

Selective hydrogenation over Pd nanoparticles supported on a pore-flow-through silica monolith microreactor with hierarchical porosity†‡

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Well-dispersed Pd nanoparticles have been synthesized inside the mesoporosity of a silica monolith featuring hierarchical porosity of homogeneous interconnected macropores (4 microns) and mesopores (11 nm). These monoliths have been implemented as microreactors for selective hydrogenation reactions. Conversion and selectivity can be tuned by adjusting the flow rates of hydrogen and substrates. In the selective hydrogenation of cyclooctadiene, a conversion of 95% and a selectivity of 90% in the monohydrogenated product, constant over a period of 70 h, have been reached. These figures correspond to a productivity of $4.2 \text{ mmol s}^{-1} \text{ g}^{-1}_{\text{MonoSil}}$ (or $0.32 \text{ mol s}^{-1} \text{ g}^{-1}_{\text{Pd}}$). In the stereoselective hydrogenation of 3-hexyn-1-ol a constant conversion of 85% was observed, with however moderate selectivity into the *cis* isomer, over a test period of 7 h. These results open the route to the synthesis of important chemicals and intermediates *via* safe and green processes.

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1. Introduction

Chemistry in flow is a promising option for the implementation of catalytic reactions enabling process intensification and simplified workups. Continuous flow chemistry allows in addition safer process operation through better control of reaction parameters such as temperature, contact time, flow rate, minimization of solvent use, etc.¹ Better control of contact time leads in turn to improved product selectivity and yield in comparison to batch reactors and represents a valuable tool for process intensification.¹ Recently, efforts have been made for the design of efficient microreactors comprising either microstructured multichannel reactors² or macroporous monoliths.³ Macroporous monoliths present the advantages of an interconnected and isotropic network of macropores allowing high surface-to-volume ratios and efficient mixing of fluids.⁴

Several approaches for the implementation of macroporous monoliths as pore-flow-through catalytic microreactors have

been reported.⁵ The very first reactors were developed by the group of Fréchet and Svec⁶ and were based on polymers. These reactors have then been further developed by the group of Kunz and Kirschning⁷ to obtain hybrid glass/polymer reactors that have been used for a large variety of organic transformations. To overcome swelling problems of polymer monoliths a new generation of unconventional monolithic inorganic (silica) microreactors for catalysis has appeared,⁸ which are formed by a combination of spinodal decomposition and a sol-gel process featuring an interconnected and homogeneous system of macropores (2–4 microns) and comprising within their skeleton homogeneously distributed mesopores adjustable in size (3–40 nm).⁹ This novel family of structured microreactors features high chemical and physical stability with a high condensation state of silica (76% of Q₄ and 24% of Q₃)^{9c} and can be readily functionalized by several catalytic active species: organic functions by organosilane grafting (e.g. aminosilane),⁸ inorganic species by surface deposition (e.g. alumina lining),^{10a} *in situ* synthesis of metal nanoparticles as Pd⁰,¹¹ *in situ* synthesis of hybrid materials as metal-organic frameworks (MOFs, e.g. CuBTC),^{10b} pseudomorphic transformation of the silica skeleton into zeolites,^{3b,c} or direct incorporation of Al¹² or Ni¹³ species during monolith synthesis. Ni species have also been incorporated by direct synthesis in similar titania monoliths.¹⁴ Sato *et al.*^{11b,12} have demonstrated first through Knudsen diffusion calculations in batch and in packed-bed reactors filled with crushed monoliths that bimodal porous silica bodies were more active than purely

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mesoporous silica because the interconnected network of macropores allows for rapid diffusion resulting in improved reaction kinetics. They have also shown that too small mesopores (<10 nm) restrict mass diffusion. The productivity in fine chemicals transformations was increased by using higher flow rates until the point where contact times were not enough to ensure high conversion.^{10,11} Previously we have shown that these new kinds of pore-flow-through silica monolith micro-reactors induced high productivity and high stability for base and acid catalyzed reactions of fine chemicals in the liquid phase under continuous flow.^{3b,8,10} The superiority of this new kind of monolith, used as a single piece microreactor, was demonstrated by the higher conversions and productivities achieved compared to packed-bed or batch reactors filled with crushed monolith.^{8,10} This result is most probably due to the more uniform contact time arising for the homogeneity of the macroporous network in the single piece monolith in comparison to the dual macroporosity (inter- and intra-particle) encountered in a packed-bed system.

In the present study, we analyze the effectiveness of these promising pore-flow-through silica monolith microreactors in a triphasic liquid/gas/solid system for selective hydrogenation reactions under conditions allowing a fine control of gas and liquid contact times on Pd nanoparticles (NPs) catalytic sites immobilized onto the silica network.

Different groups have reported on the catalytic behavior of Pd NPs supported on polymeric matrixes, dendrimers, zeolites and dispersed silica in selective hydrogenation.¹⁵ Selective hydrogenation of hydrocarbons with multiple C=C and/or C≡C and/or C=O bonds to achieve selective hydrogenation products (e.g. monoalkenes) is a highly desired and challenging process in the pharmaceutical, agrochemical and petrochemical industry sectors.¹⁶ Under comparable conditions, hydrogenation rates roughly followed the order C≡C > C=C > C=O. This behavior can be justified in terms of greater affinity of Pd for C=C than for C=O bonds in aliphatic compounds.¹⁷ Similar behavior (C=C > C=O) has been noticed using Ni-titania crushed monolith in packed-bed reactors.¹⁴ Particularly, the stereo- and chemo-selective hydrogenation of alkenes and alkynes in the presence of other functional groups is of fundamental importance in the synthesis of food additives, flavors and fragrances.¹⁸ For instance, there is growing interest in new hydrogenation processes under soft conditions that reduce the amount of double bonds in vegetable oils to product oils with higher consistency, stability and oxidation resistance, but also to avoid *trans* fatty acid esters as *trans* isomers have negative effects on health.¹⁹ The formation of *cis*-alkenes through stereo-selective addition of H₂ on alkynes is also an important step in industrial processes as in fragrance production (e.g. *cis*-3-hexen-1-ol leaf alcohol with a production of 400 tons per year).²⁰ Selective hydrogenation reactions are also crucial in polymerization processes to achieve the complete elimination of alkynes and dienes from alkene feedstocks.²¹ Flow processes could be a solution to finely tune the selectivity of these reactions by limiting the hydrogenation to one double bond. In that respect Pd NPs deposited on an

alumina membrane reactor demonstrated very promising activity for the selective hydrogenation of 1,5-cyclooctadiene.^{22a} The alumina membrane reactor proved to be more productive than batch and packed-bed reactors.^{22a} However it suffered from several drawbacks, among them a low surface area ($8\text{ m}^2\text{ g}^{-1}$), a poor dispersion of the Pd NPs at the surface, the formation of oligomers during the reaction due to residual acidity of the support which imposed intermediate reactivation steps affecting long term productivity, and the need for a relatively complex and large set-up to operate such a reactor.

Herein we present an alternative to membrane reactors for selective hydrogenation reactions using Pd-particles supported on a pore-flow-through monolith featuring a bimodal porosity and a high surface area ($600\text{ m}^2\text{ g}^{-1}$) easy to operate under soft conditions (25 °C, 2–3 bars H₂) under continuous flow. This unconventional Pd-silica monolith microreactor was used for the selective hydrogenation of 1,5-cyclooctadiene and 3-hexyn-1-ol.

2. Experimental section

2.1 Synthesis of the macro-/mesoporous silica monolith

The synthesis of the macro-/mesoporous silica monolith has been adapted from the original synthesis developed by Nakanishi.^{9a} In a flask 46.3 g distilled H₂O and 4.6 g HNO₃ (68%, Aldrich) were mixed for 15 min at 0 °C and 4.79 g of PEO (20 kDa, Aldrich 99%) were added and stirred for 1 h. Then 37.7 g TEOS (Aldrich 99%) were added and the mixture was stirred for 1 h. The resulting solution was poured into PVC tubes of 10 cm length and 8 mm internal diameter and kept at 40 °C for 3 days. The monoliths were then washed in water and treated in an ammonia solution (0.1 M) at 40 °C for 20 h. The monoliths were then dried at 40 °C for 24 h and calcined at 550 °C for 8 h. These silica monoliths (10 cm length and 6 mm diameter, 0.08 g cm^{-1}) were cut into pieces of desired size (2 cm) and are hereafter named as parent monoliths or MonoSils.

2.2 Synthesis of Pd-nanoparticles in the silica monolith (Pd-MonoSil)

A solution containing Pd(NH₃)₄(NO₃)₂ (0.141 mmol, 0.042 g, Aldrich 98%) in water (10 mL) was prepared. The pH of the Pd complex solution was adjusted to 8, 9 or 10 using a 0.1 M ammonia solution. The 2 cm length silica monoliths were immersed into these solutions. The amount of Pd in the initial solution corresponded to 1.5 Pd wt% with respect to silica. Monoliths were impregnated for 24 h at room temperature under gentle agitation at 100 rpm. The monoliths were then subsequently washed with distilled water (1 L), dried at 40 °C for 72 h and calcined at 550 °C for 8 h to form Pd oxide nanoparticles inside the silica monoliths. The reduction of PdO NPs was then performed with diluted hydrogen (3 vol% H₂ in He) at 280 °C for 2 h. The resulting monoliths are hereafter named Pd-MonoSils. For use as flow microreactors, the monoliths ended with two glass tubes and were cladded with a

heat-shrinkable DERAY® PTFE (polytetrafluoroethylene) clad (DSG-CANUSA) at 280 °C for 2 h as previously described.^{3b}

2.3. Materials characterization

The physico-chemical properties of the monoliths were characterized by nitrogen sorption at 77 K, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Supernatants of Pd complex solutions after impregnation were analyzed with UV/Vis spectroscopy.

The adsorption–desorption isotherms of nitrogen at 77 K were determined using a Micromeritics ASAP 2020 instrument after outgassing the samples (30 mg) at 250 °C under high vacuum (0.5 Pa) for 8 h with pressures between $0.001 < p/p_0 < 0.9959$ with an equilibrium interval of 5 s and 36 points in adsorption and 30 points in desorption. The mesopore volume was taken at the end of the filling of the mesopores. Surface area was determined by the BET (Brunauer Emmett Teller) equation considering the Rouquerol law to determine the highest relative pressure to use in the BET method.²³ The mesopore diameter was determined using the desorption branch of the nitrogen isotherm and the Broekhoff and De Boer method as it has been demonstrated to be one of the more accurate methods for mesoporous silica materials.²⁴ The morphology of the monoliths was examined using a Hitachi S-4500 I SEM. The chemical analysis of the monolith was performed by EDX on different parts of cut pieces of the Pd-MonoSils using a FEI instrument Quanta 200F (15 kV) in retro-diffusion. TEM images have been obtained with a JEOL 1200 EX II at 100 kV after grinding the monoliths, dispersing the powder in ethanol and deposition of the carbon grid. UV/Vis absorption spectra were recorded on a Hewlett-Packard 8452 A diode array spectrophotometer.

2.4 Selective hydrogenation of 1,5-cyclooctadiene and 3-hexyn-1-ol

For the implementation of the flow experiments a system was designed to allow for simultaneous flow of a substrate solution and hydrogen gas (up to 40 bars pressure) through a reactor tube containing the Pd-MonoSil catalysts. The reactor was completely inert, as all wet parts were made of PEEK (polyether ether ketone), PFA (perfluoroalkoxy) or PTFE (polytetrafluoroethylene). The flow of the substrate solution was regulated by an Alltech® model 426 HPLC pump in PEEK. A constant flow of hydrogen gas was adjusted by a flow controller BRONKHORST HI-TEC model F200CV-002-RGD-11-V-MFC. The hydrogen pressure in the reactor was monitored by a BRONKHORST HI-TEC P502C-AGD-11-V-6K0R-EPC meter. The concurrent flows of gas and liquid were driven through a T-shaped PEEK mixer to ensure efficient gas dispersion. The mixed hydrogen–substrate solution stream was introduced into the reactor through a 6-port Rheodyne mod. 9060 switching valve in PEEK. The Pd-MonoSils cladded into a heat-shrinkable PTFE tube together with two glass tubes (4 mm inner diameter) at each end were connected in a top-down arrangement to the system by PFA Swagelok fittings and Chemraz® O-rings (ESI Scheme S1†). At the outlet of the reactor, the product solution

was collected for GC analysis and the excess amount of the hydrogen gas released at atmospheric pressure. Commercially available H₂ (99.995%) was used as received.

In a typical experiment, the Pd-MonoSil catalyst (0.154 g, 1.3 Pd wt%) was first washed under flow with deaerated methanol at a flow rate of 0.15 mL min⁻¹ at room temperature. No leaching of Pd was observed. A deaerated solution of the substrate (cyclooctadiene or 3-hexyn-1-ol) in methanol (0.1 and 0.2 M, respectively) was then allowed to flow through the cladded Pd-MonoSil catalyst (0.154 g, 1.3 Pd wt%) at a constant flow rate of *ca.* 0.12 mL min⁻¹, together with a constant H₂ flow rate of *ca.* 0.5 mL min⁻¹ at room temperature, while the hydrogen gas was released at atmospheric pressure at the outlet of the reactor. For cyclooctadiene the substrate solution flow rate was varied between 0.05 and 0.25 mL min⁻¹ and the H₂ flow rate between 0.3 and 0.55 mL min⁻¹. This resulted in a H₂ pressure at the reactor inlet between 2.2 and 2.4 bars corresponding to a molar ratio $2.2 < \text{H}_2/\text{cyclooctadiene} < 4.5$. For 3-hexyn-1-ol the substrate solution flow rate was varied between 0.05 and 0.25 mL min⁻¹ and the H₂ flow rate between 0.2 and 1.3 mL min⁻¹. This resulted in a H₂ pressure at the reactor inlet between 2.4 and 3.1 bar corresponding to a molar ratio $0.6 < \text{H}_2/\text{hexynol} < 2.5$. Therefore, the pressure drops generated by monolithic reactors were between 1 and 2 bars. The attainment of the steady state conditions (*ca.* 1–3 h) was taken as the reaction start time. The product solution was periodically analyzed for conversion by GC, while 7.2 mL h⁻¹ aliquots were continuously sampled for subsequent Pd leaching analysis.

The content of palladium leached in the catalysis solutions was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) with a Varian 720ES instrument at a sensitivity of 500 ppb. Each sample (7.2 mL) was treated in a microwave-heated digestion bomb (Milestone, MLS-200) with concentrated HNO₃ (1.5 mL), 98% H₂SO₄ (2 mL), 37% HCl (0.5 mL) and a pellet of a digestion aid reagent (0.5 g, 0.1% Se in K₂SO₄). The solutions were analyzed directly after 1 : 5 dilution in 0.1 M hydrochloric acid.

3. Results and discussion

3.1 Characterization of Pd-MonoSil

The functionalization of the parent silica monoliths with Pd nanoparticles was carried out by impregnation of the monoliths with an aqueous solution of Pd(NH₃)₄(NO₃)₂. The initial Pd amount corresponds to 1.5 wt% with respect to silica. The increase of the pH of the impregnation solution leads to an increase of the amount of Pd incorporated within the silica monolith due to an increase of the negative charge of the surface of the silica support. Pd(NH₃)₄²⁺ ions are introduced on the silica surface by ion-exchange with the protons on the silica surface, which compensate the negative charge of the silica. Impregnations at pH 8 (Pd-MonoSil-1), pH 9 (Pd-MonoSil-2) and pH 10 (Pd-MonoSil-3) have been carried out. The amount of impregnated Pd complex was monitored by comparing

adsorption maxima at $\lambda = 300$ nm (adsorption band of Pd ($\text{NH}_3)_4(\text{NO}_3)_2$) of the initial solution and the resulting supernatant solution after the impregnation with the monolith.

The percentage of Pd incorporated within the silica monoliths increases linearly from 4 to 89% with the increase of pH from 8 to 10 and corresponds therefore to a loading of 0.06, 0.66 and 1.33 Pd wt% with respect to silica for Pd-MonoSil-1, -2 and -3, respectively (Fig. 1). Pd-MonoSil-3 with a Pd content of 1.33 Pd wt% (UV/Vis) was subsequently calcined at 550 °C and the Pd complexes in electrostatic interaction with the silica surface are changed by Pd migration into nanoparticles of PdO at the surface of the silica. Then the PdO NPs are transformed into metallic Pd⁰ NPs by reduction under H₂ at 280 °C. The reduction process changes the color of the monolith from yellow (PdO NPs) to brown (Pd⁰ NPs in the monolith) (Fig. 2). EDX analysis carried out on a cross section of the entire monolith confirms this observation with evenly distributed Pd atoms with a calculated amount of 1.28 wt%, in accordance with previous UV/Vis analysis of the supernatant solutions during impregnation.

The nitrogen sorption isotherm at 77 K of Pd-MonoSil-3 (after reduction) shows that the silica mesopores network of the monolith was kept intact throughout the synthesis of Pd NPs in the monolith (Fig. 3). In comparison to the parent silica monolith the surface area decreases slightly from 523 to 490 m² g⁻¹, the mesoporous volume from 1.19 to 1.18 mL g⁻¹ and the mesopore diameter increases slightly from 11 to 12 nm.

From TEM images it can be clearly seen that Pd-MonSil-3 contains well-dispersed Pd NPs featuring particle sizes with

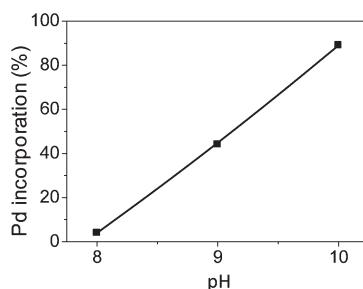


Fig. 1 Amount of impregnated $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ as a function of pH of the impregnation solution.

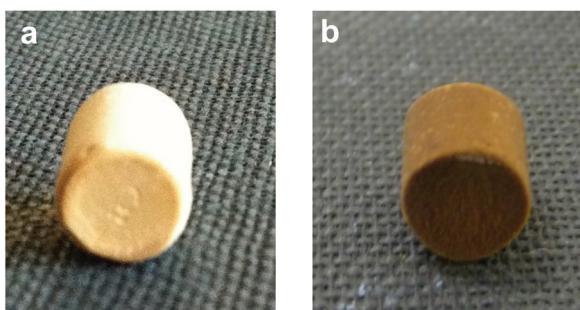


Fig. 2 Pd-MonoSil-3 after calcination at 550 °C (a) and after reduction under H₂ at 280 °C (b).

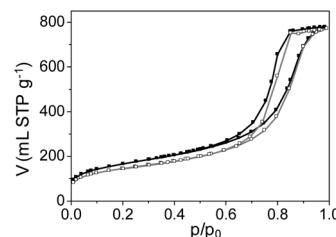


Fig. 3 Nitrogen sorption isotherms at 77 K of (black) the parent silica monolith and (grey) Pd-MonoSil-3.

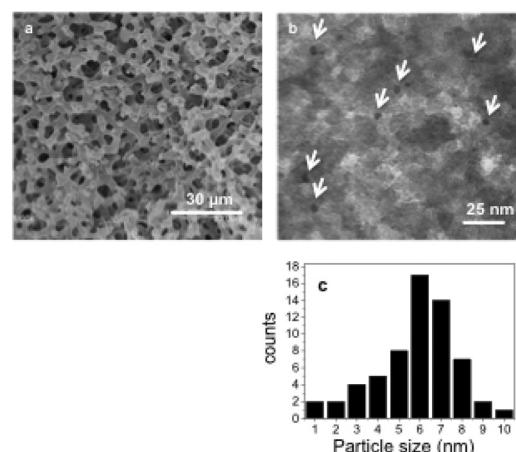


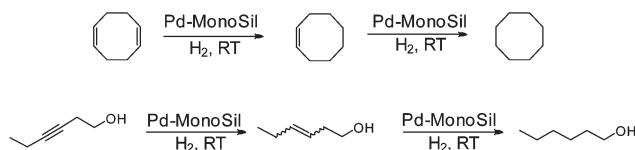
Fig. 4 SEM (a) and TEM (b) images of Pd-MonoSil-3. Arrows indicate the Pd NPs in the skeleton of the silica monolith. (c) Particle size distribution of Pd NPs in Pd-MonoSil.

average diameters of 6–7 nm within the silica monolith (Fig. 4). No particles larger than 11 nm have been detected, which indicates that the Pd NPs were formed within the mesopores (11–12 nm) of the silica monolith. The SEM image of the Pd-MonoSil-3 shows that the homogeneous and isotropic interconnected network of macropores (*ca.* 4 microns) was kept intact during the formation of Pd NPs within the monolith (Fig. 4).

3.2. Selective hydrogenation under continuous flow with Pd-MonoSil

Before performing catalytic reactions, Pd-MonoSil-3 was washed under a flow of 0.15 mL min⁻¹ of methanol. No Pd leaching was evidenced by ICP-OES analysis of the solutions. Pd-MonoSil-3 was used as a catalyst in the hydrogenation under continuous flow at room temperature and low H₂ pressure (2–3 bars) of 1,5-cyclooctadiene (COD) and 3-hexyn-1-ol using methanol as a solvent (Scheme 1).

The efficiency of Pd-MonoSil-3 (1.3 Pd wt%) was first tested for the selective hydrogenation of COD in cyclooctene (COE). As shown in Fig. 5, under the test conditions a constant conversion of 95% and a constant selectivity in COE of 90% were obtained after *ca.* 2 hours and a half under flow. The conversion and the selectivity are controlled by tuning H₂ and substrate flow rates (Fig. 6). Increasing H₂ flow rate increases the



Scheme 1 Model reactions used to evaluate the effectiveness of the pore-flow-through silica monolith in selective hydrogenation: (up) 1,5-cyclooctadiene and (down) 3-hexyn-1-ol.

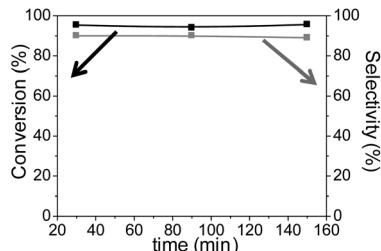


Fig. 5 Hydrogenation of 1,5-cyclooctadiene (0.1 M in methanol) over Pd-MonoSil-3 (1.3 wt Pd%) at room temperature at a H_2 pressure of 2.6 bars under continuous flow (H_2 flow rate 0.5 mL min^{-1} , substrate flow rate 0.12 mL min^{-1}).

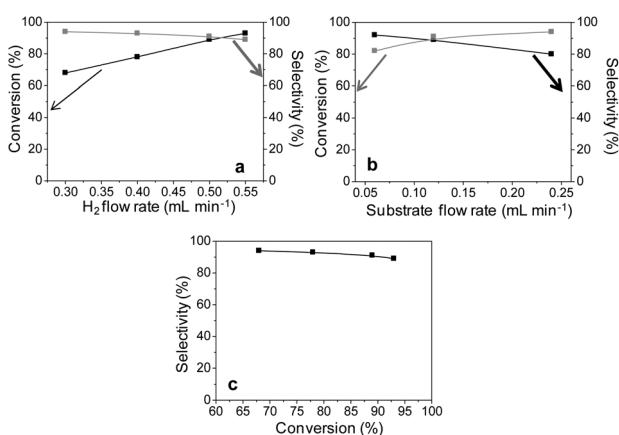


Fig. 6 Hydrogenation of 1,5-cyclooctadiene (0.1 M in methanol) over Pd-MonoSil-3 (1.3 wt Pd%) at room temperature: (a) substrate flow rate 0.12 mL min^{-1} and variable H_2 flow rate (variable $\text{H}_2/\text{substrate}$); (b) constant $\text{H}_2/\text{substrate}$ molar ratio = 4 and variable substrate and H_2 flow rates; (c) selectivity in the cyclooctene product as a function of conversion of cyclooctadiene in the same experimental conditions as in (a).

conversion and changes marginally the selectivity, with a slight decrease noticed from 94 to 89%. Increasing substrate flow rate (at the same H_2 to substrate ratio of 4) decreases slightly the conversion from 92 to 80% due to a decrease in contact time of cyclooctadiene with the catalyst, whilst the selectivity increases from 82 to 94%. The best compromise between conversion and selectivity was reached with a flow rate of substrate of 0.12 mL min^{-1} and a H_2 flow rate of 0.5 mL min^{-1} giving 95% conversion and 90% selectivity. The productivity of the reaction was $4.2 \text{ mmol s}^{-1} \text{ g}^{-1}$ MonoSil or $0.32 \text{ mol s}^{-1} \text{ g}^{-1}$ Pd. The stability of the catalyst proved remarkable as conversion and selectivity were maintained nearly constant over a period of 70 h. During the whole reaction Pd

content was below the detection limit of the ICP-OES instrument, *i.e.* 0.006 ppm, thus indicating that the Pd loss is negligible even after 70 h time-on-stream.

In that time interval only a slight decrease in conversion from 95 to 90% was noticed. Similar conversion and selectivity levels (95–100 and 92–94%, respectively) were obtained using a Pd@alumina membrane reactor for 1,5-cyclooctadiene selective hydrogenation in flow at 50°C and 10 bars of hydrogen pressure.²³ The pore-flow-through monolithic reactor loaded with Pd NPs allows one to reach the same performance under softer conditions (25°C , 2.6 bars) and, above all, demonstrates unique stability with time on stream definitely enabling continuous process operation.

The second reaction investigated using Pd-MonoSil is the stereo-selective hydrogenation of 3-hexyn-1-ol, a reaction of prime importance carried out very efficiently in industry in batch mode using the Lindlar catalyst (Pd NPs deposited on calcium carbonate) (89% selectivity in alkene). A main shortcoming in this reaction is the use of toxic additives as Pb,²³ which can further be found in food products. There is therefore a need for greener catalysts for this reaction. Different additives have been tested on Pd supported catalysts such as quinoline, carbon monoxide, organic bases, sulfides, metal ions such as copper, which are necessary to reach high stereoselectivity in this reaction, namely 99% *cis*-selectivity and 97% yield in 3-hexen-1-ol in batch mode.^{21a}

In order to determine whether this reaction could be implemented in continuous mode, we have evaluated the performance of the Pd-MonoSil (1.3 wt% Pd) microreactor in the selective hydrogenation of 3-hexenyl-1-ol at room temperature with a hydrogen flow rate of 0.7 mL min^{-1} and a substrate flow rate of 0.15 mL min^{-1} . Under these conditions a constant conversion level equal to *ca.* 85% was reached after 3 h under flow while the selectivity into 3-hexen-1-ol (*cis* + *trans*) increased steadily from 70 till 80% during the 7 h of the test (Fig. 7). The substrate conversion and the selectivity in alkene products can be tuned by adjusting the flow rates of the substrate solution and of H_2 gas. Complete conversion of 3-hexyn-1-ol was achieved by increasing H_2 flow rate, but the selectivity in alkenes decreased to 40%. As expected increasing H_2 flow rate increases the conversion by adding more H_2 in contact with the substrate and Pd NPs but decreases the selectivity by forming the 3-hexanol dihydrogenated product. The *cis*-

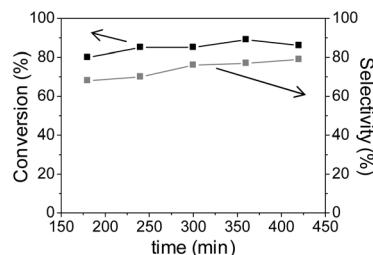


Fig. 7 Hydrogenation of 3-hexyn-1-ol (0.2 M in methanol) over Pd-MonoSil-3 (1.3 wt Pd%) at room temperature and 2.8 bars H_2 under continuous flow (H_2 flow rate 0.7 mL min^{-1} , substrate flow rate 0.15 mL min^{-1}).

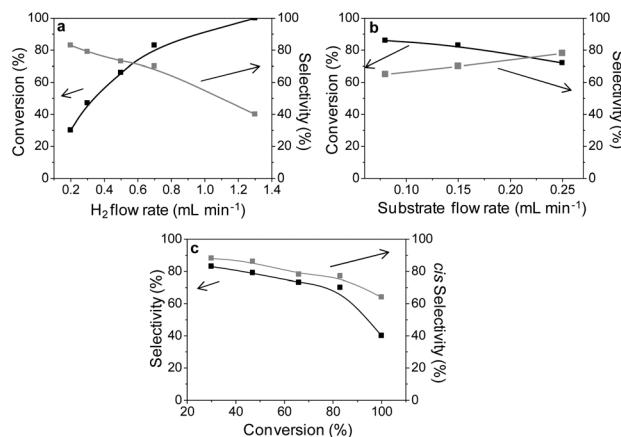


Fig. 8 Hydrogenation of 3-hexyn-1-ol (0.2 M in methanol) over Pd-MonoSil-3 at room temperature under continuous flow with (a) substrate flow rate 0.15 mL min⁻¹ and variable H₂ flow rate (variable H₂/substrate); (b) constant H₂/substrate = 2.7 molar ratio and variable substrate and H₂ flow rates; (c) alkene selectivity and *cis*-selectivity (*cis*-3-hexen-1-ol) as a function of conversion of 3-hexyn-1-ol hydrogenation (same experimental conditions as in (a)).

selectivity decreases from 88 to 64% upon increasing the hydrogen flow rate from 0.2 to 1.3 mL min⁻¹ (Fig. 8c). Higher selectivity in alkene products was achieved, up to 80%, by increasing substrate flow rate at a constant H₂/substrate molar ratio with a minimal decrease of the conversion (72%) (Fig. 8). An increase in the solution flow rate (*i.e.* a decrease of the residence time from 420 to 140 s while keeping a constant H₂/substrate molar ratio) invariably led to an increase in partial hydrogenation. For a constant conversion, the *cis*-selectivity remains constant over time. The best conversion and selectivity in *cis*-3-hexen-1-ol was achieved at a H₂ flow rate of 0.7 mL min⁻¹ and a substrate flow rate of 0.15 mL min⁻¹ and gives a productivity of 9.6 mmol s⁻¹ g⁻¹ MonoSil or 0.75 mol s⁻¹ g⁻¹ Pd.

Although the performances in terms of product selectivity stand below those of the Lindlar catalyst these preliminary results highlight the high potential and the flexibility of the Pd-MonoSil operated in continuous flow for a rather complex selective hydrogenation reaction. Pd-MonoSil can be used under flow conditions, with enormous benefits from an industrial point of view in terms of long-term productivity and space-to-time yield (STY): *e.g.* for 3-hexyn-1-ol hydrogenation, the STY (calculated from ref. 20e) of the Lindlar catalyst is 26 g l⁻¹ h⁻¹ *vs.* 270 g l⁻¹ h⁻¹ for Pd-MonoSil. Furthermore, the increase of selectivity with time on stream with Pd-MonoSil suggests some negative influence of surface sites (silanol groups), which can be amended by passivation treatments. The effect of green additives can be readily investigated. Work in these directions is in progress.

4. Conclusion

Pore-flow-through silica monoliths featuring a bimodal distribution of macropores (4–5 µm) and mesopores (11 nm) have been loaded with Pd nanoparticles and implemented as

microreactors for the continuous selective hydrogenation at room temperature of 1,5-cyclooctadiene and 3-hexyn-1-ol model substrates. In both reactions, the catalytic microreactor demonstrates remarkable stability of the activity with time on stream. The substrate conversion level as well as the selectivity into the target product can be readily controlled by independently adjusting the hydrogen and substrate flow rates. In the selective hydrogenation of 1,5-cyclooctadiene, a conversion of 95% and a selectivity of 90% in monohydrogenated product, constant over a period of 70 h, have been reached. These figures correspond to a productivity of 4.2 mmol s⁻¹ g⁻¹ MonoSil (or 0.32 mol s⁻¹ g⁻¹ Pd) and compare well with benchmark membrane based catalysts. In the stereoselective hydrogenation of 3-hexyn-1-ol a constant conversion of 85% and a selectivity of 80% into the *cis* isomer have been obtained over a period of 7 h, corresponding to a 10 times higher productivity in comparison to batch using the Lindlar catalyst. The versatility and flexibility of the monolithic microreactor in triphasic systems have been demonstrated and open new perspectives for the implementation of fine chemicals synthesis in continuous flow mode.

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