

Solvent free selective oxidation of benzyl alcohol to benzaldehyde using a membrane contactor unit

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Abstract

A new clean catalytic process for the selective oxidation of benzyl alcohol with hydrogen peroxide to benzaldehyde has been studied. 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 and the product, and the aqueous phase with the oxidant. Being the two phases separated 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.

The effect of various reaction parameters such as reaction temperature, type of membrane, type of catalyst, the addition mode of hydrogen peroxide was investigated.

Three different membranes based on hydrophobic polyvinylidene fluoride (PVDF) were prepared by phase inversion technique induced by nonsolvent and used as membrane contactor. The membranes are characterized by different thicknesses, porosity, tortuosity and hydrophobicity. The catalysts used were ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and sodium tungstate, Na_2WO_4 . In literature, both these catalysts were reported to be effective in the oxidation of alcohols with H_2O_2 in combination with a phase transfer catalyst in chlorinated solvents.

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1. Introduction

There is a growing need for “green” technologies in the synthesis of fine chemicals and pharmaceutical 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 a small scale synthesis [1].

Oxidation of alcohols to aldehydes, in particular benzyl alcohol (BzOH) to benzaldehyde (BzH), is an important organic transformation. BzH is a very valuable chemical which has widespread applications in perfumery, dyestuff and agro chemical industries [2–4].

Conventional methods for performing such transformations generally involve the use of stoichiometric or more than stoichiometric quantities of inorganic oxidants, such as

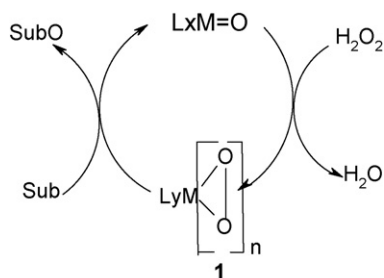
chromium (VI) reagents, dimethyl sulfoxide, permanganates, periodates or *N*-chlorosuccinimide (NCS) [4].

The increasing demand for environment-conscious chemical processes has impelled many researchers to explore truly efficient oxidation methods using aqueous H_2O_2 , an ideal oxidant in this context: hydrogen peroxide is by far the least environmentally demanding among the peroxides; in fact, water is the only by-product of these reactions. However, hydrogen peroxide is a rather weak oxidant. Thus in order to become synthetically significant, the oxidations by hydrogen peroxide need to be catalyzed [5]. Among the oldest, but very efficient, catalysts which have been well studied [6–9], the derivatives of some transition metal ions, i.e. V, Mo and W, in their highest oxidation states, are still under active investigation. The metal precursor adds hydrogen peroxide in an equilibrium process largely shifted to the right [10]. The intermediate **1** is thus formed in which *n* is usually 1 or 2 (Scheme 1).

The peroxometal complex **1** is the real oxidant in solution. Species such as **1** can be, in several instances, isolated and

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Scheme 1. Mechanism of peroxometal catalysis.

stored: they may be used as stoichiometric oxidants with synthetic relevance [11,12].

Anionic peroxomolybdenum complexes, for example, rendered soluble in chlorinated solvents by the presence of a lipophilic counter cation, allowed to obtain in a monophasic system quantitative yields of aldehydes from primary alcohols [11].

An alternative procedure consisted in a two-phase method oxidation with hydrogen peroxide under phase transfer conditions: a neutral lipophilic ligand acts as extracting agent. For example, the commercial ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in combination with a phase transfer catalyst, $(n\text{-C}_4\text{H}_9)_4\text{NCl}$, and a base (K_2CO_3), catalyzed the selective oxidation of secondary alcohols with H_2O_2 in THF solvent with a molar ratio alcohol: H_2O_2 :catalyst of 10:40:1. The more hindered alcohol moiety was selectively oxidized in the presence of a less hindered one with a conversion of 90% in 6 days [13]. $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ were used as catalysts and a lipophilic tetraalkylammonium compound as extracting agent in the oxidation of primary and secondary alcohols in 1,2-dichloroethane by Bortolini et al. [14]. The molar ratio alcohol: H_2O_2 :catalyst was of 10:20.2:1.

For all the peroxo complexes generated *in situ* by using commercial Mo(IV), W(IV), an excess of H_2O_2 was used. In fact, a problem of aqueous hydrogen peroxide as oxidant rises from its poor stability because it is liable to decompose while heated or in the presence of many metal ions. Therefore, there is a competition between the decomposition reaction and oxidation reaction. To overcome this problem, the peroxo anions of Mo(VI), W(VI) metals carrying active oxygen atoms should easily enter the organic phase. From this point of view, phase transfer agent must be able to extract the peroxo anions into organic phase. Shi and Wei [15] synthesized bis-quaternary phosphonium salts of peroxotungstate and peroxomolybdate in which the cation and counteranion are all bivalent: owing to the effective association between the two opposite charge, the peroxo anion carrying active oxygen atoms enters organic phase effectively.

In this work, we report a novel method for selective oxidation of BzOH to BzH. Neither solvent nor promoters are needed: a polymeric microporous membrane acts as a barrier to “keep in contact” the organic phase containing the BzOH and the BzH and the aqueous phase with hydrogen peroxide. The

species are transferred from one phase to the other only by diffusion: the membrane’s role in the system studied in this work was to improve the contact between the two different reactive phases, the catalyst being physically separated from the membrane, realizing an inert membrane reactor [16,17]. The reaction between the reactants, controlled by diffusion across membrane, overcomes the limit of side reactions as over oxidation of the BzH to benzoic acid (BzA).

The chemical and engineering community is already paying significant attention to the request for technologies that would lead the goal of technological sustainability [18,19]. A promising example with a lot of interest by process engineers is the strategy of process intensification. It consists of innovative equipment, design and process development methods that are expected to bring substantial improvements in chemical and any other manufacturing and processing such as decreasing production costs, equipment size, energy consumption, waste generation. Membrane operations, with their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, low energetic requirement, good stability under operating conditions and environment compatibility, easy control and scale-up, represent an interesting answer for the rationalization of chemical production. Among new unit operations involving membranes, membrane contactors are expected to play a decisive role in this scenario. The key concept is to use a solid, porous, hydrophobic (or hydrophilic) polymer matrix in order to create an interface for mass transfer and/or reaction between two phases. Whereas the design of the conventional devices is restricted by limitations in the relative flows of the fluid streams, membrane contactors give an active area, which is independent of the liquid fluid dynamics [20].

In the oxidation of BzOH to BzH using a membrane contactor unit, described in this work, various reaction parameters such as reaction temperature, type of membrane, type of catalyst, the addition mode of hydrogen peroxide were investigated. Being a pioneering study, a reaction time of 4 h without analyzing the system lifetime in long time runs was investigated.

Three different membranes based on hydrophobic polyvinylidene fluoride (PVDF) were prepared by phase inversion technique induced by nonsolvent [21] and used as membrane contactor. The membranes are characterized by different thicknesses (30 μm , 50 μm and 70 μm), porosity, tortuosity and microstructures (finger or nodular like).

The catalysts used were commercial sodium tungstate, Na_2WO_4 and ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. From both an economic and environmental viewpoints, the selective system proposed in this study working in absence of organic solvents has as consequence the reduction of toxic waste and by-products making the process ecologically more acceptable. In fact, one of the major problems encountered in various processes for producing organic fine chemicals, is the use of organic solvents. Hence, it is appropriate that organic transformations under solvent-free conditions are attracting increasing attention [22].

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