CO₂ Methanation Under Dynamic Operational Mode Using Nickel Nanoparticles Decorated Carbon Felt (Ni/OCF) Combined with Inductive Heating

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Highlights:

1. Three-dimensional (3D) composites of tuneable shape and dimension have been straightforwardly prepared and applied as catalysts in the CO₂ methanation reaction.
2. An inductive heating system has been firstly employed with success in such an exothermal process.
3. Ni@OCF catalyst exhibits high catalytic activity and stability for CO₂ methanation already under moderate reaction conditions.

Abstract

Carbon dioxide (CO_2) hydrogenation to methane (CH_4) (Sabatier reaction) is a fundamental process that meets with several key challenges of our modern society. Besides representing a convenient way to the metal-mediated conversion of a natural and abundant “waste” into a fuel of added value, its combination with H_2 from renewable resources (REs) represents a challenging technology for the REs storage. In addition, its practical exploitation can give a concrete answer to many critical societal and environmental issues largely related to the steadily increase of CO_2 concentration in the Earth’s atmosphere caused by the main anthropic activities. Although many fundamental achievements have also been reached since its discovery at the beginning of the twentieth century, alternative and conceptually new protocols for the process can provide valuable solutions to the optimization of the catalyst performance, process energetics and catalyst life-time on stream.

This contribution describes the synthesis of an efficient and robust catalyst for the CO_2 methanation, based on Nickel nanoparticles (Ni-NPs) grown on electrical conductive and macroscopically shaped oxidized carbon-felt disks (OCF), heated at the target reaction temperature by electromagnetic induction. At odds with the more classical external heat sources (based on contact heat conduction), induction heating allows the electromagnetic energy to be directly absorbed by the susceptor (OCF) who converts it into heat to be transferred to the catalyst active sites (Ni NPs). Inductive heating (IH) of Ni/OCF gives CO_2 conversion (X_{CO_2}) up to 74% and CH_4 selectivity (S_{CH_4}) close to 97% already at 320 °C, showing an excellent control of the catalyst stability under forced dynamic operational conditions.

Keywords: CO_2 methanation; Inductive heating; Oxidized carbon felt; Nickel nanoparticles; Synthetic natural gas.

1. Introduction

The restless development of renewable energy sources (REs), *i.e.* solar and wind, calls for the development of more efficient energy storage systems capable to cope with problems related to the extra and intermittent renewable energy supply. Indeed, the fluctuating nature of REs has to be taken into account while managing electricity grids in order to reduce problems linked to security and stability of power networks and ensure a constant supply of electricity on demand.[1-3] Apart from electrochemical storage devices, *i.e.* supercapacitors and batteries, chemical energy storage is a fast growing technology that allows the conversion of exceeding electricity from REs into H₂ (by water electrolysis).[4-6] The latter is supposed to be used in turn as an energy vector or an intermediate for the production of chemicals and commodities. On this regard, CO₂ hydrogenation[7-10] (Sabatier reaction) using H₂ from RE sources[11, 12] is a highly promising approach that meets with several key challenges of our modern society. Besides representing a sustainable method towards the production of chemicals and fuels[13-20] from REs it also copes with the main environmental and climate urgencies directly linked to steadily state increase of CO₂ concentration in the atmosphere. Catalytic hydrogenation of CO₂ with RE H₂ is nowadays at the forefront of many chemical technologies devoted to the production of low molecular weight olefins,[21] hydrocarbons,[22] formic acid,[23] and alcohols.[24-26] It also represents the core business of the “power to gas” (PtG) technology.[5, 6, 27-29] Indeed, it provides a powerful approach to the production of synthetic natural gas (SNG) as fuel (CO₂ methanation) that can be injected in the existing natural gas pipelines thus creating a virtuous link between existing power networks and natural gas grids.[30] CO₂ methanation is a well-established transformation promoted by a relatively large number of metal active phases [*i.e.* Ni, Ru, Rh, Co, Pd nanoparticles (NPs)] deposited on various oxide supports (*i.e.* TiO₂, SiO₂, Al₂O₃, CeO₂, MgO and ZrO₂).[31-40] It is a highly exothermic process ($\Delta H = -165$ kJ/mol) and thus,

thermal conductive supports (carbon nanotubes, graphene, and silicon carbide just to mention a few)[41-45] are generally recommended in order to prevent as much as possible the generation of local temperature gradients (hot spots) inside the catalyst bed during the process. Indeed, the generation of “hot spots” inside the catalyst can be largely detrimental both in terms of catalyst life-time and performance of the methanation process.

PtG chain urgently needs of novel concepts and breakthroughs to optimize performance of existing plants and to cope as much as possible with dynamic operational conditions that often occur within the reactor. One main dynamic parameter to be controlled is represented by the intermittent nature of reactants supply from REs. Such dynamic conditions can be responsible for the occurrence of severe temperature fluctuations within the reactor, not easy to be controlled even in apparatus equipped with external cooling systems.[46]

Induction heating (IH) represents a valid alternative to the more traditional Joule heating (JH) approach, with the former listing a series of key advantages compared to the latter in the heating of electrical conductive materials. Induction heating is likely a more clean, efficient, cost-effective, precise, and repeatable method for providing heat necessary for chemical processes to occur. Heating takes place on electrically conductive objects when they are placed in a varying magnetic field and it occurs precisely where heat is needed and not to the whole volume of the medium and the gaseous reactants; it is also defined as a noncontact heating method. Such a heating scheme allows for rapid up/down temperature ramps (*i.e.* hundred degrees per minute), with great potentials for large scale and rapid manufacturing processes and improved energy efficiencies.[47]

IH is expected to be a technique of choice for operating heterogeneous catalysis and in particular for those processes where high heat targeting along with fast heating/cooling rate provide key control on the reaction course and catalyst stability on stream, *i.e.* rapid temperature gradient control during exothermic or endothermic processes also caused by

variable reagents loads. Most importantly, the temperature control at the catalyst sites can be directly monitored by a laser pyrometer that maps the catalyst temperature in real time (and not that of the reactor) thus allowing an extremely fast response to any temperature deviation occurring at the catalyst bed. By this way, the catalyst operates under almost isothermal conditions.

IH has already been used with success for running liquid-phase catalytic reactions [48, 49] and recently for the gas-phase CO₂ methanation reaction. On the latter process, Bordet et al. [50] have elegantly demonstrated the use of the induction heating with Ni-coated iron-carbide NPs (ICNPs@Ni) or ICNPs supported on Ru-doped Silica-alumina hydrate oxides (SIRALox) as catalysts for continuous-flow reactors working under atmospheric pressure. For both their systems, the authors idea was to take advantage of ICNPs heating capacities and transfer the heat released from that NPs to activate either their Ni-coating or the neighbouring Ru NPs, thus catalysing the Sabatier process.

In this work we describe the straightforward synthesis of Ni(0) NPs on a highly defective carbon felt (Ni/OCF) support and the use of the composite as a stable and effective heterogeneous catalyst for CO₂ methanation, using an induction heating (IH) setup. We took advantage from the high and rapid heat response (heating/cooling) of OCF to magnetic stimuli of the inductive heater for a rapid temperature control at the heart of the catalytic system. Such a configuration provides an effective way to control the catalyst temperature from sudden deviations especially occurring during the start/stop of the catalytic runs where gradients of reactants loads can be formed.

2. Experimental Section

2.1. Materials and methods.

Commercial soft polyacrylonitrile (PAN)-based carbon felt (CF) was purchased from Carbone Lorraine Ltd [RVC 4002 Carbon felt (thickness: 0.01 m; $d = 100 \text{ kg m}^{-3}$; 96% carbon content; Specific Surface Area (SSA): $2.0 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$] in the form of a black carpet with a thickness of 12 mm. It can be easily adapted into various macroscopic shapes including cylinders, disks or others as a function of its downstream application. The as-received CF sample was cut into disks of external diameter of 22 mm before being oxidized upon treatment with gaseous nitric acid (68 wt.% HNO_3).^[51] In a typical oxidation procedure, CF disk is located inside a tubular quartz reactor heated to 250 °C by an external electrical furnace. Nitric acid vapors obtained by heating concentrated nitric acid (HNO_3) at 125 °C were then allowed to pass through the tubular reactor for 4 h. Afterwards, the oxidized carbon felt (OCF) was thoroughly washed with distilled water and dried in an oven at 110 °C to constant weight prior any use.

Nickel NPs were deposited on OCF by incipient wetness impregnation,^[52] using an aqueous solution of nickel nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] as to get a metal loading close to 10 wt.%. The oven-dried pre-catalyst was calcined in air at 200°C for 1 h as to convert the nickel nitrate into its oxide counterpart. Afterwards, NiO_x/OCF underwent a reduction step at 200°C for 1 h under a dynamic stream of H_2 (100 mL min^{-1}). Nickel loading was fixed by *Inductively Coupled Plasma Atomic Emission spectrophotometry* (ICP-AES) after complete acidic mineralization of $\text{NiO}_x/\text{N-CNT}$ sample, using an Optima 2000 Perkin Elmer Inductively Coupled Plasma (ICP) Dual Vision instrument; the effective nickel charge was then fixed to xx.x wt.%. *Scanning electron microscopy* (SEM) was conducted on a ZEISS GeminiSEM 500 microscope with a resolution of 5 nm. For each measurement, samples were deposited onto a double face graphite tape in order to avoid charging effect during the analysis. *Transmission*

Electron Microscopy (TEM) was carried out on a JEOL 2100F microscope working at 200 kV accelerated voltage, equipped with a probe corrector for spherical aberrations, and a point-to-point resolution of 0.2 nm. For these measurements, samples were previously dispersed in ethanol using ultrasounds (for few minutes) till a homogeneous dispersion is obtained and the resulting inks are drop-casted on a copper grid covered with a holey carbon membrane. The *Brunauer-Emmett-Teller* (BET) specific surface areas (SSA) and porosity (Based on BJH method) were calculated from N₂ physisorption isotherms recorded at 77 K on an ASAP 2020 Micromeritics[®] instrument. All samples were degassed/activated at T = 250 °C for 8 h prior their characterization. *Thermal gravimetric analysis* (TGA) and *differential thermal gravimetric* (DTG) analysis were run in the 50-800 °C temperature range (heating rate of 5 °C/min) using a TGA Q5000 instrument operating under an air flow (25 mL min⁻¹). *Inductive heater* and *laser* (still missing details).

2.2. CO₂ methanation process

The CO₂ methanation reaction (Eq. 1) was carried out under atmospheric pressure in a fixed-bed quartz tubular reactor [Ø(ID) 12 mm, length of 600 mm] charged with the disk pre-catalyst (NiO_x/OCF) and equipped with an advanced EASYHEAT induction heating system for the precise control of the reaction temperature in the 200-380 °C range. Prior of each experiment, the calcinated NiO_x/OCF pre-catalyst was reduced at 200 °C for 1 h under a stream of H₂ (100 mL min⁻¹). Finally, CO₂ and H₂ were fed into the reactor with a well-defined molar ratio by a series of calibrated Mass Flow Controllers (Brookhorst[®]). For comparative CO₂ methanation trials carried out using a classical external heater (JH), the quartz tube reactor containing Ni/OCF was housed inside an electric furnace controlled by a thermocouple for the monitoring of the temperature ramp and equipped with a second temperature controller placed in contact with the catalyst bed.

In a typical run, a 4 v/v ratio H₂-to-CO₂ gas mixture was admitted at the top of the reactor and passed downward through the catalytic disk. Gases at the reactor outlet are passed through a trap filled with silicon carbide pellets where traces of water are condensed before reaching the gas chromatograph. Reactants and products were analyzed on-line by a CP-3800 gas chromatograph (GC) equipped with a thermal conductivity (TCD) and flame ionization (FID) detectors. All exit lines were maintained at 110 °C by heating tapes to avoid condensation of water remained in the feed.

CO₂ conversion (X_{CO_2}) and CH₄ selectivity (S_{CH_4}) were calculated according to the following equations (Eq. 2 and 3):

$$\text{CO}_2 \text{ conversion: } X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2(\text{in})} - F_{\text{CO}_2(\text{out})}}{F_{\text{CO}_2(\text{in})}} \times 100 \quad (\text{Eq. 2})$$

$$\text{CH}_4 \text{ selectivity: } S_{\text{CH}_4} (\%) = \frac{F_{\text{CH}_4(\text{out})}}{F_{\text{CH}_4(\text{out})} + F_{\text{CO}(\text{out})}} \times 100 \quad (\text{Eq. 3})$$

Where $F_{\text{CO}_2(\text{in})}$ (mL/min) is the volume of CO₂ admitted to the reactor and $F_{\text{CO}_2(\text{out})}$ (mL/min) is the volume of CO₂ measured at the reactor outlet. This latter was calculated using the total volume at the reactor outlet and considering the percentage of CO₂ detected by GC analysis. The CH₄ selectivity (S_{CH_4}) was calculated by GC analysis considering CO as the unique reaction by-product.

For the present CO₂ methanation study, catalyst underwent a series of successive start and shut-down steps as to simulate the dynamic operation conditions of a CO₂ methanation plant as a consequence of the intermittent nature in reactants supply. To this aim, the start/stop process was operated as follows: at the steady-state (320 °C) the reaction temperature was decreased to 260 °C and the reactants flow was replaced by helium for 30 minutes before

raising rapidly again the reaction temperature to 320°C and re-start the reactants flow supply. Such start/stop sequences are repeated several times in order to evaluate all possible deactivation/alteration effects occurring on Ni/OCF.

2.3. Induction Heating Setup

The induction heating setup (EasyHeat LI) was purchased from Amprell Ltd (The Netherlands). It consists in a spiral 5-turn induction coil internally cooled with recirculated water (10% glycerol) provided by an external chiller. The quartz reactor containing the catalyst is placed inside induction heater coils as shown in Figure 1. Temperature regulation was ensured by a PID system (Eurotherm model 3504) connected to a laser pyrometer (Optris CT, Germany, Figure 1) working in the 150-1000 °C temperature range (with an accuracy of $\pm 0.X$ °C), for the real-time control of the temperature inside the catalyst bed. The heating/cooling rate allowed for the system is in the order of c.a. 200 °C/min.

Figure 1. Digital photos of the Ni/OCF catalyst in the quartz tubular reactor placed inside the coils of the inductive heater along with the laser pyrometer for the control of the temperature inside the catalyst bed.

3. Results and Discussion

3.1. Ni/OCF catalyst synthesis and characterization

The acid treatment of CF is used to confer a hydrophilic character to the pristine hydrophobic material as to get a more wettable surface for the impregnation step with an aqueous solution of $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$. Although such an acid treatment deeply contributes to the modulation of the chemico-physical properties (*vide infra*) of the CF surface, it negligibly affect the sample macroscopic shape. Accordingly, the catalyst shape can be fixed a priori on the pristine CF as a function of its final downstream application (Figure 2A). SEM and TEM micrographs of OCF at different magnifications show a composition made of carbon microfilaments with an average diameter of $10 \pm 1 \mu\text{m}$, featured by a highly defective and low structured C-surface morphology (Figure 2B-D). Indeed, the initial oxidation treatment with HNO_3 vapors is supposed to deeply modify the CF surface properties in terms of chemical composition (*i.e.* formation of oxygenated functional groups on highly defective C-atoms),[51] specific surface area (SSA) and pore-size distribution (*vide infra*).

Figure 2. (A) Examples of macroscopic shapes available for potential applications. (B) SEM micrograph of CF. (C to E) Representative SEM and TEM micrographs of the OCF sample after acid treatment showing the formation of disordered carbon structure at the outer material surface.

TGA/DTG profiles of CF samples before and after acid treatment are outlined in Figure 3A. OCF displays a significant decrease of the oxidation temperature compared to its pristine counterpart. This trend is in line with the presence on OCF of a reduced degree of structured carbons.[51, 53] Most importantly, the oxidative treatment translates in a significant change of the material specific surface area (SSA) that increases from about 2 (CF) to 689 m²/g (OCF) (Figure 3B and Table 1). After OCF impregnation with a solution of [Ni(NO₃)₂ 6H₂O] and calcination, the SSA of the composite is reduced down to 463 m²/g in line with a modification of the material morphology as a consequence of the calcination treatment and the partial pore clogging caused by the NiO_x NPs deposition (Figure 3B and Table 1).

Figure 3. (A) TGA/DTG profiles of the CF and OCF recorded under an oxidative flow (O₂/He : 20/80 v/v%, 50 mL/min) in the 50-850 °C temperature range; heating rate 10 °C min. (B) N₂ adsorption-desorption isotherms of OCF and NiO_x/OCF samples.

Table 1. Specific surface area (SSA), total and micropore volume of CF samples and composites.

Sample	SSA ^a [m ² g ⁻¹]	V _{p(total)} ^b [cm ³ g ⁻¹]	V _{p(micro)} ^c [cm ³ g ⁻¹] (%) ^d
CF	≈ 2	0.004	n.d.
OCF	689	0.26	0.038 (14.6%)
NiO _x /OCF	463	0.45	0.037 (8.2%)

^a Brunauer–Emmett–Teller (BET) specific surface area (SSA) measured at $T = 77$ K; ^b Total pore volume determined by using the adsorption branch of N₂ isotherm at $p/p_0 = 0.98$; ^c Micropore volume calculated by t-Plot method. ^d % of micropore volume over V_{p(total)}

Both samples (OCF and NiO_x/OCF) exhibit a Type IV isotherm with a moderate but distinctive (for OCF in particular) H4 hysteresis loop in the range of 0.4–1.0 p/p_0 , typical of mesoporous structures featured by complex pore networks of ill-defined shape.[54]

The NP distribution on the Ni/OCF catalyst, after calcination/reduction, was analyzed by Transmission Electron Microscopy (TEM) and representative images of the sample at different magnifications are given in Figure 4 (A, B). TEM micrographs reveal a roughly monodisperse and dense distribution of Ni NPs all over the sample with an average particle size of about 6 ± 2 nm, as determined from a statistical TEM analysis over 200 particles. The relatively narrow Ni NPs dispersion on OCF can be ascribed to a non-innocent role played by the oxidized nanocarrier. Indeed, relatively strong interactions between the Ni salt precursor and the highly defective and hydrophobic OCF surface are thought to be crucial for limiting NPs agglomeration phenomena throughout all thermal phases the composite undergoes. At odds with the reduction of NiO_x over polyoxydrilated supports such as alumina or silica, where strong chemical interactions between oxidized NPs and the inorganic carrier can lead to the generation of intermediates hard to be reduced, the lack of similar strong interactions on NiO_x/OCF makes much easier the conversion to its Ni(0)/OCF counterpart.

Figure 4. (A, B) Low and medium magnification TEM micrographs of Ni/OCF

3.2 CO₂ methanation trials with Ni/OCF as catalyst using inductive heating.

3.2.1 The influence of the reaction temperature

In a typical methanation run, a disk of NiO/OCF catalyst is fixed in a quartz tubular reactor, housed inside the inductor heating coils and pre-treated for 1 h at 200 °C under a stream of pure hydrogen (see Experimental Section for details). Afterwards, the temperature of the reduced Ni/OCF catalyst is fixed at the desired target value and a H₂/CO₂ mixture (4 v/v ratio) is introduced downward through the catalyst bed at ambient pressure (1 atm) and at a GHSV of 300,000 mL g_{Ni}⁻¹ h⁻¹. CO₂ conversion (X_{CO2}) and methane selectivity (S_{CH4}) measured in the 160 ÷ 380 °C temperature range are outlined in Figure 5. According to literature precedents, X_{CO2} steadily increases while increasing the reactor temperature and it rapidly approaches conversion values close to those at the thermodynamic equilibrium (Figure S1).[55-57] Noteworthy, Ni/OCF offers excellent performance already at moderately high temperature values. Indeed, it reaches a X_{CO2} up to 74% with a S_{CH4} close to 97% at 320 °C and under the same experimental conditions as mentioned above (H₂/CO₂ = 4 v/v ratio; GHSV = 300,000 mL g_{Ni}⁻¹ h⁻¹). This result is even more relevant if we consider that Ni/OCF operates under more severe reaction conditions compared to many others systems reported so far, using pure reactants flows with no need of their dilution by any inert carrier.

CO represents the unique reduction intermediate for the process detected along with CH₄ at the reactor outlet. For methanation trials at temperatures < 320 °C, S_{CH4} is rather low because of the kinetic stability of CO that makes its conversion into CH₄ hard to be accomplished under these conditions. At higher temperatures, (*i.e.* > 320 °C) both X_{CO2} and S_{CH4} decrease mainly as a consequence of side processes at work *i.e.* steam reforming (< S_{CH4}), water-gas shift (< X_{CO2}) or reverse water-gas shift reactions (< S_{CH4}).[58]

Figure 5. CO₂ methanation runs with Ni/OCF as catalyst [CO₂ conversion (X_{CO_2} ; ●) and CH₄ selectivity (S_{CH_4} ; ○)], operated by an induction heating (IH) setup. Green spheres refer to CO₂ conversion (X_{CO_2} ; ●) measured with a classical Joule heating system. Reaction conditions: catalyst weight = 0.226 g (10 wt.% of Ni), GHSV (STP) = 30,000 mL g_{Ni}⁻¹h⁻¹, [CO₂] = 20%, [H₂] = 80%, H₂-to-CO₂ v/v ratio = 4.

For the sake of comparison with a more traditional external heating system (Joule heater – JH), the methanation process was repeated on a new batch of Ni/OCF under the same catalytic conditions operated above except for the use of an electrical furnace for the set-up of the target reaction temperature. Accordingly, the reactor containing the reduced Ni/OCF catalyst was housed inside the electric furnace equipped with a thermocouple for the monitoring the temperature ramp and with a second temperature controller placed in contact with the catalyst bed. Under these conditions, Ni/OCF performance changes significantly with a X_{CO_2} that is reduced down by a factor of 56% (at 320 °C) respect to the value measured under IH at the same temperature ($X_{\text{CO}_2}^{\text{IH}}$ and $X_{\text{CO}_2}^{\text{JH}}$ at 320 °C are 74 and 32 %, respectively; Figure 5). Noteworthy, under JH conditions, Ni/OCF catalyst reaches a X_{CO_2} value of 65% ($S_{\text{CH}_4} = 92,5$ % - see Figure S2) only after increasing the reactor temperature over 380 °C. Such a result can be ascribed to the effectiveness of the induction heating approach that supplies the heat necessary for the process directly to the catalyst. Besides providing a precise and easily tuning temperature control at the catalyst bed throughout the

reaction process, IH largely prevents heat losses mainly due to conduction and convection phenomena typical of contact heating modes (*i.e.* JH). This aspect is crucial for many industrial processes where limited catalyst performance is often due to physical constraints related to an effective heat transfer to the catalyst rather than to the inherent catalyst activity. Rostrup-Nielsen and co-workers [59] have calculated that only 10% (or even less) of the external heating provided to reformer tubes is employed in the catalytic process, while the (large) remaining part is dissipated by heat transfer restrictions encountered in contact heating modes from the heat source to the catalyst. Recently, Vinum et al. [60] have described the use of dual-function Co–Ni NPs in combination with the induction heating as unique energy source for operating steam methane reforming (SMR). At odds with more classical heating supply systems, the authors have concluded that under IH the catalyst operates at its kinetic limit; *i.e.* the catalyst performance is limited by the reaction kinetic and not by the heat transfer.

Influence of dynamic operational modes on Ni/OCF. As a model trial for testing Ni/OCF under dynamic conditions, successive start/stop process cycles have been investigated while keeping the catalyst under variable reaction temperatures, GHSVs and using pure reactants as reaction feed. These trials are made possible due to the fine and almost instantaneous catalyst temperature control within the processes operated under induction heating. Indeed, heating and cooling rates with IH are extremely fast (*i.e.* $\geq 200^{\circ}\text{C}/\text{min}$) and they can be easily controlled avoiding sudden and detrimental temperature deviations on the catalyst at work. A complete overview of several start/stop CO₂ methanation cycles carried out with Ni/OCF under variable conditions (temperature and GHSV) is presented on Figure 6.

Figure 6. Ni/OCF catalyst performance miming dynamic operational condition modes in the form of successive start/stop cycles operated under different conditions (temperature and GHSV). Reaction conditions: catalyst weight = 0.22 g, GHSV (STP) = 300,000 or 600,000 mL g_{Ni}⁻¹ h⁻¹; H₂-to-CO₂ = 4 v/v ratio; operative reaction temperatures and times: 320 °C or 340 °C for 1 h; hold-on temperature value for the shut-down period: 260 °C for 0.25 h.

According to the catalytic outcomes (X_{CO_2} and S_{CH_4}), successive start/stop cycles consisting in a rapid catalyst cooling/heating in the 260-320 °C temperature range and simultaneous replacement of the H₂/CO₂ feed with Helium) do not show any appreciable modification of the catalyst performance even after several cycles. Noteworthy, such start/stop tests cannot be run under conventional heating mode (*i.e.* JH) because of longer induction times required during the cooling and heating phases. Moreover, fast heating/cooling rates along with a fine control of the target temperature at the catalyst bed provide the reactor with a powerful tool for the control (almost in real time) of those phenomena related to the discontinuous supply of reagents into the reactor. Indeed, a fine and fast temperature control is crucial to avoid sudden temperature raises at the catalyst bed, thus limiting detrimental effects for the catalyst (*i.e.* decomposition and/or NPs sintering) and the catalytic process. Besides the role played by the support thermal conductivity, the generation

of local temperature gradients (“hot spots”) inside the catalyst can be conveniently balanced by the high heating/cooling rates operated with the IH system. It is known that local temperature gradients at the catalyst bed can be generated in the CO₂ methanation even within reactors operating at low GHSVs and using reagent feeds diluted with inert carriers.[45] Accordingly, their generation can have even more drastic effects in reactors working at higher GHSV and fed with pure reactants flows. In the CO₂ methanation with Ni/OCF operated by IH, the combination of the temperature control inside the catalyst (ensured by IH mode) together with the medium thermal conductivity of the OCF support, provide a robust and effective system for the process where the generation of local “hot spots” is largely prevented if not totally suppressed. This key feature well matches with the high catalyst stability under the discontinuous (start/stop) and dynamic (temperature and GHSVs) operational modes described above for the Sabatier reaction. As an additional proof of the Ni/OCF stability on stream, long-term evaluation tests have been properly addressed under constant reaction conditions.

Long-term stability evaluation tests. The stability of Ni/OCF to perform CO₂ methanation efficiently has also been investigated as a function of the catalyst time on stream and results are presented in **Figure 7**. Ni/OCF displays a high and stable CO₂ conversion (X_{CO_2}) for more than 80 h on stream thus indicating that deactivation phenomena (*i.e.* active phase sintering, metal-nanoparticles passivation by coke deposits or metal leaching) are unlikely to occur under these conditions. Wei and co-workers [61] have recently shown how unpromoted Ni NPs decorated carbon nanotubes (Ni/CNTs) as a catalyst for the CO₂ methanation, gradually deactivates over time on stream, mainly due to the generation of coke deposits. Feng,[43] Centi [62] and Stangeland [55] have also described Ni-based catalysts for the process, using different alumina or promoted supports. Examples from this series show that catalyst deactivation can also take place through Ni NPs sintering induced by the local

generation of temperature gradients that progressively reduce the number of available active sites.

Figure 7. Long-term evaluation tests with Ni/OCF as CO₂ methanation catalyst. Reaction conditions: catalyst weight = 0.2258 g, GHSV (STP) = 300,000 mL g_{Ni}⁻¹ h⁻¹; H₂/CO₂ = 4 v/v ratio; reaction temperature = 320 °C.

TEM analysis of the exhaust Ni/OCF catalyst (Figure 8A-B) is used to unveil the high stability of the composite on stream. Indeed, a comparative analysis of Ni NPs on the exhaust catalyst (after more than 80 h on stream) with those of its freshly prepared counterpart (see Figure 4A-B) rules out the occurrence of any appreciable NPs sintering.

Figure 8. (A, B) Low and medium magnification TEM micrographs of the exhaust Ni/OCF catalyst after long-term evaluation test (> 80 h). Reaction conditions: catalyst weight = 0.2258 g, GHSV (STP) = 300,000 mL g_{Ni}⁻¹ h⁻¹; H₂/CO₂ = 4 v/v ratio; reaction temperature = 320 °C. catalytic evaluation.

TEM micrographs show that exhaust catalyst maintains a similar dispersion and distribution of Ni NPs that its pristine counterpart with an average particle size distribution of about 6 ± 2 nm (determined from a statistical analysis over 200 particles) and the absence of any macro-aggregate all over the scanned area. Such a high thermal resistance of Ni NPs throughout the whole catalytic run is also ascribed to the existence of relatively strong interactions engaged between NPs and the highly defective OCF support.

These evidences indirectly confirm the excellent thermal control at the catalyst active phase ensured by IH and the OCF thermal conductivity. Both of features have largely beneficial effects on the catalyst stability, in particular with respect to the control on the generation of local temperature gradients that can easily start NPs sintering phenomena.

4. Conclusion

In summary, an efficient and robust catalyst for the CO₂ methanation, based on Nickel nanoparticles (Ni-NPs, 10 wt.%) grown on electrical conductive and macroscopically shaped oxidized carbon-felt disks (OCF), has been prepared and heated at the target reaction temperature by electromagnetic induction. Inductive heating (IH) is proved to have largely beneficial effects on the catalyst performance compared to the more classical Joule heating methods. Indeed, the the electromagnetic energy provided by the induction heater can be directly absorbed by the electrical conductive susceptor (OCF) who convert it into heat to be transferred to Ni NPs. By this way, an almost real-time control of the target temperature at the catalyst active sites can be set-up with valuable advantages in terms of process energetics, catalyst efficiency and catalyst stability on stream. Indeed, the fast temperature regulation rate (hundreds of °C per min) ensured by IH, can control and balance undesired and sudden temperature changes at the catalyst bed. As a matter of fact, temperature fluctuation at the

catalyst bed, frequently encountered in real systems (as the consequence of a discontinuous supply of reagents loads), can be finely controlled thus allowing the reactor to operate under virtually isothermal conditions. Inductive heating (IH) of Ni/OCF gives CO₂ conversion (X_{CO_2}) up to 74% and CH₄ selectivity (S_{CH_4}) close to 97% already at 320 °C using pure reactants flows with no need of their dilution by any inert carrier. Noteworthy, the same catalyst under a more conventional JH control, reaches X_{CO_2} value of 65% and S_{CH_4} of 92,5 % for a reactor temperature set-up to 380 °C.

Ni/OCF has also shown an excellent stability upon IH when forced dynamic operational conditions are applied (reaction temperature, GHSV and reagents loads). In a model trial, dynamic operational modes have been expressly forced in the system as to mimic the process discontinuity under conditions close to those operated in real plant. Accordingly, several and sequential start/stop cycles have been run, including changes in the target reaction temperature and GHSV, thus unveiling the extremely high stability of Ni/OCF under harsh experimental conditions. Finally, a long-term experiment (> 80 h) have been used to confirm the stability of the catalyst after several hours on stream. TEM analyses of the exhaust Ni/OCF have been finally used to rule out the occurrence of any appreciable NPs sintering throughout the process. Moreover, NPs passivation by the generation of coke deposits seems to be unlikely to occur due to the efficient heat management within the process ensured by IH. Studies on Ni/OCF in CO₂ methanation under more severe reaction conditions are currently ongoing in our labs and will be reported soon elsewhere.

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