

Platinum-Catalyzed Alkene Hydrosilylation: Solvent-Free Process Development from Batch to a Membrane-Integrated Continuous Process

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The integration of a membrane separation protocol with the platinum-catalyzed hydrosilylation of olefins is investigated. The catalytic reaction is first optimized in batch where [Pt(IPr*)(dms) CI_{2} (IPr*=1,3-bis[2,6-bis(diphenylmethyl)-4-methylphenyl] imidazol-2-ylidene, dms = dimethyl sulfide) demonstrates superior activity compared to the less sterically encumbered [Pt-(SIPr)(dms)Cl₂] (SIPr = 1,3-bis(2,6-diisopropylphenyl) imidazolidine) congener. Filtration conditions are identified in membrane screening experiments. Hydrosilylation of 1-octene catalyzed by [Pt(IPr*)(dms)Cl₂] is conducted in continuous mode and the platinum catalyst is separated efficiently over the commercially available Borsig oNF-2 membrane, all under solvent-free conditions. An advantage of this process is that both reaction and separation are coupled in a single step. Moreover, at the end of the process the intact catalyst was recovered in 80% yield as an off-white solid without any further purification.

During the course of the last decade, an increasing number of large-scale industrial catalytic reactions have been carried out using continuous flow (CF) as this leads to synthesis in a more material and energy efficient fashion compared to classical batch reaction approaches. Applications of CF range from the petroleum and resources related field such as biodiesel production^[1] and valorization of raw materials,^[2] to environmentally related processes such as detoxification of liquid streams,^[3] plastic pyrolysis,^[4] and treatment of exhaust gases.^[5] Continuous flow reactors offer several advantages over the classical batch techniques, prompting nowadays substantial changes to the way catalytic reactions are carried out on large scale and influencing current development in this field.^[6] Some of the main advantages of this method include; i) better mixing and heat transfer in CF, ii) improved operational safety for

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	Supporting information for this article is available on the WWW under https://doi.org/10.1002/cssc.202101153				

better handling of reagents/reaction components, and iii) the ability to combine non-thermal energy transfer techniques, such as ultrasounds^[7] and microwaves.^[8]

Many important organic transformations rely on the use of homogeneous Late-Transition Metal (LTM) catalysts due to their unique reactivity as well as selectivity.^[9] However, the need for recycling these precious metals and the obligation of avoiding metal-contamination in the final products, especially in the food and pharmaceutical industries, render their separation a critical and an integral part of any sustainable catalytic process. Therefore, continuous flow synthesis integrated with homogeneous catalyst separation has recently gained considerable attention.^[10] Several methodologies have been applied to separate and recycle homogeneous catalysts in continuous flow, such as metal scavenging,^[11] use of liquid-liquid biphasic systems^[12] and organic solvent nanofiltration (OSN).^[13] OSN is considered a more sustainable separation technique since it does not involve the development of a biphasic system for catalyst separation. Moreover, it requires less energy compared to other typical separation techniques.^[14] Continuous processes coupled with OSN have already been applied to several reactions, such as: cross-coupling reactions, [13d,e,g,h] olefin metathesis,^[13a,c] and hydroformylation^[15] for recycling and separation of numerous platinum group metal (PGM) catalysts, such as Pd, Ru, and Rh. In contrast, platinum-based catalysts have to date not been recycled by using OSN, despite the fact that Pt-based homogeneous catalysts are widely used in the chemical industry for the production of organosilicon $\mathsf{compounds}^{\scriptscriptstyle[16]}$ These compounds are of great importance in chemical industry with their numerous applications in organic synthesis and materials science^[16a,17] and are typically obtained by hydrosilylation of olefins, which is typically performed by using homogeneous transition metal-based catalysts.^[18] The most commonly used catalysts, Karstedt's and Speier's complexes, are based on platinum.^[16b,19] Although these platinum catalysts are highly active, they possess important drawbacks, such as i) an evident instability and decomposition of the catalyst, ii) often resulting in the formation of colloidal platinum species, iii) poor selectivity, and iv) high product contamination by metal, an issue evident as some silicon oils are sold contaminated with residual platinum.

More efficient and selective hydrosilylation reactions were obtained using Pt^0 systems based on *N*-heterocyclic carbene (NHC) ligands reported by Markó et al., namely [Pt(NHC)(dvtms)] (dvtms = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane), which are highly stable under reaction conditions.^[20] Recently, our group

has reported the synthesis of Pt^0 as well as Pt^{II} complexes bearing on a number of NHC ligands using a sustainable weak base approach,^[21] and as a proof-of-concept, one of the new complexes, $[Pt(SIPr)(dms)Cl_2]$ [Pt-I; SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidine, dms = dimethyl sulfide] was employed as catalyst in a solvent-free hydrosilylation of 1-octene (1) to afford the desired 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane (3) with an excellent selectivity.

Pt-based catalysts are still expensive due to the relatively low natural abundance and the resulting high price of the platinum metal. Therefore, recycling and recovery of such an expensive metal/catalyst is highly desirable from an economic and sustainability point of view, especially for large scale industrial use. Recycling of homogeneous platinum catalysts, used in hydrosilylation reactions, has been achieved using biphasic methods in ionic liquids.^[22] Extra steps of synthesizing and optimizing a suitable ionic liquid for reaction operation/ separation are required in this instance. In contrast, a straightforward separation of the homogeneous Pt catalyst directly from the obtained product without the need of any additional recycling medium would be a significant achievement.

We recently reported a gold-catalyzed alkyne hydration reaction using a semi-continuous process coupled with OSN, in which we successfully achieved the recycling and recovery of Au-NHC catalysts.^[23] In this report, we separate and recycle the catalyst, in the end, the gold species is recovered and used to regenerate the active gold complex. This work highlighted the possibility of recovering the intact catalyst-the metal together with its ancillary ligand, since the ligands used in transition metal catalysis are oftentimes expensive. Achieving recovery of the usable catalyst would lead to a dramatic decrease in cost and environmental impact of any catalytic process. However, such catalyst recovery requires sufficient catalyst stability, which, in the cases examined, is provided by the presence of NHC ligands.

In the present work, we target the integration of the hydrosilylation of olefin reaction, catalyzed by a Pt-NHC complex, with membrane separation technology to achieve i) catalyst recyclability in a continuous manner, ii) recovery of the intact Pt-NHC catalyst, and iii) high product purity. To accomplish these goals, we proceeded to investigate the kinetic profile of the reaction and optimized the offline filtration process.

Since our initial study determined that high catalytic activity could be obtained using **Pt-I** as catalyst in the hydrosilylation of 1, further reaction and kinetic optimization was initially carried out using this complex and this reaction. We recently reported^[20] that complete conversion can be achieved in 120 min. Shorter reaction times can be achieved if the catalyst is simply added as a solid to the reagents. In this manner, regular interval sampling of the reaction indicated that complete conversion into the desired product was achieved within 30 min (Scheme 1).

Encouraged by our previously developed protocol separating Au-NHC catalysts which was achieved by using Borsig-type polymeric membranes,^[23] and the low polarity of the reaction



Scheme 1. Pt Catalysts used in the hydrosilylation of 1 to form 3. (GC yields).

system, especially in the absence of solvent, we considered that similar Borsig membranes could be suitable for separating Pt-NHC catalysts used in this study. Initially, screening filtrations for separating Pt-I were carried out in a number of organic solvents. It is important to note that, unless otherwise stated, all organic solvents were used as received without any purification. The overall Pt contents were quantified by ICP-MS analysis (Table 1). At this stage and to better streamline the optimization process, we only analyzed the recoverability as gauged by Pt content and not the Pt/ligand system as a whole. Using a Borsig oNF-1 membrane, a high Pt rejection of 93% was obtained in THF (Table 1, entry 1). When switching to the tighter Borsig oNF-2 membrane [i.e., Borsig oNF-2 with molecular weight cutoff (MWCO) = 350 Da, vs. Borsig oNF-1 with MWCO = 600 Da], an improved Pt rejection of 95.4% was observed (Table 1, entry 3). Upon performing the filtration in Me-THF, using Borsig oNF-2, the highest Pt rejection of 97.2% was obtained (Table 1, entry 4). Encouraged by the last result, the filtration of Pt-I was next carried out using the Borsig oNF-2 membrane under solvent-free conditions, targeting a more sustainable process. The solvent-free filtration of this catalyst, making use of the product itself as filtration solvent, led to a very low Pt rejection of only 39% as indicated by ICP-MS (Table 1, entry 5). Similar to the use of hexane as filtration solvent (Table 1, entry 2), we suspect this poorer rejection is due to the high affinity of the membrane toward the apolar product containing the catalyst, thus increasing catalyst permeability. We reasoned that more polar membranes, such as PuraMem selective and PuraMem 280, could be better suited for this filtration.

However, no selectivity with PuraMem selective and a low rejection with PuraMem 280 were experimentally observed (Table 1, entries 6 and 7).

Next, batch reaction optimization was carried out with [Pt(IPr*)(dms)Cl₂] (Pt-II). Since all efforts to perform the filtration in the absence of solvent, using catalyst Pt-I, were unsuccessful, our attention turned to using the bulkier Pt-II catalyst (Scheme 1). The catalytic activity of the bulky catalyst Pt-II was first studied in batch and compared to the previous results (Table 2). Under the identical reaction conditions used with catalyst Pt-I, a complete conversion into the desired product was achieved in 10 min with Pt-II (Table 2, entries 1 and 2). The reaction temperature was further investigated since most polymeric membranes are not stable at temperatures above



Table 1. Rejection and permanence data of Pt-I used in this study over polymeric membranes.					
Entry ^[a]	MembraneSolventPermeance(MWCO)[L m ⁻² h ⁻¹ bar ⁻¹]	Solvent	Permeance	Rejection [%]	
		Pt	3		
1	Borsig <i>oNF-1</i> (600 Da)	THF	8.23	93	0
2	Borsig oNF-1	hexane	10.68	86	7.79
3	Borsig <i>oNF-2</i> (350 Da)	THF	4.50	95.4	0
4	Borsig oNF-2	Me-THF	4.95	97.2	0
5 ^[b]	Borsig oNF-2	solvent-free	0.98	39	0
6 ^[b]	PuraMem selective ^[c]	solvent-free	3.48	0	0
7 ^[b]	PuraMem 280 (280 Da)	solvent-free	0.49	41.8	0

Filtration conditions: [a] Post batch reaction filtrations (69 mmol scale) carried out in solvents were diluted to a volume of 500 mL and subsequent OSN were performed at rt, P=20 bar. [b] Filtration of 0.1 mol% **Pt-I** in a total volume of 500 mL product **3**. [c] PuraMem Selective is a composite membrane, solubility (and not diffusion) dominates the membrane separation. Therefore, the cut-off of the membrane is strongly dependent on solvent/solute combination. MWCO obtained in one standard system is not characteristic for this type of membrane. Best suitable membrane for the application can be chosen by testing real solutions.

Table 2. Batch reaction optimization using catalysts Pt-I and Pt-II.					
Entry	Catalyst	t [min]	T [°C]	Conversion [%]	
1	Pt-I	30	70	>99	
2	Pt-II	10	70	>99	
3	Pt-II	10	rt	>99	
4	Pt-II	5	rt	>99	
Reaction conditions: reactions were carried out with 1 (40 mmol), 2					

(40 mmol) and catalyst (0.1 mol%) under solvent-free conditions.

60 °C. Our first attempt at tackling this problem was to perform the reaction at room temperature (22 ± 2 °C). Surprisingly, similar activity was observed at room temperature and at 70 °C (Table 2, entries 2 and 3). Moreover, sampling the reaction even at shorter time indicated full conversion into the desired product **3** in 5 min (Table 2, entry 4), which is, to our knowledge, the first efficient hydrosilylation reaction reported under solvent-free conditions at room temperature using a NHC-based platinum(II) catalyst.

In testing the membrane separation performance on **Pt-II** screening filtration over a Borsig *oNF-2* membrane gave almost a complete rejection of 99.5% (Table 3, entry 1) which is higher than the rejection obtained with catalyst **Pt-I** under identical filtration conditions (Table 1, entry 4 vs. Table 3, entry 1).

After this very promising result, a solvent-free filtration was attempted using this membrane; surprisingly, the neat filtration of **Pt-II** also gave a near complete rejection of 98% (Table 3,

Table 3. Rejection and permanence data of Pt-II catalyst over Borsig oNF-2 membrane.						
Entry	Conditions	Permeance	Rejec	tion [%]		
			Pt	3		
1 ^[a]	Me-THF	4.39	99.5	0		
2 ^[b]	Neat	1.04	98	0		
[a] Post batch reaction filtration (40 mmol scale) carried out in Me-THF was diluted to a volume of 500 mL then OSN was done at room temperature, $P = 20$ bar. [b] Post batch reaction filtration (1.13 mol scale) with a total volume of 500 mL of the product 3 .						

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entry 2), which is in contrast to the solvent-free filtration performed for **Pt-I** (Table 1, entry 5). The filtration process when using **Pt-II** seems to be more size exclusion dependent, whereas filtration using **Pt-I** is still influenced by membrane—solvent—catalyst affinity. Overall, this result brings us a step closer towards developing a greener and more sustainable separation-integrated catalytic process.

After these very promising results, a continuous flow system for the **Pt-II**-catalyzed hydrosilylation of 1-octene integrated with the Borsig *oNF-2* membrane was next designed and tested. First Borsig *oNF-2* was installed in the membrane unit. In the feed tank, 0.1 mol% of the catalyst was added together with 1.13 mol of each reagent, (equivalent to one catalytic cycle; 500 mL total volume of neat reagents) and 2.26 mol of the reagents was added together in the tank A (equivalent to two catalytic cycles; 1000 mL total volume of neat reagents). This tank was connected to an additional pump (P2) in order to add reagents under constant volume into the circulation unit (Figure 1).



Figure 1. Schematic representation of the continuous process. Reaction occurs in the unit (the shaded zone) at a flow rate of $45-52 \text{ kg} \text{ h}^{-1}$ (0.3 m s⁻¹). V-1 is always in an open position allowing permeation of the product, then reagents from the tank A are pumped continuously into the unit. P1 is a circulation pump and P2 is the pump connected to tank A to pump reagents into the unit.



After the setup was assembled, the neat reaction mixture inside the feed tank was allowed to circulate with a cross-flow velocity of 0.3 m.s⁻¹ at 3 bar for 10 min at room temperature. At this point, nothing permeated through the membrane due to the low pressure applied, this gave enough time to achieve complete conversion into the desired product 3 within the loop as indicated by GC analysis (Table 4, entry 1). Thereafter, the pressure was increased to 20 bar at which point the product began to permeate through the membrane; this pressure was then kept constant. By the time permeation of the product began, P2 started continuously supplying substrates from holding tank A in order to keep the volume inside the unit constant, regular sampling for GC analysis and ICP analysis after 55, 130 and 250 min indicated $>\!97\,\%$ of the desired linear product (3) (Table 4, entries 2-4). At the end of the process, almost full retention of Pt in all samples taken was achieved (98-99% based on the ICP-MS analysis; Table 4, entries 2-4). After 250 min, a total volume of 900 mL of colorless liquid had permeated through the membrane; and the flux throughout the whole process was stable indicating a stable membrane performance with permeance of 1.10 $(Lm^{-2}h^{-1}bar^{-1})$. The product analysis revealed a very low Pt content of 0.36 ppm, meaning that the product did not require any further purification steps.

The identity of the post-reaction catalyst was investigated next. The retained mixture was subjected to diafiltration using Me-THF, derived from renewable resources,^[24] a near complete rejection was achieved when conducting a screen filtration of **Pt-II** in this solvent (Table 4, entry 1). Three diafiltration volumes^[25] of Me-THF were washed through the membrane keeping only a solution of the catalyst in Me-THF, this will also allow for all the remaining product in the retained mixture to be separated from the catalyst at the end of the process. Almost

Table 4. Reaction yield and filtration data obtained during the continuous experiment.						
Entry ^[a]	t [min]	GC yield [%]	Volume of 3 in permeate [mL]	Permeance $[Lm^{-2}h^{-1}bar^{-1}]$	Pt rejec- tion [%]	
1 ^[b]	10	98	0	0	-	
2	55	98	150	1.1	99	
3	130	97	400	1.1	99	
4	250	97	900	1.1	98	

[a] Unless otherwise stated, continuous experiment done at a flow of 45– 52 kg h⁻¹ (0.3 ms⁻¹) at P=20 bar. [b] Reaction mixture circulation at flow of 45–52 kg h⁻¹ (0.3 ms⁻¹) at P=3 bar.

Table 5. Rejection data obtained after the continuous process using Pt-II.					
Entry ^[a]	Conditions	Permeance $[Lm^{-2}h^{-1}bar^{-1}]$	Rejection [%]		
			Pt	3	
1	1 st diafiltration volume	2.2	99	0	
2	2 nd diafiltration volume	3.3	99	0	
3	3 rd diafiltration volume	4.2	99	0	
[a] Diafiltration was done in Me-THF at flow of 45–52 kg h^{-1} (0.3 m s $^{-1}$); one diafiltration volume $=$ 500 mL.					

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full Pt rejection (98%) at all stages of diafiltration was obtained indicating a stable performance of the membrane (Table 5).

The permeance began to increase as the diafiltration proceeded, indicating a decrease in the concentration of the product in the retained phase. At the end of the diafiltration process, the retained solution of Pt-II in Me-THF was evaporated and produced an off-white solid in 80% yield. It should be noted that the 20% loss is attributed to regular sampling and losses due to the incomplete emptying of the filtration unit on completion of the reaction as no decomposition was noticed at the surface of the membrane or in the retained mixture. The 80% isolated yield of the catalyst is in our view an unoptimized recovery amount and continuous operation without the required periodic sampling associated with process optimization sets this 80% as a lower limit as far as catalyst recovery is concerned. NMR analysis of the solid confirmed the latter to be pure catalyst Pt-II and it was later successfully reused in the same reaction carried out on a 2 mmol scale without any significant loss of catalytic activity. This result clearly demonstrates that this catalyst architecture is very stable under the process conditions. Considering the high stability of both the membrane and catalyst system, this process could theoretically be continuously run for much longer time periods but due to the large reagent volumes required for efficient filtration unit operation (ca. 350 mL) and the associated costs of these reagents, we only investigated 3 cycles, which demonstrated the efficiency of this process and permitted the study of variables such as membrane performance, reaction time and reaction temperature effects.

It should be mentioned that the main goal of this study is to develop a continuous process with integrated membrane separation. Since both product and starting materials are able to cross the membrane, full conversion has to be achieved continuously so that only product can permeate without affecting overall reaction kinetics. This is crucial to a successful setup, especially since the membrane permeation is the ratelimiting step of this process. Moreover, our investigation on the catalyst recovery is only meant to showcase the possibility and ease of recovering the intact catalyst using our integrated process (no catalyst decomposition is observed in our process). Nonetheless, initial efforts to further investigate the efficiency and stability of Pt-II under the batch-mode reaction conditions were attempted; complete conversion of 1-octene, on a 20 mmol scale, was achieved with only 1 ppm of Pt-II, thus reaching a TON of 1000000 (after 9 days), which is a remarkable catalytic efficiency (see the Supporting Information). No signs of platinum colloids were noticed in the reaction mixture as evidenced by UV/Vis analysis (see the Supporting Information for details). In addition, conducting the model reaction in the presence of mercury metal did not inhibit the catalytic activity since full conversion was still observed. A more detailed investigation on the catalytic activity, stability and scope of the Pt-II catalyst in the hydrosilylation of alkenes is ongoing in our research groups and will be communicated shortly.

In summary, superior activity in the hydrosilylation reaction under very mild conditions was achieved by using [Pt(IPr*)(dms) Cl_2] (Pt-II). High activity, stability, and rejection of the bulky Pt-II



were all attained as the hydrosilylation setup was continuously operated, without any significant deactivation or catalyst decomposition, under solvent-free conditions. This process does not require any further final product purification as it leads to near complete conversion into the desired product 2 with only 0.36 ppm platinum in the permeate. In addition, at the end of the experiment, the catalyst was successfully recovered without necessitating any further treatment in 80% yield. Therefore, a straightforward sustainable process of low energy demand, high scalability, and practical catalyst recovery has been developed. These results highlight a significant breakthrough towards a sustainable hydrosilylation process under homogeneous catalytic conditions without the main drawback of expensive homogeneous catalyst recycling and recovery. To the best of our knowledge, this is the first report on homogeneous platinum catalyst recycling and recovery through OSN under solvent-free conditions. Research focusing on the development of practical homogeneous catalytic processes for industrial use is ongoing in our laboratories.

Acknowledgements

We gratefully acknowledge the support of the Special Research Fund (BOF) of Ghent University (starting and project grants to SPN) and the C3 iBOF project. TACAB thanks VITO for a PhD studentship. BPM thanks the Research Foundation – Flanders (FWO) for a strategic basic research PhD fellowship. Umicore AG is thankfully acknowledged for generous gifts of materials.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: continuous processes · homogeneous catalysis · hydrosilylation · organic solvent nanofiltration · platinum

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Manuscript received: June 2, 2021 Revised manuscript received: June 14, 2021 Accepted manuscript online: July 22, 2021 Version of record online:

COMMUNICATIONS

And on we go: Taking advantage of membrane technology for homogeneous catalyst separation, the development of the first solvent-free continuous process coupled with organic solvent nanofiltration for platinum-catalyzed hydrosilylation is described.



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Platinum-Catalyzed Alkene Hydrosilylation: Solvent-Free Process Development from Batch to a Membrane-Integrated Continuous Process