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Nickel nanoparticle/carbon catalysts derived from a novel aqueoussynthesized metal-organic framework for nitroarene reduction

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ABSTRACT

Carbon-supported, non-noble metal-based catalysts derived from metal-organic frameworks (MOFs) are attractive alternatives to noble metal-based systems, but typical syntheses of the starting MOFs are not desirable from an environmental and practical perspective (e.g., they rely on non-innocuous organic solvents and long reaction times). Here, we report the preparation of a Ni-based MOF in aqueous medium, at moderate temperature (95 °C) and in a short reaction time (<30 min), which was used as a sacrificial template to access a family of Ni nanoparticle/carbon hybrids that were then tested as catalysts in the reduction of 4-nitrophenol (4-NP). The MOF-derived hybrids exhibited a mesoporous texture, with specific surface areas between ~250 and 450 m² g⁻¹ depending on the carbonization temperature applied to the MOF, as well as high Ni contents (between ~36 and 57 wt%). Notwithstanding the latter, the metal was homogeneously distributed throughout the carbon matrix in the hybrid and was quite resistant to extensive agglomeration and sintering, even at temperatures as high as 1000 °C. With increasing carbonization temperature, the Ni component was seen to go through different crystal phases, i.e., Ni₃C phase \rightarrow Ni hexagonal close-packed phase \rightarrow Ni face-centered cubic phase. The results of the catalytic tests suggested the former and latter phases to be the most active towards the reduction of 4-NP, with catalytic activity values as high as 0.039 mol_{4-NP} mol_{N1}⁻¹ mni⁻¹.

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1. Introduction

The development of highly active and selective catalysts is of great importance in many industrial chemical processes. For many chemical reactions, the best catalysts are expensive and scarce noble metals (Pt, Pd, Au, etc), making the development of new catalysts based on cheaper metals (e.g., Ni or Cu) the subject of intense research [1–5]. Nitroarene compounds have an important role in the chemical industry, but in most of the cases they are generated as by-products of the pharmaceutical, agrochemical, dye and other industries [6–8]. Furthermore, nitroarenes are an important source of pollution from such industries and they also pose health risks due to their carcinogenic effects [9,10]. On the other hand, anilines are very important reagents in the preparation of several drugs as well as in the polymer, dye and many other industries [11]. Thus, the reduction (i.e. hydrogenation) of

* Corresponding author. E-mail address: fabian@incar.csic.es (F. Suárez-García). nitroarenes into their corresponding anilines is an important reaction that can be catalysed by different metal nanoparticles. Nowadays, the highest catalytic activity in this reaction is achieved by noble metal-based catalysts, such as Au, Ag, Pd and Pt [12–17]. One promising solution is to replace these noble metals by more abundant and cost-effective transition metals, such as Cu, Ni, or Co, which have good catalytic activities, especially when they are in the form of clusters or nanoparticles [18]. However, metallic nanoparticles have a strong tendency to form large aggregates due to their high surface energy, resulting in a remarkable reduction of their catalytic activity and limiting their industrial application [19–21]. One way to solve these problems is preparing supported catalysts, where the catalyst nanoparticles are dispersed in different materials. In the case of Ni, heterogeneous catalysts have been prepared by supporting Ni nanoparticles on carbon natotubes, graphene, porous carbons, silica, zeolites, etc. [5,7,10,20-27]. Among others, carbon materials are especially appropriate as a support due to their unique properties, such as low density and weight, high chemical and thermal stability, and the possibility of modifying their surface chemistry and porous texture.







Different methods have been studied for the dispersion of metallic nanoparticles in carbon materials, such as impregnation with metal salts followed by reduction or by means of addition of metal compounds during the synthesis of soft-templated carbons [22,24]. A novel method that allows the preparation of materials with a very high metal content and at the same time with a high dispersion of the metallic nanoparticles is the use of metal-organic frameworks (MOFs) as sacrificial materials [28]. Thus, different MOFs containing the desired metal ions or metallic clusters were synthesized and pyrolyzed in inert atmosphere at high temperature to trigger the thermal decomposition of the MOF and give metal or metal oxide/carbon nanohybrids. The large variety of MOFs with different metal nodes and organic linkers, the highly periodic arrangement of the metal ion or metallic cluster in the MOF structure and the large variety of possible pyrolysis conditions are conducive to obtaining hybrid metal/carbon materials with tunable properties.

There are only a few examples in the literature of Ni-containing MOFs that have been pyrolyzed to produce Ni/carbon catalysts [23,25,29-32]. Most of these works report the carbonization of MOFs prepared using aromatic acids (e.g., terephthalic acid or benzene-tricarboxylic acid) as organic linkers. These MOFs are generally prepared in non-innocuous organic solvents and require long reaction times [23,25,30–32], making this route unattractive from an environmental and practical perspective. To address this issue, we report here the synthesis of a new nickel-based metal organic framework (NiOF), where Ni acts as the coordinating metal and imidazole as the ligand, thus being an analogue to zeolitic imidazolate frameworks (ZIFs). To this end, an environmentally friendly water-based synthesis procedure was developed using moderate temperatures $(95 \degree C)$ and short reaction times (<30 min). This novel Ni-based MOF was carbonized at different temperatures and the resulting Ni/carbon hybrids were tested as catalysts in the reduction of 4-nitrophenol, affording a competitive activity when compared to previous Ni-based catalysts.

2. Material and methods

2.1. Materials preparation

The nickel/carbon catalysts were obtained by a simple two-step procedure: (1) synthesis of a nickel-imidazole complex (i.e. NiOF) and (2) thermal treatment to obtain a hybrid material formed by Ni nanoparticles embedded in a carbon matrix. In the first step, a novel nickel-imidazole complex was prepared following a simple method in aqueous medium. A typical synthesis procedure was the following: 20 g of nickel acetate tetrahydrate [NiOAc, Alfa Aesar, > 98% assay] were dissolved in 50 mL of deionized water and 10.102 g of 2-methyl-imidazole [2-mIm, Acros Organics, > 99% assay] were dissolved in another 50 mL of water. A molar ratio between reactants [2-mIm]:[NiOAc] = 6:1 was used. Both solutions were separately pre-heated at 95 °C, and when this temperature was reached the NiOAc solution was poured into the 2-mIm solution. The reaction started immediately and the colour of the solution was seen to change to orange, which indicated the formation of the nickel-imidazole complex [33,34]. The mixture was kept at 95 °C in argon atmosphere and under vigorous stirring for 30 min, after which it was cooled in an ice-bath and the formed solid was recovered by centrifugation after 4 washing cycles with water. After that, the obtained metal-organic framework (NiOF) was dried in vacuum at 200 °C to remove the non-reacted 2-mIm molecules that occluded the pores of the material. Finally, the NiOF was heattreated in a horizontal tubular furnace in a N2 atmosphere (99,999% pure) at different temperatures, from 400 to 1000 °C, for 30 min. The resulting materials were referred as NiCx, where "x" is a number between 4 and 10 to denote the carbonization temperature used (400–1000 $^\circ\text{C}$).

2.2. Characterization techniques

Thermogravimetric analysis (TGA) were performed in a SDT Q600 (TA Instrumets) thermogravimetric analyser. The thermal stability of NiOF was studied under an argon flow ($50 \text{ cm}^3/\text{min}$) at a heating rate of 5 °C/min up to 950 °C. The nickel content in the nickel/carbon catalysts (NiCx samples) was determined in the same thermobalance, but under air flow ($50 \text{ cm}^3/\text{min}$) with a heating program of 10 °C/min up to 950 °C and maintaining this temperature for 30 min.

Field-emission scanning electron microscopy (FE-SEM) images were obtained on a Quanta FEG 650 microscope (FEI Company). Transmission electron microcopy (TEM) studies were carried out with a JEOL 2000 EX-II instrument operated at 160 kV. Specimens for TEM were prepared by dispersing the sample in ethanol via a short sonication treatment and then drop-casting ~40 μ L of the resulting dispersion onto a copper grid (200 square mesh) covered with a lacey carbon film. Raman spectroscopy was performed with a LabRam instrument (Horiba Jobin-Yvon) using a 532 nm wavelength laser at a low incident power (0.5 mW) to avoid altering the samples. X-ray diffractograms were obtained in a D5000 diffractomer (Siemens) using Cu K_{α} radiation, with a step size of 0.015° and a step time of 1 s. N₂ adsorption-desorption isotherms were measured at -196 °C in an ASAP 2010 (Micromeritics) volumetric apparatus. The samples were previously outgassed at 150 °C overnight. From the adsorption brand of the isotherms the apparent surface area (S_{BET}) was obtained by applying the Brunauer- Emmett-Teller (BET) method in the 0.01 to 0.25 P/P₀ range, the micropore volume (V_{DR.N2}) was calculated using the Dubinin-Radushkevich (DR) equation in the 0.001 to 0.15 relative pressure range, and the total pore volume (V_T) was estimated as the volume of liquid nitrogen adsorbed at 0.975 relative pressure. Pore size distributions and microprore $(V_{\mu p})$, mesopore (V_{mp}) and total pore volumes (V_{total}) were obtained by applying the QSDFT method developed by Quantachrome [35].

2.3. Catalytic activity studies

The catalytic activity was evaluated towards the reduction of 4nitrophenol (4-NP, Sigma-Aldrich, 100% assay) to 4-aminophenol (4-AP) with NaBH₄ (Sigma-Aldrich, > 99% assay) in aqueous medium. Nickel/carbon catalysts were ground and mesh at a particle size $< 63 \mu m$ before the catalytic experiments. The experiments were carried out in a catalytic reactor (500 mL) using a total volume of 300 mL of solution. To this end, 4.5 mg of catalyst were dispersed in 292.85 mL of ultrapure water and 3.6 mL of a solution $(5 \cdot 10^{-3} \text{ M})$ of 4-NP in water were added. The temperature of the reactor was then set to a given target value (5, 15 or 25 °C) and kept for 1 h. After this time, 3.55 mL of a solution (3 M) of NaBH₄ in water were added to the dispersion to start the reduction of 4-NP. Previous work in our group [36] has demonstrated that the activity of catalysts for nitroarene reduction increases with increasing amount of NaBH₄ until a plateau is reached at a certain amount of reductant. Tests using different concentrations of NaBH₄ were carried out to determine the smallest amount needed to yield the highest catalytic activity (35.5 mM in this case) to ensure that the catalysts were working at their full potential. Additionally, the corresponding high NaBH₄ to 4-NP molar ratio ensured a large excess of the former, and thus that its concentration remained almost constant during the reaction, thus leading to simpler kinetic equations that are only dependent on the 4-NP concentration and not on NaBH₄ concentration (i.e. pseudo-first order reactions, see below).

The reaction progress was followed by UV–vis absorption spectroscopy measuring the absorption peak located at 400 nm that is characteristic of deprotonated 4-NP (i.e., 4-nirphenolate), which is generated in the basic medium induced by the presence of NaBH₄ (the corresponding absorption peak of non-deprotonated 4-NP is downshifted to 316 nm), but is absent form 4-AP [37]. 2.5 mL aliquots were taken from the reactor every 5 min until the complete transformation of 4-NP to 4-AP, which typically took place between 60 and 90 min after the start of the reaction.

The formation of 4-AP (indeed 4-amimophenolate) was guantitatively determined from the absorbance of its characteristic band at 299 nm. Calibration curves relating 4-NP and 4-AP (Sigma-Aldrich, > 99% assay) concentration and their absorbance at 400 and 299 nm, respectively, were determined using aqueous solutions of different concentrations (from 0 to 0.1 mM) in the presence of 35.5 mM of NaBH₄ (Figure S1). The reaction yields were obtained by determining the concentration of 4-AP at the end of the reduction reaction relative to the initial concentration of 4-NP. As the prepared nickel/carbon catalysts had some porosity (see below) it was necessary to rule out any potential artefacts in the catalytic tests that could be caused just by the adsorption of 4-NP on the catalysts. To this end, tests were run under the same experimental conditions as described above but in the absence of NaBH₄ and adjusting the pH to 10 by adding NaOH. In this case, the absorbance at 400 nm remained unchanged after 60 min (Figure S2) indicating that removal of 4-NP from the reaction solution by adsorption on the catalyst was negligible.

The catalyst cyclability and stability were studied for the two most active catalysts (see below). Eight consecutive reduction reactions were carried out in the cuvette of the UV–vis spectrophotometer by adding fresh 4-NP at the beginning of each cycle and measuring the absorbance decay at 400 nm. Molar ratios and concentrations similar to the ones used in the catalytic reactor were used in the cuvette experiments.

All the catalytic tests were repeated 3 times to obtain a mean value for each sample.

3. Results and discussion

3.1. Nickel-imidazole MOF (NiOF)

The method developed in this work allowed the preparation of a novel nickel-imidazole MOF (denoted as NiOF) with high yields (about 98 wt% with respect to Ni) following a simple process and using water as the solvent. The resulting solid had an ordered structure, as can be seen in the X-ray diffractogram shown in Fig. 1, with the highest intensity peak centered at $2\theta = 13.64^{\circ}$ and a shoulder at $2\theta = 15.38^{\circ}$. Low intensity peaks at $2\theta = 23.8$, 26.8, 30.7, 33.9, 46.8 and 49.1° could be also noticed. According with these peaks, the solid possessed a tetragonal structure with a D4h point group [38]. Using the two principal peaks (13.64 and 15.38°, which correspond to the (200) and (202) crystallographic planes, respectively), it was possible to calculate the unitary cell parameters: a = b = 12.973 Å and c = 29.978 Å.

The nickel content in the solid was determined by TGA in air, yielding a residual weight of 26.9 wt% (d.b.) at 950 °C which corresponds to a nickel oxide (NiO) product, as demonstrated by X-ray diffraction (XRD) (see Figure S3). This amount of NiO corresponded to a nickel content of 21.1 wt%, in reasonable agreement with a theoretical value of 18.9 wt% for a nickel di-imidazole compound, where Ni²⁺ is coordinated with four 2-mlm molecules in a square-plane configuration and two acetate anions as counter-ion [33,38].

The synthesized materials exhibited a high thermal stability in inert atmosphere, see Figure S4, showing a first small mass loss, about 3 wt%, between 180 and 381 °C, which could be due to the



Fig. 1. XRD patterns of NiOF carbonized between 400 (NiC4) and 1000 °C (NiC10) as well as the starting (non-carbonized) NiOF. The different crystalline structures involving nickel are noted: Ni₃C (Δ) (PDF 01-072-1467); Ni-FCC (\Box) (PDF 03-065-2865); Ni-HCP (\bigcirc).

volatization of residual organic ligands (i.e. 2-mIm) that were not eliminated during the drying step at 200 °C. The thermal degradation of NiOF occurred in a narrow temperature interval between 407 and 482 °C, with a mass loss of 36 wt%. Above the later temperature, a much slower and steadily mass loss is observed up to 950 °C. The final yield in inert atmosphere was ~53 wt% at 950 °C.

3.2. NiOF-derived Ni/carbon hybrids

The obtained NiOF was carbonized in inert atmosphere at temperatures between 400 and 1000 °C to obtain nickel/carbon hybrids. N₂ adsorption-desorption isotherms and pore size distributions obtained by the QSDFT method for NiOF and its carbonized counterparts are plotted in Fig. 2 and the corresponding porous textural parameters are summarized in Table 1.

All samples, including the NiOF, exhibited type IV isotherms, which are characteristic of mesoporous materials [39]. The amount of N₂ adsorbed, especially at high relative pressures, increased with carbonization temperature up to 600 °C, decreasing at higher temperatures. This fact was reflected in the different porous textural parameters, Table 1, and in their variation as a function of the carbonization temperature (Figure S4). Sample NiC6 had the maximum total pore volume $(0.73 \text{ cm}^3 \text{ g}^{-1})$ and mesopore volume (0.64 $\text{cm}^3 \text{g}^{-1}$). The largest BET surface area was obtained for the sample prepared at 500 °C (NiC5), with a value of 449 m² g⁻¹. These values could be considered moderate if they are compared with typical values for other porous materials such as MOFs or activated carbons, but it should be noted that present materials incorporated a large amount of non-porous nickel with values ranging between 35.8 and 57.5 wt% (see Table 1). Hence, the porous textural parameters were recalculated with respect to the carbon weight, and BET surface areas around 800 $m^2 g^{-1}$ and total pore volumes up to 1.37 cm³ g⁻¹ were obtained (see Table S1 and Figure S5b), indicating that the carbonaceous fraction of the samples possessed a highly developed porous texture. With respect to the carbon content, the pore texture development was seen to be maximum for the sample prepared at 700 °C (i.e., NiC7).

The carbonization temperature not only had a strong effect on the amount of Ni (Table 1) but also on the nickel particle size distribution. Figs. 3 and 4 show representative SEM and TEM images, respectively, for samples carbonized at different temperatures. The morphology of the materials (Fig. 3) evolved with temperature from a continuous, rough morphology with nanometre-sized holes



Fig. 2. N2 adsorption-desorption isotherms (a, b) and QSDFT pore size distribution (c, d) for pristine NiOF and NiOF carbonized at different temperatures (NiCx samples).

Table 1									
Yield and J	porous textural	parameters deduced from N	I_2 adsorption at	- 196 °C on	pristine NiOF	and NiOF sam	ples carbonized a	t different temp	peratures.

Sample	T (°C)	Ni (wt.%)	$V_T (cm^3 \cdot g^{-1})$	$S_{BET} (m^2 \cdot g^{-1})$	V _{DR,N2}	QSDFT (cm ³ ·g ⁻¹)			
		(cm ³ 'g ⁻¹)		$V_{\mu p} (d_p < 2 nm)$	$V_{mp} (2 < d_p < 50 nm)$	V _{total}			
NiOF	_	21.4	0.23	81	0.03	0.01	0.21	0.22	
NiC4	400	35.8	0.28	251	0.08	0.06	0.21	0.27	
NiC5	500	43.0	0.64	449	0.15	0.08	0.54	0.62	
NiC6	600	44.2	0.73	429	0.15	0.07	0.64	0.71	
NiC7	700	50.5	0.68	393	0.14	0.06	0.60	0.66	
NiC8	800	49.5	0.64	316	0.11	0.05	0.58	0.62	
NiC9	900	53.4	0.56	302	0.11	0.05	0.49	0.54	
NiC10	1000	57.5	0.50	259	0.09	0.04	0.44	0.49	

(NiC4) to an arrangement of close-packed but clearly distinct nanoparticles (NiC8). The nickel particle size tended to increase temperature (Fig. 4). It is important note that the nickel nanoparticles were homogeneously distributed throughout the carbon matrix in all the samples, as can be seen from the TEM images. While their number and size increased with treatment temperature, the nanoparticles were retained as individual, non-sintered entities, even for the sample prepared at the highest temperature (NiC10).

The nickel particle size distribution was determined from the TEM images. The particle diameter of a minimum of 1000 different nanoparticles for each sample was measured using the image treatment software ImageJ [40], and the particle size distribution histograms are given in Fig. 5. At temperatures up to 500 °C, the particle size distributions were narrow, with most sizes below

10 nm and centered on sizes around 4 nm. As carbonization temperature increased, the distributions widened and the typical particle sizes becomes larger, although for samples prepared up to 700 °C the particles were well below 20 nm. At 800 °C and above, the particle size distributions became clearly wider with a substantial percentage of the nanoparticles being several tens of nanometres in size. However, even for these samples the most frequent sized remained below 20 nm.

The average nickel nanoparticle size, L_{β} parameter, was also estimated by applying the Scherrer's equation (Equation (1)) to the X-ray diffractograms shown in Fig. 1 [41,42]. This parameter evaluated the crystal dimension using the integral breadth, b_{β} , which is defined as the total area under the diffraction maximum divided by the corresponding peak intensity. The b_{β} parameter includes an instrumental contribution, c_{eq} , that needs to be removed to



Fig. 3. Representative FE-SEM images for NiOF carbonized at: (a, b) 400 °C; (c, d) 600 °C and (e, f) 800 °C.

determine the actual integral breadth, b'_{β} , as indicated in Equation (2). In our case: $c_{eq}^2 = 7.7 \cdot 10^{-6}$. Finally, K_{β} is the Scherrer's constant, which depends on the definition of 'breadth', the crystallite shape and the crystallite-size distribution [42].

$$L_{\beta} = \frac{K_{\beta} \lambda}{b'_{\beta} \cos\theta} \tag{1}$$

$$b_{\beta}' = \sqrt{(b_{\beta})^2 - (c_{eq})^2}$$
(2)

Table 2 collects the modal and average particle size obtained from TEM images (Fig. 5) as well as the Scherrer's crystal dimension parameter for the different NiCx samples. The average values obtained from TEM and L_{β} are in reasonable agreement with each other. Both parameters increased with carbonization temperature, with a significant increase being observed between 700 and 800 °C. From 400 to 700 °C the average size and L_{β} increase from 3.8 to 7.5 and 5.8–10.7 nm, respectively, and at 800 °C these parameters change to 19.8 and 22.5 nm, respectively. On the other hand, the modal particle size did not exhibit a significant increase between 700 and 800 °C and only underwent a limited increase in the whole carbonization temperature range (from 3 to 10 nm between 400 and 1000 °C).

An interesting effect of the treatment temperature on the evolution of the crystalline phases of nickel was observed by X-ray diffraction (Fig. 1). As it is well known, a face-centered cubic (FCC) structure is the stable crystalline phase of nickel (PDF 03-065-2865), with typical peaks at $2\theta = 44.51$, 51.85 and 76.37°. These peaks were observed in all carbonized NiOF samples except in the



Fig. 4. Representative TEM images for NiOF carbonized at: (a) 400, (b) 600, (c) 800 and (d) 1000 °C.

case of NiC4, where only an intense peak at 44.74° was noticed, which could be assigned to the metastable form of Ni₃C in rhombohedral structure [43,44] (PDF 01-072-1467). The sample treated at 400 °C also displayed two peaks at 13.64 and 15.38° that corresponded to non-decomposed NiOF, i.e., this temperature was not high enough to fully decompose the NiOF as suggested by the TGA results (Figure S4). The thermal decomposition of Ni₃C is known start at around 450-475 °C [44,45], but in our case it could not observed by TGA because the thermal decomposition of the NiOF occurred in the same temperature interval (Figure S4). Samples prepared at temperatures between 500 and 700 °C exhibited additional peaks at $2\theta = 41.85$, 44.5 (this peak cannot be distinguished from the highest intensity peak of FCC Ni phase), 47.55 and 62.53°. As reported previously [45-48], these peaks can be ascribed to an intermediate phase formed during the conversion of rhombohedral Ni₃C (where carbon adopts inner atom-positions in the lattice) [44] into the stable Ni-FCC structure. In this intermediate phase, nickel atoms could be forced to adopt a compressed crystalline form of hexagonal close-packed (HCP) phase due to the loss of interstitial carbon atoms and to the effect of the graphite-like shell formed over the nickel particles, which blocks the reorganization of the Ni atoms into the FCC structure [45]. In our case, the peak position and the calculated hexagonal cell dimensions (a = 0.2492 nm and c = 0.4015 nm) were the same as those reported previously by other authors [45] and matched with PDF 00-001-1277 corresponding to the HCP structure of cobalt. Finally, samples NiC8, NiC9 and NiC10 only exhibited three intense, welldefined and narrow peaks, corresponding with high crystalline FCC nickel nanoparticles with a calculated cell dimension of a = 0.3525 nm, indicating that the stable Ni phase was attained only at a temperature of 800 °C.

Going back to the nanoparticle size histograms (Fig. 5), the discrepancies between modal values and average size and L_{β} can be understood. As can be seen, up to 700 °C the particle size distributions are narrow, but above this temperature they become wide, increasing the particle size dispersion. This is reflected in the average values (average size and L_{β}), but not in modal size. The presence of Ni₃C and HCP phases insures a strong interaction between the carbonaceous component and Ni nanoparticles, preventing their movement and therefore their sintering. Above 700 °C Ni-FCC is the only structure present in the sample and due to the evolution of the Ni crystalline phases explained above, most nickel nanoparticles are expected to continue to maintain a strong interaction with the carbonaceous support after transformation from Ni₃C to Ni-FCC, which would cause that the modal size does not increase much. However, as temperature increases a greater number of Ni nanoparticles will have less interaction with the carbon support, being able to spill over the surface and therefore sintering, increasing the particle size dispersion and therefore the average nanoparticle size.

The evolution of the carbonaceous component with heat treatment temperature was studied by Raman spectroscopy (Fig. 6). First, the Raman spectrum of non-carbonized NiOF reflected the vibrational modes of 2-mIm [49]. The most intense bands were



Fig. 5. Nickel particle size histogram distributions obtained by manually counted and measured diameters of nickel grains in TEM photographs (~1000 particles for each sample were measured).

Table 2		
Nickel particle sizes as a function	of the carbonization	temperature.

Particle size (nm)					
Modal ^(a)	Average ^(a)	Scherrer $L_b^{(b)}$			
3	3.8	5.8			
4	4.4	6.9			
6	7.3	8.6			
7	7.5	10.7			
10	19.8	22.5			
8	20.2	25.1			
6-10	36.9	26.7			
	Particle size (nn Modal ^(a) 3 4 6 7 10 8 6–10	Particle size (nm) Modal ^(a) Average ^(a) 3 3.8 4 4.4 6 7.3 7 7.5 10 19.8 8 20.2 6-10 36.9			

^a Values obtained by manually counting-measuring nickel particles (~1000 particles/sample) fromTEM images.

^b Calculated by Scherrer equation using the integral breath approximation. J.I. Langfor and A.J.C. Wilson [42].

correlated with vibrational stress of the imidazole ring (1467 cm⁻¹), symmetric tensional vibration of methyl group (2928 cm⁻¹) and symmetric tensional vibration of the HC=CH bond (3150 cm⁻¹). After heat treatment, the Raman spectra of the NiCx samples were dominated by three main features that are characteristic of graphitic (or, at least, sp²-based) carbons [50], namely, the G band (~1582 cm⁻¹), the defect-related D band (~1348 cm⁻¹), and the second-order 2D band (~2692 cm⁻¹). Samples prepared at temperatures up to 700 °C exhibited a strong overlap of very broad D and G bands as well as an absence of any 2D band, indicating a highly disordered or even amorphous carbon structure. Above this temperature, well defined D and G bands





Fig. 6. Raman spectra of pristine NiOF and NiOF carbonized at different temperatures (between 400 and 1000 $^{\circ}$ C).

were observed together with the emergence of the 2D band, which is known to be related to the development of a significant graphitic character in carbon materials with decreasing concentration of defects [51,52]. The latter was confirmed by determining the integrated intensity ratios of the D and G bands $(I_D/I_G ratio)$ as a wellknown proxy for defect content in graphitic materials. Samples NiC8, NiC9 and NiC10 had an I_D/I_G ratio of ~0.92, ~0.63 and ~0.58, respectively, indicating decreasing defect content with increasing temperature. Furthermore, Raman spectra in samples NiC9 and NiC10 showed a shoulder on the high wavenumber side of the G band, which could be assigned to the so-called D' band (~1612 cm⁻¹), which is also a defect-related band. The significant increase in the graphitic character of the samples treated at 800 °C and above could be explained by taking into account that Ni catalyses the graphitization of amorphous carbon close to the metal particles by a solution-diffusion-precipitation mechanism [48,53,54]. Indeed, TEM images for samples prepared above 800 °C showed the presence of carbon nanofilaments (see Figure S6) produced during the heat treatment.

3.3. Catalytic activity of the NiOF-derived Ni/carbon hybrids in the reduction of 4-nitrophenol

The reduction of 4-NP to 4-AP by NaBH₄ is usually employed as a model reaction to assess the catalytic activity of metallic nanoparticles [55] but has also relevance from a practical perspective (e.g., in the synthesis of certain analgesic and antipyretic drugs) [11]. The evolution of the reaction was followed with UV–vis absorption spectroscopy measuring the evolution (decrease) of the absorption band located at ~400 nm that is characteristics of 4nitrophenolate, i.e., the deprotonated form of 4-NP that is generated in the basic medium of the reaction by the NaBH₄. The formation of 4-AP was confirmed by the emergence of the 4aminophenolate characteristic band at ~299 nm (see Fig. 7 and S7). The concentration of 4-NP at the beginning of the reaction and that of 4-AP at the end were determined by means of their corresponding UV–vis calibration curves (Figure S1). Specifically, the absorbance values at 299 nm for 4-AP at the end of the reduction reaction varied between 0.113 and 0.126 (see Fig. 7 and S7 and Table S2), which corresponded to 4-AP concentrations between 0.056 and 0.062 mM. Taking into account the stoichiometry of the reaction and the initial concentration of 4-NP, the corresponding reaction yields were close to 100% (Table S2) for all the catalysts, except for NiC9 and NiC10, indicating that 4-NP was efficiently and selectively reduced to 4-AP by the Ni/carbon hybrids. The somewhat lower reaction yield for samples NiC9 (93%) and NiC10 (92%) could be simply due to the fact that reduction was not yet completed at the time of the measurement, as can be noticed in Figure S7-f1 and -g1, where some absorbance at 400 nm was observed in the latter spectra.

NaBH₄ was used in a very large excess so that the reaction approximately became pseudo-first-order with respect to 4-NP (Equations (3) and (4)). Thus, the apparent rate constant (k_{ap}) can



Fig. 7. (a) Representative evolution of the absorption spectra during the reduction of 4-NP to 4-AP with NaBH₄ catalysed by NiC7 at 25 °C; (b) corresponding plot of Ln (A/ A₀) vs time. Data for other NiCx samples are compiled in Figure S7. A denoted the absorbance measured at 400 nm at a time t, and A0 is the absorbance at the beginning of the reaction.

be calculated by a logarithmic fit of absorbance ($Ln A/A_0$) vs time (Equation (4)) as can be seen in Fig. 7b:

$$\frac{dC_{4NP}}{dt} = k_{ap} C_{4NP} \tag{3}$$

$$-Ln\frac{C_{4NP}}{C_{4NP, t=0}} = k_{ap} t \equiv -Ln\frac{A_{4NP}}{A_{4NP, t=0}} = k_{ap} t$$
(4)

, where, C_{4NP} and $C_{4NP, t=0}$ are concentration of 4-NP at the time t and at the beginning of the reaction, respectively. In order to make a better comparison of the catalyst performance, two activity parameters were defined by normalizing k_{ap} to the amount of catalyst used per unit of volume, k' (Equation 5), and to the total amount of nickel in each sample, k'' (Equation 6):

$$k' = \frac{k_{ap}}{m_{cat}/V_{react}} \tag{5}$$

$$k^{''} = \frac{k'}{\tilde{x}_{Ni}} \tag{6}$$

, where m_{cat} is the total mass of Ni/carbon hybrid used (about 4.5 mg), V_{react} is the total volume of reaction (300 mL) and \tilde{x}_{Ni} is the nickel weight percentage in each sample (Table 1). Likewise, to facilitate comparisons with other Ni-based catalysts reported in the literature, the overall catalytic activity defined as the number of moles of 4-NP reduced per mole of nickel per unit time, Act_{Ni}, was also calculated.

The different measured parameters are collected in Table 3 and for the different NiCx samples and plotted in Fig. 8 as a function of teat treatment temperature. Sample NiC4 (material prepared at 400 °C) boasted the highest catalytic activity of all samples ($K_{ap} = 0.172 \text{ min}^{-1}$, $k' = 0.191 \text{ L g}^{-1} \text{ s}^{-1}$, $k'' = 0.534 \text{ L g}_{\text{Ni}}^{-1} \text{ s}^{-1}$; Act_{Ni} = 0.039 mol_{4NP} mol_{Ni}⁻¹ s⁻¹). While an overall trend of decreasing activity parameters with increasing heat treatment temperature between 400 and 1000 °C was apparent in Fig. 8, a local maximum could be noticed at 700 °C.

To rationalize this behaviour, several points have to be taken into account. First, the monotonous increase in the size of the Ni nanoparticles in the NiCx samples with increasing the heat treatment temperature (see Table 2 and Fig. 5) entails a decrease in the specific surface area of the Ni catalyst, so a diminution in the catalytic activity of the samples when normalized to their Ni content is expected. However, although this can roughly explain the overall trend (decrease in catalytic activity with heat treatment temperature), it cannot explain the substantial increase in activity between 600 and 700 °C. Second, because the Ni nanoparticle were embedded in a porous carbon matrix (see Fig. 4), another factor that could critically impact their catalytic performance would be the accessibility of the reagent to the nanoparticle surface through the pore network of the carbon matrix. In this case, reagent access would be expected to be facilitated for carbon matrixes with a welldeveloped porous texture, particularly in terms of mesopore volume. Nevertheless, the most active catalyst (NiC4) was also the poorest regarding pore texture development, suggesting that such an effect was not a determinant of the observed catalytic trends. Third, the different crystalline phases of nickel observed by X-ray diffraction in the samples prepared at different temperatures could bear a significant influence on the reported catalytic behaviour. We note that the sharp decrease in catalytic activity between 400 and 600 °C (see Fig. 8), where the increase in Ni nanoparticle size was relatively modest, was coincident with the emergence of the HCP Ni phase (Fig. 1), and that the almost total disappearance of this

Table 3						
Kinetic constants and	catalytic activities	of the Ni/Carbon	hybrids	catalysts	at 25 °	°C.

Sample	k_{ap} (min ⁻¹)	$k' (L \cdot g^{-1} \cdot s^{-1})$	$k'' (\mathrm{L} \cdot \mathrm{g}_{\mathrm{Ni}}^{-1} \cdot \mathrm{s}^{-1})$	$Act_{Ni} (mol_{4NP} \cdot mol_{Ni}^{-1} \cdot min^{-1})$
NiC4	0.172	0.191	0.534	0.039
NiC5	0.104	0.115	0.268	0.020
NiC6	0.061	0.067	0.153	0.012
NiC7	0.129	0.143	0.283	0.020
NiC8	0.088	0.097	0.197	0.015
NiC9	0.055	0.061	0.114	0.008
NiC10	0.046	0.051	0.088	0.007



Fig. 8. Plot of the kinetic constants and ActNi at 25 °C as a function of NiOF carbonization temperature. Note that k' is referred to the total mass (carbon + nickel) and k'' is calculated with respect to the nickel amount in the catalyst.

phase at 700 °C, was concurrent with a substantial increase in catalytic activity. Such observations strongly suggest that HCP Ni is considerably less active than both FCC Ni and Ni₃C which would account for some of the peculiar catalytic trend observed in Fig. 8. Indeed, recent theoretical studies [56] on the dissociation of CO in FCC and HCP Ni catalysts have shown that the latter phase is less active than the former. In our case, this lower activity of the hexagonal phase can also be explained taking into account the mechanism discussed above for the formation of the FCC Ni phase from Ni₃C: the transformation of Ni₃C to FCC Ni occurs through the formation of the intermediate HCP phase by the diffusion of carbon atoms from the bulk to the surface of the Ni particles, where they precipitate and form a graphitic carbon shell [45]. This carbon shell can partially cover the catalyst surface, making it less accessible to the reagents, decreasing the catalytic activity of HCP Ni nanoparticles.

It is not straightforward to compare the behaviour of different catalysts reported in the literature because the conditions under which they are tested differ in the amount of catalyst used, the concentration of the reagents, the volume of the reactor and the temperature, which all have an effect on the catalyst activity. Table S3 lists different kinetic parameters and Act_{Ni} for a series of Ni catalysts supported onto carbon materials reported in the literature [7,10,22,25,29,31,32,57–61]. In several of these works, the kinetic studies were carried out in UV–Vis spectrophotometer cuvettes

(volume < 3 mL) or in low volume reactors, where the amount of catalyst to volume ratio was very high, which should favour the kinetics of the process, as we also noted in the higher values of K_{an} obtained in the cyclabilty experiments carried out in the spectrophotometer cuvettes under similar conditions than in the reactor experiments. Thus, the concentration of catalyst (i.e., Ni + carbon) and Ni used in those works were also included in Table S3. In our case, we used a reaction volume of 300 mL, which should more closely resemble a real practical situation. Taking this into account, the best catalyst prepared in this work (NiC4) displayed one the best performance for the investigated reaction and only catalysts reported by Chen et al. [58] and Xia et al. [10] (measured at 30 °C) possessed a higher activity than ours using similar catalyst concentrations. As in the case of other Ni-based catalysts, our Ni/carbon hybrids also have a ferromagnetic character (Figure S8), which allows their easy recovery comparing to non-ferromagnetic catalysts.

The cyclability of the most active catalysts (i.e. NiC4 and NiC7) was studied by means of eight consecutive reduction reaction carried out in the cuvette of the UV–vis spectrophotometer by adding fresh 4-NP at the beginning of each cycle and measuring the absorbance decay at 400 nm (Figure S9). As can be seen, after 8 consecutive cycles the reaction rate constant, K_{ap} , is maintained for both samples, thus demonstrating their stability and recyclability. Leaching of Ni into the reaction solution was not thought to be an issue. After the cyclability tests, the solid catalyst was allowed to sediment from the reaction solution, and then the latter was collected and used as a possible catalyst in a subsequent 4-NP reduction reaction. No significant catalytic activity was detected, which indicated that Ni molecular species or clusters did not leach from the solid catalyst to any substantial extent.

Finally, we studied the effect of temperature on the catalyst activity. Experiments at 15 and 5 °C were carried out with sample NiC4 and shown in Figure S10. Applying the Arrhenius equation and plotting LnK_{ap} vs. 1/T (Equation (7) and Fig. 9), the apparent activation energy (E_{act}) and the pre-exponential factor (A) could be calculated (Table 4):

$$K_{ap} = Ae^{-\frac{E_{act}}{RT}} \to Ln \ k = Ln \ A - \frac{E_{act}}{RT}$$
(7)

 E_{act} was determined to be 93.9 kJ mol⁻¹ and A was $4.34 \cdot 10^{15}$ s⁻¹. This activation energy was similar to value reported by Xia et al. [10] for Ni nanoparticles supported on carbon black (80.7 kJ mol⁻¹) and lower than that for unsupported Ni catalyst (129.3 kJ mol⁻¹) reported by same authors, but higher than those reported by other authors [7,19]. The activation energy depends on the reaction mechanism, being that of the highest energy stage. In the case of our catalysts, it seems that supporting the nanoparticles on the carbon material produces a decrease in the activation energy with respect to that presented by the not supported nickel in the reduction of 4-NP to 4-AP with NaBH₄ [10]. On the other hand, a higher activation energy is also indicative of a higher dependence



Fig. 9. Plot of Lnk_{ap} against 1/T for the reduction of 4-NP at different temperatures: 5, 15 y 25 °C.

Table 4

Kinetic parameters obtained for experiments carried out at 25, 15 and 5 °C in presence of sample NiC4. A and E_{act} were calculated using the Arrhenius equation.

T (°C)	$k_{ap} [\min^{-1}]$		$k' [L \cdot g_{cat}^{-1} \cdot s^{-1}]$		$k'' [L \cdot g_{Ni}^{-1} \cdot s^{-1}]$		$E_{act} [kJ \cdot mol^{-1}]$
	k _{ap,NiC4}	A _{,NiC4}	k' _{NiC4}	A' _{NiC4}	k" _{NiC4}	A" _{NiC4}	
25	0.172	4.34E ¹⁵	0.191	4.82E ¹⁵	0.534	1.35E ¹⁶	93,9
15	0.033		0.036		0.102		
5	0.011		0.012		0.035		

of the reaction rate with the temperature. Therefore, a small increase in temperature will produce a significant increase in the kinetic constants allowing to achieve very high reaction rates at moderate temperatures.

4. Conclusions

In this work, we have synthesized a new nickel-based metalorganic framework (NiOF) by reaction between nickel acetate and 2-methyl-imidazole in water at a moderate temperature and in a short time. This NiOF was used as a precursor for the synthesis of mesoporous Ni nanoparticle/carbon hybrids by heat treatment at temperatures between 400 and 1000 °C. The NiOF solid was a mesoporous crystalline material with a tetragonal structure (D_{4h} point group symmetry), a specific surface area of 81 m^2g^{-1} and a mesopore volume of 0.21 cm³g⁻¹. By controlling the heat treatment temperature, both the Ni nanoparticle size and the amount of nickel increased from 3.8 to 36.9 nm and from 35.8 to 57.5 wt%, respectively. Despite the large fraction of metal content, the materials exhibited a homogeneous dispersion of Ni nanoparticles with limited agglomeration or sintering, probably due to their stabilization in the porous carbon matrix. The Ni nanoparticles went through different crystalline phases during the carbonization process. At 400 °C, Ni₃C was the dominant phase, while at temperatures above 700 °C the thermodynamically stable Ni facecentered cubic phase (FCC) remained as the only crystalline form present in the samples. The nanoparticles transitioned from Ni₃C to Ni-FCC through a metastable hexagonal close-packed phase (HCP). The presence of such crystalline forms appeared to have a noticeable effect on the performance of the materials as a catalyst for the

reduction of 4-nitrophenol to 4-aminophenol. Indeed, the catalytic activity was strongly dependent on the heat treatment temperature, generally decreasing with increasing temperature, but presenting a local maximum at 700 °C. This behaviour was related to the different catalytic activity of the various nickel phases, with Ni-HCP being a relatively low activity phase. The catalyst prepared at 400 °C was the most active, boasting one of the highest kinetic parameters reported in the literature for the investigated reduction reaction using non-noble metals ($K_{ap} = 0.172 \text{ min}^{-1}$, k" = 0.534 L g_{NI}^{-1} s⁻¹ and Act_{NI} = 0.039 mol_{4NP} mol_{NI}⁻¹ min⁻¹).

CRediT authorship contribution statement

F. Julian Martín-Jimeno: Investigation, Methodology, Data curation. **Fabián Suárez-García:** Conceptualization, Methodology, Data curation, Writing – original draft, Funding acquisition. **Juan I. Paredes:** Methodology, Data curation, Writing – review & editing, Funding acquisition. **Amelia Martínez-Alonso:** Writing – review & editing, Funding acquisition. **Juan M.D. Tascón:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jallcom.2020.157348.

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