



Vanadium(III) and vanadium(IV) catalysts in a membrane reactor for benzene hydroxylation to phenol and study of membrane material resistance

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ARTICLE INFO

Article history:

Received 7 March 2012

Received in revised form 15 June 2012

Accepted 18 June 2012

Available online 26 June 2012

Keywords:

Benzene oxidation to phenol

Membrane reactor

Vanadium(III) catalyst

Physical membrane resistance

ABSTRACT

Benzene hydroxylation to phenol by using vanadium based catalysts and product recovery were performed in a two-phase membrane reactor. Benzene permeates, through the hydrophobic polypropylene membrane, in the aqueous phase containing the catalyst while phenol permeates back accumulating in the organic phase. The following fundamental aspects have been studied: dose of hydrogen peroxide, initial oxidation states of vanadium catalysts, duration of catalytic tests and lifetime of the membrane in terms of physical and chemical resistance. It was observed that feeding the oxidant by a micro pump, working in the “bulk tube” mode, phenol yield, final phenol concentration in the organic phase, phenol turnover number and system productivity increased, and no tar was formed. Initial oxidation state of vanadium catalysts influenced system performance: indeed improved results in terms of yield (35.2% vs. 25.1%), conversion of hydrogen peroxide to phenol (36.6% vs. 25.9%), productivity ($0.97 \text{ g g}_{\text{cat}}^{-1} \text{ h}^{-1}$ vs. $0.78 \text{ g g}_{\text{cat}}^{-1} \text{ h}^{-1}$) were obtained by using vanadium(III) chloride compared to vanadium(IV) acetyl acetonate. Higher phenol extraction/recovery in the organic phase (61.1% vs. 46.3%) and then higher selectivity (97.5% vs. 92.8%) were obtained by increasing test duration from 270 to 510 min. A weak membrane resistance was observed after 246 h of consecutive catalytic runs on the same membrane piece, showing degradation of the membrane material (polypropylene) caused by the OH^{\bullet} radical generated in the reacting mixture.

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1. Introduction

Phenols are important raw materials for the synthesis of a wide variety of chemicals like phenol resins, dyes, antioxidants, and pharmaceuticals [1]. Phenol production is expected to continue to grow at 6% per annum from 7 million tonnes capacity in 2002 [2]. Nowadays almost 95% of phenol production is based on the so-called “cumene process” [3]. Despite this large application, important disadvantages of this process are: (a) high and damaging ecological impact; (b) the cumene hydroperoxide is an explosive compound; (c) quantity of acetone, as by-product, equimolar to produced phenol; (d) the multistep character makes difficult to achieve high phenol yield compared to benzene [4].

Thus, the search for new routes for phenol synthesis, such as the direct hydroxylation of benzene became more intensive in the last decades [5–10]. Such a process presents various potential advantages compared to the traditional cumene process, but its selectivity is usually rather poor since phenol can be oxidized

easier than benzene [11]. The prompt removal of the produced phenol from the reaction environment represents a key point for developing such a method and, on this aspect, membranes can play an important role.

Membrane reactors (MRs) can be employed for slowing down consecutive oxidation reactions. These systems are very attractive because of their advantages related to the synergy between the chemical reaction and a membrane process [12,13]. In particular, membrane contactors permit to combine membrane separation and reaction in one device. A membrane contactor achieves gas/liquid or liquid/liquid mass transfer without dispersion of a phase within another [14,15]. One important advantage in using such a system consists in the possibility of recovering the produced phenol from the reaction mixture, achieving improvements in terms of yield and selectivity thus limiting by-products formation.

In our previous works [4,11] we proposed the use of a membrane contactor, for the one-step benzene oxidation to phenol, consisting of a flat-sheet membrane that separates two compartments: one containing an aqueous phase, with an iron catalyst and hydrogen peroxide as the oxidant, and the other one containing an organic phase (only benzene). Benzene has a double task: it is a reactant, because it permeates across the hydrophobic membrane

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