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Priority Communication

Epoxidation of propylene with H_2 and O_2 in the explosive regime in a packed-bed catalytic membrane reactor

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ABSTRACT

The vapor-phase epoxidation of propylene with H_2 and O_2 over a highly dispersed Au/TS-1 catalyst was carried out in a packed-bed catalytic membrane reactor. The membrane reactor allowed the use of high concentrations of H_2 and O_2 (40% each) that were well within the explosive regime, and the production rate of propylene oxide was improved by 100–200% compared with that from a conventional packed-bed reactor. At 180 °C, the C_3H_6 conversion was 10% and the PO selectivity was 80%, corresponding to a space–time yield of 150 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$, whereas at 212 °C, the yield increased to 200 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$. The kinetic dependency, $r_{PO} = k\,(H_2)^{0.53}\,(O_2)^{0.26}\,(C_3H_6)^{0.18}$, obtained free from mass transport and heat transfer limitations at these high concentrations was in good agreement with that reported at low concentrations.

1. Introduction

The direct oxidation of propylene to propylene oxide (PO) with oxygen is a desirable transformation but does not produce sufficient selectivity, because of the lability of the allylic hydrogens in propylene [1–3]. Recently, several industrial groups have announced new processes for PO production with hydrogen peroxide using titanosilicate catalysts [4,5]. However, hydrogen peroxide is expensive, and considerable interest has arisen in the oxidation of propylene with H_2/O_2 mixtures. This reaction was first reported on a Au/TiO_2 catalyst [6] but with limited yields due to the use of dilute reactant mixtures. Here we report the safe operation of the reaction using a ceramic membrane that selectively passes hydrogen, and thus allows the attainment of mixtures containing 40% H_2, 40% O_2, and 10% propylene in argon, which are well within the explosive region. Under these conditions, it is possible to obtain yields of PO formation using a Au/TS-1 catalyst (~200 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$) that are 100–200% higher than under standard conditions and are of commercial significance. The reaction is made possible by the recent development of a ceramic membrane with high selectivity to hydrogen that is immune to attack by oxygen, carbon monoxide, and water. The results here may be applicable to other oxidation reactions that use hydrogen peroxide as an oxidant.

The best catalysts reported for the epoxidation of propylene with H_2/O_2 mixtures consist of nanosized particles of gold supported on highly dispersed Ti oxide on silica [7] in the MFI zeolite TS-1 [8–10] or in the mesoporous support Ti-TUD [11]. Reported yields in conventional packed-bed reactors (PBRs) have ranged from 50 to 116 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$ [9,11], with the kinetics of the reaction [12] following a power-rate law of the form $r_{PO} = k\,(H_2)^{0.60}\,(O_2)^{0.31}\,(C_3H_6)^{0.18}$. Clearly, from the positive exponents, increasing the partial pressures of the reactants, especially H_2, should be beneficial for the formation of PO. But because the explosion limit of H_2 is 4.0 to 94.0% in O_2 [13], increasing the H_2 concentration in the feed gas streams of conventional reactors is dangerous. In most of the studies reported to date, the reactant streams consist of 10 vol% each of O_2, H_2, and C_3H_6 with the balance made up of inert gas. In this study, we used a packed-bed catalytic membrane reactor (CMR) to increase the concentrations of H_2 and O_2 in the reactant stream while avoiding the risk of explosion. We compare our findings with those achieved using a standard PBR.

2. Experimental

2.1. Preparation of TS-1 supports and Au/TS-1 catalyst

The TS-1 support was prepared following the method described by Khomane et al. [14]. In brief, 2.0 g of the surface

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active substance Tween 20 was dissolved in a solution of 24 g of distilled water and 27.3 g of TPAOH (20–25 wt% aqueous solution), after which 36 g of TEOS (tetraethoxyorthosilicate) was added dropwise under vigorous stirring. After continuous stirring for 1 h, 1.8 g of TBOT (tetrabutoxyorthotitanate) (dissolved in 7.2 g of 2-propanol) was added dropwise to the clear solution under stirring. The molar composition of this mixture was 1 SiO_2:0.03 TiO_2:0.12 TPAOH:0.009 Tween 20:14.5 H_2O. Stirring was continued for 1 h, after which the mixture was transferred to a PTFE-lined autoclave for hydrothermal crystallization at 160 °C for 18 h. The final product was recovered by centrifugation, washed, dried, and calcined at 540 °C for 4 h.

To prepare the Au/TS-1 catalyst by the deposition–precipitation (DP) method, 100 mL of an aqueous solution of $HAuCl_4{\cdot}4H_2O$ ($1\ \mathrm{mg\,mL^{-1}}$ or $3\ \mathrm{mg\,mL^{-1}}$) was heated to 70 °C, and the pH was adjusted to 7.0 by adding 1 and 0.1 M NaOH solutions. Then 1.0 g of TS-1 support was added to the solution, and after continuous stirring at 70 °C for 1 h, the solid was collected by centrifugation, washed with 50 mL of distilled water, and vacuum-dried overnight at room temperature.

The crystal structure of the TS-1 zeolite was confirmed by XRD analysis, the Au and Ti content in the catalyst was determined by inductively coupled plasma (ICP) analysis, and the Au particle size was determined by transmission electron microscopy (TEM) (see supplementary information).

2.2. Catalytic membrane reactor

The inorganic composite membrane tube was 42 cm long and had an outer diameter of 10 mm. The effective membrane zone was 3 cm long and was obtained by connecting a porous section of a commercial porous alumina tube (PALL Membralox TI-70-25Z) to dense alumina tubes by glass seals. The boehmite sols were prepared using a sequence of hydrolysis and peptization steps using aluminum isopropoxide (Aldrich, 98+%) in distilled water acidified with acetic acid. The silica layer was deposited on top of a multilayer porous alumina tube by chemical vapor deposition (CVD) of TEOS. Details of the membrane preparation have been reported elsewhere [15,16].

For the catalytic testing, 0.3 g of vacuum-dried catalyst was diluted with 1.8 g of quartz sand to make up a 3-cm-long (2.2 cm^3 volume) catalyst bed matched with the membrane zone. The effluent from the shell side was analyzed by an online gas chromatograph equipped with a flame ionization detector (CP-Silica and DB WAX capillary columns) and a thermal conductivity detector (Molecular Sieve 5A and Porapak Q packed columns).

3. Results and discussion

The CMR has a concentric tubular design, with the inner tube containing the membrane and the packed bed held in the annular region between the membrane tube and a quartz sleeve that prevents contact of the catalyst with the outer stainless steel body (Fig. 1). The H_2 is fed by permeation through the membrane (from the tube side), while the O_2 and C_3H_6 are fed from the opposite side (the shell side) of the reactor. The reactants come into contact and react in the catalyst bed. The danger of explosion is decreased because high concentrations of H_2 and O_2 are generated in the catalyst bed, where explosions cannot propagate due to wall quenching of radical chain reactions [17,18].

The heart of this CMR is a novel inorganic membrane, Nanosil, that is more permeable for H_2 than palladium and has >99.9% selectivity over larger species, such as CO, CO_2, and hydrocarbons [19]. This membrane is a composite formed by the deposition of a thin (20–30 nm) SiO_2 layer by CVD on a specially designed γ-alumina substrate. This substrate is obtained by the deposition of boehmite sols of controlled size on top of a porous support, so as to create a graded structure with increasingly smaller pore sizes. The size of the sol particles is tuned by precisely controlling the synthesis parameters, including acid type, acid concentration, and hydrolysis time. The topmost silica layer is placed on top of the intermediate alumina layer through CVD of a silica precursor, tetraethylorthosilicate. Cross-sectional images of the membranes obtained from scanning electron microscopy (SEM) show that the intermediate γ-alumina layers are formed from particles of progressively smaller size so as to form a smooth interface between the rough support and the topmost amorphous silica layer (Fig. 2). The resulting silica-on-alumina composite membrane has a high permeance ($5.0 \times 10^{-7}\ \mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$) and good selectivity for hydrogen over CH_4, CO, and CO_2 (>1500) at 873 K. The mechanism of permeation is physical, involving the hopping of intact molecules between adjacent solubility sites; thus, the membrane is not susceptible to poisoning or other chemical reactions [20].

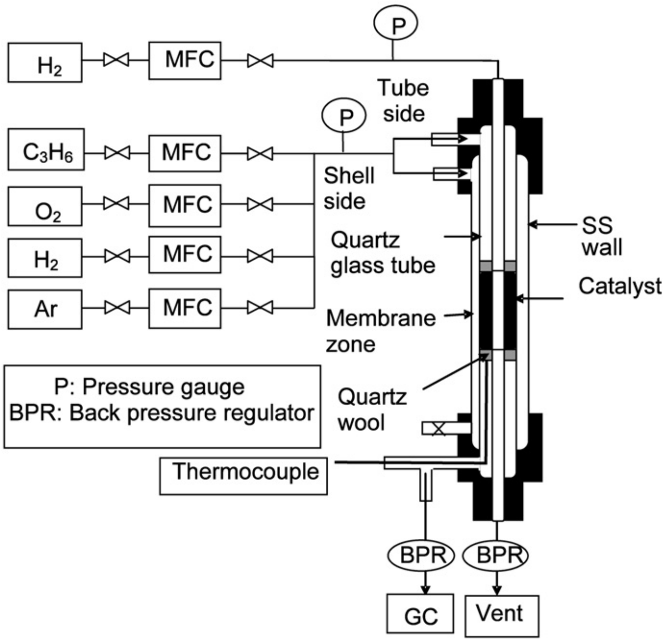


Fig. 1. Schematic diagram of the catalytic membrane reactor. MFC—mass flow controllers, BPR—back-pressure regulators, GC—gas chromatograph.

Au/TS-1 was selected as the catalyst in this study because it has been reported to have excellent stability and activity [8–10]. TEM analysis (Fig. S1 in supplementary information) showed that highly dispersed 3- to 5-nm Au particles were obtained in the Au/TS-1 catalyst. ICP analysis indicated an Au content of 0.02 wt% and a Ti content of 0.46 wt%.

The reactor was first operated as a PBR at 180 °C and 1 bar in a reaction stream consisting of 10 vol% each of H_2, O_2, and C_3H_6 diluted with Ar at a total flow rate of $35\ \mathrm{cm^3\,min^{-1}}$ and a space velocity of $7000\ \mathrm{cm^3\,g_{cat}^{-1}\,h^{-1}}$. The reaction reached steady state after around 5 h and was run continuously for 17 h, giving a C_3H_6 conversion of 2.2%, a PO selectivity of 87%, a hydrogen efficiency of 11%, and a space–time yield of $33\ \mathrm{g_{PO}\,kg_{cat}^{-1}\,h^{-1}}$, the latter corresponding to a TOF of $0.15\ \mathrm{mol_{PO}\,mol_{Au}^{-1}\,s^{-1}}$, typical for Au/TS-1 (Fig. 3) [8–10,12]. The results are given in the ovals on the left side of the figure.

The reactor was then operated as a CMR by switching the H_2 from the shell side to the tube side, where it passed through the H_2-selective silica membrane. The H_2 pressure on the tube side could be controlled to increase the concentration of H_2 in the reaction stream, and the O_2 concentration on the shell side also could be augmented while maintaining the same shell-side

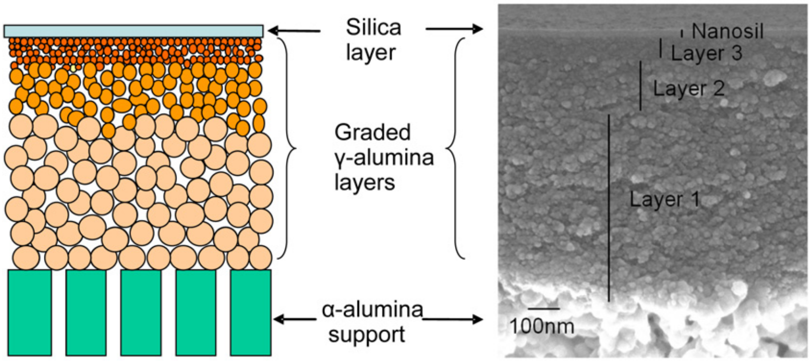
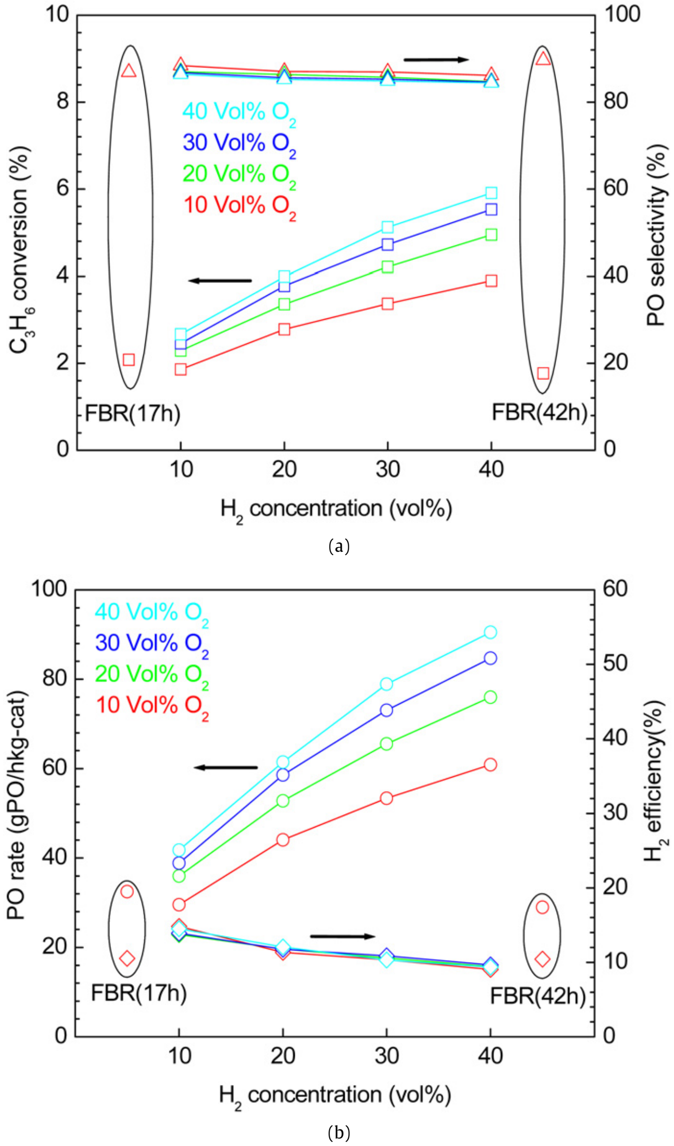


Fig. 2. Schematic diagram and scanning electron micrograph of graded membrane.

space velocity with make-up Ar. The C_3H_6 conversion and yield increased when the concentrations of H_2 and O_2 were increased, whereas the selectivity to PO decreased only slightly and the H_2 efficiency also decreased slightly. The increase in propylene oxide yield was 100–200% over that obtained in the PBR at similar conditions. With a 40 H_2/40 O_2/10 C_3H_6/10 Ar feed composition, the C_3H_6 conversion was 5.9%, the yield was 90 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$, the TOF was 0.43 $mol_{PO}\,mol_{Au}^{-1}\,s^{-1}$, and the H_2 efficiency was 9.4%. The dependence of PO rate and selectivity on H_2 concentration was found to be greater than that on O_2 concentration.



(a)

(b)

Fig. 3. Reactor performance as a function of H_2 and O_2 concentration in the PBR and the CMR. (a) C_3H_6 conversion (□) and PO selectivity (△), (b) PO rate (○) and H_2 efficiency (◇). (The Au/TS-1 catalyst was prepared with 1 mg/mL $HAuCl_4{\cdot}4H_2O$ solution, and the Au content was 0.02 wt%.)

It should be noted that in the present unoptimized operation of the membrane reactor, the conversions were low, and substantial unreacted H_2 and O_2 exited the reactor. For the inlet composition of 40 H_2/40 O_2/10 C_3H_6/10 Ar, the outlet product stream contained 37.7% H_2, 38.1% O_2, and 6.7% C_3H_6. The concentration of these reactants could be reduced by increasing the length of the packed bed beyond the membrane section. Any remaining reactants would need to be separated and recycled.

After the measurements were obtained, the reactor was returned to the PBR mode under the same initial conditions. After 42 h of total reaction time, the C_3H_6 conversion had declined only slightly to 1.8%, the PO selectivity actually rose to 90%, and H_2 efficiency remained at 10.4%, indicating that the catalyst was stable. The results are given in the ovals on the right side of Fig. 3.

Mass transport and heat transfer calculations were carried out for the highest rates in the PBR and CMR (see supplementary information). The Weisz–Prater criterion,

$$C_{WP} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{As}} < 1,$$

gave $8.0 \times 10^{-3} < 1$ in the PBR and $2.2 \times 10^{-2} < 1$ in the CMR, indicating no internal diffusion limitations [21]. The Mears criterion,

$$\frac{-r'_A R^2}{C_{Ab} D_e} < \frac{1 + 0.33\gamma\chi}{|n - \gamma_b\beta_b|(1 + 0.33n\omega)},$$

gave $2.6 \times 10^{-6} < 3$ for the PBR and $7.2 \times 10^{-6} < 3$ for the CMR, indicating no interphase and intraparticle heat transfer or mass transport limitations [22].

The reaction rate data obtained for the various concentrations was analyzed using linear regression (see supplementary information). The kinetic dependency was $r_{PO} = k\,(H_2)^{0.53}\,(O_2)^{0.26}\,(C_3H_6)^{0.18}$, in excellent agreement with the kinetics reported earlier $r_{PO} = k\,(H_2)^{0.60}\,(O_2)^{0.31}\,(C_3H_6)^{0.18}$ for Au/TS-1 [12]. This agreement supports the lack of mass transport or heat transfer limitations in the measurements.

The effect of temperature on the epoxidation of propylene with H_2 and O_2 over the catalytic membrane reactor also was studied (Fig. 4). In the CMR, mode the C_3H_6 conversion increased from 6.5% to 16% when the reaction temperature was increased from 160 °C to 212 °C, while the selectivity to PO decreased from 82% to 65%. At 180 °C, the C_3H_6 conversion was 10% and the PO selectivity was 80%, corresponding to a space–time yield of 150 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$,

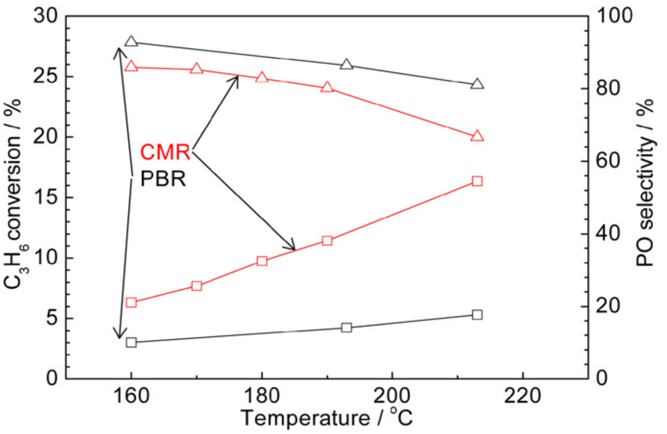


Fig. 4. Dependence of C_3H_6 conversion (☐) and PO selectivity (△) on temperature in the PBR (10 H_2/10 O_2/10 C_3H_6/70 Ar) and the CMR (40 H_2/40 O_2/10 C_3H_6/10 Ar). (The Au/TS-1 catalyst was prepared with 3 mg mL^{-1} $HAuCl_4 \cdot 4H_2O$ solution, and the Au content was 0.09 wt%.)

whereas at 212 °C, the yield increased to 200 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$. These are significant results, because the commercial ethylene oxide (EO) process operates at similar conversion and selectivity with a similar yield of 100–200 $g_{EO}\,kg_{cat}^{-1}\,h^{-1}$ [23]. The apparent activation energies for production of PO, and CO_2 were 28.8 and 74.2 kJ mol^{-1}, respectively, which are comparable with those reported earlier for Au/TS-1 [12]. Together with the kinetic results, this suggests that no change occurred in the reaction mechanism for the epoxidation of propylene with H_2 and O_2 over the CMR and PBR. Briefly, it is believed that the gold component is responsible for the activation of H_2 and O_2 to form an active oxidant, likely hydrogen peroxide, whereas the Ti component is responsible for the epoxidation reaction.

Although significant advances have been made in the application of membrane reactors for oxidation reactions [24–26], most experimentation thus far has relied on the supply of oxygen, for which selective membranes with high permeance have not been available, and, consequently, the results have been modest. The use of hydrogen to generate a high concentration of an active oxidant is attractive because of the high mobility of hydrogen both through the membrane and in the packed bed. The inert silica-on alumina membrane used here has advantages over Pd membranes [27] because it does not catalyze the hydrogen oxidation reaction.

4. Conclusion

A catalytic membrane reactor was investigated for the vapor-phase epoxidation of propylene with H_2 and O_2, and was found to improve the PO production rate by 100–200% by allowing high H_2 and O_2 concentrations in the reaction stream. A space–time yield of 200 $g_{PO}\,kg_{cat}^{-1}\,h^{-1}$ was obtained at 212 °C. This was achieved by supplying the H_2 separately via a silica membrane without the risk of explosion.

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Supplementary information

The online version of this article contains additional supplementary information.

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