

Liquid-phase oxidation of benzene to phenol using CuO catalytic polymeric membranes

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Abstract

Catalytic polymeric membranes filled with copper oxides of different particles size were prepared and tested in the liquid phase oxidation of benzene to phenol. Polyvinylidene fluoride (PVDF) was used as polymer to make the membranes. Three different solvents, dimethylacetamide (DMAc), dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (NMP) were used as polymer solvents and distilled water as a nonsolvent. The prepared membranes were characterised morphologically by scanning electron microscopy (SEM). Pore size distribution was determined using gas permeation method. Membrane characterisation tests evidenced that DMAc was the best solvent. Permeability tests were carried out for measuring the contact time of the catalyst with the reacting mixture. Catalytic membranes were tested in the liquid phase oxidation reaction of benzene to phenol by using hydrogen peroxide as oxidant in an ultrafiltration membrane reactor. The obtained results showed a higher phenol concentration using the PVDF membrane filled with the CuO nanopowder rather than CuO powder catalysts. A phenol concentration of 2.4 g L^{-1} and a benzene conversion to phenol of 2.3% were obtained using a contact time with the catalyst of 19.4 s at 35°C .

Keywords: CuO–Polyvinylidene fluoride membranes; Benzene oxidation to phenol; Copper(II) oxide catalyst; Ultrafiltration membrane reactors

1. Introduction

Different approaches have been recently studied for the design and use of membrane

technology in catalytic processes, where the membranes are employed to enhance the conversion efficiency [1–3]. Most of the recent research has been done on reactors made with inorganic membranes, due to the usually high temperatures involved and the sometimes

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aggressive chemical environments. However, there has been a recent interest in polymeric membranes [4–8], indeed they present some advantages over the most expensive inorganic membranes made from ceramic or metals. Most of the polymeric membranes can be easily manufactured in different shapes (e.g., hollow, spiral wound, flat sheet); they are elastic, have satisfactory diffusion and sorption coefficients; can be produced with incorporated catalysts as nanosized dispersed metallic clusters, zeolites and activated carbon or metallic complexes. The capability to produce a well-defined porous matrix that can serve as a support from a wide variety of catalytic materials is contributing to the production of the single-site catalysts in which all of the active sites closely resemble each other.

In this work the polyvinylidene fluoride (PVDF) has been used as the polymer to make the membrane material because of its excellent chemical resistance, particularly the oxidant resistance. The PVDF asymmetric membranes were obtained using the phase inversion method induced by nonsolvent. The effects of different solvents on membrane morphology and properties were investigated on the catalytic membranes filled with two types of the copper (II) oxide. They were tested in the liquid phase oxidation reaction of benzene to phenol using an ultrafiltration membrane reactor.

This reaction is a recent object of studies and searches [9–11] particularly for the one-step production of phenol by direct hydroxylation of benzene. Indeed, the oxidation reaction has low selectivity since the phenol is more reactive towards oxidation than benzene, and substantial formation of byproducts such as biphenyl and further oxidation compounds is found.

In order to reduce/avoid byproducts formation the control of contact time of substrate and products with the catalyst was tested. This control was obtained by feeding the oxidant

solution containing the substrate at different permeate flow rates. Some preliminary results of this novel approach are reported in this work.

2. Experimental

2.1. Materials

Commercially available polyvinylidene fluoride (PVDF) Solef[®] 6010 (Solvey Solaxis S.A. Belgium) was used as membrane material. Acetonitrile (CH_3CN , MW = 41.05 g mol⁻¹, purity 99.7%, Lab-Scan), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, MW = 60.05 g mol⁻¹, purity 99.5%, Fluka), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, MW = 176.13 g mol⁻¹, Fluka) hydrogen peroxide (H_2O_2 , 30 wt.% in water, Sigma–Aldrich), ultra-pure water Millipore ELIX 5, benzene (C_6H_6 , MW = 78.11 g mol⁻¹, purity 99.8%, Carlo Erba Reagents), were the reagents used in the catalytic tests. Phenol ($\text{C}_6\text{H}_5\text{OH}$, MW = 94.11 g mol⁻¹, purity 99.99%, Sigma–Aldrich), was used for calibration curve. *N,N*-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, MW = 73.09 g mol⁻¹, purity 99.5%, Riedel-de Haën), *N,N*-dimethylacetamide ($\text{C}_4\text{H}_9\text{NO}$, MW = 87.12 g mol⁻¹, purity 98%, Fluka) and 1-methyl-2-pyrrolidone ($\text{CH}_2 - (\text{CH}_2)_2 - \text{CON} - \text{CH}_3$, MW = 99.13 g mol⁻¹, purity 99.8%, Carlo Erba Reagents) were the polymer solvents.

The copper (II) oxides (CuO , MW = 79.54 g mol⁻¹, purity 99%, Sigma–Aldrich) in the types of powder and nanopowder were used as catalysts. Particles size of the copper oxide powder was smaller than 5 μm . The mean particles size of copper oxide nanopowder was equal to 33 nm.

2.2. Preparation of polymeric membranes catalytic and not catalytic

Flat-sheet PVDF catalytic membranes were prepared by phase inversion process induced by nonsolvent. Dimethylacetamide (DMAc),

dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (NMP) were used as solvents and distilled water as a nonsolvent. For each solvent, a solution (20 wt.%) was prepared by dissolving the polymer in the solvent by magnetic stirring at room temperature; then the CuO powder (or CuO nanopowder) at 16 wt.% was added and the resulting solution was stirred for an additional 24 h. The solution was cast on a glass plate by setting the knife gap at 250 μm , and exposed 30 s in air before immersing in a precipitation bath. The plate with casting solution thin film was firstly immersed for 10 min in a coagulation bath containing distilled water at 25°C. Secondly, the precipitate membrane was removed from the coagulation bath and leached under running water for 24 h to remove residues of solvents. Then the membranes were dried in an oven at 60°C. The same preparation procedure was employed to prepare the polymeric membranes without the catalyst.

2.3. Membrane characterization

The formed membranes were characterised by the following methods: (1) Membrane thickness was measured using a digital micrometer (Carl Mahr D7300 Esslingen a.N.) averaging five measurements. (2) Cross-section of the membranes was observed by means of FEI QUANTA 200 scanning electron microscope (SEM). Membrane samples were broken in liquid nitrogen to keep unaltered the film structure. (3) Contact angles of water droplets on the membrane surfaces were measured by the sessile drop method using a CAM 200 contact angle meter (KSV Instruments, Helsinki, Finland). (4) Pore size distribution was determined with a Capillary Flow Porometer (PMI, model CFP 1500 AEXL). The porometry tests were performed in dry-up/wet-up mode. (5) The membrane permeation properties for PVDF2, PVDF2CuOp and PVDF2CuOnanop membranes (where the number 2 present in the

membrane names means that DMAc was the solvent used for membrane preparation) were tested in an ultrafiltration membrane reactor fed with the reacting solution at different transmembrane pressures (range from 1 to 6 bar) in order to change the contact time of benzene and formed phenol with the catalyst.

2.4. Experimental plant, contact time calculations and procedure of catalytic tests

The catalytic tests were performed in the experimental plant schematised in Fig. 1. It is composed by an ultrafiltration membrane reactor where a peristaltic pump fed a dead-end permeation cell with the feed solution. The permeation cell containing the membrane had an exposed surface area of 4 cm \times 6 cm = 24 cm². This system permits to control the contact time of feed solution with the catalytic membrane by varying the permeate flow rates changing the transmembrane pressure. Calculation of contact times were performed by using the following equations:

$$\text{Contact time} = \frac{\text{Membrane thickness(cm)}}{v(\text{cm/min})}$$

$$v = \frac{\text{Permeate flow rate(mL/min)}}{\text{membrane surface(cm}^2\text{)}}$$

$$= \frac{\text{cm}^3/\text{min}}{\text{cm}^2} = \frac{\text{cm}}{\text{min}}$$

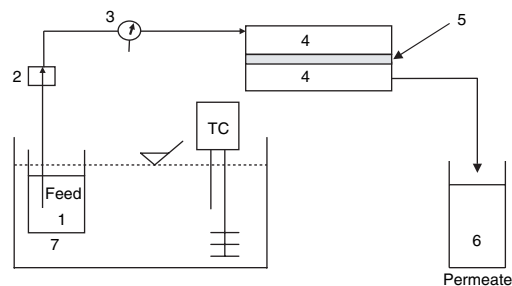


Fig. 1. Scheme of the membrane reactor: (1), feed; (2), peristaltic pump; (3), manometer; (4), permeation cell; (5), membrane; (6), permeate; (7), thermostatic bath.

where v is the permeation velocity of the reacting solutions across the membranes.

A typical procedure for oxidation tests in the membrane reactor was as follows. A solution containing 100 mL of an acetonitrile benzene mixture 8:1 (v/v) ratio and hydrogen peroxide 1:1 molar ratio with benzene was pumped in the permeation cell at different transmembrane pressures corresponding to different contact times. The permeate solution was collected and analysed in order to determine the concentrations of phenol and other byproducts.

2.5. Analysis of the solution

Phenol and oxidation byproducts in the organic phase were detected by high-performance liquid chromatography (HPLC) Agilent 1100 series using an Agilent ZORBAX Eclipse XDB-C8 (4.5 × 150 mm, 5 μm) column. The oxidation products, after extraction with diethylether, were also analysed at GC-MS (QP 2010S-Shimadzu) in order to confirm the obtained products.

3. Results and discussion

All membranes showed the so-called asymmetric morphology being characterised by a thin

skin and a porous bulk that comprises large voids extending to the central or even towards the bottom region of the membrane. The upper half of the cross section was composed by parallel finger-like voids, whereas the lower half was composed by small independent cellular pores enclosed in the polymer matrix. A uniform catalyst distribution was observed in all the polymeric membranes prepared using the copper oxide nanopowder (Fig. 2(a)). In contrast, no uniform catalyst distribution was observed in PVDF membranes prepared using the copper oxide powder (Fig. 2(b)).

For all the PVDF membranes a pore size distribution in the range from 0.02 to 0.1 μm was obtained. The permeability tests evidenced that the membrane flow rate was affected by the type of added CuO. Nanosized inorganic filler led to an increase in the PVDF membrane permeability. This can be interpreted as follows [12]: PVDF is a hydrophobic polymer and its hydrophilicity can be improved significantly by adding the CuO particles, which have hydrophilic character. Thus the permeate flow rates, at transmembrane pressure equal to 6 bar, increased from 0.5 for the PVDF2 membrane to 2.9 mL min⁻¹ for the PVDF2CuOnanop that

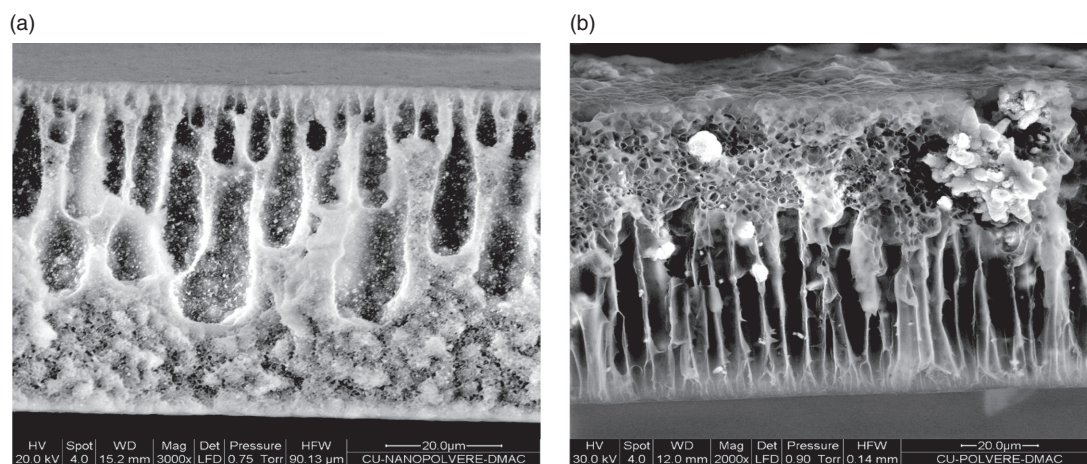


Fig. 2. Cross section images of PVDF membranes prepared with DMAc and: (a) copper oxide powder catalyst (PVDF2CuOp), (b) copper oxide nanopowder catalyst (PVDF2CuOnanop).

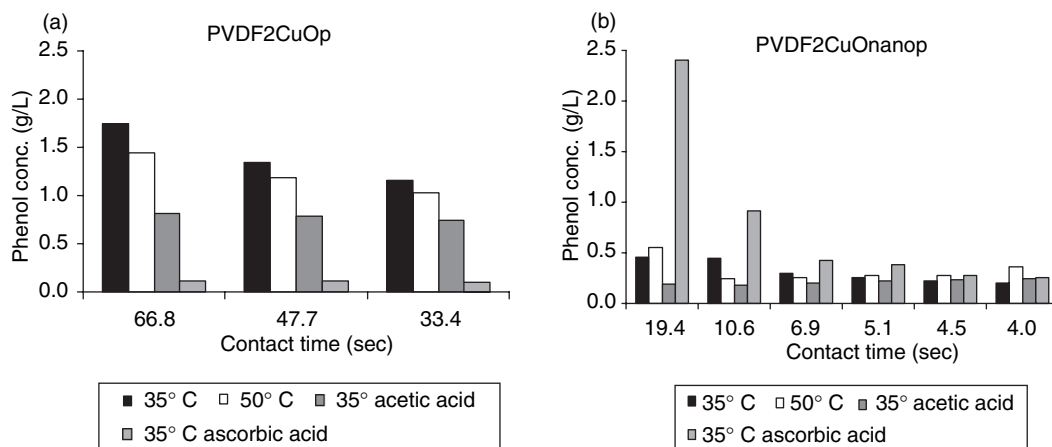


Fig. 3. Phenol concentrations at different contact time obtained by catalytic membranes prepared with DMAc and (a) copper oxide powder catalyst (PVDF2CuOp), (b) copper oxide nanopowder catalyst (PVDF2CuOnanop).

correspond to contact times of 16.7 and 4s, respectively. This trend was not evidenced when particles of powder copper oxide were used, indeed at 6 bar the value of permeate flow rates for the PVDF2CuOp membrane was the same of PVDF2 membrane and decreased at lower pressure. This behaviour was probably caused by absence of interaction between the membrane

material and the catalyst and then no alteration of membrane properties were obtained. Indeed, the advantage to entrap the CuO nanoparticles in the polymer matrix is surely the control of contact time of substrate with the catalyst but also the improvement of some properties of membranes such as the membrane permeability.

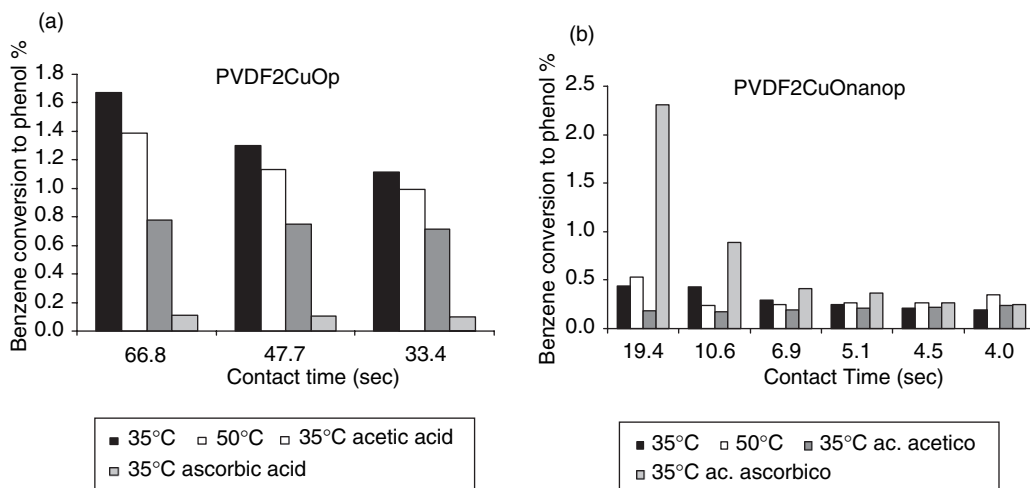


Fig. 4. Benzene conversion to phenol percentage (*) at different contact time obtained by catalytic membranes prepared with DMAc and (a) copper oxide powder catalyst (PVDF2CuOp), (b) copper oxide nanopowder catalyst (PVDF2CuOnanop). (*) Benzene conversion to phenol % = (mmol phenol / mmol benzene initial) × 100.

The study of catalytic activity of the membrane was carried out in the ultrafiltration membrane reactor (Fig. 1). In this system the catalytic (reactive) membrane has the role to confine the catalyst and to control the contact time of reactants and products with the catalyst.

Preliminary catalytic tests were performed at two different temperatures (35°C and 50°C) and the effect of acetic and ascorbic acids addition in the reacting media was studied. The results of the experimental tests using different feeding solutions at different contact times and different temperatures are reported in Figs. 3 and 4 showing phenol concentrations and benzene conversion percentage at different contact time, respectively.

The best results were obtained using the PVDF2CuOnanop membrane at 35°C and a reacting solution containing ascorbic acid at contact time of 19.4 s. Using the ascorbic acid (Fig. 3(b)) the phenol concentration increased by increasing the contact time. This behaviour indicates that an adequate contact time of ascorbic acid with the catalyst is necessary in order to reduce the Cu(II) species to Cu(I) species. Indeed the Cu(I) species react with the H₂O₂ for hydroxyl radical formation. Acetic acid and a higher temperature did not improve the phenol production.

4. Conclusion

Obtained results show a higher phenol concentration using the PVDF membrane filled with the CuO nanopowder rather than CuO powder catalysts. In particular a phenol concentration of 2.4 g L⁻¹ and a benzene conversion to phenol of 2.3% were obtained using a contact time with the catalyst of 19.6 s at 35°C. Byproducts such as benzoquinone and biphenyl were detected as traces. The results of this explorative study are encouraging and further

research is in progress to improve system performance.

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