Electronic Supplementary Material (ESI) for Green Chemistry.


# Continuous flow synthesis of menthol via tandem cyclization-hydrogenation of citronellal catalyzed by scrap catalytic converters

Alessio Zuliani,[a] Camilla Maria Cova,[a] Roberta Manno,[b] Victor Sebastian,[b,c,d] Antonio A. Romero[a] and Rafael Luque*[a,e]

[a.] *Departamento de Quımica Organica, Universidad de Cordoba, Edificio Marie-Curie (C-3), Ctra Nnal IV-A, Km 396, Cordoba, Spain. E-mail: rafael.luque@uco.es*
[b.] *Nanoscience Institute of Aragon and Chemical and Environmental Engineering Department, University of Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, Spain.*
[c.] *Networking Research Center CIBER-BBN, 28029, Madrid, Spain.*
[d.] *Aragón Materials Science Institute, ICMA, CSIC, University of Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, Spain.*
[e.] *Peoples Friendship University of Russia (RUDN University), 6 Miklukho Maklaya str., 117198, Moscow, Russia.*

**Set up of the Tandem apparatus**

The normal set up of the H-Cube® is illustrated in Fig. S1-C.

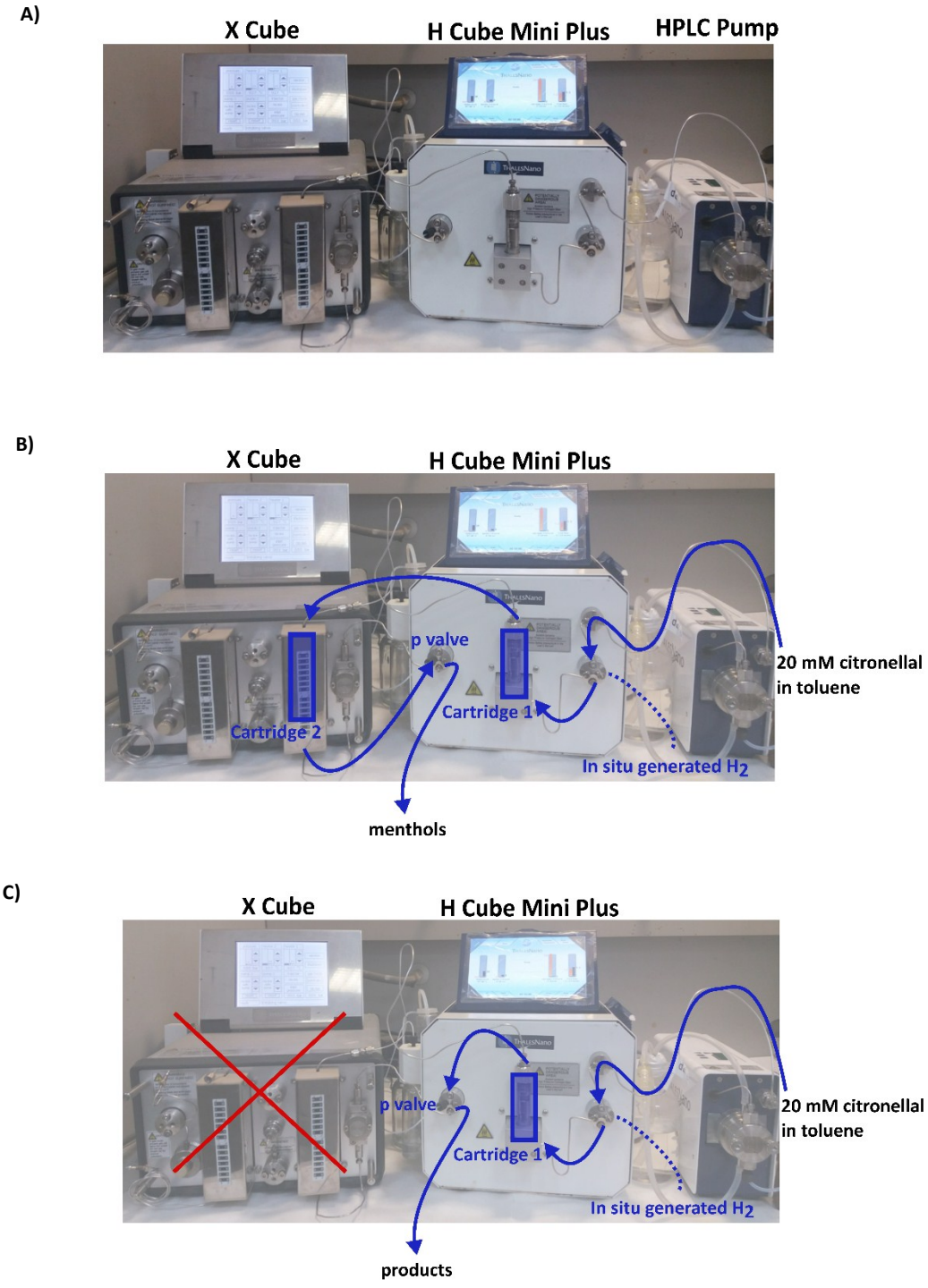


**Fig. S1**. (A) H-Cube® Mini Plus (Thalesnano Inc.) linked to an X-Cube™ (Thalesnano Inc.). (B) Flow connections of the tandem apparatus. (C) Flow connections of H-Cube®

**Experimental details**

1. **Elemental analysis of SCATs and Fe/SCATs**

Elements detected through qualitative analysis (ICP-MS) of SCATs: Mg, Al, Si, Fe, Ce, Ti, Zn, Zr, Pt

Quantitative analysis of SCATs (MP-AES): 0.97%$_{wt}$ Fe, <0.2%$_{wt}$ Pt

Quantitative analysis of Fe/SCATs (sample A) before and after reaction (MP-AES): ~7.5%$_{wt}$ Fe, <0.2%$_{wt}$ Pt

2. **STEM-HAADF of SCATs and Fe/SCATs after reaction**

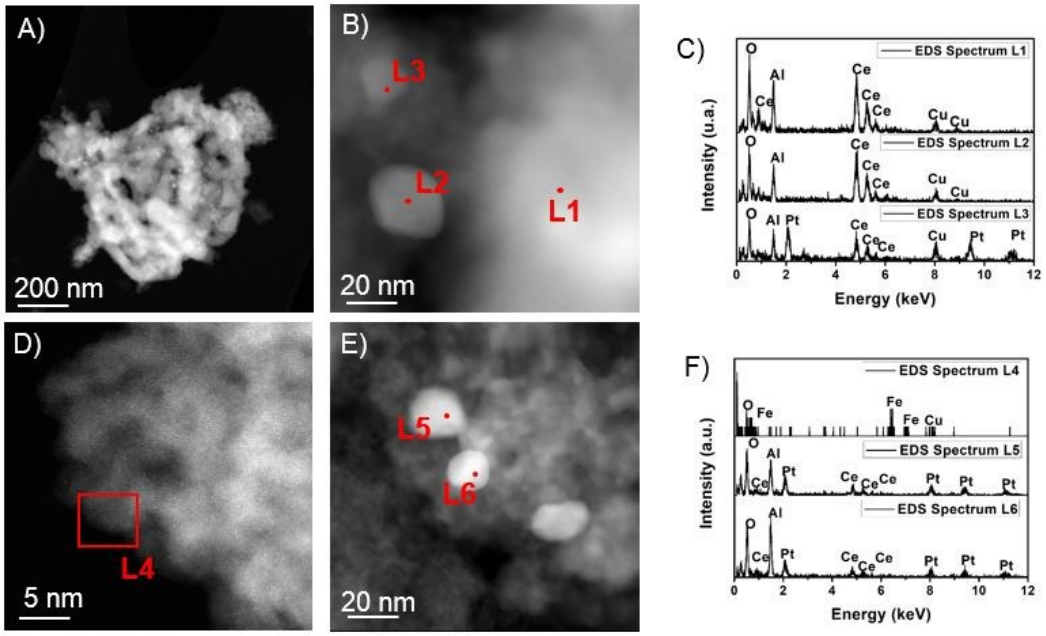


**Fig. S2** (A) and (B) STEM-HAADF images of SCATs after reaction. (C) EDS analysis of selected points (L1-L3) of SCATs after reaction. (D) and (E) STEM-HAADF images of Fe/SCATs after reaction. (H) EDS analysis of selected locations (L4-L6) of Fe/SCATs after reaction.

**Results and discussion**

### 1. Preliminary study

| Entry | $H_2$ p / bar | T[a] / K | Flow rate / mL $min^{-1}$ | $Y_{ms}$ / %[b] |
|---|---|---|---|---|
| 1 | 30 | 373-323 | 0.1 | 48.7 |
| 2 | 30 | 373-348 | 0.1 | 54.7 |
| 3 | 30 | 373-373 | 0.1 | 65.3 |
| 4 | 30 | 373-398 | 0.1 | 76.2 |
| 5 | 30 | 373-423 | 0.1 | 82.6 |
| 6 | 30 | 373-448 | 0.1 | 83.1 |
| 7 | 30 | 373-423 | 0.3 | 61.8 |
| 8 | 30 | 373-423 | 0.5 | 43.6 |

[a] Temperature of Cartridge 1 and Cartridge 2. [b] Yield % to menthols at stationary state

**Table S1.** Performances of the tandem reaction carried out using 30 mm-long Cartridge 1 and 70 mm-long Cartridge 2. Reaction parameters: (±)-citronellal 20 mM in toluene.

### 2. Influence of the flow rate

| Entry | Flow rate / mL $min^{-1}$ | $Y_{ms}$ / % [a] | $S_{(\pm)\text{-m}}$ / % [b] | $Y_{(\pm)\text{-m}}$ / % [c] |
|---|---|---|---|---|
| 1 | 0.1 | 91.8 | 84.2 | 77.3 |
| 2 | 0.3 | 68.6 | 77.7 | 53.3 |
| 3 | 0.5 | 41.6 | 73.1 | 30.4 |

[a] Yield % to menthols at stationary state. [b] Selectivity to (±)-menthol. [c] Yield to (±)-menthol.

**Table S2.** Tandem cyclisation-hydrogenation of (±)-citronellal to (±)-menthol. Reaction parameters: (±)-citronellal 20 mM in toluene, Cartridge 1 fixed at 373 K; Cartridge 2 fixed at 413 K, 5 bar $H_2$ pressure.