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High catalytic efficiency of palladium nanoparticles immobilized in a polymer membrane containing poly(ionic liquid) in Suzuki–Miyaura cross-coupling reaction

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ABSTRACT

The elaboration of a polymeric catalytic membrane containing palladium nanoparticles is presented. The membrane was prepared using a photo-grafting process with imidazolium-based ionic liquid monomers as modifying agent and microPES® as support membrane. Ionic liquid serves as a stabilizer and immobilizer for the catalytic species, i.e. palladium nanoparticles. The Suzuki–Miyaura cross-coupling reaction was carried out on the catalytic membrane in flow-through configuration. Complete conversion was achieved in 10 s through one single filtration, without formation of byproducts. The apparent reaction rate constant was three orders of magnitude greater than in a batch reactor. No catalyst leaching was detected. This membrane offers the possibility of continuous production with no need for a separation step of the catalyst from the reaction medium.

1. Introduction

Catalytic membranes have found applications in the field of fine chemistry, petrochemical industry, water treatment, etc. [1–4]. Unlike a batch reactor whose conversion rate slows down with time, a catalytic membrane gives constant conversion over time as it can be considered as a plug-flow reactor. Another advantage of a catalytic membrane is that no separation of the catalyst from the reaction medium is necessary for reuse with the catalyst immobilized inside the membrane. The mass-transfer resistance towards the catalyst is also expected to be eliminated by forcing reactants to flow through membrane pores [5]. The intensive contact between the reactant mixture and the catalyst may lead to a higher apparent conversion rate [6].

Most catalytic membranes to the date are based on inorganic materials, with applications for steam reforming of methane, alkane dehydrogenation, oxidative coupling of methane, etc. [6–10]. Polymeric membranes used in membrane reactors, however, can have some advantages over the expensive inorganic membranes, namely lower production costs, crack-free thin membranes, and large scale production [7]. However, polymeric membranes should be used under mild conditions (<150 °C), and thus require a highly active catalyst to ensure good reactivity. Metallic nanoparticles (MNP) have shown very interesting catalytic activity thanks to their high surface/volume ratio [11]. In general, their activity increases when they get smaller because of higher surface/volume ratio and higher fraction of the low-coordinated corner and edge atoms. The high surface energy of MNPs makes them thermodynamically unstable. The presence of appropriate stabilizers is necessary to prevent their aggregation, which usually results in loss of activity. The stabilization of MNPs can be accomplished by a steric effect [12], an electrostatic effect [13], a combination of both (electrosteric effect) [14], or a ligand [15].

H. Hagiwara et al., reported the immobilization of palladium acetate in an ionic liquid in silica pores [16]. Since no chemical bonding exists between the ionic liquid and silica, reaction can be carried out only in a hydrocarbon solvent to prevent removal of the ionic liquid layer from the silica. Nevertheless, palladium leaching from the silica support was still observed [16]. In our case, poly(ionic liquid) (polyIL) was chemically grafted to microPES® support membrane to stabilize palladium nanoparticles by electrosteric effect so that leaching of both nanoparticles and ionic liquid could be effectively prevented. The well-defined palladium

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nanoparticles immobilized inside the membrane provided catalytically active sites for the organic transformations envisaged [17].

2. Materials and methods

For the general aspects related to the Experimental part, see the Supplementary information.

2.1. Synthesis and characterization of ionic liquids *a* and *b*

Imidazolium-based ionic liquids (a non-cross-linking monomer **a** and a cross-linker **b**) used for MNP stabilization were synthesized according to Scheme 1. Detailed syntheses of compound **i** and **ii** were previously reported [18]. The methodologies followed for the synthesis of the monomer **a** and the cross-linker **b** and their full characterization are described in the Supplementary information.

2.2. Preparation of the catalytic membrane

2.2.1. Grafting of poly(Ionic liquid)s on the PES (polyethersulfone) support membrane

A round-shaped membrane was cut from a microPES® 2F flat sheet (purchased from Membrana Gmbh, 0.2 μm nominal pore size). A 25 wt% IL monomer solution was prepared in methanol with a cross-linker/non-crosslinker molar ratio of 1/20. 2-Hydroxy-2-methylpropiophenone (1 wt% of total monomer weight) was added to the solution as photo-initiator. The membrane was dipped in the solution for a few seconds and taken out before being exposed to UV light (Heraeus TQ 150 lamp with quartz filter, cooled by a water circuit) for 1 h in air. The distance between the membrane and the quartz filter was 4 cm. After removal from the UV light, the membrane was rinsed thoroughly with ethanol to eliminate surplus IL monomers prior to the metal loading step.

2.2.2. Metal loading

The membrane was first soaked in 10 mL solution of $K_2[PdCl_4]$ (0.05 mol/L) in H_2O/Methanol (1/1 volume ratio) for 90 min while shaking on a IKA KS 260 basic shaker at 100 rpm (1.67 s^{-1}). The membrane was then rinsed with ionized water before installation in an Amicon filtration cell with IL-grafted side of the membrane facing up. 10 mL of 0.5 mol/L $NaBH_4$ solution in H_2O/methanol (1:1 volume ratio, freshly prepared) was then filtered through the membrane (transmembrane pressure ≈ 0.2 bar). The membrane was then soaked in $NaBH_4$ for one hour before it was rinsed with and kept in deionized water. The membrane was then directly used or cut into appropriate size before use.

2.3. Permeability test

Since ethanol is the solvent used for the catalytic reaction, ethanol permeability of the catalytic membrane was measured. The flux measurements were carried out in an Amicon cell at room temperature. The permeability was determined by the slope of the plot of flux density ($L\,min^{-1}cm^{-2}$) as a function of transmembrane pressure (bar) (Eq. (1)). The permeability was corrected to 25 °C by Eq. (2) [19] to take into account the variation of viscosity with temperature. Measurements were repeated twice on each membrane.

$$L_p = \frac{J_v}{\Delta P} \tag{1}$$

where J_v is the flux density and ΔP is the transmembrane pressure.

$$L_p^{25} = L_p^T \frac{\mu_T}{\mu_{25}} = L_p^T \cdot e^{1708.1(1/T-1/298.15)} \tag{2}$$

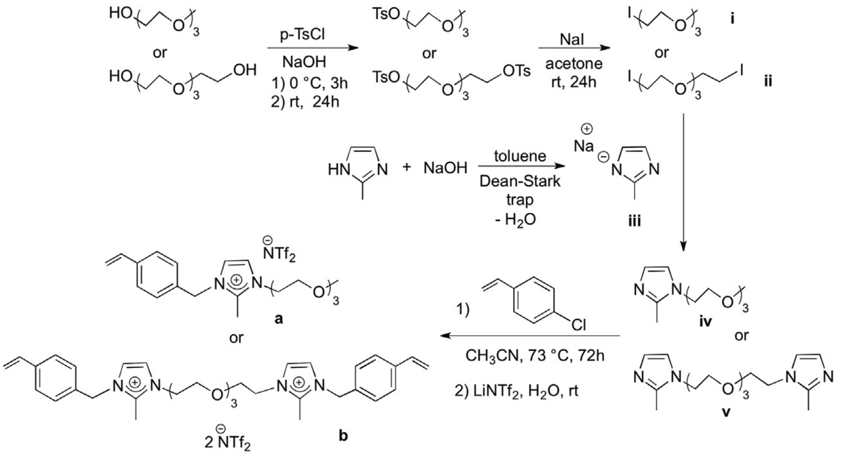
with L_p^{25} as permeability corrected to 25 °C, L_p^T as permeability measured at the temperature when the measurement was done, μ_{25} as ethanol dynamic viscosity at 25 °C, μ_T as ethanol dynamic viscosity at the temperature when the measurement was done.

2.4. Preparation of colloidal palladium nanoparticles

Palladium nanoparticles (PdNPs) were synthesized via thermal decomposition of palladium acetate [20], with the aim of obtaining a catalytic solution to perform the catalytic tests in batch conditions [21–24]. 11.5 mg (0.05 mmol) of $Pd(OAc)_2$ and 113 mg PVP (10,000 g/mol) were added in 5 mL of $[MMPIM][NTf_2]$ (1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide) and stirred at room temperature under argon in a Schlenk tube until complete dissolution. The system was then heated and stirred at 100 °C overnight to give a colloidal system (Scheme 2). PVP acts as a co-stabilizer together with the ionic liquid (molar ratio Pd/PVP monomer = 1/20).

$$Pd(OAc)_2 \xrightarrow[\substack{[MMPIM][NTf_2] \\ 100°C,\ overnight}]{PVP} PdNP\text{-}OAc$$

Scheme 2. Synthesis of colloidal palladium nanoparticles.



Scheme 1. Synthesis of imidazolium-based derivatives, the monomer **a**, and the crosslinker **b.**