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

Guillermo Minguez Espallargas, Mohanad D. Darawsheh, Dr. Mónica Giménez Marqués, Marcelo E. Domine, Pascual Oña-Burgos, Jaime Mazario, Debora M. Meira, Christian Lopes, Jordan Martinez

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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 methodology results in a compositionally homogeneous nanocomposite formed by Fedoped Pd nanoparticles and these, in turn, supported on an iron oxide-doped carbon. The nanocomposite has been fully characterized by several techniques such as IR, Raman, TEM, XPS, XAS, among others. The performance of this nanocomposite as an heterogeneous catalyst for hydrogenation of nitroarenes and nitrobenzene coupling with benzaldehyde has been evaluated, proving it to be an efficient and reusable catalyst.

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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 Jordan Martínez,b Guillermo Mínguez Espallargas*a and Pascual Oña-Burgos*b,e

Supporting Information

S1. General methods and materials
S2. Synthesis and characterization of PdFe-MOF
   S2.1. Synthesis
   S2.2. X-ray powder diffraction
   S2.3. Infrared spectroscopy
   S2.4. Thermal gravimetric analysis
   S2.5 SEM measurements
   S2.6. Sorption measurements
S3. Synthesis and characterization of PdFe-NPs
   S3.1. Synthesis
   S3.2. Chemical composition
   S3.3. High-resolution TEM
   S3.4. X-ray powder diffraction
   S3.5. X-ray photoelectron spectroscopy
   S3.6. Raman spectroscopy
   S3.7. ATR infrared spectroscopy
   S3.8. X-ray absorption spectroscopy
S4. Catalytic activity of PdFe-NPs
   S4.1. Nitrobenzene hydrogenation
   S4.2. Tandem reaction
S5. References
S1. General methods and materials

Reagents and solvents used here were of high purity grade and were purchased as follows: pyridine-3,5-dicarboxylic acid (98%) and 4-chloronitrobenzene (98%) from Alfa Aesar; Fe(NO3)3.9H2O (>98%) from Acros; benzoic acid (>99.5%), nitrobenzene (99%), benzaldehyde (99%), aniline (99.5%), N-benzylaniline (99%), chlorobenzene (internal standard, 99%), 4-methylnitrobenzene (99%) and 10wt%Pd/C from Sigma-Aldrich; methanol (reagent grade, 99.9%), toluene (99.9%) and nitrostyrene (97%) from Scharlab; and hydrogen (99.999%) from Abelló Linde S.A. For comparative purposes, a commercial catalyst Pd@C (10% wt. Pd) was purchased from Sigma-Aldrich.

Infrared spectra were recorded using Bruker Alpha II FT-IR with ATR model. Powder X-ray diffraction spectra were measured using 0.5 mm borosilicate capillaries that were aligned on an Empyrean PANalytical powder diffractometer (using Cu Kα radiation λ =1.54056 Å). Thermogravimetric analysis was done using a TGA 550 apparatus with a 5 °C·min⁻¹ scan rate and air flow in the range 25–600 °C (MOF) and a Mettler Toledo TGA/SDTA 851 apparatus, using a heating rate of 10 °C·min⁻¹ in an air stream until 800 °C (NP). ¹H NMR spectra were measured using a Bruker DRX500 (500 MHz) spectrometer.

Scanning electron microscopy SEM and Energy-dispersive X-ray spectroscopy EDS measurements were done using a Hitachi S-4800 microscope system equipped with energy-dispersive X-ray spectroscopy (EDS).

High-resolution transmission electron microscopy (HR-TEM) was done using Jeol JEM-2100F operating at 200 kV. The microscope was also equipped with a high-angle annular dark-field (HAADF) detector and an EDS X-Max 80 detector. Images from HAADF detector were used to achieve better compositional contrast. In this way, a distribution of the particle sizes for each of the samples was obtained together with its statistical parameters. In all the cases, a minimum number of 200 particles was considered. This study was possible thanks to the Software ImageJ. The interpretation of HR-TEM images as to identify interplanar distances was done with Gatan Digital Micrograph software. Thus, the crystalline substance could be known by comparing the obtained interplanar distance value with the references provided by the database of the Software X’Pert HighScore Plus. Besides, the EDS detector, with a resolution of 127 eV, supplied qualitative information about which elements were in the sample. Therefore, maps with different colours depending on the element were obtained together with single point EDAX analyses. Finally, selected area electron diffraction (SAED) was used for phase identification and determination of structural intergrowth. Electron diffraction patterns were interpreted by using Gatan Digital Micrograph software to get information about interplanar distances, thereby knowing planes and elements present in a sample.

X-ray photoelectron spectroscopy (XPS) was used to determine, at the surface of the material, the oxidation states of every metallic species, the relative abundance of every element in each one of the samples, as well as the changes in their chemical environments undertaken throughout the nanoparticle formation process and the catalysis. XPS data were collected on a SPECS spectrometer equipped with a 150-MCD-9 detector and using a non-monochromatic Al Kα (1486.6eV) X-ray source. Spectra were recorded at 25 °C, using an analyser pass energy of 30 eV, an X-ray power of 50W and under an operating pressure of 10⁻⁹ mbar. During data processing, binding energy (BE) values were referenced to the C 1s peak settled at 284.5 eV. Spectra interpretation and peak-fitting were carried out with CASAXPS software using Gaussian-Lorentzian curves, applying a nonlinear Shirley-type
background subtraction and correcting the intensity considering the transmission function of the spectrometer.

Chemical composition was determined by using an inductively coupled plasma emission (ICP) spectrophotometer Agilent 7900 (MOF) and Varian 715-ES (NP). Raman spectra were acquired by using a Labram-HR Raman spectrometer (600 mm\(^{-1}\) grating, 100 mm entrance slit) coupled to a Peltier-cooled CCD detector and an Olympus BXFM optical microscope. Raman scattering was produced by excitation at 514 nm by means of a HeNe laser with 0.1 mW excitation power on the samples. The laser beam was focused on the sample at 50 times microscope objective (numerical aperture = 0.5). Rayleigh scattering was removed by a holographic notch filter, and the Raman spectra were recorded between 200 and 2000 cm\(^{-1}\) with a resolution of 0.5 cm\(^{-1}\).

X-ray absorption near-edge structure (XANES) and extended X-ray absorption Fine Structure (EXAFS) were measured, at 20-BM-B of the Advanced Photon Source at Argonne National Laboratory. A Si (111) fixed-exit double-crystal monochromator and focused beam was used to perform the measurements at Fe and Pd K-edges (7112 and 24350 eV, respectively). For Fe-edge measurements harmonic rejection was facilitated using a Rh-coated mirror (5mrad) as well as a 15% detuning of the beam intensity at ~500 eV above the edge of interest. For the Pd-edge measurements the mirror was not used and the beam intensity was detuned 30%. Data was collected in transmission mode for Pd using ionization chambers and in fluorescence mode using a Ge 13-element detector for Fe. Details on the beamline optics and instruments can be found elsewhere.\(^\text{[1]}\) In order to study the chemical states and local environment of metallic species, the samples were prepared as pellets and measured directly at room temperature without any pre-treatments. The spectra normalization and extraction of the $\chi(k)$ functions were performed using IFEFFIT.\(^\text{[2]}\) Phase and amplitudes were calculated by FEFF6 code.

S2. Synthesis and characterization of PdFe-MOF

S2.1. Synthesis.

The metallo-ligand $\text{H}_4\text{L}$ was prepared according to the published procedure.\(^\text{[3]}\) Concerning the MOF, a solid mixture of Fe(NO\(_3\))\(_3\).9H\(_2\)O (47.2 mg, 0.117mmol), $\text{H}_4\text{L}$ (30 mg, 0.0582 mmol) and benzoic acid (3 mg, 0.0246 mmol) was briefly grounded. The mixture was placed in a thin glass tube which sealed after a cycle of vacuum. Ten of such tubes were heated for 72 h at 120 °C (heating and cooling rate of 4 °C/h). The resulting mixture was washed with DMF (7 x 20ml) and isopropanol (3 x 20ml) for 1.5 days. The as-synthesized MOF was activated using MeOH for 3 days (6 x 20 ml each day), and then heated at 130°C for 4 hours. Yield: 250 mg (64 %). Calculated composition: Pd:Cl:Fe 1:2:2; ICP found Pd:Cl:Fe: 1.0:2.0:2.2. $^1$H-NMR for digested desolvated PdFe-MOF in DMSO-HCl showed no peaks corresponding to washing solvents (DMF or methanol).

S2.2. Powder X-ray diffraction

Powder X-ray diffraction patterns of PdFe-MOF were measured using 0.5 mm borosilicate capillaries that were aligned on an Empyrean PANalytical powder diffractometer (using Cu K\(_\alpha\) radiation $\lambda =1.54056$ Å, scan step size = 0.01313, time per step = 2366.4, number of points 5180). The program (TOPAS) was used for pattern indexing, space group determination and Pawley fitting. Background subtraction, profile smoothing and application of the second
derivative method was done using the polynomial implemented procedure. The peak search algorithm was used to determine the position of 20 peaks in the region 2-30°. These positions were used for indexing, indicating a cubic system with unit cell dimensions \(a = 31.85 \text{ (18)} \, \text{Å}\) and \(V=32309 \, \text{Å}^3\) and a P-3a space group which agrees very well with Pawley fitting (Figure S1) and the morphology seen using SEM (Figure S6). To understand the difference between the current PdFe-MOF and the isoreticular In3O-Pd-MOF (cubic, \(a=22.719 \, \text{Å}\)), it is useful to call here PCN250 (Cubic cell \(a= 21.757 \, \text{Å}\)) and PCN250’ (cubic cell, \(a= 44.043 \, \text{Å}\)) MOFs. The two isoreticular MOFs with 3,3’,5,5’-azobenzenetetracarboxylic acid ligand can be distinguished by the difference in the ligand configuration. Along any axis in PCN250 the ligands in the same cube adopt a mirror configuration, then they alternatively arrange for adjacent cubes whereas in PCN250’ the ligands have the same configuration in each single cube, and the cubes are arranged in a mirror image. Therefore, similar difference in the ligand arrangement is suggested here, which could also be induced by the existence of nitrate coordinated to the axial position of iron centres (see IR and XPS below). As a result, the configuration of the ligand could be distorted, thus affecting the symmetry of the unit cell.

**Figure S1.** Pawley fitting for the Powder diffraction of PdFe-MOF. Cubic unit cell \((a=31.85(18) \, \text{Å}, \ V=32309 \, \text{Å}^3)\), Space group Pa-3. Red: experimental, Blue: fitting, grey: difference.

**Figure S2.** a) Powder diffraction of washed and activated PdFe-MOF. The MOF is stable after activation at 130 °C; b) PXRD of PdFe-MOF together with PdIn-MOF \([\text{PdCl}_2(\text{PDC})_2\text{ ligand}]\) and other MOFs with similar ligands \(3,3’,5,5’\)-azobenzenetetracarboxylic acid). PdFe-MOF is isoreticular to these MOFs (see text).
Figure S3. 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.

S2.3. Infrared spectroscopy

Figure S4 depicts the Infrared spectra of washed MOF and the metallo-ligand (H₄L). The bands at 1640, 1390, 627, and 480 cm⁻¹ correspond to the trimeric Fe₃O(COO⁻)₆ moiety. In order to investigate the existence of NO₃⁻ ion (as seen by XPS, see section 3.4), the IR spectra were compared with unpublished neutral Fe₃O-Pd-MOF (same ligand) where no NO₃ ion exists. The shoulder peaks at 720, 1339 and 1407 cm⁻¹ could indicate the NO₃ ion in PdFe-MOF, as it can be found in other metal-nitrate complexes. The NO₃⁻ indicative peaks are not clearly seen, mostly as a result of the overlapping with strong and broad carboxylic frequencies. In similar cationic MOFs, NO₃ exists and locates very close to the metal ions rather than in the centre of the pores, but not coordinated to metal ions. However, coordinated NO₃ was previously reported in oxo-iron clusters together with water molecules.
Figure S4. a) Infrared spectra of washed MOF and the metallo-ligand (H₄L). The peaks of free acid at 1718 and 1745 cm⁻¹ disappeared and instead strong peaks appeared at 1640, 1390, 627, and 480 cm⁻¹ indicating the Fe₃O(COO⁻)₆(H₂O)₃ moiety. b) Infrared spectra of washed PdFe-MOF (black) and similar unpublished Fe₃O-Pd-MOF with no NO₃. The shoulders at 720, 1339, 1407 cm⁻¹ could indicate the presence of NO₃ ion.

S2.4. Thermal gravimetric analysis

Using TGA, the thermal stability of the MOF was inspected. Under 125 °C, the MOF loses around 17.5% of its weight in one step, due to the evaporation of the adsorbed solvent molecules. In the range 125-310 °C, a gradual decrease was observed (around 10% weight loss), which corresponds to the elimination of coordinated-H₂O and NO₃⁻ molecules. Over 310 °C, the MOF decomposes as a result of breaking the metallo-ligand as seen in the TGA of the free ligand (Figure S5b). At 900 °C, 32% of residue remained, which corresponds to a mixture of Pd, PdFe and iron oxide as seen by powder diffraction.

Figure S5. a) (Black) Thermogravimetric analysis (TGA) of the PdFe-MOF using a heating rate of 5 °C/min under air flow. (Red) The derivative of weight loss with temperature. b) Thermogravimetric analysis (TGA) of the metallo-ligand H₄L using a heating rate of 5 °C/min under air flow.
S2.5. SEM measurements

Figure S6. SEM picture of the solid obtained showing the nanoparticles of PdFe-MOF with a size range between 20-70 nm.

S2.6. Sorption measurements

The N₂ sorption isotherm at 77 K of activated PdFe-MOF (at 180 °C for 2 h) corresponds to a microporous type material with type-I reversible curve below p/p₀≈ 0.8. The hysteresis loop over this value is mostly related to intergranular mesoporosity. Surface area was calculated in the range 0.0005-0.06 p/p₀, giving a value of 830 m²/g. These values are consistent with what was found for the isoreticular PdIn-MOF.[4]

CO₂ sorption isotherms were measured at 298, 313 and 333 K up to 18 bars of pressure. High CO₂ uptake was seen with 6.4 (28 wt%), 5.9 (26.0 wt%), 5.3 (23.3 wt%) mmol/g for the three temperatures, respectively. These values indicate higher CO₂ uptakes compared to isoreticular MOFs with similar ligands, with almost twice the amount of CO₂ adsorbed at room temperature.[4],[7] The three isotherms were fitted to the Langmuir equation were Q is the amount of adsorbed gas (mmol/g), Qₘ is the gas adsorbed at saturation and b₁ and b₂ are fitting constants. Clausius-Clapeyron equation was used to calculate the isosteric enthalpy of adsorption Qₛₑ using these fitted data.

Figure S7. a) N₂ sorption isotherm of PdFe-MOF at 77 K. b) CO₂ gas adsorption isotherms of PdFe-MOF at different temperatures. Lines were fitted using Langmuir equation.
As seen in Figure S8, $Q_{st0}$ is 24 KJ/mol and it slightly changes at low coverages, but then it increases up to 32 KJ/mol at high coverages. This remarkable increase mostly indicates strong intermolecular interactions.\[^9\]

**Figure S8.** Isosteric enthalpy of adsorption ($Q_{st}$) of CO$_2$ on PdFe-MOF as a function of coverage.

**Figure S9.** PXRD of desolvated PdFe-MOF before and after adsorption measurements.
S3. Synthesis and characterization of PdFe-NPs

S3.1. Synthesis

**In-situ chemically synthesized nanoparticles:** As general procedure, 10 mg of PdFe-MOF were added to a solution containing 2 mmol of nitrobenzene and 2 mL of toluene. The system was sealed and pressurized until 5 H₂ bar at 25 °C. The solution darkening due to the presence of aniline-related compounds was taken as a good indicator of the starting of the formation of nanoparticles, always occurring between 1 h and 1.5 h after the initial mixing. Once this seen, the PdFe-MOF was kept in touch with the solution for ten minutes more. Thereafter, the solid was filtered and repeatedly washed with MeOH during 24 h (as-synthesized PdFe-NP). In the case of thermal treatment of the as-synthesized NP, it was placed at 300 °C for variable times (6h, 12h or 24 h) under vacuum.

It must be pointed out that, in order to understand the influence of the components of the above reaction in the process, some additional tests were done. Firstly, 10 mg of PdFe-MOF were added to a solution containing 2 mmol of nitrobenzene and 2 mL of toluene in the absence of H₂. Secondly, 10 mg of MOF were added to a solution containing 2 mL of toluene and pressurized to 5 H₂ bar. Here no changes were observed after 24 h, being this a sign of no NP formation. Finally, the reaction was carried out with 10 mg of MOF, a solution containing 2 mmol of aniline (instead of nitrobenzene), and 2 mL of toluene in the presence of H₂. In this case, the nanoparticles were observed.

**Thermal-treating synthesized nanoparticles.** In this case, the PdFe-MOF was activated in a tubular fix-bed reactor under a H₂ flow (100 mL/min) at 500 °C during 3 h, using a heating rate of 10 °C/min.

The different nano-composite materials herein synthesized are summarized in Table S1.

**Table S1. Summary of the different materials prepared.**

<table>
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<tr>
<th>Material code</th>
<th>Description</th>
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<td>PdFe-MOF</td>
<td>Original MOF</td>
<td>-</td>
</tr>
<tr>
<td>PdFe-NP</td>
<td>Chemically as-synthesized NP (In-situ, nitrobenzene,</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td></td>
<td>toluene, H₂)</td>
<td></td>
</tr>
<tr>
<td>PdFe-NP-300-6</td>
<td>Heating PdFe-NP at 300 °C, vacuum, 6h</td>
<td>1.2±0.3</td>
</tr>
<tr>
<td>PdFe-NP-300-12</td>
<td>Heating PdFe-NP at 300 °C, vacuum, 12h</td>
<td>1.7±0.3</td>
</tr>
<tr>
<td>PdFe-NP-300-48</td>
<td>Heating PdFe-NP at 300 °C, vacuum, 48h</td>
<td>1.3±0.3</td>
</tr>
<tr>
<td>PdFe-NP-used</td>
<td>Chemically as-synthesized NP (In-situ, nitrobenzene,</td>
<td>3.8±1.4</td>
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<td></td>
<td>toluene, H₂), once the NBZ reduction is completed</td>
<td></td>
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<tr>
<td>PdFe-NP-thermal</td>
<td>NP via thermal treating of PdFe-MOF (500 °C, H₂ flow)</td>
<td>3.1±3.1</td>
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<tr>
<td>PdFe-NP-aniline</td>
<td>Chemically as-synthesized NP (In-situ, aniline,</td>
<td>2.0±1.8</td>
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<tr>
<td></td>
<td>toluene, H₂)</td>
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¹: Measured by HR-TEM by considering a minimum number of 200 particles.
S3.2. Chemical composition

Table S2 shows the results obtained by ICP and TGA for the main materials prepared in this work. As it can be seen, the transformation of the bimetallic MOF into the nanocomposite entails an increase in metal content and the corresponding decrease in the amount of organic matter.

Table S2. Compositional characterization of several PdFe-based materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Pd wt.%(^a)</th>
<th>Fe wt.%(^a)</th>
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<td>PdFe-MOF</td>
<td>9.2</td>
<td>15.7</td>
<td>64.2</td>
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<tr>
<td>PdFe-NP</td>
<td>12.6</td>
<td>17.2</td>
<td>52.1</td>
</tr>
<tr>
<td>PdFe-NP-300-6</td>
<td>15.2</td>
<td>20.6</td>
<td>47.0</td>
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\(a\): As calculated by ICP, \(b\): As calculated by TGA.

S3.3. High-resolution TEM

In order to establish the best approach to form the bimetallic nanocomposite, HR-TEM, EDAX and electron diffraction measurements were used (See Figures S10-S17). As seen in HR-TEM, the metallic nanocomposite synthesized through an in situ chemical method (PdFe-NP) has an average PdFe size \(\approx 1\) nm with most of the particles presenting a diameter below 2 nm. Therefore, considering Pd atomic radius \(\approx 140\) pm, the average nanoparticle contains around 40 Pd atoms. Thermal treatments of the nanocomposite under vacuum proved not to have any considerable effect as far as the nanoparticle size was concerned, whereas the nanoparticle size seemed to be slightly increasing at longer reaction times. Interestingly, the nanoparticles obtained after a direct thermal treatment of PdFe-MOF with \(H_2\) at 500 °C (PdFe-NP-thermal) exhibit considerably higher particle sizes than those synthesized by the chemical method at room temperature. Moreover, the well-established chemical method employing aniline together with \(H_2\) pressure over PdFe-MOF at RT in toluene (PdFe-NP-aniline) provided a broader PdFe size particle distribution \(\approx 2.0 \pm 1.8\) nm than that obtained with the \textit{in-situ} methodology.

Interplanar distances were calculated using Gatan Digital Software. In addition, electron diffraction patterns of the NPs were also recorded. The absence of narrow spacings corresponding to Pd crystalline planes in the chemical synthesized NPs points to the formation of the desired bimetallic alloy. In fact, the presence of an additional metal to palladium can be one of the reasons for the small particle size of the NPs, as previously reported in the literature.\(^{[10]}\) On the contrary, the presence of the aforementioned spacings in the sample corresponding to the PdFe-NP-thermal can be considered as an evidence of the formation of Pd NPs besides or instead of the desired alloy. Nonetheless, the resolution of both techniques could not be taken as a definitive proof of the existence of intermetallic Pd-Fe NPs, as opposed to what is reported in the literature.\(^{[11]}\) This is due to the similarities in the interplanar distances for Pd and Pd-Fe. However, the XRD indicates the existence of such intermetallic PdFe-NPs (see Figure S18a).

The presence of a small amount of Fe in the PdFe-NP was confirmed by employing EDAX punctual analysis for isolated nanoparticles from the support by an US treatment. Moreover, EDAX mapping for PdFe-NP revealed that iron is present in large amounts in the carbon. This
fact is especially interesting, as it opens up the possibility of having a material with different functionalities given by the PdFe-NPs and the presence of FeOₓ (confirmed by Raman Spectroscopy, see below) in the carbonaceous support. On the contrary, XPS and EDS analysis indicates that, for PdFe-NP-thermal, a great part of this iron should be in the bimetallic nanoparticles rather than in the support.

The XRD analysis of PdFe-NP shows the centred cubic (fcc) pattern characteristic of palladium with a shift in the diffraction peaks to higher angles with respect to the peaks expected for elemental palladium (Pd@C, 10wt%Pd). This fact corresponds to the modification of the fcc unit cell of Pd due to the presence of Fe, which is in accordance with Vegard’s law. This constitutes a definitive signal of the presence of a certain amount of Fe in the prepared nanoparticles. On the other hand, peaks related neither to metallic iron nor to iron or palladium oxides were found. Besides that, Pd@C (10wt % of Pd, commercial) has been compared with our nanocomposite, endorsing the fact that there is a shift towards higher angles for Pd in the PdFe-NP diffraction pattern. The absence of XRD peaks corresponding to iron oxide in the chemically-prepared materials along with the fact that Fe was detected in the C support by EDS and its corresponding FeOₓ seen by Raman, point to a very small size iron oxide, likely subnanometric, in the carbonaceous support. In this sense, the flattening of XAS features in comparison with those corresponding to the bulk iron oxide (Figure 5 and Table S5) can be taken as a definitive proof of the existence of such nanosized species.
Figure S10. TEM and STEM micrographs and particle size distributions of samples of a) PdFe-NP, b) PdFe-NP-300-6, c) PdFe-NP-300-12, and d) PdFe-NP-300-48.
Figure S11. TEM and STEM micrographs and particle size distributions of samples of a) PdFe-NP-used, b) PdFe-NP-aniline, c) PdFe-NP-thermal.

Figure S12. STEM micrographs (a, b) and particle size distribution (c) of samples of commercial Pd@C.
Figure S13. SAED patterns of samples of a) PdFe-NP, b) PdFe-NP-300-6, c) PdFe-NP-thermal.
Figure S14. EDS single point analyses for a) PdFe-NP sample sonicated for 30 minutes and b) PdFe-NP-thermal.

Figure S15. EDS mapping of the sample PdFe-NP.
Figure S16. EDS mapping analysis for PdFe-NP-thermal.

Figure S17. STEM images of samples of some agglomerations of PdFe-NP obtained by a) chemical treatment and b) thermal treatment.
S3.4. X-ray powder diffraction

Figure S18. a) Powder diffraction of PdFe-NP Thermal (red), b) Powder diffraction of PdFe-NP from chemical (blue) vs commercial 10%Pd@C (green). The black curves are the best fit to extract the peak positions. The black vertical lines are eye guides.

S3.5. X-ray photoelectron spectroscopy (XPS)

All the samples were manipulated under air-free conditions in order to avoid any contact with atmosphere (See Tables S3-4 and Figure 4 and S19-21).

First, the C1s signal can be deconvoluted in three different components in all spectra. The adventitious carbon together with C-C, C-H has been fixed at 284.5 eV, being all the other XPS signals calibrated with respect to this one. At around 286 eV, C bonded to N can be founded and above 288 eV the signal should correspond to carboxylates, slightly shifted at lower binding energy in the case of our chemically prepared materials, probably because of its coordination to iron.[14]
As far as the \textbf{Fe2p} region is concerned, in all the cases except PdFe-NP-thermal, the position of the \textit{2p}_{3/2} peak can be attributed to the presence of Fe (III). Although frequently deconvoluted in the literature, we consider the contributions of Fe(III) and Fe(II) too close to each other as to be properly distinguished and quantified by this technique. Nonetheless, the shoulder observed in PdFe-MOF, PdFe-NP-300-6 and PdFe-NP-300-12 can be ascribed to the presence of minor amounts of these partially-reduced species. The material PdFe-NP-thermal is the only one clearly showing the presence of Fe(0) at 706.0 eV.

On the other hand, besides the shift for metallic Pd already mentioned in the main text, the \textbf{Pd3d} area points out the presence of 100% Pd(II) and 100% Pd(0) for PdFe-MOF and for PdFe-NP-thermal, respectively. It should be noted the up-shift in the position of Pd(II) in PdFe-MOF, indicating coordination to Cl. Surprisingly, PdFe-NP, (not being thermally treated) barely shows a signal in the region of Pd at 335.0 eV corresponding to metallic Pd. If considering the total atomic \% estimated with the XPS analysis, the deposition of carbonaceous matter on the nanoparticles should be accounted for this effect. This is the reason why thermal treatments under vacuum have been used in this work, to clean the catalytic surface of the material. The XPS analysis of the materials treated at 300 °C under vacuum for different times unveil the Pd region again and thereby the good cleaning of the material. Nonetheless, the longer the treatment, the more quantity of oxidized palladium can be observed.

As far as the \textbf{O1s} is concerned, three main contributions could be identified in these samples. Taking the PdFe-MOF as a reference, the signal at 528.6 eV is to be assigned to the \textit{oxo} bridge between three irons. The upshift of this contribution observed in the supported nanoparticles unveils higher contributions of PdO to this signal. The 531.4 eV signal observed for the PdFe-MOF is due to the presence of carboxylates, with the XPS signal at lower B.E. than expected due to its coordination to iron. In fact, when forming the nanoparticles by chemical or thermal methods, this signal is shifted to higher B.E, indicating that the iron is being ripped from its original coordination environment. Finally, the signal at higher BE (533 eV) is due to contributions of nitrate ions and/or water molecules.

In the case of the \textbf{N1s}, and taking again the PdFe-MOF as a reference, the signal at 399.6 eV should be due to the pyridinic ligand coordinated to Pd, thereby shifted at higher B.E. because of the charge transfer to the metal. In PdFe-NP, the decrease in the B.E. of this N could be explained as an effect of a partial exit of the pyridinic ligand from the coordination sphere of Pd. On the other hand, a more pronounced shift towards higher BE is observed for this peak in the PdFe-NP-300-6, probably due to the presence of aniline coordinated to Pd (400.4 eV), pointing out the aniline as the key ligand from the transition from MOF to nanoparticles, which is in accordance with what has been observed in the ATR analysis (see below). For PdFe-NP-thermal only signals of oxidized N are observed, probably corresponding to nitrates and/or protonated amino groups. Additionally, for PdFe-MOF, a signal at 405.7 eV can be seen corresponding to the nitrogen of nitrate counter ion in the MOF. Ionic nitrates-N usually show signal around 407.4 eV. This low value mostly corresponds to binding nitrate (ONOO\textsuperscript{-}), as seen in the literature.
### Table S3. Atomic % obtained by XPS analysis of the different materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface atomic weight percent composition (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fe</th>
<th>Pd</th>
<th>O</th>
<th>C*</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdFe-@MOF</td>
<td></td>
<td>2</td>
<td>1</td>
<td>23</td>
<td>70</td>
<td>3</td>
</tr>
<tr>
<td>PdFe-NP</td>
<td></td>
<td>1</td>
<td>&lt;1</td>
<td>17</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td>PdFe-NP-300-6</td>
<td></td>
<td>2</td>
<td>3</td>
<td>21</td>
<td>68</td>
<td>6</td>
</tr>
<tr>
<td>PdFe-NP-300-12</td>
<td></td>
<td>9</td>
<td>3</td>
<td>39</td>
<td>46</td>
<td>3</td>
</tr>
<tr>
<td>PdFe-NP-300-48</td>
<td></td>
<td>9</td>
<td>4</td>
<td>41</td>
<td>44</td>
<td>2</td>
</tr>
<tr>
<td>PdFe-NP-thermal</td>
<td></td>
<td>10</td>
<td>1</td>
<td>31</td>
<td>45</td>
<td>13</td>
</tr>
</tbody>
</table>

### Table S4. XPS data of Fe<sub>2p</sub><sup>3/2</sup>, Pd<sub>3d</sub><sup>5/2</sup>, O<sub>1s</sub> and N<sub>1s</sub> for the different materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Binding Energy (eV) : (Atomic %*)</th>
<th>Fe&lt;sub&gt;2p&lt;/sub&gt;&lt;sup&gt;3/2&lt;/sup&gt;</th>
<th>Pd&lt;sub&gt;3d&lt;/sub&gt;&lt;sup&gt;5/2&lt;/sup&gt;</th>
<th>O&lt;sub&gt;1s&lt;/sub&gt;</th>
<th>N&lt;sub&gt;1s&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdFe-@MOF</td>
<td></td>
<td>710.6</td>
<td>337.7</td>
<td>533.1</td>
<td>531.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(13)</td>
<td>(71)</td>
</tr>
<tr>
<td>PdFe-NP</td>
<td></td>
<td>710.4</td>
<td>335.0</td>
<td>533.3</td>
<td>531.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(11)</td>
<td>(64)</td>
</tr>
<tr>
<td>PdFe-NP-300-6</td>
<td></td>
<td>710.2</td>
<td>337.2</td>
<td>533.1</td>
<td>529.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(13)</td>
<td>(37)</td>
</tr>
<tr>
<td>PdFe-NP-300-12</td>
<td></td>
<td>710.2</td>
<td>337.4</td>
<td>334.9</td>
<td>531.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(80)</td>
<td>(20)</td>
</tr>
<tr>
<td>PdFe-NP-300-48</td>
<td></td>
<td>710.3</td>
<td>337.2</td>
<td>334.7</td>
<td>533.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(95)</td>
<td>(5)</td>
</tr>
<tr>
<td>PdFe-NP-thermal</td>
<td></td>
<td>706.0</td>
<td>335.2</td>
<td></td>
<td>532.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(23)</td>
</tr>
<tr>
<td>10%Pd@C</td>
<td></td>
<td>-</td>
<td>335.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Not shown when just one species has been found.
Figure S19. C1s and Fe2p XPS signals of a) PdFe-MOF, b) PdFe-NP, c) PdFe-NP-300-6, d) PdFe-NP-300-12, e) PdFe-NP-300-48 and f) PdFe-NP-thermal.

Figure S20. N1s and O1s XPS signals of a) PdFe-MOF, b) PdFe-NP, c) PdFe-NP-300-6, d) PdFe-NP-300-12, e) PdFe-NP-300-48 and f) PdFe-NP-thermal.
Figure S21. Pd3d XPS signal of a) PdFe-MOF, b) PdFe-NP, c) PdFe-NP-300-6, d) PdFe-NP-300-12, e) PdFe-NP-300-48, f) PdFe-NP-thermal and g) Pd@C (commercial).

S3.6. Raman spectroscopy

Figure S22 shows the Raman spectroscopy of three samples corresponding to PdFe-NP, PdFe-NP-300-6, and PdFe-NP-300-48. Frequencies above 1000 cm\(^{-1}\) have been omitted because the presence of either graphene or graphitic carbon makes the analysis of features corresponding to iron oxide difficult to be properly interpreted in this area.\(^{[23]}\) Broadly speaking, the main conclusion that can be drawn is the presence of different types of iron oxide. The Raman spectra of the PdFe-NP-300-48 clearly illustrates this, as peaks at 217, 282 and 631 cm\(^{-1}\) can be observed and assigned to Fe\(_3\)O\(_4\).\(^{[24]}\) On the other hand, the peaks at 396, 591 and 690 cm\(^{-1}\) are characteristic of \(\gamma\)-Fe\(_2\)O\(_3\), whereas the band observed at 429 is usually the strongest one for the \(\alpha\)-Fe\(_2\)O\(_3\) phase.\(^{[25]}\) PdFe-NP-300-12 shows the same features but with less intensity, and for PdFe-NP just peaks at 282 and 631 cm\(^{-1}\) can be distinguished, probably due to the larger amount of carbon on the surface (see XPS Section). The magnetism exhibited by these samples fits well with Fe\(_3\)O\(_4\) being the main type of iron observed.
Figure S22. Raman spectra of different PdFe-NPs nanocomposites. (●): Fe₃O₄, (▴): γ-Fe₂O₃, (▪): α-Fe₂O₃.

S3.7. ATR-infrared spectroscopy

MOF suspensions were prepared using 5 mg of MOF in the presence of 5 bar of H₂ at 25 °C and 1 mL of toluene (PdFe-MOF-TOL) and another two with same compositions by adding 1 mmol of nitrobenzene (PdFe-MOF-TOL+NTB) or aniline (PdFe-MOF-TOL+ANI). All suspensions were stirred at 1000 rpm during 1 h, and after centrifugation of the solid, the ATR-IR was measured. The objective was to monitor the transition between PdFe-MOF and PdFe-NP, thus characterizing the material just at the beginning of the process (see Figure S23).

Despite its complexity, several interesting conclusions can be drawn from the IR spectra. No major changes were observed when the PdFe-MOF was in touch with either toluene or with a mixture of toluene and nitrobenzene. On the contrary, the presence of aniline significantly modified the structure of the material. The samples PdFe-MOF, PdFe-MOF-TOL, PdFe-MOF-TOL+NTB showed two asymmetric stretching bands corresponding to the Fe-O bond (600-650 cm⁻¹ and 450-500 cm⁻¹), this probably unveiling the mixed-valence state of iron in our MOF.[26] On the other hand, these two signals were shifted at lower frequencies for the sample PdFe-MOF-TOL+ANI, which could be indicating a change in the iron surroundings and the formation of hematite, with the iron mostly exhibiting an octahedral coordination.[27] At 1445 cm⁻¹ a weak signal usually referred to pyridine coordinated to Lewis acid sites can be assigned to the N-Pd bond.[28] In the sample in touch with aniline this signal disappeared, whereas a new one appears at 1458 cm⁻¹, which can be a sign of a ligand exchange between pyridine and aniline. Concerning the carboxylates, they also seem to be affected by the presence of aniline, since the band corresponding to symmetric vibrations of COO⁻ at 1399 cm⁻¹ seemed to partially lose its component at lower frequencies, which corresponds to COO⁻ bonded. Finally, the presence of aniline was also evident after observing the bands at 1616 and 1556 cm⁻¹ in the area of the N-H bending of primary amines.[29] Moreover, the band at
3200 cm\(^{-1}\) corresponding to NH\(_2\) can be noticed, the broad singlet feature indicating a strong hydrogen bonding and the coordination of the NH\(_2\) group.\([29]\)

![Figure S23](image)

**Figure S23.** (Top) ATR spectra for PdFe-MOF after immersion with different reactants. (Bottom) Closer view to the 1800-400 cm\(^{-1}\) region.

### S3.8. X-ray absorption spectroscopy

XAS is a powerful technique in the characterization of metal systems, providing element-selective information on local and electronic structure of metal atoms present in a matrix. Figure S24 shows the normalized XANES spectra at Fe K-edge of PdFe-MOF, PdFe-MOF, and the respective Fe-based standards. When PdFe-MOF is concerned, the main oxidation state of Fe centres lies in the region of Fe(III) (7123 eV), as already observed by XPS. Furthermore, the features of the PdFe-MOF spectrum do not resemble those of the different iron oxides used as standards, pointing out to a completely different Fe local environment in the MOF. On the other hand, when the PdFe-MOF is transformed to PdFe-NP, the spectrum presents mostly the same features as those of magnetite crystalline phase (Fe\(_3\)O\(_4\)). The similarity of iron centres in PdFe-NP in comparison to magnetite can also be seen in the EXAFS signal (Figure S24) and $|\text{FT}|$ of Figure S25(b), where all oscillations in the $\chi(k)$ and coordination shells in $|\text{FT}|$ are the same in position, despite their different intensities. These differences in intensity, especially in the higher shells (2-4 Å), can be ascribed to the (sub)nanometric character of the iron species. This behaviour has already been observed for other metal-based oxides in the literature.\([30]\) In order to verify this hypothesis, EXAFS data analysis has been performed and the results are summarized in Table S5. In fact, the first-shell Fe-O average coordination number for PdFe-NP is significantly smaller than in Fe\(_3\)O\(_4\) bulk counterpart (1.8 vs 6.0). Fitting the Fe-Fe path at higher shell (~2.8 Å – phase uncorrected) resulted in a Fe-Fe average coordination number of ~ 6, whereas in the bulk it is equal to 12. Including a Fe-Pd contribution improves the fit quality, indicating a Fe-Pd interaction, although the error bar is quite high due to the correlation between the parameters.
Figure S24. $k^2$-weighted $\chi(k)$ functions for PdFe-MOF, PdFe-NP and standards of iron oxides ($Fe_2O_3$ and $Fe_3O_4$).

Table S5. Summary of optimized parameters by fitting the Fe K-edge EXAFS data\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>Fe-O</th>
<th>Fe-Pd</th>
<th>Fe-O</th>
<th>$\sigma^2$ (Å\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN</td>
<td>R (Å)</td>
<td>CN</td>
<td>R (Å)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(6)*</td>
<td>(1.88)</td>
<td>(12)*</td>
<td>(2.73)</td>
<td>3.49</td>
</tr>
<tr>
<td>PdFe-MOF</td>
<td>3.3 ± 0.3</td>
<td>1.997 ± 0.007</td>
<td>0.0048 ± 0.0012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdFe-NP\textsuperscript{b}</td>
<td>1.8 ± 0.4</td>
<td>1.92 ± 0.01</td>
<td>6 ± 2</td>
<td>3.37 ± 0.01</td>
<td>0.001 ± 0.003</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The fits were performed over FT of the $k^2$-weighted $\chi(k)$ functions in the $\Delta k = 2.3-10.0$ Å\textsuperscript{-1} interval and $\Delta R = 1.0-2.0$ Å for PdFe-MOF and 1.0-3.5 Å for PdFe-NP. S\textsuperscript{02} = 1.0. (*) Indicates reference values. In the bulk Fe$_3$O$_4$, the first-shell Fe-O is equal to 6, pointing out that iron species on PdFe-NP are in the (sub)nanometric range since the Fe-O coordination number is much smaller.

Figure S25(a) shows the normalized XANES spectra at Pd K-edge of PdFe-MOF, PdFe-MOF, and the respective Pd-based standards. The spectrum of PdFe-MOF shows the absorption edge positioned at 24354 eV, characteristic of Pd(II). With MOF decomposition to PdFe-NP, the absorption edge immediately shifted to lower energy (24350 eV), indicating a reduction of Pd(II) species to Pd\textsuperscript{0}. The change in edge position is accompanied by the appearance of well-defined EXAFS oscillations immediately after the edge (negative and positive peaks at 24382 and 24397 eV, respectively). These strong features are due to the well-arranged local fcc structure, where 12 Pd atoms are coordinated at the same distance from the central Pd atom.\textsuperscript{[31]} The quantitative results derived from EXAFS data analysis are summarized in Table S6. For Pd metal foil, a characteristic coordination number of 12 with Pd-Pd distance of 2.74 Å was obtained, typical of noble metals arranged in a fcc local structure. For the PdFe-NP catalyst, an average coordination number of 9.6 for Pd-Pd contribution was obtained. This value is higher than expected considering the particle size distribution obtained by TEM. Notwithstanding, once XAS is a bulk-type technique and TEM is statistics dependent, the presence of unseen big particles in the sample could explain the relatively higher Pd-Pd coordination number.
Figure S25. Normalized XANES spectra at Pd K-edge (a) and |FT| of the \( k^3 \)-weighted \( \chi(k) \) functions (b) for PdFe-MOF, PdFe-NP and Pd-based standards.

Table S6. Summary of optimized parameters by fitting the Pd K-edge EXAFS data.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd-N</th>
<th>Pd-Cl</th>
<th>Pd-Pd</th>
<th>Pd-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Path</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CN</td>
<td>R (Å)</td>
<td>CN</td>
<td>R (Å)</td>
</tr>
<tr>
<td>PdFe-MOF</td>
<td>2</td>
<td>2.13 ± 0.09</td>
<td>4</td>
<td>2.23 ± 0.03</td>
</tr>
<tr>
<td>PdFe-NP</td>
<td>9.6 ± 1.1</td>
<td>2.741 ± 0.006</td>
<td>0.0054 ± 0.0009</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The fits were performed over FT of the \( k^1k^2k^3 \)-weighted \( \chi(k) \) functions in the \( \Delta k = 3.6-12.0 \text{ Å}^{-1} \) and \( \Delta R = 2.0-3.0 \text{ Å} \) intervals for PdFe-NP and \( \Delta k = 3.0-8.0 \text{ Å}^{-1} \) and \( \Delta R = 1.0-3.0 \text{ Å} \) for PdFe-MOF. Non-optimized parameters are recognizable by the absence of the corresponding error bar.

S.4. Catalytic activity of PdFe NPs

S4.1. Nitrobenzene hydrogenation with PdFe-NPs

Figure S26. a) Illustration of Pd@C not responding to magnet. b) and c) Illustration of the sequence of magnetically recovering PdFe-NP-300-6.
### Table S7. Summary of reported catalysts for hydrogenation of nitroarenes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Metal load. (wt%)</th>
<th>T(°C)</th>
<th>P(_{\text{H}_2}) (bar)</th>
<th>Conversion(%)</th>
<th>Selectivity(%)</th>
<th>TOF(h(^{-1}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdFe-MOF</td>
<td>9.2%Pd</td>
<td>r.t.</td>
<td>5</td>
<td>99</td>
<td>99</td>
<td>69</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>PdFe-NP-300-6</td>
<td>15.2%Pd</td>
<td>r.t.</td>
<td>5</td>
<td>95</td>
<td>100</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pd-CNORIT1</td>
<td>3%</td>
<td>45</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
<td>[32]</td>
</tr>
<tr>
<td>4</td>
<td>Pd-CNORITA1</td>
<td>3%</td>
<td>45</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pd-CNORITX</td>
<td>3%</td>
<td>45</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pd-HCP</td>
<td>4%</td>
<td>r.t.</td>
<td>1</td>
<td>7.7</td>
<td>99</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Co-Ndoped MC-800</td>
<td>8%</td>
<td>80</td>
<td>1</td>
<td>99</td>
<td>99</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Ni-Ndoped MC-800</td>
<td>8%</td>
<td>80</td>
<td>1</td>
<td>17.8</td>
<td>99</td>
<td>7</td>
<td>[34]</td>
</tr>
<tr>
<td>9</td>
<td>Fe-Ndoped MC-800</td>
<td>8%</td>
<td>80</td>
<td>1</td>
<td>5.6</td>
<td>99</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Pd-CHT</td>
<td>5%</td>
<td>60</td>
<td>1</td>
<td>85</td>
<td>95</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Pd-Co@C-SiO(_2)-NH(_2)</td>
<td>4.5%Pd</td>
<td>r.t.</td>
<td>1</td>
<td>100</td>
<td>-</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>NiZn-AC-350</td>
<td>10.03%Ni</td>
<td>80</td>
<td>1</td>
<td>100</td>
<td>99</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Pd-MOF-1</td>
<td>8.2%</td>
<td>r.t.</td>
<td>1</td>
<td>98</td>
<td>-</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Rh-NC-HS</td>
<td>2%</td>
<td>r.t.</td>
<td>1</td>
<td>7.3</td>
<td>99</td>
<td>5</td>
<td>[39]</td>
</tr>
<tr>
<td>15</td>
<td>Rh-NC-HS</td>
<td>2%</td>
<td>50</td>
<td>1</td>
<td>32</td>
<td>99</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Pd-PPH(_3)-FDU-12</td>
<td>0.83%</td>
<td>40</td>
<td>10</td>
<td>99</td>
<td>99</td>
<td>6</td>
<td>[40]</td>
</tr>
<tr>
<td>17</td>
<td>Pd-Al(_2)O(_3)</td>
<td>0.5%</td>
<td>r.t.</td>
<td>1</td>
<td>100</td>
<td>-</td>
<td>10</td>
<td>[41]</td>
</tr>
<tr>
<td>18</td>
<td>Pd-MgF(_2)-(OH)(_x)</td>
<td>10%</td>
<td>r.t.</td>
<td>1 (bubbling)</td>
<td>99</td>
<td>100</td>
<td>128</td>
<td></td>
</tr>
</tbody>
</table>

TOFs (h\(^{-1}\)) were calculated at the higher conversion as moles of formed aniline per moles of active metal per hour.
**S4.2. Tandem reaction**

**Figure S27.** Coupling reaction between nitrobenzene and benzaldehyde. **Reaction conditions:** 0.123 g nitrobenzene, 0.106 g benzaldehyde, 5 mg PdFe-MOF, at 5 bar H₂ pressure and 25 °C during 6.5 h.

**S5. References:**


[38] L. Bao, Z. Yu, T. Fei, Z. Yan, J. Li, C. Sun, S. Pang, *Applied Organometallic Chemistry* n/a (n/a), e5607.


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

Mohanad D. Darawsheh, Jaime Mazarío, Christian W. Lopes, Mónica Giménez-Marqués, Marcelo E. Domine, Debora M. Meira, Jordan Martínez, Guillermo Mínguez Espallargas and Pascual Oña-Burgos

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 s/n, 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, Research Centre CIAIMBITAL, University of Almería, Ctra. Sacramento, s/n, Almería, E-04120, Spain.

Abstract

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 methodology results in a compositionally homogeneous nanocomposite formed by Fe-doped Pd nanoparticles and these, in turn, supported on an iron oxide-doped carbon. The nanocomposite has been fully characterized by several techniques such as IR, Raman, TEM, XPS, XAS, among others. The performance of this nanocomposite as an heterogeneous catalyst for hydrogenation of nitroarenes and nitrobenzene coupling with benzaldehyde has been evaluated, proving it to be an efficient and reusable catalyst.
**Introduction**

Nanostructured materials and their composites have attracted a lot of attention over the last decades in catalysis, \(^1\) sensing, \(^2\) environmental \(^3\) and biomedical \(^4\) applications. Specifically, the use of nanomaterials as catalysts in organic compound synthesis is an important pathway in order to develop viable synthetic procedures in pharmaceutical and chemical industry. \(^1\) In this regard, supported metal nanoparticles (NPs) are highly valued due to their high activity, selectivity and the possibility to modulate their activity by controlling their size, distribution, composition and the nature of the support. \(^5\)

However, despite the broad applicability in different areas, high-temperature reduction of metal salts or coordination compounds is still the most common way to prepare supported metal NPs. \(^6\) A different route to successfully control the NP size under mild conditions consists in using metal complexes of low oxidation state in combination with long-chain aliphatic amines, \(^7\) although it would require the use of an inert atmosphere. An alternative approach is based on the use of templates, \(^8\) with the precursor serving as the source of both, metal and support.

In this sense, metal-organic frameworks (MOFs) \(^9\) offer a unique scenario. These porous crystalline materials formed by metal clusters and organic linkers have been studied in the last years for numerous applications, such as gas sorption and separation, \(^10\) catalysis, \(^11\) sensing, \(^12\) electronic \(^13\) and magnetic devices, \(^14\) among others. Their ordered structures act as scaffolds that result in ideal candidates for self-template precursors upon thermal conversion to well-defined nanocomposites \(^15\) that can be used in several fields such as catalysis, \(^16\) electrocatalysis, \(^17\) and energy storage and conversion. \(^18\)
An additional benefit that accompanies the use of MOFs as precursors is the possibility of preparing dispersed and homogenous multimetallic NPs, which can be easily obtained by encapsulation of metal complexes or metal NPs in the pores of the MOF prior to the thermal conversion, or by the use of core-shell MOFs. Indeed, a better control of the homogeneity of the NPs can be achieved by the use of heterometallic MOFs. Being an example of this, the preparation of Ni-Co nano-alloy from a pre-synthesized coordination polymer using temperatures over 500 °C.

Herein, we present the formation of a composite material based on Nanoparticles of PdFe (PdFe-NPs) under mild conditions (25 °C) using a heterometallic PdFe-MOF that has also been prepared under soft conditions (120 °C) in a solvent-free manner. These PdFe-NPs are directly supported on nanometric FeOx homogeneously inserted into a carbon mantle, resulting in excellent catalysts for hydrogenation reactions, forming in situ and in the absence of previous treatment.

**Discussion and Results**

**Synthesis and characterization of PdFe-MOF.**

The grinding of the solid reactants Fe(NO₃)₃·9H₂O and the palladium metalloligand PdCl₂(PDC)₂ (H₄L where PDC: pyridine-3,5-dicarboxylic acid), followed by heating at 120 °C under vacuum results in the formation, after 72 h, of the MOF [Fe₃O(L)₁.₅(H₂O)₃(NO₃)]₃, hereafter denoted as PdFe-MOF. Figure 1 represents the MOF in which the [Fe₃(μ₃-O)] building blocks are connected with six different tetra-carboxylic acid ligands to form a 3D structure with soc topology, isoreticular to an In analogue
recently reported by Steriotis, Trikalitis and co-workers.\cite{22} This solvent-free methodology, uncommon for the preparation of MOFs, has been adapted from previously reported methods\cite{23} and allows the formation of the Fe analogue, which resulted as unfruitful using the conventional synthetic route for the PdIn-MOF analogue\cite{22} yielding instead an Fe-2D network with no Pd in the structure.\cite{24} The porous nature of PdFe-MOF, as established by \textit{N}_2 sorption, reveals a total \textit{N}_2 uptake of 250 cm$^3$·g$^{-1}$ at 77 K and 0.8 bar with a calculated BET surface area of 830 m$^2$·g$^{-1}$ for the activated material, which is consistent with those found in the isoreticular PdIn-MOF. Further characterization of the MOF includes powder X-ray diffraction, SEM, infrared spectroscopy, thermal gravimetric analysis, XPS spectroscopy, EDS and ICP elemental analysis, which confirm the homogeneity of the sample (see ESI and Figures S1-9 for a more detailed discussion).

\textbf{Figure 1.} Schematic diagram of the metalloligand (H$_4$L), the oxo-centred iron carboxylate SBU, [Fe$_3$O(COO)$_6$(H$_2$O)$_3$]$^+$ 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.
Synthesis and characterization of PdFe-NPs

Scheme 1. Flow chart of the synthesis process to yield the nanocomposite (PdFe NP) from the PdFe-MOF.

Preparation of the PdFe-NPs from PdFe-MOF has been achieved by adapting a previously reported procedure by Chaudret and co-workers,[7] based on the use of an amine (aniline) in the presence of H₂ (5 bar) at room temperature. This modified approach consists in the \textit{in situ} generation of aniline, instead of using it as a solvent, in order to provide the reaction mixture with a slow supply of the amine. As a result, the heterometallic nanocomposite (PdFe-NP) is slowly formed, therefore providing a well-controlled and reproducible material. Specifically, PdFe-MOF was mixed with toluene and nitrobenzene together with a H₂ atmosphere (5 bar) at room temperature, and after 1.5 h the final nanocomposite was obtained. In this way the PdFe-MOF results in a nanocomposite (PdFe-NP) comprising both, metallic nanoparticles and a carbonaceous support, whose true nature will be thoroughly discussed over the next pages. For comparison purposes, the nanocomposite using the standard approach described by Chaudret[7] was also
prepared together with the traditional high temperature methodology based on thermal treatment of the MOF (500 °C) with a H₂ flow in a fixed bed reactor (see Supporting Section, Figure S11). The main materials prepared in this work are summarized in Table 1.

![Figure 2](image)

**Figure 2.** (a) TEM (b) STEM micrographs and (c) particle size distributions of PdFe-NP.

Electronic microscopy techniques reveal that the novel chemical methodology for the *in situ* preparation of NPs from a MOF results in ultra-small PdFe-NPs with a very narrow distribution, and an average size of 1.0±0.2 nm (Figure 2), embedded in a carbonaceous support containing FeOₓ. By HR-TEM, the obtained NPs are found to be smaller, and remarkably with a narrower distribution, than the NPs formed by the straightforward use of aniline (2.0±1.8 nm, Figure S11c) or by the thermal treatment of the MOF (3.1±3.1 nm, Figure S11b), and significantly smaller than other previously reported synthetic approaches based either on thermal and
chemical decomposition of metallic precursors ($\approx 5$ nm)$^{[26]}$ or high temperature thermal treatment methods ($\approx 10$ nm)$^{[25]}$. Based on that, it is clear that this novel methodology gives rise to NPs smaller than previously described. Moreover, in an attempt to clean the surface of the nanocomposite prior to its use in catalysis, different thermal treatments under vacuum were applied over PdFe-NP. It was concluded that these treatments did not to have any considerable effect as far as the nanoparticle size is concerned (see Figure S10).

**Table 1.** Summary of the main materials prepared.

<table>
<thead>
<tr>
<th>Material code</th>
<th>Description</th>
<th>NP size$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdFe-MOF</td>
<td>Original MOF</td>
<td>–</td>
</tr>
<tr>
<td>PdFe-NP</td>
<td>Chemically as-synthesized NP</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>PdFe-NP-300</td>
<td>PdFe-NP heated for 6h at 300 °C under vacuum</td>
<td>1.2±0.3</td>
</tr>
</tbody>
</table>

$^a$: Measured by HR-TEM by considering a minimum number of 200 particles.

The remarkably reduced size of the PdFe-NPs is consistent with a heterometallic nature of the NPs, in accordance with previous reports that show this effect on Pd-NPs upon doping with other metals.$^{[27]}$ In fact, the possible presence of Pd and Fe in the NPs has been studied by electron diffraction (Figure S13), EDAX (Figures S14-16), X-ray powder diffraction (Figure 3a and S18), XPS (Figures S19-21) and XAS (Figures S24-25). The interplanar distances of the electron diffraction patterns indicate the absence of undesired homometallic Pd crystalline phases (Figure 3b), which are however found with the common synthetic routes (Figure S13c). The presence of Fe in the NPs is confirmed by an EDAX punctual analysis of the isolated nanoparticles (Figure S14a). Further confirmation is provided by XRD (Figure 3a and S18b), which shows the centered cubic (fcc) pattern characteristic of Pd with a decrease in the cell parameter with respect to elemental palladium ($a = 3.8935(4)$ vs 3.8972), in accordance with Vegard’s law.$^{[28]}$
Besides that, no impurities corresponding to metallic iron, iron oxide or palladium oxide are detected. Moreover, EDAX mapping of the composite reveals that iron is present in large amounts in the carbon support (Figure S15), confirmed by Raman spectroscopy to be FeOₓ (see Figure S22). However, the absence of any diffraction peak corresponding to iron oxide indicates a very small size of iron oxide in the carbonaceous support, likely subnanometric. On the contrary, the classic thermal methodology ends in the formation of bimetallic NPs together with other NPs based on metallic iron (Figure S18a). These data also indicate that mild reaction conditions result in NPs with higher homogeneity in composition.

![Figure 3](image)

**Figure 3.** (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.

With the aim to provide further insights into the bimetallic nature of the nanoparticle composites, XPS measurements were carried out. XPS spectra interpretation and peak fitting of Fe2p, N1s, O1s and C1s can be found in the Supporting Information (Figures
S19-21). As can be seen in Figure 4, the Pd3d5/2 signal for the chemically prepared PdFe-NP is shifted towards lower binding energies than what is usually observed for Pd0. On the contrary, the NPs obtained by traditional thermal treatment barely present this shift (see Figure S21 and Table S4). This indicates that Pd is electronically richer in the chemically synthesized nanoparticles, which could be due to a charge transfer from either the Fe in the NP[20] or the FeOx in the support,[30] both situations having been previously described. However, as the nanocomposite obtained by the thermal treatment of the MOF, where no shift is seen, does not present FeOx in the support, this finding points to FeOx as the main responsible for this effect. These observations have been made taking as a reference the XPS spectra for commercial Pd@C (mainly Pd0, Figure 4) and they could be of great significance in catalytic applications, among others.

![Figure 4](image_url)

**Figure 4.** Pd3d XPS signal of a) PdFe-MOF, b) PdFe-NP-300, c) Pd@C (commercial).

Further details on the nature of iron species were obtained by XAS. According to both XANES and EXAFS features (Figure 5), the iron species present a structure very similar to magnetite, in good agreement with the Raman spectrum of PdFe-NP (Figure S22). The
nanosized character of the FeO\textsubscript{x} is confirmed by the flattening of EXAFS signal features in comparison with those of Fe\textsubscript{3}O\textsubscript{4} pattern, which is also reflected on the diminished Fe-O coordination number in comparison with the bulk counterpart (Figure 5, Figure S24 and Table S5). In addition, this fitting is further improved when including a Pd contribution (Figure S25 and Table S6). The position and shape of the absorption edge in the spectrum of PdFe-NP sample indicate that Pd atoms are in the reduced state in an fcc local structure.\cite{31} Therefore, the intensity of these oscillations points to the presence of a fraction of low coordinated atoms, causing the low amplitude of the EXAFS oscillations and, consequently, smaller nanoparticles in comparison with the bulk counterpart. However, the Pd EXAFS does not reveal this Pd-Fe interaction. This can be explained as a consequence of XAS being a bulk-sensitive technique. In this sense, the presence of some NP agglomerations (Figure S17), better detected than isolated NPs by this technique, may explain why, on average, this contribution is very small and cannot be distinguished.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Normalized XANES spectra at Fe K-edge (a) and |FT| of the k\textsuperscript{2}-weighted \(\chi(k)\) functions (b) for PdFe-MOF, PdFe-NP and Pd-based standards.}
\end{figure}

In order to understand the mechanism of the formation of the PdFe-NP from PdFe-MOF, a series of ATR-IR measurements were done upon exposing the MOF to different conditions for 30 minutes. Immersion of the MOF in toluene in the presence of 5 bar of
H₂ at 25 °C, or the addition of 1 mmol of nitrobenzene, neither of them causes any major changes in the IR spectrum (see Figure S23), thus indicating that the PdFe-MOF remains unmodified. On the contrary, the presence of aniline significantly modifies the structure of the material, as evidenced by a shift to lower frequencies of the bands corresponding to the Fe-O bond (600-650 cm⁻¹ and 450-500 cm⁻¹), the disappearance of the band corresponding to the coordinated pyridine (1445 cm⁻¹),[32] as well as by the presence of the characteristic bands of the N-H bending associated to aniline (1616 and 1556 cm⁻¹).[33] Thus, aniline plays a major role in the NP formation, likely via coordination to the Pd centres, displacing the pyridine and therefore initiating the rupture of the MOF. Accordingly, the evolution of XPS for N1s also supports an effect of replacement of the pyridinic ligand from the coordination sphere of Pd by aniline (Figure S20a).

**Catalytic tests for nitroderivative hydrogenation**

Considering the small size and the enhanced electronic properties of PdFe-NPs, we analysed their catalytic activity in nitroarene hydrogenations (Scheme 2). Transformation of nitroarenes into anilines is of great importance, as they are one of the main building blocks for dye and pharmaceutical industries.[34]

![Scheme 2. Nitroarene hydrogenation.](image)

More specifically, we investigated the capability of the prepared NPs in nitrobenzene hydrogenation. The turnover frequency (TOF) for different Pd-based materials was calculated as the initial reaction rate (Figure 6d). Interestingly, when the Fe-doped Pd nanoparticles were chemically prepared and their surface properly cleaned after the common thermal treatment used for NP activation, i.e. 6 h at 300
° C under vacuum (PdFe-NP-300), their activity plainly surpassed that of the commercial Pd@C (TOF = 153 vs 55, see Figure 6d). This observed improvement of the catalytic activity of our nanocomposites with respect to the commercial catalyst Pd@C could be due to the higher electronic density, observed by XPS measurements, together with the reduction in particle size (from 3 nm to 1 nm, see Figures S12 and S10, respectively).\[^{29-30}\] Moreover, TOF values of this bimetallic composite are ranked within the best catalysts under similar/identical reaction condition, thereby clearly improving many of the materials previously reported (see Table S7) for this particular reaction.

![Figure 6](image-url)

**Figure 6.** a) Nitrobenzene reduction with PdFe-MOF. b) Leaching test for PdFe-MOF in the nitrobenzene hydrogenation. Reaction conditions: 0.123 g nitrobenzene, 5 mg PdFe-MOF, at 5 bar H\(_2\) pressure and 25 ° C. 1 h of induction. c) 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 ° C during 2 h (after 1 h of induction). d) 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.
However, the most remarkable results arise from the fact that the PdFe-NPs can be formed *in situ*. Thus, since the product of nitrobenzene hydrogenation is aniline, we hypothesised that the direct use of PdFe-MOF should also act as catalyst for this reaction, as NP formation would take place in situ. In this sense, we barely see difference when comparing the activity of PdFe-MOF against the Pd@C (TOF values for PdFe-MOF and Pd@C are 47 and 55, respectively). Thus, the PdFe-MOF is acting as a Pd reservoir that, after an induction time, can generate active Pd species in the same reaction media, without the need of any thermal pre-treatment with H₂.

Looking at the overall reaction kinetics, nitrobenzene hydrogenation takes place after 1 h of induction, corresponding to the already explained MOF to NP transformation, reaching yields very closed to 100 % (conversion ≈ 99 % and selectivity ≈ 99 %) in 2 h of reaction (Figure 6a). These NPs formed in situ can be reused several cycles, with a minor catalytic deactivation (Figure 6c). This small deactivation observed could be related to the deposition of organic matter on the active centres, as it is suggested by the attenuation of the Pd3d XPS signal after reaction (Figure S21) and/or to an increase in the average particle size after the catalytic process, as it has been observed by HR-TEM (Figure S11c). Nonetheless, the loss of metals (Pd and/or Fe) from the solid to the solution during reaction could be practically discarded. In this sense, the catalyst was filtered at 45 minutes of reaction (C≤50%). The reaction was continued in the absence of catalyst until it reached 16 h, and no significant changes were observed in the conversion levels of nitrobenzene. This finding meaning that the process is purely heterogeneous. (Figure 6b). With this operation, the possibility of suffering from possible desorption and re-absorption of the active species of the catalyst during the reaction was also discarded, a phenomenon that has been widely discussed in the literature when similar materials were used as catalysts. An additional advantage of the chemically prepared solid catalysts is
the possibility of magnetically recovering them after having being used in reaction (Figure S26). As a result, we have achieved a catalytic composite material with a higher capability to hydrogenate nitrobenzene at room temperature than that exhibited by a commercial catalyst, owing to the Fe-doped Pd-NPs, and with the additional advantage of being easily recovered with the help of a magnet, due to the magnetite present in the support.

Table 2. Catalytic activity of “in-situ” formed PdFe-NPs when using different nitroderivatives.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Observed Product</th>
<th>Yield (mol.%)</th>
<th>Induction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>Aniline</td>
<td>99</td>
<td>1.0</td>
</tr>
<tr>
<td>4-methylnitrobenzene</td>
<td>4-methylaniline</td>
<td>99</td>
<td>3.0</td>
</tr>
<tr>
<td>4-chloronitrobenzene</td>
<td>4-chloroaniline</td>
<td>73</td>
<td>4.5</td>
</tr>
<tr>
<td>Nitrotyrene</td>
<td>4-ethylaniline</td>
<td>92</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.123 g nitroderivative, 5 mg PdFe-MOF, at 5 bar H₂ pressure and 25 °C. * At 2 h of reaction discarding the induction time in each case. Note: In the case of nitrostyrene the observed product (4-ethylaniline) is the complete hydrogenated molecule, both nitro and vinyl groups being reduced to amine and ethyl moieties, respectively.

Moreover, the PdFe-NPs can also hydrogenate other nitroarenes besides nitrobenzene such as nitrostyrene, 4-methylnitrobenzene and 4-chloronitrobenzene, as summarized in Table 2. Both, the induction time and the formation of the corresponding aniline, vary with the nitro-derivative used. The higher induction time observed for chloronitrobenzene with respect to methylnitrobenzene could be ascribed to the lesser reactivity of the nitro group in the presence of an electron attractor such as chloride, which can be rationalized with the Hammett parameter (σ = -0.01 for CH₃; σ = 0.47 for Cl).[^36] Nitrostyrene does not follow this trend as two hydrogenations take place, with both the nitro and the C=C being hydrogenated. The explanation for the higher induction time observed in this case is therefore more complex.

Tandem reaction
Finally, the possibility of using this new catalyst in tandem reductive amination reactions was tested (Figure 7). With this aim, the reduction reaction of nitrobenzene to aniline was coupled with the nucleophilic addition of benzaldehyde and the subsequent reduction of the formed adduct. Instead of working with an excess of benzaldehyde in the reaction mixture, slow addition of this reagent was used to decrease the rate of undesired secondary reactions resulting from benzaldehyde hydrogenation. While the one-pot reaction affords only 40 % yield to the desired product (with a 60 % selectivity to aniline, Fig. S27), slow addition of the carbonyl compound causes an increase of the selectivity to 75 % to the benzylaniline (with a subsequent decrease of the selectivity to aniline to 20 %, see figure 7). Thus, this reduction of the unreacted aniline is clear proof that the benzaldehyde is not being hydrogenated so fast when lower concentrations of it are present in the reaction mixture.
Figure 7. 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 H₂ pressure and 25 °C during 6.5 h (addition starts after 30 min of reaction, taken as t₀). The main nitrogenated by-products detected apart from the imine was aniline (∼22 mol.%)

Conclusions

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. The heterometallic nanocomposite precursor PdFe-MOF is isostructural with a previously reported PdIn-MOF and has been obtained for the first time, using a solvent-free method.

A controlled decomposition of the PdFe-MOF upon in situ generation of aniline leads to the formation of ultra-small PdFe-NP, smaller and more homogeneous than the NPs obtained by conventional thermal procedures, which also provide
other NPs based on metallic iron. In addition, PdFe-NPs obtained with our approach present excellent catalytic properties in the hydrogenation of nitroarenes, surpassing those of commercial Pd@C and offering the possibility of being magnetically recovered. Moreover, PdFe-MOF can be directly used to generate the catalyst in the reaction media. In addition, compelling evidence is provided with respect to the beneficial synergy established when both, Fe and Pd are so close enough that they can interact with each other. The size control of the Pd nanoparticles by the presence of iron, as well as the modification of their electronic charge by the FeO₅ in the support, seem to be the main facts that would define the nature of this synergy.

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.

**Experimental**

**Synthesis of PdFe-MOF**

The metallo-ligand H4L was prepared according to the published procedure.[37] Concerning the MOF, a solid mixture of Fe(NO3)3·9H2O (47.2 mg, 0.117mmol), H4L (30 mg, 0.0582 mmol) and benzoic acid (3 mg, 0.0246 mmol) was briefly grounded. The mixture was placed in a thin glass tube which sealed after a cycle of vacuum. The mixture was placed in a thin glass tube, sealed under vacuum and heated during 72 h at 120 °C.
The resulting mixture was washed with DMF and isopropanol for 1.5 days. The as-synthesized MOF was activated using MeOH for 3 days and heated at 130°C for 4 hours.

Nanoparticle synthesis

As a general procedure for the in situ chemically synthesized NP, 10 mg of PdFe-MOF were added to a solution containing 2 mmol of nitrobenzene derivative and 2 mL of toluene. The system was sealed and pressurized until 5 H₂ bar at 25 °C under vigorous stirring for 1.5 h. Then, the solid was filtered and repeatedly washed with MeOH during 24 h (as-synthesized PdFe-NP). In the case of thermal treatment of the as-synthesized PdFe-NP, it was placed at 300 °C during 6h under vacuum (PdFe-NP-300). For other times of activation (12 h or 48 h) see Supporting Information.

For conventional thermal-treating synthesis of nanoparticles, the PdFe-MOF was activated in a tubular fix-bed reactor under a H₂ flow at 500 °C during 3 h (see Supporting Information).

Material characterization

PdFe-MOF was characterized by XRD, IR spectroscopy, TG analysis, SEM and sorption measurements, while PdFe NPs and nanocomposites here prepared were characterized by means of chemical analysis (ICP), XRD, XPS, XAS, Raman and ATR spectroscopies, and HR-TEM (for more details see Supporting Information).

Catalytic tests

Hydrogenation reactions for nitrobenzene derivatives were carried out in a 6 ml batch glass micro-reactor equipped with a probe for sampling and a pressure gauge for pressure measurement. For the first catalytic experiments, 0.123 g of
nitrobenzene (1 mmol), 1 mL of toluene and 5 mg of solid catalyst (PdFe-MOF or PdFe-NP) were added in the same vessel. The reactor was sealed and pressurized with 5 bars of H\textsubscript{2} at 25 °C and maintained at 800 rpm throughout the process. In all cases, the pressure of H\textsubscript{2} in the system was kept constant at the selected value. Reusability tests were carried out for the \textit{in situ} formed PdFe-NP. The catalyst underwent four cycles, being washed with toluene for 30 minutes in-between. The tandem reaction was performed in a similar manner albeit adding 0.106 g of benzaldehyde (1 mmol) to the mixture previously described.

The progress of the reaction was followed by gas chromatography. Liquid samples (≈50 µL) were collected at different time intervals, and then diluted in a solution of 1wt% chlorobenzene (internal standard) in MeOH. The analysis of the reaction mixtures was carried out by a 3900-Varian GC equipped with FID detector and a capillary column (HP-5, 30 m length). Product identification was done by GC–MS (Agilent 6890N GC System coupled with an Agilent 5973N mass detector).

In all cases, conversion (\(x\)) and selectivities (\(s_i\)) to the different products “\(i\)”, have been estimated using the formulas below at different reaction times “\(t\)”, always taking nitrobenzene as a reference.

\[
X^t(\text{mol. %}) = \frac{n^0 \text{nitrobenzene} - n^t \text{nitrobenzene}}{n^0 \text{nitrobenzene}} \cdot 100 \quad \text{(eq. 1)}
\]

\[
S_i^t(\text{mol. %}) = \frac{n_i^t}{n^t \text{total } N\text{-products}} \cdot 100 \quad \text{(eq. 2)}
\]

TOF (Turnover Frequency) was also calculated for nitrobenzene hydrogenation and defined as the mol of aniline produced per mol of Pd present in the catalyst per time. Finally, carbon balances were estimated for each reaction with respect to
nitrobenzene, considering the total amount of products detected by GC analysis along with the remnant nitrobenzene.

\[
TOF = \frac{n_{\text{aniline}}}{n_{\text{Pd} \cdot \text{r.time}}} \quad \text{(eq. 3)}
\]

\[
CB \text{ (mol. \%) } = \left[ \frac{n_{\text{nitrobenzene}}^0 - n_{\text{nitrobenzene}}^f \cdot 6C \text{ atoms}}{n_{\text{nitrobenzene}}^0 \cdot 6C \text{ atoms}} + \sum (n_{\text{product}}^f \cdot x \text{ atoms}) \right] \cdot 100 \quad \text{(eq. 4)}
\]

**Associated Content**

**Supporting Information.**

The following files are available free of charge.

Electronic Supplementary Information (ESI) available: [General methods and materials, synthesis of PdFe-MOF, PdFe-NPs and PdFe nanocomposite, and their data characterization by XRPD, IR, TG, SEM, HRTEM, XPS, XAS and Raman].

**Author Information**

Corresponding Author

* G. M. E. guillermo.minguez@uv.es; P. O-B. pasoabur@itq.upv.es.

**Notes**

† These authors contributed equally to this work.

**Conflicts of interest**

There are no conflicts to declare.
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References


PdFe-MOF (precursor) → PdFe nanocomposite

Catalytic properties

Magnetic properties

PdFe-NP