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Immobilisation of an ionically tagged Hoveyda catalyst on a supported ionic liquid membrane: An innovative approach for metathesis reactions in a catalytic membrane reactor

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1. Introduction

Ruthenium-catalysed olefin metathesis reactions represent a powerful method for the formation of carbon–carbon double bonds allowing synthesis of various intermediate compounds useful for fine chemistry [1–8]. Among catalysts based on ruthenium, Hoveyda catalysts [9–11] are well known to be stable homogeneous metathesis catalysts used at laboratory scale. These catalysts have demonstrated their abilities to perform extremely selective organic syntheses with high yields. Nevertheless, only few industrial processes use metathesis reactions owing to the cost of homogeneous ruthenium-catalysts together with difficulties of final separation of the catalysts from the reaction media and their subsequent recycling. To overcome this major problem limiting industrial development, immobilisation of the Hoveyda catalysts in biphasic systems using ionic liquids (IL) is an attractive approach for the separation and recycling [12–16]. However, biphasic IL-organic solvent

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ABSTRACT

This study aimed at developing an innovative strategy to recycle homogeneous olefin metathesis catalysts by the combination of complementary green processes, namely organic solvent nanofiltration coupled with ionic liquid advantages. The immobilisation of an ionically tagged Hoveyda catalyst in an ionic liquid previously supported on a solvent-resistant polyimide membrane (Starmem 228) was prepared leading to an original catalytic membrane successfully used in a membrane reactor for a model metathesis reaction. © 2010 Elsevier B.V. All rights reserved.

systems induce mass transport limitations due to IL high viscosity and require large amounts of sometimes expensive ionic liquids [17,18]. Moreover, the reaction products are generally removed from the IL by solvent extraction, reducing the environmental benefits claimed for ILs but with a remaining attractivity thanks to the possible enhancement of the catalytic performances [19]. Recently, a new approach using the concept of supported ionic liquid phase (SILP) has been developed as an alternative to pure biphasic systems which consist in the immobilisation of a catalyst into an ionic liquid supported on a solid phase [20-22]. This approach reduces the amount of ionic liquid required and can overcome mass transport limitation. SILP technology has been used in various reactions such as hydroformylation [23,24], Friedel-Crafts acylations [25], Suzuki cross-coupling [26,27], allylic substitution [28], Heck reaction [29] and hydrogenation [30] using a broad range of solid phases such as silica [20,24,25,29,31], alumina [23,27], MFI zeolite [26], chitosan [28] and carbon nanotubes [32].

Even though the necessity to recycle homogeneous organometallic catalysts is commonly accepted, the applied separation technique has to be selected with an eco-design objective. Indeed, the separation steps represent up to 70% of the operating costs of a manufactured product and participate as much as 45% of its global energy cost [33]. Organic Solvent NanoFiltration (OSNF) is a recent process that allows separation of organic mixtures at molecular level by applying a pressure



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gradient across a selective and dense membrane, offering a sustainable and viable alternative for traditional separation techniques. NF processes are widely developed at industrial scale in water treatment and in food industry [34] while separations in organic solvents (OSNF) have recently started to be exploited [34–36].

The integration of OSNF within the homogeneous catalytic process of olefin metathesis represents an innovative and soft route since this separation process does not affect the reaction products that permeate through the membrane (no phase change). OSNF was already used to recycle homogeneous catalysts at laboratory scale [36-44] and the relevance of this technique has yet been highlighted by the recycling of the Co-Jacobsen's catalyst (4 cycles) [45] or the NF-coupled Heck (5 cycles) and Suzuki (10 cycles) reactions [46,47]. The OSNF of metathesis catalysts has been reported only a few times: van Koten and co-workers [48] used a dendrimer-supported metathesis catalyst in a NF reactor but a poor conversion (20%) was obtained. In 2006, Dow Chemicals patented the principle of NF separation for metathesis reactions [49] but only two questionable results were described. Firstly, one of the complexes used for the demonstration was not a metathesis catalyst and secondly, the proposed commercial membrane materials is not the one reported by the manufacturer and should not be stable in the solvent used, nevertheless the patent claimed for 87% rejection for the Grubbs's 1st generation catalyst. Using a commercial polyimide (PI) membrane (Starmem 228, MET) allowing insufficient rejection of Hoveyda catalyst (627 g mol⁻¹, 64% recovery), we proposed in 2008 the coupling of OSNF as green separation process and the use of tailor-made homogeneous Hoveyda-type catalysts with enhanced NF recovery (up to 92%), both in toluene and dimethyl carbonate, respectively known as a demanding solvent and an environmentally friendly one and allowing at least 5 cycles [50]. More recently, Plenio and co-workers also reported modified olefin metathesis catalysts displaying very good properties in nanofiltration processes [51].

If OSNF can be settled as a separate process, it can also be coupled to a reaction batch to lead to a membrane reactor or a catalytic membrane reactor (CMR) using an inert or an active membrane, respectively [52]. The membrane appearing clearly as a key point for further application, the preparation of innovative membranes is a real breakthrough. An ideal inert or active membrane must exhibit chemical, thermal and mechanical stability together with good performances, e.g. high selectivity (rejection, both based on size and affinity of the solute toward the membrane) and high permeability needed for productivity purpose. Coupling advantages based on IL route and NF appeared then as an interesting an innovative approach. Immobilisation of ILs has been already achieved in pores of microporous membranes commonly for microfiltration/ultrafiltration (supported ionic liquid membrane, SILM) useful for gas separation [53], recovery of enzyme [54] and amino acid extraction [55].

This study presents our preliminary results in achieving, according to the best of our knowledge, the first CMR for olefin metathesis. Inspired from SILM technology together with the well-known approach for membrane surface modification based on polyelectrolyte adsorption (with or without cross-linking), we propose here the modification of a PI dense membrane (Starmem 228®) by IL ([bmim][PF₆]) adsorption thus compatibilizing the membrane surface with a tailor-made IL tagged Hoveyda catalyst hoping to favour its anchorage by enhancement of polar and apolar interactions between the two ILs' parts. The resulting catalytic membrane is subsequently used in a CMR running in a discontinuous mode in toluene at low temperature ($35^{\circ}C$) with a model ring closing metathesis reaction.

2. Experimental

2.1. Reagents and solvents

Diallyltosylamide (DATA) was synthesised by a standard organic procedure using diallyltosylamine, allyl bromide and sodium hydride in DMF. Grubbs 2nd generation catalyst (Benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (tricyclohexylphosphine)ruthenium was purchased from Aldrich. Toluene was freshly distilled over Na before use. CH₂Cl₂ was freshly distilled from CaH₂.

2.2. Synthesis of the ionic liquid

The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] (Fig. 1) was prepared according to a reported procedure [56].

This ionic liquid was selected due to its low miscibility with toluene (solvent of RCM reaction) and the non coordinating PF₆⁻ anion makes this ionic liquid fully compatible with ruthenium-catalysed olefin metathesis transformations [12–16].

The ionic liquid structure was checked by ¹H and ³¹P NMR spectroscopy.

¹H NMR (200.12 MHz, CDCl₃, 25 °C) δ ppm: 0.91 (t, J_3 = 7.45 Hz, 3H); 1.39 (m, 2H); 1.89 (m, 2H); 4.15 (s, 3H); 4.31 (m, 2H); 7.65 (d, J_3 = 1.15, 1H); 7.72 (d, J_3 = 1.15, 1H); 8.93 (s, 1H).

³¹P NMR (81.019 MHz, (CD₃)₂CO) δ ppm: -142.8 (sept, J_{P-F} = 705 Hz). ¹⁹F NMR (188 MHz, (CD₃)₂CO) δ ppm: -72.6 (d, J_{F-P} = 705 Hz).

2.3. Synthesis of a new ionically tagged catalyst 2

A new tailor-made Hoveyda catalyst has been developed in order to achieve an efficient immobilisation of this complex in ionic liquids. Thus an ionically tagged ligand 1 derived from the original Hoveyda ligand was prepared and the modified complex 2 prepared in 75% yield according to reported procedure [11,15] (Fig. 2). In a Schlenck tube maintained under an argon atmosphere, Grubbs 2nd generation catalyst (50 mg, 0.06 mmol, 1.25 equiv.) and CuI (5.6 mg, 0.056 mmol, 1.2 equiv) were dissolved in 4 mL of dry and degassed CH₂Cl₂. Ligand 1 (22 mg, 0.047 mmol, 1.0 equiv.) dissolved in 4 mL of dry CH₂Cl₂ was then added and the mixture was stirred at 40 °C for 12 h. The solvent was evaporated and the crude residue was dissolved in a mixture of pentane and CH₂Cl₂ (1:1 (mL)). The unsoluble phosphine-copper adduct was filtered off. The filtrate was concentrated to dryness. 1 mL of toluene was added to dissolve the excess of Grubbs catalyst which was removed using a filtrating cannula. The new complex 2 was obtained as a greenish powder (32 mg, 75% yield). **2** was characterised by ¹H, ¹⁹F, ³¹P NMR and HRMS.

¹H NMR (200.12 MHz, CDCl₃, 25 °C) δ ppm: 1.25 (d, J_3 = 6.10 Hz, 6H, CH₃), 2.21 (m, 2H, CH₂), 2.46 (m, 21H, CH₃), 3.51 (m, 5H, CH₃ and CH₂), 4.21 (m, 5H, CH₃ and CH₂), 4.50 (s, 2H, CH₂), 4.91 (sept, J_3 = 6.15 Hz, 1H, CH), 6.90–7.05 (m, 4H, CH), 7.21 (bs, 4H, CH), 7.62 (d, 2H, CH), 16.41 (s, 1H, CH). ³¹P NMR (81.019 MHz, (CD₃)₂CO) δ ppm: -143.22 (sept, J_{P-F} = 712 Hz). ¹⁹F NMR (188 MHz, (CD₃)₂CO) δ ppm: -73.1 (d, J_{F-P} = 712 Hz). MS (ESI): m/z: [M+H]⁺ calculated for C₄₀H₅₃N₄O₂Cl₂Ru: 793.25891; found: 793.2582 (1 ppm).

PF₆

Fig. 1. Ionic liquid [bmim][PF₆].



Fig. 2. Hoveyda catalyst and synthesis of the new tailor-made catalyst 2 from grubbs 2nd generation catalyst.

2.4. Modification of the NF polyimide membrane

Three identical NF membrane coupons (Starmem 228®, 44 cm², MWCO = 280 g mol^{-1} according to the manufacturer, polyimide, MET, UK) were preconditioned by NF of toluene at 55 bar (maximum pressure according to the manufacturer) until a plateau value of flux was reached. One membrane was kept as a reference and the two other membranes were subjected to further modifications performed in two steps. First the active layer side of the membranes was impregnated by contact with a sufficient amount of IL in order to cover the entire membrane surface during two days. The excess of IL was removed by adsorption on a soft tissue. The obtained IL membranes were further called Starmem 228 [bmim][PF₆]. One membrane (no 1) was mounted in the filtration cell for measurement of the evolution of its permeability to toluene owing to the presence of IL (see below) and the second membrane (no 2) was mounted in the filtration cell and poured with N₂ gas in toluene (5 bar, t = 15 min) and then used for analysis purpose. Only the membrane no 1 was submitted to the second modification step as follows. The new complex 2 (9.5 mg, 0.01 mmol) was suspended in 9 mL of toluene and loaded into the filtration cell. A TMP of 3 bar was applied during 30 min at room temperature in order to transfer the catalyst from the toluene phase to the supported ionic liquid membrane. It was expected that 2 was quantitatively dissolved into the ionic liquid. This membrane was further called "the catalytic membrane".

2.5. Membrane material characterisations

Membrane material characterisations were achieved on the supported ionic liquid membrane using attenuated total reflectance Fourier transform infrared (ATR-FTIR), SEM-EDX microanalysis evidencing the presence of new element in order to check the IL adsorption and SEM to see the impact of the adsorbed IL on the membrane morphology. Adsorption of the ionically tagged catalyst on the supported IL membrane was indirectly checked thanks to the occurrence of the catalytic reaction (see below).

FTIR-ATR spectra were recorded on a PerkinElmer spectrometer (Paragon 1000, spectrum for windows software) with an ATR accessory equipped with a ZnSe crystal (incidence angle: 45° , 12 reflections) totally covered by the membrane coupon after registration of the background in the air (1 cm^{-1} resolution, 20 scans). The evidence of the IL adsorption was shown by comparison to the virgin polyimide membrane, for which specific PI bands were located at 1777 and 1715 cm⁻¹ for C=O and 1362 cm⁻¹ for CN.

Pictures from SEM allowed investigating the morphological evolution of the membrane surface after deposition of a thin metal layer of Au–Pd on the dried membrane sample (JEOL-



Fig. 3. NF membrane reactor.

JSM 6400, Oxoford instruments). Moreover, occurrence of both P and F element contained in the counter-anion of the ionic liquid was checked using the EDX microanalysis coupled to the SEM (SemQuant software).

For all these characterisations, membranes were dried under dynamic vacuum in a dessicator for at least one day.

2.6. NF and membrane reactor

The stirred NF dead-end filtration cell of 300 mL volume was used for permeability measurement (Fig. 3) in which a 44 cm^2 membrane, either virgin or modified one, was inserted. The transmembrane pressure (TMP) was applied with pressurised nitrogen. Standard conditions for NF were: TMP = 15 bar, rpm = 230, $T = 35 \degree$ C. Permeability (Lp) of membranes to toluene, whatever their form, was measured in the NF membrane reactor in standard conditions.

The same cell was used as membrane reactor, in which the reagents were mixed under a nitrogen atmosphere in the presence of the catalytic membrane inserted in the cell before applying pressure to recover the products in the permeate, according to a discontinuous process that must be further optimised.

2.7. Ring closing metathesis reaction

The activity of the catalytic membrane was evaluated using the ring closing metathesis reaction (RCM) of DATA (Scheme 1) directly in the CMR described above. Standard conditions for the RCM reaction used in the membrane reactor were: 100 mg of DATA (0.4 mmol) in 9 mL of toluene in the presence of 0.01 mmol (2.5 mol%) of catalyst assuming quantitative immobilisation of the catalyst in the IL. T = 35 °C, rpm = 230, 1 h (non optimised reaction time) in standard conditions. The cell was fully drained by applying TMP after each RCM reaction before starting the next one, in order to avoid the presence of c-DATA that could result in catalyst inhibition [50].



Scheme 1. RCM reaction of DATA.

DATA conversion in c-DATA was determined by gas chromatography using an apolar stationary phase made of PDMS-PDPS (95-5) in a semi-capillary column (Equity TM-5, length: $30 \text{ m} \times 0.53 \text{ mm} \times 1.5 \mu\text{m}$ film thickness, provided by Supelco). Injection at 250 °C was followed by analysis at constant temperature (230 °C) and the detection was obtained by a FID detector (250 °C). N₂ (18 kPa) was used as the carrier gas. Relative Standard Deviation on DATA and c-DATA concentrations was less than 1% thus accuracy on conversion was better than 2%.

3. Results and discussions

3.1. Analyses of the supported ionic liquid membrane

3.1.1. Membrane material analyses

The supported IL membranes were analysed by SEM-EDX. The presence of the IL on the impregnated membrane was evidenced by the detection of phosphorus and fluorine arising from the counteranion of the IL (not shown). The SEM pictures showing the different morphologies between the virgin and the impregnated membrane surfaces are presented in Fig. 4, evidencing a layer covering in an irregular way the whole membrane surface.

More sophisticated analysis was obtained from FTIR-ATR (Figs. 5–7) allowing evidencing of both the cationic and anionic part of the IL. After IL adsorption new bands appeared located at 3165 and 3118, 1574, 827 and 843, 805 and 783 emerging from local minima on the virgin membrane spectrum. To evidence the real position of the new bands, difference must be calculated between the two spectra, but as the penetration depth of the IR beam in the PI membrane varied with the thickness of the IL deposit, a correcting factor must be found as we already explained in a previous article to evidence thin deposit on polymeric membranes [57]. Considering that bands located at 1714, 1362 and 1089 cm⁻¹ only correspond to the virgin PI membrane, it is possible to substrate the virgin membrane spectra from the



Fig. 4. SEM pictures of the active layer of the virgin Starmem 228 (a) and Starmem after adsorption of [bmim][PF₆](b).



Fig. 5. FTIR-ATR raw spectra of virgin polyimide membrane and supported IL membrane region: 3400-2500 cm⁻¹.

supported IL one applying a 0.385 coefficient (supported IL– 0.385 virgin) for which these three bands are simultaneously cancelled. Thus a new band located at $834 \,\mathrm{cm^{-1}}$ emerged from the large peak located at $827 \,\mathrm{cm^{-1}}$ on the supported IL membrane (Fig. 8). Assignation of the new bands could be as follows. 3165, 3118 and $1574 \,\mathrm{cm^{-1}}$ bands correspond to the cationic part of the IL (confirmed by comparison with a similar IL after exchange of the counter-anion group, not shown here), the two first band corresponding to C–H vibrations. $834 \,\mathrm{cm^{-1}}$ is a specific band of the PF₆⁻ anion.

3.1.2. Permeability to toluene

The permeability to toluene of the reference membrane and the Starmem 228 [bmim][PF₆] membrane (no 1) were measured at 35 °C according to a standard procedure (Table 1). Applying 55 bar pressure as a preconditioning procedure increased significantly the membrane flux, probably thanks to both the removal of preservatives and to the compaction of the active layer as it is quite classical to observe in NF and UF in aqueous solution. This enhancement (about 3 times appeared irreversible over many experiments not shown here). In spite of the presence of the IL deposit on the mem-



Fig. 6. FTIR-ATR raw spectra of virgin polyimide membrane and supported IL membrane region: 1847–1398 cm⁻¹.



Fig. 7. FTIR-ATR raw spectra of virgin polyimide membrane and supported IL membrane region: 1274–549 cm⁻¹.



Fig. 8. FTIR-ATR difference spectra corresponding to supported ll membrane spectra –0.385 × virgin membrane spectra (zoom in the region 1064–647 cm⁻¹ region).

brane top layer, the permeability increased significantly for the supported ionic liquid membrane (about 2 times). Such behaviour can be explained by a modification of the polar/apolar balance of the membrane due to the IL presence, leading to a higher affinity of toluene toward the modified membrane than the virgin one, the consequence of which is a decrease in the whole membrane resistance toward the solvent transfer.

Table 1

Permea	bility	of me	embran	es to	toluene.
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Membrane	Permeability (L $m^{-2} h^{-1} bar^{-1}$)
Starmem 228 (reference)	0.35
Starmem 228 [bmim][PF ₆] no 1	0.67

Such behaviour was already observed in OSNF for membrane coated with polymer owing to polyelectrolyte properties (polycations and polyanions) or even with more simple ions issued from salts as sodium chloride adsorbed on the PI membrane [58]. The explanation based on the variation of the polar/apolar balance of the membrane was already validated in ultrafiltration for water application for polyethersulfone (PES) membrane after hydrophilic surfactant adsorption [59]. Of course in the case of NF in solvent media, as dense membranes are used, the transfer mechanisms are totally differents both for solvent and solutes. Nevertheless, the hypothesis on flux variation due to polar/apolar balance of membrane is consistent as convection is very strongly lowered (down to zero, sometimes) with NF dense membranes, increasing in a concomitant way the effect of

Table 2RCM of DATA in the membrane reactor.

Cycle	Conversion (%)	Time (h)
1	99	1
2	98	1
3	52	1
	98	2.5

physico-chemical interactions in the membrane/solute/solvent system.

3.2. Metathesis reaction in catalytic membrane reactor

The ionically tagged Hoveyda catalyst **2** immobilized in $[bmim][PF_6]$ dispersed on the Starmem membrane (catalytic membrane) was used in the catalytic reactor at 35 °C for the RCM of DATA (Scheme 1). As depicted in Table 2, the first run proceeded quantitatively in 1 h (not optimised reaction time). The reactor was then drained and reloaded with the same amount of DATA resulting in a similar result i.e. nearly quantitative conversion in 1 h. The procedure was repeated (cylcle 3) but the catalytic activity decreased and 2.5 h was necessary to ensure a high conversion (Table 2).

The decrease in activity of the catalytic membrane (Table 2) may have different origins ranging from the intrinsic stability of the catalyst to that of the catalytic membrane itself over time.

Further experiments are then needed to determine the lifetime of complex **2** under RCM conditions, conditioning of course the feasibility of long term recycling. One must notice that such kinetic studies are often lacking whatever the metathesis catalyst used.

On the other hand, the membrane stability must also be studied more extensively. Among possible problems are the transfer of the catalyst in the permeate leading to a loss not linked to natural deactivation. This leaching could also be due to the transfer mechanism itself as a too high affinity of the catalyst toward the membrane surface can sometimes lead to an enhanced transfer across the membrane in OSNF conditions not only based on size exclusion but also on physico-chemical interactions. The other bottleneck concerns the stability of the IL coating itself thanks to IL weak interactions maintaining it on the PI membrane. Then as IL is very slightly soluble in toluene it could progressively be dissolved in the solvent and consequently few leaching can occur in permeate when TMP is applied during OSNF.

At first sight, few strategies could be followed in the future to avoid such problems, if they are confirmed. On one hand grafting of IL on the PI membrane may prevent from IL leaching. On the other hand, a whole entrapping of both IL and catalyst in the polymer structure, achieved during the membrane fabrication procedure might retain both in the membrane matrix. Nevertheless, this last proposal would be probably limited thanks to the need in accessibility of substrate to the catalyst during the metathesis and probably applications would be restrained to small size substrates.

4. Conclusions

This study reports the immobilisation of an ionically tagged metathesis catalyst on an ionic liquid supported polyimide membrane to prepare a catalytic membrane, the stability of which must be carefully studied in the future according to several proposal exposed above. Nevertheless, these preliminary experiments proved, for the first time, the feasibility of the concept for metathesis catalyst as the efficiency of the catalytic membrane was demonstrated in a NF membrane reactor for a model metathesis reaction in toluene at quite gentle temperature $(35 \,^{\circ}C)$ in a discontinuous mode. Supplementary studies are ongoing to quantify the exact amount of catalyst immobilised. Another immobilisation

sequence, consisting in the dissolution of the catalyst in the ionic liquid before the impregnation step, will also be envisaged.

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