MOF-Mediated Synthesis of Supported Fe-doped Pd Nanoparticles Under Mild Conditions for Magnetically Recoverable Catalysis

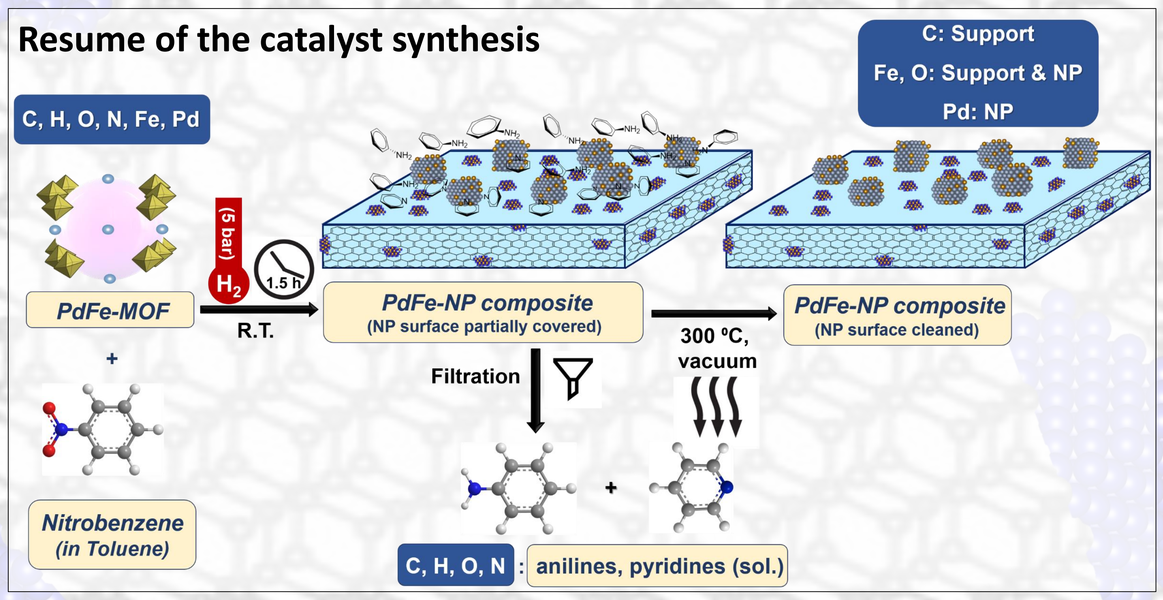
Mohanad D. Darawsheh,[a†] Jaime Mazarío,[b†] Christian W. Lopes,[c] Mónica Giménez-Marqués,[a] Marcelo E. Domine,[b] Debora M. Meira,[d,e] Jordan Martínez,[b] Guillermo Mínguez Espallargas*[a] and Pascual Oña-Burgos*[b,f]

a) Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, c/Catedrático José Beltrán, 2, 46980 Paterna, Spain.
b) Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos, 46022 Valencia, Spain.
c) Laboratory of Reactivity and Catalysis – Institute of Chemistry, Universidade Federal do Rio Grande do Sul, 91501-970 Porto Alegre, Brazil.
d)CLS@APS sector 20, Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Avenue, Lemont, IL 60439, USA.
e) Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon, SK S7N 2V3, Canada.
f) Department of Chemistry and Physics, University of Almería, Ctra. Sacramento, s/n, Almería, E-04120, Spain.

INTRODUCTION

MOF-driven synthesis is considered as a promising alternative for the development of new catalytic materials with well-designed active sites. This synthetic approach is used here to gradually transform a new bimetallic MOF, composed of Pd and Fe as metal components, via the *in situ* generation of aniline under mild conditions. This recently reported methodology results in a compositionally homogeneous nanocomposite formed by Fe-doped Pd nanoparticles and these, in turn, supported on an iron oxide-doped carbon.[1] The performance of this nanocomposite as an heterogeneous catalyst for hydrogenation of nitroarenes and coupling between nitrobenzene and benzaldehyde has been evaluated, proving it to be an efficient and reusable catalyst.

CATALYST SYNTHESIS & CHARACTERISATION



CATALYTIC ACTIVITY: Nitroderivative Hydrogenation

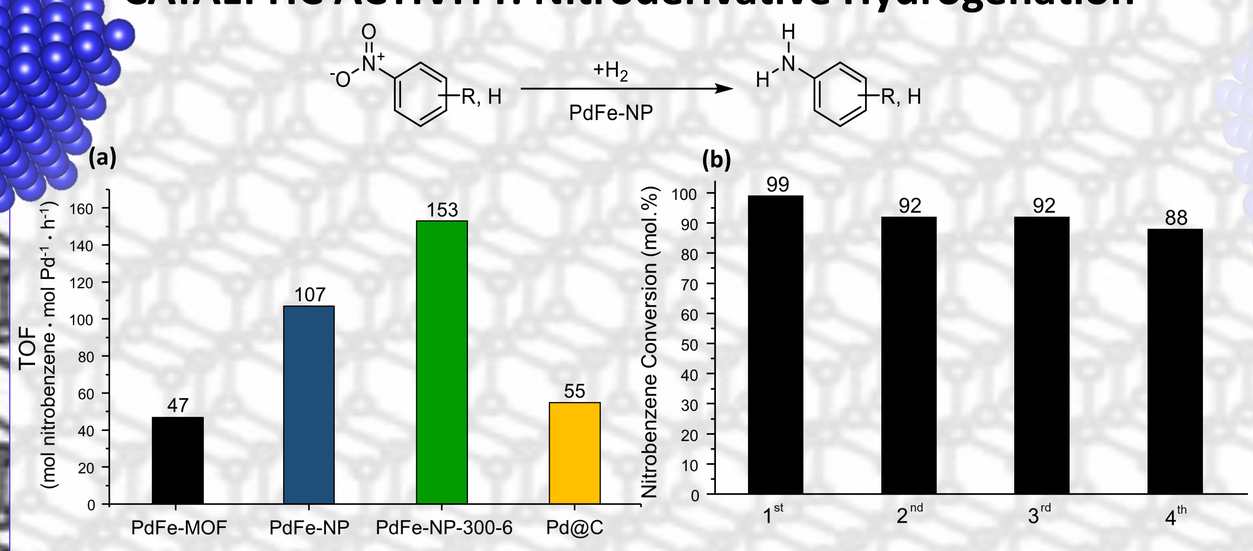


Figure 1. a) Initial reaction rates (as TOF) for different PdFe-based materials and comparison with a commercial catalyst. TOF has been calculated after the first 30 minutes of reaction plus the corresponding induction time observed. **b)** Reusability of PdFe-NP formed "in-situ" from PdFe-MOF. Reaction conditions: 0.123 g nitrobenzene, 5 mg PdFe-MOF, at 5 bar H_2 pressure and 25 ºC during 2 h (after 1 h of induction).

Table 1. Catalytic activity of "in-situ" formed PdFe-NPs when using different nitroderivatives.

Reactant	Observed product	Yield (mol.%)[a]	Induction time (h)
Nitrobenzene	Aniline	99	1.0
4-methylnitrobenzene	4-methylaniline	99	3.0
4-chloronitrobenzene	4-chloroaniline	73	4.5
Nitrostyrene	4-ethylaniline	92	7.0

Reaction conditions: 0.123 g nitroderivative, 5 mg PdFe-MOF, at 5 bar H_2 pressure and 25 ºC. [a] At 2 h of reaction discarding the induction time in each case.

CATALYTIC ACTIVITY: Tandem Reaction

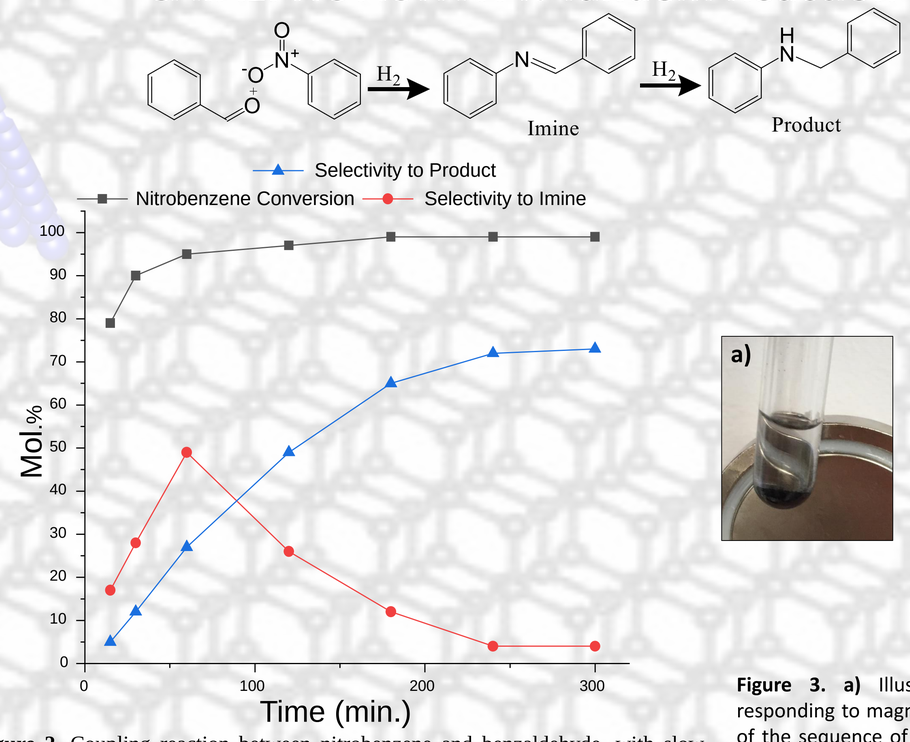


Figure 2. Coupling reaction between nitrobenzene and benzaldehyde, with slow addition of the latter. Reaction conditions: 0.123 g nitrobenzene, 0.106 g benzaldehyde (slow addition, v=102 µL/h), 5 mg PdFe@MOF, at 5 bar H_2 pressure and 25 ºC during 6.5 h.

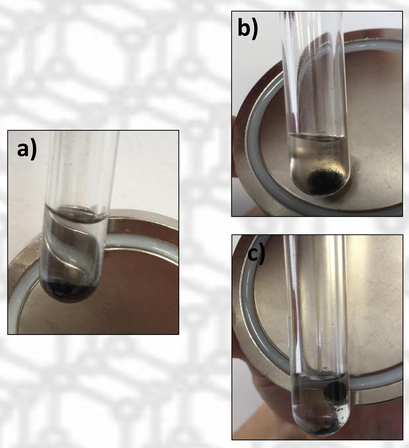


Figure 3. a) Illustration of Pd@C not responding to magnet. **b)** and **c)** Illustration of the sequence of magnetically recovering PdFe-NP-300-6.

- ***PdFe MOF***

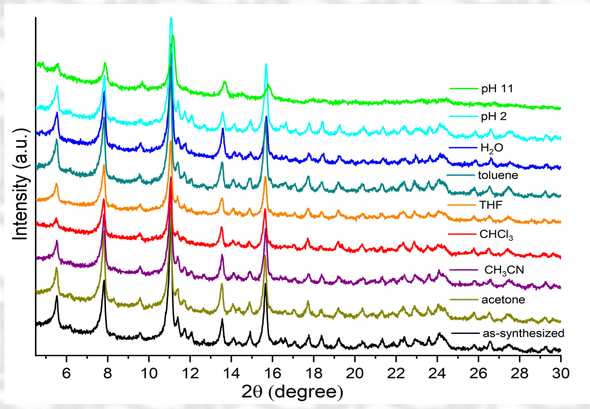


Figure 4. PXRD of PdFe-MOF after immersing in different solvents and two buffered solutions at RT during 24 h. The MOF is stable under these conditions except in highly basic solutions, where starting losing crystallinity.

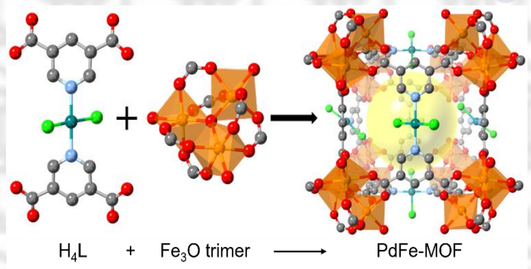


Figure 5. Schematic diagram of the metalloligand (H_4L), the oxo-centred iron carboxylate SBU, $[Fe_3O(COO)_6(H_2O)_3]^+$ and the cuboidal cage of the PdFe-MOF. Colour scheme: orange = Fe, grey = C, blue = N, red= O, dark teal = Pd, green = Cl, and yellow sphere represents the cavity. Hydrogen atoms are omitted for clarity.

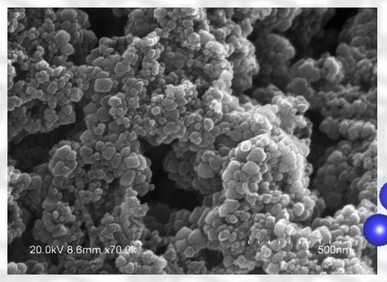


Figure 6. SEM picture of the solid obtained showing the nanoparticles of PdFe-MOF with a size range between 20-70 nm.

- ***PdFe NPs***

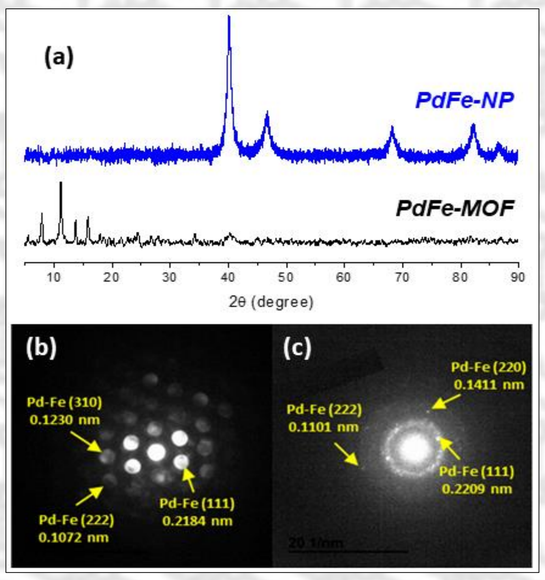


Figure 7. (a) XRD patterns for PdFe-NP and PdFe-MOF, PdFe-NP spectrum corresponds to the positions of the (111), (200), (220), (311) and (222) peaks; (b) and (c) SAED patterns of the sample PdFe-NP.

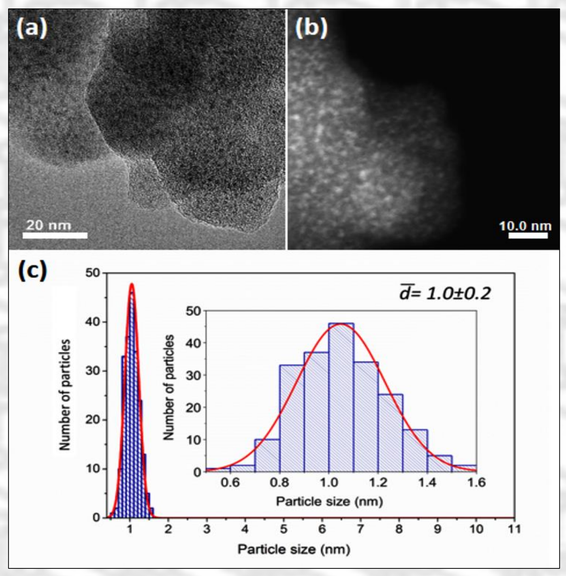


Figure 6. (a) TEM (b) STEM micrographs and (c) particle size distributions of PdFe-NP.

Table 2. Summary of the main materials prepared

Material code	Description	NP size [a]
PdFe-MOF	Original MOF	-
PdFe-NP	Chemically as-synthesized NP	1.0±0.2
PdFe-NP-300	PdFe-NP heated for 6h at 300°C under vacuum	1.2±0.3
a: Measured by HR-TEM by considering a minimum number of 200 particles.		

Table 3. Compositional characterization PdFe-based materials.

Material	Pd wt.%[a]	Fe wt.%[a]	Labile matter wt.%[b]
PdFe-MOF	9.2	15.7	64.2
PdFe-NP	12.6	17.2	52.1
PdFe-NP-300-6	15.2	20.6	47.0

IX SIMPOSIO de Investigación EN CIENCIAS EXPERIMENTALES

INSTITUTO DE TECNOLOGÍA QUÍMICA

CONCLUSION

A new family of nanocomposites based on Fe-doped Pd nanoparticles supported on an iron oxide-doped carbon has been obtained from a new bimetallic PdFe-MOF. A controlled decomposition of the PdFe-MOF upon *in situ* generation of aniline leads to the formation of ultra-small PdFe-NP. In addition, materials obtained with our approach present good catalytic properties in the hydrogenation of nitroarenes and tandem reaction. Moreover, PdFe-MOF can be directly used to generate the catalyst in the reaction media, resulting in a substantial improvement compared to the commercial Pd@C when both are used without any additional treatment. In summary, the results obtained in this work should further strengthen the confidence in the MOF-driven synthesis as a powerful tool to prepare novel nanocomposites and catalytic systems with well-defined active sites. In particular, the methodology developed in this work could be a good starting point for the controlled transformation of MOFs having similar building units into multifunctional nanomaterials.

References: [1] Darawsheh, M. D.; Mazarío, J.; Lopes, C. W.; Giménez-Marqués, M.; Domine, M. E.; Meira, D. M.; Martínez, J.; Espallargas, G. M.; Oña-Burgos, P. MOF-Mediated Synthesis of Supported Fe-Doped Pd Nanoparticles under Mild Conditions for Magnetically Recoverable Catalysis**. *Chemistry – A European Journal* **2020**, *26* (60), 13659–13667.