



Performance of vanadium based catalyst in a membrane contactor for the benzene hydroxylation to phenol

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ABSTRACT

Phenol production through the direct hydroxylation of benzene with hydrogen peroxide, as oxidant, using a vanadium catalyst in a membrane reactor has been studied. The reaction was carried out in mild condition in a liquid–liquid biphasic system separated by a polypropylene membrane. This system showed high selectivity to phenol, minimizing its over-oxidation to over-oxygenated by-products. The influence of various reaction parameters such as the addition of hydrogen peroxide mode, catalyst and sulphuric acid amounts, temperature and reducing agent effects were investigated. The vanadium catalyst avoided tar formation in all the investigated experimental conditions compared to the previous system where an iron-based catalyst was used. Use of $(C_5H_8O_2)_2VO$ as catalyst, 18 mmol of hydrogen peroxide as oxidant pumped for 4 h in the aqueous phase with the step-by-step feeding mode gave the best system performance in terms of yield (63.2%), selectivity to phenol (97.0%), and extraction quotient (76.4%).

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1. Introduction

Phenol is an important intermediate for the synthesis of petrochemicals, agrochemicals, and plastics. The current worldwide capacity for phenol production is nearly 7 million metric tonnes per year [1]. Today, almost 95% of the worldwide phenol production is based on the “cumene process”. However, this process has some disadvantages: high and damaging ecological impact, an explosive intermediate to manage (cumene hydroperoxide), large amount of acetone as by-product and a multistep character, making it difficult to achieve high phenol yield compared to benzene [2].

The search for new routes for phenol production based on the one-step direct benzene oxidation became more intensive in the last decade but this reaction is little selective because phenol is more reactive than benzene and by-products occur [3–12].

To reduce the formation of by-products the membrane reactors (MRs) and, in particular, membrane contactors, can be employed. A membrane contactor permits the combination of membrane separation and catalytic reaction in one device [13–15]. The main advantage in using a membrane in this system is the separation of phenol from the reaction mixture permitting to obtain improvements of yield and selectivity limiting side catalytic reactions.

In our research group a flat-sheet membrane contactor was used for the one-step oxidation of benzene to phenol [16–19] reducing by-products formation by employing a liquid–liquid membrane

contactor with various iron catalysts and hydrogen peroxide as oxidant. In this system phenol that did not cross the membrane rapidly remained in the reacting ambient and reacted further generating over-oxidation products such as 1–4 benzoquinone, biphenyl as trace and tars (black solid). To reduce tar formation and enhance phenol recovery in the organic phase, different aspects were studied in our previous work [20]. Despite the improved results, the black solid formation was not avoided completely. The need to avoid tar formation can be ascribed to several reasons: (i) concentration polarization and fouling phenomena that decrease membrane performance, particularly in view of the continuous operating system; (ii) bad use of a reactant (benzene); (iii) environmental impact (tar to discharge). Then the choice of the catalytic system will be a compromise between high conversion to phenol and points (i)–(iii). To avoid tar formation, catalysts different from the iron-based ones should be used considering that heavy metal oxides are generally more active than noble metal catalysts [21].

Taking into account the important role played by vanadium complexes in oxidative reactions on biological systems for the detoxification of organisms, it was interesting to investigate the performance of a vanadium catalyst in the oxidative hydroxylation of benzene, replacing the iron catalysts previously investigated. Vanadium compounds successfully oxidize benzene in most of the reactions reported in literature using H_2O_2 or oxygen as oxidants. For example, Ishida et al. [22] obtained good turnover numbers (TNs) of phenol production using a supported vanadium catalyst in mild conditions. High reaction yields were claimed by Barnhard and Hughes using vanadium complexes as catalyst and hydroquinones as reducing agents [23]. However, the concentration of

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