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ARTICLE

CO₂ Methanation over Ni/SiRAlOx Catalyst Using Magnetic Nanoparticles as a Magnetically-Induced Heating Source

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In this work, we explore the versatility of Nickel nanoparticles (NPs) supported on SiRAlOx (Ni/SiRAlOx) as catalysts in the CO₂ methanation under continuous flow. The reaction was activated by magnetic heating using Fe_{2.2}C NPs as heating agent. The combination between the good heating power of the Fe_{2.2}C NPs and the good activity of the Ni NPs allowed us to reach very high CO₂ conversions (>90%) with 100% selectivity to CH₄ after application of alternating magnetic fields oscillating at a frequency of 300 kHz. 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 values, and this activation step seems to be related to a 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 magnetic materials displaying very low values of SAR but high T_c, such as Co nano-rods (NRs), can be used as heating agents in magnetic-induced catalysis after addition of small amounts of *softer* materials with good heating power such as Fe_{2.2}C NPs. Excellent catalytic performances (90% of CO₂ and 100% CH₄ selectivity) have been obtained after applying only 32 mT at 300 kHz to trigger the reaction, suggesting that T_c also plays an important role on the catalytic performance. The excellent conversions were maintained for 2 hours by adjusting the magnetic field at 16 mT, which can be highly advantageous in terms of energy consumption.

Introduction

As a consequence of the increase in global energy consumption, CO₂ emissions are continuously increasing, which contributes to the greenhouse effect.^{1,2} The reduction of CO₂ levels, in order to minimize its negative impact, has incited the development of new technologies which make an effective use of renewable energy sources. In parallel, several research efforts have as an objective the utilization of CO₂ to produce platform molecules or fuels.³⁻⁵ In addition, the use of CO₂ as a chemical feedstock has other advantages as it constitutes a highly functional, inexpensive, renewable and environmentally friendly reagent.⁶ A possible way to use CO₂ is the catalytic hydrogenation (also known as the 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. photocatalytic or electrocatalytic water powered by wind/solar energy, biomass,

etc.).^{9,10} Besides, SNG can be further used as a fuel or a feedstock for chemical production. CO₂ methanation is a reversible and strongly exothermic reaction.¹¹ Although CO₂ methanation is thermodynamically favorable, the high kinetic barrier for the activation of the CO₂ molecule 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 the best trade-off between activity and cost.¹⁶ Traditionally, CO₂ methanation is performed in a continuous flow reactor using conventional heating, which consumes a high amount of energy.

Magnetic hyperthermia has been applied in the field of cancer therapy,¹⁷⁻²⁰ but it has been shown recently that it can also be advantageously applied in heterogeneous catalysis.²¹⁻²⁸ 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 of heating the whole reactor system. In addition, magnetic induction heating allows reaching the target temperature in a few seconds, which makes the system suitable to energetic intermittence, a main

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characteristic of renewable sources. Magnetically induced catalysis requires the design of catalytic systems combining good heating capability with high catalytic activity. The heating efficiency of metallic NPs is usually quantified by the specific absorption rate (SAR), which describes 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 Fe_xC NPs with a mean size of ca. 15 nm displaying far larger heating properties than any previously described material. The NPs were synthesized by the carbidization of pre-formed monodisperse $\text{Fe}(0)$ NPs with a mixture of *syngas* (CO/H_2). The very high SAR values were ascribed to the presence of crystalline $\text{Fe}_{2.2}\text{C}$.^{26,29}

Nevertheless, despite their high values of SAR, $\text{Fe}_{2.2}\text{C}$ NPs may not be the best choice as heating source for chemical reactions taking place at elevated temperatures since the heating properties of magnetic materials disappear above their Curie Temperature (for $\text{Fe}_{2.2}\text{C}$, $T_c \sim 450$ °C^{30,31}). Thus, ferromagnetic materials with higher T_c values, for instance, Co ($T_c > 1000$ °C³²) seem more suitable. Co is a “hard” magnetic material with a high magnetocrystalline anisotropy which requires elevated frequency and amplitude values of the applied magnetic field to release heat and therefore makes this heating source energetically unfavorable. However, by combining “hard” and “soft” magnetic materials in a single hybrid object,³³ the anisotropy of the whole system may be reduced leading to a material that would be activated at lower magnetic field amplitudes.^{34,35} Moreover, physical mixing of hard and soft materials could allow upon magnetic excitation a pre-heating of the hard material through the heat released by the soft material which would in turn render magnetic heating by the hard material possible, without the need to combine the two metals in a single nano-object. Thus, when temperature increases, the remaining energy barrier can become small enough for the magnetic moment to be returned by a small magnetic field. 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).^{36,37} This high value of H_c prevents heating upon application of a small alternating magnetic field but heating could be triggered at higher temperature, as H_c is reduced as temperature increases.

In a previous report from our group, we have demonstrated the possibility to magnetically induce CO_2 methanation in a continuous-flow reactor.²⁶ The catalyst used was composed of Ru NPs (1 wt% of Ru) supported on SiAlOx on which $\text{Fe}_{2.2}\text{C}$ NPs acting as heating agents were also present. By applying an external magnetic field of 28 mT this catalyst presented 93% of CO_2 conversion with a 100% selectivity to CH_4 . In the same work, core@shell $\text{Fe}_{2.2}\text{C}/\text{Ni}$ NPs led to solely 50% of CO_2 conversion with a CH_4 yield of 15% when applying 40 mT. Encouraged by the results obtained through the combination of $\text{Fe}_{2.2}\text{C}$ and Ru NPs, in the present study and in search for an optimized system, we have designed a new catalytic system consisting of Ni NPs supported on SiAlOx (Ni/ SiAlOx), which was associated to

$\text{Fe}_{2.2}\text{C}$ NPs, also supported on SiAlOx as a heating agent. The catalytic activity has been assessed as a function of the residence time, SAR values of $\text{Fe}_{2.2}\text{C}$ NPs and the presence or not of a pre-activation step for Ni/ SiAlOx . Furthermore, we demonstrate the concept of using *hard* magnetic *hcp*-Co NRs as a heating source by adding small amounts of a *softer* magnetic material ($\text{Fe}_{2.2}\text{C}$ NPs) as initiators.

Results and Discussion

Catalytic activity of Ni/ SiAlOx in CO_2 hydrogenation through conventional heating.

Judging from our previous results obtained with the Ru NPs deposited on $\text{Fe}_{2.2}\text{C}$ NPs/ SiAlOx ²⁶ it was found that a direct contact between the heating agent ($\text{Fe}_{2.2}\text{C}$ NPs) and the catalyst Ru NPs was not essential to obtain good catalytic performances. Considering that Ni is known to be a good catalyst in the Sabatier reaction, and that a mixture of $\text{Fe}_{2.2}\text{C}$ NPs and Ni NPs immobilized on SiAlOx ($\text{Fe}_{2.2}\text{C}/\text{Ni}/\text{SiAlOx}$) is a simpler system than the one based on $\text{Fe}_{2.2}\text{C}/\text{Ni}$ NPs immobilized on SiAlOx , a first survey using conventional heating on the effect of the deposition of Ni NPs on SiAlOx (Ni/ SiAlOx) was carried out.

Ni/ SiAlOx was prepared simply by heating a mesitylene solution of $\text{Ni}(\text{COD})_2$ at 150 °C (see Experimental Section and Fig. S1) in the presence of the support. The Scanning Transmission Electron Microscopy (STEM) images of Ni/ SiAlOx (Fig. S2) show the presence of Ni crystalline phase on the SiAlOx . To confirm the metal composition and distribution of this phase along the SiAlOx 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/ SiAlOx catalyst (400 mg) was first tested in a conventional heating set-up. The catalytic activity was tested at ambient pressure in the temperature range of 300 °C to 450 °C (Fig. 1). A $\text{H}_2:\text{CO}_2$ molar ratio of 4:1 in a continuous flow set-up, using a total flow rate of $25 \text{ mL}\cdot\text{min}^{-1}$, was used throughout the experiment.

These results show that Ni/ SiAlOx is an active catalyst in CO_2 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 led to an increase in CO_2 conversion with the simultaneous enhancement in CH_4 yield. A very high CO_2 conversion (> 95%) was observed at a set up temperature of 400 °C (376 °C measured by the thermocouple inside the reactor), with almost 99% selectivity to CH_4 formation. Further increase in temperature to 450 °C had no important influence on the reaction. The conversion values were better than anticipated from the thermodynamic equilibrium, presumably thanks to the presence of a water trap in the reactor. Removal of water assists the shifting of the equilibrium toward the formation of CH_4 .

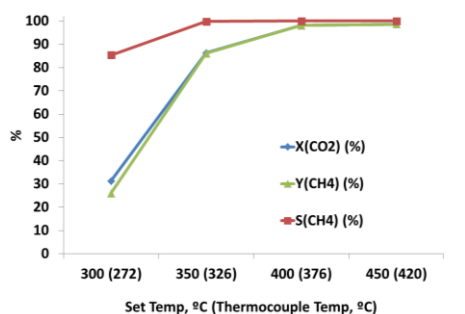


Figure 1. Catalytic results with Ni/SiRAIOx as a function of temperature in conventional heating.

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 self-citation 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 a *syngas* mixture (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 the 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 allows preparing NPs with controllable heating powers. In this respect Fe_{2.2}C NPs displaying SAR values of ~1100 W·g⁻¹ (FeC-1) and ~2100 W·g⁻¹ (FeC-2), both measured at 47 mT with a frequency of 93 kHz (see Fig. S7–14) were synthesized. *hcp*-Co NRs were prepared following a previously reported method³⁸ (see Experimental Section and Fig. S15–16). Ni/SiRAIOx was mixed with Fe_{2.2}C NPs, with *hcp*-Co NRs or with both (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 magnetic field was varied between 0 and 80 mT, and the total flow rate was set to 25 mL·min⁻¹ throughout the experiments. The magnetic field 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% Fe	wt% Ni	wt% Co
1	Ni/SiRAIOx	Ni/SiRAIOx	-	9.86	-
2	Ni/SiRAIOx pre-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/SiRAIOx as catalyst (FeC/Ni) in magnetically induced CO₂ hydrogenation

The catalysts were elaborated by supporting Fe_{2.2}C NPs (FeC-1/Ni and FeC-2/Ni) on Ni/SiRAIOx (see Figures S17–18). First, we studied the CO₂ hydrogenation under continuous flow using 400 mg of FeC-1/Ni as catalyst. The magnetic field amplitude was set to 48 mT, a value at which the reactor temperature measured by an IR camera was 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 of 280 °C. Interestingly, after this step, the reaction temperature, CO₂ conversion and selectivity to CH₄ remained stable even upon reducing the magnetic field down to 48 mT. This fact indicates that there is an induction step that corresponds to the activation of the catalyst. 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 in magnetic field up to 80 mT (see section 2.1), the improvement of the performance after activation of the catalyst is probably related to a change in the catalyst structure. It should be noted that the local temperature at the surface catalyst must be well-above to that measured with the thermal camera. 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 above 70% in all the cases and a maximum value of 85% obtained at 48 mT. The CH₄ selectivity was found 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

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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.

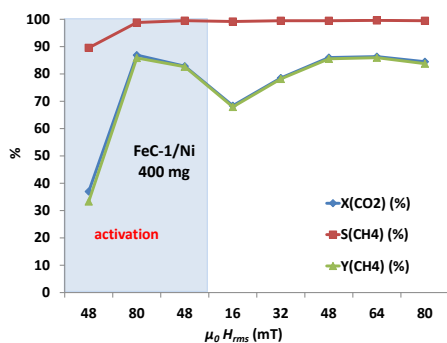


Figure 2. Magnetically induced hydrogenation of CO₂ using Fe₂C NPs FeC-1 as heating agents. CO₂ conversion, CH₄ yield and CH₄ selectivity as a function of magnetic field when using 400 mg of catalyst.

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 (~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 (~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 catalysts (see Fig. S20-22) after the catalytic reaction 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 SiRAlOx support whereas Ni is mainly concentrated in big polydisperse aggregates of 5-100 nm (see Figure 3c and d) in agreement with a sintering of the Ni NPs at high temperatures after applying the magnetic field.

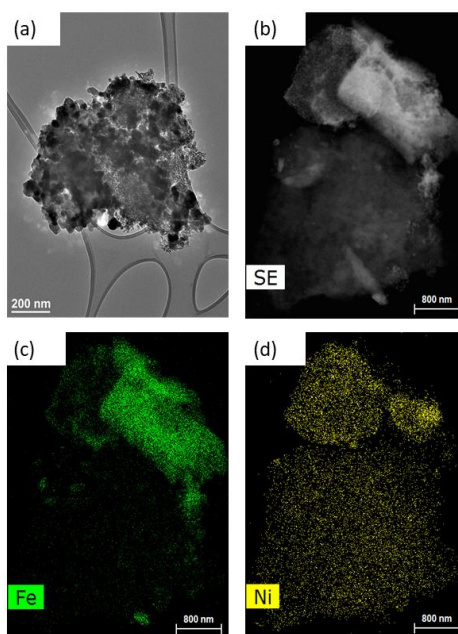


Figure 3. Characterization by HR-TEM of FeC-1/Ni after catalysis: (a) STEM-BF (Bright field) (b) STEM-HAADF (High angle annular dark field) and (c-d) EDX mapping showing the elements (c) Fe and (d) Ni.

Assuming that sintering of the NPs plays a role in the performance of the catalysts, Ni/SiRAlOx 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 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 of 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 indicating that the activation step needed for sample FeC-1/Ni is linked to the sintering of Ni 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.³⁹

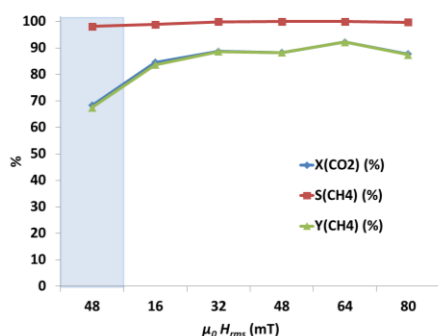


Figure 4. Magnetically induced hydrogenation of CO₂ using FeC-1/Ni-pre as catalyst.

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, as heating agents for CO₂ methanation catalysed by Ni/SiAlOx. High CO₂ conversion (94%) and CH₄ selectivity (97%) were found, even when a magnetic field of 48 mT was applied directly without previous activation at 80 mT. The reaction temperatures 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 (48 mT) 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.

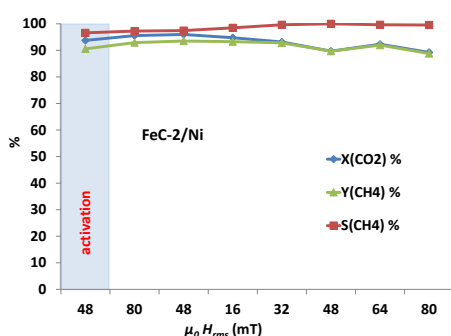


Figure 5. Magnetically induced hydrogenation of CO₂ using FeC-2/Ni as catalyst.

TEM micrographs evidenced that, similarly to FeC-1/Ni, Fe_{2.2}C NPs were completely sintered after the catalytic reaction (see Fig S29). The rather low differences in the catalytic activity between FeC-1/Ni and FeC-2/Ni in the long term (83% and 90% of CO₂ conversion at 48 mT for FeC-1/Ni 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. Interestingly, the main advantage of using Fe_{2.2}C NPs with a higher SAR is that the activation step of the catalyst can be performed at lower magnetic fields (48 mT instead of 80 mT) and in shorter times.

Co NRs supported on Ni/SiAlOx 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/SiAlOx 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 and frequencies in order 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 and hence that the Co NRs could be used as heating agents. In that case, a magnetically softer heating source, namely Fe_{2.2}C NPs, could act as a preheating agent of the Co NRs. Hence, 300 mg of Co/Ni and 100 mg of FeC-1/SiAlOx 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 temperature of the reactor 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 temperature slightly dropped down (260–280 °C). As T_c for Co is above the melting point of the glass in order 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/SiAlOx and 200 mg of FeC-1/Ni (approx. 5 wt% of Fe). In this case, the reaction temperatures were always below 200 °C and marginal CO₂ conversions were obtained (less than 5%). This experiment demonstrates that Co NRs are actually acting as heating agent in CO₂ hydrogenation. Co-FeC-1/Ni is envisaged as a good catalyst candidate for future

chemical reactions demanding high temperatures and Ni, or even Co catalysts, 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).

interest for the scaling-up of the process. Last but not least, this method can be very versatile. Indeed, by tuning the T_c , such systems can be adapted to high temperature reactions such as methane reforming.

Conflicts of interest

There are no conflicts to declare.

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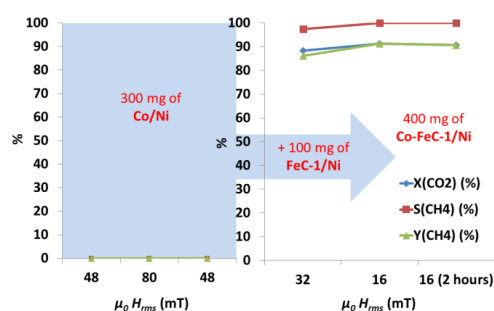


Figure 6. Magnetically induced hydrogenation of CO₂ using Co/Ni and Co-FeC-1/Ni as catalysts.

Conclusions

To conclude, we believe that magnetic heating may be a relevant method for CO₂ methanation because of its interesting properties: the energy is directly transferred to the catalyst, and there is fast warming up of the reactor (20-30 seconds) without need to heat the reactor walls. In this work we demonstrate that Ni supported on SiAlOx can efficiently catalyze CO₂ methanation by magnetic heat induction. As heating agent, 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 seems to be the reason for the improved results. Notably, 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 is highly advantageous in terms of energy consumption. As T_c of Co overpasses 1000 °C, this combined material is a promising catalyst for chemical reactions requiring high temperatures. Furthermore, the present results demonstrate that magnetic materials displaying very low values of SAR under the magnetic field amplitudes used in this work but high T_c , such as Co NRs, can be used as heating agents in magnetic catalysis after addition of small amounts of softer materials with good heating power such as Fe_{2.2}C NPs. Optimization of the reaction conditions has allowed us to improve the performance of the magnetically induced CO₂ methanation, ca. lower magnetic fields were applied, and lower amounts of catalysts were used, and this will be of further

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