Continuous Heterogeneously Catalyzed Oxidation of Benzyl Alcohol Using a Tube-in-Tube Membrane Microreactor

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ABSTRACT: A Teflon AF-2400 tube-in-tube microreactor is investigated for the continuous, solvent-free, catalytic oxidation of benzyl alcohol with oxygen. The semipermeable Teflon AF-2400 tube acts as the interface between the gaseous oxidant and the liquid substrate. Because of the inherent safety of this contacting method, the use of pure oxygen is possible. The semipermeable tube was packed with 1 wt % Au−Pd/TiO$_2$ catalyst particles and placed inside a PTFE tube to provide an annular region which was pressurized with pure oxygen. This design allowed continuous penetration of oxygen through the inner tube during the reaction, resulting in higher oxygen concentration in the catalyst bed and significantly improved conversion compared to a reactor operating with an oxygen presaturated feed. The amount of oxygen available for reaction in the tube-in-tube microreactor was 2 orders of magnitude higher than that in a nonpermeable reactor with oxygen presaturated feed. The semipermeable tube reactor performance in terms of both conversion and selectivity was enhanced by increasing the gas pressure, the catalyst contact time and by dilution of the catalyst. The highest conversion of benzyl alcohol obtained for the range of conditions investigated was 44.1%, with 73.0% selectivity to benzaldehyde, at 120 °C; catalyst contact time, 115 g$_{cat}$·s/g$_{alcohol}$; and catalyst dilution factor, 4.

1. INTRODUCTION

Heterogeneous catalytic gas−liquid reactions are an important category in synthetic chemistry, with great significance for both laboratory research and industrial applications. Conventionally, such reactions are performed in a batch reactor, and the phases are brought in contact by mechanical stirring. However, this results in a poorly defined interfacial contact area and renders scale-up more complex.[1,2] Additionally, the immediate contact of the phases raises safety concerns for hazardous reactions like oxidation reactions. Over the past decade, microreactor technology has emerged as an efficient tool for chemical synthesis.[3] The intrinsic advantages associated with such reactors are the high efficiency of heat and mass transfer, because of the high surface-area-to-volume ratio, as well as the high-resolution reaction time control.[1,2,4] The small physical scale can also significantly enhance safety.[5,6] Several types of microreactors have been developed for gas−liquid−solid reactions,[7] including the coated-wall microreactor,[5] the packed-bed microreactor,[8] and the "slurry Taylor" flow microreactor.[9]

Recently, membrane microreactors have drawn growing interest, as they combine the benefits of both the membrane reactor and the microreactor.[10,11] Gas and liquid phases can flow separately with a well-defined contacting interface and high mass and heat transfer rates. A tube-in-tube configuration employing a semipermeable Teflon AF-2400 tube as the contact interface for gas and liquid has recently been proposed by Ley's group.[12,13] This material is permeable to a wide range of gases but is impermeable to liquids. This controlled method

of gas−liquid contact could enhance safety, especially for hazardous reactions. Furthermore, because of the transfer process consisting of gas permeation solely through the Teflon AF-2400 tube and the laminar liquid flow, the mass transfer of gas in the tube-in-tube microreactor can be accurately simulated, providing insight into reactor operation.[14] Various gas−liquid reactions have been successfully performed in this type of reactor, such as ozonolysis[12] and hydrogenation of alkenes,[15] synthesis of styrenes using ethylene,[16] and carboxylation of Grignard reagents with CO$_2$.[17] Skowerski et al.[18] reported heterogeneous olefin metathesis in a tube-in-tube microreactor through packing the solid catalyst in the annulus between the inner and outer tube and improved yield and selectivity because of the efficient removal of ethylene during the reaction. O'Brien et al.[19] carried out three-phase heterogeneous catalytic reactions in which the liquid was first saturated with gas in a tube-in-tube configuration and subsequently reacted in a catalyst packed column. However, with this approach the amount of gas available for the reaction is limited by its solubility in the reaction mixture as it is not supplied in the downstream reaction section.[14] This severely affects the productivity of the tube-in-tube microreactor.

Selective oxidation of alcohols is an important reaction in chemical synthesis,[20,21] and the aerobic oxidation of benzyl alcohol using molecular oxygen is one of the most intensively studied.[5,6,22,23] A few studies investigated this reaction under flow conditions using a gold-based catalyst. Wang et al.[5] prepared a gold-immobilized capillary column reactor through cross-linking of copolymer for the oxidation of various alcohols. In our previous studies,[8,24] silicon-glass micropacked-bed reactors were used for aerobic oxidation of benzyl alcohol, with a Au−Pd/TiO$_2$ catalyst. Conversions of benzyl alcohol obtained from conventional stirred batch reactor and micro-packed reactor were found to be comparable. Oxidation of solvent-free benzyl alcohol on Au−Pd/TiO$_2$ catalyst is considered to comprise of two main steps,[8,25,26] the oxidation reaction (eq 1) and the disproportionation reaction (eq 2)

$$2PhCH_2OH + O_2 \rightarrow 2PhCHO + 2H_2O \tag{1}$$

$$2PhCH_2OH \rightarrow PhCHO + PhCH_3 + H_2O \tag{2}$$
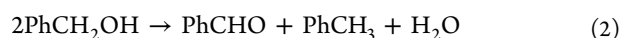
In this work, oxidation of benzyl alcohol was investigated on Au−Pd/TiO$_2$ catalyst, which was directly packed in a Teflon AF-2400 tube-in-tube microreactor. Thus, the gas transport process and the reaction section were integrated, and gas was supplied as the reaction progressed. Operating parameters were studied, with the aim of understanding reactor behavior and improving its performance.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. Au−Pd/TiO$_2$ catalyst (1 wt %) with Au-to-Pd weight ratio equivalent to 1:19 was used and was prepared by a modified impregnation method as described previously.[27,28] The gold precursor (HAuCl$_4$·3H$_2$O; Sigma-Aldrich, U.S.) was dissolved in deionized water to form a solution with a gold concentration of 9.8 mg/mL, and the palladium precursor (PdCl$_2$; Sigma-Aldrich, U.S.) was dissolved in a 0.58 M aqueous HCl solution (conc. HCl, diluted using the requisite amount of deionized water) with vigorous stirring to form a solution with a Pd concentration of 6 mg/mL. Then, the requisite amount of each metal precursor solution was charged into a 50 mL round-bottom flask fitted with a magnetic stirrer bar. The volume of the mixture was adjusted using deionized water to a total volume of 15 mL. The flask was immersed into an oil bath placed on a magnetic stirrer hot plate. The solution was stirred vigorously at 1000 rpm, and the temperature of the oil bath was raised from 27 to 60 °C over a period of 10 min. At 60 °C, 1.98 g of the TiO$_2$ support (Degussa Evonik P25, Germany) was added slowly over a period of 8−10 min with constant stirring. After the completion of the addition of the support material, the slurry was stirred at 60 °C for an additional 15 min. Following this, the temperature of the oil bath was raised to 95 °C, and the slurry was stirred at that temperature for a further 16 h until all the water evaporated, leaving a dry solid. Subsequently, the resultant solid powder was transferred into a mortar and pestle and was ground thoroughly to form a uniform mixture. A 400 mg portion of the uncalcined sample was transferred and spread out over a glass calcination boat (13 cm in length). This boat was then placed inside a calcination furnace fitted with an inlet and outlet valve. The temperature of the furnace was raised from 30 to 400 °C at a heating rate of 10 °C/min and then kept at 400 °C for 4 h under a steady flow of 5% H$_2$ in Ar. After the furnace was cooled, the resultant solid powder was pelletized, crushed, and sieved to the desired particle size range.

2.2. Tube-in-Tube Microreactor Setup. The schematic representation of the tube-in-tube microreactor used in this work is shown in Figure 1. The reactor comprises an inner

1. Gas pressure regulator
2. Pressure sensor
3. T-piece
4. Teflon AF-2400 inner tube
5. PTFE outer tube
6. Union
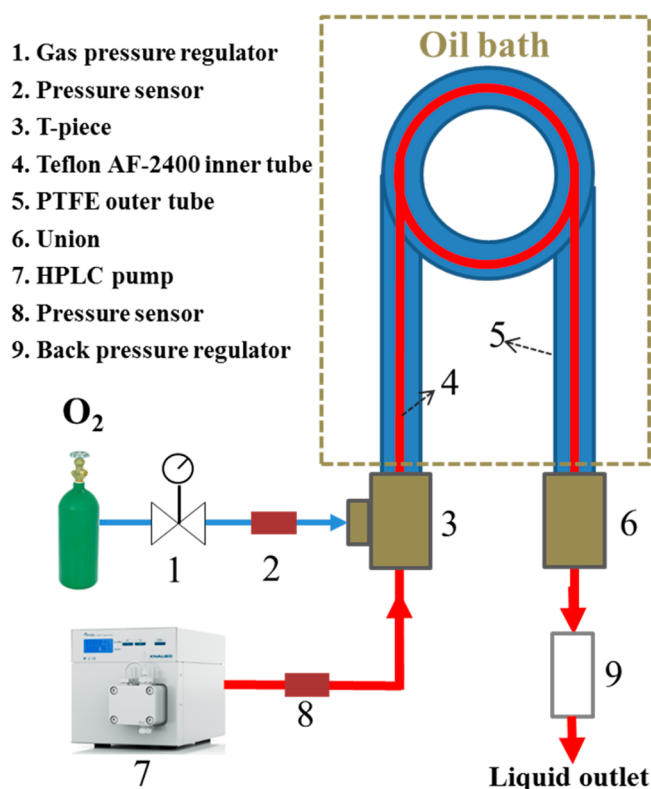7. HPLC pump
8. Pressure sensor
9. Back pressure regulator

Figure 1. Schematic of the Teflon AF-2400 tube-in-tube microreactor setup.

Teflon AF-2400 tube (Biogeneral, U.S.) and an outer PTFE tube (Agilent, U.S.). The inner diameter (ID) of the Teflon AF-2400 tube is 0.8 mm, and the outer diameter (OD) is 1.0 mm. The ID and OD of the PTFE tube are 1.59 and 3.18 mm, respectively. For the measurement of oxygen permeation, a 100 cm long tube was used without any packing. For the catalytic oxidation reaction, the total length of the reactor was 30 cm. Packing the inner tube was achieved by placing in the tube outlet a piece of silica wool which was supported by a 5 cm long stainless steel tube. Au−Pd/TiO$_2$ catalyst particles (63−75 μm) were sucked into the inner tube by a vacuum pump. The amount of catalyst used in all experiments was 20 mg. The bed length was maintained at ca. 3.0 cm. The catalyst was also mixed with silica beads (63−75 μm) before packing to investigate the effect of catalyst dilution. The inner semi-permeable tube and the outer PTFE tube were assembled together by a union and a T-piece to make up the tube-in-tube microreactor. The outlet of the inner tube was connected to a 7.9 bara back pressure regulator (BPR) (Upchurch, U.S.) (all pressures reported in this study are absolute). The pressure of the gas and liquid phases was monitored by pressure sensors placed upstream of the reactor (Zaiput, U.S.). The effluent was collected in a small vial which was placed in an ice−water bath. The reactor was immersed in a stirred oil bath, whose temperature was controlled by a hot plate fitted with a thermocouple (Stuart US152, U.K.). The reaction was carried out at 120 °C. Oxygen was fed in the annulus between the inner and outer tube, and the pressure was maintained by a gas

pressure regulator (Swagelok, U.S.). When the temperature reached the desired value, liquid benzyl alcohol (99.0%, Sigma-Aldrich, U.S.) was supplied into the tube-in-tube microreactor by a HPLC pump (Knauer P2.1S, Germany). The temperature of the fluid reached the required reaction temperature before entering the catalyst bed, as observed by temperature measurements inside the inner tube. The collected sample was quantitatively analyzed by a gas chromatograph (Agilent 6890, U.S.) fitted with a HP-INNOWax capillary column and a flame ionization detector. Benzyl alcohol conversion (X_{total}) and selectivity (S) to each product were calculated according to the following equations

$$X_{total} = \frac{C_{alcohol,in} - C_{alcohol,out}}{C_{alcohol,in}} \times 100\% \qquad (3)$$

where $C_{alcohol,in}$ and $C_{alcohol,out}$ are the concentration of benzyl alcohol at the inlet and outlet, respectively,

$$S_i = \frac{C_i \cdot \nu_i}{C_{alcohol,in} \cdot X_{total}} \times 100\% \qquad (4)$$

where ν_i is the number of moles of benzyl alcohol giving rise to 1 mol of product i.

Catalyst contact time was used to characterize the reaction time of benzyl alcohol and was defined as

$$CCT = \frac{\text{mass of catalyst } (g_{cat})}{\text{mass flow rate of benzyl alcohol } (g_{alcohol}/s)} \qquad (5)$$

For each experiment, at least three samples were collected and the results were averaged. The relative error was less than ±1.0%. Reproducibility of the experiments and the stability of the catalyst were checked every day by a standard run (120 °C; catalyst contact time, 115 $g_{cat}\cdot s/g_{alcohol}$; gas pressure, 6 bara; liquid flow rate, 0.01 mL/min; liquid pressure, 7.9 bara), and the relative differences were less than ±2%.

For comparison, a PTFE tube with ID and length the same as that of the Teflon AF-2400 tube was also packed with the same catalyst and tested. Three different feeding modes (shown in Figure 2) were investigated for the PTFE reactor: benzyl
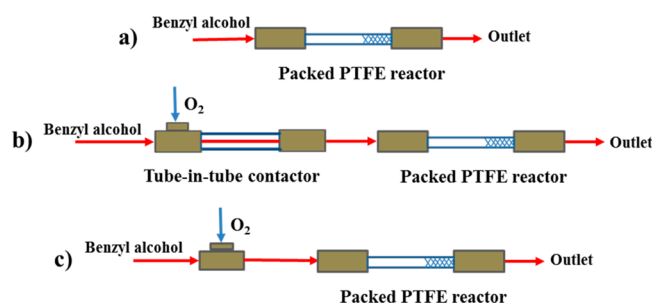

Figure 2. Packed bed PTFE reactors with different gas–liquid feed: (a) benzyl alcohol exposed to air before use, (b) benzyl alcohol presaturated with oxygen by a tube-in-tube contactor, and (c) mixture of oxygen and benzyl alcohol.

alcohol (a) exposed to air before use, (b) presaturated with oxygen at given gas pressure by an unpacked tube-in-tube contactor, and (c) mixed with oxygen. The liquid pressure for the liquid-only feed design (Figure 2a,b) was kept at 7.9 bara using a fixed BPR (Upchurch, U.S.). An adjustable BPR (Zaiput, U.S.) was used for the mixed gas–liquid feed design

(Figure 2c) to maintain the gas–liquid mixture pressure at 6 bara.

3. RESULTS AND DISCUSSION

3.1. Oxygen Permeation. The amount of oxygen dissolved in benzyl alcohol is an important factor for the evaluation of the tube-in-tube microreactor.[14] When the benzyl alcohol leaves the BPR, the dissolved oxygen escapes from the liquid because of the pressure difference between the reactor and the outlet. Assuming the residual gas in the fluid at the outlet is the same as that in the inlet (benzyl alcohol presaturated with oxygen at 1 bara and room temperature), the volume of oxygen released per unit volume of benzyl alcohol equates approximately to the oxygen permeated while the liquid is passing through the reactor. This was measured using the traditional buret method.[19] During the measurement, the tube-in-tube microreactor was kept at 120 °C, and the liquid outlet was connected to a buret filled with benzyl alcohol (presaturated with oxygen at 1 bara and room temperature). The duration for collecting a fixed volume of oxygen in the buret was recorded for different liquid flow rates and absolute gas pressures in the annulus. Thus, the outgassing rate of oxygen could be calculated. The average liquid residence time was calculated by the tube length divided by the superficial velocity of the liquid in the inner tube.

From Figure 3, it can be noted that initially the outgassing rate increased gradually with residence time at each set gas
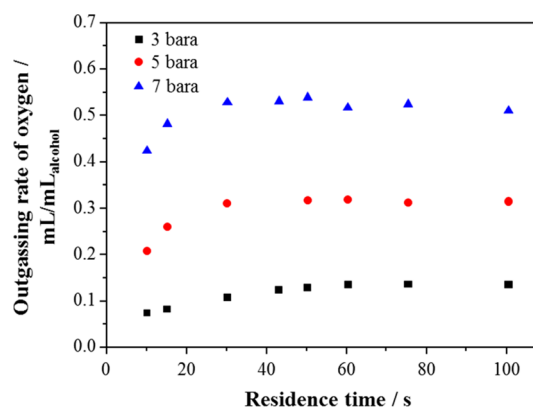

Figure 3. Outgassing rate of oxygen as a function of residence time and gas pressure in the annulus. Liquid pressure, 7.9 bara; temperature of the tube-in-tube microreactor, 120 °C.

pressure and stabilized after 50 s, indicating saturation of benzyl alcohol with oxygen. O'Brien et al.[19] reported a similar behavior for a hydrogen–dichloromethane system. The final outgassing rates at different gas pressure varied almost linearly with the gas pressure difference (between annulus and buret). These measurements show that the permeation of oxygen through the semipermeable tube can be altered by changing the liquid residence time and gas pressure.

3.2. Performance of Different Reactors. Reaction experiments of benzyl alcohol were first performed in the packed PTFE tube at 120 °C. Using the substrate without presaturation or mixing with oxygen (Figure 2a), the conversion was very low, just 1.45% (Table 1a), in the packed PTFE reactor. Equimolar amounts of benzaldehyde and toluene were formed because of the disproportionation of benzyl alcohol (eq 2).[8,25] Relatively high selectivity to dibenzyl ether was observed, which was formed by the intermolecular

Table 1. Conversions and Selectivities (%) of Oxidation of Benzyl Alcohol in Different Reactors[a]

reaction conditions	X_{total}	X_O	$S_{benzaldehyde}$	$S_{toluene}$	$S_{benzene}$	$S_{dibenzyl\ ether}$	$S_{benzoic\ acid}$	$S_{benzyl\ benzoate}$
a	1.45	0.01	40.6	40.0	0	17.6	0.32	1.51
b	1.85	0.07	44.5	40.8	0	14.2	0	0.48
c	37.3	10.7	63.1	34.4	0.74	0.98	0.23	0.65
d	78.1	45.8	75.0	16.4	0.08	0.36	1.04	7.34

[a]Reaction conditions: 120 °C; catalyst contact time, 115 g_{cat}·s/$g_{alcohol}$; liquid flow rate, 0.01 mL/min; gas pressure, 6 bara; catalyst dilution factor, 1. a: Reaction in packed bed PTFE reactor with benzyl alcohol exposed to air before use; liquid pressure, 7.9 bara. b: Reaction in packed bed PTFE reactor with benzyl alcohol presaturated with oxygen at 6 bara gas pressure; liquid pressure, 7.9 bara. c: Reaction in packed bed tube-in-tube microreactor; liquid pressure, 7.9 bara. d: Reaction in packed bed PTFE reactor with mixture of oxygen and benzyl alcohol feed; liquid pressure, 6.0 bara.

dehydration of benzyl alcohol.[25] These results indicate that practically no oxidation reaction was taking place in the absence of oxygen. To test the packed PTFE reactor under oxidative condition, benzyl alcohol was first saturated with oxygen by a tube-in-tube contactor (100 cm long; gas pressure, 6 bara; liquid flow rate, 0.01 mL/min; Figure 2b). The residence time in the tube-in-tube contactor was about 3000 s, which was long enough for the alcohol to become saturated with oxygen. Under these conditions, no obvious improvement in conversion was obtained. The main difference between the two feed approaches was the higher selectivity to benzaldehyde compared to toluene. This was due to the additional oxidation of benzyl alcohol (eq 1), besides the disproportionation reaction, because of the small amount of dissolved oxygen present in the liquid substrate.

These results confirm the two main reactions of the overall oxidation of benzyl alcohol, according to previous studies.[8,24−26] Benzaldehyde, the target product, is formed by both the oxidation and disproportionation of benzyl alcohol, while another main product, toluene, is obtained only from the disproportionation. We can quantify the amount of benzaldehyde produced by the oxidation and further calculate the amount of benzyl alcohol consumed by the oxidation reaction (X_O)[8,25]

$$X_O = X_{total}·(S_{benzaldehyde} − S_{toluene}) \tag{6}$$

This conversion in Table 1b was just 0.07%. Assuming that all the oxygen dissolved in the liquid flow (∼0.5 mL/mL$_{alcohol}$ estimated from Figure 3) was consumed through oxidation reaction, the theoretical maximum X_O would be 0.43%.

Next, the reactor with the catalyst packed in the semi-permeable tube-in-tube microreactor was evaluated (Figure 1). From Table 1c, it can be seen that the conversion of benzyl alcohol increased dramatically compared to the other two approaches at the same reaction temperature and gas pressure. The selectivity to benzaldehyde was about 30% higher than that of toluene. This improvement in the performance of the tube-in-tube microreactor was due to the increased amount of oxygen participating in the reaction, based on the corresponding X_O. The amount of consumed oxygen calculated from X_O is 12.4 mL/mL$_{alcohol}$, which is ca. 150 times higher than 0.08 mL/mL$_{alcohol}$ calculated for oxygen-presaturated benzyl alcohol. Comparing this value (12.4 mL/mL$_{alcohol}$) with the outgassing rate in Figure 3 (∼0.5 mL/mL$_{alcohol}$) shows that oxygen permeation during the reaction was enhanced, because an oxygen concentration gradient was sustained across the semipermeable tube wall. This makes the packed tube-in-tube microreactor more efficient for three-phase reactions compared with nonpermeable PTFE reactor configurations with oxygen-presaturated feed (Figure 2b).

The amount of benzyl alcohol consumed by the disproportionation reaction can be estimated by subtracting X_O from X_{total}. It was 1.78% for the conditions of Table 1b and 26.6% for those of Table 1c. This indicates that adding oxygen can accelerate the disproportionation reaction, which agrees well with previous studies that suggest two distinct pathways to disproportionation.[25] Selectivities to other products are also listed in Table 1, and the values were all lower than 2%.

To further explore the effect of oxygen concentration on the reaction performance, a mixture of oxygen and benzyl alcohol was fed into the packed PTFE reactor (Figure 2c). The gas-to-liquid volume ratio (at standard temperature and pressure, 0 °C, 1.0 bara) was 100, and the outlet pressure was kept at 6 bara. Two-phase slug flow was observed upstream of the packed bed. It can be seen from Table 1d that the conversion was 2-fold higher than that in the tube-in-tube microreactor, with 12% higher selectivity to benzaldehyde. The difference between the two approaches clearly indicates the deficiency of oxygen for the packed tube-in-tube microreactor for the conditions of Table 1c. However, the packed tube-in-tube microreactor is intrinsically safer as gaseous oxygen does not come in contact with the organic mixture.

3.3. Effect of Gas Pressure in Packed Tube-in-Tube Microreactor. To alter the amount of oxygen available for the reaction, the oxidation of benzyl alcohol was carried out with the gas pressure in the annulus changing from 3 to 7 bara. The liquid pressure was maintained at 7.9 bara by the BPR, and the catalyst contact time and reaction temperature were kept the same. The conversion of benzyl alcohol and selectivities to benzaldehyde (S_B) and toluene (S_T) are shown in Figure 4; other minor products (not shown) were all lower than 2.0%. The total conversion of benzyl alcohol increased gradually with the gas pressure. The highest conversion was 41.5% at 7 bara gas pressure. The same trend was observed for the selectivity to benzaldehyde, which reached 65.1% at 7 bara. As for the selectivity to toluene, it showed an opposite dependence on the gas pressure, decreasing from 36.2% to 32.4%. Similar behavior was also observed in a batch[26] and packed-bed microreactor.[8,24] The conversion increased from 78.5% at 2.1 bara to ca. 95% at 5 bara, and the selectivity to benzaldehyde increased from 57.7% to 77.8% in a packed-bed microreactor with oxygen−alcohol mixture feed.[8]

Additionally, X_O varied approximately linearly with the gas pressure. This directly proves that more oxygen participated in the reaction at higher gas pressure. Furthermore, it is reasonable to deduce that the oxygen concentration in the liquid was maintained at low level, and the plot of X_O also quantitatively reflects the amount of oxygen penetrating through the inner tube. Hence, increasing the gas pressure can enhance the oxygen concentration gradient between the
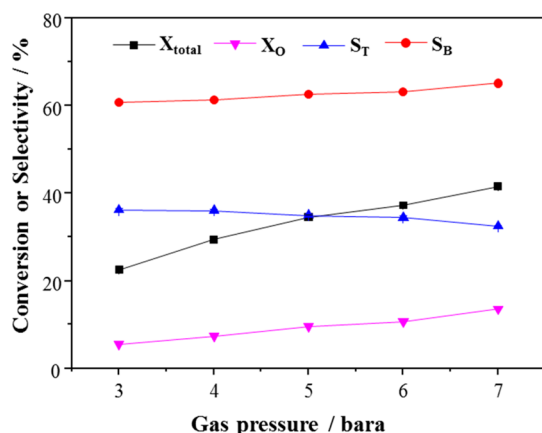
Figure 4. Effect of gas pressure in the annulus on the conversion and selectivities during benzyl alcohol oxidation. Reaction conditions: catalyst contact time, 115 $g_{cat} \cdot s/g_{alcohol}$; liquid flow rate, 0.01 mL/min; reaction temperature, 120 °C; liquid pressure, 7.9 bara; catalyst dilution factor, 1. X_{total}, total benzyl alcohol conversion; X_O, benzyl alcohol conversion through oxidation reaction; S_T, selectivity to toluene; S_B, selectivity to benzaldehyde.

annulus and the inner tube; thus, more oxygen permeates and results in more benzyl alcohol reacting.

3.4. Effect of Catalyst Contact Time in Packed Tube-in-Tube Microreactor. The effect of catalyst contact time was investigated by changing the flow rate of benzyl alcohol, keeping the same mass of catalyst. The results are shown in Figure 5. The conversion increased from 26.1% to 46.9%, and
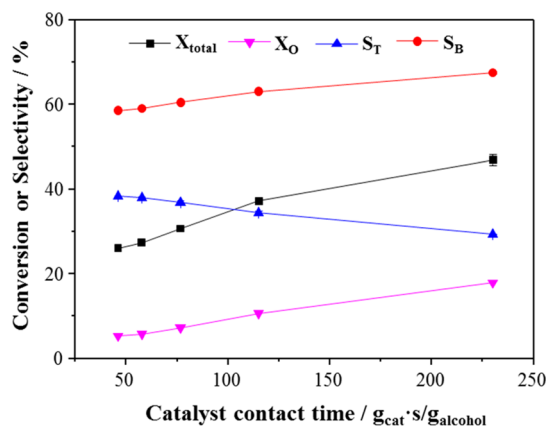

Figure 5. Effect of catalyst contact time on the conversion and selectivities during benzyl alcohol oxidation. Reaction conditions: gas pressure in the annulus, 6 bara; reaction temperature, 120 °C; liquid pressure, 7.9 bara; catalyst dilution factor, 1. X_{total}, total benzyl alcohol conversion; X_O, benzyl alcohol conversion through oxidation reaction; S_T, selectivity to toluene; S_B, selectivity to benzaldehyde.

selectivity to benzaldehyde from 58.6% to 67.5%, when catalyst contact time increased from 46 to 230 $g_{cat} \cdot s/g_{alcohol}$. Correspondingly, the selectivity to toluene decreased from 38.4% to 29.3% at the investigated catalyst contact time range. This conversion trend agrees with that in a batch and packed-bed microreactor. However, the selectivities to benzaldehyde and toluene in both batch and microreactor, where oxygen was in excess, remained practically constant with catalyst contact time.[8] The selectivity differences in the tube-in-tube micro-reactor were probably caused by the insufficient amount of oxygen in the liquid. It should be noted that the plot of X_O also

showed a linear trend. Considering the bed length was the same because of the same amount of catalyst packed, longer catalyst contact time was due to lower flow rate of the liquid, and the average residence time for the liquid through the bed was correspondingly longer. Thus, oxygen had more time to permeate and react because of longer catalyst contact time, and this resulted in an increase in the oxygen consumed by the oxidation reaction, X_O.

3.5. Effect of Catalyst Dilution in Packed Tube-in-Tube Microreactor. The effect of catalyst dilution was investigated by diluting the same amount of catalyst with different amounts of silica beads. The catalyst dilution factor is defined as the total mass of catalyst bed (catalyst + silica beads) divided by the mass of catalyst. In this case, catalyst contact time was kept constant (inlet benzyl alcohol flow rate was constant), while the bed length (and hence bed residence time) was changed. The actual bed length was about 3.0 cm for every 20 mg of packing. In Figure 6, reaction performance is shown
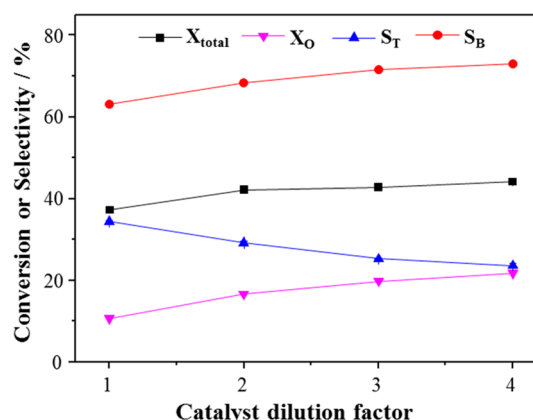

Figure 6. Effect of catalyst dilution on the conversion and selectivities during benzyl alcohol oxidation. Reaction conditions: catalyst contact time, 115 $g_{cat} \cdot s/g_{alcohol}$; liquid flow rate, 0.01 mL/min; gas pressure in the annulus, 6 bara; liquid pressure, 7.9 bara; reaction temperature, 120 °C. X_{total}, total benzyl alcohol conversion; X_O, benzyl alcohol conversion through oxidation reaction; S_T, selectivity to toluene; S_B, selectivity to benzaldehyde.

when the catalyst was mixed with the same mass of silica beads (catalyst dilution factor, 2). The conversion (42.3%) and selectivity to benzaldehyde (68.4%), as well as X_O (18.1%), were close to those when catalyst contact time was 230 $g_{cat} \cdot s/g_{alcohol}$ (46.9%, 67.5%, and 18.0%, respectively). Assuming the void fraction of the bed was the same for both conditions, the average residence time for the liquid passing through the bed with the catalyst contact time of 115 $g_{cat} \cdot s/g_{alcohol}$ and catalyst dilution factor 2 equaled that when catalyst contact time was 230 $g_{cat} \cdot s/g_{alcohol}$ and catalyst dilution factor was 1. Thus, the time for oxygen permeation was also the same. However, the main difference was that half of the bed in the former case did not contain catalyst. Therefore, similar results under these two conditions further support that oxygen permeation is a key factor controlling the performance of the tube-in-tube micro-reactor. Further dilution did not change the total conversion of benzyl alcohol very much, while the selectivity to benzaldehyde increased gradually, as well as the amount of benzyl alcohol converted by oxygen. Notably, the selectivity to benzaldehyde at catalyst dilution factor 4 reached 73.0%, which was close to the premixed alcohol−oxygen conditions (75.0%, Table 1d), as

well as the selectivity to benzaldehyde in a micropacked bed reactor (77.8%; 6 bara gas pressure; gas-to-liquid volume ratio, 200).[8] Thus, dilution of the catalyst bed allowed increasing the surface area available for oxygen transfer without increasing the oxygen demand by the catalytic bed, resulting in higher conversion and selectivity.

4. CONCLUSIONS

A semipermeable Teflon AF-2400 tube-in-tube microreactor was developed for the continuous solvent-free aerobic heterogeneous oxidation of benzyl alcohol. By comparison with nonpermeable PTFE configurations, the packed tube-in-tube microreactor allowed the continuous supply of oxygen during the reaction and therefore significantly improved both conversion and selectivity. The amount of oxygen that permeated played a vital role in reactor performance. Oxygen permeation was increased by increasing the gas pressure and catalyst contact time. When the catalyst was diluted, the average residence time of liquid in the bed increased, allowing larger oxygen permeation. All these approaches of enhancing oxygen permeation resulted in improved reactor performance. Even though the amount of oxygen available for the reaction was not enough to achieve the same total conversion of benzyl alcohol as in a packed nonpermeable PTFE reactor with a mixture of oxygen–benzyl alcohol feed, the selectivity for both reactors was similar. As gas does not come directly into contact with the organic mixture in the packed tube-in-tube microreactor, its intrinsic safety makes this type of reactor promising for wider applications in heterogeneous reactions.

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Notes
The authors declare no competing financial interest.

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