Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.


# Open cell foam materials as Pd reservoirs for Suzuki-Miyaura coupling catalysis at ppb level

## SUPPLEMENTARY INFORMATION

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## Characterization of the metallic OCF

A 11,2 x 9,3 x 7,4 mm foam sample was analysed by X-ray tomography. From the gray level images (resolution 16 µm), geometric properties of the foam were obtained with the use of Imoph software.

The global void fraction is about 0.9. The specific surface area of the analysed sample is 2700 $m^2/m^3$.

In the volume of foam analysed, 990 cells were detected, which makes possible to obtain a size distribution of the cells. The average radius of a ball that can be entirely contained in the cells is 480 ± 40 µm. Other characteristics such as the average window or the strut size are reported in Table_S 1.

*Table_S 1: Principal structural and geometric characteristics of the FeCrAl OCF obtained by analyses of X-Ray tomography volume with Imorph.*

| | |
|---|---|
| **Pore radius (included ball radius) [µm]** | 480 ± 40 |
| **Cell radius (windows radius) [µm]** | 270 ± 80 |
| **Strut thickness [µm]** | 140 ± 90 |
| **Strut length [µm]** | 400 ± 200 |
| **Void fraction (Ɛ)** | 0.89 ± 0.03 |
| **Surface area [$m^2.m^{-3}$]** | 2700 |

## Detailed preparation of the Pd NPs @ glass foam:

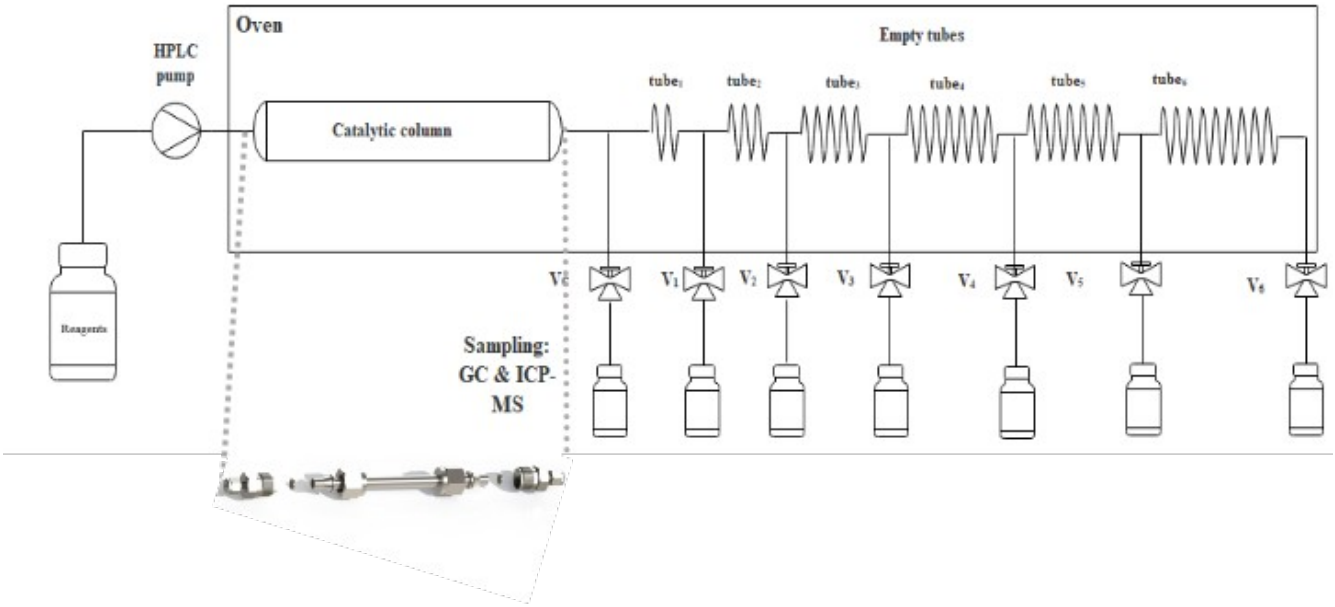
First, the glass open cell foam (OCF) was produced, starting from 200 g of crushed and sieved glass powder (< 100 µm). Then, 1.3 g of aluminium nitride (AlN), 2.5 g of titanium dioxide ($TiO_2$) and 10.4 g of manganese dioxide ($MnO_2$) were crushed and mixed with the glass powder. The mixture was introduced in a mold and pyrolysed at 850°C during 50 minutes (after a heating ramp of 10°C/min). The obtained material was characterized by helium pycnometry; a density of 0.34 kg/m$^3$ and an open porosity of 84.6% were found.

To an aqueous solution (45 mL) of *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride (HEA16Cl) salt ($2.85 \times 10^{-3}$ mol, 5.8 equiv.) was added 5 mL of a freshly prepared aqueous solution of sodium borohydride ($1.42 \times 10^{-3}$ mol, 2.9 equiv.). Then, this solution was quickly added under vigorous stirring to an aqueous solution (100 mL) of the sodium tetrachloropalladate(II) hydrate $Na_2PdCl_4$. $6H_2O$ ($4.9 \times 10^{-4}$ mol, 1.0 equiv.) to obtain a colloidal suspension of Pd(0). The reduction, indicated by a color change from yellow to black, occurred instantaneously. The suspension was kept under stirring during 12 h before use.

The glass foam was then dipped in the suitable volume of aqueous suspension according to the metal loading desired. 5 successive cycles (namely, dipping then drying at 95°C) were applied, resulting in a foam of 56 mm long and 16 mm diameter weighing 3.8 g and loaded at 0.1 wt-% of Pd. The resulting OCF is shown in Figure_S 1.

*Figure_S 1: Pd NPs@glass OCF*

## Split-flow-test set-up




*Figure_S 2: Schematic set-up of the split-flow reactor*

The experimental split flow test set-up (see Figure_S 2) is composed of a preheated (60°C) catalytic column containing the OCF followed by a PFA tube section (1.7 mm i.d., 10 m length) divided in different lengths (0.5 m, 1 m, 1.5 m, 2 m, 2 m, and 3 m respectively). Both ends of the column were equipped with appropriate Swagelok fittings, including filters (4.6 mm i.d., pore size 2 µm) (RESTEK).

The reagent solution is pumped with a previously fixed flow rate using HPLC pump. For each section of the set-up, a 2 mL sample of solution is taken to be analyzed by GC.

The residence time in tubes was calculated by using the following formula:

$$\text{Residence time (min)} = \sum_{1}^{6} \frac{V_{Tube\ i}\,(ml)}{Flowrate\,(ml/min)}$$

As an example for a flow rate of 1 mL/min the residence time for each section of the set-up is shown in Table_S 2.

*Table_S 2: Residence time in each tube at a flow rate of 1 mL/min*

| | Tube1 | Tube2 | Tube3 | Tube4 | Tube5 | Tube6 | Total |
|---|---|---|---|---|---|---|---|
| Volume (mL) | 0,99 | 1,99 | 2,99 | 3,98 | 3,98 | 5,97 | 19,9 |
| Residence time (min) | 0,99 | 1,99 | 2,99 | 3,98 | 3,98 | 5,97 | 19,9 |

## Results of the different tests with the Pd NPs@glass foam in the split flow reactor at a flow rate of 1 mL/min.

*Table_S 3: Detailed results obtained with the Pd NPs@glass foam for different ArI concentrations*

| | | **Conversion at different residence times** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Time-on-stream (min) | [ArI] | At 9.5 min, X % (col.) | At 10.5 min, X % (tube 1) | At 12.5 min, X % (tube 2) | At 15.5 min, X % (tube 3) | At 19.5 min, X % (tube 4) | At 23.5 min, X % (tube 5) | At 29.5 min, X % (tube 6) | [Pd] in tube (ppb) |
| 35 | C | 73 | 81 | 87 | 95 | 98 | 98 | 98 | 31 |
| 70 | | 68 | 75 | 78 | 89 | 94 | 98 | 99 | 33 |
| 105 | 1.5C | 32 | 42 | 44 | 58 | 69 | 71 | 74 | 16 |
| 140 | | 23 | 29 | 35 | 41 | 58 | 68 | 79 | 16 |
| 175 | C | 28 | 27 | 37 | 50 | 69 | 86 | 93 | |
| 210 | 2C | 28 | 35 | 43 | 54 | 65 | 76 | 86 | 27 |
| 245 | | 28 | 31 | 36 | 50 | 63 | 74 | 84 | 24 |
| 280 | C | 23 | 26 | 34 | 44 | 55 | 64 | 80 | |
| 315 | 2.5C | 15 | 23 | 24 | 31 | 42 | 51 | 67 | 35 |
| 350 | | 18 | 19 | 20 | 29 | 40 | 49 | 58 | 32 |
| 385 | C | 17 | - | 22 | 22 | 30 | 33 | 45 | |
| 420 | 3C | 14 | 18 | 22 | 33 | 45 | 53 | 63 | 29 |
| 455 | | 20 | 21 | 26 | 28 | 36 | 42 | 51 | 28 |

The values in red were the ones used in the main document with a mean value of Pd leaching of 30 ppb.

C is the reference concentration of 4-iodoacetophenone: 0.025 mol/L