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1 **From polysilazanes to highly micro-/mesoporous Si₃N₄ containing *in situ***
2 **immobilized Co or Ni-based nanoparticles**

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17

18 **Abstract**

19 The *in-situ* immobilization of cobalt (Co) or nickel (Ni) nanoparticles (NPs) in highly
20 micro-/mesoporous polymer-derived silicon nitride (Si₃N₄) has been achieved. It is
21 accomplished by the coordination of a polysilazane with metal chlorides (CoCl₂ or NiCl₂)
22 followed by the subsequent pyrolysis of the metal:organosilicon polymer coordination
23 complex in the temperature range 700 - 1000 °C in flowing ammonia. By coupling X-ray
24 diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM), it
25 has been shown that the phase composition and crystallinity as well as the crystal size of

1 the metal particles are controlled by tuning the synthesis conditions including the Si:metal
2 ratio, the reaction time and the type of polysilazane as well as the heat-treatment
3 temperature. This has been discussed in details. Then, to exploit the catalytic activity of
4 metal NPs towards the hydrolysis of sodium borohydride (NaBH_4), we have developed
5 the micro-/mesoporosity of the Si_3N_4 matrix using a nano-casting approach. Hence,
6 materials with BET specific surface areas (SSA) as high as $921.5 \text{ m}^2\cdot\text{g}^{-1}$ have been
7 delivered to measure their potential for catalysis.

8

9 **Keywords**

10 Polysilazane; specific surface area; non noble transition metals

11

12 **1. Introduction**

13 Clean and sustainable energy technologies such as water splitting, CO_2 reduction, N_2
14 fixation, H_2 fuel cell production or catalytic abatement of major pollutants in air such as
15 NO_x , Volatile Organic Compounds (VOCs) and CO are currently under intensive research
16 and development because of their high efficiency, promising large-scale applications in
17 the future and can be utilized with virtually no pollution or greenhouse gas emissions [1–
18 4].

19 Catalysis is highly relevant for the development of clean and sustainable energy
20 technologies. However, most of these energy technologies use noble metal catalysts (*e.g.*,
21 platinum, Pt, and the derivative Pt group metals (PGM)) to promote key chemical
22 reactions [5–7]. PGM show outstanding catalytic activities and durability under various
23 pH conditions but their limited availability and high-cost hamper large-scale applications.
24 The development of low cost, earth-abundant and highly efficient alternatives to PGM

1 via materials discovery as a key element for adoption of clean and sustainable energy
2 technologies is essential [5].

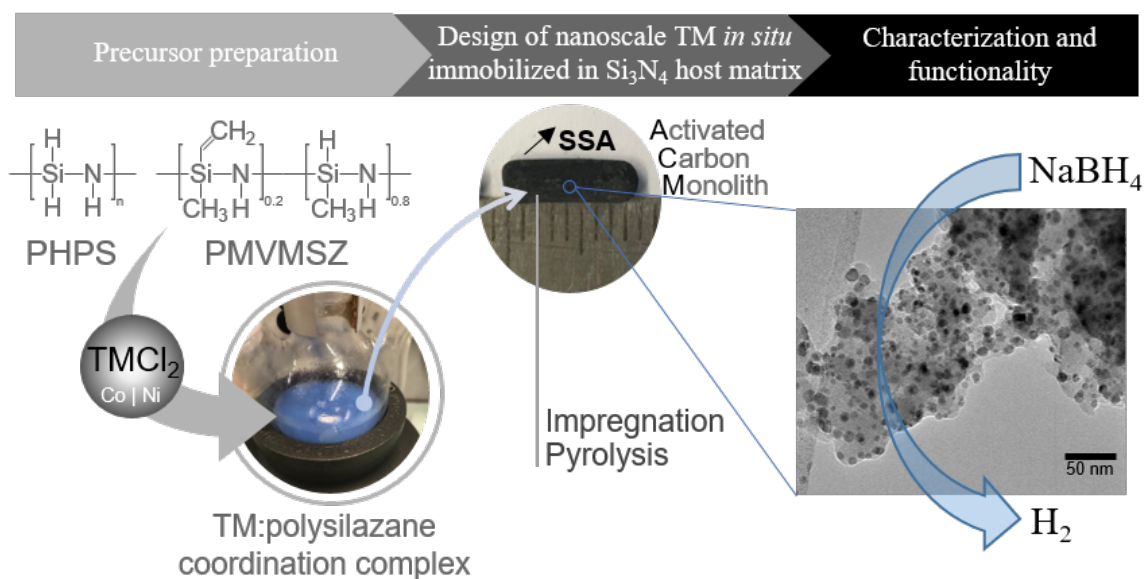
3 On the one hand, the expected high activity of non-noble transition metals (TM) such
4 as Co and Ni along with their attractive cost compared with that of noble metal catalysts
5 has sparked a growing interest in the synthesis of such metals as nanoparticles (NPs).
6 These materials are particularly relevant for use in alkaline media environments (because
7 their active oxide counterparts are stable in such an environment) to meet the
8 requirements of high activity, selectivity and long-term stability with superiority to
9 competitors (*e.g.* PGM) [6–8].

10 On the other hand, advanced ceramics are high value-added products for clean and
11 sustainable energy technologies; especially when used as durable supports on which the
12 catalyst – the metal - is deposited in form of NPs [9,10]. However, aggregation and
13 sintering of NPs usually cause loss of catalytic performance. Immobilization of
14 catalytically active metal NPs on/within a high-surface-area inorganic support may
15 partially alleviate this deficiency [11].

16 Based on these preconceptions, a very convenient precursor route - the polymer
17 derived ceramics (PDCs) route - allows the formation of the support and the catalysts in
18 an one-step process; thus, the issues related to particle agglomeration and removal from
19 the support are avoided. This approach has been recently utilized for the preparation of
20 metal/Si-based (oxy-)carbide and carbonitride compounds such as Ni/SiC [12], Ni/SiOC
21 [13], Ni/SiCN(O) [14] and M/SiCN (M = Pd and Ru [15], Pd₂Ru [16], Cu [17,18] , Ir
22 [19], Ni [20], Pt [21], Co [22], Fe [23]) derived from metal-modified polycarbosilanes,
23 polysiloxanes and polysilazanes, respectively. Likewise, the effects of TM on the
24 evolution of polymer-derived SiOC have been investigated [24,25]. Also, Co/Ni–SiOC
25 materials have been tested as electrocatalysts for the oxygen reduction reaction (ORR)

1 [26]. In contrast, the one-step immobilization of TM NPs in a Si_3N_4 matrix systems (*i.e.*,
 2 $\text{TM}/\text{Si}_3\text{N}_4$) for heterogeneous catalysis has never been demonstrated. These components
 3 may be particularly attractive as supports and catalysts themselves [27–32].

4 Very recently, the *in-situ* formation of Co [33] and Ni [34] in Si_3N_4 at a temperature
 5 as low as 400 °C using perhydropolysilazane (PHPS) as a Si_3N_4 precursor and ammonia
 6 [33] or nitrogen [34] as a pyrolysis atmosphere has been reported. Herein, the preparation
 7 of highly micro-/mesoporous Si_3N_4 -encapsulated Co or Ni NPs with various TM contents
 8 through a coupling approach based on the PDCs route and a nano-casting strategy is
 9 achieved (Fig. 1).



10

11 **Fig. 1.** Flow diagram of the general process of designing micro-/mesoporous TM (TM =
 12 Co, Ni)/ Si_3N_4 nanocomposites from polysilazanes.

13

14 The preparation has been conducted based on the preparation of a set of Co- or Ni-
 15 containing polysilazanes (Fig. 1) in the temperature range 700 – 1000 °C and as-obtained
 16 compounds have been characterized in details. They have been investigated as self-
 17 supported nanocatalysts for the hydrolysis of alkaline aqueous sodium borohydride [35],
 18 [36]. While this does not identify the most efficient material for H₂ release from NaBH₄

1 it establishes a route to the development of a novel generation of durable self-supported
2 nanocatalysts via a simple method using inexpensive precursors.

3

4 **2. Experimental**

5 *2.1 Materials*

6 The synthesis of the precursors is carried out in a purified argon atmosphere passing
7 through a column of phosphorus pentoxide and then through a Schlenk line. The cleaned
8 glassware is stored in an oven at 95 °C overnight before being connected to the Schlenk
9 line, assembled, and pumped under reduced pressure for 30 min and then filled with
10 argon. All chemical products are handled in an argon-filled glove box (Jacomex, Campus-
11 type; O₂ and H₂O concentrations kept at ≤0.1 ppm and ≤0.8 ppm, respectively).
12 Perhydropolysilazane labelled PHPS in a 20 vol% concentration in di-n-buthylether
13 (commercial name: NN120-20) and poly(methylvinyl-*co*-methyl)silazane labeled
14 PMVMSZ (commercial name: Durazane[®] 1800) were provided by durXtreme GmbH,
15 Germany, stored in a freezer and used as-received. Anal. Found (wt%): Si, 67.2; C, 2.2;
16 N, 24.0; H, 6.2; O, 0.4. [Si_{1.0}C_{0.1}N_{0.7}O_{0.0}H_{2.6}]_n (*Normalized to total 100 wt % (total of*
17 *wt% was 99.5 wt%) and reference to Si_{1.0}. Oxygen content (below 2 wt%) omitted in the*
18 *empirical formulae*). FTIR (ATR/cm⁻¹): ν(N–H) = 3377 (m), ν(Si–H) = 2141 (vs), δ(N–
19 H): 1167 (m), δ(N–Si–N) = 812 (vs). ¹H NMR (300 MHz, C₆D₆, δ/ppm): 1.6-0.3 (br,
20 NH), 5.8-4.3 (br, SiH). The Durazane[®] 1800 labelled here PMVMSZ was provided by
21 Merck Company, Germany, stored in a fridge and used as-received. Anal. found (wt%):
22 Si, 41.3; C, 27.3; N, 22.7; H, 8.3; O, 0.4. [Si_{1.0}C_{1.5}N_{1.1}H_{5.5}]_n (*Normalized to total 100 wt*
23 *% (total of wt% was 98.9 wt%) and reference to Si_{1.0}. Oxygen content (below 2 wt%)*
24 *omitted in the empirical formulae*). FTIR (ATR/cm⁻¹): ν(N–H) = 3381 (s), ν(C–H in
25 vinyl) = 3058 (m), ν(C–H in methyl) = 2954 (s), 2902 (m) and 2848 (w), ν(Si–H) = 2123

1 (s), $\delta(\text{C}=\text{C}) = 1594$ (w), $\delta(=\text{C}-\text{H}) = 1405$ (w), $\delta(\text{Si}-\text{CH}_3) = 1251$ (m), $\delta(\text{N}-\text{H})$: 1169 (s),
2 $\delta(\text{C}=\text{C}=\text{CH}_2) = 947$ (w), $\nu(\text{N}-\text{Si}-\text{N}) = 897$ (vs), $\delta(\text{Si}-\text{CH}_3) = 787$ (m); $^1\text{H NMR}$ (300
3 MHz, CDCl_3 , δ/ppm): 0.4–0.1 (br, SiCH_3), 1.1–0.5 (br, NH), 4.9–4.4 (br, SiH), 6.3–5.7
4 (br, vinyl). Toluene (99.85%, Extra Dry over Molecular Sieve, AcroSeal(R)) was
5 purchased from Acros Organics™. The metal chlorides, nickel(II) chloride 98 % and
6 cobalt(II) chloride, anhydrous for synthesis, were obtained from Sigma-Aldrich and
7 Merck KGaA, respectively. Activated carbon monoliths labelled as AC were of type
8 NORIT RX3 (Cabot Corporation) with a purity of 97 % (SSA = 989 $\text{m}^2\cdot\text{g}^{-1}$; $V_p = 0.51$
9 $\text{cm}^3\cdot\text{g}^{-1}$; $\text{Ø}_p = 4.3$ nm).

10

11 *2.2 Preparation of the precursors*

12 The precursor preparation consisted to add under argon a solution of polysilazane
13 (PHPS or PMVMSZ) in toluene (thus di-n-buthylether is first extracted from PHPS) to a
14 suspension of previously weighed (in the glove-box) CoCl_2 or NiCl_2 in toluene in a three-
15 necked round-bottomed flask and to proceed to the heating of the mixture at toluene
16 reflux. In a typical experiment, 3 g of PHPS (66 mmol) (referred to the theoretical
17 monomeric unit of the polymer) are quickly added with a syringe under flowing argon to
18 a solution of 50 mL of toluene with 1.72 g of CoCl_2 (13.25 mmol) at RT under vigorous
19 stirring. Then, the temperature is increased up to toluene reflux under static argon and
20 kept at this temperature under vigorous stirring for 72 h. After cooling down, the solvent
21 is extracted via an ether bridge (40 °C/ $1.5\cdot 10^{-1}$ mbar) to release an air- and moisture-
22 sensitive Co-modified PHPS labelled **PHCo5-72** (5 being the Si:Co ratio) that appears as
23 a blue solid polymer. Anal. found (wt %): Si 39.3, C 2.2, N 16.2, O 2.9, H 3.7, Co 16.7,
24 Cl 19.8. $[\text{Si}_{1.0}\text{C}_{0.1}\text{N}_{0.8}\text{O}_{0.1}\text{H}_{2.6}\text{Co}_{0.2}\text{Cl}_{0.4}]_n$ (Normalized to total 100 wt % (total of wt% was
25 99.2 wt%) and reference to $\text{Si}_{1.0}$. Oxygen content (below 2 wt%) omitted in the empirical

1 *formulae*). FTIR (ATR/cm⁻¹): $\nu(\text{N-H}) = 3375$ (w), $\nu(\text{Si-H}) = 2161$ (s), $\nu(\text{Co-Cl}) = 1620$
2 (s), 1400 (w), $\delta(\text{N-H})$: 1182 (m), 1016 (w), $\delta(\text{N-Si-N}) = 835$ (vs).

3 Six samples have been prepared according to this procedure by changing:

- 4 i. The Si:Co ratio from 2.5 to 25 using PHPS as a pre-formed polymer and a
5 time of reaction at toluene reflux overnight. Samples are labelled **PHCo2.5**,
6 **PHCo5**, **PHCo25**;
- 7 ii. The type of TM (Co and Ni) using PHPS as a pre-formed polymer and fixing
8 a Si:TM ratio of 5 and a time of reaction at toluene reflux of 72 h. The samples
9 are labelled **PHCo5-72** and **PHNi5-72**;
- 10 iii. The type of the preformed polymer using PMVMSZ and fixing a Si:Co ratio
11 of 5 and a time of reaction at toluene reflux of 72 h. The sample is labelled
12 **PMCo5-72**;

13

14 2.3 Heat-treatment of precursors

15 Polymer samples are then placed in alumina boats in the glovebox, introduced in a
16 sealed tube under argon atmosphere to prevent any oxygen contamination of the samples
17 during the following transfer into a silica tube inserted in a horizontal furnace (Carbolite
18 BGHA12/450B) under argon. The tube is evacuated (0.1 mbar) and refilled with ammonia
19 (99.995 %) to atmospheric pressure. Subsequently, the samples are subjected to a cycle
20 of ramping of 5 °C.min⁻¹ in the temperature range RT–1000 °C in flowing ammonia
21 (dwelling time of 2 h at the temperature selected among 700, 800, 900 and 1000 °C). A
22 constant flow (120 mL.min⁻¹) is passed through the tube during the pyrolysis cycle. After
23 cooling under argon atmosphere, as-pyrolyzed samples are stored in the glovebox for
24 characterization. Samples are labelled by adding ‘_T’ to the name of the precursors with
25 T being the first (if T < 1000 °C) or two first (if T = 1000 °C) digits of the temperature at

1 which the precursors have been exposed. For example, the **PHCo5_10** sample represents
2 the **PHCo5** sample heat-treated at 1000 °C.

3 4 *2.4 Design of micro-/mesoporous monoliths*

5 The precursors have been used to coat AC samples. The latter is previously heat-
6 treated at 600 °C under reduced pressure (3.10^{-1} mbar) for 10 hours to remove the
7 presence of any trace of oxygen, moisture, or dangling groups (-OH, -COOH, etc.)
8 without structure modification; then, they have been stored inside the glove box. A
9 specific weight of AC is taken from the glove box in a Schlenk-type flask to be put under
10 reduced pressure before deposition of the polymeric samples in solution (5 wt%). AC
11 samples are infiltrated at reduced pressure according to an optimum mass ratio between
12 the polymer and AC (1.4) [12], [37]. Then, the composites are allowed to age for 24 h
13 under static vacuum with continuous ultra-sonication. After aging for 24 h, a filtration
14 step is performed, and the composites are washed with toluene under argon flow. Excess
15 of liquid is removed using a syringe and then the solvent is evaporated at low pressure
16 (5.10^{-1} mbar) at 30 °C for 2 h to generate the coated AC. The impregnated monoliths are
17 dried and transferred under protective atmosphere into a horizontal tube furnace
18 (Thermoconcept® OS50/450/12) to be subjected to a cycle of ramping at 100 °C.h⁻¹ to
19 400 °C under nitrogen, dwelling there for 2 h. This is followed by a pyrolysis under
20 ammonia at 100 °C.h⁻¹ at the final temperature fixed in the range 700 – 1000 °C, dwelling
21 there for 2 h. Cooling to RT at 120 °C.h⁻¹ produced the porous samples labelled by adding
22 ‘m’ to the name of the ceramic product. For example, the **mPHCo5_10** sample represents
23 the mesoporous sample produced from **PHCo5** by heat-treatment at 1000 °C.

24 25 *2.5 Characterization*

1 The chemical structure of polymers has been determined by transmission FTIR
2 spectroscopy using a Nicolet 6700 Thermofisher equipment working from 4000 to 400
3 cm^{-1} . The data are collected by Omnic™ Software. Chemical analyses of the polymers
4 have been performed at Mikroanalytisches Labor Pascher (Remagen, Germany). TG
5 analyses have been carried out in flowing nitrogen at $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to $1000\text{ }^{\circ}\text{C}$ using alumina
6 crucibles at ambient atmospheric pressure (STA 449 F3, Netzsch GmbH, Selb, Germany).
7 As-obtained ceramic samples isolated at different pyrolysis temperatures are crushed into
8 fine powders and evenly spread on Si low background sample holders (Bruker™). Then,
9 their phase composition is determined by XRD analysis (Bruker AXS D8 Discover, $\text{CuK}\alpha$
10 radiation, Billerica, Massachusetts, USA). As-obtained XRD patterns have been compared
11 to reference patterns of the Powder Diffraction File of the International Centre for
12 Diffraction Data (ICDD; PDF-4+: fcc-Co: 00-015-0806, hcp-Co: 04-001-3273, CoSi: 01-
13 079-8014, Co_2Si : 04-003-2126, Co_2SiO_4 : 01-070-2115, fcc-Ni: 00-004-0850, $\alpha\text{-Si}_3\text{N}_4$:
14 04-005-5074 and $\beta\text{-Si}_3\text{N}_4$: 04-033-1160). The produced ceramic monoliths have been
15 characterized by nitrogen gas adsorption-desorption measurements at 77 K. The
16 Brunauer–Emmett–Teller (BET) method has been used to calculate the specific surface
17 area of the samples. The modal pore diameter (MPD) is derived from the desorption
18 branches of the isotherms using the *Barrett–Joyner–Halenda* (BJH) method whereas the
19 total pore volume is estimated from the amount of N_2 adsorbed at a relative pressure (P/P_0)
20 of 0.97. The data are collected using a 3Flex Physisorption equipment, from Micrometrics
21 Instrument Corporation. The chemical analysis of selected powders has been done by
22 scanning electron microscopy equipped with energy dispersive spectroscope (EDS-SEM,
23 JEOL IT 300 LV, Tokyo, Japan). The samples are positioned on metallic stubs with the
24 aid of a water-based conductive graphene carbon paint. A drop of liquid, colloidal silver
25 is placed in the side of the sample to increase conductivity. Structural and morphological

1 characterizations have been conducted on powders by Transmission Electron Microscopy
2 with a JEM-2100F model from JEOL (Japan) for **PHCo5-72_8**, **PHCo5-72_10**, **PMCo5-**
3 **72_10** and **PHNi5-72_10** samples. The hydrolysis of NaBH₄ has been performed at 80 °C
4 in a highly alkaline medium (pH > 10). In a typical experiment, 16 mg of the porous
5 samples are introduced in 1 mL solution of NaBH₄ (120 mg in 2 % NaOH) into a reactor
6 (glass tube) that is sealed with a silicon septum and Parafilm®, and connected to a water-
7 filled inverted burette (water coloured in blue) via a cold trap for steam, maintained at
8 0 °C. Then, the reactor is immersed in an oil bath kept at 80 °C. A camera records the
9 water displacement in the inverted burette due to hydrogen generation. Hydrogen starts
10 to evolve rapidly, and the evolution is video recorded for 180 min, to be then
11 computationally analysed post-hydrolysis.

12

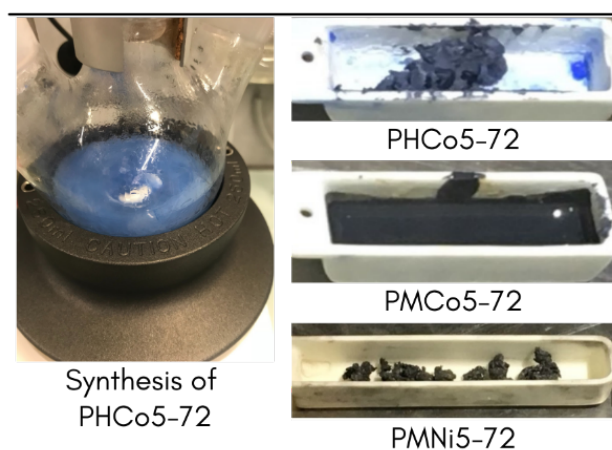
13 **3. Results and discussion**

14 *3.1 Precursor preparation*

15 Our general approach consists in the addition of a solution of polysilazane (PHPS or
16 PMVMSZ) in toluene to a suspension of nickel or cobalt chloride (NiCl₂ or CoCl₂) in
17 toluene at room temperature (RT). Then, the temperature is gradually increased to toluene
18 reflux, keeping the mixture for 72 h before cooling down and extracting the solvent. A
19 controlled molar (or atomic) ratio between metal chloride (TM) and the considered
20 polysilazane (Si) is applied. Following this strategy, we have synthesized a first series of
21 three representative polymers with a Si:TM (TM = Co or Ni) ratio of 5 by changing (1)
22 the type of pre-formed polymer (PH for PHPS or PM for PMVMSZ) and (2) the nature
23 of TM (Co or Ni). These three samples are labelled as **PHCo5-72**, **PHNi5-72** and
24 **PMCo5-72**. There is an additional series for which the Si:TM (TM = Co) ratio has been
25 changed from 2.5 to 25 according to the quantity of CoCl₂ added to the solution of PHPS.

1 The dwelling time at toluene reflux has been maintained overnight. Such polymers are
 2 denoted **PHCo2.5**, **PHCo5** and **PHCo25**.

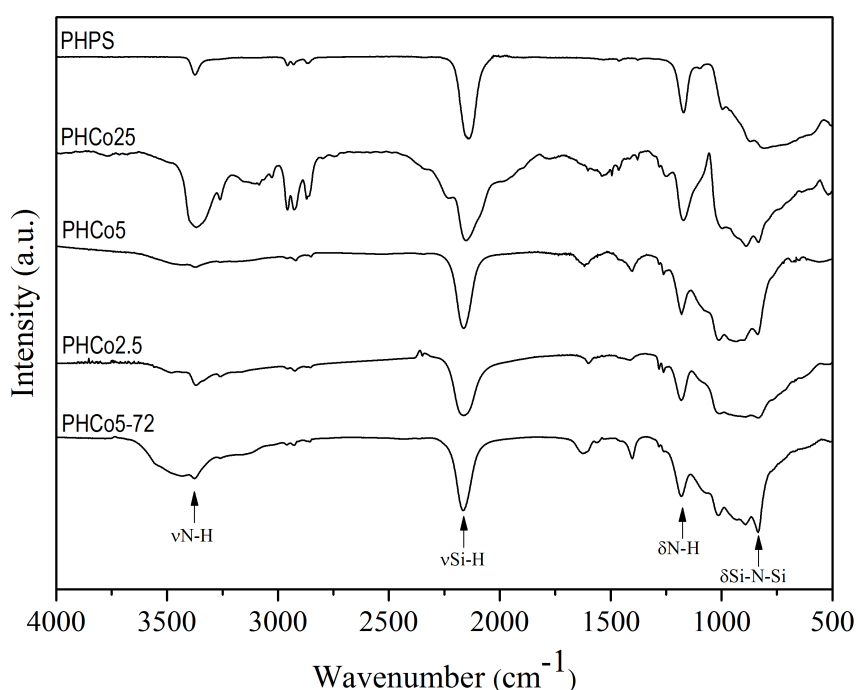
3 PHPS or PMVMSZ do not exhibit the same reactivity towards TM chlorides (TM =
 4 Co, Ni): after solvent extraction, all the samples derived from PHPS are solid and
 5 insoluble compounds whereas **PMCo5-72** (derived from PMVMSZ) remains liquid with
 6 a higher viscosity than PMVMSZ (Fig. 2). This is discussed hereafter.



7
 8 **Fig. 2.** Illustrations of the synthesis of TM-modified polysilazanes and polymers after
 9 solvent extraction.

11 The samples have been thoroughly investigated by FTIR spectroscopy (Fig. 3 and
 12 Fig. S1 (Supplementary Material)) whereas the **PHCo5-72** sample has been further
 13 selected and characterized by elemental analysis (Table 1). As reference samples, the
 14 FTIR spectra of PHPS and PMVMSZ and their elemental composition has been analyzed.
 15 As displayed in Fig. 3, the ATR-FTIR spectrum of PHPS shows the bands associated with
 16 $\nu_{\text{N-H}}$ (3377 cm^{-1}), $\nu_{\text{Si-H}}$ (2141 cm^{-1}), δ_{NH} of Si-NH-Si (1167 cm^{-1}) and $\delta_{\text{Si-N-Si}}$ (812
 17 cm^{-1}). The ATR-FTIR spectrum of PMVMSZ shows the expected absorptions of
 18 polysilazanes through the bands attributed to -Si-NH-Si- groups such as N-H stretching
 19 at 3381 cm^{-1} and the vibration of the NH unit bridging two silicon atoms at 1169 cm^{-1} . It
 20 also highlights the typical bands of i) vinyl silyl groups ($\text{CH}_2=\text{CH-Si-}$) as C-H vibrations

1 at 3056 cm^{-1} , C=C stretching at 1594 cm^{-1} , and scissoring of terminal methylene at 1405
 2 cm^{-1} , ii) Si-methyl groups with two bands located at 2954 , 2902 and 2848 cm^{-1} and
 3 assigned to the C–H stretching and at 1251 cm^{-1} ($\delta(\text{Si}-\text{CH}_3)$) and iii) Si-H groups through
 4 the strong absorption band at 2123 cm^{-1} . The large bands in the $1000\text{-}500\text{ cm}^{-1}$ range can
 5 be attributed to C=C/CH₂ groups at 947 cm^{-1} , Si-N stretching in Si-N-Si units centred at
 6 897 cm^{-1} and Si-C bond stretching at 787 cm^{-1} most probably overlapping the deformation
 7 of Si-H units.



8

9 **Fig. 3.** FTIR spectra of PHPS, **PHCo25**, **PHCo5**, **PHCo2.5** and **PHCo5-72**.

10 Although the TM-modified polysilazanes show similar spectra (except **PHCo25** that
 11 still reports toluene signature because of an incomplete extraction), minor changes are
 12 identified, as previously reported [33]: the relative intensity of $\delta\text{N-H}$ at 1167 cm^{-1} to $\nu\text{Si-}$
 13 N-Si at 812 cm^{-1} ($A_{\text{N-H}}/A_{\text{Si-N-Si}}$) in PHPS decreases with both the decrease of the Si:TM
 14 atomic ratio; thus with the increase of the TM content in all the samples (Fig. 3) and the
 15 duration of the reaction. This is evident by comparing the intensity ratios in the spectra
 16 of **PHCo5**, **PHCo2.5** and **PHCo5-72**. The spectrum of **PHCo5** displays an intensity ratio

1 of 0.72 (0.84 for PHPS) while the spectra of **PHCo2.5** and **PHCo5-72** exhibit intensity
2 ratios of 0.67 and 0.62, respectively. This indicates a lower portion of N-H bonds in
3 **PHCo2.5** and **PHCo5-72**. This tendency is also clear by comparing the relative intensity
4 of ν Si-H at 2141 cm^{-1} to ν Si-N-Si ($A_{\text{Si-H}}/A_{\text{Si-N-Si}}$) in PHPS: it decreases after addition of
5 CoCl_2 (by comparing the spectra of PHPS and Co-modified PHPS) which indicates that
6 Si-H bonds are also affected by CoCl_2 addition. In addition, it evolves with the change of
7 the Si:Co ratio from 5 (**PHCo5**) to 2.5 (**PHCo2.5**). The duration time at toluene reflux
8 (overnight or 72 h) also affects this ratio by comparing the intensity ratios in the spectra
9 of **PHCo5** and **PHCo5-72**: the former displays an intensity ratio of 1.0 (1.35 for PHPS)
10 while the latter exhibits an intensity ratio of 0.82 indicating a lower portion of Si-H bonds
11 in **PHCo5-72**. Interesting, the characteristic bands at 812 cm^{-1} (ν Si-N-Si), at 1167 cm^{-1}
12 (δ N-H) and at 2143 cm^{-1} (ν Si-H) in the spectrum of PHPS shift toward higher
13 wavenumbers in Co-modified PHPS (respectively from 812 to 835 cm^{-1} , from 1167 to
14 1182 (**PHCo2.5**) cm^{-1} and from 2141 to 2167 (**PHCo2.5**) cm^{-1}) which is attributed to the
15 highest degree of crosslinking of the delivered precursor. A hypothesis is that
16 dehydrocoupling reactions between Si-H bonds together or between Si-H bonds and N-
17 H bonds and/or transamination reactions [35–38] occur in our system by considering that
18 TM compounds are well known to catalytically activate some of these reactions in the
19 temperature range of $20 - 90\text{ }^\circ\text{C}$ [35,38]. Therefore, Co-modified PHPS are expected to
20 display a higher degree of crosslinking than PHPS. In this polymer system, both **PHCo2.5**
21 and **PHCo5-72** samples would exhibit the highest degree of crosslinking because of the
22 major occurrence of dehydrocoupling reaction and/or transamination reactions. Similar
23 observations can be made in Fig. S1A (Supplementary Material) by changing Co into Ni
24 (FTIR spectrum of **PHNi5-72**) regarding N-H bonds, but this does not affect the Si-H
25 bonds. Thus, this indicates that Ni is well suited to catalyze transamination reactions –

PHPS	2.2	6.2	24.0	0.4	-	67.2	-	$\text{Si}_{1.0}\text{C}_{0.1}\text{N}_{0.7}\text{O}_{0.0}\text{H}_{2.6}$
		3.6		2.5				
	2.2		16.7		16.5			
PHCo5-72	± 0.03	± 0.03	± 0.4	± 0.0	± 0.05	38.9	19.6	$\text{Si}_{1.0}\text{C}_{0.1}\text{N}_{0.9}\text{O}_{0.1}\text{H}_{2.5}\text{Co}_{0.2}\text{Cl}_{0.4}$
		03		2				

1

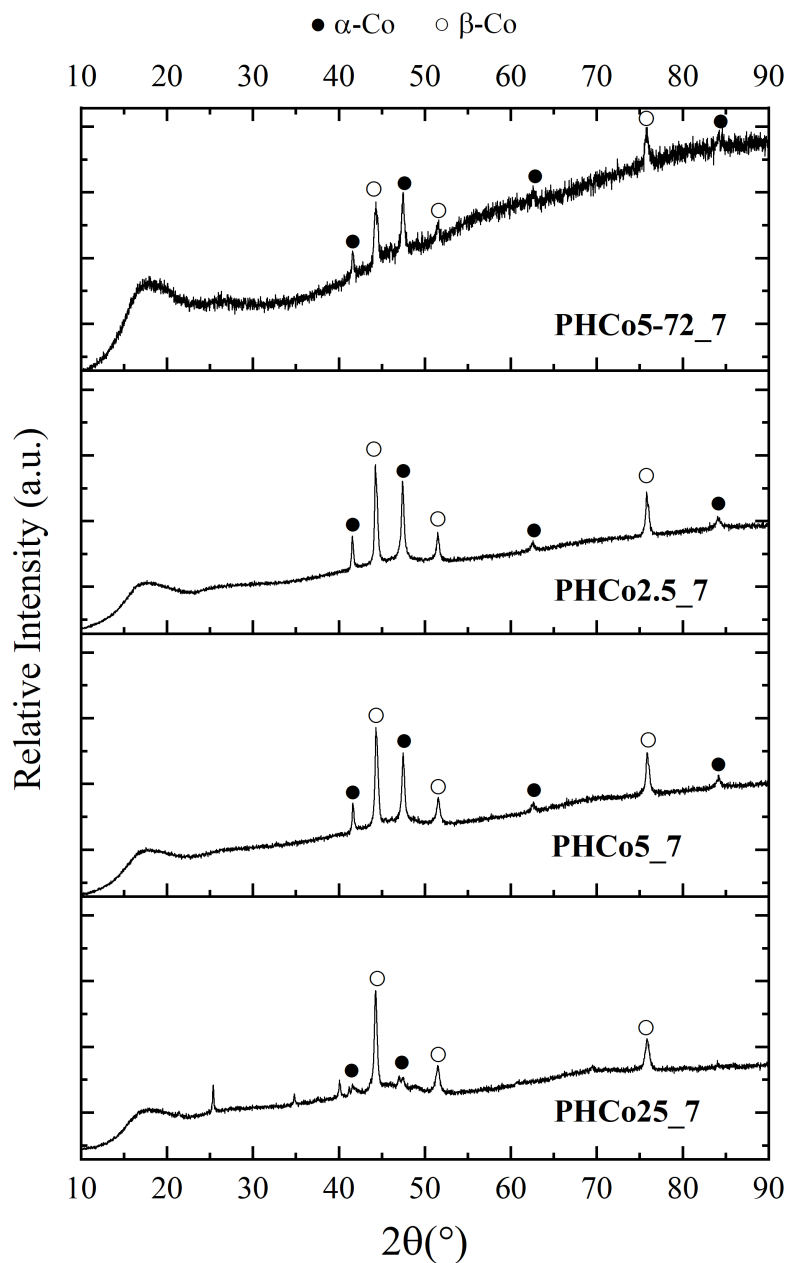
2 In a first approximation, we suggest that a blended compound with the appropriate
3 Si:Co ratio (=5) is delivered. However, the (slight) decrease of the Si:N ratio content in
4 **PHCo5-72** compared to PHPS tends to confirm the formation of Si-N bonds in **PHCo5-**
5 **72** which inherently results from dehydrocoupling reactions. Thus, TM (= Co, Ni)-
6 modified PHPS most probably represents polysilazanes coordinated by TM (= Co, Ni)
7 chlorides via silylamino groups in which dehydrocoupling reactions occur to further
8 crosslink the PHPS network.

9

10 *3.2 In-situ growth of nanoscale TM in the temperature range 700 to 1000 °C*

11 Hereafter, identification of the crystalline phase composition in the samples formed
12 by pyrolysis of precursors characterized previously from 700 to 1000 °C in flowing
13 ammonia has been explored. The temperature 700 °C has been selected as the minimum
14 temperature at which preceramic polymers is converted into ceramics [45]. 1000 °C is the
15 temperature at which the sample is considered as sufficiently stable to be explored for
16 further investigation in alkaline media. In addition, the analysis of XRD patterns has been
17 investigated to reach the crystallite size evolution upon heat-treatment. Then, micro- and
18 nanostructural information of selected samples have been collected by HR (High
19 Resolution)-TEM.

1 Fig. 4 reports the XRD evolution of the samples labelled PHCoX_Y with X being
 2 the Si:Co ratio and Y the first digit of the pyrolysis temperature: **PHCo25_7**, **PHCo5_7**,
 3 **PHCo2.5_7** and **PHCo5-72_7** samples.

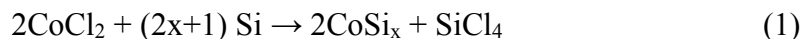


4
 5 **Fig. 4.** XRD patterns of the **PHCo25_7**, **PHCo5_7**, **PHCo2.5_7** and **PHCo5-72_7**
 6 samples.

7
 8 The addition of a low Co content in PHPS to form **PHCo25** leads to the growth of a
 9 β (fcc)-Co phase after pyrolysis at 700 °C in flowing ammonia (space group Fm-3m,

1 lattice constant $a = 0.35447$ nm, ICDD 00-015-0806) as confirmed by the indexation of
2 the peaks at $2\theta = 44.5^\circ$ (111), 51.6° (200) and 75.7° (220) [46] identified in the XRD
3 pattern of **PHCo25_7**. In addition, it can be observed the emergence of two poorly intense
4 XRD peaks at $2\theta = 41.9^\circ$ (100) and 47.6° (101); these positions are related to the
5 diffraction of the α (hcp)-Co phase (space group P63/mmc, lattice constants $a = 0.25071$
6 nm, $c = 0.408686$ nm, ICDD 04-001-3273) [46]. It is well known that at normal
7 conditions, bulk cobalt crystallizes in two phases: hexagonal closed packing (hcp, α) and
8 face-centred cubic (fcc, β) [47]. The striking difference between these two phases is the
9 stacking of atoms, i.e., in β -Co, it is ABCABC while in α -Co, it is ABABAB [48]. Earlier
10 studies on cobalt systems revealed that the synthesis conditions affect the phase
11 formations and lead to either single or mixed phases [49]. In general, it is found that a
12 single exclusive phase formation is probable when low-temperature methods are
13 employed [50], while the combination of phases is probable when high-temperature
14 methods are adopted [46]. In addition, it has been reported [51] that the stability of the
15 phase of cobalt depends on the size of the particle, reduction atmosphere, and
16 temperature. For example, cobalt nanoparticles [49] have been synthesized and,
17 depending on the particle size, either it exists in β -Co (less than 20 nm) or α -Co (above
18 40 nm) [49]. Both phases are preferred if the particle size is between 20 and 40 nm [49].
19 Herein, an average crystallite size of 21.17 nm has been calculated using Scherrer's
20 formula for the β -Co phase identified in **PHCo25_7**. Further weak peaks appear at $2\theta =$
21 $25.4, 34.8, 40.0, 41.0,$ and 46.9° in a 2θ range in which peaks related to cobalt silicide
22 (CoSi, CoSi₂, Co₂Si, ...) and/or cobalt silicate phases can be identified [52]. However,
23 given a concise and precise attribution of all the peaks is not easy: peaks at $2\theta = 34.8$ and
24 40.0° can be attributed to the (111) and (200) diffraction peaks of the CoSi (ICDD 01-
25 079-8014) [52,53] whereas the peaks at 25.4 and 46.9° can be attributed to the Co₂SiO₄

1 and Co_2Si phases, respectively [54]. The formation of CoSi_x ($x = 1, 2$) most probably
 2 results from the reaction of CoCl_2 with the Si centre of PHPS upon pyrolysis as it occurs
 3 during the synthesis of cobalt silicide NPs via microwave-assisted route of CoCl_2 and Si
 4 powders according to Eq. (1) [54].



5 CoSi is a metastable phase having the tendency to further react with Si to form the
 6 CoSi_2 phase [54].

7 In addition, CoCl_2 reacts with Si to form Co_2Si nanoparticles and SiCl_4 according to
 8 Eq. (2) [54]:

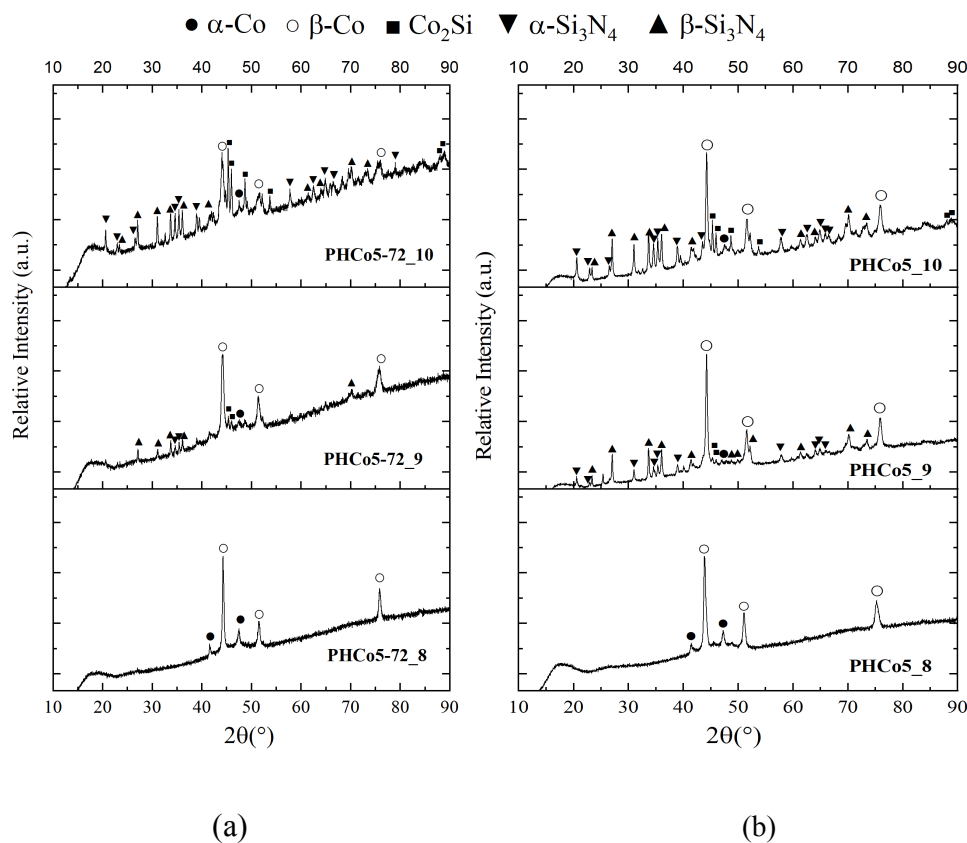


9

10 Decreasing the atomic Si:Co ratio in the precursor, thereby increasing the Co content
 11 in the early stage of the process, tends to vanish the XRD peaks of the secondary cobalt
 12 silicide phases, stabilize the β -Co phases in the derived samples and significantly increase
 13 the relative XRD peak intensities of the α -Co phase. (102) and (103) XRD peaks of the
 14 α -Co phase are even identified in the patterns of **PHCo5_7** and **PHCo2.5_7** at 62.5 and
 15 84.1°, respectively. The α -Co crystallite sizes are quite similar between all samples and
 16 range from 24.8 nm (**PHCo5_7**) to 26.1 nm (**PHCo2.5_7**) while the β -Co crystallite sizes
 17 range from 21.7 nm (**PHCo25_7**) to 28.0 nm (**PHCo2.5_7**). This agrees with previous
 18 predictions [49]. The XRD pattern of the **PHCo5-72_7** sample confirms the signature of
 19 α and β -Co phases (crystallite sizes of 25.8 and 24.4 nm).

20 Then, the evolution of the XRD patterns of **PHCo5-72_7** and **PHCo5_7** after heat-
 21 treatment at 800 °C (**PHCo5-72_8** and **PHCo5_8**), 900 °C (**PHCo5-72_9** and **PHCo5_9**)
 22 and 1000 °C (**PHCo5-72_10** and **PHCo5_10**) (Fig. 5) has been investigated. Whereas the
 23 phase composition and crystallinity of the samples remains quite stable after pyrolysis at

1 800 °C (while the average crystallite size slightly increases to 25.8 nm for **PHCo5-72_8**),
 2 the temperature rise to 900 then 1000 °C induces – as a major fact – the nucleation (900
 3 °C) then the growth (1000 °C) of α (ICDD PDF number: 04-005-5074) and β (ICDD PDF
 4 number: 04-033-1160) - Si_3N_4 . In addition, XRD peaks related to α -Co gradually
 5 disappear while the dicobalt silicide (Co_2Si) phase (ICDD 04-003-2126) is identified
 6 through the emergence of some peaks (at 45.2°, 45.9°, 48.7°, 53.7°, 88.1° and 88.8°).



7

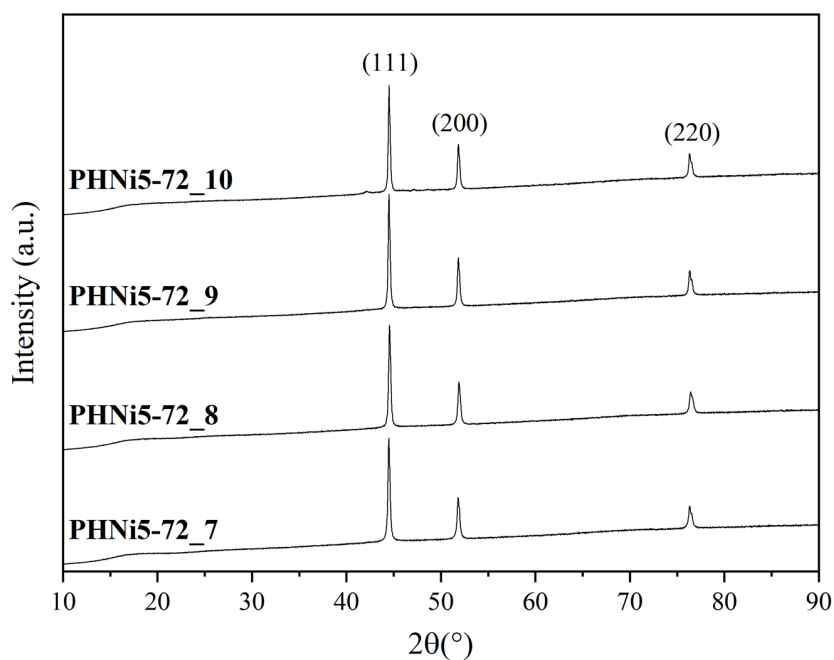
8

9 **Fig. 5.** XRD evolution of (a) **PHCo5-72_X** and (b) **PHCo5_X** (X = 8, 9 and 10) samples.

10

11 The crystallization extend of Si_3N_4 is more pronounced in the **PHCo5-72_X**
 12 compared with **PHCo5_X** (X = 9, 10) most probably because the **PHCo5-72** precursor
 13 established more Si-N bonds in its structure (higher crosslinking degree) than the **PHCo5**
 14 precursor. The growth of crystalline Si_3N_4 significantly affects the measurement of the
 15 average crystallize size of the β -Co phase for samples prepared at 900 (**PHCo5-72_9**) and

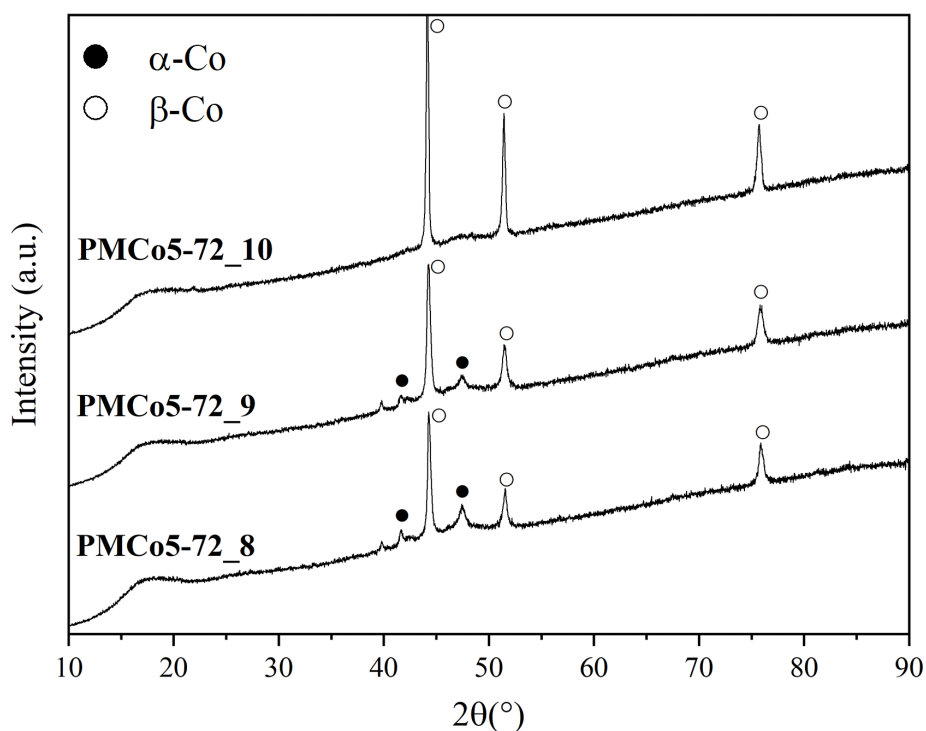
1 1000 °C (**PHCo5-72_10**). Then, the effect of Ni on the structure of samples derived from
 2 **PHNi5** (i.e., **PHNi5-72_X**; X from 7 to 10 (Fig. 6)) has been investigated.



3
 4 **Fig. 6.** XRD evolution of **PHNi5-72_X** (X = 7, 8, 9 and 10) samples.

5
 6 The heat-treatment of **PHNi5** at 700 °C results in the formation of nickel crystals
 7 (ICDD 00-004-0850) based on the identification of three characteristic diffraction peaks
 8 for pure nickel at 44.5°, 51.8°, and 76.3°. These peaks correspond to the indexed planes
 9 (111), (200), and (220) lattice planes of the stable fcc structure of Ni, respectively. This
 10 phase composition is characteristic of the whole system evolving from 700 to 1000 °C
 11 and only an increase of the average crystallite size is observed; it changes from 42.7 nm
 12 (**PHNi5-72_7**) to 56.9 nm (**PHNi5-72_10**) from the most intense peak (111) of the XRD
 13 diffraction pattern using the Scherrer formula. Therefore, the Si₃N₄ phase stays
 14 amorphous in the explored temperature range. This means that samples prepared from
 15 **PHNi5** represent Ni nanoparticles distributed in an amorphous Si₃N₄ matrix.
 16 Consequently, Co significantly promotes the crystallization of PHPS-derived Si₃N₄
 17 considering that PHPS-derived Si₃N₄ has been reported to crystallize at around 1200 °C

1 using ammonia as atmosphere [55]. Thus, following the comment on the higher catalytic
 2 effect of Co towards dehydrocoupling than Ni, the fact that the interaction between CoCl_2
 3 and PHPS upon heat-treatment is much higher than between NiCl_2 and PHPS has been
 4 confirmed; the former allowing to establish more Si-N-units in the PHPS network
 5 compared to the latter; thereby favouring the conversion (and crystallization) into (of)
 6 Si_3N_4 at lower temperature.



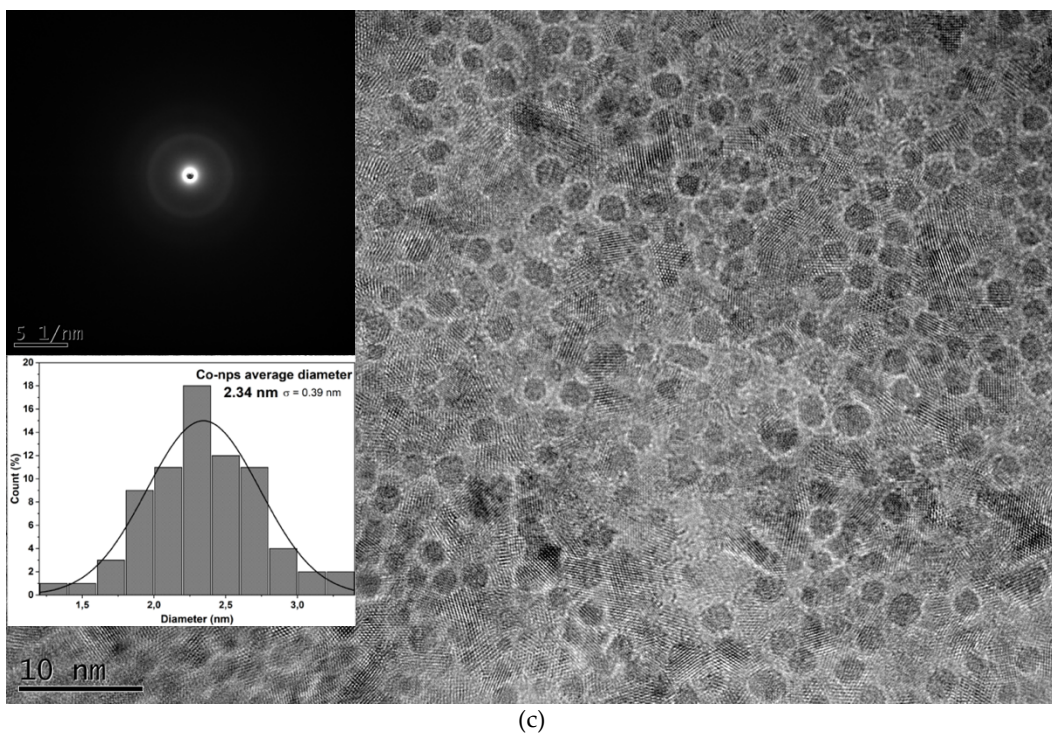
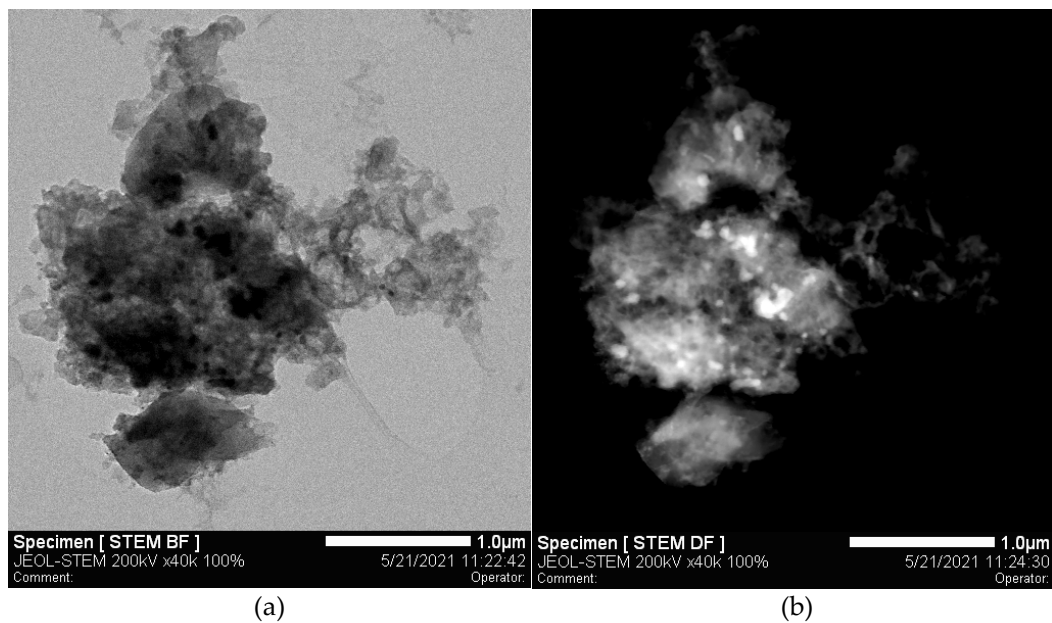
7
 8 **Fig. 7.** XRD evolution of **PMCo5-72_X** (X = 8, 9 and 10) samples.

9
 10 Similar to the structural behaviour of **PHNi5** and in total opposition with **PHCo5-**
 11 **72**, the XRD patterns (Fig. 7) of the **PMCo5-72_X** samples (X from 7 to 9) display the
 12 signature of Co including α - ($2\theta = 41.6^\circ$ (100) and 47.4° (101)) and β - ($2\theta = 44.5^\circ$ (111),
 13 51.6° (200) and 75.7° (220)) Co phases and CoSi ($2\theta = 40.0^\circ$ (200)) whereas the XRD
 14 pattern of the **PMCo5-72_10** sample exhibits the unique signature of the β -Co phase.
 15 This indicates that Si_3N_4 does not crystallize upon heat-treatment in all PMVMSZ-
 16 derived samples allowing the average crystallite sizes of β -Co particles to increase: 26.3

1 nm for **PMCo5-72_7** and 29.2 nm for **PMCo5-72_8** to be compared to **PHCo5-72-**
2 derived samples. Thus, it is noticeable that PHPS tends to form Si_3N_4 crystals at much
3 lower temperature than PMVMSZ, which can rely on the fact that dehydrocoupling
4 reactions were demonstrated to occur mainly in PHPS-based systems; thus, forming
5 further Si-N bonds which inherently tend to form at lower temperature Si_3N_4 and
6 accelerate its nucleation then growth. In both cases (**PHCo5-72_10** and **PMCo5-72_10**),
7 the XRD peaks attributed to the α -Co phase gradually disappear with the increase of the
8 exposure temperature because of the allotropic phase transformation at an equilibrium
9 temperature T_0 (at constant pressure) characteristics of a martensitic transformation [52].

10 To gather further micro- and nanostructural information on the phase formation,
11 identification and distribution, samples have been subjected to a thorough HRTEM
12 analysis that have been coupled with STEM. **PHCo5-72_8** (composed of α - and β -Co
13 phases), **PHCo5-72_10** (composed of α - and β -Co/ Si_3N_4 phases), **PMCo5-72_10**
14 (composed of the β -Co phase distributed in an amorphous matrix) and **PHNi5-72_10**
15 (composed of the Ni phase) samples are selected to investigate their micro-/nanostructural
16 features (Fig. 8-11).

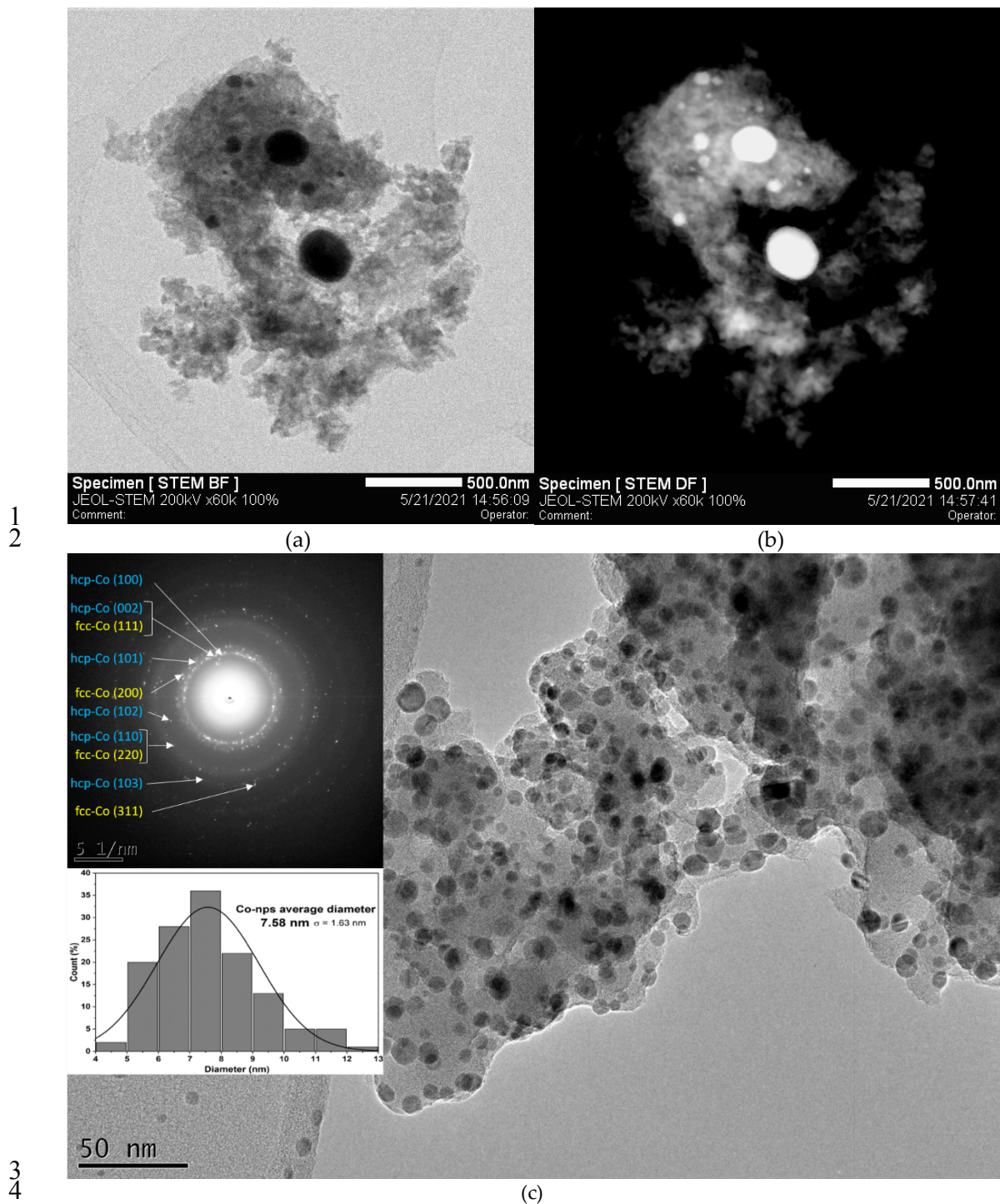
17 The STEM images of **PHCo5-72_8** sample (Fig. 8) demonstrate the localization of
18 particles as imaged in dark (DF, Fig. 8A) and bright (BF, Fig. 8B) field modes. While
19 corresponding dark spots may be found in the same location in the BF images, it appears
20 that the size of the particles can extend over several hundred of nanometers.



6 **Fig. 8.** STEM images of **PHCo5-72_8** in bright-field (BF) (a) and dark-field (DF) (b) and
7 TEM image of **PHCo5-72_8** (inset: SAED pattern and statistical measurement of particle
8 diameters) (c).

9
10 Interestingly, the occurrence of NP clustering or aggregation is limited at the
11 observed scale. Then, HRTEM in an area with the smallest particles (Fig. 8C) has been
12 assessed. It is possible to observe the local distribution of small nuclei with a calculated

1 average diameter of 2.34 ± 0.39 nm according to the size distribution of nanoparticles
2 (inset of Fig. 8C). These nanoclusters are homogeneously distributed in a featureless
3 matrix typical of amorphous (or poorly crystallized) matrix. The corresponding selected
4 area electron diffraction (SAED) pattern shows a highly diffuse ring whereas a zoom of
5 the TEM image (*See Fig. S2 in Supplementary Material*) allows measuring lattice
6 distances values of around 0.20 nm which could correspond to the (002) and the (111)
7 plane of both hcp-Co and fcc-Co phases. Thus, this provides evidence that the **PHCo5-**
8 **72_8** sample is composed of a relatively large range of NP size combining α - and β -Co
9 phase with a limited agglomeration. Upon heat-treatment to 1000 °C (**PHCo5-72_10**),
10 STEM images in BF and DF modes confirm the presence of relatively big particles (more
11 than 200 nm) along with smaller particles (Fig. 9A,B). A deeper investigation of the
12 structure of the smallest particles by HRTEM (Fig. 9C) show clear evidence for the
13 growth of the Co NPs. The latter appear as small particles with an average diameter of
14 7.58 nm ($\sigma = 1.63$) as calculated according to the particle size distribution (inset of Fig.
15 9C). The SAED pattern (inset in Fig. 9C) is composed of distinct spots at 0.217, 0.204,
16 0.190, 0.180, 0.148, 0.125, 0.115 and 0.107 nm confirming the lattice parameters of fcc
17 and hcp-Co through the attribution of the (100, hcp), (111, fcc)/(002, hcp), (101, hcp),
18 (200, fcc), (102, hcp), (110, hcp)/(220, fcc), and (103, hcp) and (311, fcc) planes. Thus,
19 it indicates the higher degree of crystallinity of the Co phases. Although the indexation
20 of the lattice planes of Si₃N₄ is not possible in the SAED pattern, we clearly distinguish
21 the presence of Si₃N₄ nanocrystals with a fringe spacing of 0.44 nm in the HRTEM image
22 of the samples (*See Fig. S3 in Supplementary Material*).



5 **Fig. 9.** STEM images in the BF (a) and DF (b) modes and HRTEM image (Inset:
6 corresponding SAED pattern and statistical measurement of particle diameters) of
7 **PHCo5-72_10**.

8
9 The heterogeneity in the Co particle size is confirmed in the STEM images of
10 **PMCo5-72_10** in BF and DF modes (Fig. 10A, B).

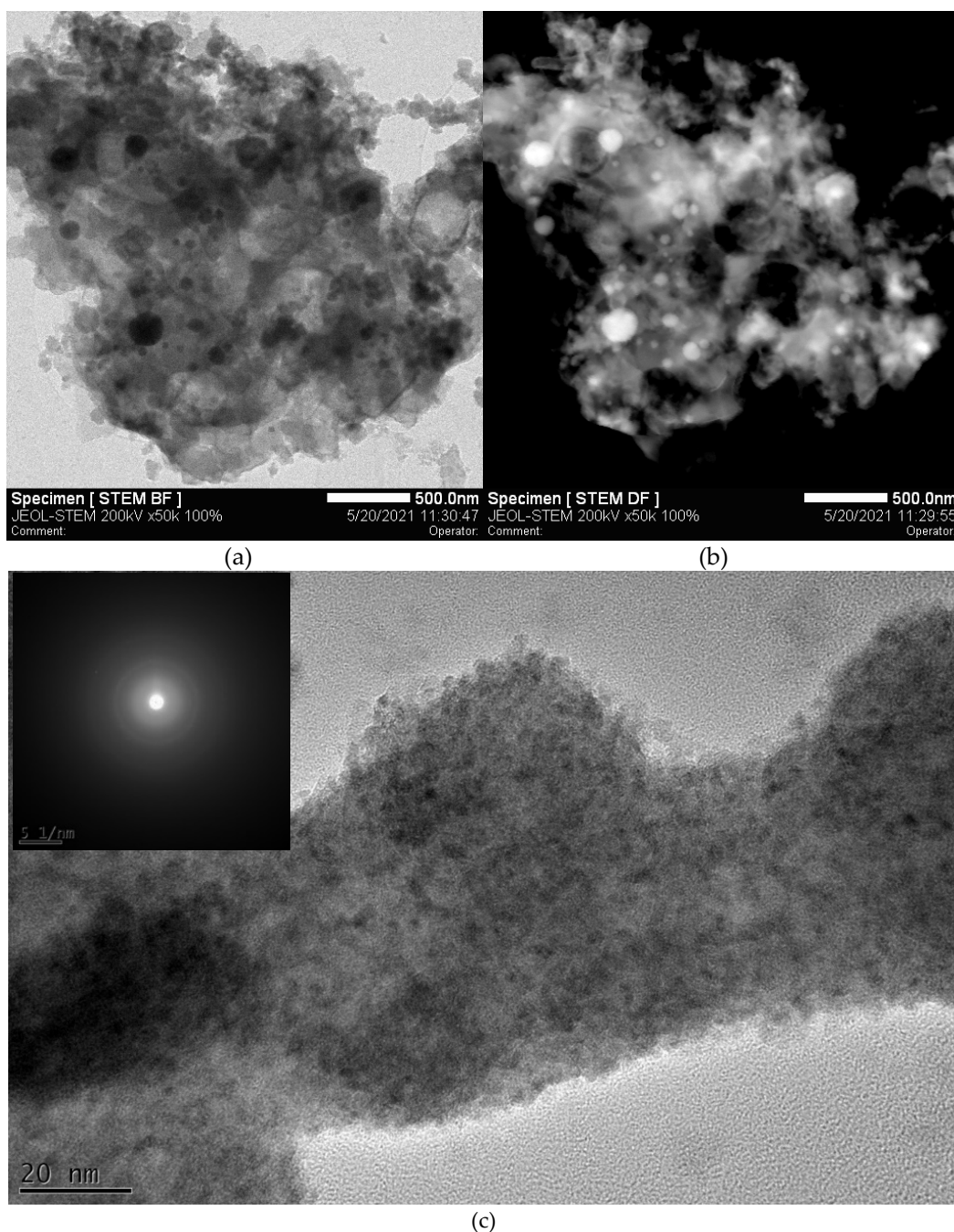
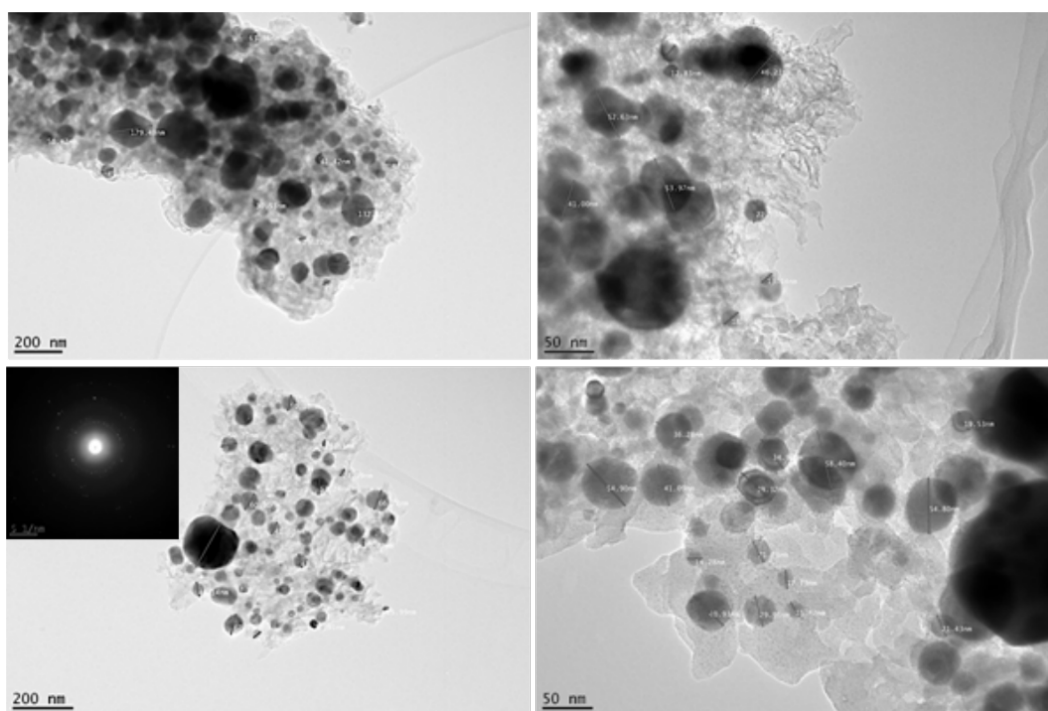


Fig. 10. STEM images of **PMCo5-72_10** in BF (a) and DF (b) mode and HRTEM image of **PMCo5-72_10** (Inset: corresponding SAED pattern) (c).

However, a strong difference in terms of microstructure definition is shown through HRTEM (Fig. 10C). The TEM investigation demonstrates that the material is less crystallized than its **PHCo5-72_10** counterpart. The diffuse character of the rings composing the SAED pattern as inset in Fig. 10C confirms these observations. The lattice

1 planes of β -Co are present in the HRTEM image of Fig. 10C as very small nuclei with a
2 fringe spacing of about 0.205 nm embedded in an amorphous matrix.

3 TEM images of the **PHNi5-72_10** samples (Fig. 11) are consistent with the XRD
4 discussion and confirm the formation of Ni nanoparticles distributed in an amorphous
5 matrix. Interestingly, the particle size is more homogeneous, and the samples is mostly
6 composed of particles with 45 nm in diameter. The associated SAED pattern - composed
7 of spots indicating the high crystallinity of the analyzed phase – confirms the XRD
8 results: the calculation of the d-spacing from the SAED gives values corresponding to the
9 (111), (200), (220), and (311) lattice planes of fcc Ni. The size of the crystals fits with the
10 average crystallite sizes calculated from XRD patterns.



11

12 **Fig. 11.** TEM images of **PHNi5-72_10** (Inset: corresponding SAED pattern).

13

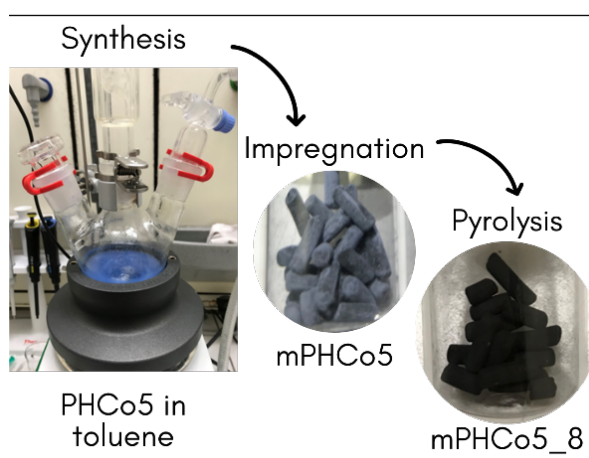
14 Because TM NPs in a matrix playing the role of a support have been generated, such
15 materials can be considered as self-supported catalysts for a large range of reactions, as
16 for the catalytic hydrolysis of sodium borohydride. However, the development of the

1 mesoporosity of the matrix has to be considered to render accessible the metal NPs. As a
2 consequence, the design of mesoporous components is considered in the following
3 section.

4

5 3.3 Design of mesoporous monolithic TM/Si₃N₄ (TM = Co, Ni) samples

6 The strategy to design mesoporous monoliths consists to firstly coat activated carbon
7 monoliths (AC) with the precursors which have been previously characterized to
8 macroscopically shape the monolithic-type structure of the support. Thus, AC is
9 deliberately kept as a support matrix to overcome the problems related to the poor
10 mechanical stability of PDCs with highly developed mesoporosity [56,57]. After solvent
11 extraction, the approach occurs via a two-step pyrolysis under nitrogen (400 °C) to
12 crosslink the precursors surrounding AC support, then under ammonia (800-1000 °C) to
13 form the mesoporous samples which reproduces the monolithic shape of AC samples
14 (Fig. 12). They are labelled with m before the labels previously used. The **mPHCo2.5_8**,
15 **mPHCo5_8**, **mPHCo25_8**, **mPHCo5-72_10**, **mPHNi5-72_10** and **mPMCo5-72_10**
16 samples have been characterized by nitrogen sorption measurements at 77 K (*See Fig. S4*
17 *in Supplementary Material*).



18

19 **Fig. 12.** General process to design micro-/mesoporous TM/Si₃N₄ nanocomposites.

20

1 It should be mentioned that the results gained from the **mPHCo5-72_8** samples are
2 close to those of the **mPHCo5_8** sample; thereby they are not reported. The analysis of
3 the nitrogen sorption isotherms by the Brunauer-Emmett-Teller (BET) method reveals
4 that all samples have similar complex isotherms composed of types II and IV [58]. This
5 observation is based on the isotherm profiles as the pressure increases. At pressures P/P_0
6 lower than 0.45, all the samples present a type II isotherm behaviour, attributed to
7 monolayer-multilayer adsorption, suggesting the presence of microporosity at such
8 relative pressures. With the pressure P/P_0 above 0.45, type IV isotherms are clear,
9 associated to capillary condensation taking place in the mesopores. This is reflected in
10 the distinct hysteresis loops which take place between the adsorption and desorption
11 curves, i.e., the saturation pressures are not equal for condensation and evaporation inside
12 the pores, so that adsorption and desorption isotherms do not coincide.

13 Considering the IUPAC classification for hysteresis loops, as-prepared monoliths
14 can be classified as type H2 [58] because of a hysteresis commonly found in disordered
15 porous materials or in ordered mesoporous materials with 3D cage-like and
16 interconnected pores [59]. Considering the activated carbon template structure [56,57],
17 investigated samples can be considered as disordered micro-/mesoporous materials
18 bearing interconnected porosity.

19 Data gained from the analyses of the N_2 adsorption-desorption isotherms such as the
20 BET specific surface area, the pore volume and the modal pore diameter (MPD) are
21 gathered in Table 2. The BET specific surface areas (SSA) are significantly high and the
22 Barrett-Joyner-Halenda (BJH) analysis suggests a narrow pore size distribution except
23 for **mPHCo5-72_10** and **mPMCo5-72_10** most probably due to the higher pyrolysis
24 temperature. Similar total pore volumes are measured while typical t-Plot micropore
25 volumes varied from 0.20 to 0.34 $\text{cm}^3 \cdot \text{g}^{-1}$ for all samples. Thus, these results prove the

1 reproducibility of the selected impregnation method and do not allow extracting a
 2 tendency regarding the effect of the Si:TM ratio, the type of polysilazane and the metal
 3 on these parameters whereas there is one report indicating a reduction on the SSA as the
 4 amount of cobalt was increased in the produced sample [60].

5

6 **Table 2**

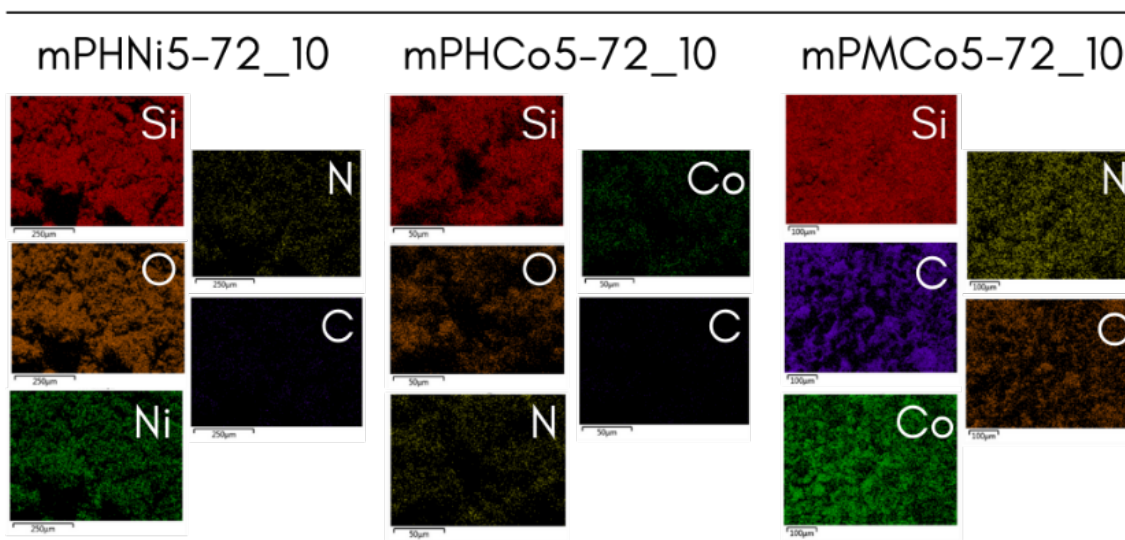
7 Specific Surface Area (SSA), Pore Volume (PV), t-plot Micropore Volume (MV) and
 8 Modal Pore Diameter (MPD) of investigated samples.

Sample	SSA (m².g⁻¹)	PV (cm³.g⁻¹)	t-plot MV (cm³.g⁻¹)	MPD (nm)
mPHCo2.5_8	859	0.45	0.31	3.95
mPHCo5_8	922	0.5	0.34	3.7
mPHCo25_8	874	0.45	0.32	3.7
mPHCo5-72_10	850	0.5	0.27	5.75
mPMCo5-72_10	756	0.5	0.20	6.3
mPHNi5-72_10	871	0.5	0.23	3.55

9

10 Although the pyrolysis temperature tends to slightly reduce the SSA, the large BET
 11 specific surface area of the samples is expected to provide selectivity and active sites to
 12 the considered sample to be effectively accessed for catalysis. Furthermore, elemental
 13 mapping (Figure 13) reveals the uniform distribution of Co and Ni along with silicon,
 14 nitrogen and oxygen at the surface of the samples. EDXS spectroscopy indicates the
 15 presence of 18 and 21 (**mPHCo5-72_10**, and **mPMCo5-72_10** samples) and 22
 16 (**mPHNi5-72_10**) wt% of Co and Ni, respectively. Thus, the TM content can be

1 controlled by adjusting the Si/TM ratio in the early stage of the process (*i.e.*, at the
2 polymer level).



3
4 **Fig. 13.** EDX mapping of **mPHNi5-72_10**, **mPHCo5-72_10** and **mPMCo5-72_10**
5 samples (SEM x550).

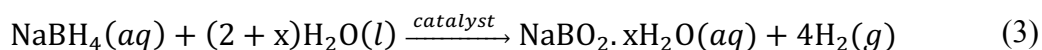
6

7 Considering the identification of Co and Ni distributed in a mesoporous Si_3N_4
8 support, we have checked the potential of these samples for heterogeneous catalysis.

9

10 3.4 Catalytic activity of micro-/mesoporous $\text{TM}/\text{Si}_3\text{N}_4$ ($\text{TM} = \text{Co}, \text{Ni}$) samples

11 From the point of view of this work, sodium borohydride (NaBH_4 ; eq. (3)) has been
12 used as a model system to explore the activity of as-produced self-supported catalysts.
13 However, it does not aim at comparing the hydrogen generation rates with previously
14 reported catalysts [61–64]; it provides a rapid overview of the potential of these materials.

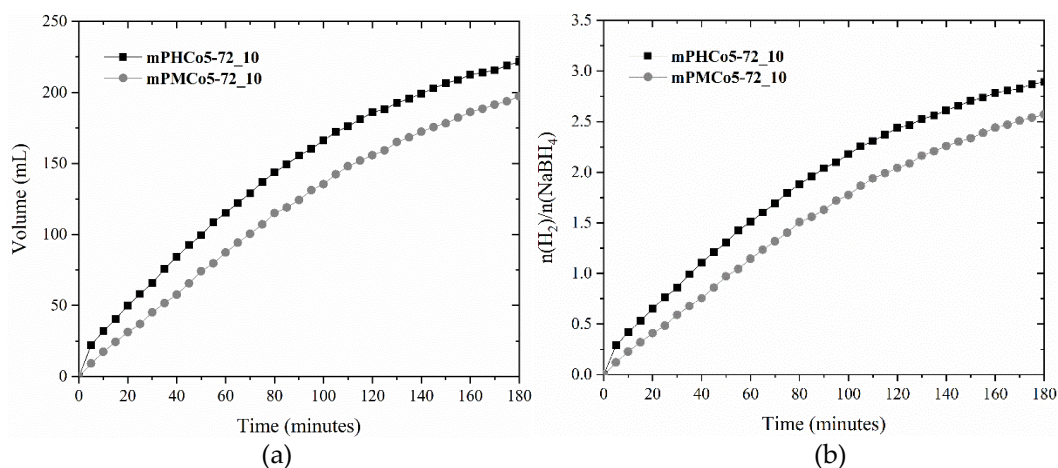


15 Before the performance of such materials is shown and compared, it is necessary to
16 bring attention to some parameters. The hydrogen generation rate is given as
17 $\text{mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{catalyst}}^{-1}$. This means that the amount of catalyst present in the sample is

1 inversely proportional to the hydrogen rate. The optimal production (OP) is the method
 2 applied to calculate this rate, according to Eq. (3), where $V_{H_2}^{op}$ is the maximum volume of
 3 hydrogen generated at an optimal time t^{op} (i.e., slope of the curve) using a known amount
 4 of catalyst m_{cat} .

$$OP = \frac{V_{H_2}^{op}}{m_{cat} \times t^{op}} \quad (4)$$

5 Because, it has been shown that Co powders show higher catalytic activity than Ni
 6 powders [65], we have selected the **mPHCo5-72_10** and **mPMCo5-72_10** samples to be
 7 used as catalysts for the hydrolysis of $NaBH_4$. Fig. 14 brings hydrogen (H_2) evolution
 8 within 180 minutes of hydrolysis.



9
10
11

12 **Fig. 14.** (a) Volume of H_2 produced during the hydrolysis of $NaBH_4$ and (b) mole of H_2
 13 per mole of $NaBH_4$ using the **mPHCo5-72_10** and **mPMCo5-72_10** samples.

14

15 It is interesting to observe that the compounds display a catalytic activity: using the
 16 **mPHCo5-72_10** sample, a release of 222 mL of H_2 is measured after 180 minutes of
 17 $NaBH_4$ hydrolysis, which is 12.4 % more than with the use of the **mPMCo5-72_10** sample
 18 (197 mL). This difference can be related to the crystallization of the matrix and/or the
 19 higher SSA of the former. Measured values correspond to a rate of 700 and 540

1 $mL \cdot min^{-1} \cdot g_{Co}^{-1}$, respectively. Even if conditions are different, the maximum value is 5
2 times lower than that obtained for support-free Co NPs [66] and PHPS-derived Co/Si₃N₄
3 compounds are not able to perform the complete release of H₂ from NaBH₄ (Fig. 14) after
4 3 h of reaction (³/₄ of the reaction is achieved). These facts do not mean that such materials
5 are not appropriate candidates for heterogeneous catalysis. They better mean that they are
6 not suited for the hydrolysis of NaBH₄ most probably because of the presence of
7 micropores in the matrix which hinder diffusion of NaBH₄ towards Co NPs. Hence, by
8 considering these hypotheses and the fact that these materials display strong nanoparticle-
9 matrix interaction with a limited active site aggregation, templates leading to fully
10 mesoporous TM/Si₃N₄ compounds would be best suitable.

11

12 **4. Conclusions**

13 As a conclusion, ceramics made of silicon (Si), carbon (C), oxygen (O) and nitrogen
14 (N) elements, surrounding cobalt (Co) or nickel (Ni) nanoparticles by coordination of
15 polysilazanes with Co and Ni chlorides have been prepared. It is shown that Co displays
16 a higher catalytic effect on polysilazanes towards dehydrocoupling than Ni which is
17 demonstrated to affect – in addition to the polysilazane nature and the Si:transition metal
18 ratio - the crystallization behavior of the derived nanocomposites. The latter are made of
19 fcc- and hcp-Co or fcc-Ni particles immobilized in a highly micro/mesoporous PDC
20 matrix via a single-step pyrolysis process at temperatures from 700 to 1000 °C under
21 flowing argon. The development of the SSA and the micro-/mesoporosity of the matrix
22 allowed exploiting the catalytic activity of the samples. Although the complete release of
23 H₂ from NaBH₄ was hindered by the presence of microporosity, this study establishes an
24 opportunity to the development of future highly durable self-supported catalysts
25 synthesized using a simple method and tailor-made templates.

1 **Appendix A. Supplementary data**

2 Supplementary material to this article can be found online at [https://doi.](https://doi.org/xx.xxxx/j.micromeso)
3 [org/xx.xxxx/j.micromeso](https://doi.org/xx.xxxx/j.micromeso). Fig. S1. FTIR spectra of PHPS and **PHNi5-72** (a) PMVMSZ
4 and **PMCo5-72** (b).; Fig. S2. Zoom of Fig. 8 to reach the lattice distance in isolated
5 particles composing the **PHCo5-72_8** sample. Fig. S3. (a) TEM image of **PHCo5-72_10**
6 (Inset: corresponding SAED pattern and statistical measurement of particle diameters)
7 and (b) HRTEM image showing Si₃N₄ crystallites. Fig. S4. N₂ adsorption-desorption
8 isotherms of **mPHCo2.5_8**, **mPHCo5_8**, **mPHCo25_8**, **mPHCo5-72_10**, **mPMCo5-**
9 **72_10** and **mPHNi5-72_10** samples.

10

11 **CRedit authorship contribution statement**

12 **M. Mallmann:** Conceptualization, Methodology, Validation, Formal analysis,
13 Investigation, Data curation, Writing - original draft preparation, Writing - review and
14 editing, Visualization. **R. Nishihora:** Formal analysis, Data curation. **E. Acosta:** Formal
15 analysis, Data curation. **P. Carles:** Formal analysis. **N. Asakuma:** Investigation. **S.**
16 **Tada:** Investigation. **Y. Iwamoto:** Writing: review and editing, Project administration,
17 Funding acquisition. **U. Demirci:** Formal analysis, Writing: review and editing. **R.**
18 **Machado:** Project administration, Funding acquisition. **S. Bernard:** Conceptualization,
19 Methodology, Resources, Writing - original draft, Writing - review and editing,
20 Visualization, Supervision, Project administration, Funding acquisition.

21

22 **Declaration of competing interest**

23 The authors declare that they have no known competing financial interests or
24 personal relationships that could have appeared to influence the work reported in this
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1

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6

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17

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