Membrane Reactor Based on Hybrid Nanomaterials for Process Intensification of Catalytic Hydrogenation Reaction: an Example of Reduction of the Environmental Footprint of Chemical Synthesis from a Batch to a Continuous Flow Chemistry Process

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Membrane processes represent a well matured technology for water treatment with low environmental footprints compared to other type of processes. We have now combined this technology with nanomaterials, ionic liquids (negligible vapor pressure), and poly(ionic liquids) in order to enlarge the field of applications while benefiting from the advantages of membranes. We have modified flat sheet water filtration membrane and used it as both catalytic support and reactor with the advantages to make the reaction and the separation of products in only one step.

For this purpose, catalytic metallic nanoparticles of palladium (diameter of ca. 2 nm) were synthesized in a gel-poly(ionic liquid) layer grafted at the surface of polymeric filtration membranes by UV-photografting method. The so obtained catalytic membrane was successfully applied in the hydrogenation of trans-4-phenyl-3-buten-2-one in forced flow-through configuration, which gave full conversion in a few seconds (2.6 s) showing advantages over the batch reactor process (in that case, palladium nanoparticles were synthesized in the ionic liquid [MMPIM][NTf$_2$] (1,2-dimethyl-3-propylimidazolium bis-(trifluoromethylsulfonyl)imide)). Nevertheless, the catalytic membrane used in submerged mode no more prevailed over the batch reactor. Catalytic nanoparticles remain highly active in the membrane after 12 cycles of reaction without need of recuperation. Results were compared to one obtains with a similar system in batch reactor conditions, showing high efficiency of our process in term of selectivity and reactivity, combined to an important compactness, the productivity of the catalytic hollow fiber membrane reactor and permitting to operate at larger scale with promising results in an environmental friendly way in term of energy and product (metal, solvent) consuming.

1. Introduction

Palladium nanoparticles (PdNPs) represent a versatile catalyst with a wide range of applications such as C-C bond and carbon-heteroatom bond formation, hydrogenation (Tsuji et al. 2004; Astruc et al. 2005; Favier et al. 2011) and carbonylation processes (Barnard et al. 2008; Gadge et al. 2014). In order to keep the chemical and physical properties of PdNPs, the formation of aggregates must be avoided during the catalytic process by stabilization of PdNPs. Despite the high intrinsic activity of such catalytic system, the production is generally limited by the process when phenomena as diffusional limitation or deactivation of the catalyst decrease the apparent reactivity. Another issue is the necessary separation step to recycle the PdNPs. In this work, we explored how catalytic membrane reactors can be used to intensify a catalytic process from batch conditions to continuous flow production. Those membranes are appropriate to be applied in catalysis due to

relevant advantages such as the catalyst immobilization and the intensification of the contact between reactants and catalyst (Miachon et al. 2004; Macanas et al. 2010). Most reported catalytic membranes are based on inorganic materials due to their high resistance (Julbe et al. 2001). However they cannot reach the high packing density offered by polymeric membranes like in the case of hollow fiber membranes assembled in modules, reaching up to 10,000 m^2 of filtration area in 1 m^3 of reactor at low cost.

In this work, PdNPs were prepared in neat room temperature ionic liquids (RTIL), taking advantage of the efficient dispersion of MNPs in this medium (Venkatesan et al. 2011). Understanding of the different catalytic behavior between the PdNPs dispersed in a RTIL and those supported on a polymeric membrane (catalytic membrane) could be gained.

The preparation of the catalytic membrane was realized through an intermatrix synthesis methodology (Gu et al. 2015). PdNPs dispersed in a RTIL were prepared by a 'bottom-up' methodology (Biswas et al. 2012), using palladium acetate as metallic precursor and PVP (polyvinylpyrrolidone) as stabilizer under thermal decomposition conditions. Parameters (such as temperature, Pd/PVP ratio, dihydrogen pressure) were optimized in order to obtain the most active catalytic system. Those catalytic systems both tested in hydrogenations in order to compare the catalytic activity difference between the PdNPs in RTIL and membrane supported PdNPs (catalytic membrane).

2. Materials and methods

2.1 Products and materials

[MMPIM][NTf$_2$] (1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide) was purchased from Solvionic, France and MicroPES (2F) Flat-sheet membrane from Membrana Gmbh (Germany), both directly used without pre-treatment. Amicon stirred ultrafiltration cell was purchased from EMD Millipore. The Ismatec SA-Reglo Analog peristaltic pump was purchased from IDEX Health & Science. Synthesis of the grafted polyRTIL membrane was published in a previous article (Gu et al. 2015).

2.2 Synthesis of colloidal palladium nanoparticles in ionic liquid

11.5 mg (0.05 mmol) of palladium acetate together with (or without) the corresponding quantity of PVP (PolyVinylPyrrolidone) were added in 5 mL of [MMPIM][NTf$_2$] and stirred at room temperature under argon in a schlenk tube until complete dissolution. The mixture was then heated and stirred at 100 °C overnight to give complete decomposition of the metallic precursor.

2.3 Procedure for hydrogenation reaction on batch reactor

1 mmol of trans-4-phenyl-3-buten-2-one (147.7 mg) was added to 1 mL of preformed colloidal palladium nanoparticles in [MMPIM][NTf$_2$] ([Pd] = 0.01 mmol/mL). The system was then pressurized with dihydrogen and stirred at regulated temperature. The mixture was then cooled to room temperature. Products were extracted with cyclohexane (5×2 mL) from the catalytic phase. The organic phases were dried over anhydrous MgSO$_4$, filtered and the solvent evaporated under reduced pressure. Conversions were determined by ^{1}H NMR spectroscopy and GC-MS chromatography, using respectively 1,3,5-trimethylbenzene and decane as internal standards.

2.4 Procedure for catalyst recycling test on hydrogenation reaction on batch reactor

The hydrogenation product (4-phenylbutan-2-one) was extracted from the reaction mixture with cyclohexane (7×1 mL). The RTIL catalytic phase from the previous run was maintained for 30 min under reduced pressure. Trans-4-phenyl-3-buten-2-one was then re-added for the next run and treated under the same conditions than those applied for the first run.

2.5 Procedure for hydrogenation reaction under flow-through configuration using the catalytic membrane

0.2 mmol of trans-4-phenyl-buten-2-one (29.53 mg) was dissolved in 50 mL of ethanol in a round bottom flask. The solution was bubbled with dihydrogen at atmospheric pressure for 30 min. The solution was then filtered through the catalytic membrane under H$_2$ pressure (0.1 bar).The permeate was collected and re-added to the round bottom flask for a second filtration. The procedure was repeated eight times with a total residence time of 2.6 s. The final permeate was collected and ethanol was evaporated under reduced pressure. The isolated product was then analyzed by ^{1}H NMR spectroscopy and GC-MS chromatography, using respectively 1,3,5-trimethylbenzene and decane as internal standards.

3. Results and discussion

3.1 Palladium nanoparticles synthesis

Although RTIL stabilizes nanoparticles by electrostatic effect, sometimes RTIL alone may still not be sufficient to well disperse metallic nanoparticles. In that case, an additional co-stabilizer is required. PVP is one of the most frequently used polymers to stabilize MNPs since it is soluble in a lot of polar solvents. L. D. Pachon et al.(2008) found that part of the PVP adsorbs on the NP surface as a protective shell, while the other part dissolves freely in the suspension, creating a second protective shell and avoiding the collision between particles. In this work, palladium acetate was used as precursor in the presence (system 1) or in absence (system 2) of PVP. During the synthesis, palladium turned from orange (color of palladium acetate) to black, indicating the formation of Pd^0 species. TEM images are given in Figure 1. Judging from the difference between system 1 and system 2, PdNPs were better dispersed with the presence of the additional polymer PVP in [MMPIM][NTf$_2$]. The PdNPs corresponding to system 1 are more homogeneous in size (2.5 ± 2.0 nm) than those related to system 2 (4.3 ± 2.0 nm). For catalytic purposes, both systems were studied to check the effect of PVP, which can also over-protect PdNPs and therefore reduce the accessibility of the reagents to the metallic surface (poison effect).
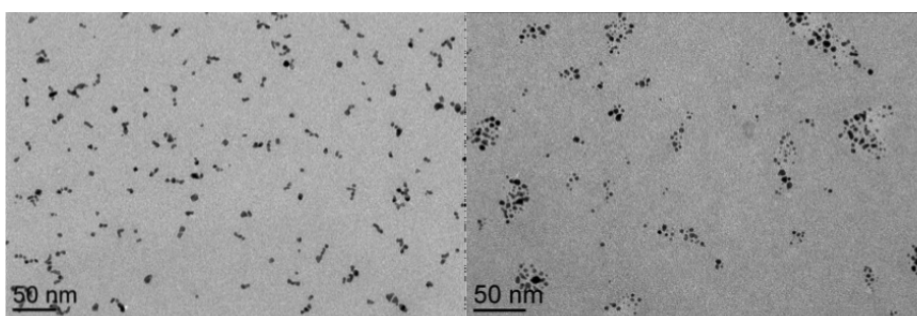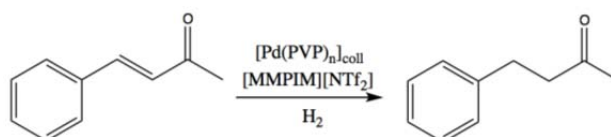

Figure 1: TEM images of PdNPs synthesized in [MMPIM][NTf$_2$]: left, system 1 (in the presence of PVP); right : system 2 (in the absence of PVP)

3.2 Catalytic hydrogenation of trans-4-phenyl-3-buten-2-one under batch conditions

Pd catalytic systems 1 and 2 were applied to the benchmark hydrogenation reaction of trans-4-phenyl-3-buten-2-one (Scheme 1 and Table 1)

Scheme 1: Pd-catalyzed hydrogenation of trans-4-phenyl-3-buten-2-one using PdNPs coming from both system 1 (in the presence of PVP) and system 2 (in the absence of PVP)

4-Phenylbutan-2-one was exclusively formed as product, which represents a model skeleton of fragrances (Jansat et al., 2009). System 1 preserved high activity under mild conditions (1-3 bar H$_2$, 1 mol% Pd; entries 1-6), even at low temperature (entry 6) and at low catalyst load (0.1 mol%, entries 7-9). Despite the similarity in NP mean diameter and the absence of PVP, system 2 was less active than system 1 (25% vs 61% conversion after 0.5h, entry 10 vs 3).

Recycling of catalytic system 1 was then run for the benchmark hydrogenation using a substrate/Pd ratio of 1,000 at 60 °C under 1 bar hydrogen pressure (for 1h each run). The catalytic system was reused 12 times without catalytic activity loss. As shown in Figure 2, the conversion rate kept above 90% through the 12 runs (product was extracted by cyclohexane after each run). Although NP agglomerations were observed after 5 recycle runs (Figure 3), high conversions were retained. Any influence of the presence of aggregates was observed during the recycling. The H$_2$ turned out to have an impact on aggregation of PdNPs in [MMPIM][NTf$_2$].

Table 1: Pd-catalyzed hydrogenation of trans-4-phenyl-3-buten-2-one under batch conditions[a]

Entry	Pd System	Substrate/Pd Molar ratio	$P(H_2)$ (bar)	T (°C)	Reaction time (hour)	Conversion[b] (%)
1	1	100	3	80	1	100
2	1	100	3	60	1	100
3	1	100	1	60	0.5	61
4	1	100	1	60	1	100
5	1	100	1	35	1	60
6	1	100	1	35	2	100
7	1	1000	3	60	1	27
8	1	1000	3	60	3	66
9	1	1000	3	60	5	100
10	2	100	1	60	0.5	25

[a]Starting from 1 mmol of substrate.
[b]Determined by ^1H NMR spectroscopy and GC-MS chromatography, using respectively 1,3,5-trimethylbenzene and decane as internal standards.
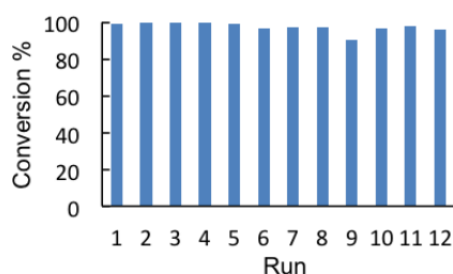

Figure 2: Recycling of system 1 for the hydrogenation of trans-4-phenyl-3-buten-2-one (conditions: 60 °C, 1 bar H_2, 1 h for each run, substrate/Pd molar ratio= 1,000).
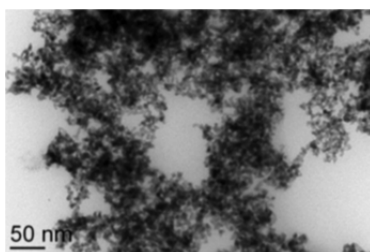

Figure 3: TEM images of system 1 after 5 recycling runs

3.3 Catalytic hydrogenation of trans-4-phenyl-3-buten-2-one under flow-through using catalytic polymeric membrane containing palladium nanoparticles

We reported in a previous work that palladium nanoparticles (diameter of ~2 nm) can be synthesized and well stabilized in a poly (ionic liquid)gel grafted by UV-polymerization at the surface of a filtration membrane (Gu et al. 2015). This type of hybrid modified membranes exhibited a high activity in catalytic reaction such as Suzuki-Miyaura cross coupling without loss of metal during the reaction.

Herein, we report the hydrogenation reaction of trans-4-phenyl-3-buten-2-one performed on the catalytic membrane under three different conditions (Figures 4 and 5).

The catalytic performance of the colloidal system on the same reaction was taken as a reference for comparison (conditions: substrate/Pd = 100 under 1 bar of H_2 at 60°C). In the flow through configuration (Figure 4-a), the reaction solution was bubbled with dihydrogen before filtered through the membrane. In the bubbling mode (Figure 4-b) and inside the autoclave (Figure 4-c), no filtration was involved. The membrane was submerged in the solution under bubbling (Figure 4-b) or under H_2 pressure (Figure 4- c).

Reaction conditions and conversions are given in Table 2. It is important to note here that this microfiltration membrane did not exhibit any retention of organic compounds nor adsorption. In the flow through

configuration, complete conversion was achieved within 2.6 s of residence time (time of the substrate presence in the grafted layer, depending on flux and grafted layer length). Thus this reaction time was much lower (~3 orders of magnitude) than that observed under batch conditions despite a lower temperature (35 °C) and lower H2 pressure.
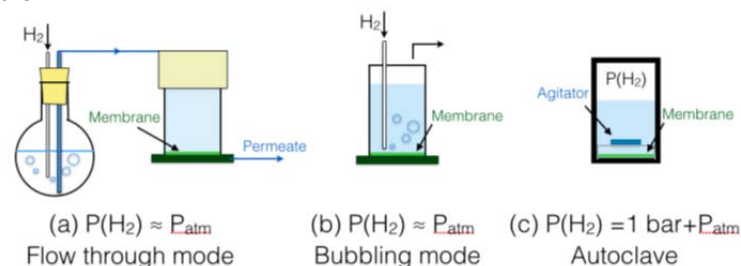

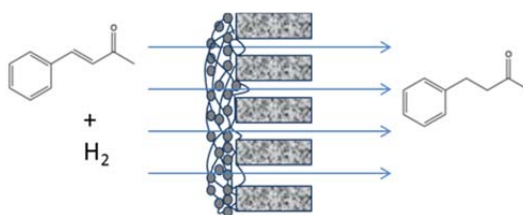Figure 4: Schematic representation of three different modes of using the catalytic

Figure 5: Schematic representation of hydrogenation reaction under catalytic membrane flow-through configuration using a poly(ionic liquid) gel grafted layer load with catalytic palladium nanoparticles.

It turned also out that the performance of the catalytic membrane was worse than the colloidal systems (see above) when no filtration was involved (i.e. bubbling vs autoclave mode). This is coherent with the reasoning on the mechanism of reaction acceleration by the catalytic membrane (Gu et al. 2015): when no forced flow through is involved, the high local catalyst concentration inside the membrane will not be able to play its role in multiplying the apparent reaction rate constant. Reaction became highly limited by diffusion of the substrate and H_2 towards the nanoparticle surface in the submerged (autoclave) mode. The striking contrast of the catalytic performance between the flow through configuration and submerged configurations highlights the necessity of forced flow in reaching remarkable reaction acceleration. It should be mentioned that liquid phase hydrogenation reaction carried out in the flow through membrane reactor is limited by the low hydrogen solubility in the solvent (ethanol). One way to overcome the low H_2 concentration is to operate the catalytic membrane reactor both feed and permeate at high hydrogen pressure keeping the transmembrane pressure at ~0.1 bar.

Table 2: Reaction conditions for hydrogenation of trans-4-phenyl-3-buten-2-one using the catalytic membrane

	Flow through	Bubbling	Autoclave
T (°C)	35	35	65
P(H$_2$)(bar)	Bubbling under atmospheric pressure		1
Reaction time (s)	2.6	1,800	3,600
Conversion (%)[a]	100	<10	27
V$_{EtOH}$ (mL)	50	20	5

[a] Determined by ^1H NMR spectroscopy and GC-MS chromatography, using respectively 1,3,5-trimethylbenzene and decane as internal standards.

4. Conclusions

The catalytic membrane reactor appeared as an efficient tool for process intensification since reaction and separation (reactants, catalyst, and product) occurred in one single step when full conversion was observed. Pure product was obtained once the process was triggered in the catalytic membrane in flow through mode but not until the end of the reaction under batch conditions. Using the flow through mode, the hydrogenation reaction was intensified by a factor ~1,000 (based on reaction time) compared to the batch reactor despite a much lower temperature (35 °C instead of 60 °C, lower thermal energy) and H$_2$ pressure. These promising results obtained with flat sheet membranes can also be intensified with hollow fiber geometry as observed in

our previous works finding applications in synthesis and catalysis (Gu et al. 2015; Emin et al. 2014; Emin et al. 2015). Due to the high efficiency of catalytic reactor membrane process in terms of reactivity, combined to a high compactness when hollow fibers are used, the productivity of the catalytic membrane reactor can reach the same level as, or outreaches microreactors (i.e. 10,000 ton per year per cubic meter). Therefore, the developed materials seem able to operate at larger scale with promising results in an environmental friendly way in terms of energy and chemicals (metal, solvent) consuming.

Acknowledgments

References

Aki S.N.V.K., Brennecke J.F., and Samanta A, 2001, How polar are room-temperature ionic liquids? Chemical Communication, 5, 413-414.

Astruc D., Lu F., Ruiz Aranzaes J., 2005, Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis, Angewandte Chemie International Edition, 44,7852-7872.

Barnard C.F.J., 2008, Palladium-catalyzed carbonylation-a reaction come of age, Organometallics, 27, 21, 5402-5422.

Baudequin C., Baudoux J., Levillain J., Cahard D., Gaumont A.C., and Plaquevent J.-C., 2003, Ionic liquids and chirality: opportunities and challenges. Tetrahedron: Asymmetry, 14, 3081-3093.

Biswas A., Bayer I.S., Biris A.S., Wang T., Dervishi E., and Faupel F., 2012, Advances in top–down and bottom–up surface nanofabrication: Techniques, applications & future prospects. Advances in Colloid Interface Science, 170, 2-27.

Emin C., Remigy J.-C., Lahitte J.-F., 2014, Influence of UV grafting conditions and gel formation on the loading and stabilization of palladium nanoparticles in photografted polyethersulfone membrane for catalytic reactions, Journal of Membrane Science, 455, 55-63.

Emin C., Gu Y., Remigy J.-C., Lahitte J.-F., 2015, Polyethersulfone hollow fibre modified with poly(styrenesulfonate) and Pd nanoparticles for catalytic reaction, The European Physical Journal Special Topics, 224,1843-1848.

Favier I., Madec D., Teuma E., and Gómez M., 2011, Palladium nanoparticles applied in organic synthesis as catalytic precursors. Current Organic Chemistry, 15, 3127-3174.

Gadge S.T. and Bhanage B.M., 2014, Recent developments in palladium catalysed carbonylation reactions. RSC Advances, 4, 20, 10367-10389.

Gu Y., Favier I., Pradel C. , Gin D. L. , Lahitte J.-F., Noble R. D., Gómez M., Remigy J.-C., 2015, High catalytic efficiency of palladium nanoparticles immobilized in a polymer membrane containing poly(ionic liquid) in Suzuki-Miyaura cross-coupling reaction, Journal of Membrane Science, 492, 331-339.

Jansat S., Durand J., Favier I., Malbosc F., Pradel C., Teuma E.; Gómez M., 2009, ChemCatChem, 1, 244-246.

Julbe A., Farrusseng D., Guizard C., 2001, Porous ceramic membranes for catalytic reactors-overview and new ideas, Journal of Membranes Science, 181, 3-20.

Miachon S., Dalmon J.A., 2004, Catalysis in membrane reactors: what about the catalyst? Topics in Catalysis, 29 ,59-65.

Macanás J., Ouyang L., Bruening M.L., Muñoz M., Remigy J.-C., Lahitte J.-F., Development of polymeric hollow fiber membranes containing catalytic metal nanoparticles, 2010, Catalysis Today,156, 181-186.

Pachón, L. D. and Rothenberg, G., 2008, Transition-metal nanoparticles: synthesis, stability and the leaching issue. Applied Organometallic Chemistry, 22, 288-299.

Tsuji J., 2004, Index, in Palladium Reagents and Catalysts: New Perspectives for the 21st Century, John Wiley & Sons, Ltd, Chichester, UK.

Venkatesan R., Prechtl M.H.G., Scholten J.D., Pezzi R.P., Machado G., and Dupont J., 2011, Palladium nanoparticle catalysts in ionic liquids: synthesis, characterisation and selective partial hydrogenation of alkynes to Z-alkenes. Journal of Materials Chemistry, 21, 3030-3036.

Wasserscheid P. and Welton T., 2007, Ionic Liquids in Synthesis, Wiley-VCH Verlag GmbH & Co. KGaA.