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Supporting information for

Continuous flow synthesis of Rh and Pd nanoparticles onto ion-exchange borate monoliths: application to selective catalytic hydrogenation of unsaturated carbonyl compounds under flow conditions

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S.1 General info

All reaction and manipulations were performed under nitrogen by using standard Schlenk techniques, unless otherwise stated. The MonoBor monolith was prepared as previously described into a commercial Omnifit Labware Glass Column (3.0 i.d. x 25 length mm) equipped with 0.2μm PE frit to ensure an optimum flow distribution [S1]. The polymer monolithic material features an isotropic microstructure based on a 'rigid' skeleton of ca. 6 μm thickness forming a narrow size distribution of interconnected flow-through pores of 10 μm size. The Pd@MonoBor catalyst was prepared as previously described [S2]. All the other reagents were commercial products and were used as received without further purification. [Rh(NBD)$_2$]BF$_4$ was obtained from Aldrich. ESEM (Environmental Scanning Electron Microscopy) measurements were performed on a FEI Quanta 200 microscope operating at 25 KeV accelerating voltage in the low-vacuum mode (1 torr) and equipped with an EDAX Energy Dispersive X-ray Spectrometer (EDS). X-ray maps were acquired on the same instrument using a 512x400 matrix, 100 μs dwell time and 25 KeV accelerating voltage. TEM (Transmission Electron Microscopy) analyses were performed using a CM12 PHILIPS instrument at 120 KeV accelerating voltage. The sample preparation was carried out by dispersing the grinded resin into about 1 ml of ethanol and treating the solution in an ultrasonic bath for 30 min. Successively, a drop of solution was deposited onto a carbon coated Cu TEM grid and the solvent left to evaporate. XRD (X-ray Diffraction) patterns were recorded with a PANanalytical XPERT PRO powder diffractometer, employing CuKα radiation (λ=1.54187 Å), a parabolic MPD-mirror and a solid state detector (PIXcel). The samples were prepared on a silicon wafer (zero background) that was rotating (0.5 rotations per second) during acquisition. All XRD patterns were acquired at room temperature in a 2θ range from 30 to 55°, applying a step size of 0.0263° and a counting time of 295.29 seconds. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded at 400.13 and 100.613 MHz, respectively, on a Bruker Avance DRX-400 spectrometer (294K). Chemical shift in ppm are relative to tetramethylsilane as external reference. The metal content in the supported catalysts was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) with a Varian 720ES instrument at a sensitivity of 500 ppb. Each sample (50-100 mg) was treated in a microwave-heated digestion bomb (Milestone, MLS-200, 20 min.@ 220 °C) with concentrated HNO_3 (1.5 mL), 98% H_2SO_4 (2 mL), and 0.5 mL of H_2O_2 30%. After filtration, the solutions were analysed. The content of metal leached in the solutions recovered after catalysis was determined by ICP-OES. The solutions were analysed after 1:5 dilution in 0.1 M hydrochloric acid. GC-analyses were performed on a Shimadzu GC 2010 gas chromatograph equipped with flame ionization detector and a 30 m (0.25 mm ID, 0.25 μm FT) VF-WAXms fused silica capillary column. GC-MS analyses were performed on a Shimadzu QP5000 apparatus equipped the same column. Reactions under a controlled pressure of hydrogen were performed using a H_2 generator Parker H2PEM-260.

S.2 Continuous flow reactor system

Reactions under continuous flow were carried out using a reactor system constructed at Istituto di Chimica dei Composti OrganoMetallici, Sesto Fiorentino (Italy). The system was designed to allow for a simultaneous flow of substrate solution and hydrogen gas through a reactor tube containing the heterogeneous catalyst. The reactor was completely inert, as all wet parts were made of PEEK, PFA or PFTE. A constant flow of 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 equipped with a 2□m filter to ensure efficient gas dispersion. The mixed hydrogen-substrate solution stream was introduced in the reactor through a 6-port Rheodyne mod. 9060 switching valve in PEEK. The solid Rh@MonoBor catalyst was fitted into a commercial tubular glass column (Omnifit, 3 mm i.d. × 25 mm length) equipped with 0.2 μm PE frits. The reactor system was equipped with a temperature controller accurate to ± 0.5 °C. At the outlet of the reactor, the product solution was collected for GC analysis and the excess amount of the hydrogen gas released to the atmospheric pressure. The reaction products were unequivocally identified by the GC retention times, mass and NMR spectra of those of authentic specimens.

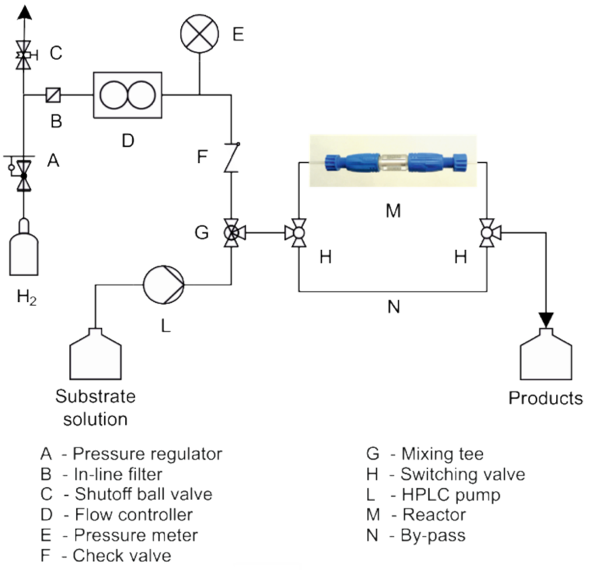


Fig. S1. Scheme of the continuous flow monolithic reactor system used.

S.3 Synthesis and characterization of Rh@MonoBor catalyst

A solution of $[Rh(NBD)_2]BF_4$ in MeOH (0.013 M) was flown through a MonoBor monolithic column (3.0 i.d. x 25 length mm, 29 mg dry material) at 0.5 ml min^{-1} for 3 h using an HPLC pump and an endless loop system. The yellow monolith obtained was then washed with methanol (0.5 ml min^{-1} for 30 min). After connection to the flow reactor system described above, H_2 (2 ml min^{-1}, typical pressure measured at the reactor inlet 1.5 bar) and methanol (0.5 ml min^{-1}) were allowed to flow simultaneously through the impregnated monolith for 3 h at r.t. The as-obtained grey material was then washed with methanol (0.5 mL min^{-1} for 15 min) under hydrogen, before being directly used as catalyst in hydrogenation reactions, or dried under a N_2 stream (0.2 mL min^{-1} for 12 h) before being analysed by ICP-EOS and EDS to give a typical Rh loading of 0.82 % (w/w). EDS spot spectra recorded on radial and longitudinal sections of the monolithic catalyst showed the metal to be evenly distributed within the support. Twenty spectra were typically recorder both for longitudinal and radial sections at different monolith depth showing the same Rh content within ± 0.04 %.

S.4. Catalytic reactions under continuous flow

In a typical experiment, a deaereated solution of substrate in methanol (0.05M) was allowed to flow through the Rh@MonoBor column catalyst (29 mg, reactor volume 176 μl) at 0.05 mL min^{-1} together with a H_2 flow of 0.29 ml min^{-1} at r.t. This resulted in a H_2 pressure at the reactor inlet of ca. 1.22 bar (corresponding to a H_2:Substarte molar ratio of ca. 5.7), while the hydrogen gas was released at atmospheric pressure at the outlet of the reactor. Therefore, the pressure drop generated by monolithic reactor was ca. 0.2 bar. The attainment of the steady state conditions (ca. 1 h) was taken as the reaction start time. The reaction was typically monitored for 7 h time-on-stream by periodically analysing the product solution for conversion and selectivity by GC, while 5.0 ml aliquots were sampled at 1 h intervals for Rh leaching determination by ICP-OES. The amount of Rh in solution was below the detection limit in each sample (0.006 ppm). Selected results are reported in Table S1.

S.5 Catalytic hydrogenation results

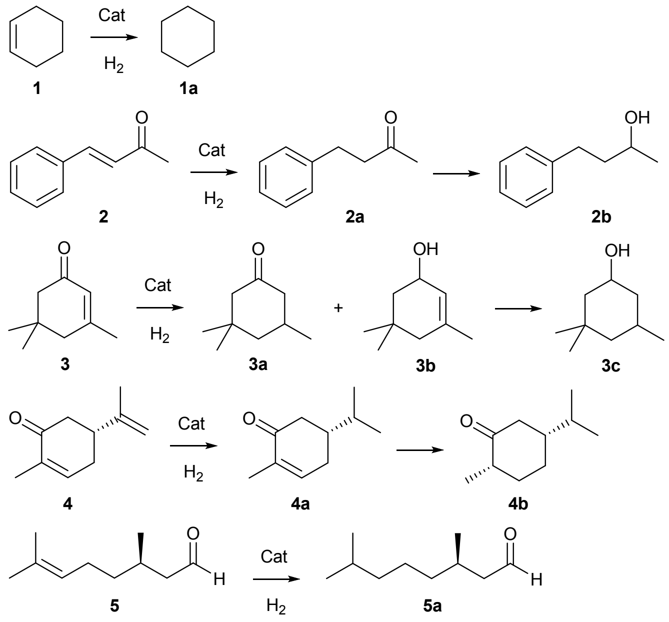


Fig. S2. Sketch of the substrates investigated and products detected, with labelling scheme adopted.

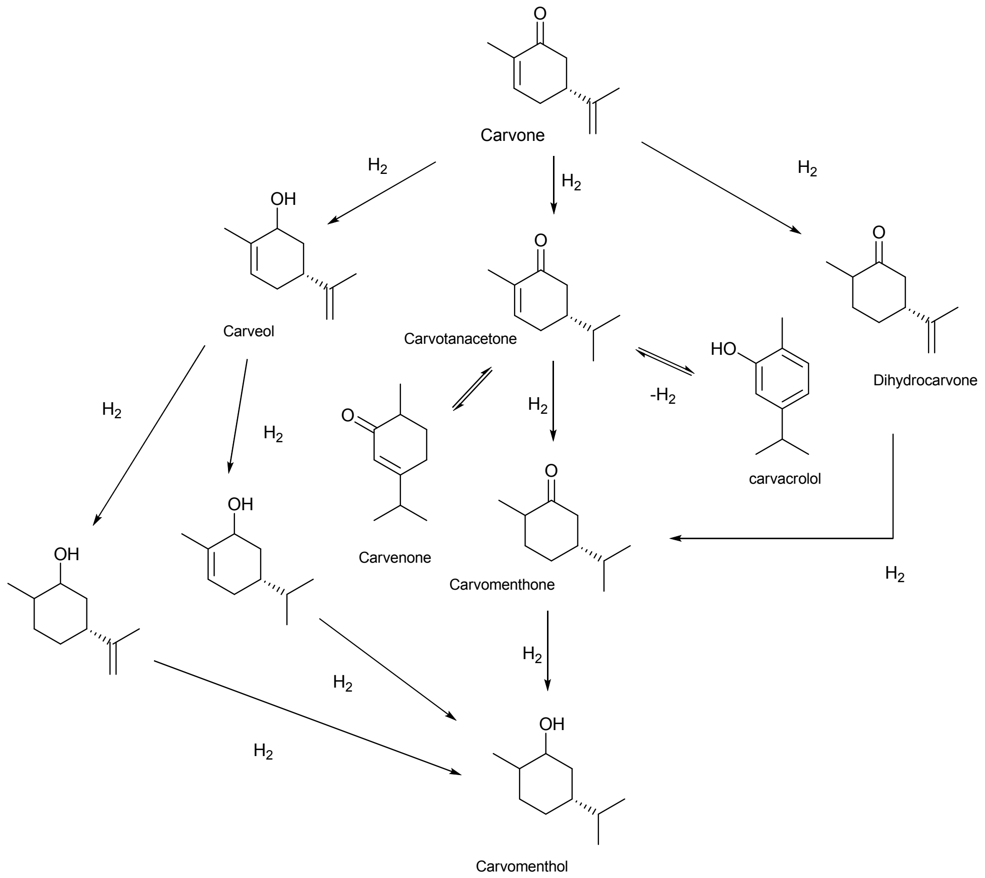


Fig. S3. Sketch of potentially accessible product from carvone under metal-catalysed hydrogenation conditions.

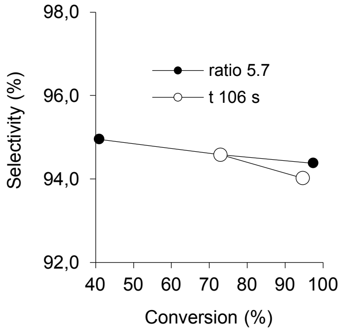
Table S1 Selected data for continuous flow hydrogenation reactions by M@MonoBor monolithic catalyst.

Substrate	Reaction conditions[a]						Conversion[e] (%)	Productivity[f]				Main product		
	Catalyst	Solution		H_2		H_2/sub.[d] ratio		$mol_{prod}\ g_M^{-1}\ h^{-1}$	TOF_{tot} (h^{-1})	TOF_{surf}[g] (h^{-1})	STY ($kg\ l^{-1}\ h^{-1}$)		Selectivity[h] (%)	Yield[i] (%)
	M	Flow rate ($ml\ min^{-1}$)	τ[b] (s)	Flow rate ($ml\ min^{-1}$)	Pressure[c] (bar)									
1 cyclohexene	Rh	0.40	26	1.95	1.8	3.6	98.1 ± 1.0	9.9	1020	3643	1.1	**1a**	100	98.1
2 *trans*-4-phenyl-3-buten-2-one[l]	Rh	0.05	211	0.29	1.2	5.7	97.4 ± 0.9	0.6	63	225	0.1	**2a**	94.4	92.0
	Pd	0.05	211	0.25	1.4	5.7	100	0.8	83	193	0.1	**2a**	94.6	94.6
	Pd	0.10	106	0.47	1.5	5.7	99.5 ± 0.1	1.6	166	386	0.3	**2a**	96.0	95.5
3 isophorone[m]	Rh	0.20	53	0.90	1.4	8.2	91.4 ± 0.4	1.4	142	507	0.3	**3a**	96.3	88.0
	Pd	0.20	53	0.90	1.4	8.2	18.5 ± 0.5	0.3	37	86	0.1	**3a**	100.0	18.5
	Pd	0.05	211	3.60	1.3	124	91.9 ± 1.0	0.4	46	107	0.1	**3a**	100.0	91.9
4 (*R*)-carvone[n]	Rh	0.18	59	0.43	1.2	11.9	92.0 ± 0.8	0.4	43	154	0.1	**4a**	77.6	71.4
	Rh	0.10	106	1.00	1.2	49	100	0.3	26	93	0.1	**4b**	85.7	85.7
	Pd	0.18	59	0.43	1.2	11.9	100	0.6	60	140	0.1	**4b**	67.1	67.1
	Pd	0.50	21	1.09	1.4	11.9	90.8 ± 0.6	1.4	151	351	0.2	**4a**	44.5	40.4
5 (*R*)-citronellal[n]	Rh	0.03	352	3.50	1.3	594	57.0 ± 0.4	0.1	4	14	0.1	**5a**	100	57.0
	Pd	0.03	352	3.60	1.2	582	97.1 ± 0.9	0.1	10	23	0.1	**5a**	99.0[p]	96.2
	Pd	0.03	352	0.25	1.1	38	95.5 ± 0.6	0.1	10	23	0.1	**5a**	99.0[p]	94.6

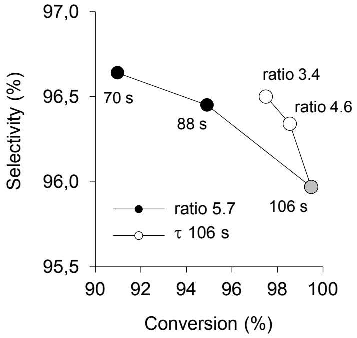
[a] Methanol solution 0.10 M, room temperature. Dry catalyst 29 mg, 0.82 % (w/w) Rh, 0.67 % (w/w) Pd. Reactor volume 176 µl. [b] τ = residence time. [c] Pressure measured at the reactor inlet. [d] Hydrogen to substrate molar ratio. [e] Data from GC analysis. Start time: attainment of steady state conditions, ca. 1h. Average value over 7 h time-on-stream. [f] Calculated from conversion average value. [g] TOF corrected for surface-exposed metal atoms, as inferred by TEM. [h] For example, **2a** selectivity = **2a**/(**2a**+**2b**). [i] Amount of indicated product in the reaction mixture. [l] 0.05 M. [m] 0.03 M. [n] 0.01 M. [p] Ca. 1% menthol.

S.6 Conversion / selectivity diagrams

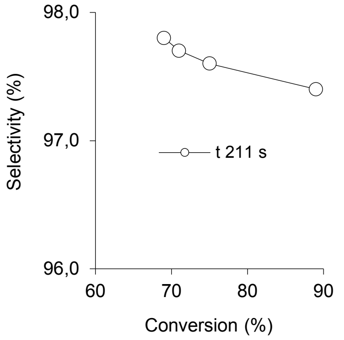
Conversion / selectivity diagrams are obtained at fixed H_2:substrate molar ratio by varying the residence time, or at fixed residence time by varying the H_2:substrate molar ratio, as indicated. Small changes in the H_2 flow rate slightly affected the H_2 pressure at the reactor inlet, while significantly modified the H_2: substrate ratio



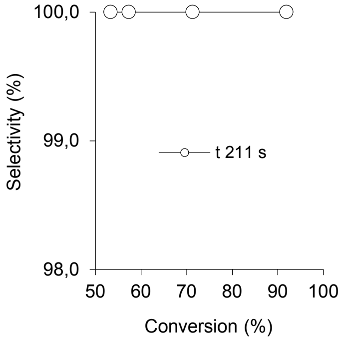
Substrate **2** over Rh@MonoBor, H_2:substrate molar ratio = 5.7 – 45.4, residence time 42 - 211 s



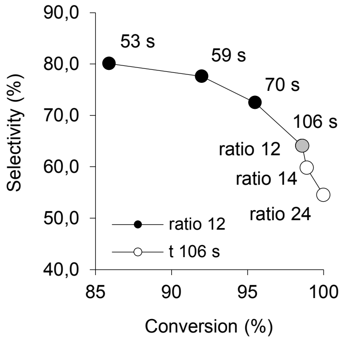
Substrate **2** over Pd@MonoBor, H_2:substrate molar ratio = 3.4 – 5.7, residence time 70 - 106 s.



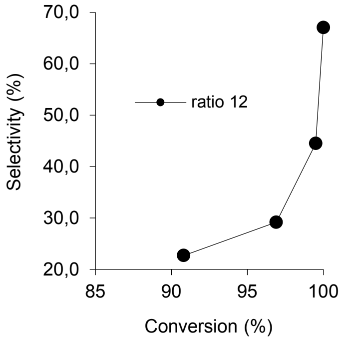
Substrate **3** over Rh@MonoBor, H_2:substrate molar ratio = 8.3 – 131, residence time 211 s



Substrate **3** over Pd@MonoBor, H_2:substrate molar ratio = 8.2 – 124, residence time 211 s



Substrate **4** over Rh@MonoBor, H_2:substrate molar ratio = 12 – 24, residence time 53 - 106 s. Selectivity to **4a**.



Substrate **4** over PdRh@MonoBor, H_2:substrate molar ratio = 12, residence time 21 - 59 s. Selectivity to **4b**.

S.7 NMR Data

2a. ^1H NMR δ: 7.25 - 7.40 (Ar-H, 5H, m), 2.80, 2.78 (CH_2, 4H, A_2B_2 spin system), 2.13 (CH_3, 3H, s). $^{13}C\{^1H\}$ NMR δ: 141.3, 127.2, 128.6, 125.9 (Ar), 206.7 (CO), 28.3 (CH_2), 43.1 (CH_2), 29.8 (CH_3).

3a. ^1H NMR δ: 2.31 (CH_2, 1H, m), 2.27 (CH_2, 1H, m), 2.06 (CH_2, 1H, m), 2.02 (CH_2, 1H, m), 1.80 (CH_2, 1H, m), 1.58 (CH_2, 1H, m), 1.98 (CH, 1H, m), 0.99 (CH_3, 6H, s), 0.97 (CH_3, 3H, d). $^{13}C\{^1H\}$ NMR δ: 210.8 (CO), 35.0 (C), 28.6 (CH), 53.3 (CH_2), 49.1 (CH_2), 57.3 (CH_2), 28.8 (CH_3), 20.4 (CH_3).

4a. ^1H NMR δ: 3.02 (CH_2, 1H, m), 2.77 (CH_2, 1H, m), 2.04 (CH_2, 1H, m), 1.80 (CH_2, 1H, m), 6.3 (=CH, 1H, m), 2.5 (=CH, 1H, m), 1.83 (CH, 1H, sept), 1.73 (CH, 1H, m), 2.43 (CH_3, 3H, s), 0.91 (CH_3, 6H, d). $^{13}C\{^1H\}$ NMR δ: 199.0 (CO), 42.0 (CH), 42.0 (CH_2), 30.1 (CH_2), 31.9 (CH), 135.2 (=CH), 145.3 (=CH), 16.0 (CH_3), 21.4 (CH_3).

4b. ^1H NMR δ: 2.31 (CH_2, 1H, m), 2.07 (CH_2, 1H, m), 1.90 - 1.65 (CH_2, 4H, m), 1.70 (CH, 1H, m), 1.82 (CH, 1H, sept), 2.35 (CH, 1H, m), 1.12 (CH_3, 3H, d), 0.99 (CH_3, 6H, d). $^{13}C\{^1H\}$ NMR δ: 213.5 (CO), 44.7 (CH), 44.0 (CH_2), 27.1 (CH_2), 31.6 (CH), 32.2 (CH_2), 31.3 (CH), 21.0 (CH_3), 15.2 (CH_3).

5a. ^1H NMR δ: 9.74 (COH, 1H, m), 2.47 (CH_2, 1H, m), 2.23 (CH_2, 1H, m), 1.30 - 1.25 (CH_2, 6H, m), 1.88 (CH, 1H, m), 1.62 (CH, 1H, m), 0.96 (CH_3, 3H, d), 0.91 (CH_3, 6H, d). $^{13}C\{^1H\}$ NMR δ: 202.5 (CO), 28.2 (CH), 39.8 (CH_2), 24.6 (CH_2), 27.5 (CH), 37.2 (CH_2), 50.5 (CH_2), 23.0 (CH_3), 20.3 (CH_3).

S.8 Abbreviations

NBD = bicyclo[2.2.1]hepta-2,5-diene; ICP-OES = inductively coupled plasma atomic emission spectroscopy; TEM = transmission electron microscopy; EDS = energy dispersive X-ray spectrometry; TOF = turnover frequency (mol product /

mol metal x h); STY = space-time-yield (kg product / litre reactor volume x h); WHSV = weight hourly space velocity (g reactant / g catalyst x hour).

S.9 Supplementary references

[S1] F. Liguori, S. Coiai, E. Passaglia, P. Barbaro, *Macromolecules* 2013, **46**, 5423.

[S2] F. Liguori, P. Barbaro, *J. Catal.* 2014, **311**, 212.