

Photocatalytic Membrane Reactor for VOC Decomposition Using Pt-Modified Titanium Oxide Membranes.

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1. Introduction

Ceramic membranes have attracted a great attention because they have excellent resistance to most organic solvents and can be used over a wide temperature range. Especially, titania (titanium oxide, TiO_2) shows excellent chemical resistance and can be used both acidic and alkali solutions, and therefore, titania is one of the most promising materials for the preparation of porous membranes; titania membranes having pore sizes in the range of nanofiltration (NF) to ultrafiltration (UF) membrane have been prepared by the sol-gel process (Tsuru 2001). Moreover, titania, which has three types of crystalline, including anatase, rutile, and brookite, shows photocatalytic activities, the principle of which is based on the generation of photoholes by ultraviolet irradiation and of OH radicals. The photocatalytic activities have been intensively investigated using TiO_2 powders or pellets.

We have proposed a photocatalytic membrane reactor where porous TiO_2 are responsible for not only selective permeation but also photocatalytic reaction (Tsuru *et al.*, 2001a, 2003a, b). As schematically shown in Figure 1, oxidation reaction by OH radicals occurs both on the surface and inside the porous TiO_2 membrane while permeating in one-pass flow. The advantages of the system are (1) the forced transport of reactants by convection to the porous TiO_2 membrane, resulting in increased reaction rate compared with conventional diffusion transport, and (2) the potential for obtaining a permeate stream oxidized with OH radicals. Photocatalytic membrane reactors were successfully applied for liquid phase reaction as well as gas phase reaction.

In this study, porous TiO_2 membranes were prepared by the sol-gel process, and applied to photocatalytic membrane reactions for the gas phase reaction of methanol and ethanol as a model volatile organic compound (VOC). The effect of feed concentration was discussed in terms of decomposition ratio and production of intermediates. Moreover modification of TiO_2 membranes with platinum was examined to increase the photocatalytic activity.

2. Experimental

Porous TiO_2 membranes were prepared by the sol-gel process using colloidal TiO_2 sol solutions prepared by hydrolysis and condensation of titanium *iso*-propoxide in isopropyl alcohol using hydrochloric acid as a catalyst or commercial TiO_2 anatase sol solutions (STS01, kindly supplied by Ishihara Sangyo Kaisha, LTD, Japan). The outer surface of cylindrical α -alumina microfiltration membranes (average pore diameter 1 μm ; 1 cm in diameter, 9 cm in length) were coated with the colloidal sol solutions, followed by firing at 450 $^\circ\text{C}$ (Tsuru *et al.*, 2001a, 2003a, b). Platinum was photo-deposited on TiO_2 porous membranes with irradiating BL lamps for 10-120 min, using chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) aqueous solutions of 0.6 and 1.9 mol m^{-3} .

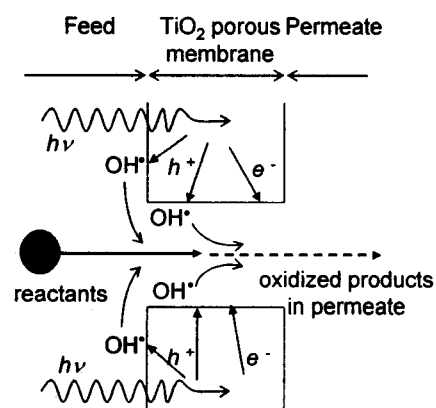


Fig.1 Schematic concept of a photocatalytic membrane reactor.

A photocatalytic membrane reactor was equipped with eight blacklight (BL) lamps (4 W, main wavelength 350 nm) mounted outside the quartz membrane cell unit (inner diameter 19 mm, thickness 1 mm). Air under the total feed flow rate of 500 cc/min from a gas cylinder was fed to the photocatalytic reactor, after the part of the feed flow was bubbled through methanol (MeOH) or ethanol (EtOH) solutions kept at suitable temperatures. Gas compositions were determined by two on-line gas chromatographs using a thermal conductive detector (TCD-GC). A Porapak T column was used for the analysis of organic components and H₂O, while a Gaskropack54 column was for the analysis of CO₂.

3. Result and Discussion

3.1 Photocatalytic membrane reactor

Figure 2 shows time course of the concentration of MeOH, CO₂, HCHO and H₂O. In the region indicated as ①, feed gas bypassed the photocatalytic reactor to adjust MeOH concentration at approximately 100ppm. In region ② where all the feed gas permeated the TiO₂ membrane under BL irradiation, MeOH concentration in permeate was reduced approximately to zero ppm. Due to photocatalytic decomposition of MeOH, the concentrations of H₂O and CO₂ were increased from the feed concentration of 750 ppm and 450 ppm, respectively, which were contained in the compressed air cylinder. HCHO was not detected in region ②. Photocatalytic membrane reaction, where all reactants were required to permeate through TiO₂ nanopores with a uniform residence time, shows enhanced reactivity (Tsuru 2001a, 2003a, b; Maria et al., 2003). In region ③, ④, and ⑤, where MeOH concentration in feed was controlled at 1100, 4400, and 2300 ppm, respectively, H₂O and CO₂ concentration in permeate were increased. Therefore, it is obvious that photocatalysis of MeOH occurred using a thin porous TiO₂ membrane. It should be noted that HCHO, one of the intermediate products of MeOH oxidation process, was not detected in region ② (low feed concentration), and detected in region ③, ④, and ⑤ (high feed concentration).

Figure 3 demonstrates the reaction rate of MeOH decomposition, and CO₂ and HCHO production as a function of feed MeOH concentration (bottom figure). With an

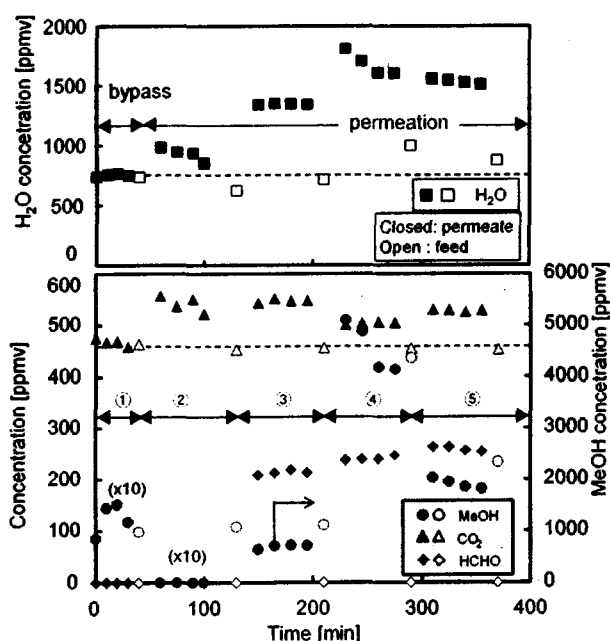


Fig.2 Time course of concentration of MeOH, CO₂, H₂O, HCHO in feed and permeate at different feed concentration. (MeOH=100 ppm for ①②, 1100 ppm for ③, 4400 ppm for ④, and 2300 ppm for ⑤).

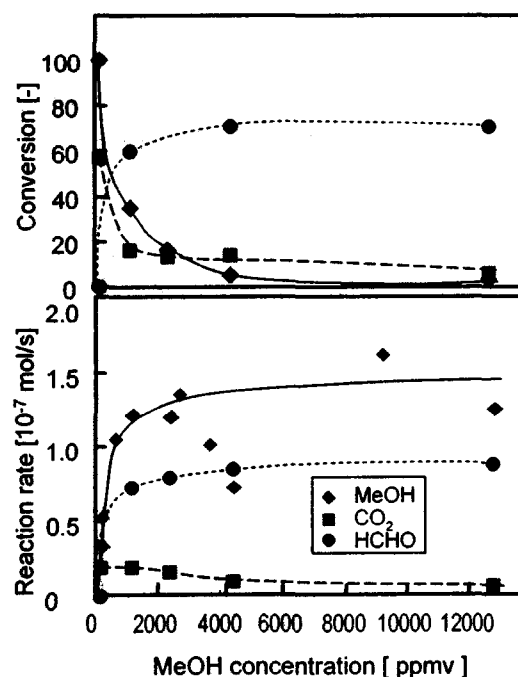


Fig.3 Conversion and reaction rate as a function of MeOH concentration in feed.

increase in MeOH feed concentration, MeOH decomposition rate increased and appears to reach a constant value, resulting in a decrease in MeOH conversion (top figure). This concentration dependency can be explained by the Langmuir-Hinshelwood mechanism, as is reported for photocatalysis of TiO_2 . CO_2 production rate appears to decrease with an increase in feed concentration, and consequently, the conversion of MeOH to CO_2 (top figure) decreased. Production rate of HCHO increased with MeOH concentration. Although the material balance of carbon molecules is not satisfied, it is obvious that intermediates including HCHO were produced in the photo-oxidation process of MeOH and increased with MeOH feed concentration.

3.2 TiO_2 membranes modified with platinum

Modification of TiO_2 with platinum has been proposed for the increased photocatalytic reaction rate. The mechanism is based on the increased electron transfer and/or electron trapping by Pt. Figure 4 shows the pore size distribution of TiO_2 membranes by nanoporometry (Tsuru et al., 2001b) The average pore sizes defined at 50 % of dimensionless permeability of nitrogen, decreased from 16 nm to 10 nm after Pt-modification, suggesting Pt was deposited on TiO_2 inner or/and outer surface and reduced the effective pore size. Figure 5 summarizes pore sizes and Pt-deposited amount as a function of BL irradiation time using two types of initial H_2PtCl_6 concentrations. The amount of deposited Pt was obtained using the concentration changes in H_2PtCl_6 aqueous solutions before and after BL irradiation. Pore sizes decreased from approximately 20 nm to 8 nm with irradiation time, while the deposited Pt amount increased. On the other hand, the initial concentration appears to have no significant effect on Pt-deposition, and therefore, Pt deposition appears to be controlled by BL irradiation time.

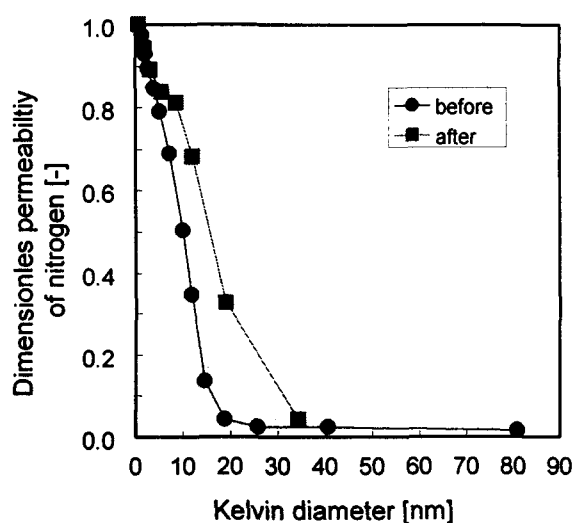


Fig.4 Pore size distribution of TiO_2 membranes before and after Pt-modification, measured by nanoporometry.

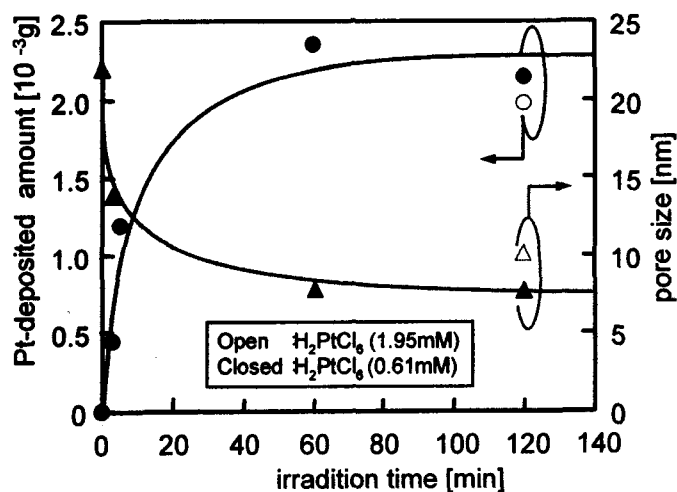


Fig.5 Average pore size and the amount of Pt-deposition as a function of irradiation time. (Initial $\text{H}_2\text{PtCl}_6\text{-6H}_2\text{O}$ concentrations: 0.61 1.95 mM)

Figure 6 shows photocatalytic decomposition of MeOH using Pt-modified TiO₂ with Pt-deposition amount of 2.0 mg. MeOH, the feed concentration of which was as high as 10000 ppm, was almost completely decomposed, and the conversion to CO₂ was approximately 100%. No HCHO was detected. It was made clear that Pt-deposition was quite effective for the enhancement of photocatalytic activity in comparison with the performance of unmodified TiO₂ membranes as shown in Fig.3. Therefore, completely purified stream was obtained in permeate stream. Figure 7 shows the photocatalytic performance for the case of EtOH as a feed VOC using two types of Pt-modified TiO₂ membranes with Pt deposition of 0.4 and 2 mg. EtOH decomposition was suggested to be restricted than the case of MeOH.

4. Conclusions

Titania porous membranes prepared by the sol-gel process were applied for a photocatalytic membrane reactor for decomposition of methanol and ethanol as model VOCs. Pt-modification was quite effective for the enhancement of photocatalytic activity.

References

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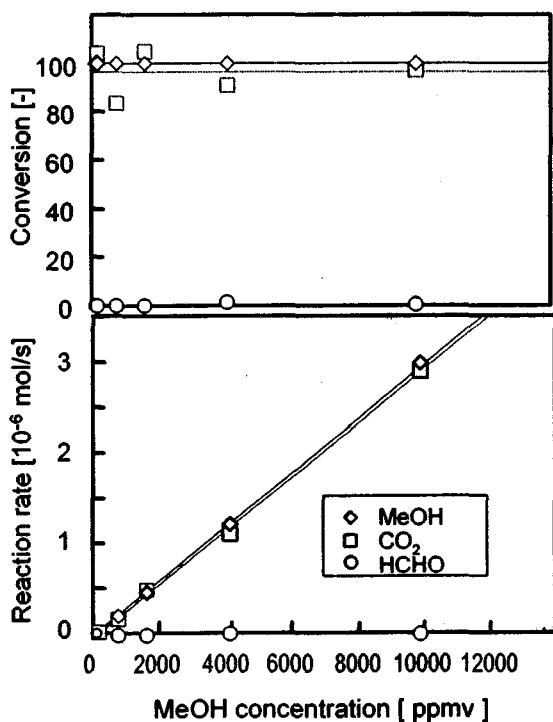


Fig.6 Conversion and reaction rate as a function of MeOH concentration in feed. (Pt-TiO₂ membrane; deposited Pt=2 mg).

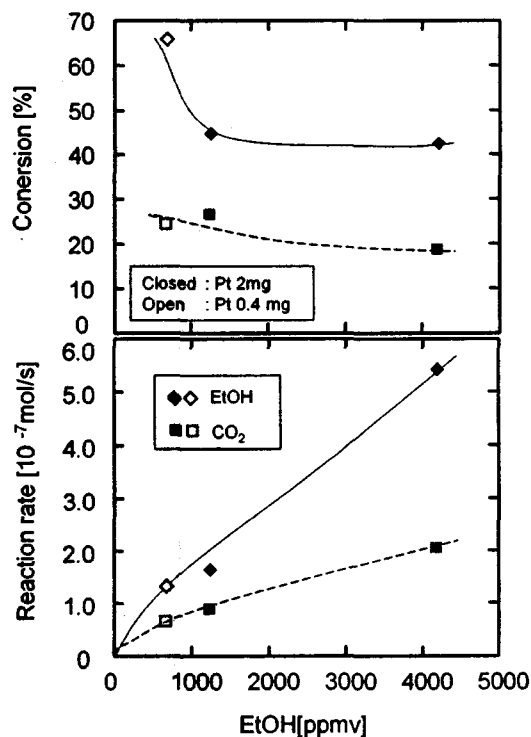


Fig.7 Conversion and reaction rate as a function of EtOH concentration in feed. (Pt-TiO₂ membrane; Pt=0.4mg, 2 mg).