# Dalton Transactions

# PAPER



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# A robust core-shell nanostructured nickel-iron alloy@nitrogen-containing carbon catalyst for the highly efficient hydrogenation of nitroarenes<sup>†</sup>

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Currently, the catalytic selective hydrogenation of nitroarenes to produce aromatic amines is one of the most important key reactions in many fine chemical processes. In particular, non-noble-metal-catalyzed hydrogenation of nitroarenes represents more sustainable chemical processes. Here, we report a new robust and recyclable core-shell nanostructured nickel-iron alloy@nitrogen-containing carbon (NiFe@NC) catalyst and the beneficial effect of alloying Ni with Fe for the above reaction. The key to this synthetic strategy was thermally transforming the Ni-Fe layered double hydroxide (NiFe-LDH)/melamine mixture to form a fixed NiFe@NC nanostructure. A series of characterization results revealed the formation of NiFe alloy nanoparticles (NPs) coated with the NC overlayer. The as-fabricated NiFe@NC catalyst with a Ni/Fe atomic ratio of 3.0 exhibited superior activity for the reduction of the nitro group in o-chloronitrobenzene, with a 99.5% yield of o-chloroaniline under mild reaction conditions. The initial reaction rate over the catalyst was nearly three times that over the monometallic Ni@NC counterpart, and even one-order magnitude higher than that over pristine NiFe-LDH-derived NiFe alloy NPs. The extraordinary activity of NiFe@NC was reasonably attributed to the unique core-shell nanostructure, where both the NiFe alloy core and the NC overlayer shell could construct a significant promotional effect, being beneficial for the selective cleavage of the N-O bond. Recycling experiments indicated that the catalyst could be easily separated and recovered under an external magnetic field and experienced excellent recyclability during seventeen cycles without an obvious loss of catalytic activity. Furthermore, the present catalyst was also highly active for the chemoselective hydrogenation of other substituted nitroarenes bearing different functional groups to the corresponding anilines.

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# 1. Introduction

Over the past half century, hydrogenation reactions have gained considerable attention due to their importance in both the academic field and the industrial production of fuels and chemicals. In particular, metal-catalyzed selective hydrogenation of nitroarenes to produce subsequent aromatic amines has been extensively investigated, because aromatic amines can be widely used as an important feedstock for the commercial manufacturing of pharmaceuticals, dyes, herbicides, pesticides, and cosmetic products.<sup>1</sup> Now, the worldwide demand for aromatic amines is substantially increasing. Various procedures involving heterogeneous catalysts and reducing agents are available for the reduction of nitroarenes.<sup>2-4</sup> As for the selective reduction of the nitro group in chloronitrobenzenes (CNBs), however, the undesired hydrodehalogenation side reaction is often involved,<sup>5,6</sup> besides the formation of main chloroanilines (CANs), as well as hydroxylamine, hydrazine, azoarene, or azoxyarene intermediates, due to the poor activities of catalysts. Despite high conversions of CNBs in this type of reaction conducted over a variety of noble metal catalysts (e.g. Pd,  $^{7,8}$  Ru,  $^9$  Pt,  $^{10,11}$  Au $^{12,13}$  and Ag $^{14}$ ), the high cost of noble metals greatly limits their practical applications. Recently, many efforts have been made towards using low-cost first-row transition metal catalysts, such as Ni/TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>,<sup>15-17</sup> as well as heteroatom-doped carbon spheres as metal-free catalysts.<sup>18</sup> In this regard, nickel-based catalysts show relatively high selectivity to aromatic amines,19-21 which represents more sustainable chemical processes. Their activities, however, usually are much lower than those of noble metal-based ones. Moreover, in some cases, weak metal-support interactions can reduce the stability of catalysts. As a result, developing costeffective non-noble-metal catalysts with robust catalytic activity



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and stability is a key issue when it comes to reducing nitroarenes to produce aromatic amines.

As one of the effective strategies for improving catalytic performance, elaborately designing or manipulating surface microstructures of catalysts always benefits the adsorption of reactants and thus the activation. Therefore, much attention has been paid to exploring alternative support materials to strengthen metal-support interactions and thus improve the reusability and recyclability of catalysts. Recently, as a kind of fascinating carbon material, nitrogen-containing carbon (NC) has been gaining considerable interest in the whole world,<sup>22,23</sup> because the introduction of highly electron-rich nitrogen atoms into the carbon framework can greatly improve the electrical and chemical properties of carbon materials, thereby bringing out a wide range of practical applications.<sup>24,25</sup> In particular, loading metallic nanoparticles (NPs) on NC materials may markedly affect the electronic character of metal species.<sup>26,27</sup> Moreover, the metallic or semimetallic nature of nanocarbons ensures strong electronic interactions with metal species to a large extent.

On the other hand, layered double hydroxides (LDHs), known as a class of two-dimensional highly ordered layered materials, are mainly composed of metal  $M^{2+}$  and  $M^{3+}$  cations distributed uniformly in the brucite-like layers.<sup>28,29</sup> Many advantages including low price, ease of preparation, and structural variability provide LDH materials high potential for various practical applications. In particular, numerous research efforts have successfully integrated LDHs into the synthesis of a variety of highly dispersed supported metal or metal oxide catalysts through the structural transformation of LDH precursors.<sup>30–32</sup> Recently, we have reported that LDHderived Ni-based catalysts possess good catalytic activity in the *o*-CNB hydrogenation to *o*-CAN,<sup>20,33</sup> despite the harsh reaction conditions employed (*e.g.* high reaction temperature and high hydrogen partial pressure).

As we know, metal catalysts often suffer from several drawbacks, such as aggregation, separation and leaching of active metal components. So, constructing magnetic metal NPs embedded into carbon nanomaterials will create a new opening for metal catalysts because of their ease of magnetic separation, cost effectiveness and high stability. Herein, we report a novel low-cost and magnetically recyclable core-shell structured Ni-Fe alloy/NC (NiFe@NC) nanocatalyst fabricated by the thermal decomposition of the NiFe-LDH/melamine mixture. The as-fabricated NiFe@NC catalyst shows excellent catalytic performance in the liquid phase selective hydrogenation of o-CNB to o-CAN in terms of activity, selectivity and stability. By virtue of the core-shell nanostructure composed of a NiFe alloy core and a thin NC layer shell, strong metalsupport interactions (SMSIs) can occur. Detailed characterization reveals that the beneficial effect of alloying of Ni with Fe is the result of the electronic modification of Ni and thus enhances the catalytic performance of the bimetallic catalyst. What's more, the unique core-shell nanostructure effectively prevents the agglomeration of NiFe alloy NPs, thus remarkably improving the catalyst stability.

## 2. Experimental

#### 2.1 Preparation of samples

NiFe-LDH precursors with different Ni/Fe molar ratios of x (x =2.0, 3.0, 4.0) were prepared by our developed separate nucleation and aging steps method.<sup>34</sup> In a typical synthesis, 100 mL of a salt solution containing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 100 mL of a base solution containing  $Na_2CO_3$  and NaOH ([ $CO_3^{2-}$ ] = 2[ $Fe^{3+}$ ], [ $OH^-$ ] = 1.6([ $Ni^{2+}$ ] + [Fe<sup>3+</sup>])) were simultaneously added into a colloid mill and vigorously mixed at a rotor speed of 4000 rpm for 3 min. Subsequently, the resulting suspension was aged at 60 °C for 6 h and centrifuged. The obtained precipitate was washed with deionized water until the pH value reached about 7.0. The synthesized NiFe-LDH was dried at 70 °C overnight in a vacuum oven, and then mixed with melamine (the mass ratio of melamine to NiFe-LDH is set at 3.0) to obtain a mixture (denoted as NiFe-LDH/M). Finally, NiFe-LDH/M was calcined under a N2 atmosphere at 600 °C for 2 h at a ramp rate of 5 °C to obtain different NiFe@NC-x samples.

For comparison, pure NiFe-LDH with a Ni/Fe molar ratio of 3.0 was reduced under a 5% H<sub>2</sub>/Ar atmosphere at 600 °C in the absence of melamine to obtain the NiFe-3 sample. In addition, the mixture of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and melamine (the melamine/Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O mass ratio = 3.0) was calcined according to the same procedure as that for NiFe-LDH/M samples. The obtained sample was denoted as Ni@NC. Meanwhile, NiFe-free pure NC was prepared from melamine without the addition of NiFe-LDH under identical experimental conditions.

#### 2.2 Sample characterization

X-ray diffraction (XRD) patterns of all samples were recorded on a Shimadzu XRD-6000 diffractometer using a Cu K $\alpha$  radiation source ( $\lambda = 0.15418$  nm).

Elemental analysis of the metal contents was performed on a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscope (ICP-AES). Before measurement, the sample was first calcined at 700 °C under air for 2 h, and then the remainder was dissolved in aqua regia. The carbon and nitrogen contents were determined by elemental microanalysis (Elementar Vario analyzer).

The morphology and microstructures of the samples were observed using a field emission scanning electron microscope (FE-SEM, Zeiss Supra 55); transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were conducted using a JEOL JEM-3010 electron microscope. High-angle annular dark-field scanning TEM (HAADF-STEM) images were observed on a JEOL2010F instrument combined with an energy dispersive X-ray spectrometer (EDX).

Low temperature nitrogen adsorption-desorption isotherms of the samples were obtained using a Micromeritics ASAP 2020 sorptometer apparatus. Specific surface areas were measured by the multipoint BET method, while total pore volumes and average pore sizes were calculated by the BJH method. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer using an Al K $\alpha$  X-ray radiation source.

A vibrating sample magnetometer (VSM, Lake Shore 7410) was used to measure the magnetic property of the samples.

Temperature-programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) experiments were conducted using a Micromeritics AutoChem 2920 II chemisorption apparatus with a thermal conductivity detector (TCD). The sample (100 mg) was degassed at 300 °C for 1 h under a He flow. Then a CO<sub>2</sub> stream (40 mL min<sup>-1</sup>) was switched into the sample tube at 100 °C for 1.5 h. Subsequently, a He flow was switched at 100 °C for 2 h. Finally, the temperature was increased to 800 °C at a rate of 10 °C min<sup>-1</sup> under a He gas flow.

Oxygen temperature-programmed oxidation ( $O_2$ -TPO) experiments were performed on a Thermo Fisher TPDRO-1100 chemical adsorption instrument with a TCD. The sample (30 mg) was degassed at 350 °C for 1 h under a He flow. TPO was performed at 30 °C in a stream of 10% v/v  $O_2$ /He at a heating rate of 5 °C min<sup>-1</sup>.

 $H_2$  pulse chemisorption was conducted on a Micromeritics AutoChem II 2920 instrument. First, the sample (100 mg) was degassed under a flow of Ar (40 mL min<sup>-1</sup>) at 500 °C for 1 h and then the temperature was decreased to 55 °C and subjected to  $H_2$  chemisorption according to a pulse titration procedure. The total hydrogen uptake was used to calculate the amount of surface active sites assuming that the ratio of H to the adsorption site is 1 : 1.

Temperature programmed desorption of hydrogen (H<sub>2</sub>-TPD) experiments were carried out on a chemisorption analyzer (Micromeritics AutoChem 2920 II sorptometer apparatus). First, the sample (0.1 g) was degassed under a flow of Ar (40 mL min<sup>-1</sup>) at 500 °C for 1 h and treated under a flow of H<sub>2</sub>/Ar (1:9, v/v; 40 mL min<sup>-1</sup>) at room temperature and held for 2 h. Finally, chemisorbed H<sub>2</sub> was desorbed from room temperature to 800 °C under a flow of Ar at a rate of 10 °C min<sup>-1</sup>.

#### 2.3 Catalytic test

In a typical run, the selective hydrogenation of o-CNB was conducted in a batch autoclave reactor (100 mL), which was loaded with o-CNB (0.5 g), ethanol (50 mL), and the catalyst (0.02 g). Before the reaction, air was flushed out of the reactor with nitrogen four times, and then the reactor was placed into a heating jacket and preheated to a certain reaction temperature and charged with pure H<sub>2</sub> to 0.5 MPa with stirring at a speed of 900 rpm. During the reaction, the reaction temperature was kept constant during hydrogenation, while the hydrogen pressure remained unchanged by continuously supplying hydrogen through the pressure regulator from the gas cylinder. Finally, the liquid products were filtered and quantitatively analyzed using a gas chromatograph (Agilent GC7890B) equipped with a flame ionization detector and an HP-5 capillary column. Under the present reaction conditions, the external mass transfer limitation was determined to be negligible at an agitation speed of 900 rpm. The conversions and selectivities were obtained based on at least 3 parallel experiments with experimental errors of less than 3%. The values of the turnover frequency (TOF) were calculated based on the moles of *o*-CNB converted per mole of surface metallic sites determined by  $H_2$  pulse chemisorption.

### 3. Results and discussion

#### 3.1 Sample characterization

As shown in Fig. 1A, the XRD patterns of pristine NiFe-LDH present a series of characteristic diffractions for the (003), (006), (012), (015), (110) and (113) planes related to the carbonate-type LDH phase (JCPDFS no. 38-0487). For NiFe-LDH/M mixtures, intensive characteristic diffractions for the melamine phase (JCPDS no. 41-1390) can be detected. Fig. 1B shows the XRD patterns of reduced samples. Conspicuously, three intensive characteristic diffractions for the (111), (200) and (220) planes of the face centered cubic (fcc) Ni<sub>3</sub>Fe alloy phase (JCPDFS no. 38-0419) can be found in the cases of NiFe@NC samples. Meanwhile, small amounts of metallic nickel (JCPDS no. 04-0850) and nickel oxide (bunsenite, JCPDS no. 47-1049) phases are detected in two cases of NiFe@NC-2 and NiFe@NC-3. For NiFe@NC-4, no metallic Ni<sup>0</sup> is observed, probably attributable to the highly dispersive nature of the formed Ni NPs with poor crystallinity. In all cases, the absence of carbon nitride or graphite carbon suggests the poor crystalline nature of the carbon-containing component. The above results suggest that the in situ formed carbon component or released ammonia upon heating melamine in the NiFe-LDH/M mixtures under an inert atmosphere can serve as reducing agents to reduce Ni<sup>2+</sup> and Fe<sup>3+</sup> species. The average particle sizes of NiFe NPs in the NiFe@NC samples estimated based on the Scherrer equation range from about 7.9 to 26.1 nm (Table 1), which are smaller than that in the NiFe-LDH-derived NiFe-3 sample (38.6 nm). As shown in Fig. S1,† different NiFe@NC samples show characteristic nitrogen adsorption-desorption isotherms of type IV with a H1-type hysteresis loop, which is characteristic of the mesoporous framework with narrow pore size distributions. In particular, the NiFe@NC-3 sample pos-



Fig. 1 XRD patterns of (A) melamine, NiFe-LDH and NiFe-LDH/M samples, and XRD patterns of (B) Ni@NC (a), NiFe@NC-2 (b), NiFe@NC-3 (c), NiFe@NC-4 (d) and NiFe-3 (e) samples.

Table 1	Analytical and	structural	data	obtained	for	different	samples
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	Content (wt%)								
Sample	Ni <sup>a</sup>	Fe <sup>a</sup>	$N^b$	$\mathbf{C}^{b}$	$S_{\rm BET}^{\ \ c} \left({\rm m}^2 \ {\rm g}^{-1}\right)$	$V_{\rm pore}^{\ \ d} \left( {\rm cm}^3 \ {\rm g}^{-1} \right)$	$d_{\rm av}^{\ e}({\rm nm})$	$D_{111}^{f}(nm)$	$D^{g}\left(\mathrm{nm} ight)$
NiFe@NC-2	23.5	12.8	10.4	52.0	40	0.198	19.02	20.8	23.9
NiFe@NC-3	35.5	12.9	8.3	42.2	58	0.335	18.72	17.9	20.6
NiFe@NC-4	47.0	12.8	6.4	31.7	46	0.168	18.93	26.1	26.2
N@NC	36.6	0	10.0	50.9	55	0.338	18.20	15.8	18.5
NiFe-3	72.5	25.2	0	0	3	0.004	21.17	38.6	40.1

<sup>*a*</sup> Determined by ICP-AES analysis. <sup>*b*</sup> Determined by element microanalysis. <sup>*c*</sup> Determined by using N<sub>2</sub> adsorption–desorption isotherms. <sup>*d*</sup> Total pore volume. <sup>*e*</sup> Average pore diameter. <sup>*f*</sup> Crystallite size of metallic NPs based on XRD line broadening of the (220) plane. <sup>*g*</sup> The extracted surface area weighted mean size of NPs calculated by TEM analysis.

sesses a relatively high surface area (58 m<sup>2</sup> g<sup>-1</sup>) (Table 1), mainly because of the smaller particle size of NiFe NPs.

The morphology and microstructure of the NiFe@NC samples were elucidated by SEM, TEM and HRTEM observations. SEM micrographs depict that all samples present a homogeneous arrangement of aggregated NPs (Fig. S2<sup>†</sup>). TEM micrographs of the samples (Fig. 2) reveal the nature of the encapsulated nanostructure of the particles. For NiFe@NC-3, numerous NPs are embedded by the carbon overlayer, and the average crystallite size (from the counting of more than 200 particles) of encapsulated NPs is about 20.6 nm, well consistent with the above result based on XRD patterns. Noticeably, single particles in NiFe@NC-3 show a clear contrast difference between heavier metallic NPs and the lighter carbon layer of about 3-8 nm thickness. Furthermore, as shown in Fig. 2e and f, two well-resolved crystalline lattice spacings of about 0.177 nm and 0.204 nm in well-defined cores are indexed to the (200) and (111) planes of the fcc Ni<sub>3</sub>Fe alloy throughout the particles. Furthermore, it is evident that the particles are

encapsulated by a few graphite layers with an interlayer spacing of about 0.36 nm. Here, pyrolyzation and graphitization of melamine contribute to the formation of the thin carbon layer upon heating the LDH/M mixture. In the present NiFe@NC system, such a carbon overlayer can inhibit the growth and aggregation of metallic NPs and strengthen the metal-support interactions. On the other side, HRTEM images of NiFe@NC-3 depict that some tiny cracks can be clearly observed on the carbon layer surface (Fig. 3), as evidenced by the partial oxidation of metallic Ni and Fe species by air after the preparation procedure (see the following part). It suggests that reactant molecules easily get access to active sites during hydrogenation reactions, due to the presence of the unclosed shell of NC layers.

HAADF-STEM-EDX observation also gives more obvious evidence of NiFe alloy NPs encapsulated into the carbon layer. As shown in the HAADF-STEM image (Fig. 4a and c), highly dispersed NPs in NiFe@NC-3 exist in the form of bright spots. EDX elemental mappings (Fig. 4b) reveal surface spatial distributions of Ni, Fe, C and N elements, indicating the complete



Fig. 2 TEM and HRTEM images of NiFe@NC-2 (a), NiFe@NC-3 (b, d, e, f) and NiFe@NC-4 (c). The insets in (a-c) show the particle size distributions.



**Fig. 3** HRTEM images (a–d) of NiFe@NC-3. The arrows point to some tiny cracks on the NC layer surface.



Fig. 4 HAADF-STEM images (a, c) of representative NiFe@NC-3 with the EDX mapping of C-K (b1), N-K (b2), Ni-K (b3) and Fe-K (b4); EDX line scan profiles of Ni, Fe, C and N populations (d1-d4) along four red lines in (c) over four single particles on the NiFe@NC-3 sample to show the formation of NiFe alloy particles covered by the NC overlayer.

overlapping of Ni and Fe signals, as well as C and N signals. It implies that Fe atoms dissolve homogeneously into Ni atoms, forming an alloyed structure. Moreover, Ni and Fe line scan spectra clearly show the same homogeneous distributions along an individual particle (Fig. 4d). Interestingly, the distributions of C and N species in the EDX scan line spectra present a two-humped distribution at the edges of particles, reflecting the formation of NC species in strong interfacial contact with metal NPs. It further confirms that carbon and nitrogen elements probably tend to distribute around NiFe particles to form a thin NC layer. In general, thanks to the unique structure of the NiFe-LDH precursor, Ni and Fe elements orderly distributed in the brucite-like layers can be easily reduced to metal particles with the help of melamine. Meanwhile, the pyrolyzation of melamine following the graphitization of carbon leads to the formation of the NC overlayer covering the surface of NiFe NPs, which effectively suppresses the aggregation of NiFe NPs.

#### 3.2 Surface properties of NiFe@NC samples

To determine the surface chemical states of C, N, Ni and Fe species, the NiFe@NC-3 sample was characterized by XPS. XPS survey shows the presence of Ni, Fe, C and N elements (Fig. 5a). There are three contributions in the C 1s spectrum (Fig. 5b), which are assigned to three kinds of carbon atoms: hybridized sp<sup>2</sup> carbon (284.6 eV), carbon in the C=N or –C–OH group (286.0 eV), and carbon in the carboxyl or C–N group (288.1 eV).<sup>35,36</sup> Meanwhile, there are four contributions in the N 1s spectrum (Fig. 5c), which are associated with four different nitrogen species: nitrogen bonded to two sp<sup>2</sup> carbon atoms in the pyridine structure (398.5 eV), nitrogen bonded to carbon as a linkage in the H–N–(C)<sub>2</sub> (pyrrolic) structure (399.7 eV), nitrogen bonded to three carbon atoms within a graphene



Fig. 5  $\,$  XPS survey spectrum (a), C 1s (b) and N 1s (c) for the NiFe@NC-3 sample.

plane (400.8 eV), and oxidized nitrogen in the N–O group (402.7 eV).  $^{37\text{--}39}$ 

In the fine Ni 2p spectra of the NiFe@NC-x samples (Fig. 6A), six fitted bands at about 853.0, 855.0, 860.8, 870.3, 872.5 and 879.6 eV are associated with the Ni 2p3/2 and Ni  $2p_{1/2}$  core levels of both metallic  $\mathrm{Ni}^0$  and  $\mathrm{Ni}^{2+}$  species as well as the satellite peaks from Ni2+ species, respectively,40,41 mainly because surface Ni<sup>0</sup> species can be easily re-oxidized to Ni<sup>2+</sup> species after preparation and exposure to air. It is noted that the binding energy for Ni<sup>0</sup> species in NiFe@NC samples shows a positive shift of about 0.6 eV, compared with the previously reported value of about 852.4 eV in the literature,42 indicative of the electron transfer from NiFe NPs to the NC layer, thus leading to the SMSI. As shown in Fig. 6B, there are three components fitted in the Fe 2p region of the NiFe@NC-2 and NiFe@NC-3 samples: a small peak at 706.4 eV corresponds to metallic Fe<sup>0</sup>, a sharp peak at 710.3 eV to Fe<sup>2+</sup> species and another one at 712.3 eV to Fe<sup>3+</sup> species.<sup>43</sup> However, in the case of NiFe@NC-4, no metallic Fe<sup>o</sup> species is detected, probably

**Fig. 6** XPS of Ni 2p (A) and Fe 2p (B) for NiFe@NC-2 (a), NiFe@NC-3 (b) and NiFe@NC-4 (c) samples.

**Binding Energy (eV)** 

720

715

710

because surface Fe<sup>0</sup> species are easily re-oxidized by air under the present synthesis conditions.

To investigate surface basicity,  $CO_2$ -TPD of the experiments was conducted over the NiFe-3 and NiFe@NC-3 samples (Fig. 7). It is noted that there is no obvious  $CO_2$  desorption peak in the range of 200 to 750 °C for the NiFe-3 sample. In contrast, the NiFe@NC-3 sample presents three  $CO_2$  desorption peaks centred at about 376 °C, 473 °C and 627 °C, respectively, which are assigned to two kinds of medium-strength basic sites below 500 °C and strong basic sites above 500 °C.<sup>44–47</sup> The fundamentally heightened surface basicity of the NiFe@NC-3 sample should originate from the presence of electron-rich nitrogen atoms in the NC layer.<sup>48,49</sup>

As a result, thanks to the unique structure of NiFe-LDH precursors, as well as the surface NC overlayer, well-dispersed NiFe alloy NPs can be generated in the NiFe@NC samples, and strong metal (NiFe alloy)–support (NC layer) interactions are formed at the core–shell interface. Moreover, the shell of the NC layer can also greatly enhance surface basicity.

#### 3.3 Catalytic performance of catalysts

Commonly, *o*-CNB can be selectively hydrogenated to produce o-CAN *via* multi-step reaction pathways.<sup>50</sup> Herein, the hydrodechlorination of *o*-CNB as a side reaction can produce aniline (AN). In some cases, undesired *o*-chloronitrosobenzene (CNSB) and *N*-chloro-phenylhydroxylamine (CPHA) intermediates can be formed. To investigate the effect of interphase transport on the hydrogenation, the agitation speed was employed from 300 to 900 rpm. Noticeably, the BA conversion over NiFe@NC-3 was unchanged at the stirring rate from 700 to 900 rpm (Fig. S3†). It demonstrates that the stirring rate of 900 rpm is appropriate enough so that the hydrogenation rate is independent of external mass transfer. Meanwhile, due to the small size of the present actual catalyst powder ( < 10  $\mu$ m), internal (or intraparticle) mass transport limitation can be ignored.



Fig. 7 CO<sub>2</sub>-TPD profiles for NiFe-3 and NiFe@NC-3 samples.

A

Relative Intensity (a.u.)

Ni 2p

885 880

Fe 2p

c

h

a

730

725

Fe 2p 1/2

890

B

Relative Intensity (a.u.)

Ni<sup>2+</sup>2p<sub>1/2</sub>

Ni<sup>2+</sup>2p<sub>1/2</sub>sat.

 $Ni^{0} 2p_{1/2}$ 

875 870 865 860

**Binding Energy (eV)** 

Ni<sup>2+</sup>2p<sub>3/2</sub>sat

Ni<sup>2+</sup>2p<sub>3/2</sub>

Ni<sup>0</sup> 2p<sub>3/2</sub>

С

b

a

Fe<sup>2+</sup> 2p <sub>3/2</sub>

2p

705

845

855 850

Paper

#### **Dalton Transactions**

Therefore, the intrinsic catalytic activity of catalysts can be assessed under the present conditions.

Fig. 8 shows the change in the o-CNB conversion and the o-CAN selectivity over different catalysts with the reaction time at 80 °C, while Table 2 summarises the catalytic results. Clearly, different catalysts present obvious differences in catalytic performance. Despite different catalysts, the o-CAN selectivity almost remains unchanged during the reaction. Notably, a quite high o-CNB yield of 99.5% is achieved over NiFe@NC-3 after a reaction time of 210 min. However, lower o-CNB yields of 62.5 and 79.3% are obtained over NiFe@NC-2 and NiFe@NC-4, respectively, despite their high o-CAN selectivities (>99.0%). In contrast, the Ni@NC catalyst with the same Ni loading as that of NiFe@NC-3 achieves a much lower o-CAN yield of 24.9%. And, the NiFe-LDH-derived NiFe-3 catalyst, with two times Ni loading as that of NiFe@NC-3, only delivers a low o-CAN yield of 7.3%. Such poor catalytic performance of the NiFe-3 catalyst can be correlated with the presence of large-sized metallic NiFe alloy particles, as identified by the above XRD results. In both of the above cases, the o-CAN selectivity is slightly decreased to about 97.0%. Previously, it was reported that the o-CNB hydrogenation easily stopped at several intermediate stages, thereby forming different undesired by-products, and the hydrodehalogenation of halogenated nitroarenes often occurred.<sup>51</sup> Obviously, the hydrogenation of nitroarene over NiFe@NC catalysts do not stop at intermediate stages. Also, all catalysts almost exhibit no activity in the dehalogenation side reaction, which is the same as the previously reported results obtained using  $Fe_3O_4$ -Ni catalysts in the hydrogenation of halogenated nitroarenes by Gawande *et al.*<sup>52</sup>

As listed in Table 2, among the tested catalysts, NiFe@NC-3 exhibits the highest initial rate for *o*-CNB conversion (18.9 µmol  $g_{cat}^{-1} s^{-1}$ ) under milder reaction conditions (*i.e.*, 0.5 MPa hydrogen pressure and 80 °C), which is nearly three times that for the monometallic Ni@NC one, and even oneorder magnitude higher than that for the NiFe-LDH-derived NiFe-3 catalyst. Moreover, the TOF value over the NiFe@NC-3 catalyst (73.8 h<sup>-1</sup>) is larger than those over other catalysts. The lower TOF values for NiFe@NC-2 and NiFe@NC-4 are probably associated with relatively low proportions of the NiFe alloy component, which are not beneficial for the activation of the hydrogen molecule. As for the Ni@NC catalyst, the absence of the NiFe alloy phase should contribute to its poor catalytic performance. The above results illustrate the importance of Ni alloying with Fe for achieving high catalytic activity in the



Fig. 8 Changes in the conversion of o-CNB (A) and the selectivity to o-CAN (B) with the reaction time over catalysts in the o-CNB hydrogenation. Reaction conditions: Hydrogen partial pressure, 0.5 MPa; reaction temperature, 80 °C.

Table 2	Catalytic performances	of different	catalysts in the	o-CNB hydrogenation <sup>a</sup>
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Entry Cata		Initial rate <sup><math>b</math></sup> (µmol g <sub>cat</sub> <sup>-1</sup> s <sup>-1</sup> )	$\operatorname{TOF}^{c}(h^{-1})$		Conv. (%)	Selectivity (%)		
	Catalysts			Yield of <i>o</i> -CAN (%)		o-CAN	AN	Others <sup>d</sup>
1	NiFe@NC-2	9.4	48.2	62.5	62.9	99.4	0.1	0.5
2	NiFe@NC-3	18.9	73.8	99.5	100	99.5	0.1	0.4
3	NiFe@NC-4	13.6	61.0	79.3	80.0	99.1	0.1	0.9
4	Ni@NC	5.0	24.9	24.2	24.9	97.1	1.3	1.6
5	NiFe-3	1.7	16.7	7.1	7.3	97.5	0.5	2.0

<sup>*a*</sup> Reaction conditions: Hydrogen partial pressure, 0.5 MPa; reaction time, 210 min, reaction temperature, 80 °C. <sup>*b*</sup> Initial rate for *o*-CNB conversion. <sup>*c*</sup> TOF of *o*-CNB converted, which was given as the overall rate of *o*-CNB conversion normalized by the number of active sites determined by  $H_2$  pulse chemisorption within the initial 40 min. <sup>*d*</sup> By-products mainly consist of CNSB and CPHA.

#### Paper

*o*-CNB hydrogenation. Moreover, pure NC only delivers a very low *o*-CAN yield of 1.1% in the *o*-CNB hydrogenation after 2 h. It suggests that the presence of metallic NiFe alloy species is a crucial key governing the catalytic performance of NFe@NC catalysts, and a single NC as a catalyst cannot contribute to the catalytic activity. Interestingly, as illustrated in Table S1,† the catalytic performance of the present NiFe@NC-3 catalyst in the *o*-CNB hydrogenation is better than or comparable with those of other Ni-based catalysts reported previously in terms of the *o*-CNB (or *p*-CNB) conversion, the *o*-CAN (or *p*-CAN) selectivity and the rate of CNB conversion within a certain period, regardless of different experimental conditions.<sup>53-56</sup>

Furthermore, to gain more information on the o-CNB hydrogenation over the NiFe@NC-3 catalyst, the kinetic curves of the hydrogenation at different temperatures of 60 °C, 70 °C and 80 °C were obtained. Here, the hydrogen pressure remains unchanged during the reaction. Noticeably,  $-\ln(1 - x)$  (x: o-CNB conversion) increases linearly with the reaction time (Fig. S4<sup>†</sup>), demonstrating that the rate of *o*-CNB hydrogenation obeys a first-order reaction. Meanwhile, NiFe@NC-2 and NiFe@NC-4 also present a similar kinetic character (Fig. S5<sup>†</sup>). Furthermore, plotting  $\ln k$  (k: reaction rate constant) vs. reciprocal of temperature gives a lower apparent activation energy  $(E_a)$  of about 38 kJ mol<sup>-1</sup> for NiFe@NC-3 than those for NiFe@NC-2 (73 kJ mol<sup>-1</sup>) and NiFe@NC-4 (61 kJ mol<sup>-1</sup>) (Fig. S4<sup>†</sup>). Therefore, the lowered activation barrier of hydrogenation evidently confirms the more obvious promotion effect of the surface combination of NiFe NPs and the NC overlayer in the case of the NiFe@NC-3 catalyst. It implies that the present hydrogenation probably follows a Langmuir-Hinshelwood mechanism.57

To determine the nature of the interactions between the catalyst and hydrogen species, the catalysts were characterized by H<sub>2</sub>-TPD (Fig. 9). For all NiFe@NC catalysts, there is strong hydrogen desorption in the range of 400–530 °C and broad desorption in the range of 550–700 °C, respectively, which are associated with the release of chemisorbed H<sub>2</sub> on the surface



Fig. 9  $H_2$ -TPD profiles of NiFe@NC-2 (a), NiFe@NC-3 (b), NiFe@NC-4 (c), and Ni@NC (d) samples.

Dalton Trans.

of metallic atoms and hydrogen spillover on the support.<sup>58,59</sup> Compared with Fe-free Ni@NC, NiFe@NC samples yield larger desorption areas, indicating that the NiFe alloy should have stronger adsorption capacity of hydrogen because of the presence of the electronic effect between Ni-Fe atoms in NiFe alloy NPs. Among the NiFe@NC samples, NiFe@NC-3 exhibits the highest adsorption capacity of hydrogen, indicative of the enhanced ability for the dissociation of H<sub>2</sub>. Meanwhile, we can find that the adsorption capacity of hydrogen for NiFe-3 is extremely weak, almost zero, mainly due to the sintering of metallic particles. Moreover, it is generally accepted that the spillover hydrogen on supports as active species, such as H\* atoms, radicals, H<sup>+</sup> ions and H<sub>3</sub><sup>+</sup> ions,<sup>60–62</sup> can be involved in hydrogenation reactions.

In the present NiFe@NC-x catalyst system, due to the formation of the solid NiFe alloy core coated with a thin NC layer shell with a thickness of 3-8 nm, there is no developed internal micro- or mesoporous structure inside catalysts, and the hydrogenation actually proceeds on the outer surface of catalysts, where o-CNB mainly is adsorbed on the NC layer shell and hydrogen is dissociated into active hydrogen species by exposed metallic species at the cracks of the NC layer surface, followed by H-transfer from metallic NiFe NPs up to the surface of the NC layer through the hydrogen spillover. In a way, the high catalytic efficiency of NiFe@NC catalysts is probably associated with the presence of a certain degree of porosity inside the NC overlayer,<sup>63,64</sup> thus facilitating the penetration of hydrogen molecules into the thin NC layer and further activation of metallic sites to some extent. In this regard, an appropriate adsorption strength for reactants, neither too weak nor too strong, is beneficial for the enhancement of the catalytic activity. For the as-fabricated NiFe@NC catalysts, surface nitrogen atoms in the NC layer with strong basicity can interact with nitrogen atoms with a partially positive change in the nitro group of o-CNB, which can induce an oriented chemisorption of o-CNB on the surface, resulting in the activation of the N-O bond to a large extent,65 followed by the catalytic hydrogenation with the spillover hydrogen from dissociated hydrogen species on active NiFe sites. This kind of interaction between the nitro group and the NC layer not only makes the nitro group easily reducible by dissociative hydrogen from active metallic species through a spillover effect, but also effectively inhibits the hydrodechlorination of the o-CNB and o-CAN product. Correspondingly, we can speculate that selective o-CNB hydrogenation over NiFe@NC catalysts may proceed according to the following route: dissociated hydrogen species from exposed metallic species at the cracks of the NC surface NiFe alloy can spill over to the NC surface, where adsorbed o-CNB is selectively hydrogenated to produce o-CAN. Therefore, the present hydrogenation mainly is a surface reaction-controlled reaction, and the internal diffusion of substrates inside catalysts can be ignored.

Based on the structural characterization and catalytic test studies, it is concluded that for NiFe@NC catalysts, exposed metallic NiFe species at the defective NC layer may serve as **Dalton Transactions** 

activation centers for the hydrogen molecule coming from the gas phase up to the surface of metallic NiFe NPs. Meanwhile, the hydrogenation of *o*-CNB adsorbed on the surface of the NC layer can occur through H-transfer from NiFe NPs. As a result, the high catalytic efficiency of NiFe@NC-3 should be associated with both easier activation of hydrogen by NiFe alloy species and favorable adsorption of *o*-CNB on the NC layer, as well as the spillover hydrogen stemming from the novel coreshell nanostructure. This is our hypothesis for the origin of enhanced hydrogenation performance of the NiFe@NC-3 catalyst. However, further investigation of the exact reason for the difference in the catalytic performance of NiFe@NC catalysts needs to be systematically explored through theoretical or experimental methods in the future.

The reusability and recyclability of heterogeneous catalysts are the two most important characters for industrial applications. Apart from the noble metal-free character of catalysts, excellent sustainability of the present NiFe@NC-3 catalyst was further revealed in terms of easy recovery and recycling properties. As shown in Fig. S6,† the magnetization curve of NiFe@NC-3 shows a high magnetic saturation (Ms) value of about 41.4 emu  $g^{-1}$ . When an external magnetic field acts on the reaction solution with the catalyst after the reaction, NiFe@NC-3 can be quickly separated from the reaction solution and recovered magnetically, mirroring an excellent magnetic separation property of the catalyst. In the cycling tests, the NiFe@NC-3 catalyst was separated from the reaction solution under an external magnetic field. The recycling results are shown in Fig. 10. Notably, NiFe@NC-3 maintains its catalytic activity even after recycling seventeen times, along with a high o-CAN yield of 95.7% only decreased by about 4%. Elemental analysis by ICP-AES reveals that the leaching losses of Ni and Fe species are almost negligible after seventeen cycles. The TEM image of the spent catalyst revealed no observable change in the morphology and micro-



**Fig. 10** Recyclability of the NiFe@NC-3 catalyst in the *o*-CNB hydrogenation.



Fig. 11 O2-TPO profiles for NiFe-3 and NiFe@NC-3 samples.

structure of the core-shell nanostructure after recycling seventeen times (Fig. S7†).

Furthermore, the catalyst was characterized by O2-TPO experiments (Fig. 11). There is an oxygen consumption peak centred at 326 °C in the case of NiFe@NC-3, which is correlated with the adsorption of oxygen on the surface of the NC layer. Correspondingly, a CO<sub>2</sub> desorption peak appears at about 407 °C, which is associated with the oxidation of the carbon content in the NC layer. With increasing temperature, no oxygen consumption can be detected, because the surface NC shell can restrain the contact of O2 with the NiFe alloy core and thus prevent metallic species from oxidation. In the case of NiFe-3, however, the initial oxygen consumption begins at 200 °C. There are two large oxygen consumption peaks at higher temperatures of 422 °C and 550 °C, indicating much more oxygen consumption. The above results reflect that NiFe NPs in NiFe@NC-3 exhibit excellent antioxidation property, thanks to the structure of the NC overlayer, which significantly prevents the sintering of NiFe NPs. Thereupon, the as-fabricated NiFe@NC-3 catalyst possesses exceptional stability in the o-CAN hydrogenation, which is ascribed to the protection of the surface NC layer encapsulating inner NiFe alloy NPs and the strong core-shell interactions, thus inhibiting the leaching, oxidation and aggregation of active species in the course of the reaction and storage.

To investigate the feasibility of the NiFe@NC-3 catalyst, selective hydrogenation of other substituted nitroarenes with Cl, Br, I, OH, CH<sub>3</sub>, and COOR functional groups was also evaluated. As shown in Table 3, NiFe@NC-3 also presents excellent catalytic performance in the hydrogenation of other halogenated aromatic nitro compounds, aromatic esters and phenolic compounds, with high conversions (>90%) and selectivities (>90%) (entries 1–12). Notably, dehalogenation still is largely avoided in all cases, and the yields of the corresponding aromatic amines reach as high as 90% or more under relatively

#### Dalton Transactions

Entry	Substrates	Products	T (°C)	Time (h)	Conv. (%)	Select. (%)
1	NO <sub>2</sub>	NH <sub>2</sub>	80	3.5	100	96.0
2			80	3	100	100
3			80	3.5	100	91.7
4	NO <sub>2</sub>	NH2	80	3.5	99.8	97.2
5	NO <sub>2</sub>	NH <sub>2</sub>	80	3.5	90.1	98.9
6	Br-NO2	Br-NH2	90	3.5	99.1	92.1
7	NO <sub>2</sub>	NO <sub>2</sub> Br	90	3.5	95.3	97.9
8		NH <sub>2</sub>	80	1	97.8	91.2
_						
9		I NH2	80	3.5	97.3	98.5
10	NO2	NH <sub>2</sub>	80	3.5	95.3	92.6
	Br	Br				
11	NO <sub>2</sub>	NH <sub>2</sub>	80	2.5	98.3	100
12	NO <sub>2</sub>		80	2.5	98.9	93.8

Table 3 Catalytic performance of NiFe@NC-3 in the hydrogenation of other nitroarenes<sup>a</sup>

<sup>a</sup> Reaction conditions: Nitroarene (0.64 mmol), catalyst (4.0 mg), ethanol (10 ml), and 0.5 MPa hydrogen pressure.

mild reaction conditions (*i.e.* low reaction temperature and low hydrogen pressure).

## 4. Conclusions

In summary, we developed highly efficient, cost-effective and magnetically recyclable core-shell structured NiFe@NC catalysts *via* a facile *in situ* decomposition-reduction of the NiFeLDH/melamine mixture. The as-fabricated NiFe@NC-3 with a Ni/Fe atomic ratio of 3.0 showed an exceptional catalytic hydrogenation performance with a high *o*-CAN selectivity of 99.5% upon complete conversion of *o*-CNB, which was much higher than that of the catalyst derived from pure NiFe-LDH. It was revealed that the NiFe alloy core and the NC overlayer shell bearing strong basicity could benefit the adsorption and activation of reactants (*i.e.*, hydrogen molecule and substrate). The catalyst could be recovered magnetically and reused 17 times

at least. Moreover, the unique NC shell, as well as strong coreshell interactions, could contribute to excellent durability. Such a NiFe@NC-3 catalyst also was highly active for the hydrogenation of other aromatic nitro compounds (*e.g.* halogenated aromatic nitro compounds, aromatic esters and phenolic compounds) to produce commercially important aromatic amines. Importantly, this present developed synthetic strategy is general and extensible for designing and synthesizing other cost-effective and stable noble metal-free, high-performing and stable heterogeneous catalysts by changing the composition of LDH precursors, which can be practically applied in a broad range of eco-friendly and sustainable catalytic processes.

# Conflicts of interest

There are no conflicts to declare.

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