

New ruthenium porphyrin polymeric membranes: Preparation and characterization

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Received 27 July 2007; received in revised form 6 November 2007; accepted 7 November 2007

Available online 17 November 2007

Abstract

In this work, the ruthenium porphyrin complex Ru(4-(CF₃)TPP)CO (**1**) (TPP = dianion of tetraphenylporphyrin) was entrapped into polymeric membranes during the phase inversion process to obtain new heterogeneous catalysts for aziridination reactions. In order to study the effect of the polymeric environment on the activity of the metallic complex, symmetric dense polymeric catalytic membranes were prepared using three different polymers: polyethersulphone (PES), polysulphone (PSf) and Hyflon AD60X. Different hydrophobicity/hydrophilicity characteristics, sorption properties and ability to retain the metallic complex characterized the catalytic polymeric membranes. On the basis of the good results compared to the other two polymers, Hyflon AD60X was selected to prepare asymmetric membranes with a skin layer on an open sublayer. The Hyflon AD60X membranes showed good catalytic activity in the aziridination reaction of α -methylstyrene by aryl azides and moreover they have been recycled without any loss in azide conversion and aziridine selectivity.

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Keywords: Polymeric membranes; Phase inversion; Hyflon AD60X; Ruthenium porphyrin complexes; Aziridines

1. Introduction

The application of new materials in bio-mimetic chemistry has been extensively studied in order to prepare catalysts that are more stable and selective under the employed reaction conditions. In the case of expensive catalysts as metal porphyrin complexes, homogeneous catalysts often provides the best results in terms of yield, whereas heterogeneous catalysis offer advantages such as an easy product purification and potential catalyst recycling [1]. Another advantage of supported metalloporphyrins is related to the possibility of mimicking the protein cavity that is present in natural enzymes. It is well known that the steric effects imposed by the active site environment are responsible for the selectivity encountered within the biological systems [2,3]. In the literature, some examples of catalytic polymeric membranes

based on poly(dimethylsiloxane) (PDMS) have been reported [4–8]. PDMS exhibits good thermal and chemical stabilities and PDMS based catalytic membranes have been successfully applied to the immobilization of metalloporphyrins [6], metallophthalocyanines [4,5], and Mn(salen) [7] for oxidation reactions. The hydrophobic PDMS acts as reactant reservoir enhancing the selectivity of the oxidation reaction avoiding over-oxidation of the products, which on the basis of different hydrophobicity/hydrophilicity compared to reagents leave the membrane phase. In general, it would be possible that a dense membrane due to its chemical nature supplies one of the reactants in a special form which is more active or selective in the reaction than in its usual form. The transition-metal-catalyzed aziridination of alkenes is an area of active investigation owing to the utility of the aziridine ring in organic synthesis [9]. In this work, new catalytic polymeric membranes entrapping the ruthenium-porphyrin complex Ru(4-(CF₃)TPP)CO (**1**) (TPP = dianion of tetraphenylporphyrin, Fig. 1) for aziridination of styrenes by aryl azides [10,11] were prepared.

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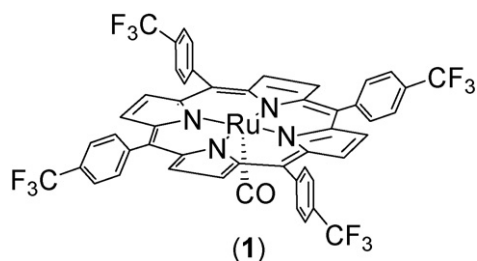


Fig. 1. The ruthenium porphyrin complex $\text{Ru}(4\text{-(CF}_3\text{)TPP})\text{CO}$ (**1**).

The catalytic membranes have been prepared by means of phase inversion induced both by evaporation of the solvent and by a non-solvent. In a first screening, three different polymers were selected and used to prepare completely dense catalytic membranes to study the effect of different microenvironments on the catalyst leaching, stability and recycling of the catalytic membranes: Hyflon, PES, and PSf. On the basis of the results obtained in this first screening, we selected Hyflon as the best polymer for the heterogeneization of the ruthenium porphyrin complex **1**. The catalyst loading in the dense Hyflon membranes was varied. Moreover, asymmetric membranes based on Hyflon, characterized by a dense skin layer on an open sublayer have been prepared to study the effect of the membrane structure on the catalytic performance.

2. Experimental

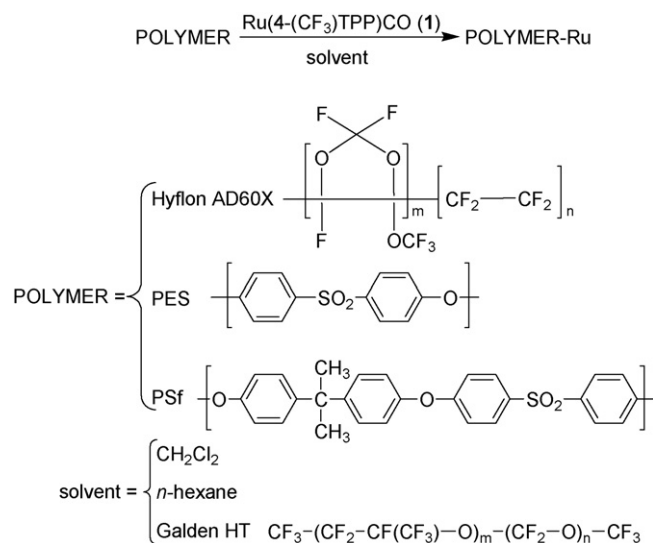
2.1. Chemicals

Commercially available reagents and solvents were used as received without further purification, for the preparation of polymeric catalytic membranes. Hyflon AD60X, Galden HT, PES (Radel[®]) and PSf (Udel[®]) were supplied by Solvay. $\text{Ru}(4\text{-(CF}_3\text{)TPP})\text{CO}$ (**1**) was synthesized according to the literature method [12].

2.2. Preparation of catalytic polymeric membranes

Flat sheet Hyflon, PSf and PES based membranes were prepared by phase inversion process (Scheme 1).

In Table 1 a summary of the experimental conditions for the preparation of catalytic membranes is given. Dense symmetric polymeric membranes were prepared by phase inversion induced by solvent evaporation. For each polymer, complex **1** (24 mg, 23.7×10^{-3} mmol) was suspended in the solvent with the polymer and the mixture was sonicated for 15 min at room temperature. The resulting solution was stirred at room temperature for 24 h and casted on a Petri disk for 12 h. Then the membrane was dried in an oven at 100°C under vacuum for 24 h. The solvent used for PSf and PES was CH_2Cl_2 . For Hyflon, Galden HT was used as solvent. In this case, two type of Hyflon catalytic membranes were prepared: dried at room temperature (Hyflon-Ru D1a) and dried at 100°C under vacuum to remove Galden HT (Hyflon-Ru D1b). Dense catalytic membranes based on Hyflon with different catalyst loading (0.79–2.37 wt% with respect to the sum of all



Scheme 1.

components in the preparation) were prepared (series Hyflon-Ru D1-D3, Table 1).

Asymmetric porous membranes were prepared by means of non-solvent (NS) induced phase inversion using n -hexane as internal and external non-solvent (series Hyflon-Ru 1P-3P, Table 1). Complex **1** (24 mg, 23.7×10^{-3} mmol) was suspended in Galden HT with Hyflon AD60X and the mixture was sonicated for 15 min at room temperature. The resulting solution was stirred at room temperature for 24 h and casted on a glass plate by means of custom made tubular casting knife (knife diameter 1.8 cm, gap 260 μm). The resulting film was coagulated in a n -hexane bath (100 mL) for 12 h. Then the film was released from the glass plate with the aid of a few drops of water and then dried in a vacuum oven at 70°C for 24 h.

2.3. Membrane characterization

The polymeric catalytic membranes were characterized by the following methods:

(1) Sorption experiments

For the sorption experiments, dried samples of catalytic membranes were immersed at 25°C in solutions of the substrate (α -methylstyrene, 0.1 M), 4-nitrophenyl azide (0.02M) or 3,5-bis(trifluoromethyl) phenylazide (0.02 M) using either of the two solvents used for catalytic reactions, i.e. n -hexane and benzene. Membrane swelling was monitored until the film had reached a constant weight. Samples were withdrawn from the solvent every now and then, and weighed after removal of the surface solvent by light blotting with a filter paper.

(2) The morphology of the membranes was evaluated by means of SEM at 20 KV (Cambridge Instruments Stereoscan 360).

(3) The membrane thickness was determined by a digital micrometer (Carl Mahr D 7300 Esslingen a.N.) and by SEM observation of the freeze-fractured cross-sections.

(4) The success of ruthenium complex **1** entrapment and its uniform dispersion in the different polymeric membranes

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