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Heterogenization of ruthenium porphyrin complexes in polymeric membranes: Catalytic aziridination of styrenes

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Abstract

In this paper we report the preparation of catalytic membranes having the complex Ru(4-(CF_3)TPP)CO (**1**) (TPP = dianion of tetraphenylporphyrin) embedded in the perfluorinated polymer Hyflon AD60X and their use in the aziridination reaction of olefins by aryl azides. The heterogeneous membrane catalysts afforded high selectivities in aziridine (90–99%). In several cases the membrane was reused three times with a catalyst leaching $\leq$6% but no decrease in selectivities upon recycle was observed.

Keywords: Ruthenium; Porphyrins; Membranes; Heterogeneous catalysis; Aziridines

1. Introduction

The development of new methods for the direct and selective synthesis of organonitrogen compounds represents an important goal for both academia and industry. Aziridines are useful building blocks for organic synthesis [1] and they also show various biological properties [2–4]. Some of the most effective routes for the synthesis of this class of compounds are the carbene transfer reaction to imines [5–7] or the nitrene transfer to olefins [1]. The direct aziridination of unsaturated hydrocarbons can be performed using several nitrene sources such as [*N*-(arylsulfonyl)imino]phenyliodinane compounds (PhI = N(SO_2)Ar) [8–10], chloramine-T [11,12], bromamine-T [13–15] or organic azides [16–19] in the presence of transition metal complexes as homogeneous catalysts. In spite of the general recognition that heterogeneous catalysis has practical advantages over homogeneous one, until now the heterogeneously catalyzed amination of unsaturated hydrocarbons has not been extensively explored. Very recently two papers on the use of Ag(1 1 0) [20] or Au(1 1 1) [21] surfaces as aziridination heterogeneous catalysts have been published but only the synthesis of 2-phenylaziridine from styrene was reported. A more general synthetic methodology to obtain *N*-substituted aziridines is represented by the use of PhI = NTs as nitrene source and various copper complexes as catalysts immobilized on the surface of zeolites [22–25] or mesoporous molecular sieves [26].

Polymeric membranes are innovative materials to immobilize transition metal complexes [27–29]. The catalyst can be dispersed into a polymer solution or co-dissolved with the polymer depending on the metal complex solubility in the preparation medium. It is also worth noting that the use of polymeric membranes to entrap homogeneous catalysts shows several practical advantages for the fine chemical synthesis: [29] (i) the homogeneous catalyst can be embedded in the membrane without any covalent bond formation avoiding any chemical modification of the complex; (ii) polymeric membranes show different affinities for different chemicals, therefore they can drive the reaction modulating the absorption and diffusion of the components of the reaction mixture; (iii) catalytic polymeric membranes can be prepared controlling the mechanical, chemical and thermal stability to yield the desired permeability and affinity for reagents

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and products; (iv) last but not least, the use of polymeric catalytic membranes allows the reaction to be performed in a catalytic membrane reactor (CMR) in which the reaction and separation processes can be combined in a single stage [30].

Porphyrin metal complexes represent a class of active and robust homogeneous catalysts for drugs synthesis [31,32] that has been embedded in micro- or mesoporous molecular sieves [33–36] or polymeric membranes [27,37] to prepare heterogeneous catalysts. In spite of the use that heterogenized metalloporphyrins have found as catalysts for hydrocarbons oxidation [35,38–43], to the best of our knowledge, they have never been employed for aziridination reactions although they are very active in a homogeneous medium [7,10,15,17].

In the last few years we have reported on the use of aryl azides as aminating agents for styrenes to form *N*-arylaziridines [44,45], for conjugated dienes to obtain *N*-aryl-2-vinylaziridines [46] and for benzylic C–H bonds to form amines and imines [47,48]. The amination of benzylic compounds is catalyzed by CO(porphyrin) complexes whereas the aziridination reaction is efficiently catalyzed in a homogeneous medium by Ru(porphyrin)CO complexes. The general procedure to yield aziridines from styrenes is illustrated in Scheme 1.

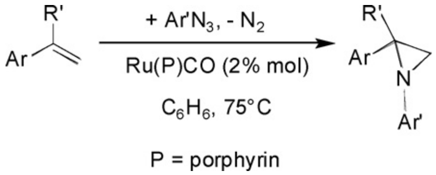
Even though our system is an atom efficient catalytic methodology in which the only by-product is molecular nitrogen and good catalytic results have been achieved, homogeneous catalysis shows some limitations for an industrial application of this methodology. First of all, reaction products are isolated by flash chromatography. Therefore an easy recovery and recycle of the fairly expensive catalyst is not immediate. In addition to that, the reaction is normally performed in benzene due to the poor solubility of porphyrin complexes in the majority of hydrocarbon solvents and the catalytic deactivation effect of coordinating solvents. In order to overcome the problems associated with homogeneous catalysis, we have decided to heterogenize the ruthenium porphyrin catalysts and, for all the reasons illustrated in the introduction, we have chosen polymeric membranes as the support [49].

Here we report on the heterogenization in polymeric membranes of ruthenium porphyrin complexes to be used as catalysts for olefins aziridination.

2. Experimental

2.1. General procedures

^{1}H NMR spectra were recorded on an Avance 300-DRX Bruker instrument, operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Infrared spectra were recorded on a Varian Scimitar FTS 1000 spectrophotometer. UV–vis spectra were recorded on a Agilent 8453E spectrophotometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere employing standard Schlenk techniques and magnetic stirring. Hyflon AD60X and Galden HT55 were supplied from Solvay. Solvents were dried prior to use by standard procedures and stored under nitrogen. 4-Nitrophenyl azide, 4-cyanophenyl azide, and 3,5-bis(trifluoromethyl)phenyl azide were synthesized by methods reported in the literature [50]. The complex Ru(4-(CF_3)TPP)CO (**1**) (TPP = dianion of tetraphenylporphyrin) was synthesized according to the literature method [51]. The thicknesses of membranes were calculated by using a MAHR digital micrometer [52].



Scheme 1. The aziridination of styrenes by aryl azides catalyzed by Ru(porphyrin)CO complexes.

2.2. Preparation of the polymeric membranes

2.2.1. Preparation of **1**-HF (7.4%)

Complex **1** (24 mg, 23.7 × 10^{-3} mmol) was suspended in Galden HT55 (1.6 mL) with Hyflon AD60X (0.3 g) and the mixture was sonicated for 15 min at RT. The resulting mixture was stirred at RT for 24 h and cast on a Petri disk for 12 h. Then the membrane was dried in an oven at 100 °C under vacuum for 24 h. Membrane thickness = 37 μm.

2.2.2. Preparation of **1**-HF (7.4%)G

This membrane was prepared with a procedure identical to that described for **1**-HF (7.4%) but it was dried at RT for 24 h at atmospheric pressure. Membrane thickness = 38 μm.

2.2.3. Preparation of **1**-HF (20%)G

This membrane was prepared with a procedure identical to that described for **1**-HF (7.4%)G by using a different amount of **1** (75 mg, 74.1 × 10^{-3} mmol). Membrane thickness = 40 μm.

2.2.4. Preparation of **1**-HF (7.4%)1p

Complex **1** (24 mg, 23.7 × 10^{-3} mmol) was suspended in Galden HT55 (1.63 mL) with Hyflon AD60X (0.3 g) and the mixture was sonicated for 15 min at RT. The resulting mixture was stirred at RT for 24 h and cast 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 an *n*-hexane bath (100 mL) for 12 h to form a porous membrane by an PI (phase inversion) process [53]. The membrane 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. Membrane thickness = 32 μm.

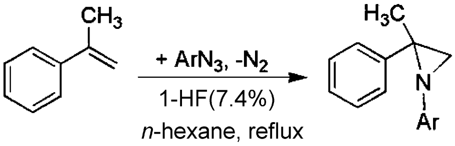
2.2.5. Preparation of **1**-HF (7.4%)2p

Complex **1** (24 mg, 23.7 × 10^{-3} mmol) was suspended in Galden HT55 (1.57 mL) and *n*-hexane (0.15 mL) with the polymer Hyflon AD60X (0.3 g) and the mixture was sonicated for 15 min at RT. The rest of the procedure was identical to that described for **1**-HF (7.4%)1p. Membrane thickness = 28 μm.

2.2.6. Preparation of **1**-HF (7.4%)3p

Complex **1** (24 mg, 23.7 × 10^{-3} mmol) was suspended in Galden HT55 (1.51 mL) and *n*-hexane (0.3 mL) with the

Table 1
Aziridination of α-methylstyrene by aryl azides catalyzed by **1**-HF (7.4%)



[a]

Entry	Ar	Run	Time (h)	ArN_3 conversion (%)[b]	Aziridine selectivity (%)[c]	**1** leached (%)[d]
1	4-$(O_2N)C_6H_4$	1st	28	82	90	9
2	3,5-$(CF_3)_2C_6H_3$	1st	8	>99	99	6
		2nd	11	>99	99	6
		3rd	8	>99	99	6
3	4-$(NC)C_6H_4$	1st	9.5	>99	99	17
		2nd	17	95	99	10
		3rd	17.5	92	99	7

[a] General procedure for aziridination reactions: **1**-HF (7.4%) (60 mg, 4.44×10^{-3} mmol of **1**) in *n*-hexane (10 mL) at reflux; molar ratios **1**/ArN_3/α-methylstyrene = 1:50:250.

[b] The aryl azide conversion was monitored by IR spectroscopy, measuring the intensity of the absorption of the azide N_3 group.

[c] Determined by ^1H NMR (2,4-dinitrotoluene as an internal standard).

[d] % of **1** leached at the end of each run measured by UV spectroscopy.

polymer Hyflon AD60X (0.3 g) and the mixture was sonicated for 15 min at RT. The rest of the procedure was identical to that described for **1**-HF (7.4%)1p. Membrane thickness = 25 μm.

2.3. UV calibrating curves

The UV calibrating curve in benzene was determined by measuring the absorbance at 414 nm of six solutions of **1** in benzene. $A = 236108 \cdot [\mathbf{1}]$ (mol L^{-1}) ($R^2 = 0.9844$).

The UV calibrating curve in *n*-hexane was determined by measuring the absorbance at 408 nm of four solutions of **1** in *n*-hexane. $A = 259764 \cdot [\mathbf{1}]$ (mol L^{-1}) ($R^2 = 0.9629$).

2.4. Catalytic reactions

In a typical run the catalytic membrane (60 mg membrane containing complex **1**, 7.4 wt%, 4.44 mg; 4.37×10^{-3} mmol) was refluxed with the desired aryl azide (0.218 mmol) and olefin (1.090 mmol) in distilled *n*-hexane (10 mL). The catalyst/azide/olefin molar ratios was 1:50:250. The consumption of the aryl azide was monitored by TLC until its spot was no longer observable and then by IR spectroscopy. The reaction was considered to be finished when the absorbance of the azide band in the IR spectrum of the solution, measured with a 0.5-mm thick cell, was at or below 0.03. At this point the amount of complex **1** leached into the solution was measured by UV spectroscopy. Then the reaction mixture was removed by cannula under dinitrogen, the internal standard (2,4-dinitrotoluene) was added and the so obtained solution was evaporated to dryness to be analyzed by ^1H NMR.

In order to recycle the catalytic membrane, it was washed with freshly distilled *n*-hexane and then a *n*-hexane solution containing the required amounts of the reagents (calculated with respect to the amount of catalyst remained in the membrane) was added.

All the reaction data for the preparation of 2-methyl-2-phenyl-*N*-(4-nitrophenyl)aziridine, 2-methyl-2-phenyl-*N*-(3,5-bis(trifluoromethyl)phenyl)aziridine, 2-methyl-2-phenyl-*N*-(4-cyanophenyl)aziridine, 2-(4-chlorophenyl)-2-methyl-*N*-(4-nitrophenyl)aziridine and 2,2-diphenyl-*N*-(4-nitrophenyl) aziridine are reported in Tables 1 and 2.

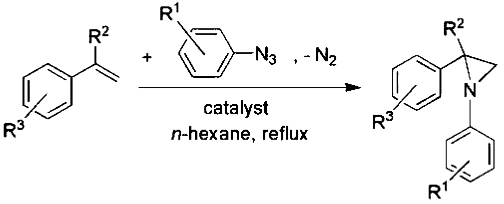
The synthesis of 2-methyl-2-phenyl-*N*-(4-nitrophenyl) aziridine was also performed with the following slightly modified procedures. (a) This procedure is similar to that described before except that distilled benzene (10 mL) at 75 °C was used as the reaction solvent. After 3 h an azide conversion = 88% with aziridine selectivity = 90% and catalyst leaching = 15% was observed. (b) This procedure is similar to that described before except that a **1**-HF (7.4%)G membrane was used as catalyst. After 3.5 h an azide conversion = 78% with aziridine selectivity = 80% and catalyst leaching = 15% was observed. (c) This procedure is similar to that described before except that a **1**-HF (20%)G membrane (60 mg membrane containing complex **1** 20 wt%, 12 mg; 1.18×10^{-2} mmol) was used as catalyst. After 3 h an azide conversion = 78% with aziridine selectivity = 85% and catalyst leaching = 13% was observed.

The analytical data for 2-methyl-2-phenyl-*N*-(4-nitrophenyl)aziridine [44], 2,2′-diphenyl-*N*-(4-nitrophenyl)aziridine [44], 2-methyl-2-phenyl-*N*-(3,5-bis(trifluoromethyl)phenyl) aziridine [45], 2-methyl-2-phenyl-*N*-(4-cyanophenyl)aziridine [45], 2-(4-chlorophenyl)-2-methyl-*N*-(4-nitrophenyl)aziridine [45], are in agreement with that reported in the literature.

3. Results and discussion

On the basis of a reported screening of the catalytic activity of different substituted ruthenium porphyrin complexes [45,46], we have decided to heterogenize one of the most active homogenous catalysts of this class, Ru(4-(CF_3)TPP)CO (**1**) (TPP = dianion of tetraphenylporphyrin), by embedding it in

Table 2
Aziridination of styrenes by aryl azides catalyzed by **1**-HF (7.4%)p catalysts



[a]

Entry	Catalyst	R^1	R^2	R^3	Run	Time (h)	ArN_3 conversion (%)[b]	Aziridine selectivity (%)[c]	**1** leached (%)[d]
1	**1**-HF (7.4%)1p	4-NO_2	CH_3	H	1st	8.5	85	99	5
					2nd	18.5	92	99	4
					3rd	36	90	99	3
2	**1**-HF (7.4%)1p	4-NO_2	Ph	H	1st	2.3	>99	99	20
					2nd	4.3	99	99	15
					3rd	6.5	95	99	4
3	**1**-HF (7.4%)1p	4-NO_2	H	4-Cl	1st	2.3	>99	99	11
4	**1**-HF (7.4%)1p	3,5-$(CF_3)_2$	CH_3	H	1st	5.1	98	99	16
					2nd	5.3	95	99	6
					3rd	5.5	92	99	9
5	**1**-HF (7.4%)2p	4-NO_2	CH_3	H	1st	5.4	85	98	10
					2nd	20.2	80	99	9.3
					3rd	40	90	99	1.9
6	**1**-HF (7.4%)3p	4-NO_2	CH_3	H	1st	8.5	>99	99	50

[a] General procedure for the aziridination: catalyst (7.4 wt%) (60 mg, 4.44×10^{-3} mmol of **1**) in *n*-hexane (10 mL) at reflux; molar ratios **1**/ArN_3/α-methylstyrene = 1:50:250.

[b] The aryl azide conversion was followed by IR spectroscopy, monitoring the intensity of the absorption of the azide N_3 group.

[c] Determined by ^1H NMR (2,4-dinitrotoluene as an internal standard).

[d] % of **1** leached at the end of each run measured by UV spectroscopy.

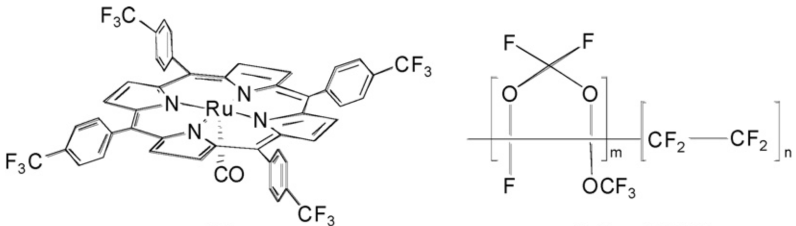
Hyflon AD60X (HF), a perfluoropolymer that shows a high thermal and chemical resistance [28,54,55] and an excellent affinity for fluorinated molecules (Fig. 1).

The catalytic membranes based on Hyflon AD60X were prepared by PI methods to yield, depending on the used technique, two different kinds of catalytic membranes. The first one, dense and symmetric, was prepared by PI induced by solvent evaporation and the second one, asymmetric with a dense skin layer and a porous sublayer, was prepared by non-solvent induced PI using *n*-hexane as internal and external non-solvent [52]. In both cases, the occlusion of catalytic complexes in polymeric membranes did not involve strong interaction forces between the complex and the polymer.

The experimental details of the characterization of these membranes are reported elsewhere [52].

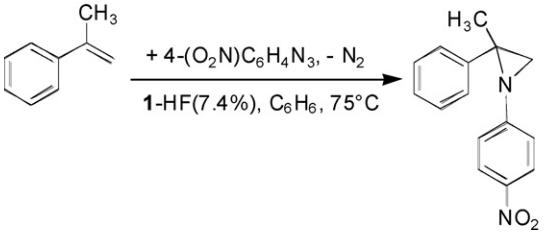
Before exploring the catalytic activity of membranes based on Hyflon AD60X we have investigated the suitability of this polymeric material as support for the aziridination reaction. For this purpose, we have performed a reaction between α-methylstyrene and 4-nitrophenyl azide in the presence of a membrane prepared without the occlusion of the catalyst **1** and using the same experimental conditions used for the homogeneously catalyzed reactions [44,45]. No reaction was observed. This proves that Hyflon AD60X is stable under the catalytic conditions and it is not responsible for any chemical transformation of the reaction components.

Before using a symmetric Hyflon AD60X membrane at 7.4 wt% loading of **1** (**1**-HF (7.4%)) in a catalytic reaction, it was stirred in benzene at 75 °C for 2 h to wash out any porphyrin complex not firmly fixed to the polymeric material. A catalyst



(**1**) Hyflon AD60X

Fig. 1. The ruthenium porphyrin complex Ru(4-(CF_3)TPP)CO (**1**) and the chemical structure of Hyflon AD60X.



Scheme 2. The aziridination of α-methylstyrene by 4-nitrophenyl azide catalyzed by the **1**-HF (7.4%) membrane.

leaching of 7.2% was determined using the UV calibrating curve reported in Section 2.

Then the solvent was removed and the membrane **1**-HF (7.4%) was used as catalyst in benzene for the reaction between α-methylstyrene and 4-nitrophenyl azide (Scheme 2).

We observed in 3 h an azide conversion of 88% with 90% aziridine selectivity. At the end of the reaction a 15% leaching of **1** indicated that the affinity of the catalyst for benzene is not compatible with the use of the latter as the reaction solvent. Considering that the choice of the reaction solvent is not limited any more by the solubility of ruthenium porphyrin complexes, we have decided to explore the use of more friendly solvents than benzene. Therefore we have employed *n*-hexane, which cannot be used in a homogeneous system due to the insufficient solubility of **1** in it, in the reaction between α-methylstyrene and three different aryl azides, catalyzed by the **1**-HF (7.4%) membrane (Table 1).

As previously described for the reaction run in benzene, firstly the membrane was stirred in *n*-hexane and, for every reaction reported in Table 1, we measured by UV spectroscopy a 1% leaching of complex **1** after 2 h.

At this stage the solution was removed to eliminate the released catalyst and then freshly distilled *n*-hexane with the required amounts of α-methylstyrene and aryl azide was added (see Section 2).

As reported in Table 1, the reaction between 4-nitrophenyl azide and α-methylstyrene (Table 1, entry 1) run in *n*-hexane yielded the corresponding aziridine in a longer reaction time than that needed using benzene as reaction solvent (28 h in *n*-hexane *versus* 3 h in benzene). At the same time the amount of **1** leached is lower (9% in *n*-hexane *versus* 15% in benzene) but the conversion of 4-nitrophenyl azide was not complete and therefore the reaction was performed only once.

On the other hand, the reactions between α-methylstyrene and 3,5-bis(trifluoromethyl)phenyl azide (Table 1, entry 2) or 4-cyanophenyl azide (Table 1, entry 3) were run for three consecutive times. At the end of each run the amount of complex **1** leached into the solution was measured by UV spectroscopy (Table 1).

Very interestingly, the reaction of α-methylstyrene with 3,5-bis(trifluoromethyl)phenyl azide yielded a complete conversion of the azide into the corresponding aziridine for three runs. It should be emphasized that the ^{1}H NMR spectrum of the complex, extracted with methylene chloride from the membrane at the end of the third run, showed only the presence of the unmodified **1**.

It is worth noting that the catalytic activity of **1**-HF (7.4%) cannot be compared to that of the homogeneous complex because the poor solubility of **1** in *n*-hexane did not allow a reaction to be performed with the same catalyst concentration used in the heterogeneous system.

As reported in entry 2 of Table 1, the leaching of **1** in each run is 6%. Although this is not a negligible quantity, it is costant for all the three runs. Moreover, a homogeneous catalytic reaction performed with a concentration of **1** equal to that lost in each run, required a three times longer reaction to reach an azide conversion of 99% with 60% aziridine selectivity. These data indicates that the aziridine formation is due to the catalytic activity of the membrane rather than to that of complex **1** present in solution.

The experimental results illustrated in Table 1 confirm that the polymeric membrane shows different affinities for different reagents, resulting in a control of the accessibility of the catalytic sites to the azide. Therefore it is not surprising that the best results have been obtained using a fluorinated azide that shows a great affinity for a fluorinated material such as Hyflon AD60X.

In order to enhance the affinity of other azides, such as 4-nitrophenyl azide, towards the Hyflon AD60X membrane, we prepared a catalytic membrane at 7.4 wt% loading of **1** (**1**-HF (7.4%)G) without removing in vacuum the solvent Galden HT55 used for the membrane preparation [56]. In fact, recent studies [52,57] have revealed that the presence of traces of this solvent, a mixture of oligomeric perfluorinated ethers that can be represented by the general formula $CF_3–(CF_2–CF(CF_3)–O)_m–(CF_2–O)_n–CF_3$, enhances the hydrofobicity and lipophilicity of the membrane. In principle it can be supposed that a more lipophilic membrane should show a better affinity for organic azides.

The catalytic reaction between 4-nitrophenyl azide and α-methylstyrene was performed in the presence of **1**-HF (7.4%)G membrane under the same experimental conditions reported in Table 1. The catalytic membrane was stirred in refluxing *n*-hexane for 2 h and 7.2% of **1** was leached. The following catalytic reaction yielded in 3.5 h an azide conversion of 78% with 80% aziridine selectivity. At the end of the reaction the leaching of the porphyrin catalyst **1** was 15%. At this point the membrane was recovered from the reaction mixture and reused for a new reaction but it was completely inactive. The same experiment was repeated with a catalytic membrane **1**-HF (20%)G prepared in the same manner but increasing the catalyst loading from 7.4 to 20 wt%. A catalytic activity (78% azide conversion with 85% aziridine selectivity in 3 h) similar to that of the membrane at 7.4 wt% loading of **1** was observed. The surface analysis of **1**-HF (20%)G membrane revealed an inhomogeneous dispersion of the catalyst and the formation of aggregated structures [52] therefore an increase of the catalyst loading from 7.4 to 20 wt% did not produce a better membrane performance. Again any attempt to recycle the membrane was unsuccessful.

In order to understand these experimental results the porphyrin complex was extracted from the membrane with methylene chloride and analyzed by NMR spectroscopy. The ^{1}H and ^{19}F NMR spectra revealed that **1** had been mostly transformed into other species. In particular, five new major signals and several weaker ones were present in the ^{19}F NMR spectrum in the region −60 to −64 ppm, which are not due to Galden HT55 itself. One of these peaks (−62.2 ppm) can be attributed to the free base porphyrin, but the others are not easily attributed. Since Galden HT55 is itself a mixture of products, we did not make any attempt to separate and characterize the individual members of this mixture. However, to test the effect on catalysis of the modification occurred we employed this mixture as catalyst for the homogeneous reaction of 4-nitrophenyl azide with α-methylstyrene. A poor catalytic activity was observed, proving that the fluorinated solvent Galden HT55 deactivates **1**. This negative effect was further proven by running two catalytic reactions in the homogeneous phase using pure **1** as catalyst and working either in the absence or in the presence of a small amount of Galden HT55 (catalyst amount: 12.4 mg, 1.20×10^{-2} mmol in 30 mL of refluxing benzene, molar ratios catalyst/azide/olefin = 1:50:250, Galden HT55, if added, 200 μL). The reaction was about three times slower in the latter case.

To increase the catalyst accessibility, we decided then to move from dense symmetric membranes, in which the activity of surface layer is more prominent than the catalytic activity of the bulk material because the transport of the components follows the solution-diffusion model, to asymmetric ones in which a dense skin layer is supported on a porous sublayer. These membranes, **1**-HFp, have been prepared occluding 7.4 wt% of **1** in Hyflon AD60X by PI technique in the presence of a non-solvent. Three asymmetric membranes, **1**-HF (7.4%)1p, **1**-HF (7.4%)2p and **1**-HF (7.4%)3p, characterized by a different type of skin layer on the porous sublayer (see Section 2), have been prepared in order to identify the optimal relationship between the membrane structure and the reagents permeability. In particular, it was found that increasing the quantity of internal non-solvent in the casting solutions membranes, the skin layer, completely dense in **1**-HF (7.4%)1p, is characterized by the presence of nanopores and mesopores in **1**-HF (7.4%)2p and **1**-HF (7.4%)3p, respectively [52]. The membranes **1**-HF (7.4%)p have been used as catalysts in several aziridination reactions of styrenes and the experimental results are reported in Table 2.

The analysis of data illustrated in Table 2, reveals that the porous sublayer in the membrane structure is responsible for shorter reaction times, indicating a better accessibility of the catalytic sites. The reaction of α-methylstyrene with 4-nitrophenyl azide in the presence of **1**-HF (7.4%)1p yielded for three consecutive times the corresponding aziridine with good azide conversion, aziridine selectivity and reaction time (Table 2, entry 1). In all three runs the quantity of **1** leached was ≤5%.

When 4-nitrophenyl azide was reacted with an olefin with different lipophilicity such as diphenyl ethylene (Table 2, entry 2), we observed a drastic change of the reaction behaviour indicating that the membrane performance depends not only on the lipophilic nature of the azide but also on the nature of the olefin. In fact, comparing entries 1 and 2 of Table 2, in spite of a similar azide conversion and aziridine selectivity, the reaction times and the catalyst leaching are very different. The data indicates that the amount of the metal complex leached during the catalysis depends on the nature of the interaction between the organic species present in solution and the metal centre. Surprisingly, the catalytic membrane used in the reaction between 4-nitrophenyl azide and 4-chlorostyrene (Table 2, entry 3) was not any more active after the first run. The interpretation of this experimental result is still in progress.

Comparing data reported in Table 1 (entry 2) with those in Table 2 (entry 4), it emerges that the reaction of 3,5-bis(trifluoromethyl)phenyl azide with α-methylstyrene yielded the corresponding aziridine in a shorter reaction time when the porous **1**-HF (7.4%)1p membrane was used as catalyst, but an increase in the catalyst leaching was also observed. These experimental results confirm that the porosity of the membrane favours, at the same time, the substrate access to catalytic active centres and the leaching of the porphyrin complex **1** during the catalysis.

In order to confirm that the amount of **1** leached during the catalysis depends not only on the affinity of the metal complex for the reaction solvent but also on the nature of all reaction components, we have refluxed four different samples of the membrane **1**-HF (7.4%)1p in *n*-hexane for 2 h. A 6–7% leaching was always registered. However, a leaching range from 3 to 20% was observed using the membrane **1**-HF (7.4%)1p as catalyst of the aziridination of different olefins by different aryl azides (entries 1–4, Table 2).

In order to identify the best equilibrium between the porosity and the catalytic activity of **1**-HF (7.4%)p membranes, we have prepared **1**-HF (7.4%)2p and **1**-HF (7.4%)3p membranes with an increased porosity and tested them in the reaction between α-methylstyrene with 4-nitrophenyl azide. As reported in Table 2 (entries 5 and 6), the aziridine formation is associated to a leaching of the catalyst too high to be acceptable for any synthetic application.

4. Conclusion

In this paper we have reported a new catalytic method to obtain aziridines using porphyrin metal complexes embedded in Hyflon AD60X membranes. The catalytic data indicated that our methodology shows a synthetic applicability with an easy catalyst separation, recovery and recycling. Moreover, it should be emphasized that the heterogeneous system allows the reaction to be performed in a more friendly solvent such as *n*-hexane.

In conclusion, to the best of our knowledge, this is the first heterogeneous method employing polymeric membranes to obtain aziridines with, in most cases, quantitative azide conversion and aziridine selectivity. The development of this innovative catalytic method should improve the synthesis of useful fine chemicals such as aziridines using environmentally benign technologies.

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