Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

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Materials and methods

The solvents mesitylene (99%) and toluene (99%) were purchased from VWR Prolabo while decane was purchased from Sigma Aldrich, dried on alumina desiccant and degassed by passing Ar through for 20 min. The reactants and substrates: palmitic acid, furfural, 5-hydroxymethylfurfural, cyclopentanone, diphenyl ether, benzyl phenyl ether, cyclohexyl phenyl ether, phenol, benzene, cyclohexanol and dodecane were purchased from Sigma-Aldrich and used without further purification. The bis(amido)iron(II) dimer $\{Fe[N(SiMe_3)_2]_2\}_2$ and the amidinate nickel(II) complex $Ni[^iPrNC(CH_3)N^iPr]_2$ were purchased from Nanomeps. All the synthesis and catalytic experiments were prepared under Ar using Schlenk techniques or glove box.

The TEM grids were prepared by depositing a drop of colloidal NPs solution in a copper grid covered with amorphous carbon. The TEM images were recorded in a JEOL 1400 microscope working at 120 kV. The metallic composition of the NPs was determined by Thermogravimetric analysis (TGA), performed in a TGA/DSC 1 STAR System equipped with an ultra-microbalance UMX5, a gas switch GC200 and DTA and DSC sensors. The magnetically induced catalytic experiments were performed using a magnetic coil of 5 cm height and 4 cm width working at 300 kHz with an amplitude adjustable from 0-64 mT. The catalytic mixtures were analyzed by gas chromatography (GC PerkinElmer 580) and a FID detector and using H_2 as carrier gas. The GC is coupled to a Clarus SQ8T mass spectrometer. Conversion and yields were obtained by comparison of the peak areas of reagent, products and internal standard.

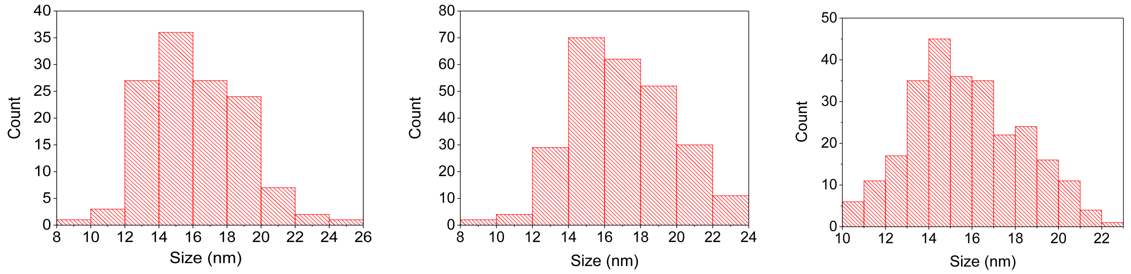
Catalyst synthesis

$FeNi_3$@Ni NPs were synthesized in two steps following the procedure previously reported by our group.[1] In the glove box in a Fisher–Porter bottle, 682 mg of $Ni[^iPrNC(CH_3)N^iPr]_2$ (2 mmol) were dissolved in 8 mL of mesitylene and added to a solution of $\{Fe[N(SiMe_3)_2]_2\}_2$ (301 mg, 1 mmol) in 4 mL of mesitylene. Then, 185 mg of palmitic acid (0.72 mmol) were dissolved in 8 mL of mesitylene and added to the mixture under vigorous agitation. The Fisher–Porter was pressurized at 3 bar of H_2 and stirred at 150 °C for 24 h. The NPs were separated from the solution by magnetic decantation, washed with 3x5 mL of toluene and dried under vacuum. Approximately 130-160 mg of black $FeNi_3$ NPs were obtained using this procedure, with a metallic content ca. 80 % and a composition of 28 wt% Fe and 67 wt% Ni.

To obtain the Ni-enriched NPs (FeNi$_3$@Ni), 80 mg of FeNi$_3$ NPs (ca. 1.31 mmol of metal) were dispersed in 10 mL of mesitylene together with 128 mg of palmitic acid (0.5 mmol, ca 0.4 eq) in a Fisher–Porter bottle. 171 mg of Ni[^{i}PrNC(CH$_3$)N^{i}Pr]$_2$ were dissolved in 5 mL of mesitylene and added to the mixture under vigorous agitation. The bottle was pressurized at 3 bar H$_2$ and the mixture stirred at 50 °C for 24 h. FeNi$_3$@Ni NPs were recovered by magnetic decantation and washed with 5 x 5 mL of toluene. The resulting black powder was dried under vacuum to yield about 95 mg of NPs with a metallic content of ca. 88 % and a composition of 19 wt% Fe and 68 wt% Ni.

Catalyst characterization

The structural and magnetic properties of FeNi$_3$@Ni NPs have been already investigated and are discussed in a previous publication.[1] The heating power of magnetic NPs can be quantified by the Specific Absorption Rate (SAR), which describes the amount of heat released as a function of time and mass of NPs. The SAR depends on the magnetic properties of the NPs which are governed by intrinsic parameters linked to the material (chemical composition, crystalline structure), to the NP features (size and shape), and to the environment (NP-NP interactions, temperature…). The two main parameters to be optimized are: i) the magnetization, which should be as high as possible and ii) the magnetic anisotropy, which dictates the magnetic field amplitude required to activate the heating and governs the tendency of NPs to form "chains".[2-6] For spherical particles, the anisotropy is essentially due to the magnetocrystalline anisotropy and thus can be tuned by the material properties. Moreover, the heating efficiency of NPs strongly depends on their capability to arrange in "chains" following the direction of the magnetic field. For this phenomenon to happen, the NPs must present a rather low anisotropy.[2, 4]



A

B

C

Figure S1. Size distributions of $FeNi_3$@Ni NPs before catalysis (A), after reaction with cyclopentanone (B) and after reaction with diphenylether (C). The average sizes are respectively 16.1 ± 2.7, 16.9 ± 2.7 and 15.7 ± 2.6 nm

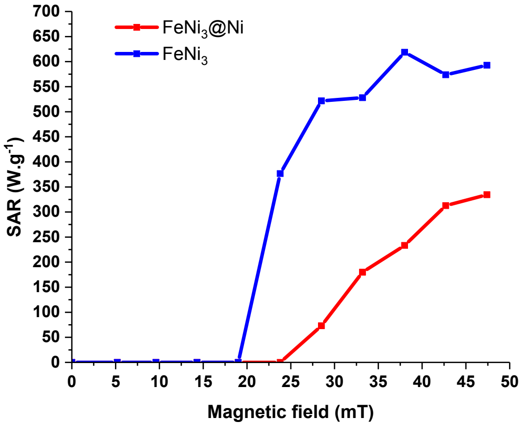
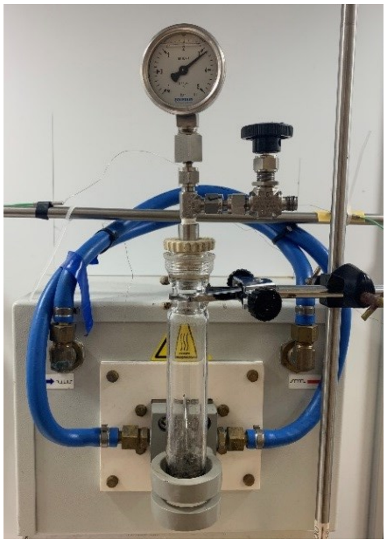


Figure S2. Specific Absorption Rate measured as a function of the applied field ($\mu_0 H_{rms}$)and for a fixed frequency of 93 kHz for $FeNi_3$ (in blue) and $FeNi_3$@Ni NPs (in red).[1]



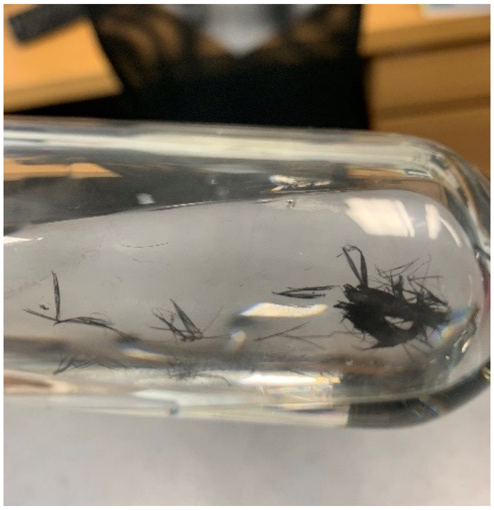


Figure S3. Fisher–Porter bottle placed in the center of the coil after catalysis experiment (left) and the NPs' chains formed during catalysis.

Catalytic procedure

In a typical experiment, 1 mmol of substrate, 1 mmol of dodecane (227 µL) used as internal standard, and ca. 10 mg of $FeNi_3@Ni$ (12 mol % based on Ni content) were mixed in 5 mL of mesitylene or decane in a Fisher–Porter bottle in the glove box. The reaction was pressurized with 3 bar of H_2, the Fisher–Porter bottle placed in the center of the magnetic coil and the amplitude settled to the desired value for the required time. At the end of the reaction, the pressure was released and an aliquot was taken and dissolved in dichloromethane, furfural or mesitylene for GC-MS analysis.

GC method

Furfural derivatives

The initial temperature, 50 °C, was increased to 80 °C at 5 °C min^{-1}, then increased to 200 °C at 15 °C min^{-1} and hold for 6 minutes. The injector temperature was settled at 250 °C and the carrier gas flowed at 7 psi.

Aryl ethers

The initial temperature, 35 °C, was hold for 5 min, then increased to 80 °C at 14 °C min^{-1} and hold for 3 min. Then, it was increased to 200 °C at 20 °C min^{-1} and hold for 6 minutes. The injector temperature was settled at 250 °C and the carrier gas flowed at 7 psi.

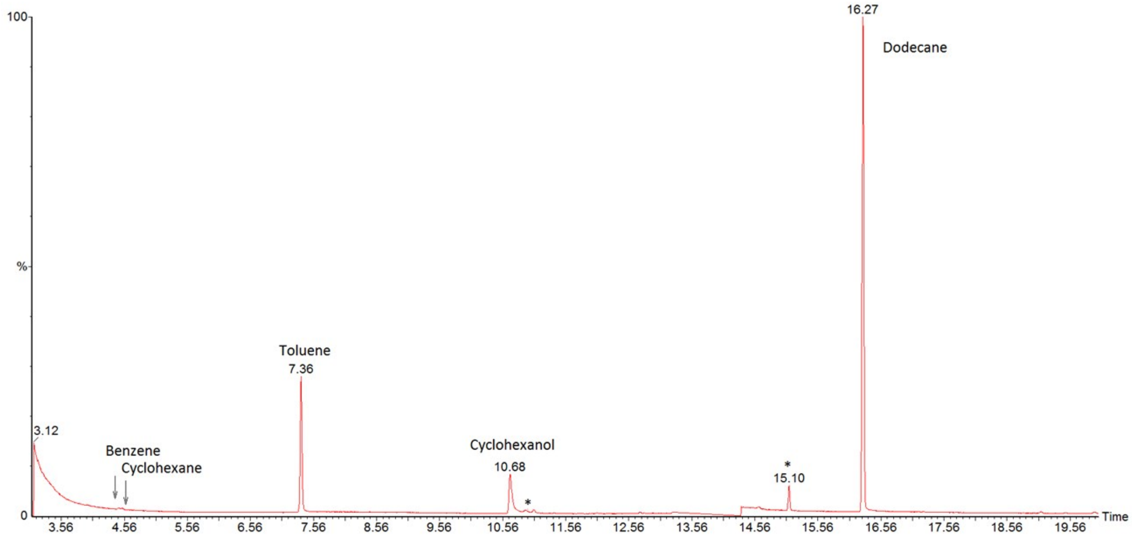


Figure S4. Example of chromatogram. In this case resulting from the catalysis of benzyl phenyl ether. Marked with a * the signals derived from solvent.

Yield and selectivity calculation

- Furfural derivatives and cyclopentanone

$$Conversion = \frac{A\ (substrate)}{A\ (dodecane) \times CF\ (substrate)}$$

Where A is the area of the peak and CF the conversion factor as the relation between the area of the substrate and that of the reference (dodecane) calculated at a ratio 1:1 as follows:

$$CF = \frac{A(substrate)}{A(dodecane)}$$

Since the products of catalysis of furfural and HMF, as well as those of cyclopentanone oligomerization, were not easily accessible, their conversion factor could not be calculated. Thus, it was supposed to be the same as that of the starting material. Therefore, the selectivity was calculated as follows:

$$Selectivity = \frac{A(product\ 1)}{A(product\ 1) + A(product\ 2)}$$

- Diphenyl ether and benzyl phenyl ether:

$$mol\ product = \frac{A(product)}{A(dodecane) \times CF}$$

In this case the conversion factor was obtained by a calibration curve obtained at different ratios product:dodecane, with the exception of cyclohexyl benzyl ether the conversion factor of which was supposed to be the same as that of cyclohexyl phenyl ether. The conversion, yields and selectivities were calculated as follows:

$$Conversion = \frac{mol\ substrate\ consumed}{initial\ mol\ substrate} \times 100$$

$$Yield = \frac{mol\ product\ i}{mol\ substrate\ introduced}$$

References

1. D. De Masi, J. M. Asensio, P. F. Fazzini, L. M. Lacroix and B. Chaudret, *Angewandte Chemie International Edition*, 2020, **59**, 6187-6191.
2. D. Serantes, K. Simeonidis, M. Angelakeris, O. Chubykalo-Fesenko, M. Marciello, M. d. P. Morales, D. Baldomir and C. Martinez-Boubeta, *The Journal of Physical Chemistry C*, 2014, **118**, 5927-5934.
3. J. M. Asensio, J. Marbaix, N. Mille, L.-M. Lacroix, K. Soulantica, P.-F. Fazzini, J. Carrey and B. Chaudret, *Nanoscale*, 2019, **11**, 5402-5411.
4. B. Mehdaoui, R. P. Tan, A. Meffre, J. Carrey, S. Lachaize, B. Chaudret and M. Respaud, *Physical Review B*, 2013, **87**, 174419.
5. E. Myrovali, N. Maniotis, A. Makridis, A. Terzopoulou, V. Ntomprougkidis, K. Simeonidis, D. Sakellari, O. Kalogirou, T. Samaras, R. Salikhov, M. Spasova, M. Farle, U. Wiedwald and M. Angelakeris, *Scientific Reports*, 2016, **6**.
6. C. Martinez-Boubeta, K. Simeonidis, D. Serantes, I. Conde-Leborán, I. Kazakis, G. Stefanou, L. Peña, R. Galceran, L. Balcells, C. Monty, D. Baldomir, M. Mitrakas and M. Angelakeris, *Advanced Functional Materials*, 2012, **22**, 3737-3744.