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(54) Title: NI-SILICA-BASED CATALYSTS WITH HIGHLY DISPERSED NICKEL PARTICLES

(57) Abstract: A nickel-silicon catalyst, wherein the nickel is present in an elemental weight percent of 1 to 7.5% considering the total weight of the catalyst, said nickel-silicon catalyst comprising a silicon oxide support bearing the nickel nanoparticles; and wherein the dispersion of the catalyst is at least 15%.

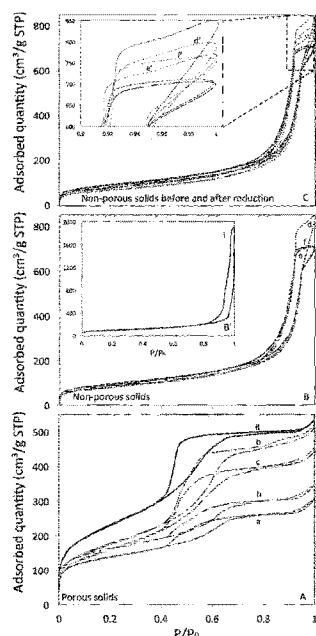


Fig. 1

SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN,
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Description

Ni-silica-based catalysts with highly dispersed nickel particles

- [0001] The present invention relates to catalysts comprising nickel (Ni) and silica (Si), and demonstrating good abilities in the dry reforming of methane reaction (DRM).
- [0002] The DRM converts two major greenhouse gases, CH₄ and CO₂, into a useful chemical feedstock: a mixture of H₂ and CO “syngas” with an H₂/CO molar ratio equal to the unity adapted for Fischer-Tropsch procedure, as reported by B. Abdullah et al. in *J. of Clean. Prod.* 162 (2017) 170-185. Different strategies and siliceous supports have been developed and used in order to improve the nickel dispersion and interaction with the support, those features being particularly important in order to protect the Ni nanoparticles from sintering and to avoid side reactions; such side reactions are exemplified in different publications such as in the article of L. Espinosa-Alonso et al. published in *J. Am. Chem. Soc.* 131 (2009), 131, 16932-16938.
- [0003] Until now, supported nickel-based materials have been intensively investigated as catalysts for the DRM - named « DRM catalysts » in the following description - as well as in the methanation of coal synthesis gas. Nickel-based catalysts usually suffer from rapid deactivation, due to partial metal oxidation as described by S. M. Kim et al. in *J. Am. Chem. Soc.* 139 (2017) 1937-1949 or K. Nagaoka et al. in *Appl. Catal. A* 268 (2004) 151-158; particle sintering as described by Z. L. Zhang et al. in *J. Catal.* 158 (1996) 51-63 or L. Xu et al. in *ACS Catal.* 2 (2012) 1331-1342; and coke formation as described by J. H. Kim et al. in *Appl. Catal. A Gen.* 197 (2000) 191-200 or F. Frusteri et al. in *Carbon* 40 (2002) 1063-1070. Different strategies have been developed in order to protect Ni nanoparticles and to avoid side reactions, see for example the article published by J. R. A. Sietsma et al. in *Angew. Chem. Int. Ed.* 46 (2007) 4547-4549. Porous supports and especially mesoporous ones have been extensively studied. Their ordered pore structures, high specific surface areas and the resulting confinement effect inside the pore channels are expected to afford highly dispersed nanoparticles with an increasing number of thermodynamically

high-energy active surface atoms (see the article published by L. Tarpani et al. in *Catal. Commun.* 74 (2016) 28–32) and to lead to a more resistant catalyst toward the sintering and coke deposition owing to physical barrier of the pore walls. Most of those catalysts containing Ni developed for the DRM must be obtained by the impregnation of a porous support: SiO₂ proved to be one of the best candidate for this purpose, in particular the so-called « SBA-15 » prepared from silica gel is known to be a good support for the Ni containing material, as described in the above mentioned article published by Sietsma and coworkers.

- [0004] In the context of DRM, nickel nitrate (Ni(NO₃)₂.xH₂O) is the most used Ni precursor for the preparation of Ni/Silica catalysts and one-pot preparation methods have already been investigated in order to generate highly stable silica-based catalysts as described by O. Daoura et al. in *Int. J. Hydrogen. Energ.* 43 (2018) 17205-17215. Nevertheless, siliceous support prepared in acidic medium such as mesoporous SBA-15, make the one-pot preparation difficult due to the amphoteric properties of silica surface. In acidic conditions, Si-OH groups transform into Si-OH₂⁺ and the resulting surface charge does not favor interactions with the Ni(II) aqua complexes.
- [0005] One siliceous support prepared in acidic medium is mesocellular silica foam (MCF); Daoura et al. report the preparation of Ni catalyst containing MCF in *J. CO₂ Util.* 24 (2018) 112-119. The classical preparation of those Ni/MCF catalysts requires long steps - at least two days - of hydrothermal treatment rendering thus the synthesis of DRM catalysts difficult. Moreover, under those conditions, organic porogen molecules, such as swelling and amphiphilic agents are required; and taking into account those agents have to be removed afterward, usually by calcination, thus such a process from the prior art is not suitable for a high-scale catalyst synthesis under a green pathway.
- [0006] Besides, an important parameter for the catalyst efficiency is the amount of metal and in particular the Ni content, and the dispersion (fraction of Ni atoms available for catalysis) has to be kept as high as possible, as mentioned above. Many Ni catalysts have been developed, but it is noteworthy that improving the Ni content usually causes a drastic lowering

of the dispersion: L. Qian et al. report the preparation of a Ni catalyst for DRM with a Ni wt% (Mass Fraction) of 0.5 having a dispersion of 40 in *Microp. Mesop. Mater.* 243 (2017) 301-310 ; while C. Wang et al. report the preparation of a Ni catalyst for DRM with a Ni wt% of 5-12 having a dispersion rate of only 11 in *Catal. Sci. Technol.* 8 (2018) 4877-4890. To date, the methods developed to produce catalysts are not efficient enough to obtain DRM catalysts containing the ideal average of Ni content together with a dispersion sufficiently high to perform the DRM in good conditions and to reach very good yield together with great turnover number.

[0007] The main aim of the present invention is to provide a nickel containing DRM catalyst easily obtainable with a high Ni content and good dispersions and demonstrating the same or even better activity toward DRM, compared to the nickel catalysts from the prior art.

[0008] The present invention concerns a nickel-silicon catalyst, wherein the nickel is present in an elemental weight percent (wt%) of 1 to 7.5% considering the total weight of the catalyst, said nickel-silicon catalyst comprising a silicon oxide support bearing the nickel nanoparticles; and wherein the dispersion of the catalyst being more than at least 15%. The dispersion is calculated using the H₂ chemisorption method. The dispersion refers here to the molar percentage of surface Ni atoms compared to the total number of Ni atoms in the sample:

$$D = \frac{Q_{\text{ads}}}{Q_{\text{max}}} = \frac{\sqrt{KP}}{1 + \sqrt{KP}}$$

D: Fractional occupancy of the adsorption sites

Q_{ads}: Quantity adsorbed

Q_{max}: Quantity adsorbed on saturation

K: Equilibrium constant

P: Partial pressure of the adsorbate

In order to visualize the nickel dispersion and location, STEM/HAADF and EDX/mapping were also performed on a JEOL® 2020 microscope on ultra-thin sections of selected samples. The inventors have developed a new preparation method, very simple to carry out in comparison to known

technologies in this field, giving rise to nickel-derived catalysts exhibiting tiny nanoparticles, high metal support interaction and excellent particles dispersion compared to other known materials. The nickel-silicon catalysts according to the present invention prove to be more readily obtainable compared to the already known nickel DRM catalysts, and demonstrate better activity toward DRM, with excellent stability.

Nanoparticles of Ni in the context of the invention are objects with sizes below 100 nm, preferably below 10 nm, ideally in the range of 2 to 5 nm. Bigger particles are detrimental to catalysts activity per gram of metal and can be responsible of side-reactions. The sizes were established by using direct observations by Transmission Electron Microscopy as well indirect evaluations using H₂ chemisorption measurements.

- [0009] Advantageously the dispersion of the catalyst being more than at least 18%.
- [0010] Advantageously the dispersion of the catalyst being more than at least 25%. Preferably, the dispersion of the catalyst being more than at least 30%, and most preferably more than at least 35%, and most preferably at least 40%.
- [0011] Advantageously the nickel is present in an elemental weight percent of 1.5 to 6.5%.
- [0012] More advantageously the nickel is present in an elemental weight percent of 2 to 6% and even 2.5 to 5.5%.
- [0013] Advantageously the silicon oxide support is non-porous. A non-porous silica material is an “essentially non-porous” silica material wherein a pore diameter, if present, cannot be determined under standard methods. The inventors have noticed, in a completely unexpected manner, that using a non-porous support gives rise to higher nickel dispersion that leads to active and stable catalysts. Non-porous powders, such as non-porous silica, are identified by a characteristic type II isotherm (IUPAC classification) in porosity measurements by N₂ adsorption.
- [0014] The textural properties were determined using N₂ adsorption-desorption method. Thus, before porosity measurements the samples were dried under vacuum for 2 hours at 250 °C. Then, specific surface areas were determined using BET equation, and Pore diameters and volumes were determined using BJH model according to the description provided by E. P. Barrett, and

al. in the article: "The determination of pore volume and area distributions in porous substances. 1. Computations from nitrogen isotherms" *Journal of the American Chemical Society*, (1951), vol 73(1), pages 373-380.

- [0015] Advantageously the silicon oxide support comprises Nickel (Ni) phyllosilicate. Using Ni phyllosilicates as precursors gives rise to excellent activity and stability. Moreover, the catalysts developed by the inventors exhibit excellent particles dispersion compared to other materials comprising phyllosilicate described in the literature; see for example the article published by Z. Li et al. in *Catal. Sci. Technol.* 8 (2018) 3363-3371, for which the dispersion rate does not exceed 3%.
- [0016] Phyllosilicates are an important group of minerals constituted of tetrahedral and octahedral sheets. In case of nickel-silica-supported phyllosilicates material developed for DRM, tetrahedral sheet consists of Si^{4+} , bonded to 4 oxygen atoms and the octahedron consists of Ni^{2+} , coordinated with six anions, which can be O^{2-} or OH^- . In general, the formation of phyllosilicates needs the combination of three factors, i.e. a metal precursor, a silica source and a basic environment. Superficial silica is partially dissolved due to the alkaline environment, hence generating soluble silicate anions. Those silicate anions then react with Ni cations, and hydroxide anions in the solution to form the phyllosilicate structure that is further deposited on the remaining silica support as described in *Catal. Today* 339 (2020) 3-23 and *J. CO₂ Util.* 18 (2017) 345-352, by Z. Bian et al.
- [0017] Advantageously the nickel-silicon catalyst according to the invention does not comprise any added cobalt(Co) atom, or does not comprise essentially any cobalt (i.e. less than 0.01 wt%). Co atoms can make the catalyst vulnerable to oxidation leading to deactivation.
- [0018] Advantageously the nickel-silicon catalyst according to the invention does not comprise any element selected in the group of lanthanide (for example La, Ce) and actinide, and does not contain indium (In), thallium (Tl), tin (Sn) or lead (Pb). A catalyst free of these elements is safer to use considering the toxicity of those elements.
- [0019] Advantageously the particle size is below 6 nm, preferably below 5 and even below 4 nm. The inventors have demonstrated that using NH_3 during

preparation of the catalysts led to the improvement of the dispersion. This could be reflected by higher accessible nickel surface area due to smaller particle sizes. The particle sizes were measured using Transmission Electron Microscopy (TEM). TEM analyses were performed on a JEOL® 1011 (LaB) or JEOL® 2010 (LaB) microscope operating at 200 kV. The sample powder was ultrasonicated in ethanol and 2 drops of the resulting suspension were deposited on a copper grid coated with a porous carbon film. Observations were made once ethanol was evaporated at room temperature.

[0020] The present invention concerns also the process for the preparation of a metal(M)-silicon(Si) catalyst for the DRM comprising the following steps:

- 1- siliceous support $(\text{SiO}_2)_n$ is suspended in water (preferably distilled water) ;
- 2- $\text{M}(\text{NO}_3)_2$ is added into the suspension prepared according to step 1;
- 3- the mixture obtained in step 2- is maintained under stirring during at least 2 hours at a temperature maintained between rt. (room temperature is supposed to be 20°C) and 60°C ;
- 4- the solvent is evaporated;
- 5- the material obtained at step 4- is calcinated at least 2 hours at 550°C.

Advantageously, the metal used in the process disclosed in the present invention is nickel.

Advantageously, step 1- comprises the addition of at least 2 mL of 30 wt.% NH_3 , or an equivalent concentration of aqueous NH_3 , per gram of silica. The catalyst prepared with NH_3 proved to be more active and stable.

Advantageously, during step 1- the reaction time does not exceed 6 hours, or even 4 hours, at 1 bar.

Advantageously, the process does not require any hydrothermal treatment under pressure (i.e. autoclave process), or at high temperatures (i.e. $>100^\circ\text{C}$) for Ni incorporation into the siliceous support before the calcination step.

Advantageously, said siliceous support used is selected between mesoporous silica material and non-porous silica material, wherein said silicon oxide support is considered non-porous when it presents a type II N_2

adsorption isotherm. A mesoporous material is a material containing pores with diameters between 2 and 50 nm, according to IUPAC nomenclature. For comparison, IUPAC defines microporous material as a material having pores smaller than 2 nm in diameter and macroporous material as a material having pores larger than 50 nm in diameter. A non-porous silica material is an “essentially non-porous” silica material wherein a pore diameter, if present, cannot be determined under standard methods. Non-porous powders, such as non-porous silica, are identified by a characteristic type II isotherm (IUPAC classification) in porosity measurements by N₂ adsorption. Non-porous silica is a well-known type of silica, as well as a commercially available type of silica (i.e. Aerosil®).

The present invention concerns also any of the catalyst presented previously according to the present invention that are obtainable by the process presented above in the frame of said invention.

[0021] Other advantages and characteristics of the present invention are described in details in the following experimental part in connection with the figures, which is only made for explanatory purposes and cannot serve to limit the scope of the invention.

[0022] EXPERIMENTAL PART

[0023] I. Analysis and characterisation methods

[0024] A- Textural properties were determined from N₂ adsorption-desorption isotherms recorded on a Belsorp®-max (from BEL JAPAN™) or ASAP™ 2020 (from Micromeritics®) apparatus. Before measurements, the samples were degassed under vacuum for 2 h at 250°C on BelprepII-vac unit or ASAP 2020 (Micromeritics). Specific surface areas were obtained using the BET equation. Pore diameters and specific pore volumes were determined using the BJH model (E. P. Barrett, and al. *Journal of the American Chemical Society*, (1951), vol 73(1), pages 373-380.). It must be noted that the textural properties were calculated taking into account the siliceous support weight only (without Nickel).

- [0025] B- Wide angles XRD measurements were performed on a Brüker® D8 Advance diffractometer ($\text{CuK}\alpha = 1.54 \text{ \AA}$). The data were recorded in the 2 theta range between 5 and 90° using 30 kV and 10 mA conditions, a step size of 0.01° and 1 s per step. The average nickel/nickel oxide particles size was calculated from the Scherrer equation: $D = K\lambda/\beta\cos\theta$, where K is a constant ($K=0.9$), $\lambda = 1.54 \text{ \AA}$, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the peak position.
- [0026] C- The X-ray photoelectron spectra (XPS) were collected on an Omicron® Argus™ X-Ray photoelectron spectrometer using a monochromatic Al K α ($h\nu = 1486.6 \text{ eV}$) X-ray source having a 300 W electron beam power. The emission of photoelectrons from the sample was analyzed at a take-off angle of 45° under ultra-high vacuum conditions ($1 \times 10^{-8} \text{ Pa}$). XP spectra were collected at pass energy of 20 eV for C 1s, Si 2p, Ni 2p and O 1s core XPS levels. The charging effects were corrected by adjusting the binding energy of the C 1s peak from carbon contamination to 284.6 eV. The peak areas were determined after subtraction of a Shirley background (Nagash and al. *Chem. Mater.*, (2006), 18, 10, 2480-2488). The atomic ratio calculations were performed after normalization using Scofield factors. Spectrum processing was carried out using the Casa™ XPS software package under the condition described by M. P. Seah in, *Surface and Interface Analysis*, (1980), vol.2, Iss.6, 222-239.
- [0027] D- Thermogravimetric analyses (TGA) were performed in order to quantify the amounts of carbon deposited on the spent catalysts using a TA® SDT Q600™ thermal analyzer instrument. Measurements were carried out from rt. to 900°C (heating rate $10^\circ\text{C min}^{-1}$) in flowing air (100 mL.min^{-1}).
- [0028] E- Temperature-Programmed Reduction (TPR), carried out on an AutoChem™ 2910 or a Micromeritics® 2920 apparatus equipped with a thermal conductivity detector (TCD), was used in order to study the nickel reducibility of calcined materials. The samples (80 mg) were heated on quartz wool in a U-shaped quartz tube from rt. to 900°C at a rate of $10^\circ\text{C min}^{-1}$ using a 5 vol% H_2/Ar gaseous mixture (25 mL.min^{-1}). An isopropanol-

liquid N₂ mixture (AutoChem™ 2910) or an ice and salt bath (Micromeritics® 2920) was used before the TCD detector to trap the water molecules formed during NiO reduction. The nickel loading was deduced from the amount of H₂ consumed during the TPR experiment after controlling that the Ni loading of a reference material was found to be coherent with that determined by inductively-coupled plasma optical emission spectrometry (ICP-OES (Crealins-Villeurbanne)). The AutoChem and Micrometric apparatus were also used to perform high-temperature H₂ reductions mimicking the *in situ* reduction (detailed later) carried out as a pretreatment step prior to the catalytic test.

[0029] F- Transmission Electron Microscopy (TEM) analyses were performed on a JEOL®-1011 (LaB) or JEOL®-2010 (LaB) microscope operating at 200 kV. The sample powder was ultrasonicated in ethanol and 2 drops of the resulting suspension were deposited on a copper grid coated with a porous carbon film. Observations were made once ethanol was evaporated at room temperature.

Microtomed Solids: transmission electron microscopy (TEM) images and HRTEM images were taken on a JEOL® JEM-2010 UHR operating at 200 kV, equipped with an energy dispersive X-ray (EDX) detector. Materials were analyzed after ultramicrotomy. A few mg of powder were deposited in the bottom of a Beem capsule. Some embedding resin (AGAR™ 100) was added and polymerized for 48 h at 60°C. The polymerized blocks were then cut into ultrathin sections (about 70 nm thick) using a diamond knife of a Leica® microtome (ULTRACUT UCT) and deposited on carbon-coated copper grids. In order to visualize the nickel dispersion and location, a scanning transmission electron microscope (STEM) technique was used: which is named High-angle annular dark-field imaging (HAADF); and EDX/mapping was also performed on a JEOL® 2020 microscope on ultrathin sections of selected samples.

[0030] G- H₂ Chemisorption experiments: were performed on a BELSORB-max™ equipment from BEL JAPAN™. The samples (about 200 mg) were reduced *in situ* under a flow of H₂ (50 mL min⁻¹) at 650°C for 2 h using a ramp of

10°C min⁻¹. The sample was then outgassed at 620°C for 2 h under vacuum (about 5.10⁻¹ Pa). A first, H₂ chemisorption measurement was performed at 25°C, the pressure at equilibrium being recorded when the pressure variation was below 0.02% per minute. The sample was then outgassed for 2 h at 25°C before a second H₂ chemisorption was performed under the conditions described for the first H₂ chemisorption. Nickel particle size estimations are based on truncated octahedron geometry, assuming complete reduction, semi spherical particles and a H/Ni adsorption stoichiometry factor of 1. The experimental data were fitted with a Langmuir adsorption equation (Equation 1) and the amount of surface nickel was calculated from the quantity adsorbed at saturation (Q_{max} in the model). The dispersion refers here to as the molar percentage of surface Ni atoms compared to the total number of Ni atoms in the sample.

$$D = \frac{Q_{ads}}{Q_{max}} = \frac{\sqrt{KP}}{1 + \sqrt{KP}}$$

D: Fractional occupancy of the adsorption sites

Q_{ads} : Quantity adsorbed

Q_{max} : Quantity adsorbed on saturation

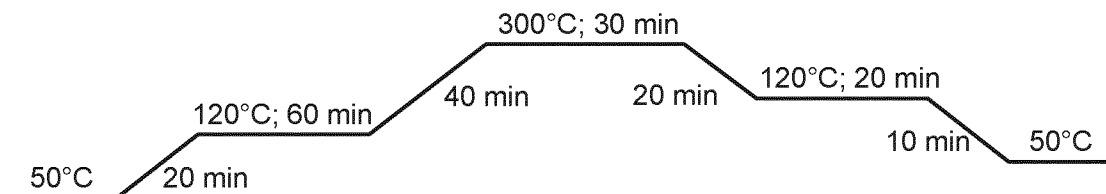
K: Equilibrium constant

P: Partial pressure of the adsorbate

[0031] H- Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS):

[0032] -> The experiment was performed using a Tensor II Bruker® spectrometer with a DRIFTS cell (Praying Mantis™ Diffuse Reflectance Accessory). Diffuse reflectance infrared spectra were recorded in the 4000–600 cm⁻¹ range (resolution 4 cm⁻¹, 128 scans/spectrum, Mercury cadmium telluride (MCT) detector).

The sample compartment of the cell was filled with the powder (approximately 30 mg), which was heated *in situ* under an Ar flow (20 cm³ min⁻¹) using the following program:



- [0033] All spectra were recorded *in situ* and were converted into Kubelka-Munk units after subtraction of the spectrum recorded on the dehydrated KBr sample (Fluka®, purity >99.5%), according to Kubelka P., et al. in Zeitschrift für technische Physik, (1931), Vol.12, pp. 593-601.
- [0034] -> When information dealing with wavenumbers below 600 cm⁻¹ were needed (in the 4000–200 cm⁻¹ range), the diffuse reflectance infrared spectra were recorded using a Brüker® Vertex 70 spectrometer (4 cm⁻¹ resolution, 512 scans/spectrum, DLATGS detector and wide range FIR-MIR beamsplitter). About 40 mg of powder, corresponding to a mechanical mixture of 20 mg of sample in 20 mg of diamond powder, was placed inside a heated crucible located in a Thermo Spectra-Tech high temperature cell equipped with two diamond windows and with appropriate gas inlet and outlet connections as to pass the gas flow through the sample bed. The reference spectrum was recorded with the diamond powder itself (size 6 µm).
- [0035] I- ²⁹Si MAS NMR: spectra were recorded at 79.5 MHz with a Brüker® Avance 500 spectrometer and 7 mm (external diameter) zirconia rotors at 6 kHz spinning speed. Chemical shifts of silicon were measured by reference to tetramethylsilane (TMS). ²⁹Si MAS NMR spectra were obtained with 3.5 µs excitation pulse duration and 10 s recycle delay.
- [0036] J- Catalytic measurements
- The different catalysts were tested using a PID ENG&TECH™ Microactivity Effi Reactor (from Micromeritics®). The solids were loaded on a plug of quartz wool and treated *in-situ* at 650 °C for 2 h (10 °C.min⁻¹) in a 5 vol.% H₂/Ar flow (30 mL min⁻¹) in order to achieve a complete reduction of NiO into metallic nickel. After this pretreatment step, the temperature was decreased to 200°C and the dry reforming of methane reaction was started under atmospheric pressure, using a CH₄/CO₂/Ar (5/5/90) reacting mixture and at

a total Gas Hour Space Velocity (GHSV) of 144 (50 mg of catalyst and 120 mL min⁻¹ total flow) or 960 L g⁻¹ h⁻¹ (10 mg of catalyst diluted with 90 mg of fumed silica (Aldrich 381276) and 160 mL min⁻¹ total flow of reactants mixture).

[0037] Firstly, the activity of the catalyst was measured by increasing the reactor temperature from 200 up to 650°C (using a rate of 5°C min⁻¹). The temperature was then maintained at 650°C for 12 h for stability measurements. The gaseous products were analyzed online by a micro-GC (Agilent 490) equipped with Plot-U and Molecular sieves channels and TCD detector. The conversions of methane and carbon dioxide were calculated according to Equations 2 and 3, respectively, and the H₂/CO ratios were estimated using Equation 4:

$$\text{CH}_4 \text{ conversion, \%} = \frac{(\text{CH}_4(\text{in}) - \text{CH}_4(\text{out}))}{\text{CH}_4(\text{in})} \times 100 \text{ (Equation 2)}$$

$$\text{CO}_2 \text{ conversion, \%} = \frac{(\text{CO}_2(\text{in}) - \text{CO}_2(\text{out}))}{\text{CO}_2(\text{in})} \times 100 \text{ (Equation 3)}$$

$$\text{H}_2/\text{CO} = \frac{\text{H}_2(\text{out})}{\text{CO}(\text{out})} \text{ (Equation 4)}$$

The catalytic performances were also compared to thermodynamic curves calculated using the HSC Chemistry Software (version 7.1) at 1 atm, from 0 -1000 °C, at inlet feed ratio of CO₂/CH₄ =1 and assuming no carbon formation occurring during reaction.

[0038] II. Preparation of the materials

[0039] In this part, the preparation of the siliceous supports and the nickel incorporation method will be detailed.

[0040] II.1 Silica supports

[0041] The silica supports used were commercially available, such as SBA-15 (Sigma-Aldrich® CAS number: 7631-86-9 with 4 nm as pore size), Aerosil® 380 (nSiO₂) from Evonic®, or were synthesized (pSiO₂) as shown below.

The later was prepared by using a mixture of cetyltrimethylammonium bromide (CTABr) and Pluronic (P123) as surfactants. The mixture of CTABr and P123 with an appropriate ratio leads to a porous material with high specific surface area, 4 nm as pore size and a higher wall thickness than SBA-15 according to *Microp. Mesop. Mater.* 89 (2006) 179-185 published by W.-H. Zhang et al. The synthesis of pSiO₂ was performed according to the procedure described by W.-H. Zhang et al. (*Microp. Mesop. Mater.* 89 (2006) 179-185) using 4 g of the triblock copolymer (EO₂₀PO₇₀EO₂₀, Pluronic P123) dissolved in a mixture of 37 wt% HCl (20 mL) and distilled water (130 mL) at 40°C. Three hours later, 1 g of CTABr was added to the solution and stirred for 30 min. After total dissolution, 6.6 g of tetramethylorthosilicate (TMOS) were added and the resulting suspension was stirred at 40°C for 20 h. After hydrothermal treatment for 24 h at 100°C, the suspension was filtered and the recovered solid (pSiO₂-N) was washed, dried and calcined at 550°C for 5 h (heating rate 1°C min⁻¹) affording pSiO₂-C.

[0042] II.2 Insertion of Ni

[0043] Six Ni-based catalysts were prepared, a first one by the impregnation of commercially available SBA-15 by two solvents, three by the impregnation of nSiO₂ with or without NH₃ and two starting from pSiO₂. Table 1 summarizes the preparation methods of the solids.

[0044] Table 1: Description of siliceous supports and the Ni/silica materials

Ni_{5%}/SBA-15-TS	SBA-15 impregnated by Ni (5 wt.%) using the "Two-Solvents" (TS) method
Ni_{5%}/nSiO₂	nSiO ₂ impregnated by Ni (5 wt.%) without NH ₃
Ni_{5%}/nSiO₂-NH₃	nSiO ₂ impregnated by Ni (5 wt.%) in presence of NH ₃
Ni_{3.5%}/nSiO₂-NH₃	nSiO ₂ impregnated by Ni (3.5 wt.%) in presence of NH ₃
Ni_{5%}/pSiO₂-NH₃-N	pSiO ₂ non calcined (N) impregnated by Ni (5 wt.%) in presence of NH ₃
Ni_{5%}/pSiO₂-NH₃-C	pSiO ₂ calcined (C) impregnated by Ni (5 wt.%) in presence of NH ₃

[0045]

[0046] Preparation of Ni_{5%}/SBA-15-TS: The Ni/SBA-15-TS sample was prepared by the "Two-Solvents" (TS) method. To do so, 1 g of a commercial SBA-15 was suspended in 35 mL of cyclohexane, then a volume of water equal to

the silica pore volume (as previously determined by N₂ physisorption) and containing the appropriate amount of nickel precursor (0.25 g of Ni(NO₃)₂·6H₂O for 5 wt. % Ni) was added dropwise. The solid was dried one day at room temperature, then overnight at 60°C, and it was finally calcined at 550°C for 5 h (heating rate 1°C min⁻¹).

- [0047] Preparation of Ni5%/pSiO₂-NH₃-N and Ni5%/pSiO₂-NH₃-C: The support pSiO₂ prepared according to procedure described in the above II.1 section, was impregnated by nickel nitrate in presence of NH₃ before (leading to Ni5%/pSiO₂-NH₃-N) and after (leading to Ni5%/pSiO₂-NH₃-C) removal of surfactants from the porosity.
- [0048] The effect of NH₃ on the stabilization of Nickel was also studied on non-porous siliceous support. Commercial (Aerosil® 380) non-porous silica (named nSiO₂) was impregnated with two different amounts of nickel 5 wt. % and 3.5 wt. % (Ni3.5% and Ni5%/nSiO₂-NH₃).
- [0049] Preparation of Ni5%/nSiO₂: it was prepared using a wet impregnation method. To do so, 1 g of Aerosil® 380 was suspended in 30 mL of water with 0.25 g of Ni(NO₃)₂·6H₂O under vigorous stirring for 2 h. Then, the mixture was dried at 60°C and finally calcined 2 h at 550°C (heating rate 1°C min⁻¹).
- [0050] The other solids, synthesized in the presence of NH₃ (Ni5%/nSiO₂-NH₃, Ni3.5%/nSiO₂-NH₃, Ni5%/pSiO₂-NH₃-N and Ni5%/pSiO₂-NH₃-C), were prepared using a modified wet impregnation method. Briefly, 1 g of siliceous (nSiO₂ or pSiO₂-C or -N) support was suspended in 30 mL of distilled water and a volume (around 2-3 mL) of NH₃ 30% (pH = 9) at 60°C for 10 min. Then, the adequate quantity of Ni(NO₃)₂·6H₂O dissolved in 5 mL of distilled water was added dropwise to the SiO₂ suspension under vigorous stirring. After 2 h of stirring at 60°C, the suspension was filtered and the solid washed with water, dried at 60°C during 24 h and finally calcined 2 h at 550°C (heating rate = 1°C min⁻¹).

[0051] III. Results

[0052] The impact of the preparation method on the textural properties of the solids as well as on the nickel characteristics will be analyzed in this part.

[0053] III.1 Physico-chemical properties of calcined and reduced solids

[0054] Figure 1 displays the nitrogen adsorption-desorption isotherms of the solids and, Table 2, their textural parameters.

[0055] Table 2: Physico-chemical properties of calcined Ni-silica based materials and of their respective parents.

Materials	Isotherms	Ni ^a (wt. %)	S _{BET} (m ² g ⁻¹)	V _{BJH Des.} ^b (cm ³ g ⁻¹)	D _{pores} ^c (nm)
SBA-15	(h)	---	567	0.4	4
Ni _{5%} /SBA-15-TS	(a)	4.7	355	0.3	4
pSiO ₂	(g)	---	832	0.8	4
Ni _{5%} /pSiO ₂ -NH ₃ -N	(b)	5.1	592	0.8	4
Ni _{5%} /pSiO ₂ -NH ₃ -C	(c)	5.1	581	0.7	4
nSiO ₂	(i)	---	341	2.8	---
Ni _{5%} /nSiO ₂	(d)	4.8	315	1.4	---
Ni _{5%} /nSiO ₂ -NH ₃	(e)	5.8	340	1.0	---
Ni _{3.5%} /nSiO ₂ -NH ₃	(f)	3.5	300	1.0	---

^a Nickel content estimated from H₂ consumption during TPR measurements; ^b Total N₂ volume from BJH desorption; ^c Average pores diameter deduced from BJH desorption pore size distribution.

[0056] According to the IUPAC classification, Ni_{5%}/SBA-15-TS (a), Ni_{5%}/pSiO₂-NH₃-N (b), and Ni_{5%}/pSiO₂-NH₃-C (c) as well as their corresponding supports pSiO₂ (g) and SBA-15 (h) (Fig. 1 A) are characterized by type IV isotherms in agreement with those of mesoporous materials described in *C. R. Chimie*, 21 (2018) 514-522, by M. Boutros et al.

- [0057] In Figure 1: N₂ adsorption-desorption isotherms at -196°C of a: Ni₅%/SBA-15-TS, b: Ni₅%/pSiO₂-NH₃-N, c: Ni₅%/pSiO₂-NH₃-C, d: Ni₅%/nSiO₂, d': reduced Ni₅%/nSiO₂, e: Ni₅%/nSiO₂-NH₃, e': reduced Ni₅%/nSiO₂-NH₃, f: Ni_{3.5}%/nSiO₂-NH₃, f': reduced Ni_{3.5}%/nSiO₂-NH₃, g: pSiO₂, h: SBA-15 and i: nSiO₂.
- [0058] Discussion: contrary to what could be expected for SBA-15, the hysteresis observed in the case of the commercial SBA-15 used in this work (Figure 1 (h)) before and after impregnation, was closer to H5 type that can be associated with certain pore structures containing both open and partially blocked mesopores (e.g., plugged hexagonal templated silicas). Compared to its support, Ni/SBA-15-TS displayed a decrease in the pore volume (-25%) and the specific surface area (-40%). Such modifications in the textural parameters could be related either to the incorporation of Ni in the porosity and/or more preferentially to some pores blocking since the plug observed on the impregnated solid was relatively more important than on the corresponding naked support. On the other hand, as expected, compared to its parent support (pSiO₂ (g)), Ni₅%/pSiO₂-NH₃-C (c) showed a decrease in the pore volume which is not the case for Ni₅%/pSiO₂-NH₃-N (b) due to the presence of the surfactant inside the porosity of pSiO₂-N during impregnation. Moreover, both Ni₅%/pSiO₂-NH₃-C and N exhibited around 20% decrease of the specific surface area. These two solids with their support exhibited (Fig. 1 A) H2(a) hysteresis loops shapes in agreement with more complex pore structures (Fig. 1 A). Such observation is the consequence of using a mixture of two structure-directing agents, *i.e.* P123 and CTABr. Compared with the literature, pSiO₂ prepared with P123: CTABr molar ratio of 1:4 exhibited typically the same isotherms, hysteresis loop, pore size and volume with relatively larger surface area (832 instead 650 m² g⁻¹). It has also to be mentioned that the hysteresis loop in the case of Ni₅%/pSiO₂-NH₃-C seems to be a little bit flattened. Such modification may be related either to the prolonged contact of the calcined siliceous support with NH₃ (which could deteriorate the support) and/or to the double calcination of Ni₅%/pSiO₂-NH₃-C (before and after impregnation).

- [0059] $\text{Ni}_{5\%}/\text{nSiO}_2$ (d), $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ (e) and $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$ (f) samples as well as the corresponding naked support nSiO_2 (i) (Fig. 1 B and B') exhibit type II isotherms (IUPAC classification) whose shapes are characteristic of the aggregation of their non-porous grains [25]. The presence of hysteresis loop for such solids can be related to inter-granular porosity, which also explains the high N_2 volume adsorbed (BJH) especially in the case of the support nSiO_2 . Compared to their support, $\text{Ni}_{5\%}/\text{nSiO}_2$ (d), $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ (e) and $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$ (f) are characterized by a decrease of the adsorbed N_2 volume. However, the specific surface area remained more or less unchanged (*c.a.* $300 \text{ m}^2 \text{ g}^{-1}$) for the whole series. It is noteworthy that all of the non-porous solids showed some microporosity that could be detected from their isotherms at very low P/P_0 .
- [0060] Reduced $\text{Ni}_{5\%}/\text{nSiO}_2$, $\text{Ni}_{3.5\%}$ and $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ were also analyzed by N_2 sorption (Fig. 1 C) showing very similar isotherms before and after reduction. However, the specific surface areas decreased for the three reduced samples (265 , 291 and $260 \text{ m}^2 \text{ g}^{-1}$ for $\text{Ni}_{5\%}/\text{nSiO}_2$, $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ and $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$, respectively), which may be caused by the heat treatment during the reduction step. In addition, it could be noticed that the total N_2 adsorbed volume was somewhat higher after reduction in the case of solids prepared in presence of NH_3 (1.2 *vs.* $1.0 \text{ cm}^3 \text{ g}^{-1}$ for both $\text{Ni}_{3.5\%}$ and $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$) compared to those prepared without ammonia (1.3 *vs.* $1.4 \text{ cm}^3 \text{ g}^{-1}$ for $\text{Ni}_{5\%}/\text{nSiO}_2$).
- [0061] III.2 NiO and Ni^0 characterizations
- [0062] XRD patterns for the calcined samples (NiO) (Fig. 2 A) showed a wide peak between $2\theta^\circ = 15\text{--}30^\circ$ due to diffusion effects by the amorphous silica walls. Five intensive diffraction peaks at $2\theta^\circ = 37.3^\circ$, 43.1° , 62.8° , 75.4° and 77° corresponding to NiO (JCPDS no. 89-7130) were also detected on the calcined $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a) and $\text{Ni}_{5\%}/\text{nSiO}_2$ (d). Particles size for these two samples, estimated from Scherrer equation, were 5.7 nm and 13.8 nm (Table 3), respectively thus highlighting the advantages of porous materials such as SBA-15. In contrast, no peaks corresponding to crystalline NiO were detected for all the other solids prepared in the presence of NH_3 .

However, three peaks were noticeable at $2\theta = 34.1^\circ$, 36.7° and 60.5° for those solids. After reduction in conditions similar to those used just before the catalytic test (2 h at 650°C) (Fig. 2 B), three peaks corresponding to Ni^0 at $2\theta = 44^\circ$, 52° and 76° (JCPDS no. 70-1849) were detected for $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a) and $\text{Ni}_{5\%}/\text{nSiO}_2$ (d).

[0063] Figure 2 : XRD diffraction patterns of calcined (A) and reduced (B) a: $\text{Ni}_{5\%}/\text{SBA-15-TS}$, b: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$, c: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-C}$, d: $\text{Ni}_{5\%}/\text{nSiO}_2$, e: $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ and f: $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$.

[0064] Table 3: NiO and Ni^0 particles size and dispersion estimated from different techniques.

Materials	Before catalytic tests					Spent
	NiO size ^a	Ni^0 size ^a	Ni^0 size ^b	D ^c	Ni^0 size ^d	Ni^0 size ^a
	(nm)	(nm)	(nm)	(%)	(nm)	(nm)
$\text{Ni}_{5\%}/\text{SBA-15-TS}$	5.7	6.5	6.1	16.0	6.2	6.7
$\text{Ni}_{5\%}/\text{nSiO}_2$	13.8	17.1	19.3	4.8	21.2	16.7
$\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$	PS ^e	No Peaks	3.3	28.0	3.6	n.d. ^f
$\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$	PS ^e	No Peaks	n.d. ^f	41.7	2.4	No Peaks
$\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$	PS ^e	No Peaks	4.2	19.6	5.1	3.8

^a From the Scherrer equation (XRD); ^b From TEM images by counting more than 400 particles;

^c Nickel dispersion calculated from H_2 chemisorption; ^d From H_2 chemisorption; ^e PS: Phyllosilicates; ^f n.d.: Not determined.

[0065] Discussion: no significant changes in the particles size occurred during the reduction of NiO in the case of $\text{Ni}_{5\%}/\text{SBA-15-TS}$. On the contrary, after reduction, $\text{Ni}_{5\%}/\text{nSiO}_2$ showed bigger Ni^0 particles (17.1 nm) than the NiO ones (table 3) which evidences sintering.

[0066] In the same line with the XRD results of the calcined solids, no peaks could be noticed after the reduction of the materials synthesized in the presence

of NH_3 despite Ni loading values comprised between 3.5 and 5 wt.%. Such observations (no NiO/Ni^0 peaks) could be related to the small size of the nanoparticles and their good dispersion on the support when NH_3 was used.

[0067] Additional results:

[0068] X-Ray Photoelectron Spectroscopy (Fig. 3) and Temperature-programmed reduction (Fig. 4) analyses were carried out on the calcined solids in order to study, first, the presence of nickel (especially for the solids prepared in presence of NH_3), then its oxidative state and to investigate their reduction behaviors.

[0069] XPS measurements performed on $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a), $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$ (b), $\text{Ni}_{5\%}/\text{nSiO}_2$ (d), $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ (e) and $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$ (f) exhibited, for all those solids, two main peaks corresponding to $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ with their satellites.

[0070] In figure 3: XPS spectra of calcined a: $\text{Ni}_{5\%}/\text{SBA-15-TS}$, b: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$, d: $\text{Ni}_{5\%}/\text{nSiO}_2$, e: $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ and f: $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$.

[0071] In figure 4: H_2 -TPR profiles of calcined a: $\text{Ni}_{5\%}/\text{SBA-15-TS}$, b: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$, c: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-C}$, d: $\text{Ni}_{5\%}/\text{nSiO}_2$, e: $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ and f: $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$ recorded with a H_2 5 Vol. %/Ar flow of 30 mL min^{-1} and a heating rate of $10^\circ\text{C min}^{-1}$.

[0072] Discussion: The $\text{Ni } 2p_{3/2}$ peak assigned to NiO for both $\text{Ni}_{5\%}/\text{nSiO}_2$ (d) and $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a) could be deconvoluted into two different peaks. Due to their binding energy, those peaks could be attributed to nickel in strong (856 eV) or weak (854.7 eV) interaction with the support (to our knowledge, binding energy of $\text{Ni } 2p_{3/2}$ of bulk NiO is 853.6–854.4 eV). XPS also showed one peak at higher binding energy (approximately 857 eV) for $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$ (b), $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$ (f) and $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ (e). This higher energy identified only for those solids, could be related to nickel in stronger interaction with the support which is not the case for $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a) and $\text{Ni}_{5\%}/\text{nSiO}_2$ (d).

[0073] The TPR profiles displayed in figure 4 showed that the solids prepared in

the presence of NH_3 are characterized by higher reduction temperatures with one ill-defined and broad peak located between 450 and 900°C (b, c, e, f). In contrary, the catalysts prepared in the absence of NH_3 exhibited two more defined reduction peaks (a, d). The first, at lower temperature, (400°C) can be attributed to the reduction of bulk NiO with low metal-support interaction and/or big aggregates. However, the second (600-650°C) was tentatively assigned to the reduction of the NiO species strongly interacting with SiO_2 . In parallel, the Ni wt.% values estimated from the consumed H_2 quantity are summarized in table 3. Further, we checked, by ICP-EOS for $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ (e) that the value obtained by H_2 -TPR (5.8%) are very similar to that obtained by ICP-EOS (5.9%).

[0074] Monitoring of calcined and reduced solids:

[0075] Figure 5: TEM images of calcined microtomed A: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$, B: $\text{Ni}_{5\%}/\text{SBA-15-TS}$, C: $\text{Ni}_{5\%}/\text{nSiO}_2$ and D, D': $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$.

[0076] Figure 6: TEM images of reduced microtomed; a: $\text{Ni}_{5\%}/\text{SBA-15-TS}$, b: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$, c: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-C}$, d: $\text{Ni}_{5\%}/\text{nSiO}_2$, e: $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ and f: $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$.

[0077] The calcined (Fig. 5) and reduced (Fig. 6) solids were analyzed by transmission electron microscopy in order to evaluate the morphology of the nickel particles, as well as their size (summarized in table 3) and their dispersion on the supports. Calcined $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (Fig. 5 B) and $\text{Ni}_{5\%}/\text{nSiO}_2$ (Fig. 5 C) materials prepared without using NH_3 , clearly exhibited NiO particles. In particular, $\text{Ni}_{5\%}/\text{nSiO}_2$ showed big nickel aggregates. Those results are in good correlation with XRD analyses. TEM images of $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (Fig. 5 B) revealed small particles inside the porosity but big aggregates on the external surface of the grains. In the presence of NH_3 , no nickel particles could be observed but some branch-like structures were detected on the external surface of the siliceous grains for both porous ($\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$) and non-porous ($\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$) solids (Fig. 5 A and D, respectively). It has to be noticed also that, after their reduction, TEM of $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (Fig. 6 a) and $\text{Ni}_{5\%}/\text{nSiO}_2$ (Fig. 6 d)

emphasized no significant modification in their morphologies (dispersion, porosity etc...).

[0078] In contrast, the lamellar structures observed on the calcined solids prepared in presence of NH_3 (Fig. 5 A and B) were not detectable anymore after the reduction step. Instead of them, well-dispersed and tiny nanoparticles of, normally, Ni^0 (because it appears after reduction) on the grains surface could be detected in the case of the non-porous support (Fig. 6 e and f). In the case of porous solids, ($\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$ and $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-C}$ (Fig. 6 b and c, respectively)) most of the observed particles coated the outer grains surface of the porous support and no nickel particles were detected in their porosity.

[0079] EDX/MAPPING and EDX analyses:

[0080] Figure 7: A: TEM-MAPPING and B: TEM-EDX results for microtomed $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$.

[0081] EDX/MAPPING (Fig. 7 A) and EDX (Fig. 7 B) analyses were carried out on the reduced $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$ in order to confirm the absence of nickel (Ni^0) inside the porosity. Indeed, both techniques revealed that Ni mainly occupied the external surface of this material.

[0082] The nickel dispersion and its accessibility were estimated from H_2 chemisorption measurements (table 3). The determination of Ni dispersion was estimated on the basis of the first H_2 isotherm (including reversibly and irreversibly chemisorbed hydrogen) as recommended by Bartolomew C.H. in *Catal. Lett.* 7 (1990) 27-51.

[0083] Discussion: Clearly, these analyses emphasized that the use of NH_3 during the impregnation step, led to the improvement of the dispersion. This could be reflected by higher accessible nickel surface area due to smaller particles sizes. The $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$ sample was characterized by the highest dispersion value (*c.a.* 42%) which corresponds to the smallest nanoparticles (2.4 nm). Despite its higher nickel content, $\text{Ni}_{5\%}/\text{nSiO}_2\text{-NH}_3$ showed also a good nickel dispersion (28%) with nickel particle sizes of 3.6 nm.

- [0084] The comparison of the particle dimensions in Ni_{5%}/nSiO₂-NH₃ (3.6 nm) with Ni_{5%}/nSiO₂ (19 nm) clearly indicates that ammonia has an important effect on the dispersion (see Table 3). Surprisingly, for the sample based on porous supports impregnated in presence of NH₃ (Ni_{5%}/pSiO₂-NH₃-N), despite the deposition of nickel mainly on the outer grains surface, this last showed good dispersion and relatively small particles. Compared with Ni_{5%}/SBA-15-TS, where the nickel was incorporated into the porosity, Ni_{5%}/pSiO₂-NH₃-N (Table 3) exhibited better dispersion (19.6% vs. 16%) and smaller particles (5.1 nm vs. 6.2 nm).
- [0085] Infrared - FT-IR
- [0086] FT-IR spectra of the calcined samples collected at 120°C (after treatment at 300°C under air flow) are shown in Fig. 8A. All of them were characterized by an absorption band assigned to isolated silanol groups at 3733 cm⁻¹ [29] in the O-H stretching region.
- [0087] In figure 8: A and B: DRIFT and C: ²⁹Si solid state (HPDEC) NMR spectra of calcined d: Ni_{5%}/nSiO₂, e: Ni_{5%}/nSiO₂-NH₃, f: Ni_{3.5%}/nSiO₂-NH₃, and i: nSiO₂. IR spectra in Fig. 8 B were collected using samples diluted in diamond powder. NMR spectra were normalized on Q4.
- [0088] Nickel-based solids prepared in presence of NH₃ (Fig. 8 A e and f) showed an additional band at 3621 cm⁻¹ that would be due to the vibration of the OH group linked with Ni atoms or H₂O molecule encapsulated between two layers of a phyllosilicate structure in connection with the work reported in *J. Phys. Chem. B* 101 (1997) 7060-7074 by Burattin P. et al. Indeed, such band did not appear in the spectrum of pure nSiO₂ treated with NH₃ (Fig. 9).
- [0089] In figure 9: IR spectrum (DRIFT) of calcined SiO₂ after treatment with NH₃ without nickel.
- [0090] Discussion: The frequency range lower than 1500 cm⁻¹ of the spectra of Ni_{5%}/nSiO₂, Ni_{5%}/nSiO₂-NH₃, and nSiO₂ (Fig. 8 B d, e and i respectively) was further analyzed after the dilution of those samples with up to 50% of diamond powder. On the contrary to what is observed for nSiO₂ and

Ni_{5%}/nSiO₂; Ni_{5%}/nSiO₂-NH₃ exhibited a different signature between 750 and 625 cm⁻¹ which could be due to the presence of a small band (at around 665 cm⁻¹) in this region (see the zoomed part from Fig. 8 B).

[0091] ²⁹Si solid-state NMR spectrum (HPDEC) is widely used to characterize amorphous silica. This technique enables the silicon atoms of bulk silica (Q⁴= Si(OSi)⁴) to be distinguished from silanol groups, also terminal silanol groups (Q³= Si(OSi)₃(OH)) from geminal silanol groups (Q² = Si(OSi)₂(OH)₂). In addition, this method facilitates the evaluation of the chemical environment of the Si atoms. A modification in this environment will be reflected by certain chemical shift (ppm). Figure 8 C shows the ²⁹Si solid-state NMR spectra of Ni_{5%}/nSiO₂ (d), Ni_{5%}/nSiO₂-NH₃ (e), Ni_{3.5%}/nSiO₂-NH₃ (f), and nSiO₂ (i) samples. From those results, a tiny shift (around 1 ppm) toward lower magnetic field of the Q⁴ peak in the case of the solids prepared in presence of NH₃ could be revealed. Such shift is in agreement with a certain modification of the chemical environment of the Si atoms when ammonia was used.

[0092] IV. Activity of the catalysts toward DRM

[0093] The catalytic performances of selected solids were analyzed under two different set of conditions: Y: Catalyst weight: 50 mg, CH₄ and CO₂ conversion: 200-650 °C (5 °C min⁻¹), conversions stability at 650 °C during 12 h, GHSV = 144 L g⁻¹ h⁻¹ and Z: Catalyst weight: 10 mg diluted with 90 mg of fumed silica (Aldrich, CAS 381276), CH₄ and CO₂ conversion: 200-650 °C (5 °C min⁻¹), conversions stability at 650 °C during 12 h, GHSV = 960 L g⁻¹ h⁻¹.

[0094] IV.1 Catalytic test under GHSV = 144 L g⁻¹ h⁻¹

[0095] Ni_{5%}/pSiO₂-NH₃-N (b), Ni_{5%}/SBA-15-TS (a), Ni_{3.5%}/nSiO₂-NH₃ (f) and Ni_{5%}/nSiO₂ (d) (see in Figure 10: Catalytic performances of a: Ni_{5%}/SBA-15-TS, b: Ni_{5%}/pSiO₂-NH₃-N, d: Ni_{5%}/nSiO₂ and f: Ni_{3.5%}/nSiO₂-NH₃) were chosen to be tested in the DRM reaction in order to check the influence of the preparation method (two porous solids with and without NH₃ and two non-porous ones characterized by the higher (42%) and lower

(approximately 5%) nickel dispersion also with and without NH_3).

- [0096] After *in situ* reduction under H_2 (5 vol.% flow: 30 mL min^{-1}) at 650°C during 2 h, their performances were evaluated firstly in terms of CH_4 and CO_2 conversions versus temperatures until 650°C then at the same temperature during 12 h for the stability test.
- [0097] The conversions of CH_4 and CO_2 rise while increasing the temperature (Fig. 10 A and B). Under these conditions, the solids prepared in presence of NH_3 $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$ (b) and $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$ (f) were very active with CH_4 and CO_2 conversions (approximately 80% at 650°C) very close to the thermodynamic equilibrium ones and reached an H_2/CO ratio close to 1 (good selectivity). $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a) solid exhibited also good performances. On the other hand, $\text{Ni}_{5\%}/\text{nSiO}_2$ (d) turned out to be less active with CH_4 and CO_2 conversions of approximately 30%. Those results emphasized that i) adding NH_3 during the synthesis seems to be very interesting since both mesoporous and non-porous supports led to very good performances, ii) when NH_3 was not used, the mesoporosity played a crucial role towards enhancing the catalytic behavior of the solids.
- [0098] From the stability test, the samples prepared in the presence of NH_3 turned out to be more stable and selective than the others, with the same reactant's conversions and H_2/CO ratio close to unity during 12 h. On the contrary, $\text{Ni}_{5\%}/\text{nSiO}_2$ (d) and $\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a) showed a decrease up to 15% of the conversions just after 1 h on steam and a H_2/CO molar ratio < 1 .
- [0099] Characterization of the spent catalysts at $\text{GHSV} = 144 \text{ L g}^{-1} \text{ h}^{-1}$: the coke deposition after catalytic test was evaluated by thermogravimetric analyses. From the results displayed in figure 11 A, it can be noticed that the higher weight loss (amount of deposited carbon) was detected for $\text{Ni}_{5\%}/\text{nSiO}_2$ (d).
- [00100] In figure 11: A: TGA profiles and B: XRD patterns of spent a: $\text{Ni}_{5\%}/\text{SBA-15-TS}$, b: $\text{Ni}_{5\%}/\text{pSiO}_2\text{-NH}_3\text{-N}$, d: $\text{Ni}_{5\%}/\text{nSiO}_2$ and f: $\text{Ni}_{3.5\%}/\text{nSiO}_2\text{-NH}_3$.
- [00101] The quantity of coke was reduced when a mesoporous SBA-15 support was used instead of non-porous silica ($\text{Ni}_{5\%}/\text{SBA-15-TS}$ (a)), which could be related to the confinement of nickel inside the regular and ordered pores of SBA-15. The solids prepared in the presence of NH_3 (d and f) did not show

any coke deposition, which confirms the stabilization of Ni NPs. In addition, the spent solids were analyzed by XRD and the particles sizes of Ni⁰ were estimated using the Debye Scherrer equation. From XRD patterns (Fig. 11 B), no significant sintering occurred during the catalytic tests when comparing the Ni⁰ particles sizes before and after the catalytic test (Table 3).

[00102] IV.2 Catalytic test under GHSV = 960 L g⁻¹ h⁻¹

[00103] In order to better evaluate the catalytic properties of Ni/nSiO₂-NH₃ solids prepared without any surfactant, which could be more advantageous for industry, additional catalytic tests were performed.

[00104] To do so, the impact of the dispersion and Ni loading on the reactivity (see Ni_{3.5%} - Ni_{5%}/nSiO₂-NH₃ samples) was studied under kinetic regime (GHSV = 960 L g⁻¹ h⁻¹), far from the equilibrium conversion (Fig. 12).

[00105] In Figure 12: Catalytic performances of e: Ni_{5%}/nSiO₂-NH₃ and f: Ni_{3.5%}/nSiO₂-NH₃ under GHSV = 960 L g⁻¹ h⁻¹.

[00106] According to U. Oemar U. et al. in *Catal. Sci. Technol.* 6 (2016) 1173-1186, most of the studies conducted for Ni/silica are carried out at low gas hourly space velocities (GHSVs). Thus, it is important to know that the GHSV used here (960 L g⁻¹ h⁻¹) is among the highest one found in the literature for the DRM while using Ni-silica based catalysts especially. As discussed before and owing to the endothermic nature of this reaction, the conversions of CH₄ and CO₂ increase with temperature (Fig. 12 A and B). Ni_{3.5%}/nSiO₂-NH₃ exhibited very good conversions (higher than Ni_{5%}/nSiO₂-NH₃) under this severe reforming environment despite its lower Ni percentage. Those results can be referred to the better dispersion of Ni particles (42 % *vs.* 28% for Ni_{5%}) obtained in the case of this sample. In addition, both solids exhibited a very good stability during 12 h at 650°C (Fig. 12 A' and B'). It can also be noted that those catalysts let to a very selective DRM reaction since the H₂/CO ratio remained equal to approximately 1 during 12 h (Fig. 12 C and C').

Claims

- Claim 1. A nickel-silicon catalyst, wherein the nickel is present in an elemental weight percent of 1 to 7.5% considering the total weight of the catalyst, said nickel-silicon catalyst comprising a silicon oxide support bearing the nickel nanoparticles; and wherein the dispersion of the catalyst is at least 15%.
- Claim 2. A nickel-silicon catalyst according to claim 1, wherein the dispersion of the catalyst is at least 18%, and preferably at least 25%.
- Claim 3. A nickel-silicon catalyst according to any of claim 1 to 2, wherein the dispersion of the catalyst is at least 30%, preferably 35% and most preferably at least 40%.
- Claim 4. A nickel-silicon catalyst according to any of claim 1 to 3, wherein the nickel is present in an elemental weight percent of 1.5 to 6.5%.
- Claim 5. A nickel-silicon catalyst according to any of claim 1 to 4, wherein the nickel is present in an elemental weight percent of 2 to 6%.
- Claim 6. A nickel-silicon catalyst according to any of claim 1 to 5, wherein the silicon oxide support is non-porous, wherein said silicon oxide support is considered non-porous when it presents a type II N₂ adsorption isotherm.
- Claim 7. A nickel-silicon catalyst according to any of claim 1 to 6, wherein the silicon oxide support comprises nickel phyllosilicate.
- Claim 8. A nickel-silicon catalyst according to any of claim 1 to 7, wherein the nickel-silicon catalyst according to the invention does not comprise essentially any cobalt atom, or any added cobalt atom.
- Claim 9. A nickel-silicon catalyst according to any of claim 1 to 8, wherein the nickel-silicon catalyst according to the invention does not comprise any element selected in the group of lanthanide and actinide, and does not contain indium, thallium, tin or lead.
- Claim 10. A nickel-silicon catalyst according to any of claim 1 to 9, wherein the particle size is below 6 nm.
- Claim 11. Process for the preparation of a metal-silicon catalyst for the dry reforming of methane reaction comprising the following steps:

- 1- suspending siliceous support in water ;
- 2- adding $M(NO_3)_2$ in the suspension according to step 1- ;
- 3- the mixture obtained in step 2- is allowed under stirring during at least 2 hours at a temperature and maintained between 20 and 60°C ;
- 4- evaporating the solvent ; and
- 5- the material obtained at step 4- is calcinated at least 2 h at 550°C.

Claim 12. Process according to claim 11, wherein the metal used is nickel.

Claim 13. Process according to any of claim 11 to 12, wherein step 1- comprise the addition of at least 2 mL of 30 wt.% aqueous NH_3 , or an equivalent concentration of aqueous NH_3 , per gram of silica.

Claim 14. Process according to any of claim 11 to 13, wherein during step 1- the reaction time does not exceed 4 hours at 1 bar.

Claim 15. Process according to any of claim 11 to 14, wherein said siliceous support used is selected between mesoporous silica material and non-porous silica material, wherein said silicon oxide support is considered non-porous when it presents a type II N_2 adsorption isotherm.

Claim 16. A nickel-silicon catalyst according to any of claim 1 to 10, obtainable by the process according to any of claim 11 to 15.

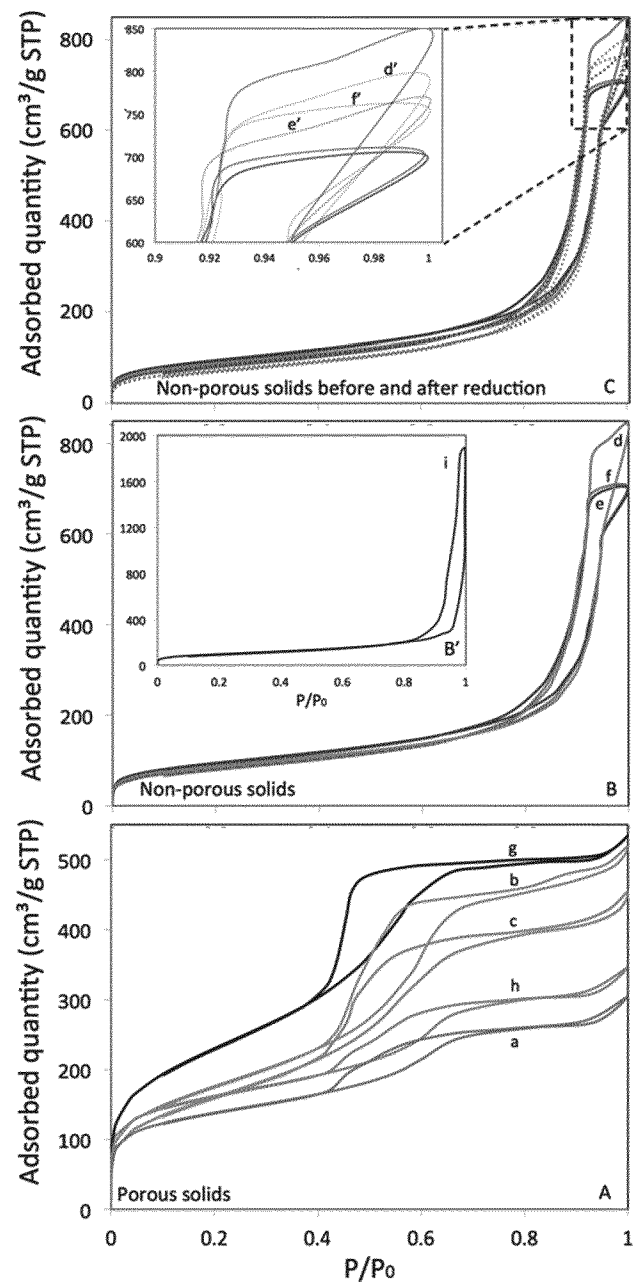


Fig. 1

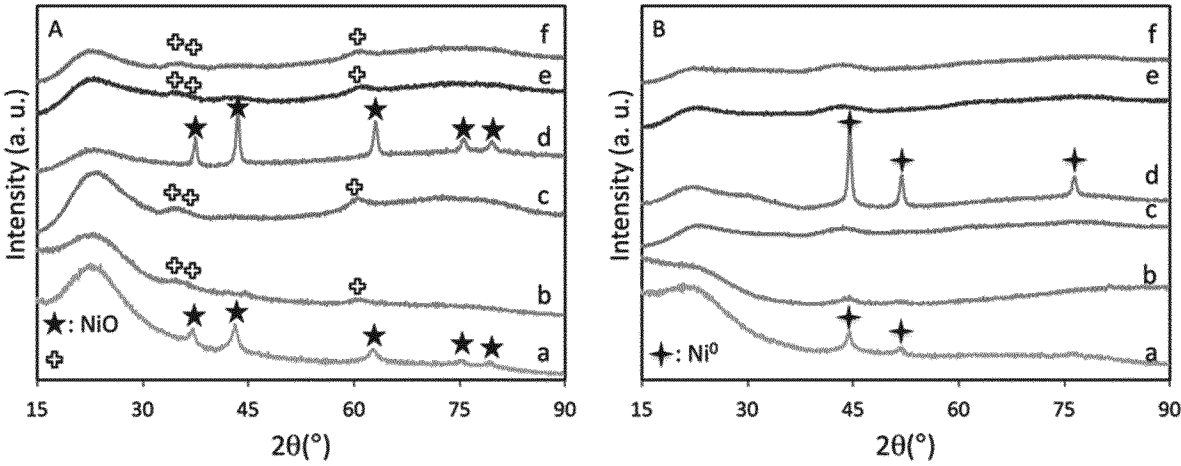


FIG. 2

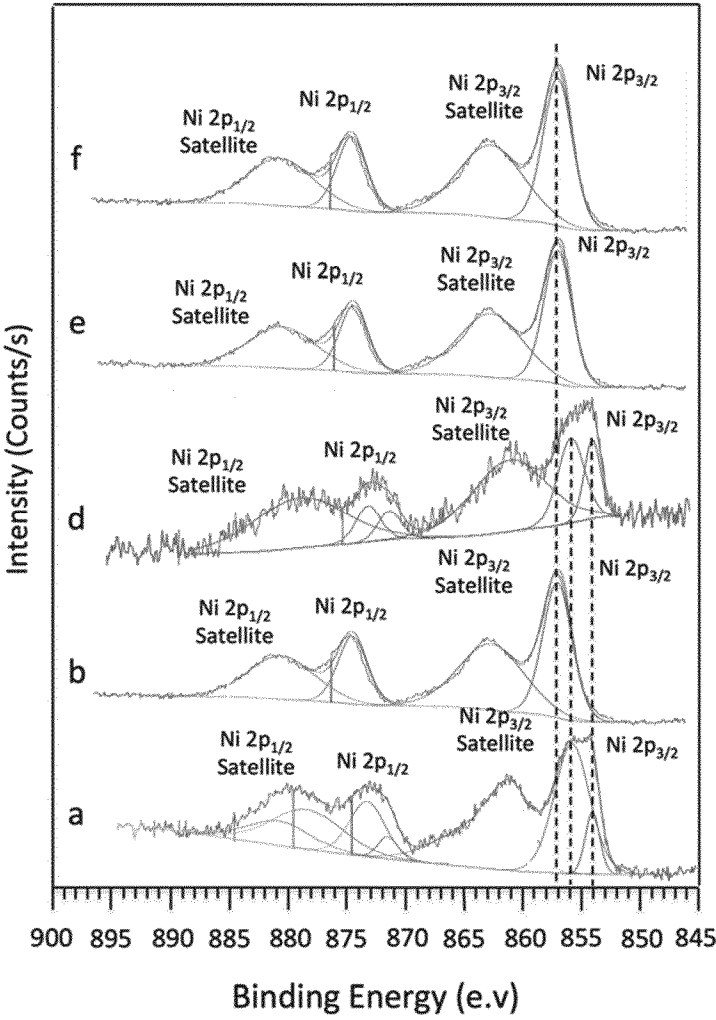


FIG. 3

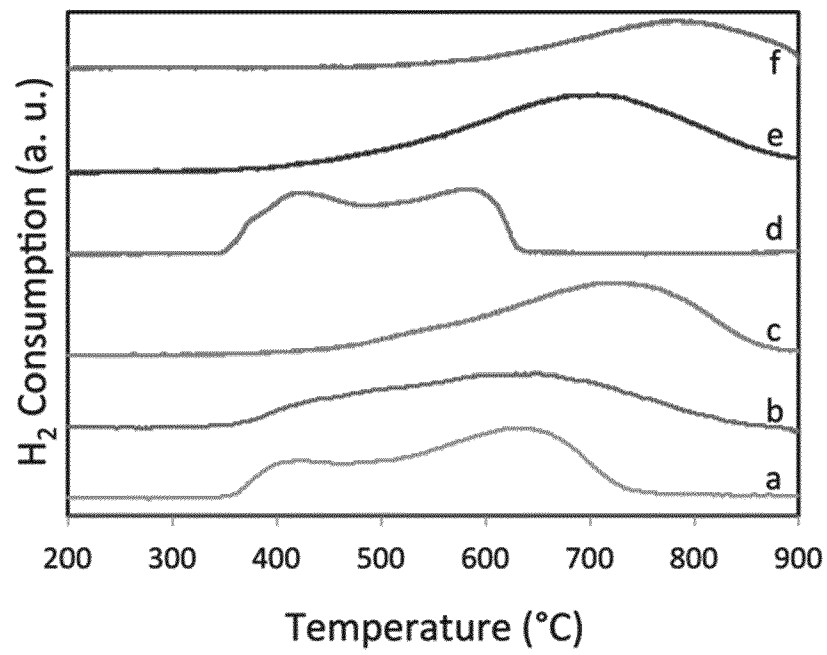


FIG. 4

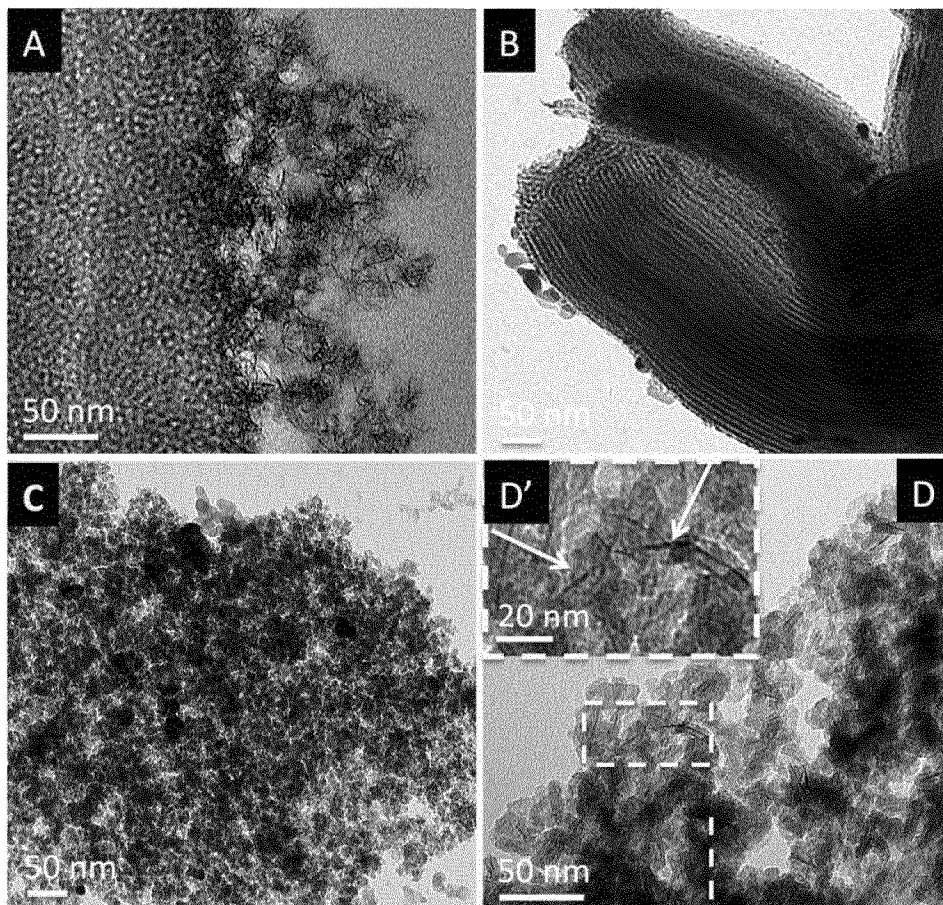


FIG. 5

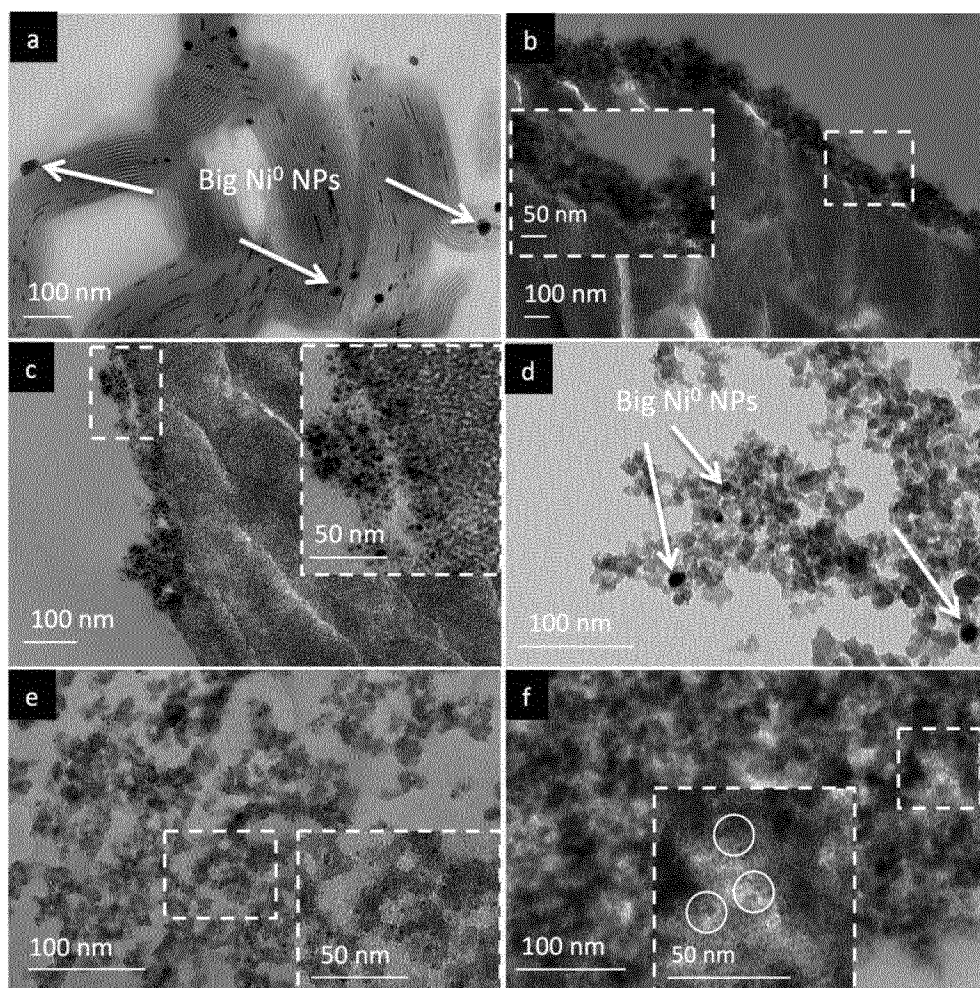


FIG. 6

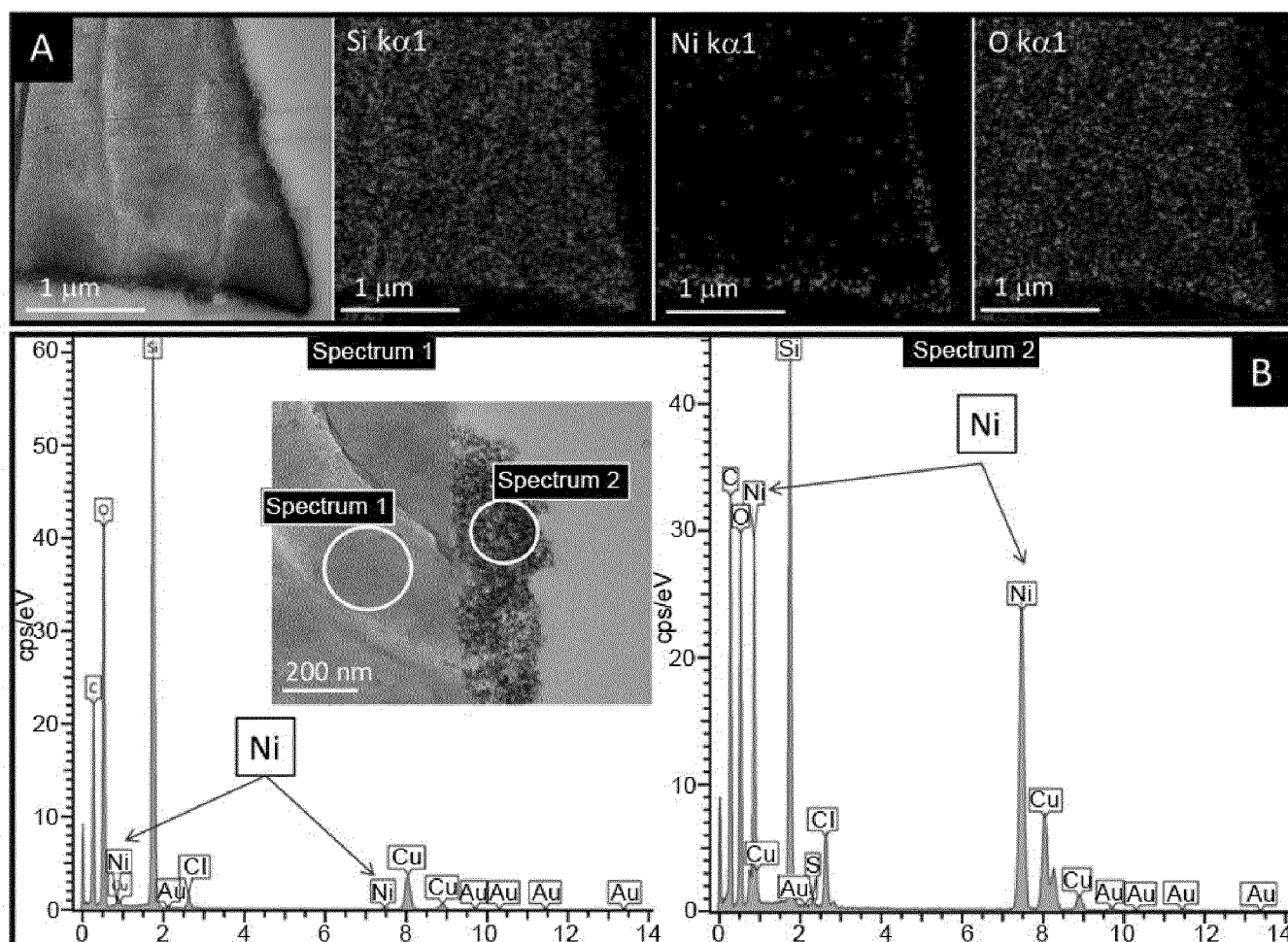


FIG. 7

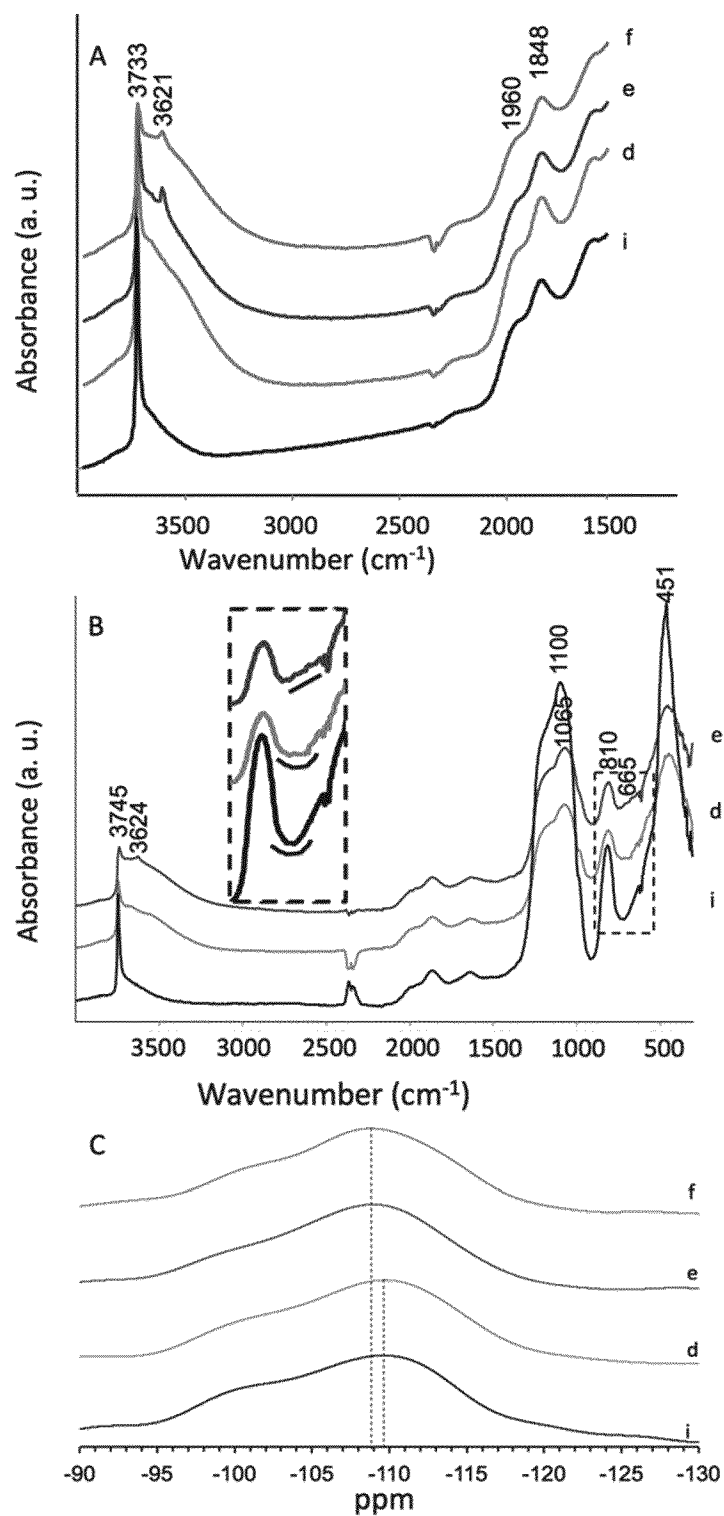


FIG. 8

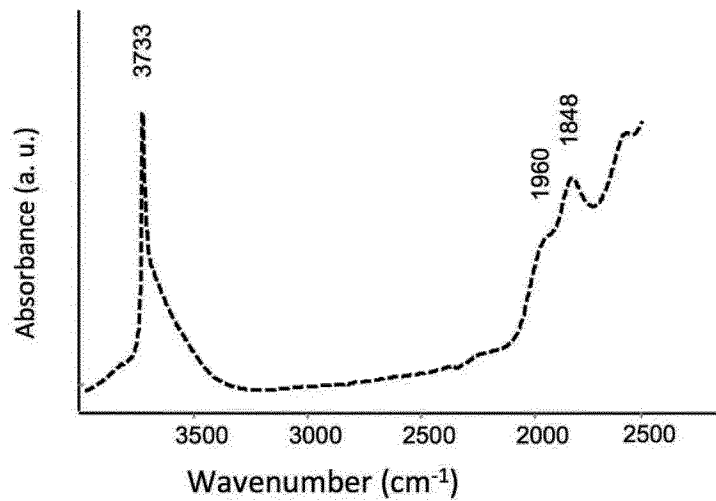


FIG. 9

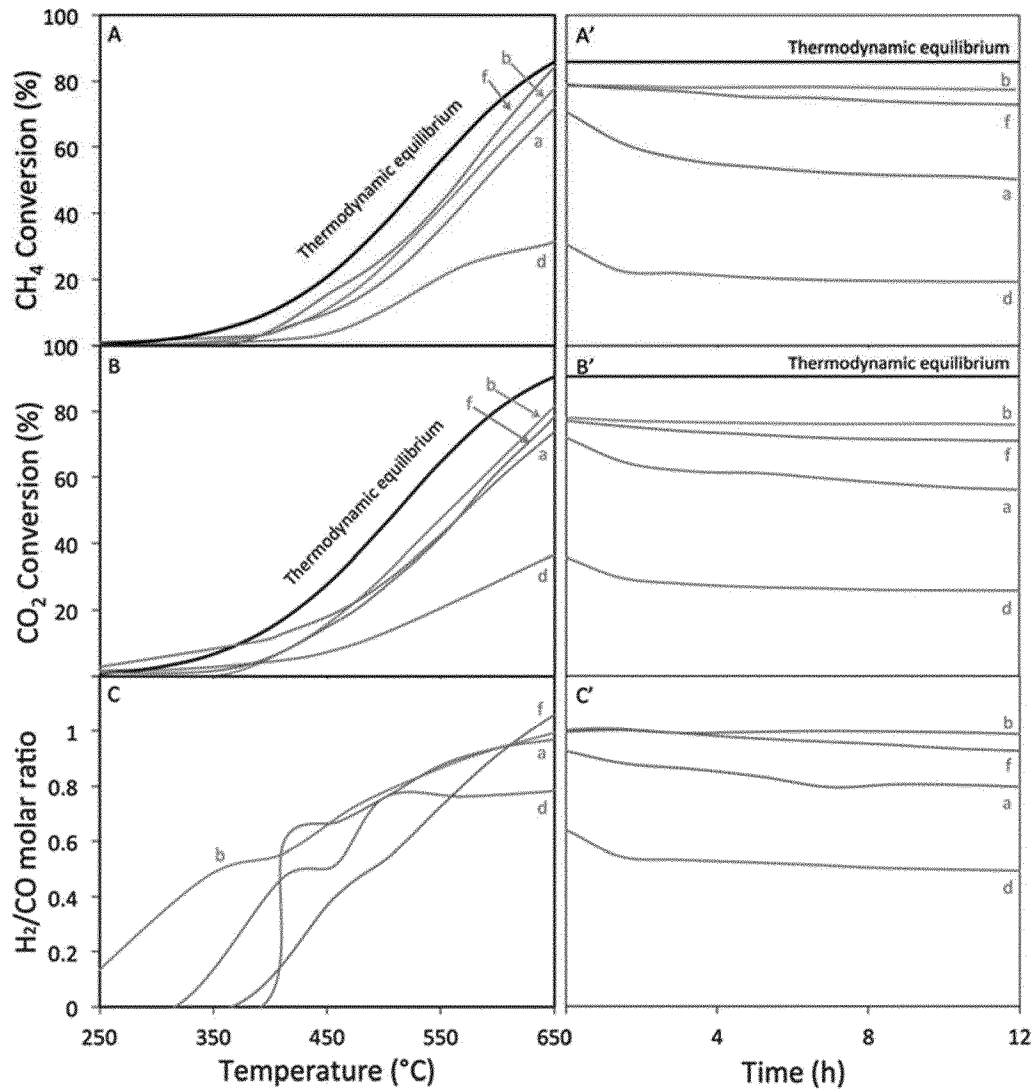


FIG. 10

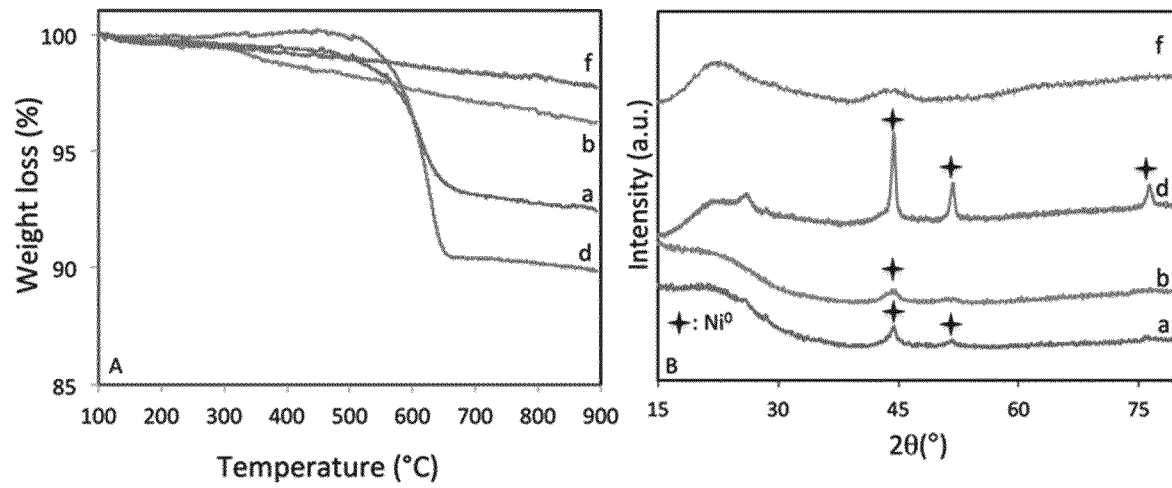


FIG. 11

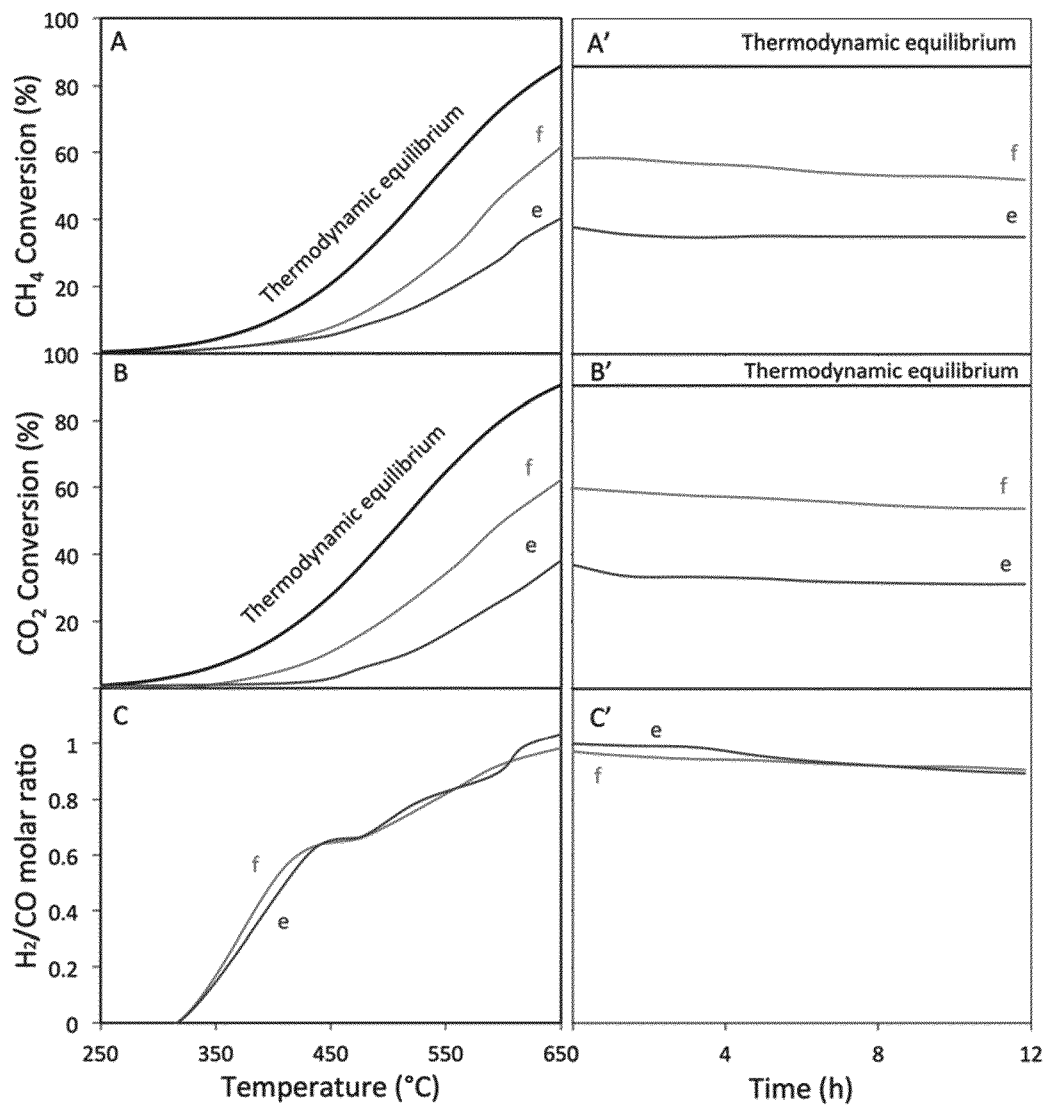


FIG.12