

Interests and challenges of organic solvent nanofiltration for sustainable chemistry: the case of homogeneous catalysis of metathesis

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Abstract

The development of chemical reactions catalysed by homogeneous organometallic complexes has allowed a significant breakthrough in synthesis chemistry, but now research axes must integrate catalysts recycling at the early stage of their conception. Catalyst recycling by nanofiltration in organic solvent (OSN) may represent an innovative route since this separation process at a molecular level is a low energy consumer. Challenges for OSN are membrane stability in organic solvents and the mastering of filtration conditions. Molecular engineering of catalysts based on slight structural modifications is also proposed to associate activity and high retention for OSN recycling. This paper deals with the integration of OSN within the homogeneous catalytic olefin metathesis reaction.

Keywords: nanofiltration, homogeneous catalysts, catalyst recycling, membrane material, olefin metathesis.

1 Introduction

Catalyzed transformations are recommended in the 12 principles of green chemistry as they can increase reactions efficiency and reduce the production of wastes by enabling selective and atom economy transformations [1]. However, it



is quite clear that if the catalysts are not recyclable, the use of catalyzed reaction is less advantageous in terms of sustainable production. The recycling of catalysts is therefore an important scientific and technical challenge for fine chemistry. The most common approach, following the usual practices of organic synthesis, is to isolate the catalyst from the reaction medium at the end of reaction. Classically, extractions based on state changes (precipitation) are used that can often lead to more or less catalyst inactivation. To improve these separations several alternatives were considered:

- carry out the synthesis in non-conventional media [2], such as ionic liquids or supercritical carbon dioxide, perfluoroalkanes and water
- grafting catalysts on soluble supports in the synthesis medium but extractable by solvent change [3]
- grafting catalysts on insoluble supports [4], which facilitates recovery but is generally associated with poorer reaction kinetics and thus lower productivity.

All these solutions exist at the laboratory scale, but have drawbacks that have limited their transfer to industrial scale until now. The use of ionic liquids is a solution that has proven its effectiveness for the recycling of various catalysts, but have the disadvantage of not being eco-friendly solvent. Nowadays, chemists are looking for more reactive catalysts that could be used at “homeopathic” level and lost in the synthesis media. However, this prospect is not entirely satisfactory as the reaction products would be contaminated by metal residues. We put ourselves in a different perspective by proposing to separate the catalyst from the reaction medium using a membrane process (nanofiltration), which has the advantage of not requiring a change of state neither from the catalyst nor from the solvent. We thus expect a longer life cycle of the catalyst. Consequently, nanofiltration is an athermal process, which limits the energy required and its concomitant environmental impacts.

In this study, we apply this approach to olefin metathesis [5] which allows the efficient transformation of carbon-carbon double bonds. The three major contributors to olefin metathesis development and achievements shared the Nobel Prize in Chemistry in 2005 [6–8]. These reactions, usually conducted in toluene, can be catalyzed by homogeneous catalysts (soluble) containing ruthenium, as Grubbs or Hoveyda-type (figure 1) whose molecular weights are around 600 g mol^{-1} [9].

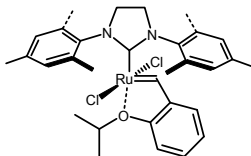


Figure 1: Hoveyda II catalyst (627 g.mol^{-1}) for olefin metathesis.

2 The challenges ahead for organic NF

Nanofiltration is a separation process at the molecular scale, widely used industrially in aqueous media and for which applications in organic solvent

medium already exist for the recycling of solvents such as in the Max Dewax process [10]. Various studies at laboratory scale have been published dealing with the retention of homogeneous organometallic catalysts and recycling by organic nanofiltration (OSN) most often in methanol or other polar solvents: Co-Jacobsen (4 cycles) [11], Heck (5 cycles) and Suzuki (10 cycles) reaction catalysts [12, 13] and more rarely in an aromatic solvent (toluene) as for Hoveyda catalysts for the olefin metathesis [14]. However, to be widely used on an industrial scale, the NF in organic medium faces several challenges. The challenges are at different levels. The first bottleneck is the stability of membrane material in the solvent used for OSN which is also that of the organometallic synthesis. Obviously in practice inorganic membranes (zirconia, titania + zirconia on alumina support) can be selected at start as promising solvent resistant materials; but their pore size is generally too large to ensure a high enough level of retention of molecules less than 2000 g mol^{-1} , which will be the case of homogeneous catalysts. Hence actually the attention is focused on solvent resistant polymeric membranes, but this class of membranes is not yet well developed and there are only few commercially available polymer membranes that allow retention of smaller molecules. Basically, these membranes have composite structure having a tight skin layer on one side to ensure the retention and selectivity of separations. In these composite membranes, the skin layer is made of either polydimethylsiloxane (PDMS) or polyimide(s) deposited on a macroporous support (PAN, ...) chosen to provide mechanical strength to the overall structure. Contrary to aromatic polyimides, which are polar glassy materials, PDMS membranes, which are hydrophobic rubbery materials, do not exhibit the same stability and permeability in aromatic solvents such as toluene. For instance, PDMS composite structures can suffer from the separation of the skin layer from the macroporous support one after some time exposure to toluene due to different swelling of both polymers in toluene. Thus, there is a need to provide new membrane materials to develop more widely the OSN applications. Besides the solvent resistance, these membrane materials should ideally allow full retention of the catalyst. The development of such specific membranes is a long-term research. In the following, our research program proposes to develop two original routes. The first is based on an entirely homogeneous polymer membrane based on copolyurethane materials. Conversely, the second one makes use of an organo-ceramic composite membrane obtained by the modification of a ceramic nanofiltration membrane by grafting of organo-titanate to improve the compatibilization of the membrane toward the organic medium. The second bottleneck is the mastering of the separation process itself. In aqueous media it is well known that retention performance depends on many physico-chemical and hydrodynamic aspects. Physico-chemical aspects takes place at different levels. First, the membrane fouling that is due to weak interactions between membrane and solute that adsorbs on it. Then solute-solute interactions that promote the establishment of deposit whose consequence is the permeate flux limitation and consequently a decline in productivity. The physico-chemical interactions are also involved in the transfer mechanisms of solute through the membrane:



attractive interactions (e.g. electrostatic or van der Waals type leading to adsorption on the membrane) generally favoured the transfer that is not only controlled by the relative size of the solute to the membrane pores. The intensity of these interactions is generally modulated by the filtration environment, for instance changes in retention should be expected by varying concentrations as well as impact of the overall physico-chemical environment. The hydrodynamics is involved in controlling the development of a more or less important fouling deposit and the phenomenon of concentration polarization upstream of the membrane. Concentration polarization is reversible and consists of an accumulation of solute on a few microns thickness. Both deposit and concentration polarization layer can be lowered by applying tangential filtration at high cross-flow velocity instead of dead-end filtration. First studies of the process mastering can be achieved with commercial membranes to draw trends but in fact the results will be dependent on the membrane/catalyst couple. Moreover, the membrane-solvent affinity controls the membrane swelling and thus opening of pseudo-pores in the polymer structure, thus allowing the occurrence of more or less convection inside the membrane in addition to diffusion controlled by the membrane/solute affinity. Consequently, for a given membrane and a given molecule the transfer mechanism can vary with the OSN solvent. Thanks to the lack of optimized membrane for the target separation, a complementary approach is to synthesize prototype catalysts which have good catalytic performances and improved retention with commercially available polyimide membranes. Considering the overall strategy, the OSN integration can be achieved in different ways according to the separation performance and to the metathesis conditions. Either OSN is made after the reaction performed in batch mode, according to a classical cascade: synthesis reactor then separation (figure 2), or OSN intervenes to set up a coupled process, which is then a synthesis membrane reactor (figure 3) that will be the most efficient regarding

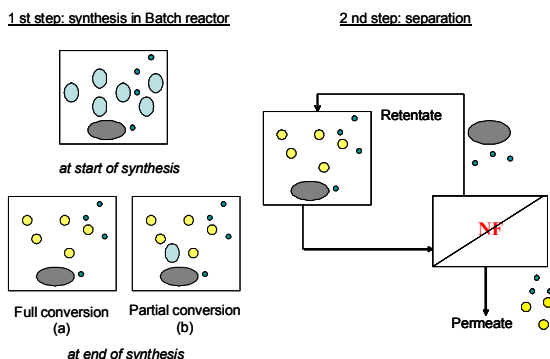


Figure 2: Integration of nanofiltration (NF) in synthesis process after reaction.

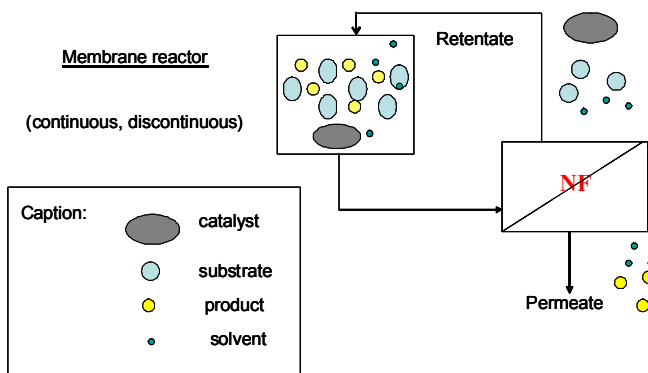


Figure 3: Integration of nanofiltration (NF) in a membrane reactor for synthesis.

sustainable requirements. There is no single answer. The choice depends on the reaction substrate and on the selectivity of the membrane towards the substrate and products of the metathesis. In the following we give some examples of the various approaches we have experienced.

3 Modifying catalysts to achieve high retention in OSN

We used pseudo-tangential filtration, meaning that tangential filtration was performed with very low cross-flow velocity ($v < 0.01 \text{ cm.s}^{-1}$) actually corresponding to dead-end filtration. The membrane used was a polyimide one: Starmem 228 (MET, Evonik, UK). Its molecular weight cut-off (MWCO) is 280 g.mol^{-1} , which very roughly means that a 90% retention is expected for this molecular weight. Filtration is achieved until final volume reduction ratio $\text{VRR} = 2$, that is to say, with continuous extraction of permeate until halving the initial feed volume. At 25°C and 25 bar the commercially available Hoveyda II (figure 1) catalyst (0.53 mmol.L^{-1} in toluene) is 67% recovered, that is highly insufficient for recycling [14].

3.1 Synthesis and recovery of prototype catalysts

To increase the recovery of the catalyst, we have introduced modification in the Hoveyda II structure to increase its size by adding rigid phenyl groups decorated by sterically hindering substituents (figure 4). Recovery was actually increased up to 92% in standard conditions of OSN further used (figure 5). Nevertheless, the increase in the catalyst recovery was not only related to its size increase and to the increasing fouling as demonstrated by the “low” recovery of the heavy, bulky and rigid catalyst 5 (82%). This underlines the important role of the affinity between membrane and phenyl groups of prototype catalysts leading to higher transfer through the membrane despite size increase [14].

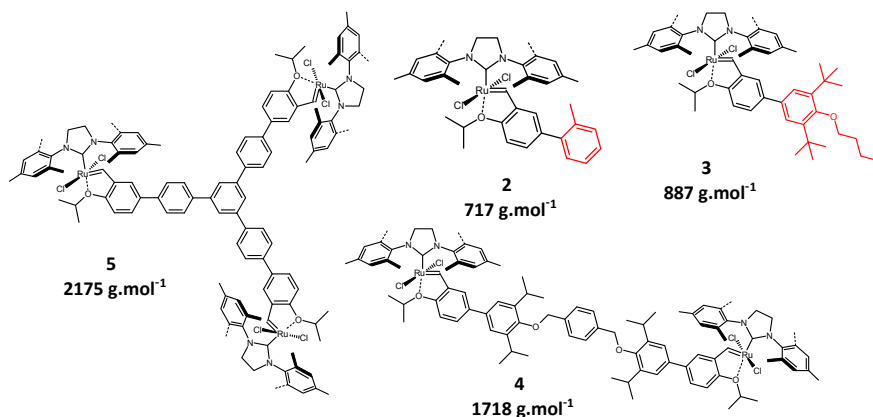


Figure 4: Prototype catalysts of Hoveyda II type.

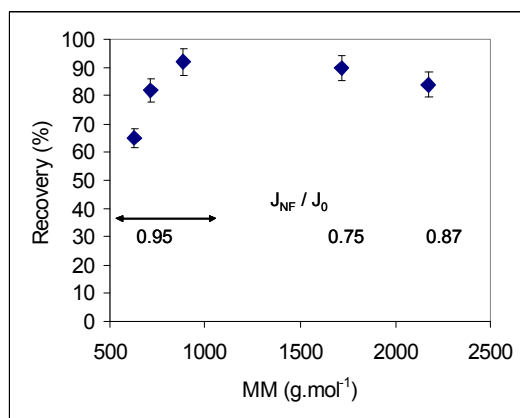


Figure 5: Recovery of Hoveyda II and prototype catalysts by OSN in toluene at VRR=2, 25 bar, room temperature, catalyst initial concentration: 2.5 to 3.1 mmol.L⁻¹, Starmem 228, pseudo-tangential (dead-end) filtration.

3.2 Recovery and recycling of prototype catalysts

As catalyst 3 (887 g.mol⁻¹) was the more retained, it was engaged in a series of model reaction of ring closing metathesis (RCM, figure 6). Each cycle was performed as follows. First, the metathesis reaction was achieved with 9 mg of catalyst 3 in 4 mL of solvent (toluene or dimethylcarbonate) and 100 mg of substrate (DATA). At the end of the reaction (monitored by gas chromatography) the reaction medium was diluted until a catalyst concentration of 2.6 mmol.L⁻¹ (calculated from initial amount) was reached and OSN was then

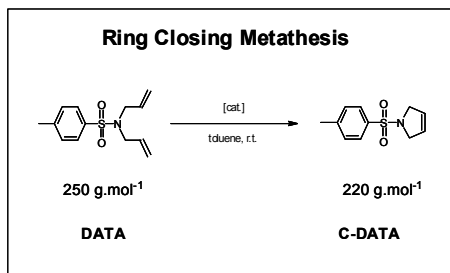


Figure 6: Model metathesis reaction.

performed in the standard conditions described before. The final retentate was then engaged in a further reaction with 100 mg DATA and so on. Up to 5 cycles were achieved with acceptable performances [14].

4 The control of transfers by the role of hydrodynamics

As the Starmem 228 membrane was no more commercially available, we change for the Starmem 122 ($\text{MWCO} = 220 \text{ g.mol}^{-1}$, MET-Evonik, UK) also made of polyimide (not exactly the same as for the Starmem 228 as seen from FTIR spectra) and for the Duramem 300 ($\text{MWCO} = 300 \text{ g.mol}^{-1}$, MET-Evonik, UK) that is cross-linked polyimide contrary to the two others. Actually, the MWCO of the 3 membranes are not significantly different. Hoveyda II catalyst was dissolved in toluene ($0.53 \pm 0.03 \text{ mmol.L}^{-1}$, 1/5 diluted compared with OSN with Starmem 228 membrane) and filtered at room temperature either with Duramem 300 in pseudo-tangential filtration (dead-end) or with Starmem 122 in tangential filtration (MET Cell, cross flow velocity close to 0.1 m.s^{-1} , as in spiral membrane). Pressure varied between 5 and 25 bar. The final VRR was between 1 (batch mode, total recycling of retentate and permeate) and 4. No variation of retentions was observed here by varying VRR. Figure 7 shows retention

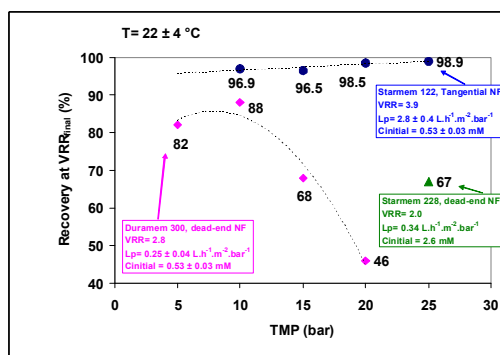


Figure 7: OSN of Hoveyda II commercial catalyst with different polyimide membranes and various hydrodynamics.

variation versus transmembrane pressure (TMP), clearly different from one membrane to the other. The most permeable membrane, namely Starmem 122 (Lp permeability was ten times that of Duramem 300) offers the better retention also thanks to tangential conditions.

5 The challenges of developing prototype membranes

It is important to be aware that even a small change in the membrane material composition can modify all the physico-chemical interactions in the filtration medium. Moreover, at constant chemical composition, slight change in the membrane porosity alters the transfer mechanisms and thus the selectivity.

5.1 Ceramic membranes modified by grafting of hydrophobic groups

The lower cut-off of nanofiltration (NF) ceramic membranes commercially available is $\text{MWCO} = 1,000 \text{ g mol}^{-1}$. We tested such a membrane (Kerasesp 1 kg.mol^{-1} , Novasep Process, France) in conditions close to dead-end filtration (tangential filtration with v close to 2.2 cm.s^{-1}) at very low and not optimised $\text{TMP} = 1.5 \text{ bar}$. The retention of $0.030.10^{-3} \text{ mol.L}^{-1}$ Hoveyda II in toluene was less than 5% at $\text{VRR} = 2$. In addition, the membrane was strongly fouled as the permeate flux decreased by more than $1/3$. To reduce the strong irreversible adsorption of the catalyst on the membrane we develop a surface modification by grafting of organo-titanate bearing highly hydrophobic functional groups (Figure 8). The chosen organo titanate was the isopropyl-isostearoyl-titanate. The retention of Hoveyda II catalyst ($0.053 \pm 0.001 \text{ mmol.L}^{-1}$) by the grafted membrane was increased up to 40% (2.2 cm.s^{-1} , 1.5 bar, $\text{VRR} = 2$, 20°C) These results are encouraging and must be improved in the future.

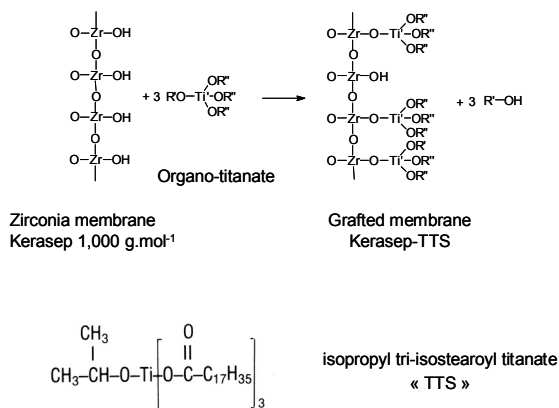


Figure 8: Scheme of zirconia membrane grafting according to [15].

5.2 Polymer membranes

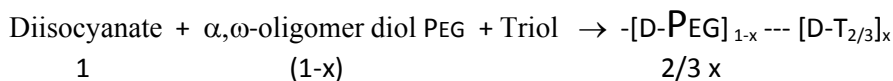
As said previously, the number of available commercial NF membranes is yet rather low and the related molecular cut-off are not so well predictable; moreover the NF properties of these membranes are known to vary with the applied NF conditions. Hence the synthesis of a series of original polymer membranes was carried out and the type of polymer network was chosen according the analysis of the metathesis reaction medium to be nanofiltrated as explained below. The targets to be reached by OSN membranes are very challenging and have been recalled in the above section. The first criterion to meet is the membrane chemical stability in the solvent under the OSN conditions, i.e. 8 to 15 bar at 40°C. Toluene and dimethylcarbonate (DMC) are the two solvents considered as the potential reaction medium of the metathesis reaction; they have quite distinct physical and chemical properties (table 1). Except the close molecular weights, toluene is a liquid having a low polarity whereas DMC is strongly polar as it can be seen from the solubility parameters. These distinct polar features are well reflected by their strong differences of solubility in water. Obviously it means that the polarity of the selected NF membrane will affect significantly the solvent OSN flux: as far as materials of similar glass transition are considered, a polar membrane will induce more affinities for DMC whereas a hydrophobic one will conversely have more affinities for toluene.

Table 1: Physical chemical properties of the solvent selected for the reaction.

	M (g.mol ⁻¹)	Boiling point (°C)	Viscosity (mPa.s) 25°C	Solubility parameter δ (MPa ^{1/2})	Solubility in Water (g.L ⁻¹)
Toluene	92	110.5	0.64	18.2	0.53
DMC	90	90	0.53	22.5	139

The second criterion to meet is the highest possible retention of the catalyst. Among the relevant parameters known to control the retention, some are linked to the catalyst characteristics, such as its molecular weight and its affinity for the membrane material. Others are also linked to the extent of the membrane interactions with the solvent: the stronger the interactions, the higher will be the membrane swelling, and the lower the catalyst retention. So the choice of the membrane polymer, either polar or non polar, will affect directly the retention efficiency in relation with the type of solvent used. To be able to control and tailor the polarity of the membrane and, thus, to adjust the membrane structure and properties, the synthesis of block co-polyurethanes (co-PU) was carried out. The reason of this choice is twofold. Firstly previous works have shown that this polymer structure is well stable at least in toluene up to 80°C [16]; secondly, the block co-polymerization route is rather a flexible one because it allows the easy incorporation of oligomer blocks, which can be used to tune the membrane polarity and to control the swelling extent of the network. The applied synthesis route follows the general polymerization reaction:





with:

block D: -NHCO-R-NH-CO-, block P: -PEG-O-, block T: T(-O-)₃

This scheme corresponds to the classical step polyaddition of difunctional reagents, i.e. diisocyanate and diols, under molar stoichiometric ratio; as diols, aliphatic polyethylene glycols (PEG) were used. The structures of the diisocyanate are given in the figure 9. To ensure chemical resistance, a third trifunctional reagent can be added as well; here we used a low molecular weight triol molecule. The polymer network was synthesis according to two successive steps: the initial formation of linear PEG urethane oligomers follow by the network extension and crosslinking. Thus the overall polymer network can be seen as the chemical association of two types of urethane units. Looking to the co-PU structure (Figure 10), it turns out that the polarity of the network can be varied by adjusting several keys parameters: (i) the PEG molecular weight, (ii) the diisocyanate molecular weight, and the extent of crosslinker versus PEG.

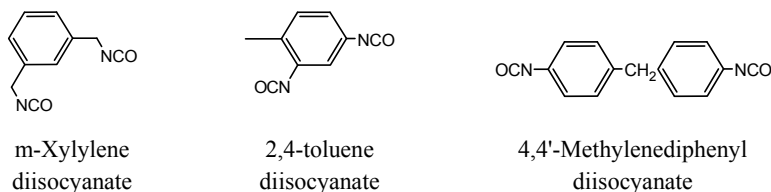


Figure 9: Diisocyanate structures used to prepare block copolyurethanes.

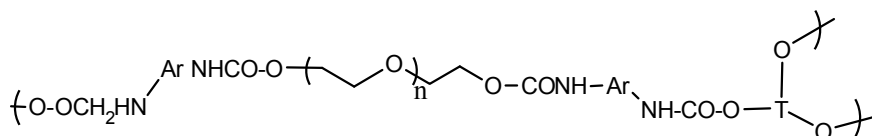


Figure 10: Chemically crosslinked block co-polyurethane-alcoxyether (PUE).

Accordingly to the above synthesis analysis, three membrane structures were first prepared to check the membrane feasibility; then the solvent compatibility was evaluated with a series of experimental data corresponding to immersion test in the pure liquid. The results gathered in table 2 showed a marked difference of swelling extent between the two solvents; going from toluene to DMC, the swelling increases from a factor 5 to 9.

Clearly the more polar solvent favored the swelling of PUE membranes. It can be explained by the polar PUE networks created from the aromatic isocyanates and the PEG of low molecular weight. Indeed, the aromatic urethane fraction is above 0.40 and so corresponds to a significant rigid, polar structure moiety compared to the PEG block. These preliminary results are in good agreement with the expected results and validate our synthesis membrane approach.

Table 2: Results of swelling experiments in organic liquids ($t=20^{\circ}\text{C}$, $P=1\text{MPa}$).

Diisocyanate	Membranes	Aromatic fraction	δ^*	Swelling extent (wt%)	
				Toluene	DMC
TDI	PUE1	0.43	32.5	4.5	36
XDI	PUE2	0.45	26.4	8.5	40
MDI	PUE3	0.52	23.9	3.5	31

*Calculated for the equivalent aromatic urethane moiety (δ in $\text{MPa}^{1/2}$).

6 Conclusion

Our main long term goal is the integration of organic solvent nanofiltration within the homogeneous catalytic olefin metathesis reaction. It aims at achieving high retention of Hoveyda II type catalyst(s) to increase its(their) life cycle and decrease its(their) environmental impact due to loss at various steps. This example can be used as a model case to understand the various challenges facing fine chemistry nowadays and how integration of membrane separation processes can contribute to a solution that could be further scaled-up at industrial level.

The development of chemical reactions catalysed by homogeneous catalysts are recommended for sustainable production in fine chemistry according to the green chemistry concepts, but now, research axes must integrate catalysts recycling at the early stage of their conception, leading to an integrated approach including molecular engineering of catalyst together with recycling process. A dual objective has to be reached: (i) to increase catalyst productivity by increasing its recycle ability and simultaneously lower the environmental impact partly due to impossible re-use up today, (ii) to lower residual metal content in the reaction products and fulfil requirement for pharmaceutical uses, for instance. At laboratory scale, catalysts recycling by nanofiltration proved to be an innovative alternative route for recycling. This separation process is few energy consuming compared to other separation methods and the catalyst is not damaged thanks to the absence of phase change. Moreover, it is a friendly process toward fragile substrates and products that permeate through the membrane. Nanofiltration can be settled as a separation process or coupled to a reaction batch to lead to a membrane reactor. Membrane reactor is probably the best choice according to the sustainable requirements and to process intensification but not always well adapted depending on the target chemical reaction itself. Whatever the choice, separate separation or membrane reactor for synthesis, there are two main challenges for organic solvent nanofiltration. The first one is the membrane stability in organic solvents. Only few membranes able to highly retain homogeneous catalysts in polar, non polar or aromatic solvents are commercially available. Thus there is a need in preparation of new (selective) membranes to be able to widely extend OSN applications to various systems. We have shown here two types of membrane materials that can be developed for filtration in toluene that is one of the most difficult cases. One is an integrally polymeric membrane, the other is an organo-ceramic composite one. For both membranes, we only showed preliminary results that are promising.



Developments of these two membranes are still in progress. The second aspect concerned the mastering of the filtration process itself, needing a better fundamental understanding of transfer mechanisms not fully understood in OSN. Retentions are correlated to physico-chemical environment and hydrodynamics and synergies between these two types of parameters. For a given solvent/catalyst solution it was clearly shown how change in transmembrane pressure or filtration mode (dead-end or tangential) can strongly affect the catalyst recovery, in addition with the role played by the membrane material itself. Finally, in the future, we hope to be able to determine the best way for the eco-design of a whole process involving metathesis reactions in good agreement with the sustainable chemistry requirements.

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