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## ARTICLE

## Induction heating applied to anisole HDO using Formic Acid as hydrogen source

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Magnetically induced heating catalysis using encapsulated magnetic nanoparticles as heating agents presents itself as a new efficient method for carrying out high-temperature reactions. In this work, magnetic Fe, Co, and FeCo nanoparticles encapsulated in carbon were synthesized using various methods. Rhenium oxide supported on high-surface-area graphite was used as a catalyst for the gas-phase HDO reaction of anisole, a model molecule for HDO studies of biomass-derived compounds. The characterization confirmed the formation of metallic nanoparticles, the alloying of FeCo and the successful coating with a graphitic like carbon film around the NPs, resulting in core-shell type materials. According to the catalytic results, the activity and the selectivity was similar when using formic acid (FA) or hydrogen (H<sub>2</sub>). Furthermore, by comparing the use of conventional and magnetic heating, it was concluded that carbon encapsulation is an effective strategy to generate a bed that heats but does not catalyze. The ReO<sub>x</sub> catalyst stood out for its capacity to break the OCH<sub>3</sub> bond, forming benzene as the major product. Among the different MNPs, FeCo@CHT presented the best properties and performance.

**Keywords:** magnetic nanoparticles, carbon encapsulation, HDO, biomass valorization.

## 1. Introduction

Nowadays, the treatment of biomass for its transformation into chemicals and fuels is emerging as a great alternative to the traditional fossil fuel model, which currently accounts for approximately three-quarters of the global energy supply.<sup>1</sup> More specifically, the treatment of lignocellulosic biomass presents itself as an environmentally friendly alternative.<sup>2,3</sup> Among its components (hemicellulose, cellulose, and lignin), lignin is interesting, as it is the only constituent composed of polymeric aromatic chains.<sup>4,5</sup> These chains can be broken down through processes such as pyrolysis.<sup>6</sup> However, the resulting products are rich in oxygen (over 40% wt.) and must be processed to obtain high-value compounds, such as bio-oil and fine chemicals.<sup>7</sup> Hydrodeoxygenation (HDO) is the process used to remove oxygen, and in the laboratory, model molecules such as anisole<sup>8,9</sup> or guaiacol<sup>10,11</sup> are used to study the process, with appropriate catalyst and conditions of high temperature and pressure.<sup>12</sup> The HDO process is highly hydrogen demanding and

around 94% of hydrogen is currently obtained from fossil sources.<sup>13</sup> Utilizing molecules derived from various biomass treatments as a hydrogen source represents a sustainable and innovative alternative for biorefineries. This has led to the use of molecules such as alcohols<sup>14</sup> or formic acid<sup>15</sup>, a by-product of cellulose hydrogenolysis<sup>16</sup> as hydrogen donors in different types of reactions in liquid<sup>17</sup> and gas phase.<sup>18</sup> Formic acid (FA) is the simplest carboxylic acid, with a specific energy of 5.3 MJ per kg, corresponding to a relatively high hydrogen content (4.4 wt%).<sup>15</sup> Additionally, FA exhibits low flammability, low toxicity, and is stable at room temperature.<sup>19</sup> The decomposition of FA can follow two competing pathways: dehydrogenation ( $\Delta G^\circ = -32.9 \text{ kJ mol}^{-1}$ ;  $\Delta H^\circ = 31.2 \text{ kJ mol}^{-1}$ ), producing H<sub>2</sub> and CO<sub>2</sub>, or dehydration ( $\Delta G^\circ = -12.4 \text{ kJ mol}^{-1}$ ;  $\Delta H^\circ = 29.2 \text{ kJ mol}^{-1}$ ), yielding H<sub>2</sub>O and CO. Both reactions can occur simultaneously, so if hydrogen production is the primary goal, dehydration must be minimized, also preventing carbon monoxide formation, which can poison the catalyst leading to lower efficiency of the process. As previously discussed, HDO reactions require elevated temperatures due to their endergonic nature and/or high activation energy barriers.<sup>20</sup> To address these issues, including the potential for energy savings, a novel approach in the field of heterogeneous catalysis has emerged: magnetic heating. This technique, originally applied in cancer therapy (magnetic hyperthermia),<sup>21,22</sup> is based on the principle that ferromagnetic materials generate heat through relaxation or hysteresis losses when exposed to a high-frequency alternating magnetic field.<sup>23,24</sup> The primary advantage of magnetic induction heating is its ability to deliver localized heating

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Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



directly to the catalytic bed, without heating the entire reactor,<sup>25–27</sup> resulting in faster system response times, improved energy efficiency, and greater control over reaction conditions.<sup>20</sup> Moreover, induction heating can induce localized heating on the nanoparticles surface, while keeping the medium relatively cold. This is beneficial for the operation of systems in outside conditions, which is useful in the systems that consist of endothermic and exothermic steps. In our case, the localized heating is useful for: (i) selectively pairing the endothermic path conventional. Moreover, magnetic heating also has advantages in exothermic reactions, since it can help start exothermic reactions by providing rapid, localized heat to overcome the activation energy barrier. Unlike conventional heating, it directly warms conductive materials or catalysts, allowing precise control and efficient initiation. Once the reaction becomes self-sustaining, the induction can be switched off, avoiding excess heat and improving safety and energy efficiency.<sup>28</sup> This new heating approach opens new challenges in the development of nanomaterials.

The heating efficiency of these materials is typically characterized by their specific absorption rate (SAR).<sup>29</sup> In heterogeneous catalysis, catalysts with a high SAR would offer several advantages: (i) near-instantaneous heating to rapidly initiate or stop reactions, (ii) eliminating the need to heat the entire reactor and focusing solely on the catalytic bed and (iii) energy transfer would occur via induction, a process more efficient than conduction, as heating would originate within the material itself rather than from the exterior of the reactor.<sup>30</sup> However, it should be taken into account that magnetic nanoparticles, in addition to generating heat, may also catalyze reactions to undesired products or suffer modifications on the magnetic properties after prolonged use in reactions. To avoid these drawbacks, one way to ensure that nanoparticles act solely as heating agents is by coating them with carbon<sup>31</sup> or silica.<sup>32</sup> Carbon coatings, in particular, enhance the sintering resistance of these materials due to their high thermal stability and strong confinement properties.<sup>31</sup> This novel heating method has been scarcely used for HDO reactions of biomass molecules, using iron carbide<sup>33</sup> or iron and cobalt based nanomaterials as heating material.<sup>34,35</sup> Recently, Mustieles Marin et al.,<sup>36</sup> carried out the HDO of acetophenone and furfural through magnetic induction heating in liquid phase. They employed nanoparticles with a core composed of a Ni-Fe alloy and a Ni-enriched surface as both the heating material and catalyst. Under reaction conditions of 3 bar H<sub>2</sub> pressure and a magnetic field of 49 mT, they achieved complete conversion for acetophenone and partial conversion for furfural (60–70%). For this study, hydrogenation of anisole with formic acid was carried out under magnetic induction heating in gas phase, using rhenium oxide supported on high-surface-area graphite as catalyst. Rhenium is a relatively rare transition metal, known for its excellent catalytic properties,<sup>37</sup> particularly in hydrogenation and hydrodeoxygenation reactions.<sup>38–42</sup> When supported on materials with high surface area and conductivity, such as graphitic carbon, rhenium oxide can exhibit enhanced catalytic performance.<sup>43</sup> Graphitic materials, provide several advantages as catalyst supports. Their high thermal and electrical conductivity, combined with a large specific surface

area, enables excellent dispersion of the active metal species, improving the overall catalytic activity.<sup>44</sup> In addition, graphite exhibits high stability under acidic conditions.<sup>45</sup> We investigated a system in which the catalyst is mixed with the heating agent, in order to combine the heating capacity of the coated metallic nanoparticles based on Fe and Co with the properties of supported rhenium as a catalyst. With this aim several synthetic procedures for magnetic nanoparticles have been investigated.

## 2. Experimental

### 2.1 Catalysts' preparation

The Re-based catalysts were synthesized on a commercial high-surface-area graphite (G, Timcal,  $S_{\text{BET}}$ : 400 m<sup>2</sup>/g) using the incipient wetness impregnation method. A 50:50 vol.% aqueous-ethanol solution of NH<sub>4</sub>ReO<sub>4</sub> was employed to achieve a 10 wt.% Re loading, followed by drying at 100 °C for 12 hours. The resulting material was activated as described in the catalytic reaction experimental section.

### 2.2 Magnetic nanoparticles preparation

**Hydrothermal Synthesis.** Graphite-encapsulated metal core-shell nanoparticles were synthesized through a hydrothermal process followed by heat treatment, a variation of that reported by Lee et al.<sup>46</sup> A solution consisting of metal source (Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O = 5 mmol and Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O = 5 mmol) and glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> = 8 mmol) was stirred in water until the solution became clear. The mixture was then transferred to a 100 mL stainless steel autoclave and heated at 190 °C for 9 hours (pressure of 15 bars). The products were washed several times with distilled water, filtered off, and finally dried in an oven at 100 °C for 12 h. Finally, the dried products were heat-treated at 800 °C for 3 h under an He atmosphere to grow a graphite shell on the surface of the metal nanoparticles. The three types of MNPs were labelled Fe@C<sub>HT</sub>, Co@C<sub>HT</sub> and FeCo@C<sub>HT</sub>.

**Coprecipitation Synthesis.** Maghemite nanoparticles were synthesized by a modified Massart coprecipitation method<sup>47</sup> using FeCl<sub>3</sub> and FeCl<sub>2</sub> (2:1) as precursors and NH<sub>4</sub>OH (25%) to form an alkaline solution. The resulting Fe<sub>3</sub>O<sub>4</sub> nanoparticles were converted to maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) through a thermal acid treatment. After the synthesis, the nanoparticles underwent surface modification with dextran (40 kD) as carbon source and heat-treated at 800 °C for 3 h with He. The resulting material was named Fe@C<sub>CP</sub>.

**Impregnation Synthesis.** Commercial nanoparticles (Sigma-Aldrich CAS-No: 1317-61-9) of Fe<sub>3</sub>O<sub>4</sub> were encapsulated using a simple impregnation method and posterior thermal treatment. Glucose was dissolved in water and impregnated in a Fe<sub>3</sub>O<sub>4</sub> surface (molar ratio of 1:1) and then dried at 100 °C for 12 hours. Finally, the resulting product was heat-treated with the same conditions as in the hydrothermal synthesis to carry out the graphite encapsulation. This material was denoted as Fe@C<sub>I</sub>.

### 2.3 Characterization

The X-ray diffraction (XRD) patterns were recorded using a Polycrystal X' Pert Pro PANalytical diffractometer with Ni-filtered Cu Kα radiation ( $\lambda$  = 1.54 Å). The measurements were conducted at 45 kV and 40 mA, covering a 2θ range of 4° to 85° with a step size of 0.04 °/s.



X-ray photoelectron spectroscopy (XPS) was performed using non-monochromatic Al K $\alpha$  radiation (200 W, 1486.61 eV) with a SPECS GmbH UHV system and a PHOIBOS 150 9MCD energy analyzer. Survey spectra were obtained with a 50 eV pass energy, and region spectra with a 20 eV pass energy. Binding energies were referenced to the C1s peak of graphitic carbon at 284.6 eV, with an equipment error of less than  $\pm 0.01$  eV.

Further structural characterization was conducted using High-Resolution Transmission Electron Microscopy (HRTEM). Both images and electron diffraction (ED) patterns were captured with a JEOL JEM 3000F microscope operating at an acceleration voltage of 300 kV. Samples were prepared by crushing the powders in ethanol and dispersing them onto copper grids coated with a holey carbon film. Additional chemical composition analysis was performed using energy-dispersive X-ray spectroscopy (EDX) within the same JEOL JEM 3000F microscope.

Thermogravimetric analysis (TGA) was carried out in a TA Instruments TGA 500, with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ , in an air atmosphere from room temperature to  $850\text{ }^{\circ}\text{C}$ .

Vibrating Sample Magnetometry (VSM) was performed using an MLVSM9 Mag Lab 2 T (Oxford Instruments). Samples were precipitated, dried, weighed, and placed in gelatin capsules. After saturating the samples to a 2 T magnetic field, magnetization (M) vs. applied magnetic field (H) curves were acquired at room temperature. Saturation magnetization ( $M_s$ ), expressed in emu per g of material, was determined from the experimental M(H) data in the high-field region, where magnetization exhibits a linear relationship with  $1/H$ . These values were extrapolated to an infinite field ( $1/H = 0$ ). The mass of magnetic material was calculated by correcting the sample weight based on thermogravimetric analysis (TGA) data.

Qualitative and quantitative analyses using TXRF were conducted using the S2 PicoFox TXRF spectrometer, a benchtop model from Bruker Nano based in Germany. This apparatus featured a Mo X-ray source functioning at 50 kV and 600  $\mu\text{A}$ , along with a multilayer monochromator that achieved 80 percent reflectivity at 17.5 keV (Mo K $\alpha$ ). It also incorporated a XFlash SDD detector, boasting an effective area of 30 mm<sup>2</sup> and an energy resolution superior to 150 eV for 5.9 keV (Mn K $\alpha$ ). The deconvolution and integration of data were managed with the Spectra v. 7.5.3 software package provided by Bruker. For the sample digestions, two different systems were utilized. The first method involved an open vessel digestion using the DigiPREP block digestion system from SCP Science in Canada, which operates at temperatures of up to  $180\text{ }^{\circ}\text{C}$  and includes a graphite heating block for processing 24 reactors containing 50 mL Falcon type tubes. The second method employed high-pressure and temperature microwave acid digestion technology utilizing the UltraWAVE digestion system from Milestone, Italy, which features a single reaction chamber capable of functioning at pressures reaching 199 bar and temperatures of up to  $270\text{ }^{\circ}\text{C}$ .

Temperature programmed desorption (TPD) was employed to study the adsorption of reactants in the spent catalysts. The experiments were performed in an ultrahigh vacuum (UHV) apparatus equipped with a UTI quadrupole mass spectrometer (Prisma Pro QMG 250). The TPD experiments were carried out in a fixed catalytic reactor system placing 0.1 g of catalyst and a thermocouple in the middle of the catalyst bed and applying a temperature ramp of  $5\text{ }^{\circ}\text{C/min}$  to  $400\text{ }^{\circ}\text{C}$  in He (99.999 %).

## 2.4 Catalytic reaction

The gas phase anisole hydrodeoxygenation was performed at atmospheric pressure in a fixed-bed glass reactor (int. d. 1.3 cm). The sample, 285 mg was charged in the reactor and was then treated at  $350\text{ }^{\circ}\text{C}$  ( $5\text{ }^{\circ}\text{C min}^{-1}$ ) in a He (99.999%, 50 ml min<sup>-1</sup>) or H<sub>2</sub> atmosphere (99.999%, 50 ml min<sup>-1</sup>) for one (under H<sub>2</sub>) or two hours (under He) to obtain the ReO<sub>x</sub>/G and/or Re/G catalyst respectively.

The reagent mixture (ANISOLE-FA mol ratio 1:6) was added using a syringe pump (IPS-14S Independent Double Channel Syringe Pump) with a total flow of 1.38 ml/min, diluted in 50 ml/min of helium flow (99.999%) and a gas hourly space velocity of  $2\text{ h}^{-1}$ . All flow lines were heated at  $100\text{ }^{\circ}\text{C}$ . The HDO reaction was carried out in two different ways. Initially, preliminary tests were carried out using either pure hydrogen or formic acid (2.3% He diluted) as a hydrogen source using either Re/G or ReO<sub>x</sub>/G as catalysts in a continuous reactor heated by conventional heating. The reaction was carried out at  $320\text{ }^{\circ}\text{C}$ . Also, a test using ReO<sub>x</sub>/G 285 mg and 2 g of commercial Fe<sub>3</sub>O<sub>4</sub> was performed using conventional heating. Alternatively, magnetic induction was used with the same conditions and a catalytic bed composed of a physical mixture of 285 mg of ReO<sub>x</sub>/G and 2 g of magnetic nanoparticles (MNP). The reactor was a high frequency coil working at 100 kHz (IDPartner) that allows to control the magnetic field amplitude between 0 and 42 mT. The catalyst (with or without MNP) was loaded in the reactor and the reaction temperature was monitored by a thermocouple placed in the middle of the catalytic bed. Control experiments confirmed that the thermocouple did not influence the induction heating. Also, prior to testing, a series of blank tests were performed with the MNPs: The commercial MNPs without the catalyst were placed in both a conventional reactor and a magnetic reactor. A blank test was also performed using only SiC in the conventional reactor.

The reaction products and reactants were analyzed *online* using a gas chromatograph (Agilent 8860) equipped with a flame ionization detector (FID) with a DB-Fatwax capillary column and a thermal conductivity detector (TCD) with a Carboxen 1010 column. To identify the reaction products a mass spectrometer (Agilent 5977B GC/MSD) connected to the chromatograph was used.

Anisole conversion and products selectivity are calculated as follows:

$$\text{Conversion}(\%) = \frac{\eta_{C_i \text{ products}}}{\eta_{C_i \text{ reagents}}} \cdot 100$$

$$\text{Selectivity}(\%) = \frac{\eta_{C_i \text{ products}_i}}{\sum \eta_{C_i \text{ products}}} \cdot 100$$





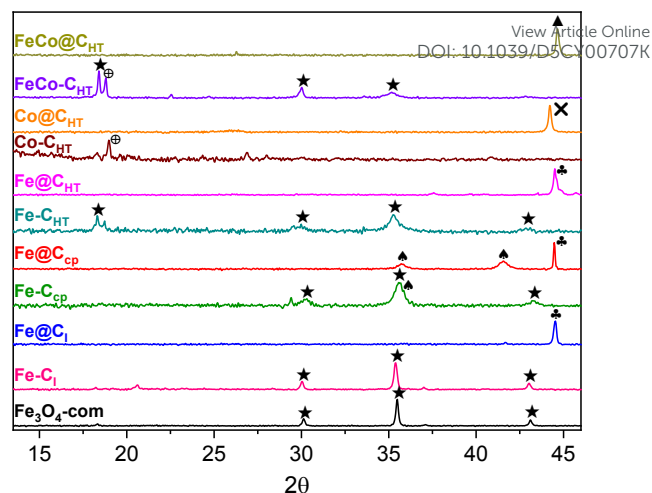
The carbon balance was better than 95%, estimated by comparing the calibrated GC peak areas of the blank anisole with the sum of unreacted anisole and detected products. For the HDO with FA, the estimation included the carbon introduced by FA and the carbon contained in CO and CO<sub>2</sub> formed during the reaction.

### 3. Results and discussion

#### 3.1 Characterization results

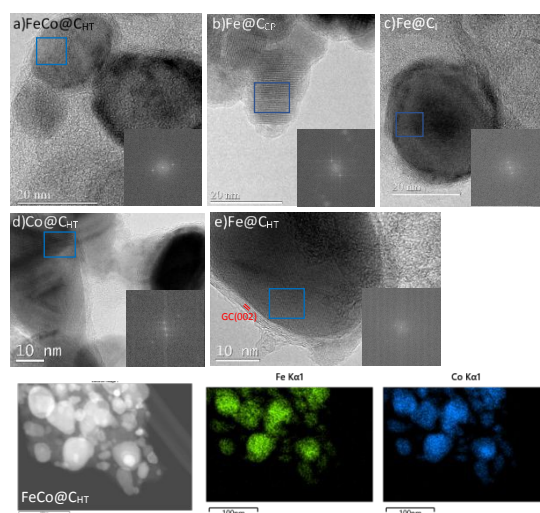
The X-ray diffraction patterns of the bare support and the catalysts, in Fig. S11 are dominated by the diffraction at  $2\theta$  of  $26.3^\circ$ , which is characteristic of highly structured graphitic carbon (002) (Graphite, JCPDS#01-075-1621). For the sample ReO<sub>x</sub>/G, it can also be observed a small peak at  $37.3^\circ$  which corresponds to ReO<sub>2</sub> (JCPDS#24-1009). This may indicate that ReO<sub>3</sub> is found as larger particles than Re(0). Regarding the XRD analysis of the magnetic nanoparticles, measurements were conducted before and after thermal treatment, with the results presented in Figure 1. The non-encapsulated commercial sample, Fe<sub>3</sub>O<sub>4</sub>, exhibited peaks at  $30.1^\circ$ ,  $35.5^\circ$ , and  $43.1^\circ$  characteristics of Fe<sub>3</sub>O<sub>4</sub>, (JCPDS#26-1136), corresponding to the (220), (311) and (400) planes of inverse cubic spinel magnetite. While, Fe-C<sub>i</sub> displayed a similar pattern compared to Fe<sub>3</sub>O<sub>4</sub>, the diffractions of Fe-C<sub>CP</sub>, Fe-C<sub>HT</sub> and FeCo-C<sub>HT</sub> are slightly wider. These peaks confirm the presence of Fe<sub>3</sub>O<sub>4</sub>, already formed during hydrothermal synthesis in the autoclave. For Co-C<sub>HT</sub>, the pattern exhibit a single peak at  $18.1^\circ$ , corresponding to the (001) plane of Co(OH)<sub>2</sub> (JCPDS#46-0605). This compound may be formed during the initial stages of the hydrothermal process, which possibly occurs due to the hydrolysis of the homogeneous aqueous solution of cobalt nitrate.<sup>48</sup> This peak is also present in FeCo-C<sub>HT</sub>. For the Fe-based heat-treated samples, Fe@C<sub>i</sub>, Fe@C<sub>CP</sub> and Fe@C<sub>HT</sub>, a single peak is observed at  $44.5^\circ$ , corresponding to the (110) plane of metallic Fe (JCPDS#06-0696).<sup>49</sup> Additionally, Fe@C<sub>CP</sub> exhibits two peaks at  $35.7^\circ$  and  $41.6^\circ$  ascribed to FeO (JCPDS#01-074-1886).<sup>50</sup> In the case of Co@C<sub>HT</sub>, the presence of metallic cobalt is confirmed by the peak at  $44.2^\circ$ , due to the (111) plane (JCPDS#05-0727).<sup>51</sup> For FeCo@C<sub>HT</sub>, a single peak at  $44.6^\circ$  is found, which for this sample can be ascribed to the (110) plane of an iron-cobalt alloy.<sup>52</sup> Moreover, the characteristic diffraction of graphite at  $26.3^\circ$  is not observed on the patterns. The absence of this peak was expected as the thermal treatment led to the formation of a thin layer of graphite, as will be verified by microscopy. The XRD patterns demonstrated that during the pyrolysis at  $800^\circ\text{C}$ , the metal oxides were reduced to metal nanoparticles.<sup>53</sup>

Figure 2a-e displays selected TEM images of all the magnetic materials, and 2f STEM-EDS images along with the elemental mapping of FeCo@C<sub>HT</sub>. The images reveal the formation of quasi-spherical nanoparticles. Furthermore, all the samples exhibit a well-defined carbon layer surrounding the particles, with the exception of Fe@C<sub>CP</sub>. This phase shows an interplanar spacing of  $0.34\text{ nm}$ , corresponding to the d-spacing of (002) plane of graphitic carbon, and its thickness is between  $3\text{--}8\text{ nm}$ . Fe@C<sub>i</sub> graphitic coating is formed by fewer carbon layers. In contrast, Fe@C<sub>CP</sub> displays a carbon coating environment, but it does not show the formation of a graphitic layer.



**Figure 1.** XRD patterns of the encapsulated MNP before and after heat treatment ( $800^\circ\text{C}$ , 3h, He) and commercial magnetite. ★Fe<sub>3</sub>O<sub>4</sub> ▲FeO ◆Fe(0) ⊕Co(OH)<sub>2</sub> ✕Co(0) ▲FeCo.

The elemental mapping of FeCo@C<sub>HT</sub>, also in Figure 2, which shows a homogeneous distribution of Fe and Co, confirms the formation of a FeCo alloy throughout the materials as the XRD indicated. The particle size of the MNPs was in the range  $20\text{--}40\text{ nm}$ . Selected area electron diffraction (SAED) patterns of the MNPs showed interplanar spacings were in good agreement with XRD. Reflections at  $d \approx 0.20\text{ nm}$  in Fe@C<sub>i</sub> and Fe@C<sub>HT</sub> matched the (110) plane of metallic Fe, while  $d \approx 0.22\text{ nm}$  in Co@C<sub>HT</sub> corresponded to the (100) plane of metallic Co. For FeCo@C<sub>HT</sub>, the spacing of  $d \approx 0.20\text{ nm}$  was assigned to the (110) plane of the FeCo alloy, consistent with the EDS analysis. In Fe@C<sub>CP</sub>, a spacing of  $d \approx 0.28$  was observed, characteristic of Fe<sub>3</sub>O<sub>4</sub>. These results confirm the strong correlation between SAED and XRD analyses.



**Figure 2.** Selected TEM images of a) FeCo@C<sub>HT</sub>; b) Fe@C<sub>CP</sub>; c) Fe@C<sub>i</sub>; d) Co@C<sub>HT</sub>; and e) Fe@C<sub>HT</sub> magnetic nanoparticles; HAADF-STEM images of f) FeCo@C<sub>HT</sub> and EDS mapping of Fe (green) and Co (blue) in FeCo@C<sub>HT</sub>.

The ReO<sub>x</sub>/G and the *in situ* reduced catalyst Re/G were studied by XPS. The Re 4f regions of the Re/G and ReO<sub>x</sub>/G catalysts are shown in Fig. 3, and could be decomposed into two components corresponding to the 7/2 and 5/2 orbitals which are split by  $2.4\text{ eV}$ .<sup>54</sup> The 4f region of ReO<sub>x</sub>/G in Fig. 3a can be deconvoluted in one



**Table 1.** XPS C1s, Fe and Co binding energies (eV) of the magnetic nanomaterials.

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DOI: 10.1039/D5CY00707K

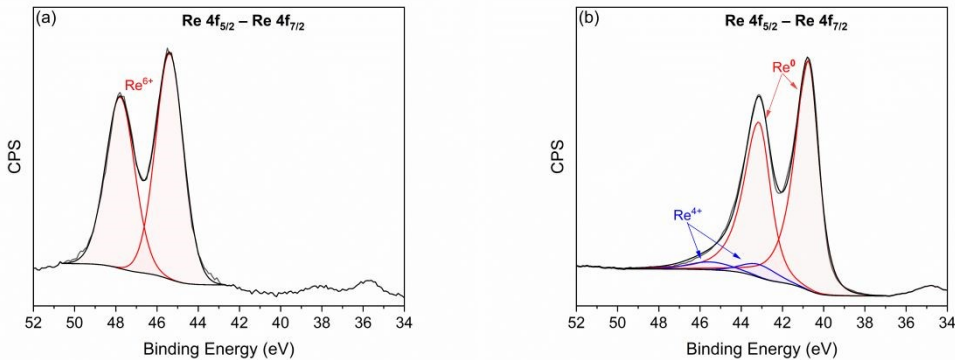
	BE, eV (at. %)												
Phases	C 1s					Fe 2p <sub>3/2</sub>			Co 2p <sub>3/2</sub>				
	C-C sp2	C-O	C=O	π-π*	CO <sub>3</sub> <sup>2-</sup>	Fe <sup>0</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Co <sup>0</sup>	Co <sup>2+</sup>	Co <sup>3+</sup>	Fe/C	Co/C
Fe@C <sub>HT</sub>	284.6 (68.0)	285.7 (17.9)	288.0 (6.7)	291.0 (7.4)	-	707.0 (37.2)	710.1 (29.6)	711.5 (33.1)	-	-	-	0.03	-
Co@C <sub>HT</sub>	284.6 (72.7)	286.2 (8.2)	288.3 (8.2)	290.5 (10.9)	-	-	-	-	778.2 (60.2)	780.7 (18.9)	782.3 (20.8)	-	0.07
FeCo@C <sub>H</sub>	284.6 (69.1)	286.2 (12.9)	288.3 (11.4)	290.8 (6.6)	-	707.0 (26.2)	710.2 (42.0)	711.3 (31.8)	778.5 (42.9)	780.8 (25.1)	782.3 (32.0)	0.08	0.06
T													
Fe@C <sub>CP</sub>	284.6 (51.8)	286.2 (6.7)	288.5 (16.9)	291.0 (2.5)	289.6 (22.2)	-	710.3 (47.9)	711.6 (52.1)	-	-	-	0.12	-
Fe@C <sub>I</sub>	284.6 (51.0)	285.9 (34.0)	288.5 (11.0)	290.5 (4.0)	-	707.0 (7.7)	710.5 (45.9)	711.8 (46.4)	-	-	-	0.08	-

component at 45.4 eV and 47.8 eV for the 7/2 orbital and the 5/2 orbital respectively, which correspond to Re<sup>6+</sup>. For the Re/G catalyst in Fig. 3b, the Re 4f<sub>7/2</sub> region displayed contributions at 40.6 eV and 43.5 eV which correspond to Re<sup>0</sup> and Re<sup>4+</sup>.<sup>55</sup> The relative contribution of Re<sup>0</sup>, 93.3%, confirms that Re is mainly found in the most reduced phase. Regarding the Re/C ratio, for the Re/G catalyst it is 4.0x10<sup>-2</sup> and for the ReO<sub>x</sub>/G it is 6.7x10<sup>-3</sup>, which indicates that rhenium is more dispersed on the support on the Re/G catalyst as also the DRX suggested.

The XPS spectroscopy was employed to analyze the chemical state of the carbon, iron and cobalt atoms. The C 1s XPS spectra of the materials is included in Fig S12, and could be well-fitted into four components. The peak at 284.6 eV is attributed to the C-C bonds of graphitic carbon, which illustrates the delocalized sp<sup>2</sup>-hybridized carbon. The peaks at 285.7-286.2, 288.0-288.5 and 290.5-291.0 eV are attributed to the C-O and C=O bonds and to the π-π\* satellite respectively.<sup>56</sup> The samples prepared by hydrothermal method show similar binding energies and similar relative atomic percentages of C-C sp<sup>2</sup> which are included in Table 1. The sample Fe@C<sub>CP</sub> presents a significant contribution at 289.6 eV corresponding to the presence of carbonates on the surface. The reason for the appearance of this phase is not clear, but it could be due to the higher amount of iron oxides, as the XPS in Table 1 also shows, which could serve as adsorption sites for CO<sub>2</sub>.<sup>57,58</sup> Also, the sample Fe@C<sub>I</sub> displays a higher contribution of C-O species compared to the other materials.

The Fe 2p 3/2 and Co 2p 3/2 regions, are shown in Figure 4, and Table 2 summarizes the binding energies (BE) and relative proportion for all the catalysts. As shown in Fig. 4, the Fe 2p<sub>3/2</sub> region for Fe@C<sub>HT</sub>, FeCo@C<sub>HT</sub>, Fe@C<sub>I</sub> and Fe@C<sub>CP</sub> could be deconvoluted into two components with binding energies at 711.8-711.3 eV and 710.5-710.1 eV which correspond to Fe(III) and Fe(II) respectively in the Fe-O bond. In addition, Fe@C<sub>HT</sub>, FeCo@C<sub>HT</sub> and Fe@C<sub>I</sub> also display a component at 707 eV due to metallic Fe.<sup>59</sup> As included in Table 1, the relative contribution of Fe(0) is 37.2%, 23.4% and 7.7% in Fe@C<sub>HT</sub>, FeCo@C<sub>HT</sub> and Fe@C<sub>I</sub>, respectively. As long as the Co 2p<sub>3/2</sub> region is concerned, shown in Fig. 4, for Co@C<sub>HT</sub> and FeCo@C<sub>HT</sub>, it can be deconvoluted into three components with binding energies at 782.3, 780.7-780.8 and 778.2-778.5 eV which can be attributed to Co(II), Co(III), and metallic Co respectively.<sup>60</sup> The relative contribution of Co(0) is 60.2% and 42.9% in Co@C<sub>HT</sub> and FeCo@C<sub>HT</sub>. The BE values obtained in the Fe 2p and Co 2p regions for the FeCo alloy agree with the values reported in the literature.<sup>61-63</sup>

The discrepancies between XRD and XPS can be explained by considering that XPS is a surface-sensitive technique and that the graphite layer over the MNP is 3-8 nm depth. Hence, the results obtained for the Fe 2p and Co 2p regions arise mainly from oxidized species that have remained unencapsulated and from the most outer Fe and Co layers of the nanoparticles which can be partially oxidized. For the sample Fe@C<sub>I</sub>, the low percentage of Fe(0) may be due to the lesser extent of encapsulation. Similarly, although the XRD of Fe@C<sub>CP</sub> shows a metallic iron phase, the lack of proper encapsulation results in XPS detecting only the oxide components.



**Figure 3.** *In situ* XPS of a) the Re 4f region for the ReO<sub>x</sub>/G catalyst and b) the Re 4f region for the Re/G catalyst.

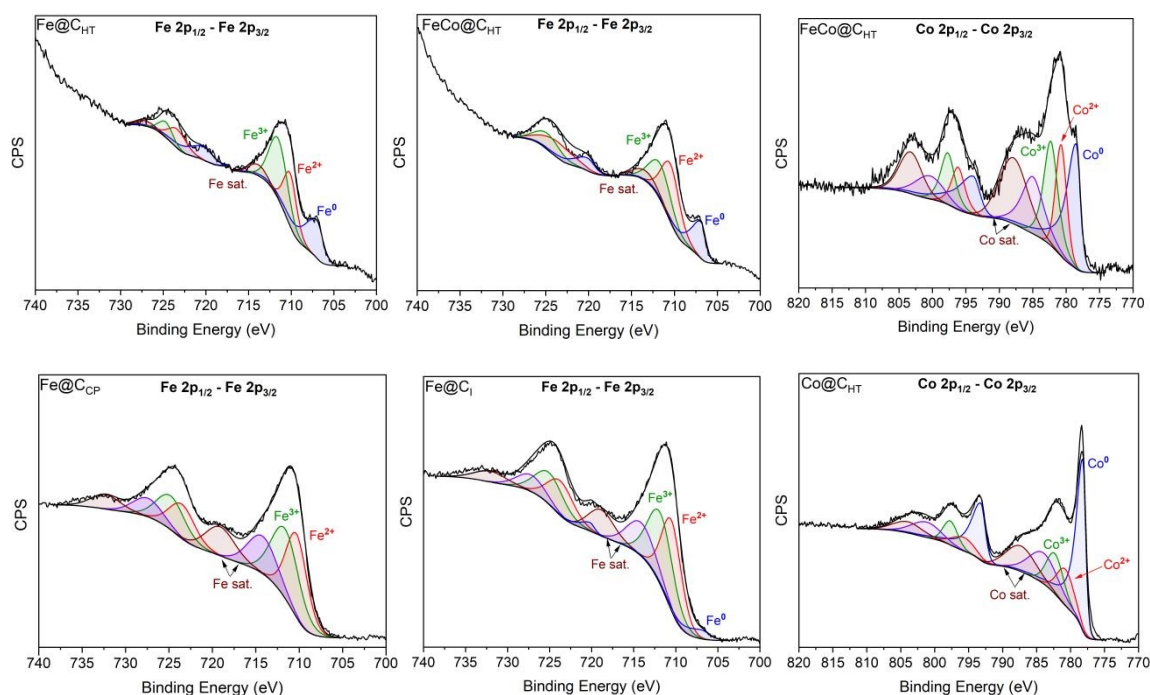
TGA measurements were conducted on Fe@C<sub>HT</sub>, Co@C<sub>HT</sub>, FeCo@C<sub>HT</sub>, Fe@C<sub>i</sub> and Fe@C<sub>CP</sub> (Figure S3). The samples exhibit both weight gain and weight loss, which can be attributed to different processes taking place under the oxidative atmosphere.

Firstly, Fe@C<sub>HT</sub> and Co@C<sub>HT</sub> showed a weight gain of 5-10% with a maximum around 400 °C which can be assigned to the oxidation of non-encapsulated Fe and Co metallic phases into oxides. This was followed by a weight loss, much more pronounced for Co@C<sub>HT</sub>, consistent with the combustion of the more reactive, poorly graphitized carbon shell, likely accelerated by the catalytic effect of Co. FeCo@C<sub>HT</sub> shows a pronounced and sustained weight gain starting above 500 °C, suggesting extensive oxidation of the Fe-Co alloy core, with carbon combustion playing only a minor role. Fe@C<sub>i</sub> only showed a weight gain and it started at temperatures above 500 °C. This may suggest either a more stable carbon layer or a higher encapsulation degree of the metallic phases. In contrast, Fe@C<sub>CP</sub> only exhibited weight loss: after an initial decrease below 200 °C, two steps centered at ~250 and ~300 °C are observed, attributed to oxidation of graphitic and amorphous carbon,<sup>46</sup> in agreement with microscopy observations. The absence of weight gain for this sample is consistent with XPS results showing no detectable metallic Fe; once

The magnetic properties of Fe@C<sub>HT</sub>, FeCo@C<sub>HT</sub>, Co@C<sub>HT</sub>, Fe@C<sub>i</sub> and Fe@C<sub>CP</sub> as well as commercial magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles, have been measured using vibrating sample magnetometry (VSM). The saturation magnetization (*M<sub>s</sub>*) and coercivity (*H<sub>c</sub>*) were determined from the hysteresis loops, shown in Figure 5, at 300 K and the values are compiled in Table 2. All materials have saturation magnetization values that correspond to those typical of ferromagnetic materials.<sup>25,30</sup> Ferromagnetic particles exhibit distinctive magnetization (*M/H*) profiles that allow for the conversion of radiofrequency into heat through hysteresis losses. Among the materials, those MNP prepared by the HT method presented the most interesting magnetic properties for their use in heterogeneous catalysis. Specifically, FeCo@C<sub>HT</sub> showed the highest saturation magnetization and the lowest coercivity among the studied samples, with a saturation value close to those previously reported in the literature (233-237 emu/g).<sup>52</sup> In contrast, Co@C<sub>HT</sub> exhibited the lowest saturation and highest coercivity.

Notably, although the graphite-encapsulated iron-based materials form metallic iron, they exhibit variations in both saturation magnetization and coercivity. As mentioned in the experimental Section, the hydrothermal synthesis was a modification of Lee et al.<sup>46</sup>

Figure 4. XPS of the Fe 2p and Co 2p region for the Fe@C<sub>HT</sub>, FeCo@C<sub>HT</sub>, Fe@C<sub>CP</sub>, Fe@C<sub>i</sub> and Co@C<sub>HT</sub> MNPs.



Fe is already oxidized, no further oxidation can be registered by TGA. Overall, the results indicate that carbon reactivity follows the trend C<sub>HT</sub>>C<sub>CP</sub>>C<sub>i</sub>, while the extent of core oxidation is most pronounced for FeCo@C<sub>HT</sub> and Fe@C<sub>i</sub>. The different temperatures and magnitudes of these processes reflect the varying encapsulation efficiency and the intrinsic stability of the carbon supports employed. To summarize, the weight changes can be ascribed to the transformation of the unencapsulated iron/cobalt phases under the oxidative atmosphere and/or to the decomposition of the carbon layer.<sup>46</sup>

method. They achieved graphite encapsulation of Fe and Co MNPs with a *M<sub>s</sub>* values of 86.6 and 43.8 emu/g, respectively. In our research, the MNPs Fe@C<sub>HT</sub> and Co@C<sub>HT</sub> exhibited *M<sub>s</sub>* values of 164 and 94 emu/g which is greater than those found in the original study. These results demonstrate that the revised synthesis technique produces MNPs with improved magnetic characteristics, making them suitable for applications in catalytic magnetic induction. Among the tested samples, Fe@C<sub>CP</sub> is the material with the lowest *M<sub>s</sub>* which can be associated to the higher percentage of carbon on this sample, related to the TGA mass loss (9.7%).



### 3.2 Catalytic performance

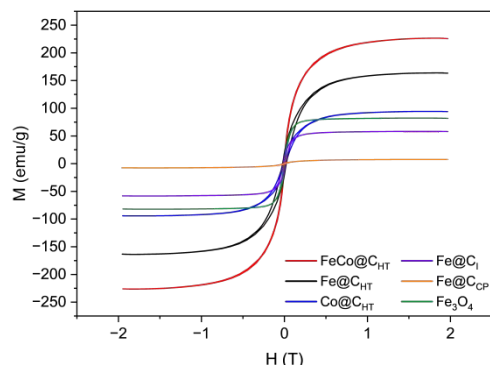
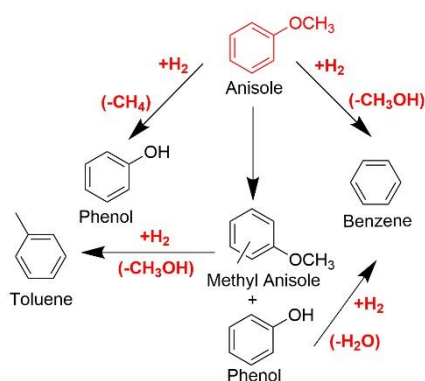


Figure 5. Hysteresis loop measured by VSM on the MNP and  $\text{Fe}_3\text{O}_4$  at 300 K.

Table 2. Coercivity ( $H_c$ ) and saturation magnetization ( $M_s$ ) of MNPs.

	$H_c$ (Oe)	$M_s$ (emu/g)
$\text{Fe}@C_{HT}$	228	164
$\text{Co}@C_{HT}$	183	94
$\text{FeCo}@C_{HT}$	44	226
$\text{Fe}@C_{CP}$	119	7
$\text{Fe}@C_1$	160	58
$\text{Fe}_3\text{O}_4$	97	82

The hydrogenation of anisole can follow multiple pathways, as shown in Scheme 1. During the hydrogenation of the  $-\text{OCH}_3$  group, the  $\text{O}-\text{CH}_3$  bond may break, leading to the formation of phenol and methane, i.e. hydrogenolysis, or alternatively, cleavage may occur at the oxygen-aromatic bond, resulting in methanol and benzene, i.e. demethoxylation (DMO). Without the intervention of hydrogen, intermolecular alkylation can occur forming phenol and methyl anisole, which can react with  $\text{H}_2$  to form toluene.<sup>64,65</sup>



Scheme 1. Possible reaction pathways for anisole conversion for HDO reactions. Reactions are postulated on the basis of the products identified.

Figure S4 shows the preliminary results using a conventional heating set-up and  $\text{Re}/\text{G}$  or  $\text{ReO}_x/\text{G}$  as catalysts, for this latter evaluating both  $\text{H}_2$  and FA as hydrogen source. In all the reaction tests, an initial

In this work, rhenium-based catalysts were used for the hydrodeoxygenation reaction of anisole with formic acid in the vapor phase at ambient pressure and 320 °C, employing conventional heating and magnetic induction heating.

pronounced deactivation of the catalyst occurs until 150 min, where the conversion and selectivity to benzene decreased. This stage was followed by a more stable conversion and selectivity profile, although conversion seems to smoothly decay. From this time, both catalysts show a similar conversion, 5-6%, and the selectivity was directed towards benzene, ca. 65-70% and phenol ca. 28-32%, while toluene and methyl anisole (data not shown) were only produced with a selectivity below 5%. Also, the results of conversion and selectivity obtained using  $\text{ReO}_x/\text{G}$  and  $\text{H}_2$  or FA as hydrogen source are similar. An additional test was conducted to study the conversion and selectivity obtained with the physical mixture of  $\text{ReO}_x/\text{G}$  and commercial  $\text{Fe}_3\text{O}_4$  using conventional heating. A notable increase in conversion up to 14% was observed, as well as a change in selectivity, yielding 35% benzene and 65% phenol. This indicates that the presence of iron oxides is negative for the efficiency of the hydrodeoxygenation reaction, likely due to the lower activity of iron oxides in breaking C-O bonds.<sup>66</sup> In this reaction, iron acts as a promoter when combined with supported rhenium oxides which explains the higher conversion.<sup>67</sup> Anisole HDO has been previously evaluated using Re-based catalysts. However, data about their use in the gas-phase HDO is scarce. Rezaei et al.<sup>67</sup> evaluated  $\text{FeReO}_x/\text{ZrO}_2$  catalysts in the HDO of anisole in gas phase at 350 °C and WHSV of 19.9  $\text{h}^{-1}$ , and observed a selectivity to benzene of 43.3% and only 4.4 % selectivity to toluene. The initial deactivation observed may be due to strongly adsorbed anisole and formic acid molecules occupying the available active sites as evidenced by the post-reaction TPD experiment (Fig. S5), where signals corresponding to the characteristic masses of the mentioned molecules were detected, indicating surface blockage.

Besides Re, Mo catalysts have been evaluated in gas phase also taking advantage of the variety of its oxidation states. Shetty et al.<sup>65</sup> reported that toluene was a minor product in the HDO of anisole over  $\text{MoO}_3/\text{ZrO}_2$ , obtained via a secondary reaction pathway from m-cresol intermediates. In the reaction at 320 °C they obtained benzene as the main product at 27% and phenol at 23%. The HDO of anisole has been studied using molybdenum carbides at low temperatures (150-250 °C), using kinetic conversions below 15%, achieving a benzene selectivity of 80-90%.<sup>12,68</sup> More literature is found related to the use of Re-based catalysts for HDO of anisole in liquid phase. For example, Ghampson et al.<sup>69</sup> investigated  $\text{ReO}_x/\text{CNF}$  catalysts in liquid-phase HDO at 300 °C, showing that Re species of the type  $\text{Re}^{6+}$  promote direct C-O bond cleavage. Similarly, Wang et al.<sup>70</sup> examined  $\text{Cu}-\text{ReO}_x/\text{SiO}_2$  catalysts at 320 °C in liquid phase, finding that the Cu-Re interaction enhanced anisole adsorption while facilitating benzene desorption, resulting in 50% BTX yield at optimal Cu/Re ratios. Despite the key role of the solvent in the liquid phase reactions, the reported literature has shown that rhenium provides several oxidation states, i.e.,  $\text{Re}^{7+}$ ,  $\text{Re}^{6+}$ ,  $\text{Re}^{4+}$ , that can facilitate  $\text{H}_2$





activation and subsequent C–O bond cleavage, even at relatively low temperatures.<sup>71</sup>

For these catalytic systems, the selectivity towards benzene can be attributed to the strong oxophilicity of Re species, which may favor the hydrogenolysis of both anisole and phenol.<sup>71,72</sup> Interestingly, the use of formic acid as a hydrogen source does not significantly modify the conversion or the selectivity. This result is in contrast with other studies, where formic acid outperforms molecular H<sub>2</sub> in other HDO reactions such as benzylic ketones using Pd/HPC–NH<sub>2</sub> as catalyst.<sup>73</sup> This improvement was also observed in the hydrogenation and HDO of lignin-derived monomers, including guaiacol and syringol, yielding various aromatics with a lower oxygen weight content compared to the use of external H<sub>2</sub>. Nevertheless, those reactions were performed in liquid phase and the reaction mechanism and hydrogen availability would differ from our system. In our previous research on the gas phase hydrogenation of crotonaldehyde using Cu and Re on a graphite support,<sup>74</sup> we found that the type of hydrogen source (formic acid or molecular hydrogen) significantly impacts both activity and selectivity. Specifically, catalysts based on Re, which showed no activity with H<sub>2</sub>, became active when formic acid was utilized. This indicates that the enhancing effect of formic acid is not the same for all systems, but depends on various factors, including the reaction phase and the interactions between the substrate and the surface.

ReO<sub>x</sub>/G was selected as the catalyst to further evaluate the use of magnetic heating employing FA as the hydrogen source. Hence, the same reaction was carried out at 320 °C using magnetic induction and varying the MNP. When the reactor was placed inside the coil a magnetic field was applied to reach the target temperature of 320 °C.

The results, in Figure 6, show a similar trend in the conversion to that of conventional heating. At the beginning of the reaction, the conversion was in the range 11–17%, and falls to around 7% when using the encapsulated materials. However, when commercial nanoparticles Fe<sub>3</sub>O<sub>4</sub> were used, the conversion of anisole was close to 14% as seen in conventional heating reaction.

Differences are also observed in the selectivity values. While encapsulated nanoparticles reached 65 % selectivity to benzene, the unencapsulated Fe<sub>3</sub>O<sub>4</sub> showed selectivity to benzene of 30 %. This again reflecting that MNPs, if not encapsulated, can influence conversion and selectivity.

Table 3 summarizes the magnetic fields required to heat different MNPs to the reaction temperature at 100 kHz. Each material exhibits a unique value within the range of 16 to 34 mT. When FeCo@C<sub>HT</sub> were used, the required field was the lowest, 16 mT. The MNPs based solely on encapsulated iron show comparable values (20, 21 y 23 mT). The Co@C<sub>HT</sub> nanoparticles required a field of 34 mT, making them the material with the highest field demand. Commercial nanoparticles, required a slightly higher field (26 mT), exhibit a notable change in selectivity due to the lack of encapsulation. These slight variations can be attributed to differences observed in XRD analyses, where Fe@C<sub>CP</sub>, after heat-treatment, retained traces of iron oxide (FeO).

The decomposition of formic acid was evaluated using ReO<sub>x</sub>/G as catalyst and Fe<sub>3</sub>O<sub>4</sub> since iron has been reported to be active on the dehydration of FA resulting in CO + H<sub>2</sub>O.<sup>75</sup> The results for conversion

and CO<sub>2</sub> selectivity are presented in Figure S6 and indicate thermal decomposition as the main path under these conditions. Formic acid conversion at 320 °C reached a value of 100% in all three reactions including a previous blank test. The selectivity towards CO<sub>2</sub> was 80–84% with conventional heating and 76% with magnetic heating. Therefore, the CO values obtained in the catalytic system were in the range of 0.8–1.4 × 10<sup>−5</sup> mol min<sup>−1</sup>, corresponding to approximately 16–24% of the formic acid decomposition pathway. With these results, H<sub>2</sub> can be supplied in excess for the hydrodeoxygenation reaction of anisole, with H<sub>2</sub>/ANISOLE ratios of 5.0–4.6 (Table S1). The lower selectivity to CO<sub>2</sub> obtained with magnetic heating could be attributed to the presence of Fe<sub>3</sub>O<sub>4</sub>.

In the HDO of anisole performed under magnetic heating with Fe<sub>3</sub>O<sub>4</sub> as heating agent, a full conversion was achieved without losing CO<sub>2</sub> selectivity of 80%, complemented by a CO formation rate of 1.06 × 10<sup>−5</sup> mol min<sup>−1</sup> and a H<sub>2</sub>/anisole ratio of 4.8. The same trend was observed for FeCo@C<sub>HT</sub> where complete conversion was measured, with a CO<sub>2</sub> selectivity of 90%. The latter gave the lowest CO produced (5.29 × 10<sup>−6</sup> mol min<sup>−1</sup>) and highest H<sub>2</sub>/anisole ratio (5.4), marking the positively significant impact of FeCo encapsulation to reduce dehydration of formic acid, and promote generation of H<sub>2</sub> for the HDO reaction.

**Table 3.** Catalytic performance of magnetically induced of anisole HDO using various MNP at 320 °C with ReO<sub>x</sub>/G.

Heating Agent (HA)	Field (mT)	Conv. (%)	S Benzene (%)	S Phenol (%)	S Toluene (%)
Fe@C <sub>HT</sub>	20	7.6	69.3	30.4	<1
Co@C <sub>HT</sub>	34	7.4	67.5	27.9	4.6
FeCo@C <sub>HT</sub>	16	7.0	67.1	30.1	2.8
Fe@C <sub>CP</sub>	23	8.1	67.4	31.8	<1
Fe@C <sub>I</sub>	21	8.1	67.0	27.4	5.5
Fe <sub>3</sub> O <sub>4</sub>	26	16.4	34.7	63.1	<1

Methylanisole selectivity <1

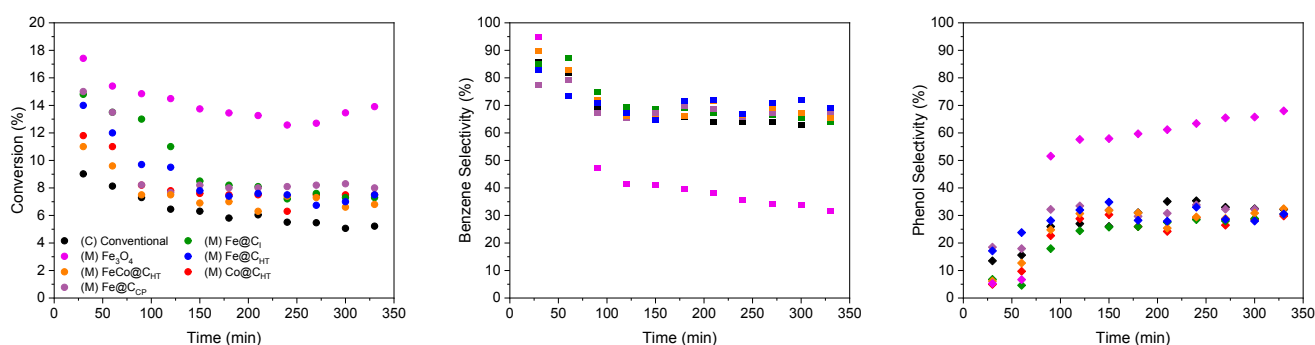


We have performed TXRF and XPS analyses of the spent catalyst  $\text{ReO}_x/\text{G}$  after the HDO reaction included in Table S2. The TXRF measured values are consistent with the nominal Re loading, and the Re/C values of spent catalyst after reaction under  $\text{H}_2$  or FA are similar to that of the fresh catalyst confirming that no leaching occurred.

To check the stability of the MNP, the XRD analysis (Figure S7) of the used MNPs in the catalytic experiments was performed. All the MNP showed diffractions at  $44.5^\circ$ , ascribed to  $\text{Fe}(0)$  and/or at  $44.2^\circ$  attributed  $\text{Co}(0)$ . Moreover, the materials  $\text{FeCo@C}_{\text{HT}}$ ,  $\text{Fe@C}_{\text{CP}}$ ,  $\text{Fe@C}_i$ , and  $\text{Fe}_3\text{O}_4$  exhibited diffractions at  $30^\circ$ ,  $35.5^\circ$ ,  $37^\circ$ , and  $43.1^\circ$ , which are attributed to  $\text{Fe}_3\text{O}_4$ , indicating that in the encapsulated

that MNPs are linked to the catalytic phase, which can create small hot areas that go beyond the boiling point of the solvent, allowing full HDO of acetophenone, furfural, and HMF under 3 bar of  $\text{H}_2$ . The reaction took place under less severe conditions than those required for heterogeneous catalysis. This shows the potential of magnetically induced “nanoreactors” to facilitate demanding transformations through rapid, localized, and efficient heating. Crucially, the intimate contact between the heating agent ( $\text{Fe}_{2.2}\text{C}$ ) and the active phase (Ru) was essential to achieve high selectivity and avoid an undesired hydrogenation of the aromatic ring. In addition to the above, in these works the synthesis of MNPs reported in the literature is usually

**Figure 6.** Conversion (circles), selectivity to benzene (squares) and phenol (diamond) as a function of time during conventional (C) and magnetically induced (M) Anisole HDO over  $\text{ReO}_x/\text{G}$  catalyst and MNP at variable magnetic-field amplitudes. Reaction conditions:  $\text{H}_2$  source: FA, 2.7% vol. Anisole, 100 kHz,  $320^\circ\text{C}$ .



MNP, oxidation of metallic iron has occurred during the reaction. In  $\text{Co@C}_{\text{HT}}$ , metallic cobalt remains as the only observable phase. In fact, metallic phase is observed in all the compounds, which indicates that the encapsulation helped to maintain the structure of the MNPs throughout the reaction, as since complete oxidation of the material has not occurred during the reaction time, which would lead to a change on its magnetic properties and a change in the magnetic field necessary to reach  $320^\circ\text{C}$ . This aligns with earlier studies that emphasize the significance of thermal stability in catalysis and the role of graphite encapsulation.<sup>31,35</sup> In these studies, magnetic non-encapsulated nanoparticles have been observed to experience sintering and loss of effectiveness when subjected to high temperatures for long periods. To address this limitation, Martínez-Prieto et al.<sup>31</sup> developed  $\text{FeCo}$  and  $\text{Co}$  nanoparticles encapsulated in carbon ( $\text{FeCo@C}$  and  $\text{Co@C}$ ), which were capable of sustaining high temperatures ( $>600^\circ\text{C}$ ) during gas-phase reactions such as  $\text{CO}_2$  methanation, propane dehydrogenation and dry reforming. These carbon-encapsulated MNPs retained their morphology and heating performance over time. Similarly, Cerezo-Navarrete et al.<sup>35</sup> reported the synthesis of  $\text{FeCo@Ni}$  nanoparticles via an organometallic approach in mesitylene. Although effective under magnetically induced catalytic conditions for the hydrogenation of HDO of vanillin in water (conversion of 35%), those materials required carbon encapsulation to mitigate deactivation due to thermal sintering and magnetic agglomeration during prolonged exposure to high-frequency alternating magnetic fields (50–100 mT at 300 kHz). Finally, the carbon-coated MNPs demonstrated recyclability and stability and they achieve over 90% conversion. Magnetic induction heating has also been applied in different biomass valorization reactions, particularly in hydrogenations and HDO processes in liquid phase (typically at 30–100 mT at 300 kHz). Asensio et al.<sup>20</sup> demonstrated

more complex, since it requires organometallic precursors. For instance, Mustieles Martín et al.<sup>36</sup> used  $\{\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2\}_2$  and  $\text{Ni}[\text{iPrNC}(\text{CH}_3)\text{NiPr}]_2$  as precursors for the formation of nanoparticles with a  $\text{FeNi}$  core in the HDO of vanillin (47 mT at 100 kHz). However, its application in gas phase systems remains less explored. Regarding gas-phase reactions, magnetic induction has also been used in processes such as  $\text{CO}_2$  hydrogenation,<sup>26,76</sup> although these studies are still less common. In our work, we provide a new approach to the application of magnetic induction, demonstrating their efficiency in catalytic gas phase reactions involving biomass-derived molecules.

## 4. Conclusions

The characterization revealed that the MNP formed by thermal showed variable carbon coverage depending on the carbon source used, with glucose being the most effective in promoting the formation of a graphitic layer. Encapsulation was not complete in all cases, as some materials remained partially coated or formed oxides. Thermal treatments allowed the *in situ* reduction of metal oxides to metallic nanoparticles. MNPs synthesized by the hydrothermal method exhibited the best magnetic properties for magnetic induction catalysis. In particular,  $\text{FeCo@C}_{\text{HT}}$  showed the highest saturation magnetization and the lowest coercivity, making it the most suitable material for this purpose. The presence of a graphite layer contributed to the thermal stability and oxidation resistance of the nanoparticles during the reaction. Additionally, a higher percentage of metallic iron and cobalt correlated with better encapsulation, enhancing nanoparticle stability, while poor encapsulation favored oxide formation, negatively impacting magnetic properties. Regarding the catalytic performance, the



ReO<sub>x</sub>/G catalyst showed an anisole conversion of around 8%, regardless of whether hydrogen or formic acid was used as the hydrogen source. The use of magnetic induction did not significantly affect the conversion, but commercial Fe<sub>3</sub>O<sub>4</sub> nanoparticles, when non-encapsulated, achieved a higher conversion of 13%, with a predominant selectivity towards phenol. Materials with graphitic encapsulation, such as FeCo@C<sub>HT</sub>, displayed better magnetic properties and greater stability during the reaction process. In this system, the reaction is slightly to moderately endothermic (+70 to +140 kJ mol<sup>-1</sup> anisole), requiring continuous external energy input to proceed. Nevertheless, even in exothermic HDO reactions, magnetic heating offers additional advantages, where a rapid and localized energy input facilitates the initiation step. Once the reaction becomes self-sustaining, the magnetic field can be switched off, thereby minimizing the risk of overheating while improving both energy efficiency and operational safety. In summary, the results highlight the importance of selecting the appropriate synthesis method to achieve the desired magnetic properties and effective encapsulation, as these factors significantly influence nanoparticle stability and product selectivity. The combination of rhenium with encapsulated magnetic nanoparticles emerges as a promising strategy to enhance catalytic efficiency in hydrogenation processes, with potential applications in the conversion of anisole and other phenolic compounds. Furthermore, since all samples were subjected to the same thermal treatment, it can be concluded that the hydrothermal process is the most suitable for achieving greater coverage and better carbon crystallinity.

### Author contributions

VNO: investigation, writing – original draft; MD: investigation; GS: conceptualization, review and editing, funding acquisition; ABD: conceptualization, project administration, supervision, writing, review and editing, funding acquisition.

### Conflicts of interest

There are no conflicts to declare.

### Data availability

Data for this article, was obtained during PhD thesis of VNO at Universidad Autónoma de Madrid. Other data, not included in the SI can be requested to authors.

### Acknowledgements

This investigation received financial support from the European Commission through the H2020-MSCA-RISE-2020 BIOALL project (Grant Agreement: 101008058 and MCIN (TED2021-130525A-I00)). IMDEA Nanociencia acknowledges support from the 'Severo Ochoa' Programme for Centres of Excellence (Ministerio de Ciencia e Innovación, CEX2020-001039-S).

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View Article Online  
DOI: 10.1039/D5CY00707K

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DOI: 10.1039/D5CY00707K

## Data availability

Data for this article, was obtained during PhD thesis of VNO at Universidad Autónoma de Madrid. Other data, not included in the SI can be requested to authors.

