New porous monolithic membranes based on Supported Ionic Liquid-Like Phases for oil/water separation and homogenous catalyst immobilisation

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Supporting information

1. Schemes, Figures and Tables:

Scheme S-1 Synthesis of the SILLPs-based membranes

Fig. S-1 Schematic representation of the method used for the preparation of the polymeric membranes

Fig. S-2 FT-IR-ATR spectra of the materials obtained by chemical modification of **M-1** and **M-2** according to Scheme S-1

Fig. S-3 Illustration of the results of the NBP-test for the different synthetic steps involved in the preparation of the membranes **M-(1-2)-SILLP-Cl-(a-b)**

Fig. S-4 SEM images for membranes M-1, M-2, M-2-SILLP-Cl-b and M-2-SILLP-NTf₂-b.

Fig. S-5 a) Picture of the set-up used for the biphasic aldol condensation of furfural with acetone under flow conditions and continuous membrane separation. b) Schematic representation of the system used for O/W separation

Fig. S-6 Results obtained for the O/W separation of a dispersed mixture of n-hexane/water (1:1)

Fig. S-7 Results obtained for the O/W separation of an emulsioned mixture of *n*-hexane/water (95:5)

Fig. S-8 Kinetic analysis of the biphasic aldol condensation of furfural with acetone in a 2-Me-THF:water (1:1) mixture under batch conditions

Fig. S-9 Results for the integration of reaction and separation of the biphasic aldol condensation of furfural with acetone in a 2-Me-THF:water (1:1) mixture under batch conditions using the **M-2-SILLP-NTf₂-b** membrane

Fig. S-10 Results for the integration of reaction and separation of the biphasic aldol condensation of furfural with acetone in a 2-Me-THF:water (1:1) mixture under continuous flow mode, using the **M-2-SILLP-NTf₂-b** membrane

Table S-1 Polymerization mixtures tested for the preparation of tubular membranes

Table S-2 Loading of IL-like units based on Elemental Analysis

Table S-3 Main physico-chemical properties of the different porous monolithic tubular

 membranes considered in this work

2. General experimental procedures

3. Synthesis of the tubular membranes by bulk polymerization

4. Oil/water separation

5. Study of the kinetics of the aldol condensation of furfural with acetone in batch mode

6. Evaluation of the integration of reaction and separation in the aldol condensation

of furfural with acetone under flow conditions in batch mode

7. Evaluation of the integration of reaction and separation in the aldol condensation

of furfural with acetone under flow conditions in the continuous flow mode

9. Characterization of (1E,4E)-1,5-di(furan-2-yl)penta-1,4-dien-3-one

10. NMR Spectra

11. References

Scheme S-1 Synthesis of the SILLPs-based membranes





M-1 (n:m:x:y:z = 0.13:0.30:0.30:0.27:0) **M-2** (n:m:x:y:z = 0.13:0.30:0.30:0.22:0.05)



LiNTf ₂	M-1-SILLP-NTf ₂ -(a-b)	a)	R	=	CH ₃ -
		b)	R	=	C_4H_9
	M-2-SILLP-NTf ₂ -(a-b)	a)	R	=	CH ₃ -
		b)	R	=	C_4H_9

M-1-SILLP-CI-(a-b) a) $R = CH_3$ b) $R = C_4H_9$ **M-2-SILLP-CI-(a-b)** a) $R = CH_3$ b) $R = C_4H_9$ **Fig. S-1** Schematic representation of the method used for the preparation of the polymeric membranes. a) Set-up of the mould used for the preparation of the membranes: The outer cylinder was a 15 x 1 cm Omnifit® glass column and the inner cylinder was 0.6 cm diameter glass bar located concentrically to the Omnifit® column using Omnifit® connectors. b) Photograph of the mould once assembled. c) Photograph of one of the membranes after demoulding. d) Visual comparison between a commercial ceramic membrane and one of the prepared polymeric membranes



Fig. S-2 FT-IR-ATR spectra of the materials obtained by chemical modification of **M-1** and **M-2** according to Scheme S-1. Arrows indicate the main changes observed associated to the expected transformations



Fig. S-3 Illustration of the results of the NBP-test for the different synthetic steps involved in the preparation of the membranes M-(1-2)-SILLP-Cl-(a-b). Violet = (+) test (presence of chloromethyl groups), non-coloured = (-) test (absence of chloromethyl groups). The initial membranes M-1 and M-2 gave a clear positive NBP-test. Membranes M-(1-2)-SILLP-Cl- (a-b) all gave negative NBP tests indicating the full substitution of the CH₂-Cl groups for the corresponding imidazolium chloride salt

NBP Test





Positive NBP Test





Fig. S-4a SEM images for membranes M-1 and M-2



Fig. S-4b SEM images obtained for M-2, M-2-SILLP-Cl-b and M-2-SILLP-NTf₂-b.



Fig. S-5 a) Picture of the set-up used for the biphasic aldol condensation of furfural with acetone under flow conditions and continuous membrane separation. b) Schematic representation of the system used for O/W separation

a) Picture of the reactor set-up



b) Schematic representation of the ultrafiltration system for the O/W separation Pressure regulator





Fig. S-6 Results obtained for the O/W separation of a dispersed mixture of n-hexane/water (1:1)

Fig. S-7 Results obtained for the O/W separation of an emulsioned mixture of n-hexane/water (95:5)



Fig. S-8 Kinetic analysis of the biphasic aldol condensation of furfural with acetone in a 2-Me-THF:water (1:1) mixture under batch conditions. Yields calculated by ¹H-NMR. Triangles: Yield (%) found in the aqueous phase. Circles: Yield (%) found in the 2-Me-THF phase



Fig. S-9 Results for the integration of reaction and separation of the biphasic aldol condensation of furfural with acetone in a 2-Me-THF:water (1:1) mixture under batch conditions using the **M-2-SILLP-NTf2-b** membrane. Yields calculated by ¹H-NMR. Red dots represent the permeate mass flow, while the bars correspond to the permeate volumetric flow



Fig. S-10 Results for the integration of reaction and separation of the biphasic aldol condensation of furfural with acetone in a 2-Me-THF:water (1:1) mixture under continuous flow mode, using the **M-2-SILLP-NTf2-b** membrane. Yields calculated by ¹H-NMR. Red dots represent the permeate mass flow, while the bars correspond to the permeate volumetric flow



Table S-1 Polymerization mixtures tested for the preparation of tubular membranes^{a,b}

Entry	CIVB (%) ^d	MMA (%) ^d	EGDMA (%) ^d	VB (%) ^d	DVB (%) ^d	Mon. (%) ^e	Por. (%) ^f	Dod. (%) ^g	Tol. (%) ^g	M.S. ^h
1	30				70	40	60	75	25	(-)
2	10				90	40	60	75	25	(-)
3	40	30	30			40	60	75	25	(±)
4	40	30	30			40	60	90	10	(±)
5	40	30	30			40	60	100		(+)
6 (M1) ^c	13	30	30	27	-	70	30	100	-	(+)
7 (M2) ^c	13	30	30	22	5	70	30	100	-	(+)

^a All percentages are given as weight percent. ^b The polymerization was kept at 70°C for 24h, unless otherwise stated, and the mixture of polymerization contained 1% in weight of AIBN over monomers. c. 60°C for 24h; at 70°C these membranes presented a lower porosity and were relatively fragile. ^d Percentage of each monomer in the monomeric mixture. ^e Percentage of monomers in the polymerisation mixture (monomers + porogens). ^f Overall percentage of porogens in the polymerisation mixture (100 - % monomers). ^g Percentage of each porogen in the porogenic mixture; Dod.: dodecanol; Tol.: toluene. ^h M.S.: mechanical strength = (-) very week, (±) middle , (+) strong

Entry	Membrane	Experimental loading of IL-like units (mmol IL/g)	Theoretical loading of IL-like units (mmol IL/g) ^a
1	M-1-SILLP-Cl-a	0.77	0.82
2	M-1-SILLP-NTf ₂ -b	0.85	0.79
3	M-2-SILLP-Cl-a	0.82	0.82
4	M-2-SILLP- NTf ₂ -b	0.83	0.79

Table S-2 Loading of IL-like units based on Elemental Analysis

^a According to the composition of the monomeric mixture.

Entry Membrane		BET Surface	Median Pore Diameter	Total Intrusion	al Intrusion Porosity ^b		Surface Tension. CA (°)			
		Area (m²/g) ^a	(Volume)(nm) ^b	Volume (mL/g) ^b		Water	2-Me-TFH	Hexane		
1	M-1	39.42	21.0	0.3833	31.41%	43.66	-	-		
2	M-1-SILLP-Cl-a	-	27.3	0.4730	36.79%	-	-			
3	M-1-SILLP-Cl-b	-	36.3	0.4968	37.43%	24.86	-	-		
4	M-1-SILLP-NTf ₂ -b	-	32.5	0.5003	40.01%	51.79	-	-		
5	M-2	36.40	44.5	0.4671	36.05%	-	-	-		
6	M-2-SILLP-Cl-a	-	42.1	0.4649	35.61%	-	-	-		
7	M-2-SILLP-Cl-b	-	35.0	0.4584	36.32%	-	-	-		
8	M-2-SILLP-NTf ₂ -b	-	32.1	0.4492	36.45%	99.78	-	-		

Table S-3 Main physico-chemical properties of the different porous monolithic tubular membranes considered in this work

^a The test was made with the use of argon. ^b Mercury Intrusion Porosimetry.

2. General experimental procedures

All reagents were purchased from Sigma-Aldrich. Furfural was purified by distillation under reduced pressure. ¹H-NMR experiments were obtained using a Bruker Avance III HD 300 MHz (¹H, 300 MHz) spectrometer. The chemical shifts are given in delta (δ , ppm) values and the coupling constants (*J*) in Hertz (Hz).

FTIR spectra were recorded on a JASCO 4000 spectrometer equipped with a PIKE ATR MIRacle accessory. Elemental analyses were performed on an Elemental Carlo Erba 1108 apparatus. Thermal analyses were carried out using a TG-STDA Mettler Toledo model TGA/SDTA851e/LF/1600 analyser under a flow of N₂.

3. Synthesis of porous monolithic tubular membranes: The monomeric mixture, which was composed for at least a functional monomer and a cross-linking monomer, and the porogenic agents were weighed according the polymeric composition (see Table S-1 for each porous polymeric membrane). The resulting homogeneous solution was purged with N_2 during 15 minutes and after that 1% of AIBN was added. The solution was stirred and sonicated for 15 minutes and poured into a mould (see Fig. S-1). The mould was sealed and introduced in an oven at 60°C (or 70°C) for 24 h. After this time, the porous monolithic tubular membranes were demoulded and washed for 24 h with methanol to eliminate the porogens. Finally, the polymeric membranes were vacuum dried at 60°C until constant weight.

Synthesis of SILLPs-based M-1(2)-SILLP-Cl-a(b) membranes: The porous monolithic tubular membrane (M-1 or M-2) was submerged in the corresponding neat imidazole (methyl or butyl imidazole) for 24 h at 80°C. After this period of time, the modified porous monolithic tubular membrane was washed with methanol to eliminate the excess of imidazole for 24 h and then finally vacuum dried at 60°C until constant weight.

Synthesis of SILLPs-based M-1(2)-SILLP-NTf₂-a(b) membranes The former modified porous monolithic tubular membranes containing imidazolium chloride fragments were immersed in 150 mL of a solution of 5 equivalents of LiNTf₂ in H₂O:MeOH (1:3 v:v) for 24 h under stirring. After this period of time, the corresponding membrane was washed with methanol for 24 h and then finally vacuum dried at 60°C until constant weight.

These synthetic protocols had been previously optimized by our group and described in detail, allowing a quantitative transformation of the chloromethylated fragments into alkyl benzyl imidazolium groups.¹ The resulting materials were characterized by different techniques, such as FT-IR (Fig. ESI-2)² and the NBP test (Fig ESI-3,³ which is able to easily determine the presence of reactive chloromethyl groups and confirmed their expected structures and the full conversion of the chloromethyl groups into the corresponding supported imidazolium salts for all the polymeric membraned prepared.

4. Oil/water separation

Oil/water separation experiments were conducted with a membrane filtration system that can be operated in cross-filtration flow mode (Fig. S-5). The system included a feed tank, a feed pump, a feed flow meter, a feed pressure gauge, a membrane module, a back pressure regulator, and a permeate tank.

The feed tank was loaded with 60 mL of the O/W mixture (1/1 v/v dispersion of *n*-hexane/water, $74 \pm 4 \mu m$ droplet size or a 95/5 v/v emulsion of *n*-hexane/water, $31.3 \pm 1.9 \mu m$ droplet size) and then maintained under magnetic stirring (1200 rpm) and pumped through the filtration module at different recirculation tangential flows (0.3, 0.6 and 1.2 L·h⁻¹) at 6 ± 1 bar back-pressure, obtaining a yellow steady permeate flow, which was collected at fixed time intervals to determinate its composition and the permeate flow.

5. Study of the kinetics of the aldol condensation of furfural with acetone in batch mode

The aldol condensation of furfural with acetone was carried out using six different emulsions of furfural (**3**, 3.8 g, 0.04 moles), acetone (1.16 g, 0.02 moles) and NaOH (0.34 g, 0.008 moles) in 2-MeTHF (15 mL)/distilled H₂O (15 mL). These emulsions were stirred in an orbital stirrer at 500 rpm and rt, stopped at different times and the phases separated. The organic phase (2-MeTHF) was concentrated under reduced pressure and the crude obtained analysed by ¹H-NMR. The aqueous phase was extracted with 5 mL of CHCl₃, dried with anhydrous MgSO₄ and concentrated under reduced pressure to be analysed by ¹H-NMR. The results obtained are summarised in Fig. S-8.

6. Evaluation of the integration of reaction and separation in the aldol condensation of furfural with acetone under flow conditions in batch mode

The reactor system consisted of a stirred tank (250-mL total capacity) connected through a HPLC pump with the ultrafiltration module, containing a cylindrical tubular SILLPsbased membrane (5.3 cm length, 1 cm e.d. and 0.6 cm i.d., 9.99 cm² filtration surface area) (see Fig. S-5a). Firstly, the reactor tank was loaded with 15 mL of a solution of furfural/acetone in 2-Me-THF (253 mg/mL furfural and 176 mg/mL acetone) and 15 mL of aqueous NaOH (22.7 mg/mL). Both solutions were emulsioned under high magnetic stirring (1200 rpm, 150 \pm 8 µm droplet size) until a homogeneous suspension was observed. Then, the pumping was started applying a 5 mL min⁻¹ recirculation flow rate through the membrane module at 5 \pm 1 bar back-pressure, obtaining a slightly yellow and clear permeate, which was collected at fixed time intervals. The 2-Me-THF in the permeate samples was removed under vacuum and the resulting product weighted and analyzed by NMR (¹H-NMR in CDCl₃). All experiments were carried out in duplicate. The results are summarized in Fig. S-9.

7. Evaluation of the integration of reaction and separation in the aldol condensation of furfural with acetone under flow conditions in the continuous flow mode

The reactor system consisted of a stirred tank (250-mL total capacity) connected through a HPLC pump with the ultrafiltration module, containing a cylindrical tubular SILLPsbased membrane (5.3 cm length, 1 cm e.d. and 0.6 cm i.d., 9.99 cm² filtration surface area) (see Fig. S-5a). Firstly, the reactor tank was loaded with 15 mL of a solution of furfural/acetone in 2-Me-THF (253 mg/mL furfural and 176 mg/mL acetone) and 15 mL of aqueous NaOH (22.7 mg/mL). Both solutions were dispersed under high magnetic stirring (1200 rpm, 150 ± 8 µm droplet size) until a homogeneous suspension was observed. Then, the pumping was started applying a 5 mL min⁻¹ recirculation flow rate through the membrane module and at 5 ± 1 bar back-pressure, obtaining a slightly yellow and clear permeate, which was collected at fixed time intervals. The reactor tank was continuously fed with fresh furfural/acetone in 2-Me-THF solution at the same flow than the one for the permetate. The 2-Me-THF of the permeate samples, obtained at regular time intervals, was removed under vacuum and the resulting product weighted and analyzed by NMR (¹H-NMR in CDCl₃). All experiments were carried out in duplicate. The results are summarized in Fig. S-10.

9. Characterization of (1E,4E)-1,5-di(furan-2-yl)penta-1,4-dien-3-one



(1E,4E)-1,5-di(furan-2-yl)penta-1,4-dien-3-one was obtained as a yellow solid. ¹H-NMR (CDCl₃, 300 MHz): δ 7.51 (d, J = 2.0 Hz, 2H), 7.45 (s, 2H), 6.91 (d, J = 15.6 Hz, 2H), 6.68 (dd, J = 3.3, 0.6 Hz, 2H), 6.50 (dd, J = 3.4, 1.8 Hz, 2H) ppm.^{4,1}

10. NMR Spectra

RP1182E-20 h







11. References.

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