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Development of a Flat Membrane Microchannel Packed-Bed Reactor for Scalable Aerobic Oxidation of Benzyl Alcohol in Flow

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Highlights

- A Teflon AF-2400 flat membrane microchannel reactor was demonstrated for safe and scalable oxidation of solvent-free benzyl alcohol with molecular oxygen on Au-Pd/TiO_2 catalysts.
- Oxygen transfer processes in the microchannel reactor were studied, and the main transfer resistance was indicated to be the transverse mass transfer in the bed.
- An effectiveness factor analysis akin to internal/external mass transfer and reaction in a catalytic particle was proposed, which provides guidance on catalyst choice and membrane reactor design.

1. Introduction

Oxidation of alcohols is one of the most important processes in organic chemistry and often performed with stoichiometric inorganic reagents [1]. In order to improve the atom efficiency and reduce the environmental costs, heterogeneous catalysts have been developed for selective oxidation of alcohols by use of molecular oxygen, and significant advances have been reported [2, 3]. However, large-scale applications of aerobic oxidation of alcohols are still limited by potential safety issues caused by the oxidant-organic reactant mixtures [2, 4]. Recently, several approaches have been proposed to ensure intrinsic process safety [5, 6]. Among these, membrane reactors have attracted attention, since a membrane can act as a well-defined contacting interface for gas and liquid phases [7]. In prior work, we investigated a tube-in-tube membrane microreactor [8]. In this study, a scalable Teflon AF-2400 flat membrane microchannel reactor was developed and applied for continuous-flow aerobic oxidation of solvent-free benzyl alcohol on Au-Pd/TiO_2 catalyst.

2. Methods

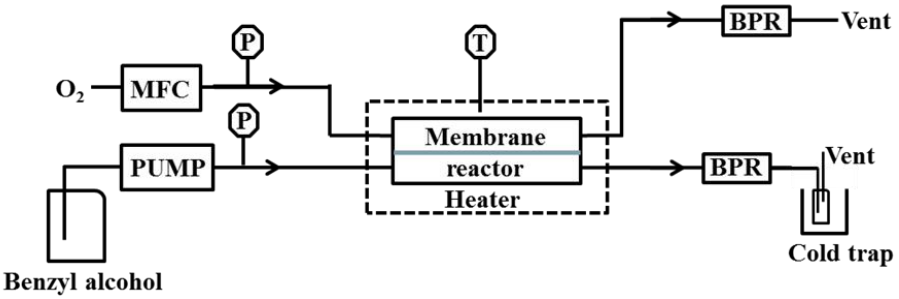

Figure 1. Schematic of the experimental set-up (MFC, mass flow controller; P, pressure sensor; T, thermocouple; BPR, back pressure regulator)

A schematic of the experimental set-up is shown in Figure 1. Neat benzyl alcohol (99.0%, Sigma-Aldrich) was delivered to the reactor liquid inlet with a HPLC pump (Knauer P2.1S), and gas (pure oxygen or air) was regulated by a mass flow controller (Brooks, GF40) and directed to the gas inlet of the reactor. Au-Pd/TiO_2 catalyst particles (total metal loading, 1 wt%; metal particle size, 1-2 nm) were packed in the liquid flow channel.

3. Results and discussion

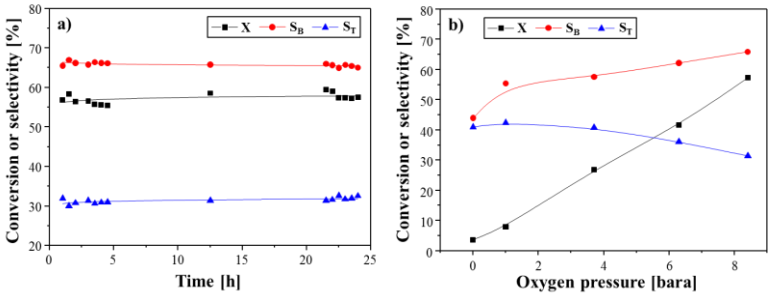

Figure 2. Aerobic oxidation of benzyl alcohol in the flat membrane microchannel reactor: a) stability study of Au-Pd/TiO_2 catalyst and b) effect of oxygen pressure. Reaction conditions: Au-Pd/TiO_2 catalyst (90-125 μm), 100 mg; neat benzyl alcohol, 10 μL/min; catalyst contact time, 577 g_{cat}·s/$g_{alcohol}$; oxygen pressure, a) 8.4 bara and b) 0-8.4 bara; liquid pressure, 10 bara; reaction temperature, 120 ºC. X, conversion; S_B, selectivity to benzaldehyde; S_T, selectivity to toluene.

Initially, a stability study was conducted, and the results (shown in Figure 2a) demonstrate the high stability of the prepared Au-Pd/TiO_2 catalyst and the excellent performance of the reactor. The productivity of benzaldehyde was calculated to be 2.3 g_B/(g_{cat}·h). The effect of oxygen pressure was studied, and higher reaction rate and benzaldehyde selectivity were observed at higher oxygen pressure (shown in Figure 2b). This indicates the importance of oxygen concentration for the reaction within the membrane reactor. Doubling the membrane thickness led to a 20% drop of oxygen consumption rate, which suggests that the main oxygen transfer resistance was not in the membrane. When changing the catalyst particle size and the liquid flow rate, no significant effect was observed on the oxidation reaction rate. An effectiveness factor approach, considering oxygen membrane permeation and transverse mass transfer in the catalyst packed in the membrane reactor, utilising permeability and transverse dispersion from literature, indicated that the oxidation of benzyl alcohol on the highly active Au-Pd/TiO_2 catalyst was controlled by the transverse oxygen mass transfer in the bulk liquid within the catalyst bed. Scale-up of the flat membrane microchannel reactor was demonstrated through widening the liquid channel width by ~10 times, which increased the reactor production rate by a factor of 8.

4. Conclusions

A Teflon AF-2400 flat membrane microchannel reactor was demonstrated for heterogeneously catalysed aerobic oxidation of alcohols. As compared to previous tube-in-tube membrane microreactors, the flat configuration provides wider operating pressure range and is easier to scale-up. The reactor can be combined with plate heat exchangers to realize better temperature control for highly exothermic reactions. Furthermore, mass transfer analysis provides guidance on catalyst choice and membrane reactor design. The simple assembly of the flat membrane microchannel reactor suggests that other similar flat membranes could be used for scalable flow oxidation of alcohols with molecular oxygen.

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Keywords
Gold-palladium catalyst; Teflon AF-2400 membrane; microchannel reactor; aerobic oxidation of alcohol.