PVA composite catalytic membranes for hyacinth flavour synthesis in a pervaporation membrane reactor

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1   Introduction

Hyacinth flavour, a high value product used in food and cosmetic industry, is generally synthetized by acetalization of phenylacetaldehyde with glycerol under acid catalysis. One of environmental and economic gains of this reaction is the reuse of the glycerol in biorefineries, a byproduct of the increasing biodiesel production by transesterification of vegetable or animal oil [1].

Since acetalization is a reversible reaction it is equilibrium limited. Reactive azeotropic distillation has been proposed for removal the water formed in the reaction, in order to improve conversion [2]. However this thechnique requires large amounts of toxic solvents, oversized equipment and consequently leads to high energetic costs.

Polymeric catalytic membrane reactors (PCMRs) can ofer specific advantages by combining in a single step chemical reaction and separation [3-4].

In the present work, catalytic composite membranes consisting in poly(vinyl alcohol) (PVA) crosslinked with glutaraldehyde and zeolite HUSY dispersed in the polymeric matrix, were prepared and used in the acetalization of phenylacetaldehyde. Catalytic runs were performed in batch conditions and in a pervaporation assisted catalytic membrane reactor. The effects of catalyst loading, polymer crosslinking and hydrophilic/hydrophobic balance in the catalytic behaviour of the prepared membranes were evaluated, as well as the application of a pervaporation catalytic membrane reactor as an alternative method to azeotropic distillation.

2   Experimental

2.1   Preparation of membranes

PVA (Aldrich, ≥99% hydrolysed) was dissolved in water at 80 ºC. In order to obtain membranes with different catalyst loadings, 20 mL of aqueous 8 wt.% PVA solution were mixed with 5, 10, 15 and 20 wt.% of H-USY zeolite (Zeolyst, CBV 720), sonicated for 1 h and then mixed with 2 wt.% glutaraldehyde (Aldrich, aqueous solution, 50 wt.%). In order to prepare membranes with different crosslinking degrees, 20 mL of the PVA solution were mixed with 10 wt.% of the zeolite), sonicated for 1 h and then mixed with 4, 6, 8 and 10 wt.% of glutaraldehyde aqueous solution (50 wt.%).

The solutions were poured in a Petri dish and allowed to concentrate and crosslink at 40 ºC for 135 min. Finally phase inversion was obtained by adding methanol to the Petri dish.

In order to prepare more hydrophobic membranes, PVA acetylation was carried out by reaction with acetic anhydride (>99%, Riedel-de Haën) at 110 ºC and atmospheric pressure during 24 h, followed by acetone extraction and drying at 80 ºC for 4 h. The parcilly acetylated PVA was then subjected to the procedure previously described with 10 wt.% of zeolite and 2 wt.% of glutaraldehyde.

2.2   Membranes' characterization

The catalytic membranes were characterized by measurement of thickness, water contact angle and swelling degree as well as by Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2.3   Catalytic experiments

Catalytic tests in batch conditions were carried out in a batch reactor at 100 ºC using catalytic membranes cut in 0,6 cm diameter disks. The reactor was loaded with 14 mL of glycerol, a known amount of membrane's mass (0.5-0.8 g) and 12 mL of phenylacetaldehyde. Samples were taken at regular time periods and analyzed by gas chromatography (GC).

Catalytic runs in membrane reactor operating under sweep gas pervaporation conditions were performed using a reactor composed of two metal slabs, each having an inlet and an outlet. The reactor was heated at 100 ºC and the reaction mixture (35 mL of glycerol and 30 mL of phenylacetaldehyde) was pumped at 12.4 mL/min. Dry nitrogen gas (flow rate of 170 mL/min), was used to sweep the downstream side of the membrane into an succinic anhydride/1,3-dioxane solution. In order to quantify permeated water, samples from this solution were also taken to GC analysis.

3   Results and Discussion

3.1   Membranes' characterization

Swelling tests and contact angle mesaurements showed that by increasing the catalyst loading, the membranes' ability to swell with water goes through a maxi-

mum on 10 wt% of zeolite, possibly due to the spacer role of zeolite particles. On the other hand, the increase of crosslinking and acetylation degree leads to a decrease in the percentage of water swelling due to the decrease in hydrophilicity.

The changes in the PVA chemical structure were evaluated by FTIR spectroscopy, where the typical PVA pattern was recognized. From a semi-quantitative analysis by comparing the intensity of matrix bands and that of the characteristic acetal band at 1650 cm^{-1}, it was found a decrease of O-H ratio intensity and an increase of C-O ratio intensity with the increase of the amount of glutaraldehyde, supporting the thesis that crosslinking consumes OH groups, replacing them by acetal bridges. Moreover, the addition of excessive crosslinking agent seems to lead to some partial crosslinking reaction, resulting in a free aldehyde group from one unreacted glutaraldehyde ending.

Membranes' surface morphology was examined by SEM and AFM. Results (Fig. 1) show asymmetric membranes with two distinct layers and a possible correlation between the average roughness and hydrophilicity: the increase of membranes' hydrophilicity can lead to higher water content in the polymeric matrix, which leads to membranes' increased plasticity, reducing its surface roughness.
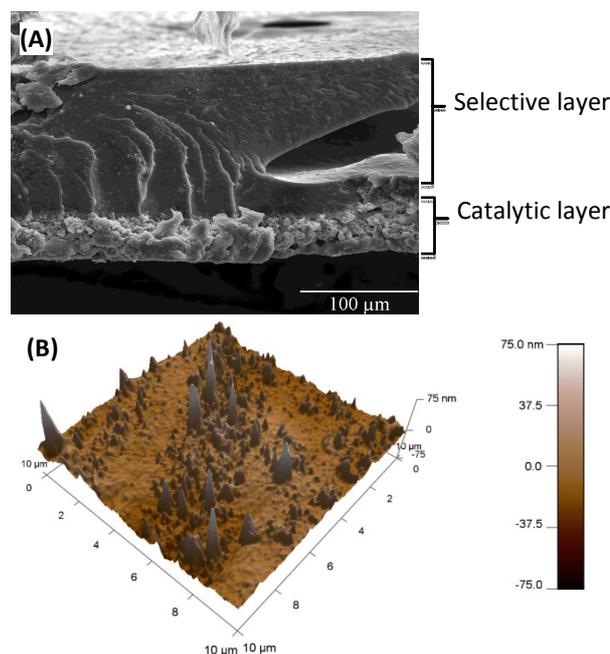

Fig. 1. (A) SEM section image and (B) 3D AFM image of PVAC10GU2 (10% H-USY zeolite; 2 wt.% glutaraldehyde).

3.2 Catalytic experiments

Fig. 2 shows the profiles of phenylacetaldehyde conversion and permeated water for the acetalization reaction carried out in the pervaporation assisted membrane reactor, assembled with a PVA membrane loaded with 10% H-USY and crosslinked with 2% glutaraldehyde (PVAC10GU2). The observed initial induction period is likely to be due to the acetal sorption in the polymer matrix. The amount of permeated water was calculated from the amount or succinic acid formed in the dioxane solution. Only trace

amounts of phenylacetaldehyde or glycerol esters were detected in this solution, showing the good selectivity of the membrane to water. The fitting of a diffusion-kinetic model assuming fickian transport and dependence of the diffusivity of phenylacetaldehyde on the concentration of the formed acetal supports that hypothesis. It was observed, in batch experiments, that the increase of crosslinking leads to the decrease of the calculated initial diffusivity probably due to the increasing limitation of membrane swelling.
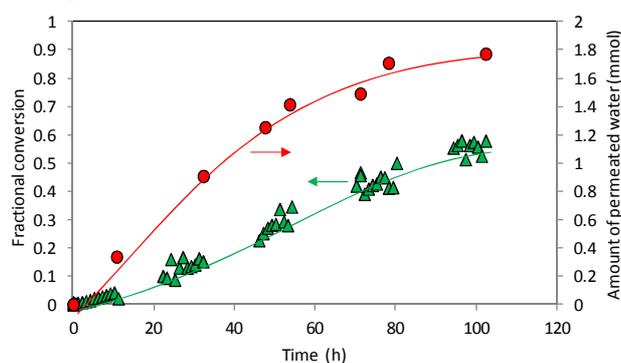

Fig. 2. Conversion and permeated water profiles obtained in the membrane reactor assembled with a PVAC10GU2 membrane.

4 Conclusions

PVA membranes were successfully crosslinked with glutaraldehyde and have shown good catalytic activity in the acetalization reaction of phenylacetaldehyde with glycerol.

The increase of catalyst loading seems to improve the membranes' transport properties. The polymer crosslinking also strongly affects the membranes' transport properties.

Permeation in membrane reactor was well accomplished with good selectivity to water.

5 Acknowledgements

6 References

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