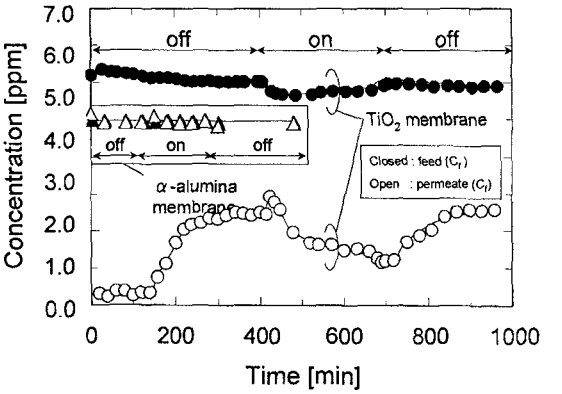

Fig. 5 Methylene blue concentration in feed and permeate as a function of elapsed time. (TiO_2 M-1(type-B) and αAl_2O_3; $J_v = 8.9 \times 10^{-6}$ ms^{-1}, ΔP=30kPa, 25°C)

permeate concentration was almost zero as long as 170 min, and then the permeate concentration increased with time before reaching a steady concentration of 2.5 ppm. The observed rejection of MB, the molecular weight of which is 320, was 0.58, which seems to be larger than estimated from data in Fig. 4. Therefore, by considering the time dependency of permeate concentration, the adsorption of MB on TiO_2 surface, causing smaller effective pore sizes, was suggested. When the TiO_2 membrane was irradiated by BL, permeate concentration gradually decreased to 1.5 ppm. After switching off BL lamps, permeate concentration increased to the concentration without BL. For the comparison, permeate concentration using the α-alumina support under the condition of approximately the same permeate flux as the TiO_2 membrane, was also shown in the figure. No change in permeate concentration was observed with and without BL irradiation. Therefore, it is clear that MB was decomposed by photocatalytic reaction of the TiO_2 membrane.

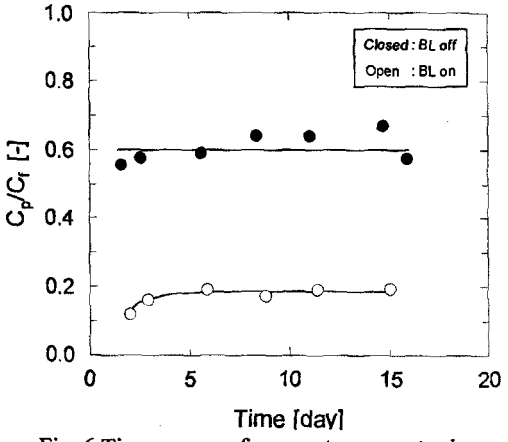

Fig. 6 Time course of permeate concentration normalized with feed concentration. (M-2 (type-B), ΔP=30kPa, 25°C)

Figure 6 shows the time course of permeate concentration normalized with feed concentration, C_P/C_F, indicating the photocatalytic activity was maintained as long as15 days.

3.3 Performance of photocatalytic membrane reactors

Figure 7 shows permeate volume flux, J_v, MB permeate molar flux, J_{MB}, and permeate concentration normalized with feed, C_P/C_F, as a function of permeation temperature. Permeate concentration without BL increased with an increase in temperature, that is, rejection by the TiO_2 porous membrane decreased with temperature, probably because of larger diffusivity of MB and/ or smaller adsorption thickness. On the other hand, permeate concentration under BL irradiation remained constant in the experimental range of temperature. Photocatalytic reaction rate was suggested to be enhanced at high temperature.

Figure 8 demonstrates the effect of feed concentration. Normalized permeate concentration, C_P/C_F, was approximately constant at 0.4 probably because the rejection of MB was caused by the molecular sieving mechanism. On the other hand, C_P/C_F under BL irradiation seems to increase with feed concentration, that is, larger decomposition ratio at low concentration, suggesting Langmuir-Hinshelwood mechanism [6, 7].

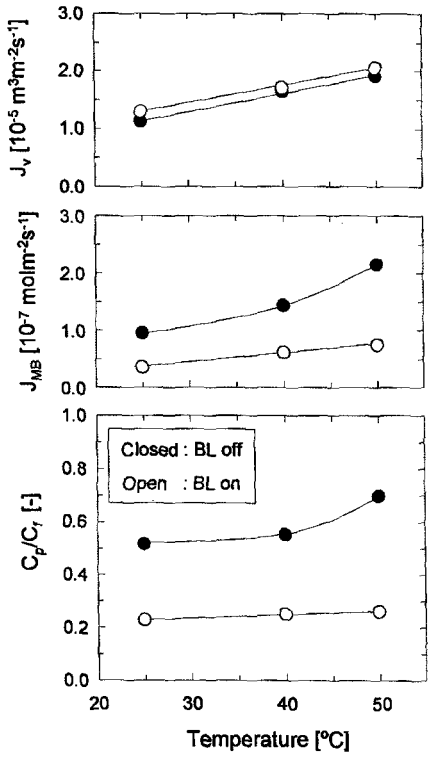

Fig. 7 Permeate volume flux, J_v, permeate flux of MB, J_{MB}, and normalized permeate concentration, C_p/C_f, as a function of temperature. (M-3 (type-B), ΔP=20kPa)

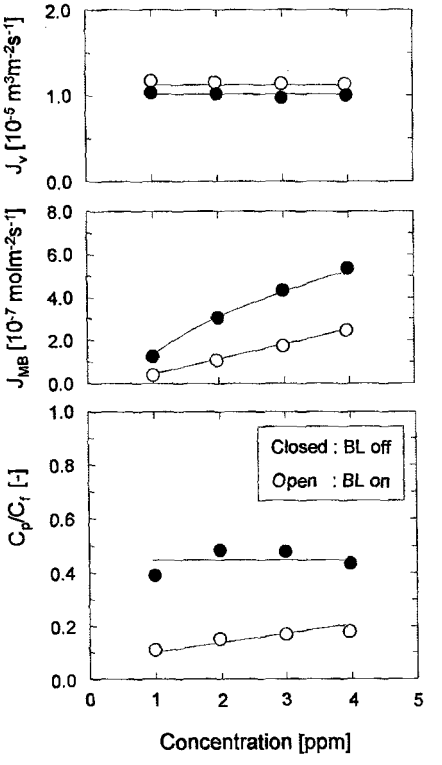

Fig. 8 Permeate volume flux, J_v, permeate flux of MB, J_{MB}, and normalized permeate concentration, C_p/C_f, as a function of feed concentration. (M-4 (type-B), ΔP=30kPa)

Figure 9 shows permeate volume flux, J_v, as a function of MB concentration with and without BL irradiation. Without BL irradiation, J_v decreased with feed concentration, because the adsorption amount of MB, which could be a resistance of permeation, probably increased with concentration. With BL irradiation, J_v was approximately constant irrespective of feed concentration. This is because MB was decomposed by photocatalysis and therefore permeate volume flux was recovered.

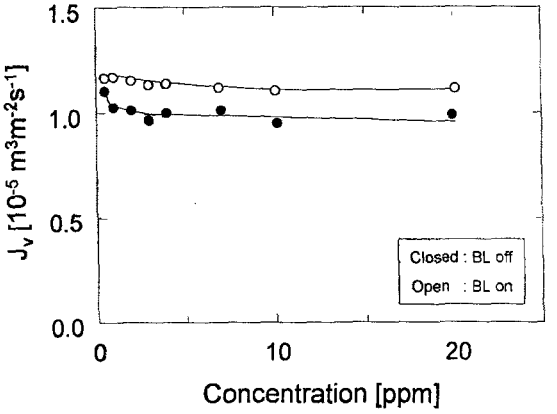

Fig. 9 Permeate volume flux, J_v, with and with out BL as a function of feed concentration. (TiO_2 (M-B1), ΔP=30kPa)

Table 1 summarizes normalized permeate concentration, C_P/C_F, with and without BL irradiation. A TiO_2 membrane of small pore size shows lower C_P/C_F, that is, larger rejection of MB, based on the molecular sieving effect. With BL irradiation, C_P/C_F, was decreased for both the two types of TiO_2 membranes. Therefore, it was demonstrated that pore size of TiO_2 membranes is one of the significant factors controlling performance of photocatalytic membrane reactors. Moreover, combining the molecular sieving and the photocatalytic reaction was found to be effective for improving selectivity of photocatalytic membrane reaction.

Table 1 Summary of photocatalytic performance.

membrane	Pore diameter [nm]	BL	C_p/C_f	$L_p \cdot \mu$ [m]
M2	13	off	0.56	3.09×10^{-13}
		on	0.12	3.23×10^{-13}
M3	3	off	0.43	1.62×10^{-14}
		on	0.07	1.76×10^{-14}

3.4 Optical transmission of TiO_2 membranes

UV/Vis spectra of TiO_2 films, which were coated on quartz substrates and fired at 450 °C, were recorded by a double beam spectrophotometer (Jasco, V-570), as shown in Fig. 10. Film thickness, estimated by photo-interference method, was approximately 440 nm. Transmission of 350 nm, which is a main wave length of BL lamps, was approximately 60 % for TiO_2 films with and without MB adsorption. Since the film thickness

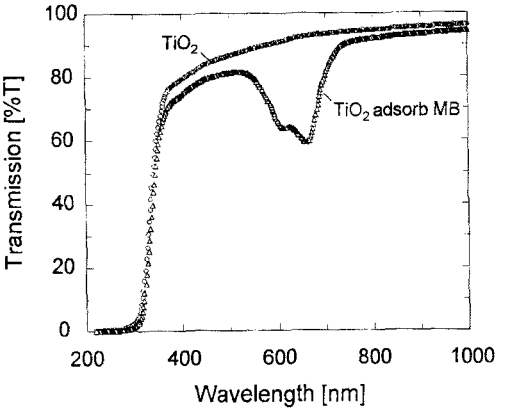

Fig. 10 Transmission spectra of fresh and MB-adsorbed TiO_2 films.

was 440 nm, approximately 30 % of BL was estimated to be transmitted in TiO_2 membranes having approximate thickness of 1 μm. Therefore, it was suggested that BL light penetrated throughout the TiO_2 layer coated on α-alumina supports.

4. CONCLUSIONS

Nanoporous TiO_2 membranes were applied to a photocatalytic membrane reactor. The molecular sieving and the photocatalytic reaction were explored to be combined to improve the selectivity. Methylene Blue (MB) was used as a model solute under the irradiation of blacklight lamps (BL) for a photocatalytic reaction. TiO_2 membranes, having an average pore diameter of 10nm, showed 60% rejection of MB based on the molecular sieving effect without BL irradiation. The rejection of MB increased under BL irradiation, depending on experimental conditions such as feed concentration, applied pressure. Permeate flux without BL irradiation decreased with an increase in feed concentration of MB because of pore blocking by MB. On the other hand, the permeate flux increased with BL irradiation and showed approximately constant value irrespective of MB concentration. It was suggested that the permeate flux was recovered by photocatalytic degradation of MB which fouled the membranes.

5. Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (B) from Japan Society for the Promotion of Science (JSPS) and The Salt Science Research Foundation.

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(Received October 13 2003; Accepted March 31, 2004)