Direct O_2 Epoxidation of Propylene by the Membrane Reactor Loaded with Ag–Sr Catalyst

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A novel membrane reactor process using porous α-Al_2O_3 tube loaded with silver–strontium catalyst realized direct O_2 epoxidation of propylene with notable selectivity of propylene oxide. Segregated feed of propylene and O_2 combined with facile permeation of reactants and products across the membrane was essentially important for the membrane epoxidation process.

Currently, over 5×10^6 metric tons of propylene oxide (PO) are being produced in the world industry annually.[1] The major industrial routes to manufacture PO involve multistepped chlorohydrine process, which generates large quantity of by-products including chlorinated compounds.[2] Therefore, more environmentally benign processes are required, particularly those of direct epoxidation with much safer oxidizing agents.

Use of hydrogen peroxide (H_2O_2) solution has been considered as one of the attractive green processes.[3] Recently, Degussa Headwaters Co. has adopted this process in industrial production of PO. Direct epoxidation of propylene with molecular oxygen (O_2) as an ultimate oxidant is another alternative in terms of environmentally benign process. To date, the synthesis of PO by molecular O_2 have been attempted by conventional fixed-bed reactors with silver or other transition-metal catalysts.[4] Despite of the high temperature input (250 to 450 °C), the PO yield remained at most 3% owing to poor PO selectivity.

Recently, attention has been paid to the catalytic membrane reactors in the selective oxidation reactions[5] since they often provide improved reaction conversion combined with high selectivity.[6] Here, we report the direct epoxidation of propylene with molecular O_2 by use of tubular α-Al_2O_3 membrane reactor impregnated with silver–strontium catalyst.[3]

The tubular membranes were prepared by coimpregnation of silver and strontium (Supporting Information).[12] Figure 1 depicts the configuration of the present membrane reactor, where the tubular membrane based on porous α-Al_2O_3 is placed at the center of cylindrical stainless steel shell. A mixture of propylene, water steam, and N_2 was supplied into the inner alumina tube (tube side), whereas O_2 and N_2 were introduced from the outer tube (shell side).

The flow rate at the tube-side was always kept larger than that of the shell-side. The organic products from the inner and outer sides of the tubular membrane were separately analyzed by an online gas chromatograph. Water steam was continuously supplied with propylene from an equilibrated saturator during the reaction. As has been pointed out by Bare and colleagues,[7] water steam can decrease the desorption energy of PO from silver surface and that prevents the PO degradation or secondary reactions.

The XPS measurement of the catalytic zone evidenced the predominant presence of metallic Ag (binding energy = 268.3 eV). The SEM image and EDX analysis of the membrane

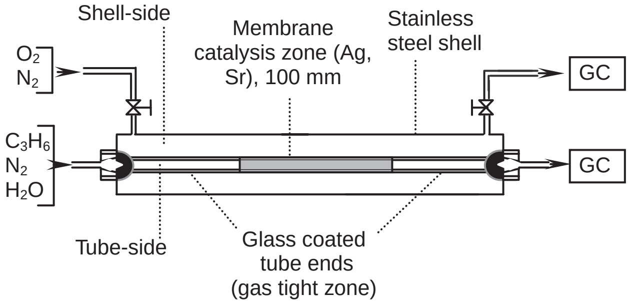

Figure 1. The schematic configuration of the present catalytic membrane reactor used in the O_2 epoxidation of propylene.

Table 1. O_2 epoxidation of propylene over porous alumina tubes impregnated with Ag and Sr at 240 °C[a]

Membrane	Support	Loaded metals /mg[b]	$C_3{}^{=}$ Conv. /%	Consumed O_2 /%	Selectivity/%			PO yield /%	Pressure/hPa	
					PO	CO_2	Others[c]		Tube side	ΔP[d]
A	α-Al_2O_3	34	6.5	56.2	57.4	39.6	2.6	3.7	1030	10
B	α-Al_2O_3	99	4.9	57.4	53.9	42.5	3.4	2.6	1070	40
C	α-Al_2O_3	156	4.7	61.6	51.4	45.4	4.2	2.4	1050	15
D	2-layered α-Al_2O_3	18	3.5	29.9	47.1	48.3	4.3	1.6	1110	60
E	2-layered α-Al_2O_3	53	3.0	28.3	46.8	48.9	4.1	1.4	1110	60

[a]Feedstock: inner of the tube (propylene noted as $C_3{}^{=}$: 10.3 mL·min^{-1}, N_2: 4 mL·min^{-1}, water: 0.9 atm carried by N_2: 27 mL·min^{-1}), outer of the tube (O_2: 4.8 mL·min^{-1}, N_2: 0–4 mL·min^{-1}). [b]Total weight of (Ag + Sr) loaded onto the support, with keeping Ag/Sr = 10 for each membrane. [c]Acetone, propanal, and acrolein. [d]ΔP is the total pressure difference across the membrane (tube side pressure – shell side pressure).

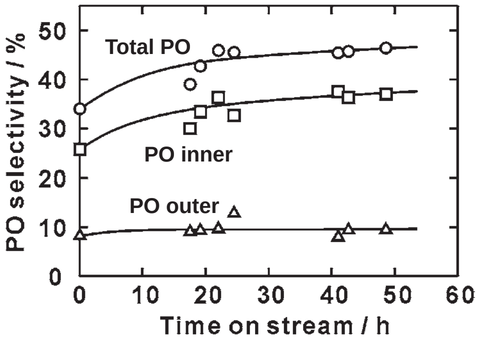

Figure 2. Selectivity for propylene oxide at inner and outer side of the membrane tube as a function of time. AgSr content: 6.5 wt % in Al_2O_3 tube.

surface have demonstrated a well-dispersed and homogeneous distribution of Ag and Sr. Double layered α-Al_2O_3 tube was used as the supports of the membranes D and E. In this case, the top surface of the α-Al_2O_3 tube was coated with smaller size alumina particles (ϕ 0.05 µm).

Table 1 shows the numerical data of the propylene epoxidation by a series of membrane reactors. Noteworthy, the major reaction products are PO and CO_2 in the present reaction system. The segregated feeding of substrate and oxidant has resulted in better conversion and selectivity than cofeeding of two reactants.[8] The conversion increased by elevation of temperature, yet resulted in decrease of selectivity due to enhanced CO_2 formation. The optimized temperature with respect to PO yield ranged 220–240 °C. The highest selectivity up to 57.4% of PO was attained by the membrane A at 240 °C with propylene conversion of 6.5%, resulting 3.7% of PO yield. PO was mostly found from inner tube side, but nearly 25% of it was found from shell side (Figure 2). This ratio depends on the metal loading that affects the permeation of O_2 and PO. When the metal loading is extremely low, amount of PO found at inner and outer tube side became closer. The conversion and PO selectivity decreased with increase of metal loading (membranes A, B and C). This trend is accompanied by the increase of O_2 consumption leading to an enhanced formation of CO_2 and other C3 mono-oxygenates by successive oxidation of PO. Large amount of silver enhances particle agglomeration or clustering which could decrease the number of Ag^0 sites accessible by propylene.[9] It is essential to control the feed rate of O_2 lower than $5.0\,mL{\cdot}min^{-1}$ in order to prevent further oxygenation of hydrocarbon while keeping better conversion and selectivity.

In the cases of membranes D, E, the permeation of gases was retarded by the presence of narrow channels at the top layer. In these cases, propylene conversion as well as oxygen consumption is apparently low. In addition, PO selectivity is decreased owing to the successive oxidation of PO yielding large amount of CO_2 and ring-opened products of PO. Thus, facile permeation of reactants and transportation of product across the membrane are essentially important for the membrane epoxidation system.

A similar epoxidation (267 °C) examined by the membrane loaded only with silver resulted in significantly poor PO selectivity (0.7%) and yielded mainly CO_2 (96.5%). Coloading of strontium combined with silver has remarkably improved the PO selectivity by promotion of the catalytic activity of silver. By changing Ag/Sr ratio, it appeared that around 25 wt % of strontium content gave maximum performance in terms of both conversion and selectivity. Addition of strontium can modify the chemical, ionic, or electrical properties of transition metals and leads to suppress the particle growth and sintering.[10] Positive promotion effect of the alkaline metals, including Na, Rb, and Cs, and Ba has been demonstrated particularly in the epoxidation of ethylene by silver catalyst.[11,4b] Lowering of apparent activation energy for the olefin epoxidation has been pointed out by the presence of cesium as silver promotor.[4a]

Unlike membrane reactor system, the conventional fixed bed reactor gave only low yield of PO (less than 0.5%) despite of increased loading of catalysts. Combustion of propylene oxide and propylene was predominant yielding large amount of CO_2 and ring-opened products of PO and their isomerized by-products. The advantage of segregated feeding of propylene and O_2 is it can prevent successive reactions including further oxidation of PO.

In conclusion, a novel membrane reactor process to manufacture PO was presented. Use of Ag–Sr catalysis loaded in porous alumina membrane combined with a segregated feed of O_2 and propylene realized O_2 epoxidation of propylene with notable PO selectivity.

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