

Supplementary Materials : Direct Synthesis of Hydrogen Peroxide under Semi-Batch Conditions over Un-Promoted Palladium Catalysts Supported by Ion-Exchange Sulfonated Resins: Effects of the Support Morphology

Francesco Frison¹, Chiara Dalla Valle¹, Claudio Evangelisti², Paolo Centomo^{1,*} and Marco Zecca.¹

Materials and apparatus.

All the chemicals employed herein are listed in Table SM1. They were used as received, if not otherwise stated.

Table SM 1. List of chemicals

<i>Chemical</i>	<i>Formula</i>	<i>Molar mass (g/mol)</i>	<i>Density (g/mL)</i>	<i>Supplier</i>
Tetrahydrofuran (THF)	C ₄ H ₈ O	72.11	0.89	Sigma-Aldrich
Methanol (MeOH)	CH ₃ OH	32.04	0.79	Sigma-Aldrich
1,2-dichloroethane (DCE)	CH ₂ Cl-CH ₂ Cl	98.97	1.25	Prolabo
Potassium iodide	KI	166	/	Sigma-Aldrich
Sodium molybdate	Na ₂ MoO ₄	205.92	/	Carlo Erba
Soluble starch	/	/	/	Acros
Sulfuric acid 98%	H ₂ SO ₄	98.09	1.84	Sigma-Aldrich
Chloridric acid 37%	HCl	84.46	1	Sigma-Aldrich
Sodium Hydroxide	NaOH	40	/	Prolabo
Phenolphthalein	C ₂₀ H ₁₄ O ₄	318.33	/	Merck
Sodium tiosulfate	Na ₂ S ₂ O ₃	158.11	/	J.T. Baker

Potassium dicromate (0.1N Normex vial)	$K_2Cr_2O_7$	294.19	/	Carlo Erba
Tetraminepalladium(II) sulfate	$[Pd(NH_3)_4]SO_4$	270.49	/	Alfa-Aesar
Palladium on carbon, 1% w/w, reduced (Pd/C)	/	/	/	Alfa-Aesar
Divinylbenzene, technical grade (DVB; mixture of isomers, 85 %, and ethylstyrene)	$C_{10}H_{10}$	130.18	0.91	Sigma-Aldrich
Azobisisobutyronitrile (AIBN)	$[(CH_3)_2C(CN)]N_2$	164.21	/	Janssen
Dihydrogen (gas cylinder)	H_2	2.02	/	Air Liquide
Dioxygen (gas cylinder)	O_2	32.00	/	Air Liquide

The macroreticular co-poly{styrene-divinylbenzene} resin (15 % cross-linked; m-pSDVB) was supplied by Spolchemie (Czech Republic).

The gaschromatographic (GC) analysis of the off-gas from the reactor for the DS was carried out with a micro-gaschromatograph Agilent 3000 μ -GC. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyses were carried out with an Ametek Spectro Genesis. Transmission electron microscopy (TEM) and HAADF-STEM (high angular annular dark field scanning electron microscopy) micrographs were taken with a ZEISS LIBRA200FE microscope equipped with a 200 kV FEG source. The samples were finely ground in an agate mortar, suspended in isopropanol and sonicated. Then a few drops of each suspension were deposited onto a lacey carbon coated copper grid (300 mesh) and the solvent removed by evaporation. Histograms of the particle size distribution were obtained by counting about 100 particles (or more) onto the micrographs. The mean particle diameter (d_m) was calculated by using the formula $d_m = \sum d_i n_i / \sum n_i$ where n_i was the number of particles of diameter d_i .

Polymerization of DVB [1,2].

In a typical experiment 6.00 g of DVB, 0.1650 g of AIBN, 60 mL of THF and 6.0 mL of distilled water were introduced into a teflon vessel and magnetically stirred for 4 h. A steel autoclave was the lined with the vessel, closed, heated and kept at 100 °C for 72 h. At the end the polymer was recovered as monolith, which was coarsely broken and dried under laboratory conditions for 2 weeks and finally ground to a relatively uniform powder with pestle and mortar. The amounts for the three batches of pDVB employed in this work are reported in Table SM 2.

Table SM2. Analytical details on support preparation

<i>Batch number</i>	<i>DVB (g)</i>	<i>AIBN (g)</i>	<i>THF (mL)</i>	<i>H₂O (mL)</i>
1	6.0231	0.1648	60	6
2	6.0440	0.1609	60	6
3	5.9587	0.1636	60	6

Sulfonation of the macroreticular resin and of pDVB.

The sulfonation was carried out according to a well-established literature procedure [3]. 30 mL of 1,2-dichloroethane were introduced into a jacketed glass vessel and ca 2 g of the resin suspended in the liquid. The precise values are reported in Table SM3.

Table SM3. Analytical data on supports

<i>Sulfonation</i>		<i>Titration</i>				<i>Sulfonated aromatic rings (%)</i>
<i>Amount of starting resin (g)</i>	<i>C_{NaOH} (M)</i>	<i>V_{HCl} (mL)</i>	<i>Amount of titrated resin (g)</i>	<i>IEC (mmol·g⁻¹)</i>		
mS-pSDVB	2.0468	0.1020	5.30	0.0976	5.0	108%

μ S-pDVB_1	1.8683	0.0940	7.40	0.1021	2.0	31%
μ S-pDVB_2	2.0090	0.1020	7.00	0.1013	3.2	56%

After 2 h 100 mL of concentrated sulfuric acid were slowly added to the suspension of the swollen resin. Then the vessel was heated to 80 °C with oil circulating in the jacket from an external thermostat. The mixture was magnetically stirred for 3 h at this temperature. After this time all the polymer moved into the bottom inorganic layer and the organic layer removed by decantation. The inorganic layer was diluted with the drop-wise addition of a number of aqueous solutions of H₂SO₄ with progressively decreasing concentrations (10, 5, 2.5, 1.25, 0.5 M; 20 mL each). The sulfonated resin was eventually recovered upon filtration, washed with distilled water up to neutrality of the liquor and finally rinsed with methanol. The solid was finally dried in an oven at 110 °C overnight, under air and sieved to recover the 180-400 μ m fraction.

Titration of sulfonated resins.

Dried samples of the sulfonated resins (mS-pSDVB; μ S-pDVB) were titrated to assess their ion-exchange capacity (IEC, mmol·g⁻¹ of -SO₃H groups; **Error! Reference source not found.**). For this purpose 100 mg of the discarded fraction with grain diameter lower than 180 μ m were dried again at 110 °C and then suspended in 10.0 mL of a ca. 0.1 M aqueous solution of NaOH, which was standardized prior each titration with standard 0.1 M HCl (from a concentrated Normex solution). After stirring overnight, the unreacted NaOH was back-titrated with standard 0.1 M HCl using phenolphthalein as the indicator. IEC was calculated from the following equation:

$$IEC(\text{mmol} \cdot \text{g}^{-1}) = \frac{C_{\text{NaOH}} \cdot V_{\text{NaOH}} - 0.1 \cdot V_{\text{HCl}}}{m_r} (C \text{ in mol} \cdot \text{L}^{-1}; V \text{ in mL}; m_r \text{ in g})$$

Catalyst preparation.

The sulfonated resin (180-400 μm , 2 g) was let to swell in about 10 mL of distilled water for 2 h. Then the amount of $[\text{Pd}(\text{NH}_3)_4]\text{SO}_4$ precisely required to achieve the desired metal load in the catalyst (25.4 and 89.0 $\text{mg}\cdot\text{g}_{\text{support}}^{-1}$, for 1 % and 3.5 % w/w, respectively) was dissolved into 10 mL of distilled water and the solution added to the suspension. The amounts of metal precursor and of support employed are reported in Table SM3.

Table SM3. Analytical details on catalysts preparation

<i>Palladium-exchanged resin</i>	<i>Support amount (g)</i>	<i>Pd precursor amount (g)</i>
$\text{Pd}^{\text{II}}/\text{mS-pSDVB10}$	1.9889	0.0504
$\text{Pd}^{\text{II}}/\mu\text{S-pDVB10}$	1.8200	0.0475
$\text{Pd}^{\text{II}}/\mu\text{S-pDVB35}$	1.4954	0.1401

The mixture was gently stirred on a swirling plate for 24 h, then the palladium-exchanged resin was recovered upon filtration. All the aqueous liquor fractions (filtrate) were collected together in a stoppered flask and saved for ICP-OES analysis of the residual metal. The solid was washed on the filter with 50 mL of peroxide-free THF obtained upon purification with neutral alumina according to a literature procedure [4]. was packed inside a column for liquid chromatography, until the bed was ca 10 cm high. Then a slow THF flow was started: the first 20 mL were used simply to better pack the stationary phase and discarded. The purified THF was collected and stored, in the dark and under nitrogen, in a double-neck round bottom flask equipped with a glass stopcock.

The sample for the ICP-OES analysis was prepared by simply pouring each filtrate into a graduated flask and diluting it with distilled water to the exactly known volume of the flask. The final volumes of the solutions to be analyzed and the concentrations of Pd found therein are reported in Table SM4.

Table SM4. Analytical data on metal analysis in the catalysts

<i>Filtrate source</i>	<i>Final volume (mL)</i>	<i>Pd concentration (ppb, $\mu\text{g/L}$)</i>
------------------------	--------------------------	---

Pd ^{II} /mS-pSDVB10	500	60.0
Pd ^{II} /μS-pDVB10	500	1468.0
Pd ^{II} /μS-pDVB35	500	1724.0

To reduce palladium(II) to palladium(0) 2 g of the palladium-exchanged resin were suspended in 50 mL of purified THF inside a low-mid pressure glass autoclave, containing a magnetic stirring bar, and let to swell for 2 h. The autoclave was immersed in a water bath initially at room temperature, flushed with H₂ three times and eventually closed. The H₂ pressure was raised to ca 455 kPa at 25 °C and then heated to 60 °C, so that a final inner gas pressure of ca 506 kPa was attained. The mixture was kept under magnetic stirring for 5 h. The autoclave was then cooled to room temperature, vented and opened to recover the suspension. The catalyst was eventually separated upon filtration, washed on the filter with 50 mL of purified THF and dried overnight at 70 °C in an oven, under air.

Catalytic runs.

The catalytic runs were carried out in a semi-batch reactor formed by a home-built jacketed 500 mL Schott-Duran. The threaded cap was modified to arrange a teflon head with ports for the introduction of the catalyst, the sampling of the liquid phase, the gas inlet, the gas outlet and the introduction of a thermocouple. All the ports were equipped with stopcocks or valves. A gas sparger was applied to the bottom of the gas inlet port, to improve its mixing with the liquid. For the same purpose, four internal baffles prevented the formation of the vortex upon stirring (magnetic bar). H₂ and O₂ were fed through separate dedicated lines, each equipped with a respective mass-flow controller (MFC) and mixed immediately before entering the reactor. The gas outlet line was equipped with a condenser cooled to -9 °C to condense and separate volatiles from gases prior the on-line GC analysis. Some representative chromatographs illustrated in Figures SM1 and SM2.

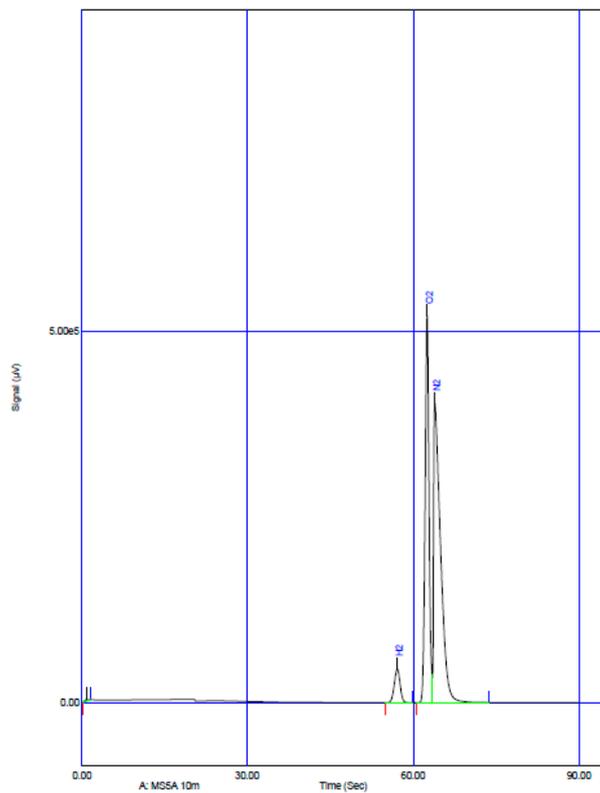


Figure SM1. Chromatogram of the off-gas during the stabilization of the reactor

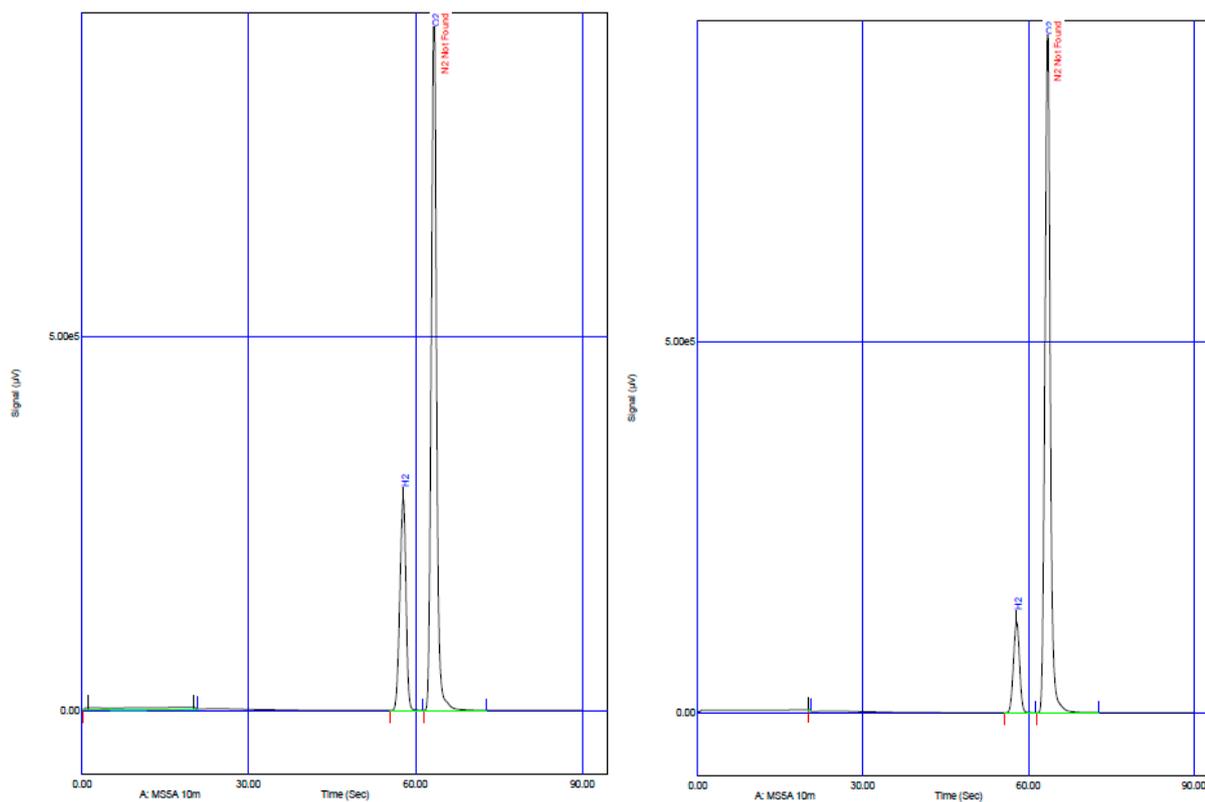


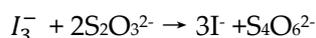
Figure SM2. Chromatogram of the off-gas at the beginning (left) and at half-time (2, h; right) of a catalytic run

The set-up parameters for the GC analysis are reported in Table SM5

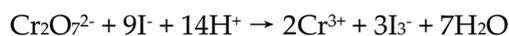
Table SM5. Set-up parameters for GC analysis

Column	Molecular Sieve 5 Å (MS5A)
T_{inj} (°C)	60
T_{col} (°C)	100
Sampling time (s)	5
Injection time (ms)	300
Backflush time (ms)	20
Run time(s)	90
P_{col} (psi)	30

After pouring 300 mL of MeOH into the reactor, it was closed and the H₂ and O₂ flows were started (101.3 kPa, 1 and 24 mL·min⁻¹, 4 and 96% v/v, respectively). Immediately thereafter the rotation of the magnetic bar (1250 rpm) and the circulation of water from an external thermostatic bath (25 °C) to the jacket were switched on. During the stabilization of the chromatographic areas of the gases (about 2 h), 100 mg of the catalysts were suspended in 1-2 mL of MeOH and let to swell for at least 2 h. The catalysts was then introduced into the reactor through the dedicated port and this operation was taken as the start of the reaction (t=0). If not otherwise stated, the reaction time was 4 h per single run. Every 20 min ca 1 mL of the alcoholic H₂O₂ solution was withdrawn, into a weighed glass vial, for the iodometric determination of the product:



The mass of the sample was transformed into its volume assuming that the solution had the same density of MeOH. It was the quantitatively transferred into a beacker and then 2.0 mL of an aqueous solution of Na₂MoO₄ (0.13·g⁻¹) and H₂SO₄ (10⁻³ M) were added, followed by 3 mL of an aqueous solution of KI (10 g·L⁻¹). The titration was carried out with an aqueous solution of Na₂S₂O₃ ca 10⁻³ M. The solution was standardized upon titration of a known amount of I₃⁻ generated upon reacting KI with a known volume of standard K₂Cr₂O₇ 1.667·10⁻² M (0.1 N), $V_{\text{Cr}_2\text{O}_7^{2-}}^{\text{stand}}$, from a concentrated Normex solution [5]:



From the equivalent volume of Na₂S₂O₃ consumed in the titration, $V_{\text{PE,S}_2\text{O}_3^{2-}}^{\text{stand}}$, its concentration was calculated as:

$$C_{\text{S}_2\text{O}_3^{2-}} = 6 \cdot \frac{C_{\text{Cr}_2\text{O}_7^{2-}} \cdot V_{\text{Cr}_2\text{O}_7^{2-}}^{\text{stand}}}{V_{\text{PE,S}_2\text{O}_3^{2-}}^{\text{stand}}}$$

The moles of H₂O₂ in the sample (-ΔnH₂O₂) were eventually calculated as:

$$\Delta n_{H_2O_2} = \frac{C_{S_2O_3^{2-}} \cdot V_{S_2O_3^{2-}}}{2}$$

On-line analysis of the off-gas

The down-stream flow of H₂ (ΦH_{2,out}, mL·min⁻¹) was determined from the chromatographic area of the H₂ peak measured with the μGC directly connected to the gas outlet port, using the following calibration method. The reactor was filled with 300 mL of MeOH and thermostated at 25 °C. After switching on the rotation of the stirring rod (1250 rpm) the gas flow started. For each point of the calibration curve a different mixture of H₂ and O₂ of known composition, set by changing the H₂/O₂ flow ratios, was fed (Table SM6).

After the equilibration of the system, the chromatographic area of H₂ (A_{H₂}) was measured at least five times for each mixture and the respective calibration obtained as the average of the five values. A strictly linear relationship between A_{H₂} and X_{H₂} was observed (Figure SM3): the intercept (a) and the slope (b) of line were obtained from the linear interpolation (R² = 0.99978) of the calibration data.

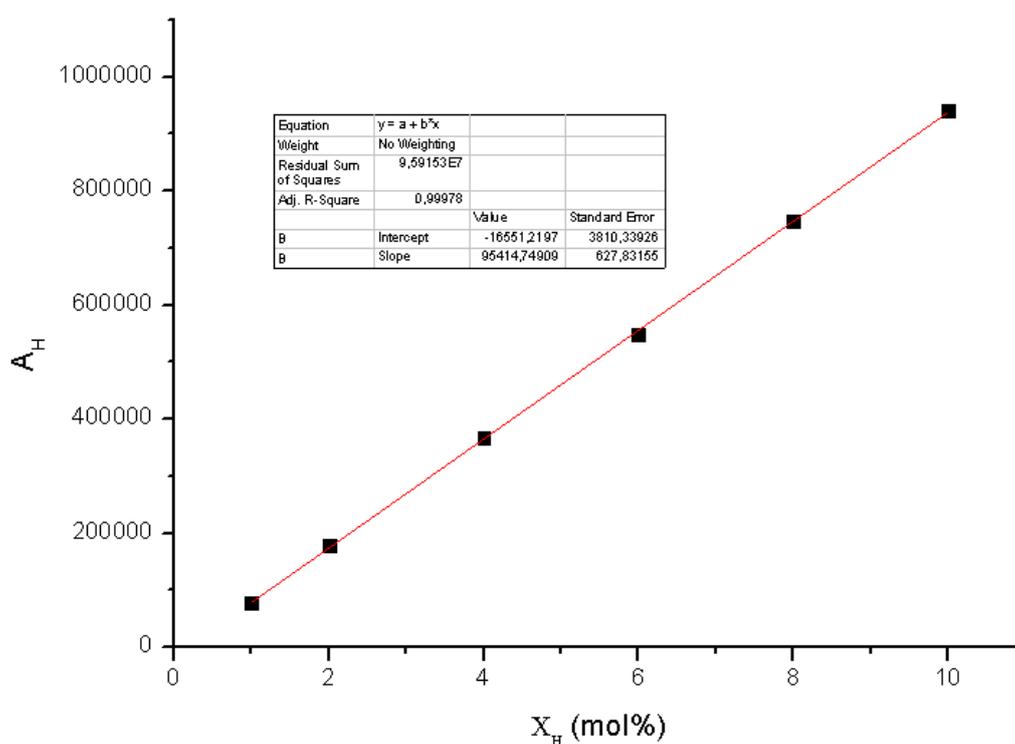


Figure SM3. Calibration plot for the GC analysis of H₂

Table SM6. Composition of gas mixtures for calibration

Gas flow (Φ , mL·min ⁻¹)		X_{H_2} (mol%)	X_{O_2} (mol%)
H_2	O_2		
0.5	49.5	1	99
1	49	2	98
1	24	4	96
1.5	23.5	6	94
2	23	8	92
2	18	10	90

During the catalytic runs H_2 was fed at 1.0 mL·min⁻¹ ($\Phi_{H_2,in}$; $X_{H_2,in} = 0.04$) and the off-gas was sampled and analyzed for A_{H_2} every 3 min. $\Phi_{H_2,out}$ was calculated as follows:

$$\Phi_{H_2,out} = \frac{(A_H - a) \Phi_{H_2,in}}{b X_{H_2,in}}$$

$(\Phi_{H_2,in} - \Phi_{H_2,out})$ represents the actual instant rate of H_2 consumption and was corrected by subtracting the apparent instant consumption rate at $t = 0$, if any.

The overall amount of H_2 consumed at time τ ($-\Delta n_{H_2,\tau}$) would be given by:

$$-\Delta n_{H_2,\tau} (mmol) = \frac{1}{V_m^{298.15K}} \cdot \int_0^\tau (\Phi_{H_2,in} - \Phi_{H_2,out}) dt$$

which was approximated in this work as:

$$-\Delta n_{H_2,\tau} (mmol) = \frac{1}{V_m^{298.15K}} \cdot \sum_{i=0}^n (\Phi_{H_2,in} - \Phi_{H_2,out})_i \cdot (t_i - t_{i-1})$$

Determination of the initial rates ($t < 80$ min) from the kinetic plots of H_2 consumption or H_2O_2 formation.

The values of $-\frac{\partial n_{H_2}}{\partial t}$ and $\frac{\partial n_{H_2O_2}}{\partial t}$ reported in Tables 3, 4 and 5 in the article were calculated from the slopes of the plots of $-\Delta n_{H_2}$ and of $\Delta n_{H_2O_2}$ vs time illustrated in Figures SM4-13. In fact, after the initial delay and/or induction time (if any), these plots are linear up to 240 min ($-\Delta n_{H_2}$) or 80-90 min ($\Delta n_{H_2O_2}$) in the case of fresh Pd/ μ S-pDVB10, Pd/ μ S-pDVB35, Pd/mS-pSDVB10 and Pd/C (used within 24 h from the preparation). For the aged catalysts, Pd/ μ S-pDVB35-2A/3N/4AR and Pd/mS-pSDVB10-2A/3N/4AR, clearly linear portions were found only in the $-\Delta n_{H_2}$ plots, with initial and final slopes sometimes different.

The interpolations of the linear plots or portions thereof provided the slopes from which the values of $-\frac{\partial n_{H_2}}{\partial t}$ and $\frac{\partial n_{H_2O_2}}{\partial t}$ were readily obtained with a simple change of the time unit from min to h.

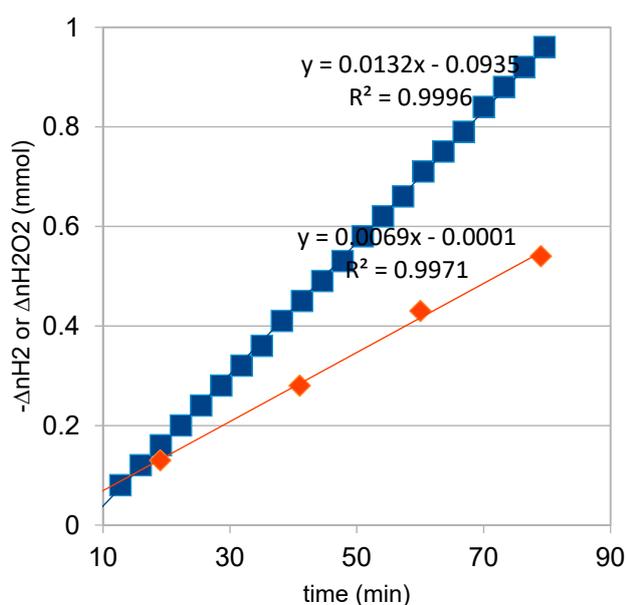


Figure SM4: Pd/ μ S-pDVB10 (squares: $-\Delta n_{H_2}$; diamonds: $\Delta n_{H_2O_2}$)

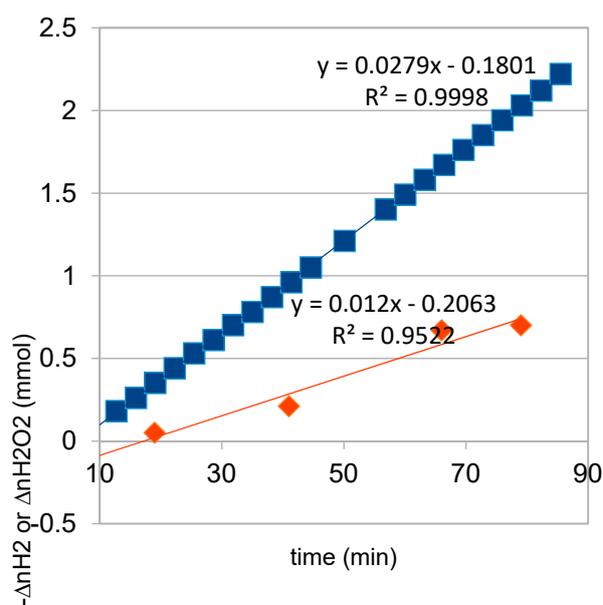


Figure SM5: Pd/ μ S-pDVB35 (squares: $-\Delta n_{H_2}$; diamonds: $\Delta n_{H_2O_2}$)

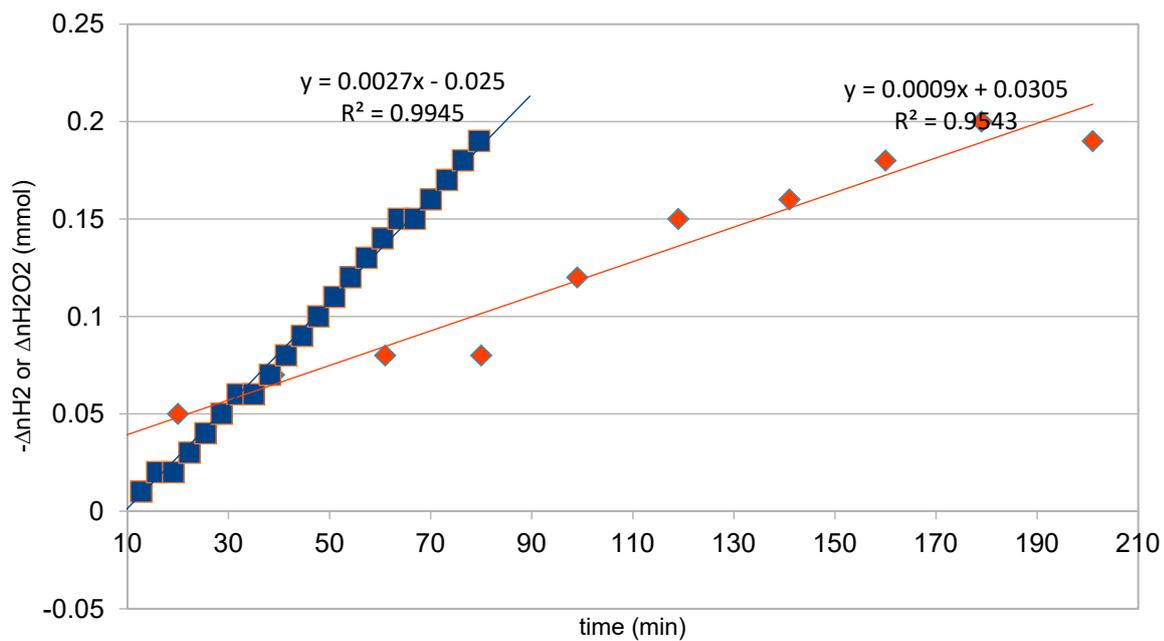


Figure SM6: Pd/mS-pSDVB10 (squares: $-\Delta nH_2$; diamonds: ΔnH_2O_2)

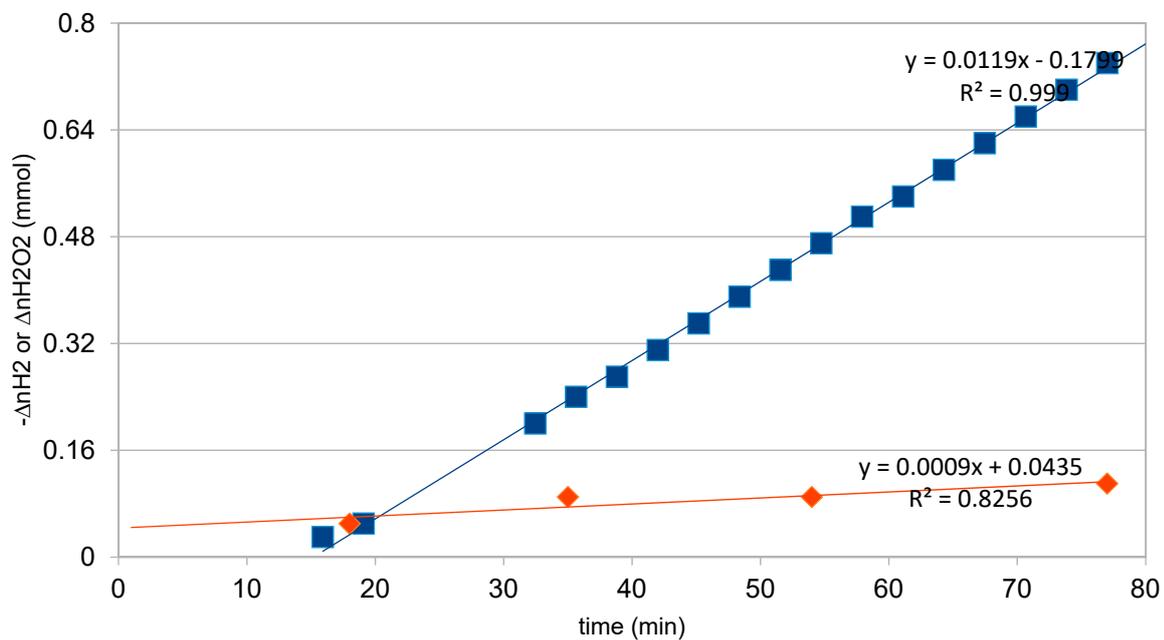


Figure SM7: Pd/C (squares: $-\Delta nH_2$; diamonds: ΔnH_2O_2)

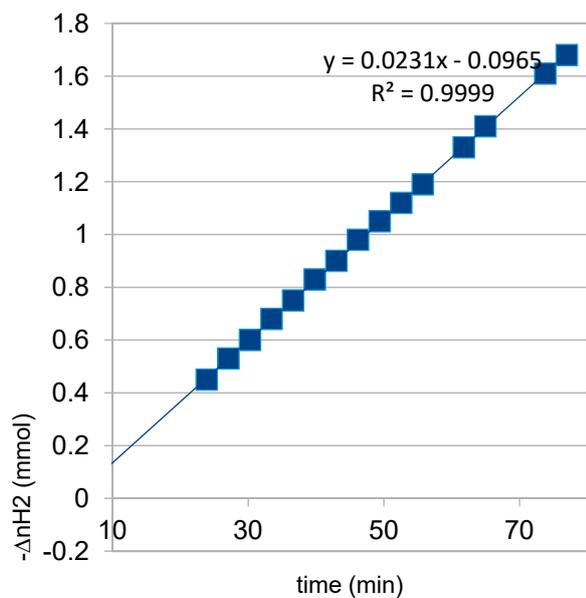


Figure SM: $Pd/\mu S-pDVB35-2A$

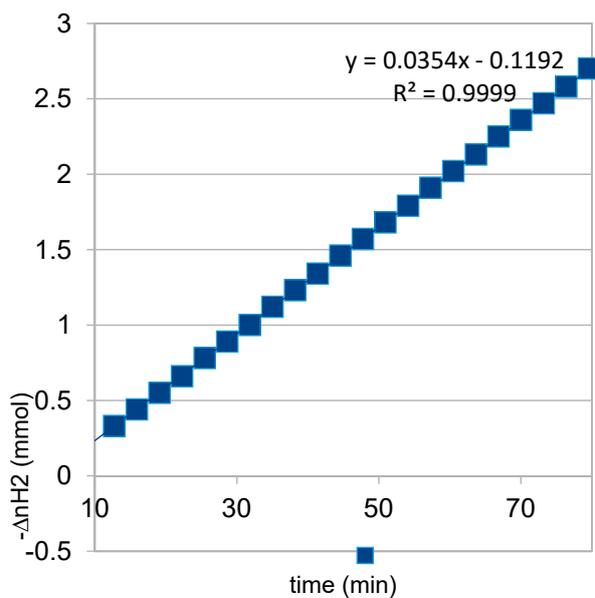


Figure SM9: $Pd/\mu S-pDVB35-3N$

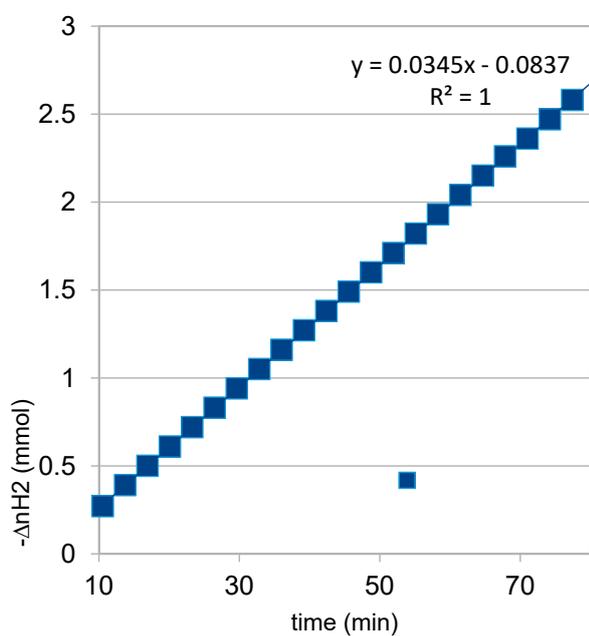


Figure SM10: $Pd/\mu S-pDVB35-4AR$

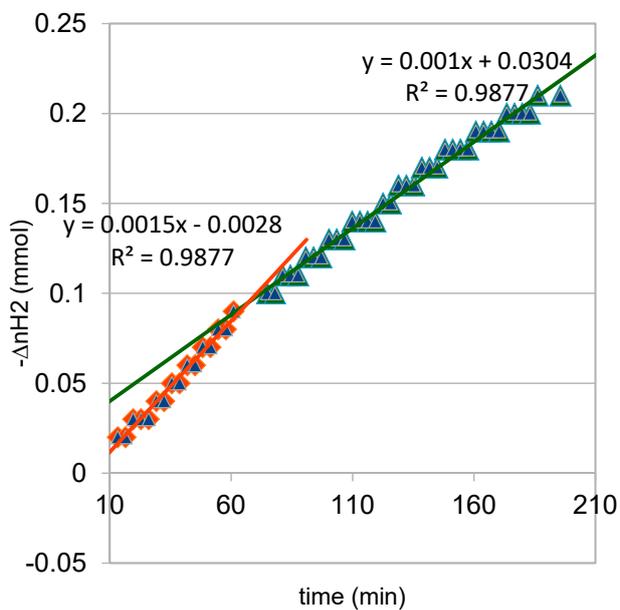


Figure SM11: $Pd/mS-pSDVB10-2A$ (initial: red diamonds; final: green inverted triangles)

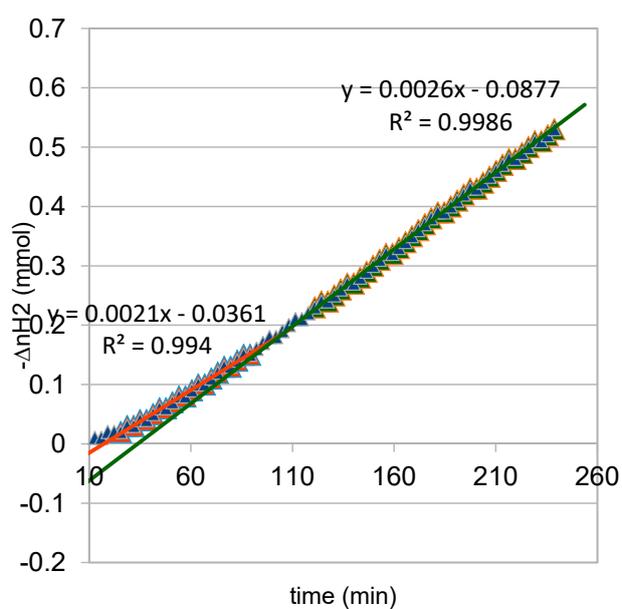
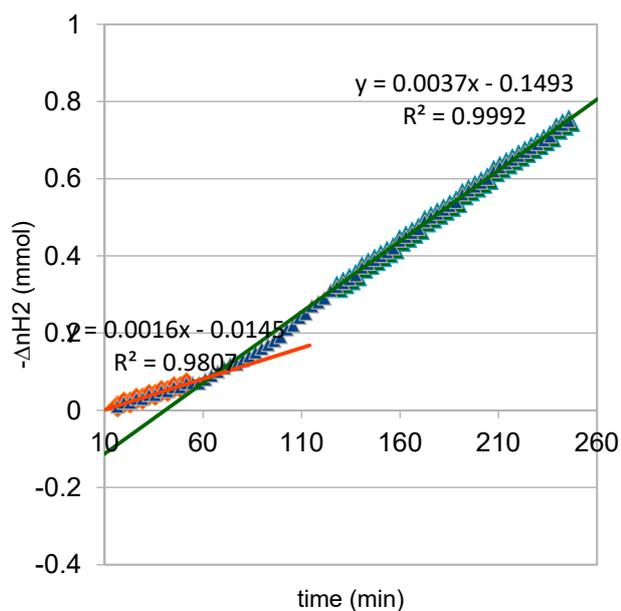


Figure SM12: Pd/mS-pSDVB10-3N (initial: red diamonds; final: green inverted triangles) Figure SM13: Pd/mS-pSDVB10-4AR (initial: red diamonds; final: green inverted triangles)

Table SM7. Rates ($\text{mmol}\cdot\text{min}^{-1}$) of H_2 consumption or of H_2O_2 formation at the beginning (80 min) and at the end (240 min) of the reaction, obtained from interpolation of the kinetic plots in Figures SM4-13.

Catalyst	$-\frac{\partial n_{\text{H}_2}}{\partial t}$		$\frac{\partial n_{\text{H}_2\text{O}_2}}{\partial t}$
	80 min	240 min	80 min
Pd/ μS -pDVB10	0.0132	-	0.0069
Pd/ μS -pDVB35	0.0279	-	0.0120
Pd/mS-pSDVB10	0.0027	-	0.0009
Pd/C	0.0119	-	0.0009
Pd/ μS -pDVB35-2A	0.0231	-	-
Pd/ μS -pDVB35-3N	0.0354	-	-
Pd/ μS -pDVB35-4AR	0.0345	-	-

Pd/mS-pSDVB10-2A	0.00146	0.00096	-
Pd/mS-pSDVB10-3N	0.00160	0.00367	-
Pd/mS-pSDVB10-4AR	0.00211	0.00260	-

References to the Supplementary Material

1. Zhang, Y.; Wei, S.; Liu, F.; Du, Y.; Liu, S.; Ji, Y.; Yokoi, T.; Tatsumi, T.; Xiao, F.-S. Superhydrophobic nanoporous polymers as efficient adsorbents for organic compounds. *Nano Today* **2009**, *4*, 135–142.
2. Hanková, L.; Holub, L.; Meng, X.; Xiao, F.-S.; Jeřábek, K. Role of water as a coporogen in the synthesis of mesoporous poly(divinylbenzenes). *J. Appl. Polym. Sci.* **2014**, *131*, n/a-n/a.
3. Hanková, L.; Holub, L.; Jeřábek, K. Relation between functionalization degree and activity of strongly acidic polymer supported catalysts. *React. Funct. Polym.* **2006**, *66*, 592–598.
4. Jackson, H.L.; McCormack, W.B.; Rondestvedt, C.S.; Smeltz, K.C.; Viele, I.E. Control of peroxidizable compounds. *J. Chem. Educ.* **1970**, *47*, A175.
5. Bray, W.C.; Miller, H.E. The standardization of thiosulfate solution by the permanganate-iodide and dichromate-iodide methods. *J. Am. Chem. Soc.* **1924**, *46*, 2204–2211.