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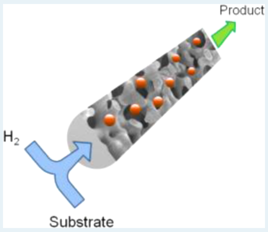
Continuous Partial Hydrogenation Reactions by Pd@unconventional Bimodal Porous Titania Monolith Catalysts

Noemi Linares,[†] Sarah Hartmann,[‡] Anne Galarneau,*[,‡] and Pierluigi Barbaro*[,†]

[†]Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche, 50019 Sesto Fiorentino, Italy
[‡]Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, 34296 Montpellier, France

Supporting Information

ABSTRACT: Pd nanoparticles are immobilized by a green procedure onto unconventional dual porosity titania monoliths. The material is used in catalytic continuous-flow hydrogenation reactions showing excellent efficiency, selectivity, and durability.



KEYWORDS: *Pd nanoparticles, catalysis, monolith, flow reaction, hydrogenation*

Continuous-flow catalytic processes represent a convenient alternative to heterogeneous phase batch systems in terms of efficiency, safety, waste emission, purification, automation, space and energy consumption,[1−3] thus providing a considerable contribution to the sustainability of long-term production of chemical compounds, particularly fine-chemicals.[4,5] To this purpose, different types of microfluidic flow reactors have been developed so far.[6−10] Monolith-based reactors have attracted increasing interest in recent years[11] because of their significant advantages compared to conventional packed-bed systems, including better heat and mass transfer, lower pressure drop, narrow residence time distribution, which ultimately result in higher productivities.[12] Polymeric materials were the first to demonstrate the utility of monoliths in the catalytic fine-chemicals production under flow.[13−16] However, despite their unquestionable interest, polymer-based monoliths may present some drawbacks from an engineering point of view, such as volume and porosity changes with swelling, thermal, mechanical, and chemical stability, shrinking phenomena, back pressure evolution at high flow rate due to limited porosity, which adversely affect their performance as catalyst supports.[17−19] To avoid these problems different types of inorganic monoliths have been synthesized, including conventional ceramic monoliths obtained by extrusion, that are largely employed in conversion of raw materials, pollutant abatement, and automotive exhaust gas treatment.[20,21] Only two types of unconventional inorganic monolith materials were reported for continuous flow operations in fine chemical synthesis, and both based on silica. One was obtained by emulsion templating synthesis and featured a disordered macropores network for transesterification reactions;[22] the other one, showing a well-defined hierarchical porosity network of flow-through macropores (2−10 μm) and diffusive mesopores within the struts (2−20 nm), was obtained by a combination of spinodal decomposition and sol−gel transition, and it was used for diverse organic catalysis.[23] These latter materials can be particularly useful in the synthesis of fine chemicals, being able to address the need of both efficient processing (within small pores) and fast diffusion (by macropores).[24,25] Despite these favorable features, this type of monoliths have never been explored in highly selective transition-metal catalyzed reactions, for example, in hydrogenation reactions. Selective hydrogenation of hydrocarbons with multiple C═C and/or C≡C bonds to achieve partial hydrogenation products is a highly desired and challenging process in the pharmaceutical, agrochemical, and petrochemical industries.[26,27] 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. Partial hydrogenation reactions are also crucial in industrial polymerization processes to achieve the complete elimination of alkynes and dienes from alkene feedstocks.[28]

Herein we report the first example of a microreactor based on metal nanoparticles (MNPs) supported onto well-defined hierarchical porosity titania monolith and its use in continuous flow catalytic partial hydrogenation reactions under mild conditions. Motivations for the choice of titania as inorganic support were multiple: (1) TiO_2 features a better chemical resistance compared to other oxide materials,[29] (2) titania often shows a positive influence on the activity of the immobilized catalyst with respect to other supports,[30,31] (3) use of TiO_2 may contribute to reduce sintering of Pd NPs.[32] Apart from the use in chromatography and in photolysis reactions,[33,34] previous uses of bimodal TiO_2 in catalysis are restricted to reactors packed with powdered materials for the CO_2-reforming reaction of methane and for the hydrogenation of crotonalde-

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hyde under high temperatures and pressures.[35,36] In the present work, single-phase anatase monoliths with typical dimensions 4 × 30 mm (diameter × length) were prepared, featuring a reproducible, homogeneous, and isotropic open-cell network with a dual porosity: (1) uniformly distributed flow-through macropores of average diameter 2.5 μm (mercury porosimetry, X-ray tomography, SEM), (2) diffusive mesopores of 6.0 nm size, with a large surface area of 150 $m^2 g^{-1}$ (N_2 sorption), due to the interstices of TiO_2 nanocrystallites (7−8 nm X-ray diffraction (XRD), transmission electron microscopy (TEM)) forming the monolith skeleton of about 1 μm thickness (scanning electron microscopy (SEM)) (Figure 1, Table 1) (see Supporting Information). After cladding the monolith into a heat shrinkable Teflon tube, and connecting it to the continuous-flow system described below, Pd NPs were effectively synthesized in situ by a smooth, one-pot procedure involving an appropriate flow of $Pd(NO_3)_2$ aqueous solution through the monolith, followed by reduction under a H_2 flow (3 bar, 2.0 mL min^{-1}, 21 °C, 1 h). The procedure led to a slight restructuring of the titania crystallites, resulting in larger mesopores (7.4 nm cavity; 4.1 nm windows) suitable to accommodate Pd NPs (5 nm) with a narrow size distribution (TEM, Figure 2) and evenly distributed within the monolith skeleton, as shown by the uniform radial and longitudinal loading of the metal (energy dispersive spectroscopy (EDS), Figure 3).[22] Typical Pd content was 0.24 wt % (ICP-OES).

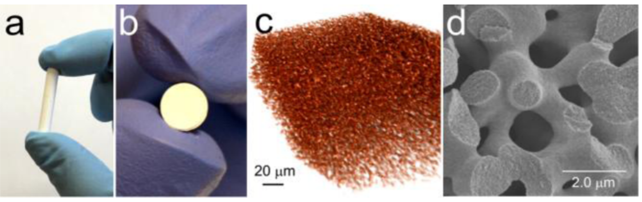


Figure 1. Images of the bimodal TiO_2 monolith with well-defined macroporosity: (a, b) optical; (c) X-ray tomography; (d), SEM.

Table 1. Textural Characteristics of Tested Porous Materials[a]

	macropores		mesopores		
material	*D* (μm)	*V* ($cm^3 g^{-1}$)	*D* (nm)	*V* ($cm^3 g^{-1}$)	*S* ($m^2 g^{-1}$)
TiO_2 monolith	2.5	1.10	6.0	0.16	148
$Pd@TiO_2$ monolith[b]	2.5	1.10	7.4	0.16	122
TiO_2 xerogel[c]			6.9	0.29	217
$Pd@TiO_2$ xerogel[d]			6.8	0.23	166
SiO_2 monolith[e]	4.0	1.80	12.5	1.15	550
$Pd@SiO_2$ monolith[f]	4.0	1.80	12.5	1.11	552

[a]BET surface area (*S*), porous volume (*V*), pore diameter (*D*). [b]0.24 wt % Pd. [c]Xerogel powder. [d]0.73 wt % Pd. [e]See ref 23. [f]0.32 wt % Pd.

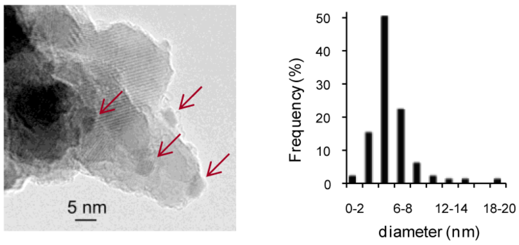


Figure 2. Left: TEM image (340 k magnifications) of $Pd@TiO_2$ monolith showing the diffraction planes of anatase nanocrystals and supported spheroidal Pd NPs (arrows). Right: size distribution of Pd NPs.

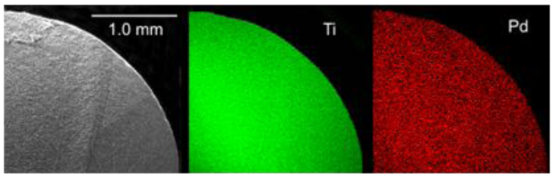
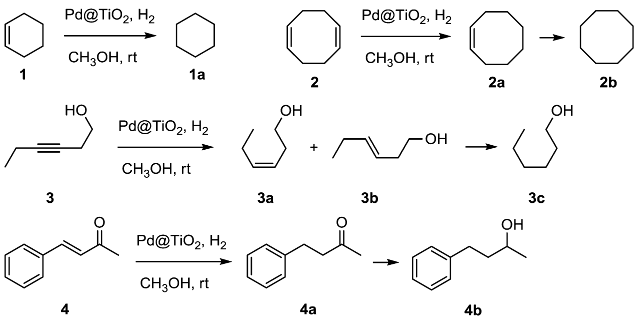


Figure 3. ESEM image (30 keV, 50 magnifications) and EDS maps of a quadrant of an equatorial section of $Pd@TiO_2$ monolith. Left: secondary electrons image; center: Ti map (Ti Kα1); right: Pd map (Pd Lα1).

The as-prepared $Pd@TiO_2$ cladded monoliths were employed as catalyst in continuous flow hydrogenation reactions of unsaturated C−C bonds, using a homemade microreactor based on concurrent flows of substrate solution and gas reactant (see Supporting Information). Various probe substrates were chosen to test the efficiency of the catalyst in terms of productivity and selectivity in partial hydrogenation: cyclohexene **1**, 1,5-cyclooctadiene **2**, 3-hexyn-1-ol **3**, benzylideneacetone **4** (Scheme 1). All reactions were monitored for conversion and selectivity with time. Different flow rates of solution and H_2 gas were examined.

Scheme 1. Catalytic Hydrogenations over $Pd@TiO_2$ Monoliths



The hydrogenation reaction of **1** was used to evaluate the productivity of the novel $Pd@TiO_2$ monolith catalyst and to compare it with that of the corresponding packed-bed and batch (stirred tank) systems and of the parent SiO_2 monolith (Table 1), under similar reaction conditions. Representative results are reported in Table 2 in terms of both turnover frequency (TOF = mol $_{product}$/mol $_{Pd}$ × h) and space-to-time yield (STY = kg $_{product}$/liter $_{reactor\ volume}$ × h).[37] Several solvents were tested, of which methanol was the most appropriate. Cyclohexene conversion using $Pd@TiO_2$ monolith was about 90% under very mild conditions (room temperature (rt), H_2 2.4 bar -3.0 mL min^{-1}, methanol 0.12 mL min^{-1}).[38,39] Noteworthy the catalyst exhibited excellent long-term stability as *it retained >99% of its starting activity after 3 days time-on-stream,* providing an overall turnover number (TON) > 125000 (Figure 4). In addition, the $Pd@TiO_2$ monolith could be reused *with no need of any reactivation treatment* while no Pd leaching in solution was detected by ICP-OES. Three comparative elements can be highlighted from Table 2. (1) *Monolithic versus packed-bed and batch reactors.* A crushed fraction of Pd@

Table 2. Productivities for Batch and Flow Hydrogenations of 1 Using Solid Supported Pd NPs Catalysts[a]

entry	reactor		catalyst	TOF (h^{-1})	STY ($kg\ L^{-1}\ h^{-1}$)
1	batch		$Pd@TiO_2$ ground monolith	932	0.01
2	flow	packed-bed	$Pd@TiO_2$ xerogel	295	0.47
3			$Pd@TiO_2$ ground monolith	1131	0.95
4	flow	monolith	$Pd@TiO_2$ monolith	1673	4.02
5			$Pd@SiO_2$ monolith	272	0.27

[a] Reaction conditions: methanol, rt. The productivity in the batch reactor was calculated after conversion of the same amount of substrate per mol of Pd as in the flow system, using the same catalyst under similar conditions. Productivities in the flow reactors were calculated at comparable conversions. Sieved fraction 60−120 μm for batch and packed-bed.

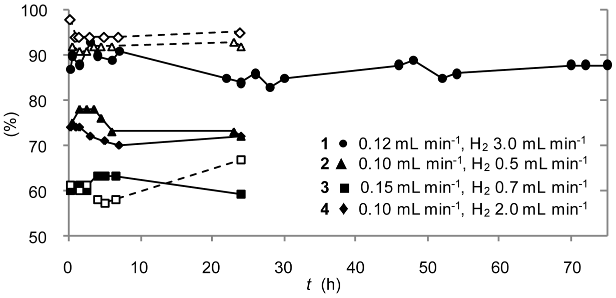


Figure 4. Selected results of conversion (filled symbols, solid lines) and selectivity (empty symbols, dashed lines) to the monohydrogenated products in continuous-flow hydrogenations by $Pd@TiO_2$ monolith catalysts (0.24% Pd w/w) as a function of time-on-stream (rt, methanol). Start time: attainment of steady state conditions (ca. 1 h).

TiO_2 monolith catalyst (60−120 μm grain size) was used both in a standard batch device and in the continuous flow system using a packed-bed arrangement. In agreement with previous results on metal-free bimodal porous SiO_2 monolithic catalysts,[23] the entire $Pd@TiO_2$ monolith in flow was more efficient than both the batch and packed-bed systems, under analogous conditions. Compared to the classical laboratory flask, the $Pd@TiO_2$ monolith exhibited about 2 times higher TOF and about 400 times higher STY (Table 2, entry 1 and 4). Compared to the packed-bed system, the productivity of the monolith was about 50% higher in terms of TOF and about 4 times higher when referred to the reactor volume (Table 2, entry 3 and 4).[22] These findings highlight the superiority of the monolithic reactor with respect of packed-bed and batch design.[40] (2) *Mesoporosity versus bimodal meso-/macroporosity.* Flow experiments were carried out using a commercial tubular reactor packed either with Pd@mesoporous TiO_2 xerogel or $Pd@TiO_2$ ground monolith (same sieved fractions), providing a remarkable higher STY and about 4 times higher TOF in the case of the meso-/macroporous catalyst (Table 2, entry 2 and 3). This result can be attributed to the specific texture of the hierarchical monolith which avoid the site inhibition effect usually found in purely mesoporous powdered material due to pore clogging.[41] (3) *TiO_2 versus SiO_2 monoliths.* These monoliths have similar hierarchical porosity textures (Table 1). Pd NPs were immobilized onto SiO_2 monoliths using the same procedure adopted for TiO_2, which resulted in comparable Pd loading (0.2−0.3 wt % Pd). Under analogous flow conditions, the $Pd@TiO_2$ monolith catalyst showed much higher TOF (6 times) and STY (15 times) than the $Pd@SiO_2$ monolith (Table 2, entry 4 and 5). A combination of factors may be responsible for this effect, including the different surface chemistry of the materials[32,42] and the strong metal−support interactions of TiO_2 anatase.[32,43] The above results demonstrate the advantages of the $Pd@TiO_2$ monolith catalyst for the development of long-tem hydrogenation reactions under continuous flow.

Having established a highly active catalytic system, we turned our attention to examine the selectivity performance. Representative results are graphically reported in Figure 4 for the substrates investigated (see Supporting Information). Yields in the monohydrogenated products were tuned by adjusting the H_2 and the solution flow rates, as illustrated as follows for the hydrogenation reaction of **2** as representative example. At a fixed solution flow rate (i.e., for the same residence time), an increase of the H_2 flow resulted in significantly higher conversions (up to 100%) and in small selectivity drop (Figure 5a). The effect is attributed to the change in the H_2:substrate molar ratio upon varying the hydrogen flow rate, as the overall H_2 pressure at the reactor inlet was not significantly affected by small differences in the H_2 flow. An increase of the solution flow rate (i.e., a decrease of the residence time while keeping a constant H_2:substrate molar ratio) invariably led to an increase of selectivity in partial hydrogenation reactions, which could be easily brought to 100%, although with some conversion decrease (Figure 5b). Accordingly, in the case of **2**, the monohydrogenated product **2a** could be obtained in 77% yield by appropriate selection of the above experimental parameters (Supporting Information, Table S4).[22] The best compromises between conversion and selectivity for all substrates were obtained for residence times in the range 40−80 s, room temperature and about 2 bar H_2. Under these conditions, all reactions were typically accomplished with good conversions

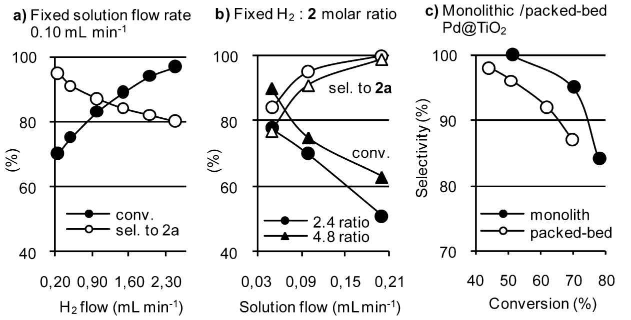


Figure 5. Continuous-flow hydrogenations of **2** over $Pd@TiO_2$ monolith catalysts (0.24% Pd w/w, rt, methanol) as a function of the: (a) H_2 flow rate at fixed 0.1 mL min^{-1} solution flow (residence time 68 s, H_2:**2** ratio 2.4−24.0); (b) solution flow rate at fixed H_2:**2** ratios (H_2 0.14−0.93 mL min^{-1}, residence time 34−135 s); (c) reactor design: entire vs ground monolith (fixed H_2:**2** ratio = 2.4). Selectivity to **2a** = **2a**/(**2a** + **2b**).

(60–90%) and selectivity: **2a** 91%, **3a+b** 63% (87% of which **3a**), **4a** 95% (Figure 4). Pd leaching in solution was below the ICP-OES detection limit in any case. Finally, compared to the packed-bed configuration using the crushed material, the monolith catalyst provided a higher selectivity at the same conversion, as graphically shown if Figure 5c and Supporting Information, Figure S10 for the partial hydrogenation reaction of **2**. This demonstrates that the entire monolith is superior to a packed-bed system also in terms of selectivity.

The hydrogenation of **2** to **2a** under continuous flow conditions was previously reported using an inorganic flow-through catalytic membrane reactor (0.04%Pd@Al_2O_3).[44,45] Compared to the Pd@TiO_2 monolith catalyst (91% selectivity at 75% conversion), similar selectivity was obtained at greater conversion (95%@100% conversion), under 50 °C and 10 bar H_2. However, our system offers significant advantages in terms of energy requirements, process miniaturization, catalyst lifetime, and reusability (no need of regeneration). *Cis*-3-hexen-1-ol leaf alcohol **3a** is an important fragrance component with a production of about 400 t y^{-1}.[46] It is industrially obtained by the batch hydrogenation of **3** using the Lindlar catalyst (Pd on $CaCO_3$ doped with Pb).[47] Even if the industrial process is slightly more selective, to the best of our knowledge the Pd@TiO_2 monolith system represents the first example of flow process for this reaction and also avoids the use of toxic Pb, with clear benefits in terms of safety, environmental impact, and productivity, as previously shown.

In conclusion, we have described the first example of a microfluidic flow reactor based on metal nanoparticles embedded onto an entirely inorganic, unconventional TiO_2 monolith. The system exhibits very good efficiency and excellent durability in catalytic partial hydrogenation reactions of simple substrates under a continuous flow of liquid and gas phases and very mild conditions. This remarkable performance can be attributed to the dual porosity of the monolith, featuring a narrow size distribution of meso- and macropores which guarantee a small pressure drop, a high mass transfer, and a uniform residence time for reactants throughout the catalytic material,[48] to well dispersed Pd NPs homogeneously distributed within the solid support, and to the intrinsic chemical interactions of titania with Pd. The results obtained highlight the great potential of Pd@TiO_2 monolithic reactors in the sustainable production of fine-chemicals. They offer the possibility to implement effective hydrogenation reactions in flow for long-term productivity, coupled with decreased reactors size compared to conventional batch and packed-bed systems, and to grant cleaner and less energy demanding processes.

The devised catalytic system displays some additional advantages: (i) the procedure for the preparation of the supported Pd NPs is extremely simple, effective, and environmentally friendly: it does not require long procedures (e.g., batch impregnation), harsh conditions (high temperatures or pressures, calcination), elaborate apparatus (chemical vapor deposition), use of an excess of hazardous/polluting reducing agents ($NaBH_4$, N_2H_4), thus satisfying most Principles of Greener Nanomaterial Production,[49] (ii) the catalyst is generated in situ, hence there is no need to isolate nor store it, (iii) the Pd NPs are immobilized using a flow approach, which represents a significant practical advantage for potential industrial applications, and also eliminates the presence of any erratic metal particle, in fact, (iv) no Pd is leached into solution even upon prolonged exposure to catalytic conditions, (v) the inorganic material eliminates most of potential drawbacks associated with polymeric monoliths, as above-discussed. The implementation of MNPs-based monolithic reactors represents an important step forward in a topical area of chemistry.[50,51] It also opens up the exciting perspective to engineer effective bifunctional flow reactors combining chemical- and photocatalysis.[52]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of synthesis, characterization, and catalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pierluigi.barbaro@iccom.cnr.it (P.B.), anne.galarneau@enscm.fr (A.G.).

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Notes

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