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Iron Carbide or Iron Carbide / Cobalt Nanoparticles for Magnetically-Induced CO₂ Hydrogenation over Ni/SiRAIO_x Catalysts

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ABSTRACT. Magnetic nanoparticles have recently been used as heating agents in heterogeneously catalyzed reactions such as CO₂ hydrogenation into methane. In the present work, we explore the potential of heating agents presenting different heating properties in the activation of a supported catalyst based on nickel nanoparticles (NPs) (Ni/SiRAIO_x) for the CO₂ methanation under continuous flow. Two types of Fe_{2.2}C NPs presenting distinct heating properties have been tested. For Fe_{2.2}C NPs displaying lower heating powers of ca. 1 kW·g⁻¹, an activation of the catalyst at a magnetic field amplitude of 80 mT is necessary to achieve high conversion and selectivity, this activation step being attributed to a partial sintering of the Ni NPs. When using Fe_{2.2}C NPs displaying much higher heating powers of 2 kW·g⁻¹ as heating agents, the magnetic field amplitude required to activate the catalyst can be reduced to 48 mT. Finally, we demonstrate that *hard* magnetic materials displaying very low heating power but high Curie temperatures, such as Co nanorods (NRs), can be used as relay heating agents when mixed with small amounts of *softer* materials with high heating power. Thus, by mixing Co NRs with Fe_{2.2}C NPs, excellent catalytic performances (90 % of CO₂ and 100%

CH₄ selectivity) have been obtained after applying only 32 mT to trigger the reaction. Once the reaction initiated, these performances are maintained even after lowering the magnetic field to 16 mT, which is advantageous in terms of energy consumption.

INTRODUCTION

As a consequence of the fast development of global energy consumption, CO₂ emissions are continuously increasing, hence enhancing the greenhouse effect.^{1, 2} Thus, research efforts have as an objective the use of CO₂ as a chemical feedstock to produce platform molecules or fuels.³⁻⁶ A possible way to use CO₂ is the catalytic hydrogenation (Sabatier process^{7, 8}) for methane production, the so-called synthesis of natural gas (SNG). The process is industrially applicable, and favorable in terms of carbon balance, provided that the hydrogen is obtained from renewable and sustainable sources (e.g. photocatalysis or electrocatalysis of water powered by wind/solar energy, biomass, etc.).^{9, 10} CO₂ methanation is a reversible and strongly exothermic reaction.¹¹ Although it is thermodynamically favorable, the high kinetic barrier for the activation of CO₂ is the main challenge to achieve high CH₄ yields at low temperatures.¹²⁻¹⁴ Hence, selecting the appropriate catalyst is the key step to overcome the kinetic limitation. During the past years, several supported metal-based catalysts have been investigated, in particular, transition metals such as Ni, Fe, Co, Ru, Rh, etc. dispersed on various supports like Al₂O₃, SiO₂, TiO₂, ZrO₂, CeO₂, etc.^{11, 15} Among them, Ni based catalysts are the most widely studied due to the best trade-off between activity and cost.¹⁶ Traditionally, CO₂ methanation is performed in a continuous flow reactor using conventional heating.

Magnetic hyperthermia has been applied in the field of cancer therapy,¹⁷⁻²⁰ but it has been shown recently that the same principle can also be advantageously applied in heterogeneous catalysis.²¹⁻²⁹ The concept is based on the fact that ferromagnetic materials placed in a high-frequency alternating magnetic field release heat through hysteresis losses. Hence, by using

magnetic nanoparticles (NPs) the heat is directly and homogeneously distributed within the catalyst without the need for heating the whole reactor system. In addition, magnetic induction heating allows reaching the target temperature in a few seconds, which makes the system well-adapted to intermittent energies. Magnetically induced catalysis requires the design of catalytic systems combining good heating capacity with high catalytic activity. The heating efficiency of metallic NPs is quantified by the specific absorption rate (SAR), which represents the amount of energy absorbed per unit of mass in the presence of an alternating magnetic field and can be measured in units of watts per gram of metal ($\text{W}\cdot\text{g}^{-1}$). Recently, we have reported the synthesis of FeCx NPs with ca. 15 nm mean size displaying much higher heating properties than any previously described material. The NPs were synthesized by the carbidization of pre-formed monodisperse Fe(0) NPs by a mixture of *syngas* (CO/H₂). The very high SAR values were ascribed to the presence of crystalline Fe_{2.2}C.^{26,30}

However, the heating power of magnetic materials is reduced with increasing temperature as a result of the reduction of the area of the hysteresis loop and becomes zero at the Curie Temperature. For FeCx, the Curie temperature (T_C) is close to 450 °C^{31,32}, depending on the exact stoichiometry of the carbide and therefore, the heating power will start to decrease at high temperatures. Thus, ferromagnetic materials with higher T_C values may retain a large enough coercive field to allow efficient heating at lower magnetic field amplitudes even at high temperature. For example, Co is a *hard* magnetic material with a high magnetocrystalline anisotropy and a high Curie Temperature ($T_C > 1000$ °C³³), which would require at room temperature very high field amplitudes to release heat and, therefore, which cannot be used for heat production. However, by combining *hard* and *soft* magnetic materials in a single hybrid object,³⁴ the anisotropy of the whole system may be reduced, leading to a material that would be activated at lower magnetic field amplitudes.^{35,36} A different configuration would be a simple mixing of *hard* and *soft* nanomaterials that do not interact directly and which

could allow upon magnetic excitation a pre-heating of the *hard* material through the heat released by the soft material. This would in turn decrease the coercivity of the *hard* material and render magnetic heating by the *hard* heating agent possible. In this respect, *hcp*-Co nanorods (Co NRs) previously prepared in our laboratory are good candidates to act as a *hard* ferromagnetic material, as they possess high magnetocrystalline and shape anisotropies, and hence high values of coercive fields (H_c).^{37, 38} $Fe_{2.2}C$ NPs could then function as “starters” for reaching the temperature above which Co NRs can be easily activated by lower magnetic fields.

In a previous report from our group, we have demonstrated the possibility to magnetically induce CO_2 methanation in a continuous-flow reactor.²⁶ In that work, core@shell $Fe_{2.2}C@Ni$ NPs/SiRAIOx led to solely 50% of CO_2 conversion with a CH_4 yield of 15% when applying 40 mT. However, a catalyst composed of Ru NPs supported on SiRAIOx on which $Fe_{2.2}C$ NPs were present but without being directly associated to Ru, presented 93% of CO_2 conversion with a 100% selectivity to CH_4 , when activated by an external magnetic field of only 28 mT. Therefore, a direct contact between the heating agent ($Fe_{2.2}C$ NPs) and the catalyst Ru NPs is not indispensable for obtaining good catalytic performances.

Considering that Ni is a good catalyst for the Sabatier reaction, and that a mixture of $Fe_{2.2}C$ NPs and Ni NPs immobilized on SiRAIOx ($Fe_{2.2}C/Ni/SiRAIOx$) is a simpler system than the one based on $Fe_{2.2}C@Ni$ NPs immobilized on SiRAIOx, in the present study and in search for an optimized system, we have designed a new catalytic system consisting of Ni NPs supported on SiRAIOx (**Ni/SiRAIOx**) which was associated to $Fe_{2.2}C$ NPs as a heating agent. The catalytic activity has been assessed as a function of the SAR values of $Fe_{2.2}C$ NPs and the presence or not of a pre-activation step for **Ni/SiRAIOx**. Furthermore, we explore here the concept of implementing *hard* magnetic *hcp*-Co NRs as a stable heating source by using small amounts of a *soft* magnetic material ($Fe_{2.2}C$ NPs) as initiators.

RESULTS AND DISCUSSION

Catalytic activity of Ni/SiRAIOx in CO₂ hydrogenation through conventional heating.

Ni/SiRAIOx was prepared simply by heating a mesitylene solution of Ni(COD)₂ at 150°C (see Experimental Section and Fig. S1 ESI†) in the presence of the support. The Scanning Transmission Electron Microscopy (STEM) images of **Ni/SiRAIOx** (Fig. S2) show the presence of crystalline Ni NPs on SiRAIOx. To confirm the metal composition and distribution of this phase along the SiRAIOx support, TEM and STEM-HAADF (High Angle Annular Dark Field) images combined with Energy-Dispersive X-Ray Spectroscopy (EDX) were recorded (Fig. S3), revealing the presence of Ni NPs with a mean size of 2-3 nm over the whole support.

The **Ni/SiRAIOx** catalyst (400 mg) was first tested in a conventional heating set-up. The catalytic activity was evaluated at ambient pressure in the temperature range of 300 °C to 450 °C (Fig. 1). A H₂:CO₂ molar ratio of 4:1 in a continuous flow set-up, with a total flow rate of 25 mL·min⁻¹, was used throughout the experiment.

The results show that **Ni/SiRAIOx** is an active catalyst for CO₂ hydrogenation, the optimal global temperature of the catalyst (for conversions higher than 80%) being above 300 °C. Increasing the temperature from 300 °C to 400 °C leads to an increase in CO₂ conversion with the simultaneous enhancement in CH₄ yield. A very high CO₂ conversion (> 95%) was observed at a set up temperature of 400 °C (376 °C measured by a thermocouple inside the reactor), with almost 99% selectivity to CH₄ formation. Further increase in temperature to 450 °C had no important influence on the reaction. Thanks to the presence of a water trap in the reactor, water removal shifts the equilibrium toward the formation of CH₄, thus, conversion

values are better than the anticipated ones based on the thermodynamic equilibrium values (description of the reactor is given in ESI-14).

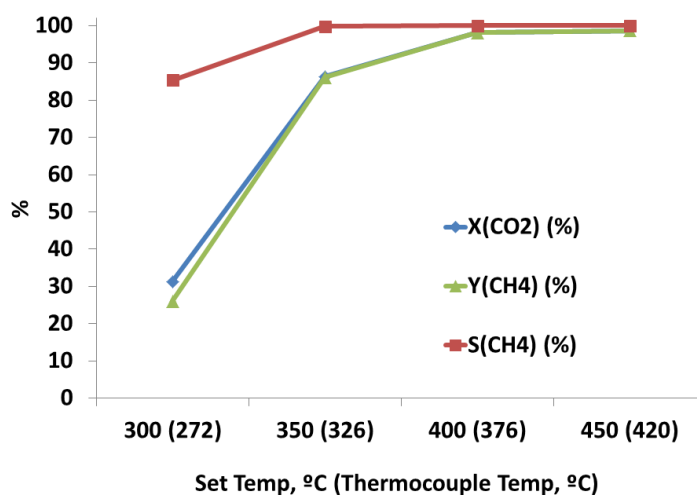


Figure 1. Catalytic results with Ni/SiRAIOx as a function of temperature in conventional heating.

Catalytic activity of Ni/SiRAIOx in CO₂ hydrogenation by magnetic heat induction

Three different magnetic heating agents were used in the following catalytic experiments, two types of Fe_{2.2}C NPs and *hcp*-Co NRs. Fe_{2.2}C NPs with a mean size of ca. 14-15 nm were synthesized through carbidization of pre-formed Fe(0) NPs of ca. 12.5 nm (see Fig. S4-6) under *syngas* (CO:H₂) following a recently described procedure (see Experimental Section). In our previous work, we have observed that dipolar couplings strongly affect the heating power displayed by Fe_{2.2}C NPs. Thus, the SAR of the Fe_{2.2}C NPs can be modulated by adjusting the amount of ligands at the beginning of the carbidization which permits preparing NPs with controllable heating powers.³⁹ In this respect Fe_{2.2}C NPs displaying SAR values of ca. 1100 W·g⁻¹ (**FeC-1**) and ca. 2100 W·g⁻¹ (**FeC-2**) were synthesized, both measured at 47 mT with a frequency of 93 kHz (see Fig. S7-14). *hcp*-Co NRs were prepared following a previously reported method⁴⁰ (see Experimental Section and Fig. S15-16). Three catalytic

mixtures were tested. They were composed of the above-mentioned **Ni/SiRAIOx** catalyst which was then mixed (i) with Fe_{2.2}C NPs, (ii) with *hcp*-Co NRs and (iii) with both Fe_{2.2}C NPs and *hcp*-Co NRs (see Experimental section for details). The list of these catalysts and their abbreviations along with the corresponding ICP analyses are given in Table 1.

The CO₂ hydrogenation activity of the prepared samples was evaluated in a glass reactor (Internal Diameter of 1 cm) with a H₂:CO₂ molar ratio of 4:1 in a continuous flow under ambient pressure using an alternating magnetic field oscillating at a frequency (*f*) of 300 kHz. The total flow rate was set to 25 mL·min⁻¹ throughout the experiments. The magnetic field was varied between 0 and 80 mT, and for each amplitude value it was maintained constant for one hour during which 3 injections into the Gas Chromatograph (GC) were performed.

Table 1. List of catalysts and their abbreviations used in the CO₂ methanation and ICP analyses.

No	Catalysts	Name	wt%	wt%	wt%
			Fe	Ni	Co
1	Ni/SiRAIOx	Ni/SiRAIOx	-	9.86	-
2	Ni/SiRAIOxpre-activated ^a	Ni-pre	-	n. a.	
3	FeC-1 (SAR~1100 W·g ⁻¹) ^b on Ni/SiRAIOx	FeC-1/Ni	9.57	7.31	-
4	FeC-2 (SAR~2100 W·g ⁻¹) ^b on Ni/SiRAIOx	FeC-2/Ni	8.92	7.01	-
5	FeC-1 (SAR~1100 W·g ⁻¹) on Ni-pre	FeC-1/Ni-pre	6.83	6.37	-
6	Co-NRs on Ni/SiRAIOx	Co/Ni	-	-	9 ^c
7	Co-NRs on Ni/SiRAIOx + FeC-1 (SAR~1100 W·g ⁻¹) on SiRAIOx	Co-FeC-1/Ni	1.45	5.86	6.60

a) Pre-activated in the oven at 400 °C. b) SAR measured in mesitylene solution at a $\mu_0 H_{rms}$ of 47 mT and a *f* of 93 kHz. c) Estimated from Thermogravimetric Analysis

Fe_{2.2}C NPs as heating agent supported on Ni/SiAlOx as catalyst (FeC/Ni) in magnetically induced CO₂ hydrogenation

The first configuration was explored with the two types of Fe_{2.2}C NPs (**FeC-1** and **FeC-2**) described hereabove and differing by their heating capacities. The catalysts were elaborated by supporting Fe_{2.2}C NPs on **Ni/SiAlOx** hereafter called **FeC-1/Ni** and **FeC-2/Ni** (see Figures S17-18). First, we studied the CO₂ hydrogenation under continuous flow using 400 mg of **FeC-1/Ni** as catalyst. The Fe_{2.2}C loadings were fixed to 10 wt%, as this concentration is close to the minimum required to activate the reaction.²⁶ Heating agent loadings of 5 wt% were not enough to reach the working temperatures (see below), whereas Fe_{2.2}C loadings above 10 wt% did not have a significant influence on the CO₂ conversion. The temperature at the surface of the reactor was monitored using an infrared (IR) camera (see ESI-14). The magnetic field amplitude was set to 48 mT, a value at which the reactor temperature measured by the IR camera was found in the range of 240-260 °C. A rather low (35%) CO₂ conversion was obtained, although the catalyst was highly selective towards CH₄ formation. Subsequently, the magnetic field was set to 80 mT, where the catalyst showed a remarkable improvement in CO₂ conversion to 85% with a 99% selectivity to CH₄. At this point the temperature measured by thermal camera was 280 °C. It should be noted that the local temperature at the surface of the catalyst must be well-above that measured with the thermal camera. Thus, to obtain a similar conversion through conventional heating an oven temperature of 350 °C should be set (see Fig 1). Interestingly, after this step, the reaction temperature, the CO₂ conversion and the selectivity for CH₄ remained stable even upon reducing the magnetic field down to 48 mT. As the global temperature of the reactor was comparable when applying a $\mu_0 H_{rms}$ of 48 or 80 mT, and the temperature necessary to activate CO₂ was reached at 48 mT before increasing the magnetic field up to 80 mT, the

improvement of the performance after activation of the catalyst is probably related to a change in the catalyst structure. This fact indicates that there is an induction step that corresponds to the activation of the catalyst. After catalyst activation, the catalytic activity was evaluated by varying the magnetic field from 16 mT to 80 mT, maintaining each value constant for at least 45 minutes (see Figure 2a). The CO₂ conversion was found to be above 70% in all the cases and a maximum value of 85% was obtained at 48 mT. The CH₄ selectivity was above 99% even at low magnetic field amplitudes. Finally, the stability of the catalyst **FeC-1/Ni** was evaluated by stopping the application of the magnetic field, stopping the CO₂ flow and cooling down to room temperature under inert atmosphere, and then restarting. The system maintained its catalytic activity exhibiting the same reaction profile as a function of the magnetic field but without the need for catalyst activation.

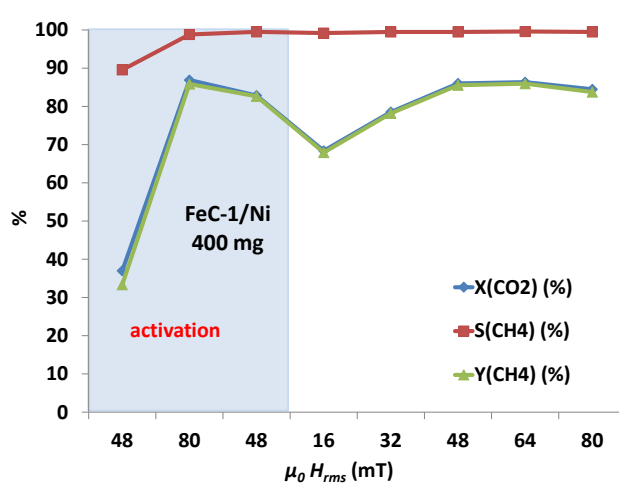


Figure 2. Magnetically induced hydrogenation of CO₂ using Fe_{2.2}C NPs **FeC-1** as heating agents. CO₂ conversion, CH₄ yield and CH₄ selectivity as a function of magnetic field when using 400 mg of catalyst.

The residence time or weight hour space velocity (WHSV) of the gas flow was optimized for **FeC-1** (see Fig. S19). When using 300 mg of the **FeC-1/Ni** catalyst (ca. 1.2 cm of catalyst-bed

height), a significant decrease in CO₂ conversion (35%), CH₄ yield (30%) and CH₄ selectivity (70-80%) was observed both at 48 and 80 mT, producing CO as by-product. However, the temperature of the reactor was similar to that measured when employing 400 mg of catalyst, suggesting that the differences were more related to WHSV rather than to the temperature. In addition, the catalyst notably improved its performance after addition of 100 mg of the same batch of **FeC-1/Ni**. When performing the reaction using 600 mg of the catalyst **FeC-1/Ni** (ca. 2.3 cm of length), CO₂ conversion and CH₄ selectivity reached values of 88% and 99% respectively at 48 mT, without the need of any activation of the catalyst at 80 mT. Further variation on the magnetic field did not affect the performance of the catalyst.

TEM images of the spent catalysts (see Fig. S20-22) evidence changes in their morphology (see Fig. 3). STEM-BF, STEM-HAADF and EDX images show that Fe is present in large particles between 20 and 200 nm homogeneously distributed throughout the SiRAIOx support whereas Ni is mainly concentrated in big polydisperse aggregates of 5-100 nm (see Figure 3c and d) due to sintering of the Ni NPs at the high temperatures induced by the applied magnetic field.

Assuming that sintering of the NPs plays a role in the performance of the catalysts, **Ni/SiRAIOx** was thermally pre-treated in the presence of H₂ for 1 h at 400 °C, a temperature similar to the global temperature reached during the catalytic experiments, to give the sample **Ni-pre**. As can be observed by TEM and STEM-EDX mapping (see Fig. S23-25), a coalescence of the Ni NPs occurred to give big nano-objects in the range of 5-50 nm. **FeC-1** NPs were subsequently supported on **Ni-pre** and 400 mg of **FeC-1/Ni-pre** catalyst (see Fig. S26-28) were evaluated in CO₂ hydrogenation under the same conditions of flow and magnetic field previously described. Interestingly, CO₂ conversion was 73% with nearly 100% selectivity to CH₄ at 48 mT (see figure 4). The catalyst was then submitted to different magnetic fields (16 mT to 80 mT). A remarkable CO₂ conversion of 80% was obtained at 16

mT further supporting that the activation step needed for **the FeC-1/Ni** catalyst is linked to the sintering of Ni. This is in agreement with a recent report which showed that larger Ni NPs can afford better conversions in CO₂ methanation because CO adsorption, which is the rate-limiting step, is more efficient in that case.⁴¹

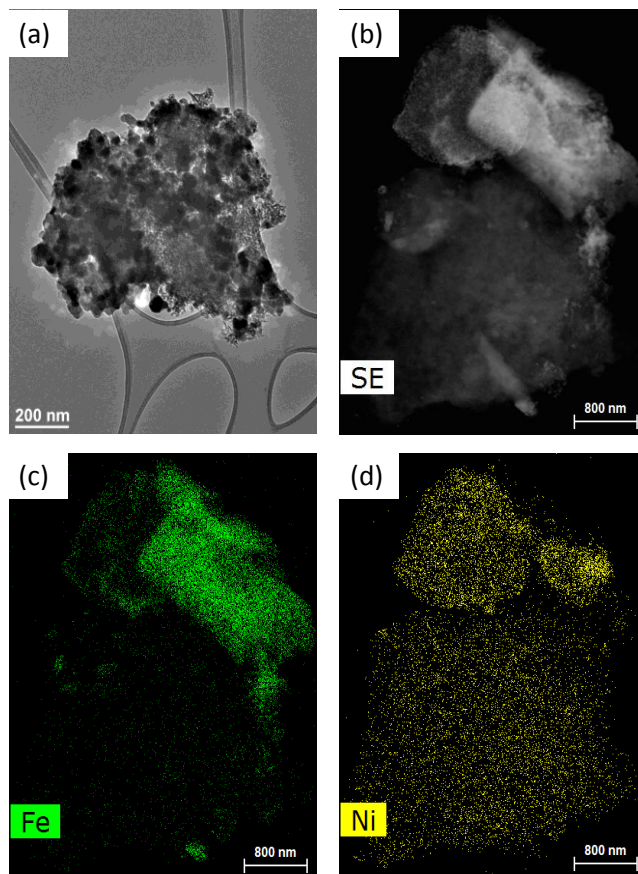


Figure 3. Characterization by HR-TEM of FeC-1/Ni after catalysis: (a) STEM-BF (Bright field) (b) STEM-HAADF (High angle annular dark field) and (c-d) EDX mapping showing the elements (c) Fe and (d) Ni.

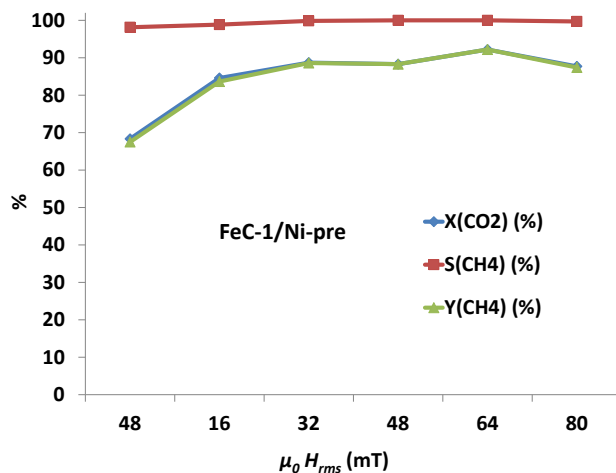


Figure 4. Magnetically induced hydrogenation of CO₂ using **FeC-1/Ni-pre** as catalyst.

Having optimized the catalytic procedure, we then evaluated the performance of the **FeC-2/Ni** catalyst in which the iron carbide NPs display a much better SAR value of ca. 2100 W·g⁻¹. High CO₂ conversion (94%) and CH₄ selectivity (97%) were obtained, even when a magnetic field of 48 mT was directly applied without previous activation at 80mT. The reaction temperatures measured by thermal camera are in the same range (280-300 °C) as for **FeC-1/Ni** after the activation step. Increasing the magnetic field amplitude to 80 mT did not result in significant changes neither in the reaction temperature, nor in the CO₂ conversion and CH₄ selectivity, and these performances remained stable when decreasing the field back to 48 mT (Figure 5). These results indicate that, in contrast to **FeC-1/Ni**, the **FeC-2/Ni** sample reaches its maximum catalytic performance at lower magnetic field amplitudes (48mT) when using 400 mg of catalyst. As in the previous case, the catalytic activity was further investigated by gradually varying the magnetic field from 16 mT to 80 mT. The CH₄ selectivity reaches 100% above 32 mT with only a slight variation in CO₂ conversion, which was of more than 90% in all the cases. The catalyst was also found to be more active at 16 mT than **FeC-1/Ni**.

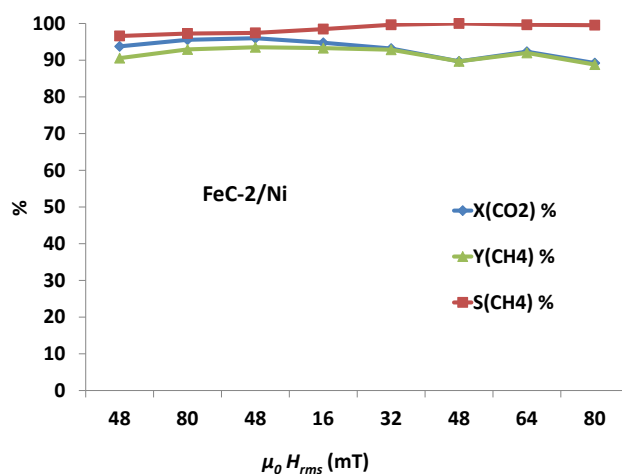


Figure 5. Magnetically induced hydrogenation of CO₂ using **FeC-2/Ni** as catalyst.

TEM micrographs evidenced that, similarly to **FeC-1/Ni**, **FeC-2/Ni** NPs were completely sintered after the catalytic reaction (see Fig S29). The rather small differences in the catalytic activity between **FeC-1/Ni-pre** and **FeC-2/Ni** in the long term (85% and 90% of CO₂ conversion at 16 mT for **FeC-1/Ni-pre** and **FeC-2/Ni**, respectively) suggest that the SAR of Fe_{2.2}C NPs does not dramatically affect the performances of the catalyst once activated. However, the advantage of using Fe_{2.2}C NPs with a higher SAR is the absence of activation step.

Co NRs supported on Ni/SiRAIOx as heating agent in magnetically induced CO₂ hydrogenation.

Aiming at exploring other nanomaterials as heating agents for magnetically induced catalysis, Co NRs were assessed as they possess a high T_C (> 1000 °C) in contrast to Fe_{2.2}C NPs. Briefly, pre-synthesized Co NRs of ca. 80-90 nm length (see Experimental Section for synthesis details and SI for TEM and Vibrating Sample Magnetometry characterization, Fig. S15-16), were supported on **Ni/SiRAIOx** to afford the catalyst **Co/Ni** (Fig. S30). 300 mg of the latter were placed inside the glass reactor and 25 mL·min⁻¹ of a 4:1 mixture of H₂:CO₂

were flowed through. Although the magnetic field was varied from 0 to the highest possible value, i.e. 80 mT, as expected, no variation of the temperature was observed during the experiment (see Fig. 6). Thus, owing to their high magnetocrystalline and shape anisotropies, Co NRs need much higher applied magnetic fields to start the rotation of the magnetic moment which is fixed along the easy magnetization axis (the long axis of the nanorod). Given that the magnetocrystalline anisotropy decreases with temperature, it is reasonable to anticipate that at higher temperature, the rotation of the magnetic moment of the NRs could be triggered, enabling the use of Co NRs as heating agents. For this to occur, a magnetically softer heating source, namely Fe_{2.2}C NPs, should act as a preheating agent of the Co NRs. Hence, 300 mg of Co-NRs on **Ni/SiRAIO_x (Co/Ni)** and 100 mg of **FeC-1/SiRAIO_x** were mechanically mixed to give the catalyst **Co-FeC-1/Ni**. The latter was placed inside the reactor in the presence of a CO₂/H₂ flow and submitted to a magnetic field of 32 mT, which was the minimum field required to activate the system. Under these conditions, the measured temperature increased up to 280-300 °C, leading to 88% of CO₂ conversion and 97% selectivity to CH₄ (see Fig 7). Importantly, by subsequently decreasing the magnetic field down to 16 mT, both CO₂ conversion (90%) and selectivity to CH₄ (100%) increased, even though the measured temperature slightly decreased (260 °C). As T_c for Co is above the melting point of the glass and to avoid reactor melting, the field amplitude was not increased further. As a control experiment, the reaction was carried out under the same conditions after mixing 200 mg of **Ni/SiRAIO_x** and 200 mg of **FeC-1/Ni** (approx. 5 wt% of Fe). In this case, the measured temperatures were always below 200 °C and marginal CO₂ conversions were obtained (less than 5%). This experiment demonstrates that Co NRs are acting as relay heating agent for CO₂ hydrogenation. **Co-FeC-1/Ni** is envisaged as a good catalyst candidate for chemical reactions requiring high temperatures, such as methane dry reforming. The stability of **Co-FeC-1/Ni** catalyst over time was evaluated at 16 mT for 2 hours. A slight

decrease in CO₂ conversion, probably related to water accumulation in the reactor trap, was observed. After the catalysis, Co NRs and Fe_{2.2}C NPs are no longer present, only big nano-objects being observed (Fig. S31).

Finally, 400 mg of the **Co-FeC-1/Ni** catalyst were evaluated in CO₂ hydrogenation through conventional heating under the same values of flow rate. The reaction profile as a function of temperature of **Co-FeC-1/Ni** was comparable to the one obtained with the **Ni/SiRAIOx** (see Fig S32), although the selectivity to CH₄ was slightly lower at high temperatures (ca. 95% at T=380 °C). These results suggest that the presence of Fe_{2.2}C NPs and Co NRs does not have a strong influence on the catalytic performance of **Ni/SiRAIOx**.

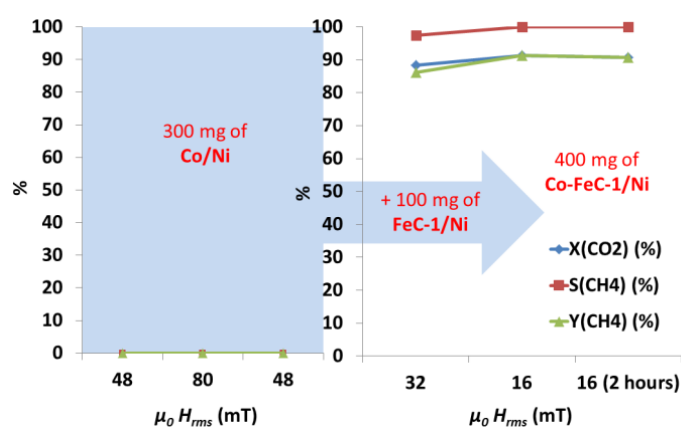


Figure 6. Magnetically induced hydrogenation of CO₂ using **Co/Ni** and **Co-FeC-1/Ni** as catalysts.

CONCLUSIONS

In this study, we show that magnetically induced heating can trigger CO₂ methanation catalyzed by supported Ni catalysts. Once the temperature needed for the reaction onset is reached, the energy is directly transferred to the catalyst, and the warming up of the reactor (20-30 seconds) is fast without the need to heat the reactor walls. The choice of the heating agent determines the magnetic field amplitude necessary for the catalyst to become

operational. As heating agents, we have used either *soft* magnetic Fe_{2.2}C NPs or the combination of Fe_{2.2}C NPs with the *hard* magnetic *hcp*-Co NRs (**Co-FeC-1/Ni**). In contrast to the Fe_{2.2}C@Ni NPs previously reported by our group, where both the catalytic and the heating agent were part of a single nano-object, in the current systems the two components are separated, which constitutes an advantage as this system is a simpler catalyst. Furthermore, combining a magnetically hard (Co NRs) and a magnetically soft material (Fe_{2.2}C NPs) as heating agents permits exploiting the soft material to attain a temperature necessary for the hard material to start heating. Thus, for the combined **Co-FeC-1/Ni** system, excellent catalytic performances (90 % of CO₂ and 100% CH₄ selectivity) are achieved even at a very low field, namely 16 mT. This value allows a reduction of energy by a factor of 2. Optimization of the reaction conditions has allowed to improve the performance of the magnetically induced CO₂ methanation (low magnetic fields and small amounts of catalysts). Last but not least, as the T_c of Co overpasses 1000 °C, this combined material is a promising catalyst for chemical reactions requiring high temperatures such as methane reforming.

CONFLICTS OF INTEREST

The authors declare no conflict of interest

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