

SUPPORTING INFORMATION

A) Catalyst preparation

Preparation of MIL-101: Cr³⁺-MIL-101 was prepared according to the reported procedure.ⁱ Briefly, 500 mg of terephthalic acid and 800 mg Cr(NO₃)₃·9H₂O were dissolved in 15 mL H₂O and 40 μL HF (40%). The solution was placed inside an autoclave and kept at 200°C for 8h in an oven. The resulting material was recovered by filtration, washed with DMF and hot ethanol, and dry at RT in air.

Preparation of Pd@MIL-101: The preparation procedure for this material was adapted from that reported by Pan et al.ⁱⁱ Briefly, 500 mg of Cr³⁺-MIL-101 were dried under a vacuum at 120°C, and impregnated with 0.5 mL of an aqueous solution containing 10 mg mL⁻¹ of Pd(NO₃)₂·2H₂O. The solid was then dried in air and heat treated up to 200°C under a N₂ atmosphere and kept at this temperature under a H₂ atmosphere for additional 2 h to reduce the palladium precursor. According to ICP, the Pd content of this samples was 0.28 wt% Pd.

B) Catalytic tests

The citronellal isomerization reaction was performed at 80°C under a N₂ atmosphere. 60 μl of racemic citronellal and 30 mg of MOF was placed inside a round bottom flask with 0.5 ml of cyclohexane. The reaction was followed by GC-MS, using dodecane as external standard.

For the tandem isomerization/hydrogenation reaction, the N₂ atmosphere was replaced by a H₂ atmosphere ($p(\text{H}_2) = 0.8 \text{ MPa}$). upon completion of the isomerization reaction.

C) Textural properties of the catalysts

Table S1

Sample	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)
Cr ³⁺ -MIL-101	2336	1.40
Pd@MIL-101	2182	0.97
Pd@MIL-101 used ^a	1619	0.72

^a Material recovered after one catalytic cycle (tandem one-pot two steps isomerization/hydrogenation of citronellal to menthol at 80°C and $p(\text{H}_2)=0.8 \text{ MPa}$).

D) XRD analysis

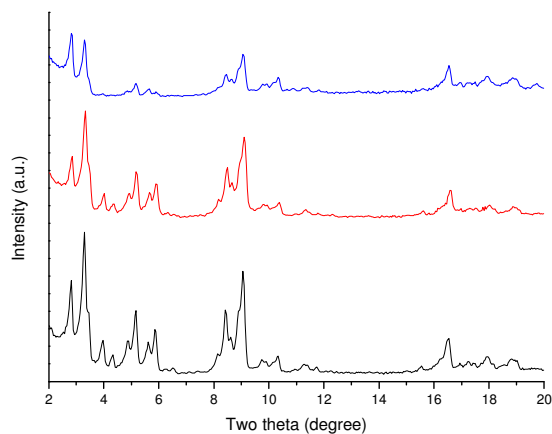


Fig. S1. XRD patterns (Cu K α radiation) of MIL-101 (black), Pd/MIL-101 before the reaction (red) and Pd/MIL-101 after the reaction (blue).

E) TEM analysis

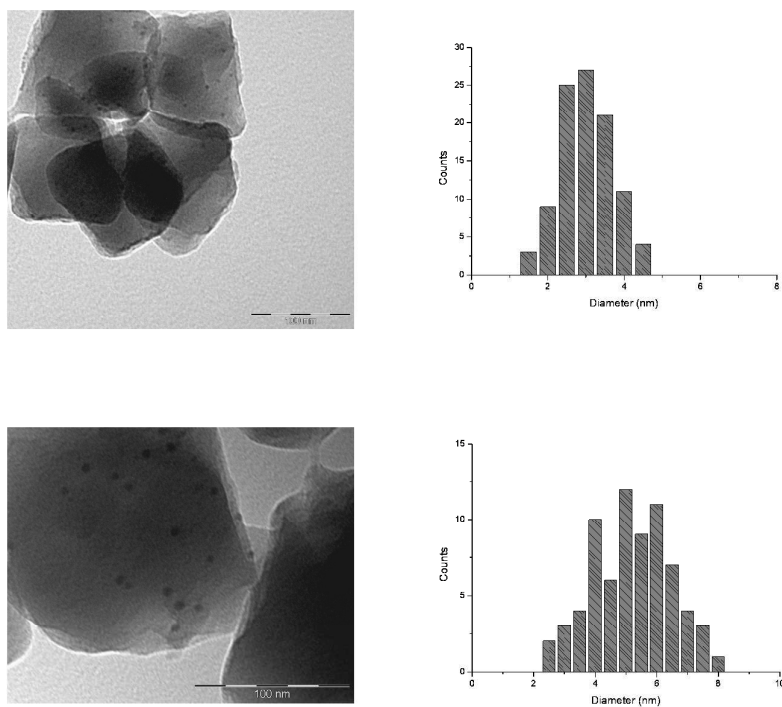


Fig. S2. TEM images and particle size distributions of (top) fresh and (bottom) used Pd@MIL-101.

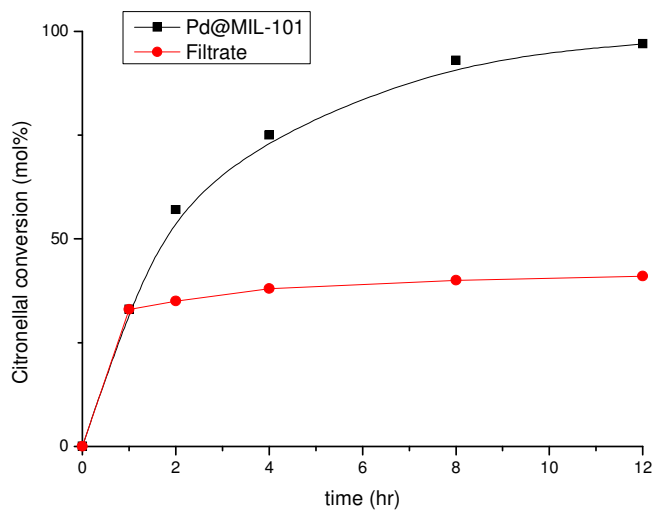


Fig. S3. Hot filtration test. Black curve: Conversion of citronella over Pd@MIL-101. Red curve: The reaction was carried out in the presence of Pd@MIL-101 for 1 hr. Then the catalysts was removed by filtration at the reaction temperature and the reaction was followed in the filtrate at the same temperature.

ⁱ G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.

ⁱⁱ Y. Pan, B. Yuan, Y. Li and D. He, *Chem. Commun.*, 2010, **46**, 2280-2282.