

Selective oxidation of benzyl alcohols to benzaldehydes using a membrane contactor

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In this work, we report a novel method for selective oxidation of benzyl alcohols to benzaldehydes. Neither solvent nor promoters are needed: a polymeric microporous membrane acts as a barrier to “keep in contact” the two phases: the organic phase containing the substrate, benzyl alcohols and the products, benzaldehydes and the aqueous phase with the catalyst and the oxidant, hydrogen peroxide. This system showed a high selectivity to benzaldehyde (>98%), operating at 1.7×10^3 mL/h and 10×10^3 mL/h flow rates for organic and aqueous phase, respectively. Increasing the organic flow rate to 4.7×10^3 mL/h, an higher concentration of over-oxidation product (benzoic acid) is observed, lowering the selectivity to 85%. Noteworthy, in the tests with substituted benzyl alcohols as substrates, i.e. 2-chloro benzyl alcohol and 2-methyl benzyl alcohol, the structure-reactivity behaviour has been induced by the substrate interaction with the polymeric membrane.

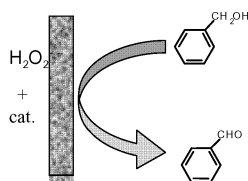
1. Introduction

There is a growing need for “green” technologies in the synthesis of fine chemicals and pharmaceuticals intermediates. In this context, an important target is to achieve the highest possible selectivity and thus minimize the additional costs of separation of by products and waste removal that may be a critical factor in chemical synthesis (Opre *et al*, 2006).

Frequently improvements in process are obtained by changing the process flowsheet, making compromises between capital improvements and operating cost savings. In other cases, efficiency gains can be realized without significant capital investment by redesigning the reaction system (Nehelsen *et al*, 2007).

Oxidation of alcohols to aldehydes, in particular benzyl alcohol to benzaldehyde, is an important organic transformation. Benzaldehyde is a very valuable chemical which has widespread applications in perfumery, dyestuff and agro chemical industries (Hudlicky, 1990; Bortolini *et al*, 1987). Conventional methods for performing such transformations generally involve the use of stoichiometric or more than stoichiometric quantities of inorganic oxidants, such as chromium (VI) reagents, dimethyl sulfoxide, permanganates, periodates or N-chlorosuccinimide (NCS) (Hudlicky, 1990). Furthermore, these methods are usually carried out in halogenated organic solvents, typically chlorinated which are environmentally undesirable and often require one or

more equivalents of these relatively expensive oxidizing agents. In this work, a new method for selective oxidation of benzyl alcohols to benzaldehydes has been reported. A polymeric microporous membrane keeps in contact the two phases: the organic phase containing the substrate (benzyl alcohol) and the product, (benzaldehyde) and the aqueous phase with the oxidant, hydrogen peroxide, and the catalyst (Scheme 1).



Scheme 1-Schematization of oxidation of benzyl alcohol to benzaldehyde using a membrane at the interface of aqueous phase and organic phases, containing respectively the oxidant and the substrate and product of reaction.

Being the two phases separate by the membrane, there is no mix of them and dispersion phenomena do not occur. The species are transferred from one phase to the other only by diffusion.

2. Materials and methods

2.1 Chemicals

Benzyl alcohol (MW= 108.14 g/mol , purity 99.99%), 2-chlorobenzyl alcohol (MW=142.58 g/mol, purity 99.99%) and 2-methyl benzyl alcohol (MW= 122.16 g/mol, purity 99.99%) from Sigma-Aldrich were used both as reagent and as solvents. Ammonium molybdate tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (MW=1235.86 g/mol, purity 99.98 %), from Sigma-Aldrich were employed as catalysts. H_2O_2 (30 wt% solution in water) from Sigma-Aldrich was the oxidant.

M1 is a commercial membrane supplied by Alfa Laval (former DSS) (Sweden). Some characteristics have been reported in Table 1.

Table 1-Characteristics of polymeric membrane used as membrane contactor

Type	Material	δ (μm)	r_p (μm)	α ($^\circ$)	
				Top layer	bottom layer
Composite	Fluoropolymer (top layer) PP (bottom layer)	238	0.2	90 ± 2	140 ± 3

2.2 Apparatus

Experimental tests were carried out at 353K in a reactor made with a two compartment cell to separate the organic and the aqueous phases. The system was in a flat sheet configuration with a membrane surface area of $4.91 \times 10^{-4} \text{ m}^2$.

The volume of the aqueous and organic solutions in each compartment of the experimental apparatus was 37 cm^3 . During the reaction tests, the membrane was located in the membrane reactor with the top layer from the aqueous phase side.

The aqueous and organic solutions were continuously re-circulated on both membrane surfaces using two pumps at a fixed flow rates (Figure 1). The reaction progress was monitored by periodically sampling the organic and aqueous phases.

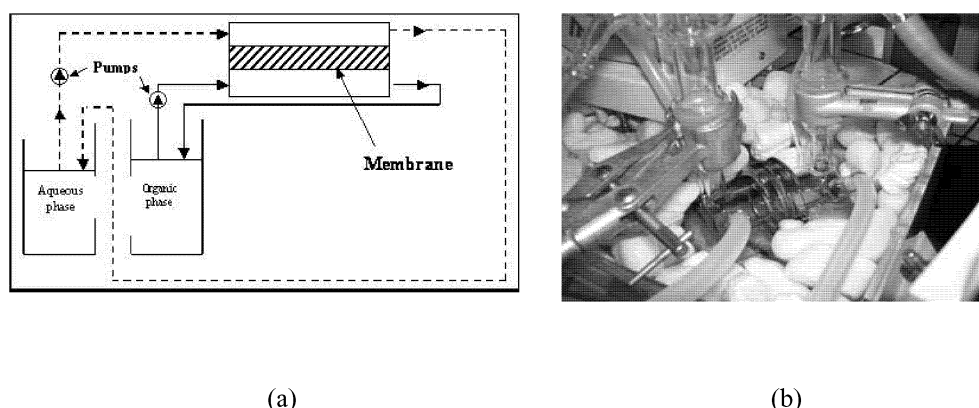


Figure 1- Schematization of the used membrane reactor (a) and picture of the cell (b).

The morphology of the dried membranes (at 60°C overnight) was examined using Scanning Electron Microscopy (SEM), Cambridge, Stereoscan 360, at 20kV. For cross-section analysis the membrane samples were freeze fractured in liquid nitrogen. All samples were sputter-coated with gold before analysis. EDX microanalyses were performed using Philips EDAX analysis system.

Membrane pore dimensions were determined by means of a capillary Flow Porometer CFP 1500 AEXL (Porous materials Inc. PMI, Ithaca, New York, USA).

Contact angles of water droplets on the membrane surfaces were measured by sessile drop method using CAM 200 contact angle meter (KSV Instruments LTD, Helsinki, Finland).

2.3 Oxidation reaction

In a typical experiment, the membrane was located between the cell compartments with the top surface from aqueous phase side. 200 mmol of benzyl alcohol in a one of the two cell compartment and in the other one, 15 mL of water, 4 mmol of catalyst and

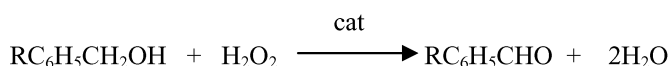
199 mmol of H_2O_2 were loaded. Obtained results are reported as selectivity to benzaldehydes, benzyl alcohol conversion to benzaldehydes, a reaction time of 4h.

2.4 Analysis

The analysis of the organic and aqueous phases was carried by GLC using a 6890 network GC system of Agilent on a HP-5 (30m x 0.320mm x 0.25 μm) column.

2. Results and discussion

Oxidation of benzyl alcohols, tested in this work, to corresponding benzaldehydes occurs by the following reaction:



1: R=H

2: R= Cl

3: R= Me

Using hydrophobic membrane (Buonomenna *et al*, 2007) three steps happens: (i) benzaldehyde permeation across the membrane from the organic phase to the membrane interface aqueous side; (ii) interfacial oxidation reaction ; (iii) benzaldehyde permeation across the membrane to the organic phase where it takes shelter from over-oxidation (Scheme 1).

The aim of the reported tests was to compare the system performance, in the oxidation of benzyl alcohol, by changing the flow rate in the compartment of organic phase operating in counter-current mode and to study in the proposed system the oxidation of substituted benzyl alcohols.

Effect of organic phase flow rates

Effect of organic phase flow rates on the progress of oxidation of benzyl alcohol was studied using as flow rate 1.7×10^3 and 4.7×10^3 mL/h. Experimental results are reported in Table 2 and Figures 2(a-b).

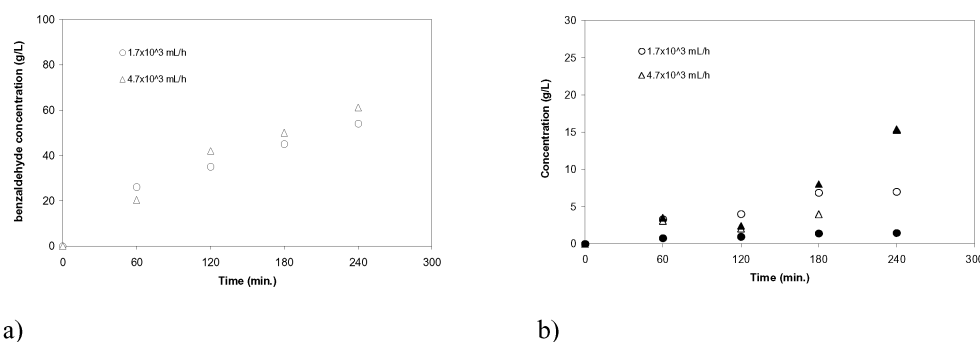
Table 2- Selectivity, benzyl alcohol conversion varying flow rate of organic phase (aqueous phase flow rate= 10×10^3 mL/h, counter-current mode).

Organic Phase Flow rate (mL/h) $\times 10^3$	Selectivity to BzH (%) ^a	Benzyl alcohol conversion to benzaldehyde (%) ^b
1.7	98.2	5.97
4.7	85	7.48

^a Selectivity to BzH = $[\text{mmol BzH}/(\text{mmol BzH} + \text{mmol BzA})] \times 100$.

^b BzOH conversion to BzH = $(\text{mmol BzH}/\text{mmol BzOH initial}) \times 100$.

It is observed in these experiments that benzyl alcohol conversion to benzaldehydes increased (from 5.97% to 7.48%) as flow rate was raised with a loss of reaction selectivity, from 98.2 % to 85 %. In fact, increasing the liquid flow rate will enhance the mass transfer. However, in practice, the liquid flow velocity cannot be elevated without bound. At a higher liquid velocity, in fact, the liquid has a greater potential to wet the membrane which reduces the mass-transfer rate (Malek and Teo, 1997). Specifically, the effect on the reaction progress operating at different flow rates is clearly visible from the plots of benzaldehyde and benzoic acid in the two reaction phases, i.e. organic (Fig. 2a) and aqueous (Fig. 2b).

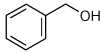
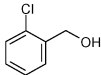
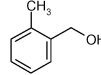


a) b)
Figure 2-a) benzaldehyde concentration in the organic phase and b) benzaldehyde (open symbols) and benzoic acid (closed symbols) concentration in the aqueous phase vs. time at different flow rates of organic and aqueous phases (counter-current mode).

In the organic phase, an higher concentration of product, benzaldehyde was achieved during the time at the highest flow rate. Analysis of the aqueous phase for detecting benzaldehyde and over-oxidation product, i.e. benzoic acid, was carried out to examine the effect of the two different flow rates on the extraction capability of the membrane from the aqueous compartment to organic one. It is noteworthy that operating at 4.7×10^3 mL/h flow rate of organic phase, in the aqueous phase, the highest concentration of benzaldehyde produced during the reaction was detected, determining an overall conversion to desired product of 7.48 %, but with lower selectivity (85 %), due to higher production of benzoic acid in the aqueous phase. Although a better selectivity has been obtained operating at organic flow rate of 1.7×10^3 mL/h, nevertheless next experiments with substituted benzyl alcohols **2** e **3** were carried out with 4.7×10^3 mL/h in order to ensure that the two alcohols do not solidify in the pump tubes due to their relatively high melting points (342K and 306K for **2** and **3**, respectively). The experimental results have been reported in Table 3. The reactions have been carried out in monophasic system to have a reference, without compartmentalization by membrane and separation of catalyst by substrate and product: a polar solvent, acetonitrile, has been used. In fact, alcohols **2** and **3** **do not react in solvent free conditions using the homogeneous catalyst** $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Mo7).

Inspection of data reported in Table 3 show that, in all cases, the homogeneous mono-phase oxidation is faster. The interesting observation is that the structure-reactivity behaviour may indeed be induced by the nature of the polymeric membrane.

Table 3- Selectivity, benzyl alcohols conversion by the membrane contactor MC-Mo7 (aqueous phase flow rate= 10×10^3 mL/h, organic phase flow rate= 4.7×10^3 , counter-current mode) and with the homogeneous catalyst using acetonitrile as solvent $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Mo7)

Benzyl alcohol	System	Selectivity to BzH (%)	Benzyl alcohols conversion to benzaldehyde (%)
 1	MC-Mo7	85	7.48
	Mo	97	22.5
 2	MC-Mo7	96	3.15
	Mo	95	24.3
 3	MC-Mo7	98	6.64
	Mo	97	18

In particular, considering the series of aromatic alcohols a preferential reactivity towards benzyl alcohol **1** and lower conversion for **2** is registered, which stands in contrast with the homogeneous reference. These observations point to a specific substrate recognition exerted by the polymeric matrix of the membrane; the preferential interaction with the polymeric membrane (mutual affinity) promotes the oxidation favouring the sorption equilibria and leading to an enrichment of the substrate concentration on the membrane-aqueous phase interface. However, if the interaction between the fluoropolymer layer of composite membrane and substrate is too strong, no complete extraction of the product in the organic phase (from membrane –aqueous phase interface) is obtained and a lower concentration of benzaldehyde has been detected in the organic compartment (Table 3, benzyl alcohol **2**, 3.15 % of conversion) This fact is also consistent with the EDX analysis of the membrane cross section before and after the test with benzyl alcohol **2** (Figure 3).

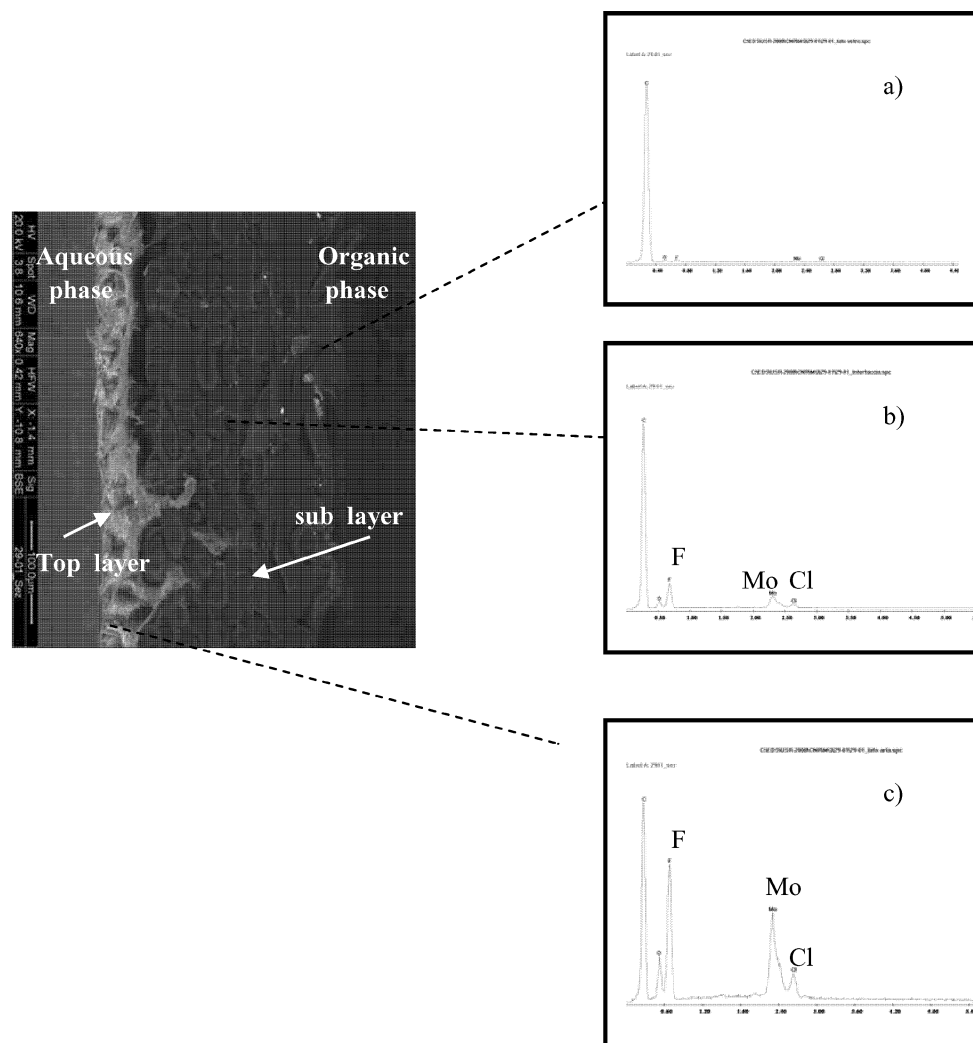


Figure 3- Cross section (left) of composite polymeric membrane (see Table 1) and corresponding EDX analyses at different depths of membrane cross section (right). (a) interface membrane-organic phase; (b) membrane sublayer; (c) interface membrane-aqueous phase.

In other words, the membrane-assisted process favours the accumulation of the chloride reagents and products at the interface membrane-aqueous phase without complete transport of the reaction product at the organic phase-membrane inter-phase.

4. References

- Bortolini, O., S.Campestrini, F. Di Furia, G. Modena, 1987, Journal of Organic Chemistry , 5467, 52.
- Buonomenna,M.G.,E.Drioli,2007,Appl.Catal.B-Environ.
doi:10.1016/j.apcatb.2007.10.003
- Hudlicky, M. Oxidations in Organic Chemistry; ACS:Washington, DC, 1990.
- Malek, A., K. Li, W.K. Teo, 1997, Ind. Eng. Chem.Res., 784, 36.
- Nehelsen, J., M. Mukherjee, R.V. Porcelli, 2007, Chem Eng Prog , 103, 31.
- Opre, Z., D. Ferri, F. Krumeich, T. Mallat, A. Baiker, 2006, Journal of Catalysis, 241, 287.