

# AEROBIC OXIDATION OF BENZYL ALCOHOL IN A CATALYTIC MEMBRANE REACTOR

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## *Abstract*

A catalytic ceramic membrane reactor was studied for the continuous catalytic oxidation of liquid phase benzyl alcohol with oxygen. Pd/Au catalyst was impregnated on the inner side of the ceramic membrane using a rotating impregnation device. The reactor was comprised of an inner tube that together with the membrane created an annulus containing glass beads through which the liquid phase flowed. The membrane consisted of layers of alumina and a titania top layer with an average nominal pore size of 5 nm. Pure oxygen was fed to the opposite side of the membrane in the outer shell of the reactor. The role of the membrane was to provide an interface for gas and liquid to come in contact. The catalyst remained active for at least a month. Conversion of benzyl alcohol increased with increasing pressure and decreasing liquid flowrate, while selectivity of benzaldehyde remained nearly constant at 93-97%. The membrane reactor offers safer operation as compared to a batch slurry reactor, since flammable oxygen/organic mixtures are avoided.

## *Keywords*

Aerobic oxidation, Impregnated membrane reactor, Multiphase reactor, Gold/palladium catalyst

## **Introduction**

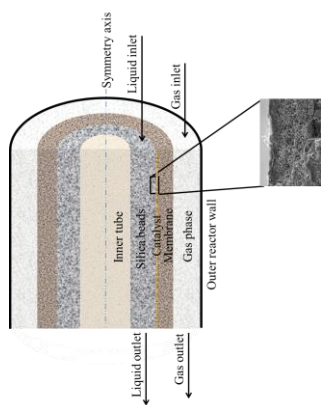
Aldehydes, produced by catalytic oxidation of alcohols, are valuable precursors for the production of pharmaceutical compounds, dyes and fragrances. Oxygen is a clean oxidant for their production, but is not used in industry due to safety concerns. Membrane contactors allow two phases to come into direct contact with each other to achieve efficient interfacial mass transfer, without the need to disperse one phase into the other providing safer operation.

Ceramic membranes have a great potential to be applied to gas-liquid-solid reactions due to their chemical resistance and high gas permeability. They allow controlled dosing of gas reactants, which can affect product selectivity. In our previous work we studied benzyl alcohol oxidation using a packed-bed ceramic membrane reactor (Constantinou et al., 2015) where mass transfer resistances affected adversely the selectivity to benzaldehyde under certain operating conditions. In this work, a continuous catalytic membrane reactor was employed for benzyl alcohol aerobic oxidation. Impregnating the catalyst on the inner side of the ceramic membrane is beneficial in terms of oxygen mass transfer

and gas-liquid contacting. As a consequence selectivity to benzyl aldehyde can be improved. This configuration allows continuous addition of the oxidant along the length of the reactor in a safer way, since gas-liquid dispersions are avoided and concentration of volatiles in the gas phase can be better controlled.

## **Membrane Reactor Description**

The reactor comprised of four concentric sections (see Figure 1). The inner tube created an annulus which was packed with glass beads (particle size 100-200  $\mu\text{m}$ ) through which the liquid phase (pure benzyl alcohol) flowed. Glass beads were used to improve the liquid distribution. This was followed by the ceramic membrane tube, which consisted of layers of alumina and a titania top layer with nominal pore size 5 nm. Pd/Au catalyst was impregnated on the inner  $\text{TiO}_2$  layer. An aqueous solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{PdCl}_2$  was injected into the membrane tube and by rotating the membrane horizontally using a rotating device, liquid was evaporated in order to achieve homogeneous distribution of the catalyst along the inner side of the membrane.



The membrane was dried at 110 °C for 16 hr and calcined at 400 °C for 2 hr. Pure oxygen was fed to the opposite side of the membrane. Heating was achieved by flexible heaters placed outside of the reactor. The reactor effluent was analyzed by gas chromatography.

Figure 1. Schematic of the catalytic membrane reactor with SEM picture of the ceramic membrane.

## Results and Discussion

Figure 2 shows the stability test performed on the catalytic membrane over a period of 670 hr. Conversion of benzyl alcohol was stable during that period and it was around 25% while the selectivity to benzaldehyde was around 97% and remained stable as well. In contrast, in our previous work (Constantinou et al., 2015) a similarly prepared Pd-Au/TiO<sub>2</sub> catalyst that was used as a packed bed, was active for 4-5 days, and showed lower selectivity. The high selectivity to benzaldehyde obtained in this work might be due to improved oxygen mass transfer to the catalytic sites.

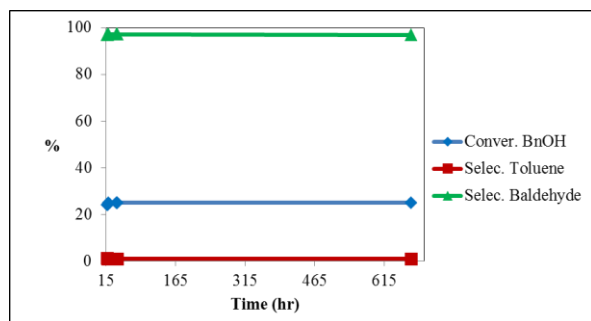


Figure 2. Stability test of the catalytic ceramic membrane.  $F_L = 0.01$  ml/min, gas pressure  $\approx 3$ bara, pure BnOH, temperature  $\approx 115^\circ\text{C}$ .

In order to alter the availability of oxygen for the reaction, gas pressure was changed from 2 to 5 bara (see Figure 3). Benzyl alcohol conversion increased up to 20% with benzyl aldehyde selectivity was 92-97%. Increasing the gas pressure would increase dissolved oxygen concentration. As a result more oxygen was available for the reaction and hence benzyl alcohol conversion increased.

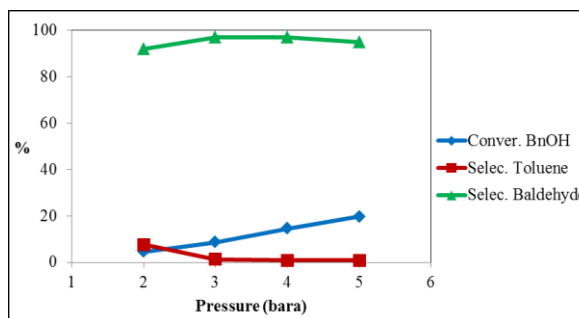


Figure 3. Effect of pressure on conversion and selectivities.  $F_L=0.04$ ml/min, pure BnOH temperature  $\approx 115^\circ\text{C}$ .

The effect of catalyst contact time was studied by varying the benzyl alcohol flowrate from 0.005 to 0.04 ml/min. Figure 4 shows that benzyl alcohol conversion increased up to 40% for 0.005 ml/min while selectivity of benzaldehyde was nearly constant at 93-97%.

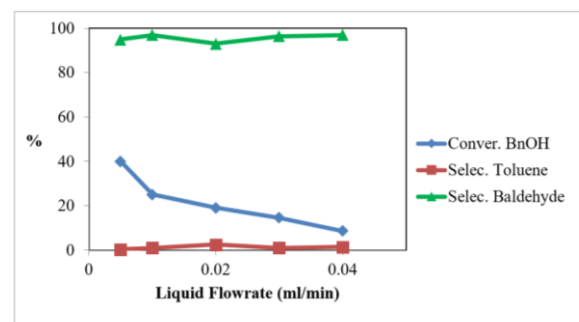


Figure 4. Effect of liquid flowrate on conversion and selectivities.  $F_L=0.005-0.04$ ml/min, gas pressure  $\approx 3$ bara, pure BnOH, temperature  $\approx 115^\circ\text{C}$ .

## Conclusions

A ceramic membrane impregnated with Pd/Au catalyst was developed and used for the continuous heterogeneously catalyzed aerobic oxidation of benzyl alcohol. The catalytic membrane reactor showed excellent stability, compared to our previous work where the catalyst was employed as a packed bed. Experiments showed that increasing pressure and decreasing liquid flowrate led to increased conversion of benzyl alcohol, while selectivity to benzaldehyde was nearly constant at  $>95\%$ . The catalytic ceramic membrane showed high selectivity to benzaldehyde possibly due to improved oxygen mass transfer to the catalyst. This configuration allows safer operation than batch operation, since gas does not come in direct contact with the organic mixture.

## Acknowledgments

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## References

Constantinou, A., Wu, G., Corredera, A., Ellis, P., Bethell, D., Hutchings, G. J., Kuhn, S., Gavriilidis, A. (2015). *Org. Proc. Res. Dev.*, accepted for publication.