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Christian Cerezo-Navarrete, Irene Mustieles Marin, Carlo Marini, Bruno Chaudret, Luis Martínez-Prieto. Structural transformation of carbon-encapsulated core-shell CoNi nanoparticles during magnetically induced CO<sub>2</sub> reduction into CO. *Applied Catalysis B: Environmental*, 2024, 347, pp.123780. 10.1016/j.apcatb.2024.123780 . hal-04816147

**HAL Id: hal-04816147**

**<https://hal.science/hal-04816147v1>**

Submitted on 3 Dec 2024

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# *Structural transformation of carbon-encapsulated core-shell CoNi nanoparticles during magnetically induced CO<sub>2</sub> reduction into CO*

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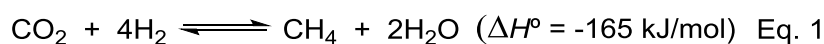
## **Abstract**

Controlling product distribution in CO<sub>2</sub> hydrogenation is of great scientific interest, the selective CO production through the reverse water-gas shift reaction (RWGS) being one of the most investigated processes. Herein, we report the synthesis of new core-shell **Co@Ni** NPs encapsulated in carbon (**Co@Ni@C**) to prevent their aggregation at the high-temperatures reached during magnetically induced catalysis. This bifunctional system has been simultaneously used as heating agent and catalyst for the magnetically induced hydrogenation of CO<sub>2</sub>. While at low magnetic fields **Co@Ni@C** produces CH<sub>4</sub>:CO mixtures, at higher field amplitudes it selectively generates carbon monoxide. Indeed, **Co@Ni@C** has shown to be one of the most active catalysts reported to date, which reaches a maximum conversion of 74.2 % with complete selectivity towards CO at 53 mT and XXX kHz. In addition, recycling and cyclability experiments have demonstrated that **Co@Ni@C** becomes fully selective for CO after being exposed to high field amplitudes (i.e. reaction temperature above 400 °C),

even when it exposed to low magnetic fields again. This change in the selectivity is due to an atomic rearrangement of the core-shell structure, as was confirmed by EDX, XAS, TPR and TPD analysis.

## 1. Introduction

The excessive production and release of greenhouse gases (GHS) leading to global warming is a worldwide problem, the main contributor being CO<sub>2</sub>, and, as a result, its capture and subsequent use as feedstock or chemical reagent is one of the main present challenges for the scientific community.[1] In this respect, the hydrogenation of CO<sub>2</sub> to obtain highly valuable compounds is both of great scientific and applied interest. CO<sub>2</sub> can be reduced into methane through the Sabatier reaction (Eq. 1).[2] but another attractive way for reducing CO<sub>2</sub> is the Reverse Water-Gas Shift reaction (RWGS, Eq. 2),[3,4] which produces CO and H<sub>2</sub>O.[5–7] The great versatility of CO as a C1 building block, as well as its use as a raw material for countless industrial processes,[8] makes the RWGS an interesting option for the valorisation of CO<sub>2</sub>. RWGS is usually favoured at high temperatures due to its moderate endothermic character and the high energy required for the activation of the CO<sub>2</sub> molecule.[9,10] At low temperatures (below 400 °C), RWGS is normally accompanied by the formation of CH<sub>4</sub> as a secondary product *via* CO<sub>2</sub> methanation,[11,12] CO being the main product above 600-700 °C. Although this is one of the main limitations of the RWGS, it is already being exploited at an industrial level. Therefore, it is necessary to develop new catalytic processes that do not require large energy supplies to reach such working conditions.[13]



Numerous catalysts based on supported metal nanoparticles (Pd,[14,15] Pt,[16,17] Fe,[18,19] Ni,[20,21] Cu,[22,23] etc.) have been reported to catalyse RWGS reaction. The use of supported-alloy metal nanoparticles, such as Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,[24] Pd-In/SiO<sub>2</sub>,[25] Cs-Cu/Mo<sub>2</sub>C,[26] has also been studied for RWGS, leading to conversions between 20-50 % with high selectivity towards CO (> 99

%). One of the most active catalysts based on Ni in RWGS (Ni/SiO<sub>2</sub>) was recently reported by Rossi *et al.*. It shows good results in terms of conversion and selectivity (up to 70 % conversion and 100 % selectivity towards CO).[27,28] However, Ni/SiO<sub>2</sub> requires extremely high temperatures (□ 800 °C) to reach such conversions, which is accompanied by a substantial energy consumption. It is therefore necessary to explore novel reaction technologies that offer enhanced energy efficiency for selective CO<sub>2</sub> reduction to CO.

Magnetic induction heating by applying a high-frequency alternating magnetic field (AMF) has been known for a long time,[29] and when considering nanoparticles, has found uses in biomedical applications such as cancer therapy (magnetic hyperthermia).[30] Magnetic induction heating is based on the principle that ferromagnetic materials can produce heat by hysteresis losses when exposed to an AMF.[31] In this line, magnetic nanoparticles (MagNPs) have been successfully used to activate a multitude of catalytic reactions both in solution (*e.g.*, hydrogenation,[32–35] amide condensation,[36–38] water splitting,[39,40] hydrogenolysis[41]) and in the gas-phase (*e.g.*, Fischer-Tropsch,[42] CO<sub>2</sub> hydrogenation,[43–46] methane reforming[47–49] or alkane dehydrogenation[50]), since they can simultaneously act as heating agents and catalysts. The heating power of MagNPs is commonly quantified by the specific absorption rate (SAR), which intimately depends on the physicochemical properties of the MagNPs (size, shape, composition, etc.).[51,52] The main advantage of magnetic heating is that it is a non-contact technique since the energy is directly transferred inside the ferromagnetic material to be heated, and thus displays the highest power transmission. This, together with its extremely short warming time, makes magnetically induced heating a very energetically efficient method and well-adapted to intermittent energy supply.[31] This is also why magnetic catalysis is a promising technology to carry out endothermic reactions that require high temperatures, such as RWGS.

On the other hand, understanding the function and location of active sites of heterogeneous catalysts in the same way that they can be determined in homogeneous systems is still a challenge. In most cases, the species active during catalysis are not found in the as-synthesized catalyst, due to atomic rearrangements that take place under reaction conditions.[53,54] That is why a multitude of analytical

techniques such as HRTEM, EDX, XPS or XRD, have been efficiently employed for the determination of these active sites. In situ catalysts modifications can be due to diverse factors, such as change of crystal phase,[55] alteration of the particle size,[56] reactant-induced atomic displacement,[57] being one of the most observed atomic restructuring.[58–60] This type of structural reorganization usually occurs in multimetallic catalysts, where the migration of the atoms from the core to the surface of the nanoparticles and vice versa is observed. For example, in 1995 Bradley and coworkers observed a Pd-enrichment of the surface of bimetallic alloy-CuPd nanoparticles after exposing them to a CO atmosphere.[61] Years later, Somorjai *et al.* also reported how bimetallic nanoparticles of Rh<sub>0.5</sub>Pd<sub>0.5</sub> underwent a dynamic transformation in composition and chemical state as a function of the reaction atmosphere.[62] More recently, Liu and colleagues reported the atomic rearrangement of core-shell AuNi NPs during CO<sub>2</sub> hydrogenation. More specifically, they observed a reversible change in the core-shell structure at high-temperatures forming a transient reconstructed alloy surface promoted by the CO adsorption generated during the reaction.[63] Thus, the atomic rearrangement of the catalysts can be due to the affinity of the different metals for the reactants,[64] as well as the reaction conditions itself.[65]

Herein, we report an efficient magnetic catalyst based on core-shell **Co@Ni** nanoparticles encapsulated in carbon (**Co@Ni@C**). Similarly to our previous results,[66] the encapsulation in carbon prevents the sintering of MagNPs due to the high temperatures reached during the catalysis. The synthesized catalyst has been fully characterized by state-of-the-art techniques, such as TEM, HRTEM, EDX, XPS, XAS, TPR and TPD measurements. **Co@Ni@C** has proven to be an exceptional catalyst for magnetically induced RWGS. In addition, we have found that **Co@Ni@C** undergoes a structural transformation under catalytic conditions, which is somewhere in between core-shell and pure alloy, making it highly active and selective for CO<sub>2</sub> hydrogenation to CO even at low field amplitudes (or low temperatures).

## 2. Experimental Section

### 2.1. *Synthesis of Co@Ni@C*

This synthesis followed a three-step procedure. (i) First, the monometallic Co NPs were prepared according to previously reported procedure.[66] More specifically, Co precursor,  $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{THF})]$  (180 mg, 0.8 mmol), was reduced under 3 bar of  $\text{H}_2$  upon heating at 150 °C for 24 h in mesitylene (20 mL) and in the presence of long chain surfactants, hexadecylamine (HDA; 386 mg, 1.6 mmol) and hexadecylamine hydrochloride ( $\text{HDA}\cdot\text{HCl}$ ; 333, 1.2 mmol). After reaction, a black solution with the magnetic Co NPs stabilized by HDA/HDA·HCl was obtained. (ii) In a second step,  $\text{Ni}(\text{COD})_2$  (220 mg, 0.8 mmol) was added to the Co NPs solution, and then reduced under 3 bar  $\text{H}_2$  at 70 °C for 20 h. (iii) Once the Co@Ni NPs were formed, 920 mg of activated carbon (Norit D10) dispersed in 10 mL of mesitylene were added to the Fischer-Porter bottle that contains the suspension of Co@Ni NPs (92 mg). After vigorous stirring, Co@Ni NPs were adsorbed on the activated carbon. Then, carbon-supported Co@Ni NPs were washed with hexane three times, and dried at 60 °C overnight. The resulting black powder was then subjected to a pyrolysis process (2 h at 300 °C under  $\text{N}_2$  pressure, with a heating ramp: 10 °C·min<sup>-1</sup>), producing the Co@Ni NPs encapsulated in carbon (**Co@Ni@C**). The size of the carbon-coated NPs was measured by TEM for at least 100 nanoparticles, which afforded a mean value of  $12.4 \pm 2.8$  nm (Figure 2). ICP: Co: 5.1 wt%, and Ni: 5.3 wt%.

### 2.2. *Synthesis of CoNi@C*

The bimetallic CoNi alloy nanoparticles were synthesized through the simultaneous decomposition of the metal precursors  $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{THF})]$  (150.5 mg; 0.4 mmol) and  $\text{Ni}(\text{COD})_2$  (110.0 mg; 0.4 mmol) under 3 bar  $\text{H}_2$  at 150 °C for 24 hours in mesitylene (20 mL), in the presence of HDA (386.0 mg; 1.6 mmol) and  $\text{HDA}\cdot\text{HCl}$  (333.5 mg; 1.2 mmol). After the reaction, a black solution containing the magnetic CoNi nanoparticles stabilized with HDA/HDA·HCl is obtained. The carbon encapsulation of these MagNPs was carried out in the same manner as described for **Co@Ni@C**. The

size of the carbon-coated NPs was measured by TEM for at least 100 nanoparticles, which afforded a mean value of  $9.3 \pm 2.2$  nm (see SI section S2, Figure S13). ICP: Co: 4.4 wt%, and Ni: 4.9 wt%.

### 2.3. Digestion experiments

Following the procedure of Bao and co-workers,[67] who concluded that CoNi NPs were completely encapsulated in graphene because they were not soluble in a strong acid, we demonstrated that the carbon layer of **Co@Ni@C** and **CoNi@C** present a great number of cracks. Specifically, 10 mg of the sample were practically dissolved in a  $\text{H}_2\text{SO}_4$  solution (2M, 5 ml) at 80 °C after 2 h. Upon analyzing the resulting solutions by ICP-AES, we observed a metal content of Co: 4.9 wt%, and Ni: 5.2 wt% for **Co@Ni@C**, and Co: 4.8 wt%, and Ni: 5.2 wt% for **CoNi@C**. This indicates that practically all metals presents were dissolved due to the presence of a large number of gaps in the carbon layer. On the other hand, when the same digestion experiment was performed on **Co@Ni@C** pyrolyzed at 600 °C, the metal contents were Co: 3.9 wt%, and Ni: 4.1 wt%, which indicates a lower number of cracks or gaps in the carbon layer.

### 2.4. Catalytic reactions

Catalytic experiments were performed in a quartz tube continuous-flow reactor of 1 cm diameter which was placed at the centre of an inductor delivering an AC magnetic field oscillating at a frequency of 300 kHz with a root-mean-square (rms) amplitude adjustable between 0 and 65mT. The induction coil is 3 cm wide and 2 cm high.

For the **Co@Ni@C**, **CoNi@C**, and **Co@C** catalysts, 400 mg of catalytic bed material was used for the RWGS reaction, supplying a flow rate of  $25 \text{ mL}\cdot\text{min}^{-1}$  with a  $\text{CO}_2:\text{H}_2$  molar ratio of 1:4 (GHSV:  $70.7 \text{ L}\cdot\text{h}^{-1}\cdot\text{g}_{\text{Ni}}^{-1}$ ;  $70750 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{Ni}}^{-1}$ ).

In all cases, the outlet gases were injected into a GC-MS (Gas Chromatograph PerkinElmer 580 coupled to a Mass Spectrometer Clarus SQ8T). Gas injection calibration and GC analysis method were performed using pure gases. The response factor of the analytes ( $\text{RF}_i$ ) was determined by injecting known quantities of each analyte  $i$  into the column. The area of the peak of species  $i$  in the

chromatogram ( $A_i$ ) allowed for the determination of the conversion of  $i$  ( $X_i$ ) and selectivity based on the following calculations.

$$X_{CO_2} = \frac{\sum RF_{products,i} \cdot A_{products,i}}{\sum RF_{products,i} \cdot A_{products,i} + RF_{reactant,i} \cdot A_{reactant,i}}$$

$$Selectivity = \frac{RF_{product,i} A_{product,i}}{\sum RF_{products,i} \cdot A_{products,i}}$$

### 2.5. $H_2$ -TPR connected to mass-spectrometer

In a typical experiment, 50 mg of **Co@Ni@C<sub>after</sub>** was heated from 25 to 450 °C at 5 °C min<sup>-1</sup> under  $H_2$  flow (10 vol%  $H_2$  in Ar; 14 mL min<sup>-1</sup>). The possible formation of  $CH_4$  due to carbide hydrogenation was followed by online MS. During the entire experiment, the mass signals corresponding to an  $m/z = 16, 15$  and  $14$  did not increase at all, indicating the absence of  $CH_4$  species. Thus, this online experiment is not in agreement with the presence of nickel surface carbides **Co@Ni@C<sub>after</sub>**.

### 2.6. Regeneration experiment

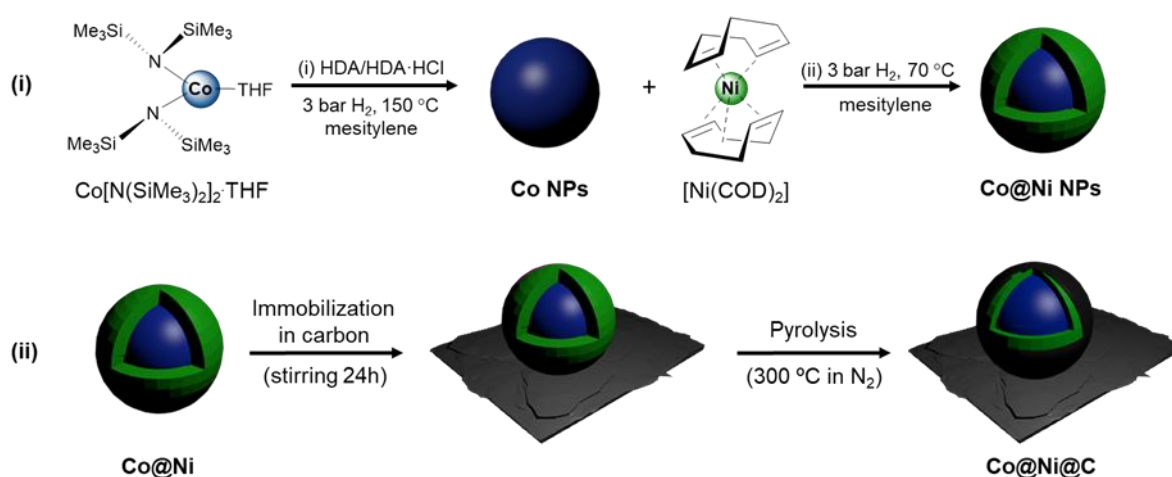
For this regeneration experiment, 400 mg of **Co@Ni@C<sub>after</sub>** was placed into a quartz tube continuous-flow reactor. While heating to 500 °C, a  $H_2$  stream (25 mL·min<sup>-1</sup>) was flowed through the catalyst during 5 h with the aim of removing any pollutants or nickel carbide species formed during the magnetic catalysis. After this regeneration treatment, **Co@Ni@C<sub>after</sub>** was used as catalyst under magnetic heating and in the standard reaction conditions (25 mL min<sup>-1</sup>,  $CO_2:H_2$  1:4 molar ratio at different field amplitudes), observing that the catalyst keeps the selective towards CO at low magnetic fields/temperatures. Therefore, the high CO selectivity of this regenerated material suggests that the change in the selectivity is not due to the presence of pollutants or nickel carbide species.

## 3. Results and discussion

### 3.1. Synthesis and characterization

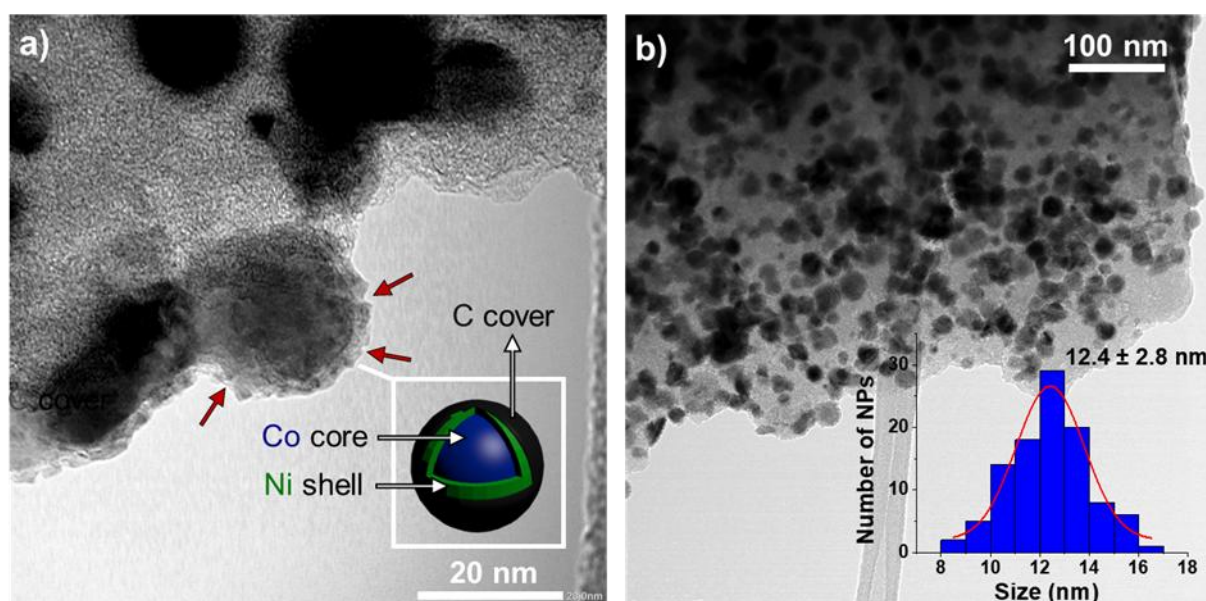


MagNPs encapsulated in carbon were synthesized according to a two-step procedure (Figure 1). (i) First, core-shell **Co@Ni** NPs were prepared through a two-fold decomposition process following an organometallic synthesis. More specifically,  $\text{Ni}(\text{COD})_2$  is decomposed under 3 bar  $\text{H}_2$  at 70 °C in the presence of HDA-stabilized Co NPs dispersed in mesitylene, which were in turn previously synthesized by decomposition of  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2\text{THF}$  under 3 bar  $\text{H}_2$  at 150 °C. (ii) Once core-shell **Co@Ni** NPs were obtained, they were first immobilized on activated carbon and then, through a pyrolysis process (300 °C, 2 h, 10 °C/min), encapsulated into carbon (**Co@Ni@C**) according to a previously reported procedure.[35,66] The carbon encapsulation of **Co@Ni** NPs is important to prevent their sintering when exposed to the high temperatures reached during the magnetically induced catalysis. However, it is key to carry out the encapsulation process at 300 °C for two reasons: (i) to keep the core-shell structure of the carbon-coated **Co@Ni** NPs, since at higher pyrolysis temperatures these MagNPs become alloyed, and (ii) to form a cracked carbon layer with a large number of gaps that allow the access of substrates to the active metal surface. The metal content of **Co@Ni@C** was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using an already reported digestion method.[67,68] In detail, **Co@Ni@C** has a total metal content of 10.4 wt % (Co: 5.1 wt%, and Ni: 5.3 wt%), corresponding to a NP composition of  $\text{Co}_{49}:\text{Ni}_{51}$ , which is very close to the theoretical value ( $\text{Co}_{50}:\text{Ni}_{50}$ ).



**Figure 1.** Synthesis of **Co@Ni@C** following a two-step synthetic procedure: (i) generation of core-shell **Co@Ni** NPs by the controlled decomposition of  $\text{Ni}(\text{COD})_2$  on the surface of Co NPs and (ii) formation of **Co@Ni@C** by encapsulation of core-shell **Co@Ni** NPs on carbon through a pyrolysis process (2h at 300 °C under a  $\text{N}_2$  flow, 10 °C/min).

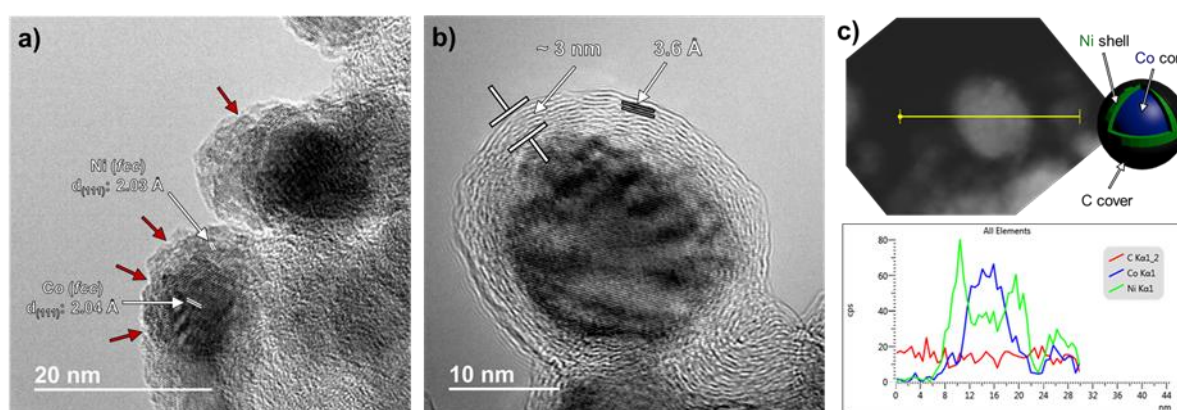
TEM images of Co NPs before the formation of the Ni shell show spherical and well-distributed nanoparticles with a mean size of  $10.1 \pm 1.9$  nm (see SI section S2, Figure S1). After the controlled decomposition of the Ni precursor, uniform core-shell **Co@Ni** NPs were obtained with a slightly larger size due to the incorporation of the Ni layer ( $11.1 \pm 2.5$  nm) (see SI section S2, Figure S2). Finally, after the encapsulation into carbon, the NP size slightly increases to  $12.4 \pm 2.8$  nm, due to a minor sintering of the MagNPs during the pyrolysis process (Figure 2).



**Figure 2.** (a, b) TEM micrographs and (b) size histogram of **Co@Ni@C**. The cracks of the carbon layer are highlighted by red arrows.

The crystallinity and metallic composition of **Co@Ni@C** were studied by high-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) using a high-angle annular dark-field detector (HAADF) coupled to Energy-dispersive X-ray (EDX) spectroscopy. HRTEM images of **Co@Ni@C** show crystalline core-shell NPs, with a *fcc* (face-centered cubic) cobalt core and a *fcc* nickel shell (Figure 3a). In addition, it was observed by HRTEM that these crystalline NPs are covered with a turbostratic cracked carbon coat of *ca.*  $\sim 3$  nm, with a separation between the carbon layers of  $3.6 \text{ \AA}$  (Figure 3b). Despite the large number of cracks observed in this carbon layer, it prevents the sintering of **Co@Ni** NPs at the high temperatures reached during the magnetic catalysis (*vide infra*). The presence of these cracks was confirmed by a simple digestion experiment, where carbon-

encapsulated **Co@Ni** NPs were totally disaggregated using a  $\text{H}_2\text{SO}_4$  solution (10.1 wt% of metal content, calculated by ICP-AES). This large number of gaps is due to the incomplete encapsulation of MagNPs when the pyrolysis is carried out at 300 °C. The chemical order was studied by STEM-HAADF coupled with EDX analysis. The EDX line scan profile of **Co@Ni@C** shows core-shell NPs coated by a carbon layer with an atomic composition of  $\text{Co}_{47}:\text{Ni}_{53}$  (Figure 3c), which is very close to the ICP results (*vide supra*) and matches very well the theoretical composition ( $\text{Co}_{50}:\text{Ni}_{50}$ ). Note that, as mentioned before, the encapsulation temperature is critical since, for example, at 600 °C core-shell **Co@Ni** NPs undergo a complete atomic restructuring, where surface Ni atoms diffuse into the core forming alloy-type NPs (see SI section S3, Figure S4).



**Figure 3.** (a) HRTEM micrographs of **Co@Ni@C**. (a) Lattice spacings of *fcc* Co (2.04 Å) and Ni Co (2.03 Å) are highlighted in white. The cracks of the carbon layer are highlighted by red arrows. (b) Separation of the carbon layers (3.6 Å) and the thickness of the carbon coat (~ 3 nm). (c) STEM-HAADF image and EDX line scan profile of **Co@Ni@C**.

A raman spectrum of **Co@Ni@C** (see SI section S4, Figure S7) shows two major peaks at  $1348\text{ cm}^{-1}$  and  $1606\text{ cm}^{-1}$ , associated to bands D and G respectively, which are characteristic of carbon based materials.[69] The high intensity of the D band is in turn associated with the presence of a large number of defects in this carbon material.

The X-Ray diffractogram of **Co@Ni@C** exhibits a series of low intensity peaks corresponding to *fcc*-Co and *fcc*-Ni together with peaks attributed to CoO and NiO, confirming the partial oxidation of the MagNPs encapsulated in the cracked carbon layer after air exposure (see SI section S5, Figure S8).

The chemical composition and oxidation states of **Co@Ni@C** NPs were investigated by X-ray photoelectron spectroscopy (XPS). Figure S9a (top, see SI section S6) shows the Ni 2p and Co 2p

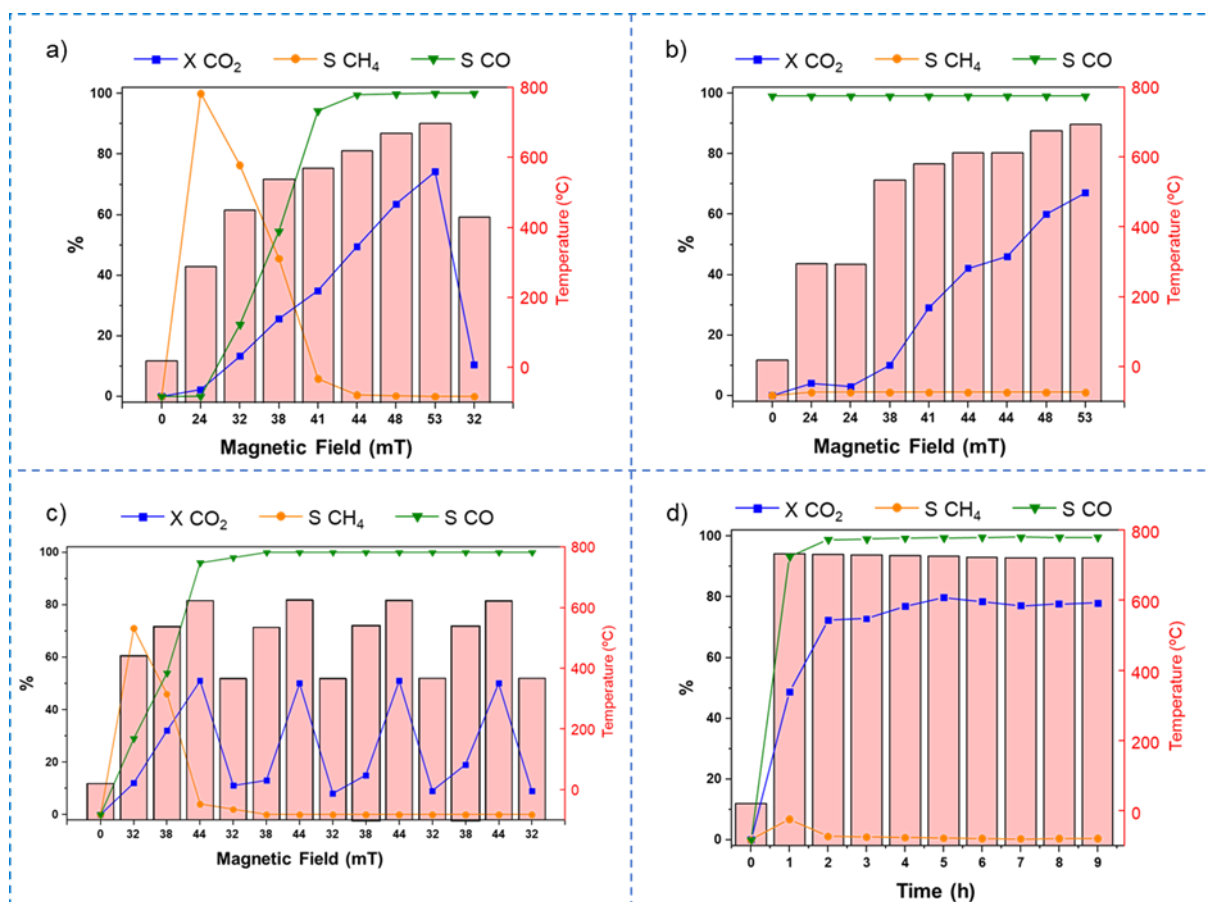
areas of these carbon-encapsulated **Co@Ni** NPs. The Ni 2p area presents a main peak at 855.1 eV, which can be deconvoluted into two components: (i) a major contribution at 855.5 eV that corresponds to Ni oxide (NiO) and (ii) a minor one at 853.0 eV belonging to metallic Ni (Ni<sup>0</sup>). In the same way, the Co 2p region exhibits a strong emission at 780.3 eV, which after deconvolution displays two bands, a big one at 780.9 eV corresponding to Co oxide (CoO) and a small one at 778.9 eV of Co<sup>0</sup>. Therefore, by analysing Ni 2p and Co 2p XPS regions, we can deduce that the surface of as-synthesized **Co@Ni@C** NPs are mostly oxidized due to their purification under air. Remarkably, after catalysis under reductive conditions (see SI section S6, Figure S9a bottom), **Co@Ni@C** are partially reduced (*vide infra*).

The magnetic properties of **Co@Ni@C** NPs were measured by Vibrating Sample Magnetometry (VSM) applying a magnetic field between - 3 and 3 T at 300 K and 5 K. The obtained hysteresis loops provide the corresponding saturation magnetization ( $M_s$ ) and coercive field ( $H_C$ ) values for **Co@Ni@C** (see SI section S7, Figure S10a). The  $M_s$  obtained are 65 A·m<sup>2</sup>·g<sup>-1</sup> at 300K and 70 A·m<sup>2</sup>·g<sup>-1</sup> at 5 K, which are considerably lower than that reported for the same cobalt NPs encapsulated in carbon (**Co@C**;  $M_s$  of 120-130 A·m<sup>2</sup>·g<sup>-1</sup>) due to the incorporation of the Ni shell.[35] The existence of a perceptible *exchange bias* field in the hysteresis loops (shifted along  $\mu_0 H_C$  axis) confirms the partial oxidation of **Co@Ni@C** (see SI section S7, Figure S10b).

The heating capacity of **Co@Ni@C** NPs was evaluated by determining their specific absorption rate (SAR) by calorimetry using a previously reported procedure (see SI, section S8).[42,43,70] The SAR values at different field amplitudes (from 0 to 47 mT) were determined in the solid state after the application of an alternating magnetic field ( $\mu_0 H_{rms}$ ) with a frequency of 93 kHz (see SI section S8, Figure S13). **Co@Ni@C** starts to heat up at 19 mT, reaching a maximum SAR value of 76 W·g<sup>-1</sup> at 47 mT. This value is slightly lower than the one obtained for the analogous reported material based on carbon-encapsulated cobalt NPs (**Co@C**; 120 W·g<sup>-1</sup>), due to the presence of the nickel-shell which is a magnetically softer material. Although these SAR values are somewhat low, they have proven to be enough to reach very high temperatures under high frequency AMFs.[66]

### 3.2. Catalytic studies

**Co@Ni@C** was simultaneously used as heating agent and catalyst in continuous flow magnetically induced CO<sub>2</sub> hydrogenation, employing a gas feed of CO<sub>2</sub>:H<sub>2</sub> mixture with a 1:4 molar ratio (5 mL·min<sup>-1</sup> CO<sub>2</sub> and 20 mL·min<sup>-1</sup> of H<sub>2</sub>). At low field amplitudes (from 24 to 38 mT), the conversions are low (< 25 %), producing mixtures of methane and CO (Figure 4a). For example, at 32 mT the conversion is only 13.2 % with 76 % selectivity towards CH<sub>4</sub> and 24 % to CO. However, at 41 mT **Co@Ni@C** begins to selectively convert CO<sub>2</sub> into CO (34.9 % of conversion with 94 % selectivity to CO). At 44 mT, the selectivity towards CO is 100 % with a conversion of 49.5 %. Increasing the field amplitude led to higher conversions keeping the high selectivity toward CO, which reaches a maximum conversion value of 74.2 % at 53 mT. The bulk temperature (T<sub>bulk</sub>) of the system, determined by an ultrathin thermocouple located in the middle of the catalytic bed, also increases with the field amplitude from 289 °C at 24 mT to 698 °C at 53 mT. Remarkably, the conversion at 53 mT (T<sub>bulk</sub> = 698 °C) is slightly higher than the expected conversion at the thermodynamic equilibrium at the estimated temperature (~ 70 %; Table 1, entry 1 and Figure S14), which suggests that surface temperature (T<sub>surf</sub>) of **Co@Ni@C** is above the measured T<sub>bulk</sub> value, as was previously observed in similar systems.[35,71] According to the conversion observed at 53 mT (74.2 %), it can be estimated that the catalyst surface is above 750 °C (see SI section S9, Figure S14). In comparison to the catalytic systems already reported in the literature, **Co@Ni@C** seems to be one of the most active catalysts in the selective hydrogenation of CO<sub>2</sub> to CO (RWGS) (see SI section S10, Table S1). Finally, after decreasing the field amplitude to 32 mT, the high selectivity to CO observed at high temperatures is retained, leading to 10.5 % of CO<sub>2</sub> conversion with 100 % selectivity towards CO. The later result indicates that the change observed in the selectivity is not only a matter of temperature (normally in CO<sub>2</sub> hydrogenation the RWGS is favoured at high temperatures and Sabatier reaction at lower ones). Thus, this change in the selectivity of **Co@Ni@C** NPs must be due to a structural transformation of the catalyst and/or the formation of new active sites during the magnetically induced catalysis, since both the nanoparticle size and morphology remain practically unchanged as can be observed by TEM images after catalysis (see SI section S2, Figure S3).

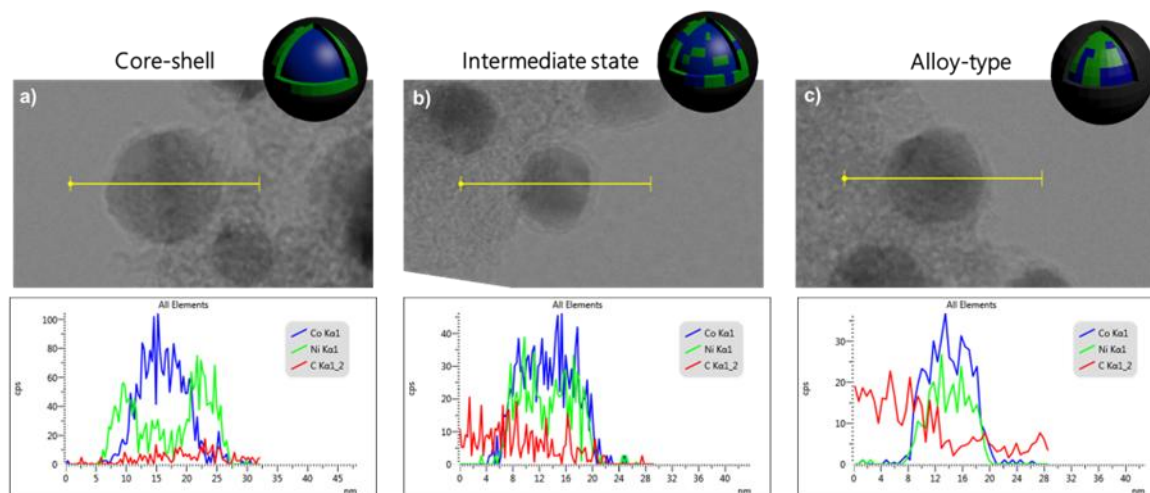


**Figure 4.** Magnetically induced  $\text{CO}_2$  hydrogenation reaction using (a)  $\text{Co@Ni@C}$  and (b)  $\text{Co@Ni@C}_{\text{after}}$ . (c) Cyclability study of magnetically induced  $\text{CO}_2$  hydrogenation reaction using  $\text{Co@Ni@C}$ . (d) Catalytic performances of  $\text{Co@Ni@C}$  over time. Gas flow: 25 mL/min  $\text{CO}_2:\text{H}_2$  (1:4) ( $\text{GHSV} = 70750 \text{ mL}\cdot\text{h}^{-1} \text{ g}_{\text{Ni}}^{-1}$ ). X = conversion, S = selectivity, and Y = yield. Temperatures (red bars) were recorded by an ultrathin thermocouple directly located in the catalytic bed and confirmed by IR thermometry.

To confirm the change observed in the selectivity of  $\text{Co@Ni@C}$ , recyclability and cyclability experiments were carried out. First, the same continuous flow catalytic test was performed with an already used and recovered  $\text{Co@Ni@C}$  catalyst ( $\text{Co@Ni@C}_{\text{after}}$ ). As shown on Figure 4b, the selectivity toward CO is 100 % even at low field amplitudes and conversions, which indicates that the catalyst becomes magnetic selective during the first catalytic cycle. Here, the conversion also increases linearly in all the range of magnetic field amplitudes, reaching a 67 % of conversion of  $\text{CO}_2$  at 53 mT, which is slightly lower than the value obtained with fresh  $\text{Co@Ni@C}$  catalyst (Figure 3a). This may be due to a higher degree of encapsulation of the MagNPs when reaching temperatures above 600 °C during the first catalytic cycle, which would reduce the number of available active sites. Secondly, a cyclability experiment at variable field amplitudes (from 32 to 44 mT) was also performed for  $\text{Co@Ni@C}$ . More

specifically, conversions and selectivities at 32, 38 and 44 mT were measured cyclically (Figure 4c). Remarkably, **Co@Ni@C** exhibits almost perfect cyclability in terms of temperature (620 °C) and CO<sub>2</sub> conversion (~ 50 %). Regarding selectivity, at low field amplitudes (*i.e.* 32 mT), the conversion is low (12 %) and the reaction products are a CH<sub>4</sub>:CO mixture, methane being the major product (71 % selectivity). After increasing the magnetic field to 38 mT, the conversion increases to 32 % but the selectivity changes, CO being the main product (54 % selectivity). A drastic change in selectivity occurs when a certain  $T_{\text{bulk}}$  value is reached (> 500 °C), leading exclusively to CO as the main reaction product. Accordingly, the change in the selectivity of **Co@Ni@C** occurs when this temperature is reached, since by decreasing the field to the initial values (32 mT) the formation of methane is no longer observed. In addition, **Co@Ni@C** has been shown to be stable for at least 9 hours under reaction conditions, without showing any significant loss in activity or selectivity (~ 75 % conversion and > 99 % selectivity to CO after 9 hours of reaction; Figure 4d). Therefore, we can conclude that the carbon coat significantly increases the stability of these MagNPs, avoiding their agglomeration and allowing them to maintain both their activity and heating capacity during long reaction periods.

As previously mentioned, the encapsulation of **Co@Ni** NPs was carried out at 300 °C, since at higher temperatures (*i.e.* 600 °C) the core-shell structure undergoes an atomic rearrangement where Ni atoms diffuse from the shell towards the nanoparticle nucleus, forming alloy-type nanoparticles (see SI section S3, Figure S4). In a similar way, during the catalysis at field amplitudes higher than 44 mT (above 500 °C), an irreversible structural transformation occurs in the MagNPs, forming alloy-type CoNi nanoparticles. This structural change was confirmed by STEM-EDX analysis of **Co@Ni@C<sub>after</sub>**, where diverse types of MagNPs can be observed with different degrees of atomic arrangements: core-shell like, alloy type and intermediate states between alloy and core-shell (Figure 5). Possibly, the change in selectivity observed during the catalysis is due to the atomic rearrangement that **Co@Ni@C** undergoes under high field amplitudes, resulting in an intermediate state between core-shell and alloy with enhanced magnetic properties, as was observed by VSM measurements (higher values of  $M_S$  and  $H_C$ ; see SI section S7, Figure S11).



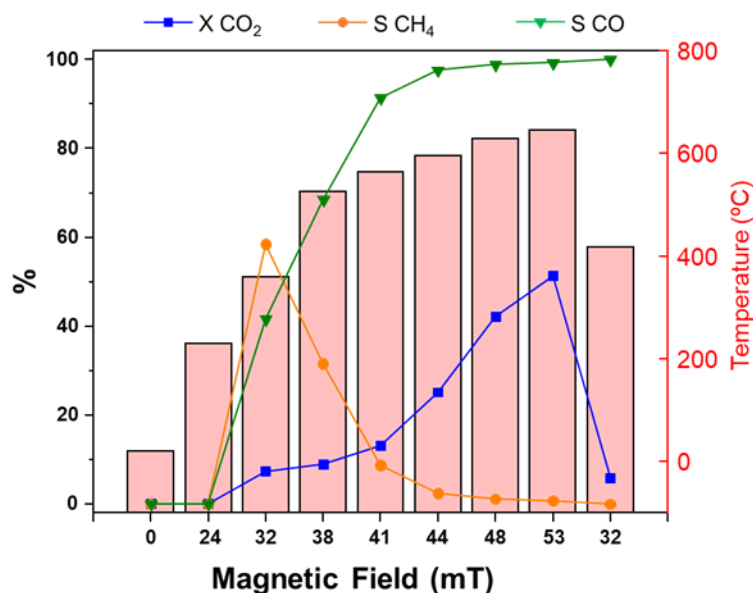
**Figure 5.** STEM-BF images and their corresponding EDX line scan profiles of **Co@Ni@C<sub>after</sub>**.

After observing the atomic rearrangement in **Co@Ni@C** that takes place during the magnetic catalysis, where most of the MagNPs evolve from core-shell to alloy, we proceeded to synthesize the analogous alloy type material (**CoNi@C**) and test it in the same catalytic reaction. More specifically, the alloy-type CoNi NPs were prepared following a co-decomposition of Co and Ni precursors under 3 bar H<sub>2</sub> at 150 °C, which were subsequently encapsulated in carbon by the same pyrolysis process described above (2 h at 300 °C, 10 °C/min under N<sub>2</sub>). The metallic content of **CoNi@C** is very close to the theoretical value, presenting 4.4 wt% Co and 4.9 wt% Ni. In addition, by TEM and STEM-EDX analysis it was possible to confirm that these MagNPs were alloy type and display a particle size of  $9.3 \pm 2.2$  nm (see SI section S3, Figure S5), very similar to the size observed for the core-shell type catalyst (**Co@Ni@C**).

After the characterization of the surface of **CoNi@C** by XPS (see SI section S6, Figure S9), showing that it is mostly oxidized, it was tested in the magnetic hydrogenation of CO<sub>2</sub> (Figure 6) under the catalytic conditions previously described (gas flow: 25 mL min<sup>-1</sup>, molar ratio CO<sub>2</sub>:H<sub>2</sub> 1:4). In the same way as **Co@Ni@C**, at low field amplitudes (32 mT) **CoNi@C** produces CO:CH<sub>4</sub> mixtures, the main product being methane (7.3 % conversion and 58.5 % selectivity to CH<sub>4</sub>). However, at field amplitudes higher than 44 mT, CO becomes the only reaction product. At 53 mT (maximum field amplitude reached by our equipment) the yield of CO is 51.3 % (T<sub>local</sub> = 646 °C). Similarly to **Co@Ni@C**, if we decrease the magnetic field applied again to 32 mT, the selectivity to CO is



maintained, even at low  $T_{\text{bulk}}$  and conversion ( $\square$  400 °C and 5.8 % conversion). Although **CoNi@C** presents a very similar catalytic behavior to **Co@Ni@C**, this catalyst is less active. At the same field amplitude value (53 mT), the alloy-type catalyst reaches a maximum conversion of 51.3 %, while **Co@Ni@C** shows a conversion of 74.2 %. This difference in activity is probably due to the higher bulk temperature reached with the core-shell catalyst at 53 mT ( $T_{\text{bulk}}$  of 698 °C), since with **CoNi@C** the  $T_{\text{bulk}}$  is only 646 °C, which is attributed to the lower magnetic properties ( $M_S$  and  $H_C$ ) of **CoNi@C** (see SI section S7, Figure S12). The cyclability studies of **CoNi@C** revealed a similar behavior to that previously observed for **Co@Ni@C** (see SI section S11, Figure S15), but with less activity. In the first cycle, at low field amplitudes (*i.e.* 32 mT) the conversion is 6.3 % with 63 % selectivity towards methane. However, when the field is increased to 44 mT only CO is obtained (18.2 % conversion and >99 % selectivity). After performing successive 32-38-44 mT cycles, methane formation is no longer observed. The latter results show that in the same way than for **Co@Ni@C**, at a certain local temperature (> 500 °C) a change in selectivity takes place, with CO being the only product of the reaction.



**Figure 6.** Magnetically induced CO<sub>2</sub> hydrogenation reaction using **CoNi@C**. Gas flow: 25 mL/min CO<sub>2</sub>:H<sub>2</sub> (1:4) (GHSV = 1500 h<sup>-1</sup>). X = conversion, S = selectivity, and Y = yield. Temperatures (red bars) were recorded by an ultrathin thermocouple directly located in the catalytic bed and confirmed by IR thermometry.

To confirm that high temperatures ( $> 500\text{ }^{\circ}\text{C}$ ) are responsible for the atomic restructuring and the change in the selectivity observed in **Co@Ni@C** during the catalysis, we proceeded to perform the hydrogenation of  $\text{CO}_2$  under conventional heating and the standard reaction conditions ( $25\text{ mL min}^{-1}$ ,  $\text{CO}_2:\text{H}_2$  1:4 molar ratio) with fresh **Co@Ni@C** (see SI section S11, Figure S16). The conversions are significantly lower over the entire temperature range. For example, at  $400\text{ }^{\circ}\text{C}$  the conversion is only 5.3 % with 57.9 % selectivity towards  $\text{CH}_4$  and 42.1 % to CO. As temperature increases, the conversion increases too and the selectivity shifts towards CO, reaching a maximum conversion of 16.6 % at  $600\text{ }^{\circ}\text{C}$  (maximum operation temperature of the conventional heating reactor) and a selectivity of XXXX%. Comparing the latter result with that obtained by magnetic induction at similar  $T_{\text{bulk}}$  (*i.e.*  $T_{\text{bulk}}$  of  $620\text{ }^{\circ}\text{C}$  at 44 mT), we observe a much higher conversion when the catalyst is magnetically heated (conversion of 16.6 % vs. 49.5 %). As was previously observed, under an oscillating magnetic field the surface temperature of the catalyst ( $T_{\text{surf}}$ ) is much higher than the measured  $T_{\text{bulk}}$ , which is normally reflected in higher conversions at the same  $T_{\text{bulk}}$ . In terms of selectivity, under conventional heating **Co@Ni@C** shows the same behaviour than a magnetically heated sample. It maintains the high selectivity towards the formation of CO even after reducing again the temperature (6.8 % conversion with 100% selectivity towards CO at  $400\text{ }^{\circ}\text{C}$ ) (see SI section S11, Figure S16). STEM-EDX analysis of **Co@Ni@C** after conventional heating indicates a similar structural transformation to the one previously observed after magnetic catalysis (see SI section S3, Figure S6). Thus, we can propose that the structural transformation that produces the change in the selectivity of the catalyst is caused by the temperature reached during the catalytic reaction.

In order to determine the role of Co in the reactivity of these catalysts, the analogous monometallic material was prepared (**Co@C**),<sup>[66]</sup> and tested in the magnetically induced  $\text{CO}_2$  hydrogenation (see SI section S11, Figure S17a). In summary, when **Co@C** was used as a catalyst under the standard reaction conditions ( $25\text{ mL min}^{-1}$ ,  $\text{CO}_2:\text{H}_2$  1:4 molar ratio), at low field amplitude (32 mT) the conversion is very low (1.8 %) and produces mixtures of  $\text{CH}_4:\text{CO}$  (53.7 % selectivity towards  $\text{CH}_4$ ). As the field amplitude increases, the conversion and selectivity towards CO increase, reaching a maximum conversion at 53 mT with high selectivity towards CO (44.3 % of conversion with 97 %

selectivity) ( $T_{\text{bulk}} = 635 \text{ }^{\circ}\text{C}$ ). However, unlike the bimetallic catalysts (**Co@Ni@C** and **CoNi@C**), when low field amplitudes are again applied (*i.e.* 32 or 24 mT) mixtures of  $\text{CO}:\text{CH}_4$  are observed (see SI section S11, Figure S17a). This latter result indicates that the presence of Ni not only increases the activity of these catalysts, but also significantly improves their selectivity to CO after being exposed to AMF. This behavior was corroborated by a cyclability study (see SI section S11, Figure S17b). Contrary to bimetallic catalysts, **Co@C** follows the same pattern during the successive cycles;  $\text{CH}_4:\text{CO}$  mixtures are produced at low magnetic fields and CO at high fields. Therefore, we can confirm that **Co@C** does not suffer any change in the selectivity after exposing it to high magnetic fields. In addition, we can assume that if any Co carbide species are formed during the magnetic catalysis at high temperatures, they are not responsible for the change in the selectivity observed for the CoNi bimetallic systems. On the other hand, since the formation of Ni carbide species may be responsible for this change in selectivity towards CO, as was recently reported,[27] we decided to better analyze **Co@Ni@C<sub>after</sub>** looking for Ni-C species. Neither by direct (XRD, XPS or XAS) nor indirect techniques ( $\text{H}_2$ -TPR connected to a MS[72] to probe methane formation and testing of catalytic activity after a regeneration treatment;[73] see Experimental section, sections S1) were able to demonstrate the presence of Ni carbides. Thus, the change in selectivity should be due to the atomic restructuring observed at high magnetic fields/temperatures.

In summary, as can be seen in Table 1, core-shell MagNPs (**Co@Ni@C**) present the highest activity in the selective hydrogenation of  $\text{CO}_2$  to CO, being one of the most active catalysts reported to date (see SI section S10, Table S1). The lower activity of the alloy-type catalyst (**CoNi@C**) indicates that, even when an atomic rearrangement occurs on **Co@Ni@C** NPs during magnetic catalysis, they do not form a perfect alloy but remain in an intermediate state which favours their heating capacity and activity in the selective reduction of  $\text{CO}_2$  to CO. On the other hand, the selectivity change observed during the magnetic catalysis with bimetallic catalysts (**Co@Ni@C** and **CoNi@C**), suggests that these catalysts can also undergo some type of structural transformation that make them selective towards CO.

**Table 1.** Magnetically induced CO<sub>2</sub> hydrogenation using **Co@Ni@C**, **CoNi@C** and **Co@C** as catalysts.

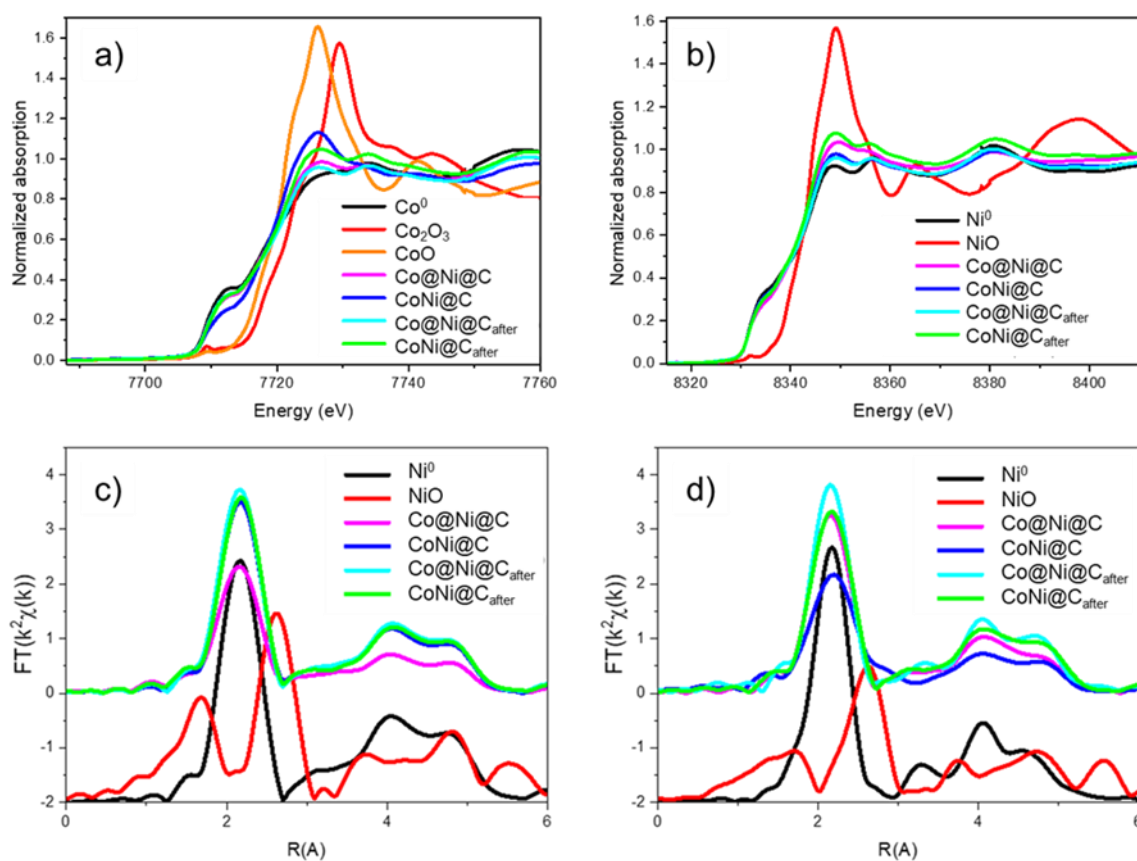
Catalyst	Conversion (%)	Selectivity (%)	T <sub>bulk</sub> (°C) <sup>a</sup>	Conversion at thermodynamic Eq. (%) <sup>b</sup>
<b>Co@Ni@C</b>	74.2	>99	698	72
<b>CoNi@C</b>	51.3	>99	646	68
<b>Co@C</b>	44.3	97	635	67

<sup>a</sup>T<sub>bulk</sub> was recorded by an ultrathin thermocouple directly located in the catalytic bed. <sup>b</sup>Conversions at thermodynamic equilibrium were estimated employing the Gibbs free energy minimization method.

### 3.3. Structural transformation studies

With the intention of studying the change in selectivity of **Co@Ni@C** and **CoNi@C** during the magnetically induced catalysis at high field amplitudes, the atomic composition of these bimetallic catalysts before and after catalysis was examined by XAS experiments (XANES and EXAFS). In this way it was possible to study in depth the oxidation state and coordination number of metal centers of these heterogeneous catalysts. The normalized XANES spectra at the Co-K and Ni-K edges of the bimetallic catalysts before (**Co@Ni@C** and **CoNi@C**) and after catalytic conditions (**Co@Ni@C<sub>after</sub>** and **CoNi@C<sub>after</sub>**) can be observed on Figure 7a-b. When comparing the XANES spectra of the bimetallic samples with the Co and Ni references, we can observe that in all samples both Co and Ni are present mainly as zerovalent metals (Table 2). This observation is not in agreement with the results previously observed by XPS (see SI section S6, Figure S9), where it was seen that MagNPs were mostly oxidized before applying reducing conditions. However, XPS is a surface characterization technique, and it is only capable of determining the oxidation states of atoms located in the outer layers, which are more exposed to air. On the other hand, in line with XPS data, **Co@Ni@C<sub>after</sub>** is more reduced than the as-synthesized catalyst. More specifically, before catalysis, 89.5 % of the cobalt is found as Co<sup>0</sup> and 81.2 % of the nickel is as Ni<sup>0</sup>, while after catalysis, 93.9 % of the cobalt and 92.8 % of the nickel are found in their respective zerovalent states (Table 2, entries 1 and 2). Under reductive reaction conditions (25 mL min<sup>-1</sup> of CO<sub>2</sub>:H<sub>2</sub> 1:4) and magnetic induction heating, the small fraction of metal oxides present on the catalyst surface is mostly reduced. In the case of the alloy-type catalyst (**CoNi@C**) a similar trend is observed for cobalt, which is reduced under reaction conditions

(from 67.8 % to 82.0 %; Table 2, entries 3 and 4). The higher amount of CoO in **CoNi@C** than in **Co@Ni@C** is due to the fact that Co is more exposed to air in alloy-type MagNPs. In the core-shell catalyst (**Co@Ni@C**), the Ni shell acts as a protective layer against the oxidation of the Co core. However, in the case of nickel we can observe that **CoNi@C<sub>after</sub>** presents a higher proportion of NiO than **CoNi@C** (9.0 % and 23.5 %, respectively; entries 3 and 4). This can be related to an enrichment in Ni of the NP surface after catalytic conditions, where without forming a core-shell NP it approaches to the mentioned intermediate state that makes the catalyst completely selective to CO even at low magnetic fields. Thus, the higher oxidation degree of Ni in **CoNi@C<sub>after</sub>** can be explained by a greater number of Ni atoms on the NP surface after catalysis.



**Figure 7.** (a, b) XANES spectra and (c, d) EXAFS Fourier transform at the Co-K and Ni-K edges of **Co@Ni@C**, **CoNi@C**, **Co@Ni@C<sub>after</sub>** and **CoNi@C<sub>after</sub>** together with reference materials of Co (Co<sup>0</sup>, Co<sub>2</sub>O<sub>3</sub> and CoO) and Ni (Ni<sup>0</sup> and NiO).

**Table 2.** Oxidation states of **Co@Ni@C** y **CoNi@C**, before and after catalytic conditions calculated by XANES.

Entry	Catalyst	Co <sup>0</sup> (%)	CoO (%)	Ni <sup>0</sup> (%)	NiO (%)
1	Co@Ni@C	89.5	10.5	81.2	18.8
2	Co@Ni@C <sub>after</sub>	93.9	6.1	92.8	7.2
3	CoNi@C	67.8	32.2	91.0	9.0
4	CoNi@C <sub>after</sub>	82.0	18.0	76.5	23.5

To shed some light about the local structure of the intermediate state between core-shell and alloy observed in bimetallic systems after catalysis, EXAFS spectroscopy analysis of Co@Ni@C and CoNi@C before and after catalytic conditions was performed. EXAFS data of these samples together with metallic foils and their oxides are shown in Figure 7 (see also Figure S18, section S12). Co@Ni@C<sub>after</sub> exhibits values of number of neighboring atoms (N) different from those observed for Co@Ni@C and for the alloy type catalyst, CoNi@C (Table 3, entries 1, 2 and 3). However, after comparing Co@Ni@C<sub>after</sub> and CoNi@C<sub>after</sub> they show N values very similar, suggesting that an atomic restructuring takes place on both catalysts since they present similar local structure (Table 3, entries 2 and 4). Therefore, from EXAFS data it has been possible to confirm the existence of an intermediate state between core-shell and pure alloy, which is produced as a consequence of an atomic rearrangement of the MagNPs under catalytic conditions at high reaction temperatures (> 500 °C), and turns the catalysts highly selective towards CO even at low field amplitudes.

**Table 3.** Number (N) and distances (R) between neighbouring atoms of Co@Ni@C y CoNi@C, before and after catalytic conditions calculated by XANES.

Entry	Catalyst	N				R			
		Co-M	Co-O	Ni-M	Ni-O	Co-M	Co-O	Ni-M	Ni-O
1	Co@Ni@C	10.08	-	6.81	5.81	2.492	-	2.489	2.002
2	Co@Ni@C <sub>after</sub>	10.76	-	9.24	-	2.497	-	2.488	-
3	CoNi@C	9.17	5.31	8.81	-	2.496	2.035	2.493	-
4	CoNi@C <sub>after</sub>	10.75	-	10.55	4.06	2.518	-	2.494	2.029

Finally, TPR (temperature-programmed reduction) and TPD (temperature-programmed desorption) of CO and CO<sub>2</sub> experiments were carried out in order to investigate the high selectivity towards the CO

formation of **Co@Ni@C<sub>after</sub>** and **CoNi@C<sub>after</sub>** catalysts. First, the reducibility of the different catalysts, **Co@Ni@C**, **CoNi@C** and **Co@C**, was compared (see SI section S13, Figures S19 and S20). The TPR profile of the monometallic catalyst **Co@C** shows a reduction peak at ~320 °C (Figure S19). On the other hand, the reduction of CoO in the bimetallic catalysts observed in their TPR profiles takes place at lower temperatures, which is due the presence of Ni (Figures S20), as previously reported.[74,75] More specifically, **Co@Ni@C** exhibits two reduction peaks at 168 and 232 °C, which are attributed to the reduction of CoO and NiO species present in this catalyst. Interestingly, above 460 °C a negative peak is observed, which is normally associated to the desorption of a gas. Since the change in the selectivity towards CO during catalysis occurs around a similar temperature (see Figure 4), this negative peak in the TPR profile could be a consequence of the structural transformation at this particular temperature. Above 400 °C, the desorption of an adsorbed gas on the MagNP surface is observed (probably H<sub>2</sub> strongly chemisorbed to the metal surface)[76,77] and may be related to the atomic restructuring that **Co@Ni@C** undergoes at this temperature. After losing the core-shell structure, H<sub>2</sub> previously adsorbed on the MagNP surface are desorbed.[78] When analyzing the TPR profile of **Co@Ni@C<sub>after</sub>** (Figure S20a), we observe a displacement of the Co and Ni reduction peaks to higher temperatures (244 and 319 °C) and a negligible contribution of the negative peak. Thus, the gas desorption is no longer observed after the afore mentioned intermediate state is reached during catalysis. The same trend was found for **CoNi@C** (Figure S20b). Before catalysis the reduction peaks of the oxidized species are observed (144 and 206 °C) together with a negative peak (413 °C). And after catalysis, the reduction peaks shift to higher temperatures and the negative contribution disappears, suggesting that there has been a change in the metallic distribution of the catalyst. Therefore, TPR provides us further information about the structural change observed, which is responsible for the high selectivity towards CO of the bimetallic catalysts. However, it is worth mentioning that this structural transformation does not generate two identical catalysts, since although both systems present high selectivity to CO even at low reaction temperatures, **Co@Ni@C** is much more active due to its higher heating capacity (74.2 vs. 51.3 % at 53 mT, see Table 1).

TPD-CO<sub>2</sub> was performed to explore the affinity of the different catalysts towards CO<sub>2</sub> adsorption, which is crucial for CO<sub>2</sub> conversion. As can be seen in Figure S21a (see SI section S14), TPD-CO<sub>2</sub> of **Co@Ni@C** exhibits two weak signals at *ca.* 266 y 582 °C, and a more intense one at 362 °C. However, **Co@Ni@C<sub>after</sub>** shows a significantly different profile, where only two signals can be observed at 276 and 623 °C, the latter being much more intense. This indicates that CO<sub>2</sub> desorption takes place at higher temperature in **Co@Ni@C<sub>after</sub>** because CO<sub>2</sub> is strongly adsorbed to this catalyst surface. Likewise, TPD-CO<sub>2</sub> of **CoNi@C** (Figure S21b) shows a main peak centered at 400 °C that switches to higher temperature after catalytic conditions (i.e. 595 °C). Similar to TPR measurements, the difference between TPD-CO<sub>2</sub> profiles before and after catalysis provides further evidence of the structural transformation observed under catalytic conditions.

TPD-CO was also measured to determine the capacity to desorb CO of **Co@Ni@C** and **CoNi@C** before and after the structural change. As can be seen in Figure S22a (see SI section S15), TPD-CO of **Co@Ni@C** shows a peak at *ca.* 381°C assigned to the desorption of CO by the catalyst at this temperature. However, the TPD-CO of the same catalyst after magnetic catalysis (**Co@Ni@C<sub>after</sub>**) does not exhibit any noticeable desorption peak. This indicates that **Co@Ni@C<sub>after</sub>** presents a high CO desorption capacity, and CO is probably desorbed during the signal stabilization time at room temperature, so its detection was not possible. The same trend was also observed for **CoNi@C** NPs (see SI section S15, Figure S22b), where before catalysis it is possible to observe a peak centered at *ca.* 348 °C, while after magnetic induction catalysis (**CoNi@C<sub>after</sub>**) the TPD-CO spectrum does not show any perceptible desorption peak. This result could explain the great selectivity of **Co@Ni@C<sub>after</sub>** and **CoNi@C<sub>after</sub>** towards the formation of CO, since for the formation of CH<sub>4</sub> it is necessary that the CO is more strongly adsorbed to the catalyst surface to be subsequently hydrogenated to methane.[28]



#### 4. Conclusions

Magnetic core-shell **Co@Ni** NPs encapsulated in carbon (**Co@Ni@C**) have been simultaneously used as heating agent and catalyst in the magnetically induced hydrogenation of CO<sub>2</sub> to CO. First, it was concluded that the encapsulation process of the MagNPs by pyrolysis of the carbon-supported **Co@Ni** NPs needs to be carried out at a maximum temperature of 300 °C for two reasons: i) to preserve the core-shell structure of the MagNPs, since at higher temperatures they become alloy type MagNPs; and ii) to keep a large number of cracks/gaps in the carbon layer that favors the accessibility of the substrates to the active metal surface of the catalyst. Catalytic studies on the hydrogenation of CO<sub>2</sub> showed that at low field amplitudes, **Co@Ni@C** produces mixtures of CO:CH<sub>4</sub>, while at higher field amplitudes (*i.e.* 53 mT, T<sub>bulk</sub> = 698 °C) it presents a high conversion and selectivity towards CO (74.2 % conversion and 100 % selectivity), being one of the most active catalysts reported to date (see SI section S10, Table S1). Interestingly, recycling and cyclability studies showed that after exposing **Co@Ni@C** to high magnetic fields (*i.e.* temperatures > 400 °C) it becomes fully selective to CO even at low field amplitudes (or temperatures). Microscopic (STEM-EDX), spectroscopic (XANES and EXAFS) and adsorption/desorption (TPR and TPD) studies have demonstrated that during magnetic catalysis, **Co@Ni@C** undergoes a structural transformation where surface Ni atoms diffuse towards the core of the nanoparticle, losing the core-shell structure and forming MagNPs that resembles an alloy type. However the structure of this alloy is not homogeneous but could contain a gradient of concentration of Cobalt into Nickel. Similar behavior was observed for pure alloy type carbon-encapsulated CoNi NPs (**CoNi@C**), where a change in selectivity was also observed after exposing the catalyst to high field amplitudes. However, the activity of alloy-type CoNi NPs in CO<sub>2</sub> hydrogenation is much lower (51.3 % conversion at 53 mT, 646 °C) due to their lower heating capacity. On the other hand, the monometallic Co catalyst (**Co@C**) is not only the least active catalyst (44.3 % conversion at 53 mT, 635 °C), but also it does not suffer any change in the selectivity at high fields, producing CH<sub>4</sub>:CO mixtures at low fields/temperatures. Thus, we can conclude that **Co@Ni@C** and **CoNi@C** catalysts undergo structural transformations during magnetic catalysis that make them highly selective in the hydrogenation of CO<sub>2</sub> to CO even at low fields/temperatures and we

propose that a gradient of concentration of one metal in the structure of the other be present. Such structures have been previously observed in FeCo NPs and could be interesting in catalysis.

## Acknowledgements

The authors thank Instituto de Tecnología Química (ITQ), Instituto de Investigaciones Químicas (IIQ), Consejo Superior de Investigaciones Científicas (CSIC), Universitat Politècnica de València (UPV) and Universidad de Sevilla (US) for the facilities. We also thank the Electron Microscopy Service of the UPV for TEM analysis. The authors also acknowledge European Union's Horizon 2020 research and innovation program H2020-LC-SC3-2020 (LAURELIN; n°: 101022507), Agencia Estatal de Investigación, Ministerio de Ciencia e Innovación (PID2021-126080OA-I00, TED2021-132087A-I00 and RYC2020-030031-I), Junta de Andalucía (ProyExcel\_00706) and University of Seville (VI PP A.TALENTO; 2022/00000400) for financial support. We gratefully acknowledge Dr. Raf Roelant for his help with thermodynamic equilibrium calculations. C. Cerezo-Navarrete thanks Generalitat Valenciana predoctoral fellowship (GVA: ACIF/2019/076).

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### Graphical Abstract

