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***Metal loaded nanoporous silicas with tailor-made properties through
hyperbranched polymer assisted templating approaches***

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Abstract

Over the last years, mesoporous silicas have gathered considerable interest especially in the field of catalysis, singled out as excellent catalytic supports owing to their intriguing textural features. Herein, the synthesis of novel nanoporous silicate materials containing copper or palladium nanoparticles, by means of co-assembly and one-pot templating pathways is described. Inclusion of metal nanoparticles within the porous network of the silicate materials is accomplished with the use of hyperbranched Polyethyleneimines (PEIs), serving both as chelating and secondary structure directing agents. The co-assembly method involves the introduction of PEI into the initial reaction mixture containing the triblock copolymer Pluronic P123 as the main template and TEOS as the silica source, **whereas incorporation of metal nanoparticles is performed at a second step**. The one-pot approach, achieves metal loading in a single step through the direct insertion of PEI already complexed with the desired metal, into the synthetic gel. Several parameters are investigated including solution's pH, reaction path and PEI's molecular weight. Results from TGA, XRD, N₂ porosimetry, electron microprobe, SEM, **TEM** and UV-DR analyses, confirm that both synthetic strategies can produce nanoporous materials with advanced and tunable textural and morphological characteristics and thus widened application prospects. Among the examined synthesis parameters, PEI molecular weight and synthetic gel's pH were found to have the most pronounced effect on final material pore architecture, morphology, **metal** loading and dispersion. Preliminary deNO_x activity tests in the NO + CO reaction indicated that the developed materials could find use in environmental applications.

Keywords: mesoporous silica; copper oxide; palladium; hyperbranched polyethyleneimine; NO reduction.

1. Introduction

Mesoporous inorganic solids have received immense attention in recent years, due to their unique pore architecture namely their high internal surface area, pore volume and tunable mesochannels within the nanometer range. These appealing structural features render mesoporous materials excellent candidates as catalyst supports, facilitating the mass transport of reagent and product gas molecules and the high dispersion of active species [1-2]. Indeed, the confinement of nanoparticles into mesoporous hosts is considered a very effective way to control the size and shape of nanoparticles as well as to inhibit growth phenomena, providing higher dispersions compared to more conventional non-porous carriers [1-3]. It is well documented that particle size is closely related to materials' catalytic properties, having a tremendous impact on both selectivity and conversion [4]. Another important factor influencing the dispersion, thus the catalytic performance of metal and metal oxide nanoparticles, is the methodology followed for their immobilization within the mesoporous channels [5-6]. Within this context, research efforts have been directed towards the uniform deposition of catalytic active species and thus the increase of surface active centres.

The most frequently used approaches include incipient wetness impregnation, functionalization of mesoporous framework with specific organic moieties acting as metal sorbing agents and direct incorporation of the catalytically active components during synthesis of the mesoporous support [2-3, 6-11]. Traditional impregnation of the metal salts into the mesoporous channels is a synthetic route of particular interest, given its simplicity, low cost and easy scalability. However, its major drawback is associated with the lack of finely dispersed nanoparticles and the formation of aggregates, especially in cases of high metal loadings [6].

Modification of mesoporous surfaces, prior to the deposition of active species, is considered a more efficient approach for the preparation of homogeneously dispersed nanosized supported catalysts. Several protocols have been reported, concerning the

functionalization of mesochannels' interior with specific organic molecules, especially organosilanes, bearing functional groups able to entrap metal ions. Introduction of these organic species is accomplished through post-grafting or co-condensation routes [7, 12]. Direct or in situ pathways are also applied, involving the introduction either of pre-formed metal nanoparticles or metal precursors into the synthetic gel [5, 13]. However, most of the aforementioned methods are time and energy consuming and too sophisticated, requiring several synthetic steps and the utilization of various reactants and solvents for the inclusion of metal or metal oxide nanoparticles within the mesoporous support [14].

Lately, hyperbranched polymers are gaining growing scientific interest due to their multifunctionality and diversity of applications arising from their characteristic molecular architecture in addition to their low cost and high availability [15-16]. **Hyperbranched Polyethyleneimine (PEI)** is a highly branched cationic polymer, inexpensive and readily available in several molecular weights. This hyperbranched molecule possesses a large number of amino groups (primary, secondary and tertiary), being therefore able to **adsorb large CO₂ amounts and to** chelate a wide variety of metal ions dissolved in water, such as Pt²⁺, Pd²⁺, Au³⁺, Ag⁺, Cu²⁺, Ni²⁺, Ru³⁺, Mn²⁺, Fe³⁺ [15-20]. **Consequently, its use as structure directing agent and its integration into an inorganic matrix can easily yield adsorption materials for water purification or CO₂ capture, as well as metal functionalized nanoporous materials with potential use in catalysis [15-20].**

In the present study, motivated by PEI's unique structural and chemical properties, two novel synthetic strategies are described for the production of metal loaded mesoporous silicas, combining simplicity and cost-effectiveness. Our proposed methodologies rely on the exploitation of PEI both as chelating and secondary structure directing agent. The two synthetic pathways employed, include: i) incorporation of PEI

during initial material synthesis and subsequent metal loading through impregnation of the organically modified mesoporous silica into metal nitrate solution **for the metal sorption to take place** (co-assembly route) and ii) nanoparticles incorporation in a single synthetic step through the introduction of PEI preloaded with copper or palladium, into the reaction mixture (one-pot route). The effect of the hyperbranched polymer addition on the formation of silica's mesostructure along with final copper loading and dispersion was determined through XRD, N₂ porosimetry, electron microprobe, SEM and UV-DR analyses. The deNO_x activity of the derived materials was assessed through NO reduction using CO as a reducing agent under stoichiometric conditions.

2. Experimental

2.1 Synthesis

2.1.1 Co-assembly synthesis

The experimental protocol for the production of nanoporous silicas containing metal nanoparticles through co-assembly and one-pot pathways is illustrated in Scheme 1. Co-assembly methodology involved dissolution of the triblock copolymer Pluronic P123 (2.5 gr) in 50 ml of H₂O, overnight stirring at RT and then drop wise addition of tetraethyl orthosilicate TEOS (3.11 ml) at 35 °C in two different pH environments (strongly acidic and neutral initial pH), with subsequent introduction of a specific amount of PEI, Mw=2000 or 5000 BASF, (1.56g). An appropriate amount of NaF (NaF/TEOS ≈ 5 mol %) was added into the reaction mixture, only when neutral initial pH conditions were employed. After stirring for 24 h, the synthetic gel was transferred into an autoclave and hydrothermally treated at 100 °C for 72h under static conditions. The resulting solids, obtained by centrifugation, were **either dried and calcined to produce the metal free reference samples or** dried and subjected to acetone extraction at 56 °C for 24h, for the removal of the main organic template (P123). Metal **loaded**

samples were derived by impregnation of the dried organically modified silica samples. Specifically, 250 mg of the dried sample was added to 2.5 ml, 10500 ppm aqueous copper nitrate solution and was left under stirring for 24h at RT. During this time Cu^{II} sorption is taking place, given the retained chemical and chelating properties of PEI integrated into the siliceous matrix. The solid samples after centrifugation were washed with a small amount of distilled H_2O to remove uncomplexed Cu, dried overnight at 50 °C and finally calcined under airflow (100 ml/min) at 500 °C (heating rate 1°C min^{-1}) for 8 h.

2.1.2 One-pot synthesis

In one-pot synthesis, metal loaded nanoporous silicas were produced in a single step. For this purpose, an appropriate amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.249 gr) or $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.0113 gr) was added into an aqueous solution of PEI, $M_w=2000$ or 5000 BASF, (1.56 gr polymer in 10 ml H_2O) and the system was subjected to overnight stirring. The formed solution containing the PEI- Cu^{2+} or PEI- Pd^{2+} complexes was pipetted dropwise into the initial synthetic mixture containing P123 and TEOS. Then, the same amount of NaF was added, followed by stirring for 24h at 35 °C, hydrothermal treatment at 100 °C for 72h, centrifugation and drying. All the final products were calcined at 500 °C for 8 h at a heating rate of 1°Cmin^{-1} .

2.2 Characterization

N_2 adsorption isotherms were collected at 77 K on an automated volumetric system (AUTOSORB-1-Krypton version – Quantachrome Instruments). Specific surface area was determined using the Brunauer–Emmett–Teller (BET) method. The pore size distribution was calculated using the Nonlocal Density Functional Theory (NLDFT) model (Quantachrome Instruments, AS1Win, v. 2.01, DFT software). Prior to the

measurements, the samples were outgassed at 250 °C for 24 h. Scanning Electron Microscopy analysis was conducted with a Jeol (JSM 7401F field emission) instrument equipped with Gentle Beam mode. **Materials' properties in the nanoscale were examined utilizing an FEI CM20 TEM operating at 200 kV accelerating voltage.** Low and wide angle XRD diffraction patterns were acquired using a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA, nickel-filtered CuK α 1 radiation) and an R-Axis IV image plate. Samples were sealed in Lindemann capillaries. Thermogravimetric analysis was performed on a SETARAM SETSYS Evolution 18 Analyser, at a heating rate of 10 °C/min, in an alumina crucible using dried air as the carrier gas. UV-visible diffuse reflectance (UV-vis-DR) analysis was carried out on a Nicolet Evolution 500 spectrophotometer. The spectra were obtained in the range of 200-800 nm and the samples were diluted in KBr (2 wt %). The copper and palladium composition of the various catalysts were determined by electron microprobe analysis on a JEOL JXA 733 (AXES UA). The material powders were grinded and dispersed on a copper grid coated with a carbon film. For each sample, three measurement points were taken in order to calculate average metal loading. Carbon–hydrogen–nitrogen (CHN) analysis was conducted using a PerkinElmer 2400 CHN elemental analyser.

2.3 Catalytic measurements

The apparatus used for the experiments of NO + CO reaction consists of an automatic gas supply unit, a quartz fixed-bed reactor (i.d. 4 mm) loaded with 0.08 g of catalytic material mixed with 0.160 g of inert material (SiC, 46 grit, Alfa Aesar) and an analysis unit. The catalytic sample was retained between two plugs of quartz wool. The reactor was mounted axially in a temperature-controlled electric furnace and catalyst temperature was continuously monitored by two thermocouples located upstream and downstream of the bed. Before the measurements, the catalyst was pretreated overnight

under N₂ flow at 300 °C (5 °C min⁻¹ heating rate) and subsequently (temperature was set to 200°C or remained at 300°C) the gas feed was switched to a mixture of 500ppm NO and 500ppm CO. Two total flow rates, 40 ml/min and 80 ml/min corresponding to space velocities (GHSV) of approximately 30,000 and 60,000 L⁻¹h⁻¹kg⁻¹, were employed. Catalyst temperature was stepwise increased from 200 to 500 °C and NO concentration at the reactor outlet was recorded when steady state conditions were reached (stabilised NO concentration at the reactor outlet). Nitrogen oxides (NO and NO₂) at the reactor inlet and reactor outlet were monitored using a chemiluminescence NO/NO₂/NO_x analyzer (Thermo 42i-HL). The conversion of NO (X_{NO}) was calculated as follows:

$$X_{NO} = \frac{(NO_{in} - NO_{out})}{NO_{in}},$$

Where NO_{in} : NO concentration at the reactor inlet and NO_{out} : NO concentration at the reactor outlet.

3. Results and Discussion

3.1 EPMA analysis

Estimation of materials final metal loading was carried out by means of EPMA analysis with results shown in Table 1. In co-assembled samples, despite the same initial amount of copper precursor, final metal content varies depending on the synthesis' parameters. Specifically, samples prepared under a strong acidic environment contain only trace amounts of copper (low incorporation yield). Interestingly, sample PEI-A-2000-Cu-NE, which was not subjected to acetone extraction, exhibits a higher copper content (2.1 wt. %). On the other hand, materials prepared under neutral environment contain a significantly higher copper loading (high incorporation yield). All these results are in agreement with CNH elemental analysis which revealed a

significantly higher PEI incorporation degree into the final solid when neutral (25 wt. %) instead of acidic (less than 10 wt. %) conditions are applied. Apart from solution pH, PEI's molecular weight is another parameter influencing final metal loading. Lower molecular weight PEI (PEI2000 instead of PEI5000) gives higher copper content samples. Given that equivalent amounts of hyperbranched polymers into the initial reaction mixture represent equal number of amine ligands per unit mass, these differences in metal loadings could be attributed to limited accessibility of metal ions to the internal nitrogen atoms of high Mw PEI, due to its more compact macromolecular structure resulting in reduced metal-ion-binding capacity [21-22]. Finally, the lower copper incorporation yield of the one-pot compared to the two-step synthesis (co-assembly followed by Cu^{II} sorption) is a consequence of the lower initial Cu amount added into PEI's solution. This was done to avoid formation of copper hydroxide precipitates given the highly basic nature of PEI's aqueous solution.

For the Pd loaded sample, driven by the current needs for partial replacement and minimization of noble metals (NMs) [23], the intention was to keep metal content at a low level. In this context, a low final Pd loading in sample PEI-1-5000-Pd (0.8 wt. %) was achieved by introducing a very small amount of Pd precursor into PEI's aqueous solution.

3.2 TGA analysis

Thermogravimetric weight changes were recorded with the aim to examine the incorporation and the interaction of the surfactant P123 and the hyperbranched polymer with the siliceous framework. The respective TGA and DTG profiles, along with those of two reference samples one produced under acidic conditions with addition of P123 and one under neutral with the use of PEI shown for comparison reasons, are presented in Figs. 1 and 2. All samples exhibit an initial weight loss around 75 °C related to the

desorption of physically adsorbed water, whereas weight losses occurring at higher temperatures can be assigned to the decomposition of the two polymers integrated into the siliceous matrix. Very useful remarks can be derived from the temperature range of polymers' decomposition. In the case of the silica sample, synthesized under highly acidic conditions with no addition of PEI (used as a reference), a single sharp weight loss associated with the thermal removal of the organic triblock polymer P123 is observed at 180 – 320°C. Samples produced with the use of PEI, under the same pH environment, displayed additional weight losses. The major steep weight loss, attributed primarily to P123, is now shifted to much higher temperatures around 210 – 380 °C, accompanied by two broad ones at about 160 °C and 550-600 °C. The significant delay in P123 decomposition signifies a stronger interaction between the polymer template and the silica framework in the presence of PEI, under strongly acidic pH conditions. This conjecture can be further validated by inspecting the respective TGA and DTG profiles of the samples prepared in neutral initial pH environment. In this case, different thermal analysis profiles are obtained, characterized by multi – step weight losses with the one ascribed to P123 placed in much lower temperatures about 220 °C instead of 280 °C (Fig. 2). More importantly, thermal decomposition of PEI is now well resolved, differentiating from the respective of P123. This is evidenced in the respective DTG spectra where the peaks around 210, 300 and 530 °C assigned to PEI decomposition are clearly visible (Fig. 2A-D). Moreover, the higher peak intensity indicates a larger amount of PEI when neutral conditions are employed, supporting the results of CNH elemental analysis. Fig. 1 also illustrates the TGA curves of a blank sample produced only with the aid of PEI and of samples PEI-N-5000 and PEI-A-2000 subjected to acetone extraction. The great similarity observed by comparing these profiles demonstrates the removal of P123 and the existence of PEI after acetone extraction. However, closer inspection of sample's PEI-A-2000 DTG spectra (Fig. 2G) reveals

signs of pluronic residue after the extraction procedure (peak at 270 °C). This confirms the previous assumption regarding the stronger interaction of P123 with the siliceous framework mediated by PEI under acidic conditions.

Finally, in the case of copper loaded samples derived from one-pot pathway the main weight loss is observed at much higher temperatures. This finding could be justified by the presence of PEI-Cu²⁺ complexes into the reaction mixture possibly interfering in the formation of the mesophase. In addition it should be mentioned that complete removal of the organic content is taking place at much lower temperatures in the case of metal (Cu or Pd) loaded samples (indicated by dashed lines in Fig. 1) suggesting a catalytic decomposition process due to the metal species [24-25].

3.3 XRD

X – Ray diffraction patterns of the metal free materials in the low angle area are depicted in Figs. 3A-F. Samples produced under highly acidic initial pH conditions display well resolved patterns with three distinct diffraction peaks which could be assigned to the (100), (110), and (200) planes of the 2D hexagonal p6mm symmetry (Fig. 3A). This result indicates that under such conditions uniform channel-like materials with hexagonal arrangement of mesopores similar to that of SBA-15 can be obtained despite the incorporation of the hyperbranched polymer into the initial reaction mixture. On the other hand, neutral initial pH environment resulted in the formation of poorly ordered nanoporous materials since a single broad diffraction peak in the range of $2\theta = 1.42^\circ$ was observed in the respective diffractograms (Fig. 3B). These XRD data are in agreement with N₂ adsorption analysis results, described below, pointing out the substantial effect of solution's pH on the geometry of the formed mesophases. Evidently, a strongly acidic medium favors the assembly of charged PEO units of P123 and cationic silica species and the formation of the hexagonal mesophase through a

$N^0H^+X^-S^+$ type interaction [12]. Although addition of PEI to the synthesis medium under these conditions, resulted in a small increase of the pH value from 0 to 0.5, it did not disrupt the interaction between the surfactant P123 and the silicates. On the contrary, PEI's introduction under neutral initial conditions causes a shift towards the basic pH region ($pH \approx 10$) completely altering the reaction mechanism which directs the formation of assembled mesophase and thus the final nanoporous structure.

Introduction of metal species within the nanoporous framework had a clear effect on the materials' structural properties. In the case of samples synthesized in acidic medium, structure regularity was reduced, especially in acetone extracted samples as demonstrated by the broad asymmetrical peak detected at 2θ around 1.1° (Fig. 3A). Interestingly in the case of metal loaded samples produced under neutral conditions, a broad shoulder or even additional weak signals emerge at higher angles suggesting a greater degree of pore structure ordering (Figs. 3B-C).

In the wide-angle diffraction regime, the very broad reflection detected at $2\theta \approx 22^\circ$ indicates the amorphous nature of silica network walls (Figs. 3D-F). In almost all Cu loaded samples produced in neutral environment the two most intense diffraction peaks ascribed to CuO tenorite crystal phase (JCPDS #03-0884) can also be distinguished (Figs. 3E-F). The average crystallite sizes calculated from the fitted Gaussian CuO (111) reflection peak using the Scherrer formula are compiled in Table 1. The absence of copper oxide X-ray signals in sample PEI-1-5000-Cu suggests an excellent dispersion of copper species into the porous silica network with a size smaller than the detection limit, whereas in the case of samples PEI-A-2000-Cu and PEI-A-5000-Cu it can be associated with the very low final metal loading, as demonstrated by EPMA analysis. Finally, in the case of mesoporous silica loaded with Pd, broad and weak peaks corresponding to PdO crystal phase could be detected (JCPDS #41-1107), reflecting the

nano-crystalline nature of Pd species. As determined by applying the Scherrer equation the average PdO crystal size was around 4 nm.

3.4 N₂ adsorption

Textural characteristics of the as – developed samples were assessed by N₂ adsorption analysis (after thermal treatment at 500 °C) and the respective isotherms are illustrated in Figs. 4-6. From N₂ adsorption data, different behaviors can be distinguished in terms of pore network architecture depending on the employed synthesis parameters. All metal free samples synthesized through the co-assembly pathway under neutral initial conditions exhibit type IV isotherms accompanied by a very broad hysteresis loop corresponding to type H2, according to the IUPAC classification. An initial uptake is observed at low relative pressures, associated with the presence of micropores, followed by a gradually increasing adsorption at higher pressures. An additional characteristic detected in these samples, is the delayed capillary evaporation and the sharp desorption step around $P/P_0 = 0.45$. As documented in the literature, a wide hysteresis loop combined with a steep desorption branch and a closure point at relative pressures around 0.45 is related to ink-bottle type pore geometry encountered in disordered and highly connected networks or in materials with a well-organized mesoporous structure such as FDU-1 and SBA-16 [26-27]. Taking into consideration the results from the XRD analysis, a disordered network of interconnected ink-bottle pores is more likely for this group of materials.

Reliable data for estimating mesopore size distributions can only be acquired from the adsorption branch, given the shape of the respective isotherm plots [28-31]. Pore size distribution (PSD) evaluated from the adsorption branches is illustrated in Fig. 4 (insert). As it can be observed, these samples exhibit PSD curves characterized by a maximum in the micropore area and a very broad distribution in the mesopore area, as

was expected based on the sloping shape of the adsorption branch. On the other hand, the desorption branch can provide information on the size of pore constrictions, i.e. the width of narrow entrances of the pore bodies [28, 32]. However, if the underlying evaporation mechanism – percolation or cavitation – has not been clarified, desorption analysis can lead to misleading conclusions [28-29, 33], as it has been acknowledged that in the case of cavitation, artificial and not realistic PSD related to the pore neck size is obtained from the desorption data. In our case, the fact that all isotherm plots feature sharp desorption steps at the same P/P_0 values can be regarded as a strong indication of cavitation phenomenon [34].

Metal free samples synthesized in a highly acidic environment display a type IV isotherm with a H1 hysteresis loop typical of ordered mesoporous solids with channels of cylindrical geometry (Fig. 5). The well-defined hysteresis and the steepness observed in the adsorption and desorption branches are indicative of pore size uniformity. This is further supported by the very narrow monomodal PSD curve estimated from the desorption branch with a maximum at 8.5 nm. Hence, it can be suggested that introduction of PEI into the initial reaction mixture in strongly acidic medium does not downgrade the pore structure regularity of SBA-15, in agreement with low angle XRD analysis.

Remarkably, metal loaded samples demonstrate superior textural properties compared to the parent nanoporous silicas, quite the opposite of the established usual trend. Indeed, metal incorporation has a pronounced effect on silica's porous network since it induces a strong increase up to 80 % in surface area and 71 % in pore volume and generates a larger fraction of micropores, as shown in Table 1. The latter is manifested by the stronger uptake at low relative pressures in the respective isotherm plots (Figs. 4-5) as well as by the mean pore diameter shifting to lower values. Micropore formation can be justified, taking into account the catalytic properties of the

metal species that assist PEI's decomposition, generating additional polymer-free nanocavities [24-25]. The catalytic effect of Cu^{2+} and Pd^{2+} is further supported by thermogravimetric analysis results, where decomposition of both organic templates in metal loaded samples was observed at much lower temperatures than in metal free ones.

Metal loaded samples derived from one – pot synthetic pathway display similar pore structural characteristics compared to their analogues obtained by the co-assembly route, in the same pH environment (Fig. 6). However, the Cu loaded sample formed by employing PEI of higher molecular weight exhibits a strongly microporous texture (Fig. 6B). The corresponding isotherm plot could be assigned to type II, with a very strong contribution of micropores evidenced by the sharp uptake at low P/P_0 . The increased adsorption at high relative pressures reflects substantial interparticle porosity, confirmed also by SEM analysis (next section). Interestingly, the Pd loaded sample produced under the same conditions (one-pot synthesis under neutral environment with the use of PEI5000) exhibits different pore structure, more similar to that of sample PEI-1-2000-Cu, i.e. coexistence of micropores and mesopores (Fig. 6C). This is validated by the broad H2 type hysteresis loop and the bimodal nature of the pore size distribution, with the second PSD curve located in the mesoporous area (Fig. 6C insert). Therefore, it can be inferred that the type of metal ion complexed with the hyperbranched polymer also exerts a notable impact on the final pore topology.

A final observation derived from N_2 adsorption analysis concerns the effect of the employed extraction procedure, particularly in the case of samples developed under strongly acidic conditions. By comparing the isotherm plots of copper loaded (PEI-A-5000-Cu and PEI-A-5000-Cu-NE) samples before and after acetone extraction, a completely different behavior can be noticed (Figs. 5 and S1 C-D). Clearly, acetone extracted samples do not retain pore structure uniformity as verified by both the collapse of the hysteresis loop and the low angle XRD patterns. This could be possibly

related to the stronger interaction between polymers and silica framework as discussed previously in the thermal analysis section. Finally, it is worth mentioning that the non-extracted PEI-A-5000-Cu-NE sample possesses the highest specific surface area reaching up to 990 m²/g.

3.5 SEM and TEM microscopy

Morphological characteristics of nanoporous solids before and after metal incorporation were investigated by means of scanning electron microscopy. SEM micrographs of the samples produced under neutral initial pH environment, depicted in Figs. 7-8, reveal a homogeneous morphology featuring spherical agglomerated particles. However, a strong dependence of particle size on PEI's molecular weight is observed, as PEI of lower molecular weight yields uniform particles with size around 200 nm (Fig. 7a, c and 8a-b), whereas by employing PEI of higher molecular weight particles' size is reduced to approximately 50-70 nm (Figs. 7b, d and 8c-f). These small sized spherical particles, in the latter case, form closed packed aggregates accounting for the strong adsorption at high relative pressures in the respective isotherm plots. On the other hand, samples synthesized in highly acidic media demonstrate a rod-like morphology similar to that of SBA-15. As illustrated in Figs. 9a-f these rod-like particles exhibit a high coalescence degree forming fused fiber-like macrostructures.

Metal loading did not alter significantly the materials' morphology. Differences in surface texture are clearly visible only in the case of samples produced under neutral synthesis conditions. In the magnified SEM images of copper loaded samples (Figures 7c and 8b) the porous texture of the surface is visible, confirming the N₂ adsorption findings.

Detailed information regarding materials' pore network and metal oxide nanoparticles size and location were acquired by TEM microscopy. TEM micrographs

of three selected metal loaded materials are depicted in Fig. 10. All samples investigated are highly homogeneous demonstrating a disordered interconnected cage-like pore structure with pores of different sizes, in line with low angle XRD and N₂ adsorption analyses. Spots of darker contrast, possibly palladium or copper oxide nanoparticles, are distinguished inside the pore bodies indicating that metal oxide species are highly dispersed and located mainly within the porous silica system. PdO nanoparticles detected in PEI-1-5000-Pd sample (Fig. 10 e-f), exhibit sizes varying between 1 to 4 nm, in agreement with wide angle XRD findings. In the case of copper containing silica samples, especially in PEI-N-5000-Cu, apart from small CuO nanocrystallites (Fig. 10 a-d), larger particles of phylloidal shape (Fig. S2) can be spotted - although in much lesser extent - on the external silica surface, possibly due to a combination of high metal loading and incomplete removal of uncomplexed Cu species through washing. Finally, the estimated size of silica nanospheres is consistent with SEM analysis results and ranges between 50 to 100 nm for samples PEI-1-5000-Pd and PEI-N-5000-Cu produced with higher Mw PEI, while for PEI-1-2000-Cu, produced with PEI 2000, their size reaches around 200 nm.

3.6 UV-Vis analysis

The dispersion degree of the catalytically active elements was elucidated by means of UV-vis DR analysis. Cu-loaded samples prepared by the one-pot pathway (Fig. 11A) displayed an intense band situated between 240-300 nm assigned to charge-transfer between mononuclear Cu²⁺ ion and oxygen, suggesting that isolated copper cations are the dominant Cu species. In the UV spectra of sample PEI-1-2000-Cu an additional band between 320 nm and 440 nm can be observed related to the existence of the oligomeric [Cu-O-Cu]_n clusters [35]. In both materials, the absence of the adsorption band between 600-800 nm corresponding to bulky CuO, implies an excellent dispersion

of copper species. In the spectra of samples PEI-A-5000-Cu-NE, PEI-N-2000-Cu and PEI-N-5000-Cu, apart from the appearance of an intense band located at 240-300 nm, bands at higher wavelengths (ranging from 320 nm and 440 nm) are well distinguished indicating a stronger contribution from oligomeric copper oxide clusters. Moreover, UV signals, around 600-800 nm, related to the presence of bulky copper oxide were also identified. In the case of PEI-N-2000-Cu, this signal is stronger reflecting a higher population of copper oxide aggregates, as expected given its high copper loading.

Apparently, the controlled deposition of copper species in a highly dispersed state is provided by the hyperbranched polymer. As evidenced in the UV spectra of PEI-A-2000-Cu and PEI-A-5000-Cu (Fig. 11C), adsorption bands emerge only at high wavelengths, around 430 nm and 700 nm, indicating a high agglomeration degree despite the trace amount of copper present in these samples. This poor dispersion of copper species can be attributed to the low amount of PEI and its interaction with pluronic, as demonstrated by CHN elemental and TGA analysis, leading to a lower amount of amino groups available for complexation with Cu ions.

Finally, regarding the Pd loaded PEI-1-5000-Pd, its UV-vis Dr spectrum (Fig. 11D) features a well resolved band centered at ~ 250 nm ascribed to highly dispersed Pd(II)O clusters or small PdO particles and a small shoulder between 300-500 nm associated to larger PdO particles [36-39].

3.7 Effect of synthesis parameters

In this work, two templating approaches (co-assembly and one-pot) were followed for the design of new nanoporous silicate materials containing copper or palladium nanoparticles, by making use of PEI's chemical and structure directing properties. EPMA, XRD, N₂ adsorption, SEM, TEM, UV-Vis-Dr and CHN elemental analyses

were performed to probe the effect of different synthesis parameters on materials' final properties.

As demonstrated, strongly acidic initial pH conditions favour the formation of a long-range two-dimensional hexagonal pore arrangement through a $N^0H^+X^-S^+$ type interaction between protonated P123 and positively charged silica species mediated by Cl^- counter anions. On the other hand in neutral initial pH medium, solids exhibiting a disordered network of ink-bottle pore geometry are generated due to a different assembly mechanism directing the formation of the mesophase [12]. This change in the reaction mechanisms induced by different pH environments has also an effect on particle morphology, with rods vs uniform spherical particles formed under acidic and neutral initial conditions respectively. Several studies in the literature refer to the templating action of amine terminated dendrimers in general as well as to that of PEI for biomimetic silica nanospheres production [16, 40-41]. M. Arkas et al. [16] in their work describe the synthesis of hybrid PEI/silica nanospheres under mild environmentally friendly conditions and propose the interaction of partially protonated amines with silanolate groups as the formation mechanism. In this context, it is likely that in our system under neutral initial pH conditions, PEI acts primarily as structure directing agent interacting electrostatically with the negatively charged silica species thus controlling the final pore architecture and morphology. Apart from pore structure and morphology, the system's pH also regulates the material's final metal content and dispersion, by determining PEI's incorporation degree into the siliceous framework and its interaction with P123. Interaction between the two polymers not only reduces the amino groups available for complex formation with metal species, but also results in PEI's partial removal during the P123 extraction procedure. The latter is supported by the higher Cu content (2.1 wt. %) and the retained pore structure uniformity in PEI-A-5000-Cu-NE which is not subjected to acetone extraction.

An additional synthesis parameter influencing final metal loading and particle size, when neutral conditions are employed, is PEI's molecular weight. For example, PEI-N-2000-Cu derived from PEI 2000 has a higher Cu content than PEI-N-5000-Cu derived from PEI 5000. A similar effect of PEI's molar mass on Cu^{II}-PEI complex formation has been previously observed and ascribed to the smaller number of nitrogen atoms able to participate in Cu complexation, in PEIs of higher molecular weight, due to steric hindrance [22]. Another interesting finding is the production of smaller spherical particles in the presence of high Mw PEI. In general, it is recognised that in dendrimer mediated silica production, activation of silica poly-condensation is driven by the concentration of primary amino moieties [40-41]. Consequently, in the case of high Mw PEI the larger number of surface primary amines per molecule (amines in closer proximity) could accelerate silica condensation and increase nucleation rate resulting in the generation of smaller sized particles. On the other hand, low generation dendritic macromolecules have been reported to form aggregated structures due to their increased intercalation degree, providing a larger surface for silica polycondensation. This could be an additional factor accounting for the growth of larger sized nanospheres when low Mw PEI is used [40].

Different reaction paths, on the other hand, did not have a significant impact on materials' properties, producing samples with similar morphological and pore structural characteristics. Each pathway, however, has different practical merits: the co-assembly route enables the preparation of composite silica/PEI materials in two different pH environments whereas one-pot downsizes the synthetic steps into a single one, resulting in significant time, cost and energy saving. Finally, it is worth mentioning that a common asset of both synthetic procedures is their versatility allowing the fabrication of silicate materials with various metal species owing to PEI's chemical and chelating properties.

3.8 Reduction of NO by CO

A preliminary catalytic evaluation of selected Cu and Pd containing silicas prepared in this work was prompted by the well-established NO catalytic properties of Cu and Pd based systems [6, 42-48]. To this end, the catalytic activity of one palladium and four copper loaded samples, produced in a neutral pH environment, towards NO reduction by CO was evaluated under steady state conditions using a stoichiometric mixture of reactants (500 ppm each). Samples prepared under acidic conditions were not tested given their low metal loading. It should be noted that NO₂ formation was not detected by the chemiluminescence NO_x analyzer for any of the investigated catalysts. NO conversion over Cu loaded catalytic materials as a function of temperature is depicted in Fig. 12. In all samples NO reduction by CO was observed above 300 °C and increased progressively with temperature rise. The highest NO activity was provided by sample PEI-N-5000-Cu which reached 54% NO conversion at 470 °C. Sample PEI-1-2000-Cu demonstrated a similar performance with slightly lower maximum NO removal (44 %) recorded however at lower temperature (40 % at 400 °C). Surprisingly, PEI-1-5000-Cu, the sample with the highest dispersion of copper species according to the UV-Vis findings, exhibited the worst performance (40 % at 400 °C). Low NO activity was also observed for PEI-N-2000-Cu, 15% NO conversion at 500 °C. Thus the acquired catalytic activity trend in terms of overall NO removal is the following: PEI-N-5000-Cu \approx PEI-1-2000-Cu > PEI-N-2000-Cu > PEI-1-5000-Cu.

According to these results it can be deduced that deNO_x activity on copper loaded silicas is determined by several factors, including pore network architecture, copper dispersion and loading. One-pot methodology with the use of higher molecular weight PEI provides a highly microporous material (PEI-1-5000-Cu) with an excellent dispersion of copper species confined within, as revealed by N₂ adsorption and UV-vis

DR techniques. However, this porous system, comprised of small sized interconnected channels, inhibits the reactant molecules' access to the catalytic active sites resulting in a negligible NO conversion. Apparently, the presence of mesoporosity facilitates diffusional phenomena and results in significant enhancement of the catalytic activity. Indeed, between PEI-1-5000-Cu and PEI-1-2000-Cu, samples of similar copper content and dispersion characteristics, sample PEI-1-2000-Cu performs better due to its considerably larger fraction of mesopores. Copper loading, on the other hand, exerts a positive but not monotonic effect on catalytic activity. Gradual increase of copper content up to 5.2 % wt. favors NO_x reduction. However, further increase to 6.6 % wt. produces a high population of CuO aggregates, as identified by XRD and UV-vis DR analyses, and a corresponding drastic drop in catalytic performance. Even though samples such as PEI-N-2000-Cu and PEI-1-5000-Cu were not found suitable for NO reduction, they could be proven promising for use in other applications. The retained chemical and structural properties of hyperbranched polyethyleneimine integrated into the siliceous matrix before calcination, could make them excellent candidates in applications such as heavy metal ions and organic molecules removal in water purification or CO₂ capture.

In the case of the Pd loaded material, catalytic tests were performed by employing two flow rates 40 and 80 ml/min corresponding to different space velocities, 30,000 and 60,000 L⁻¹h⁻¹kg⁻¹. As evidenced by the acquired NO profiles (Fig. 13) this material exhibits remarkable NO reduction activity. Initiation of NO conversion was recorded at very low temperatures (> 150 °C) followed by an abrupt increase in the temperature interval of 225 – 250 °C and complete conversion below 300 °C. The same sample was subjected to a second run with an increased flow rate and consequently a higher GHSV (60,000 L⁻¹h⁻¹kg⁻¹). The only difference noticed was a conversion profile shift to slightly higher temperatures whereas 100 % NO conversion was achieved at 280 °C.

Considering the results on similar catalytic materials reported to date [44-48] as well as the employed experimental conditions (CO concentration, GHSV) and final metal loading, the Pd loaded silica prepared in this work exhibits a noteworthy deNO_x activity making it a promising candidate for catalytic applications. Further studies will be directed to a **detailed investigation** of its catalytic NO_x reduction properties under a more realistic operation environment, including a more complicated feed mixture **e.g. presence of O₂, co-existence of SO₂ or H₂O, stability tests and products selectivity.**

4. Conclusions

The proposed templating methodologies are able to deliver metal containing nanoporous silicas with advanced and tailor-made properties and thus widespread application prospects. The key factor for the easy and controlled synthesis of metal loaded silicate materials is the introduction of hyperbranched polyethyleneimines during initial self-assembly and material synthesis, simplifying significantly the synthetic procedure. These polymers contribute to the formation of the porous network and can host various metal guest species in a highly dispersed state, due to their chelating properties. In this work, new materials incorporating copper or palladium oxide nanoparticles were developed, demonstrating the versatility of the described templating approaches. Fine tuning of the synthesis parameters, especially the synthetic gel's pH and PEI's molecular weight, allows the production of materials with diverse pore architectures, morphologies, metal content and distribution. De-pollution performance of the developed materials, assessed by preliminary experiments towards NO reduction by CO, was found to be strongly dependent on both accessibility and dispersion of the active sites confined in the porous matrix. Maximum NO conversion over copper loaded silicas reached up to 54 % whereas the palladium loaded sample demonstrated an excellent deNO_x activity under two different space velocities.

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Table 1. Samples coding, textural characteristics, particle size and final copper loadings

Samples	Synthetic procedure	Initial pH	PEI Mw	Metal ^a wt %	SSA ² (m ² /g)	TPV ³ (cm ³ /g)	Mean Pore Diameter (nm)	Mean crystal size ^b (nm)
PEI-A-2000	Co-assembly	Acidic	2000	—	686	1.02	5.96	—
PEI-A-5000	Co-assembly	Acidic	5000	—	737	1.05	5.7	—
PEI-A-2000-Cu	Co-assembly & impregnation	Acidic	2000	0.0	852	0.61	2.9	—
PEI-A-5000-Cu	Co-assembly & impregnation	Acidic	5000	0.4	779	0.47	2.4	—
PEI-A-5000-Cu-NE	No extraction	Acidic	5000	2.1	990	0.84	3.4	—
PEI-N-2000	Co-assembly	Neutral	2000	—	167	0.20	4.8	—
PEI-N-5000	Co-assembly	Neutral	5000	—	112	0.11	3.7	—
PEI-N-2000-Cu	Co-assembly & impregnation	Neutral	2000	6.6	594	0.45	3.1	13
PEI-N-5000-Cu	Co-assembly & impregnation	Neutral	5000	5.2	561	0.37	2.7	13
PEI-1-2000-Cu	One – pot	Neutral	2000	3.9	464	0.34	2.96	15
PEI-1-5000-Cu	One – pot	Neutral	5000	3.7	587	0.35	2.4	—
PEI-1-5000-Pd	One – pot	Neutral	5000	0.8	558	0.38	2.7	4

^aDetermined by EPMA analysis^bCalculated from the Scherrer equation according to the [111] diffraction peak of CuO.

Figure Captions

Scheme 1: Schematic illustration of co-assembly and one-pot synthetic pathways

Fig. 1: TGA profiles of samples produced through co-assembly and one-pot pathways and of two reference samples, one produced under acidic conditions with addition of P123 (SiO₂ blank) and one under neutral with addition of PEI (PEI-blank).

Fig. 2: DTG profiles of A) PEI-blank, B) PEI-N-5000-Extracted, C) PEI-N-5000, D) PEI-N-2000, E) PEI-A-5000, F) PEI-A-2000 and G) PEI-A-2000-Extracted samples.

Fig. 3: Low-angle XRD patterns of the A) co-assembled samples produced under acidic conditions, B) co-assembled samples produced under neutral conditions, C) samples derived from one-pot approach and Wide-angle XRD patterns of the D) co-assembled samples produced under acidic conditions, E) co-assembled samples produced under neutral conditions and F) samples derived from one-pot approach.

Fig. 4: N₂ sorption isotherms of co-assembled samples prepared under neutral initial pH conditions (Insert: dV-dlogD and CPSD curves of PEI-N-2000 sample estimated from the adsorption branch), metal free reference samples with open symbols and metal loaded ones with filled symbols. A) PEI-N-2000, B) PEI-N-2000-Cu, C) PEI-N-5000, and D) PEI-N-5000-Cu.

Fig. 5: N₂ sorption isotherms of co-assembled samples prepared under acidic initial pH conditions, metal free reference samples with open symbols and metal loaded ones with filled symbols. A) PEI-A-2000, B) PEI-A-5000, C) PEI-A-2000-Cu, D) PEI-A-5000-Cu and E) PEI-A-5000-Cu-NE.

Fig. 6: N₂ sorption isotherms of samples derived from one-pot approach (Insert: dV-dlogD and CPSD curves) of: A) PEI-1-2000-Cu, B) PEI-1-5000-Cu and C) PEI-1-5000-Pd samples.

Fig. 7: SEM micrographs of the co-assembled samples produced under neutral conditions, a) PEI-N-2000, b) PEI-N-5000, c) PEI-N-2000-Cu and d) PEI-N-5000-Cu.

Fig. 8: SEM micrographs of a-b) PEI-1-2000-Cu, c-d) PEI-1-5000-Cu and e-f) PEI-1-5000-Pd samples.

Fig. 9: SEM micrographs of the co-assembled samples produced under acidic conditions, a) PEI-A-2000, b) PEI-A-2000-Cu, c) PEI-A-5000, d) PEI-A-5000-Cu, e) and f) PEI-A-5000-Cu-NE.

Fig. 10: TEM micrographs of a-b) PEI-N-5000-Cu, c-d) PEI-1-2000-Cu and e-f) PEI-1-5000-Pd samples.

Fig. 11: UV-DR spectra of A) PEI-1-2000-Cu (black line) and PEI-1-5000-Cu (red line) samples, B) PEI-N-2000-Cu (black line) and PEI-N-5000-Cu (red line), C) PEI-A-5000-Cu-NE (black line), PEI-A-5000-Cu (red line) and PEI-N-2000-Cu (blue line) samples and D) PEI-1-5000-Pd sample.

Fig. 12: NO conversion profiles as a function of temperature over Cu loaded samples, PEI-N-2000-Cu (\blacktriangle), PEI-N-5000-Cu (\blacksquare), PEI-1-2000-Cu (\bullet) and PEI-1-5000-Cu (\blacklozenge). Conditions: Total flow rate 40 ml min^{-1} , Feed gas composition 500 ppm NO + 500 ppm CO with balance He, Catalyst weight 80 mg, GHSV 30000 h^{-1} .

Fig. 13: NO conversion profiles as a function of temperature over Pd loaded sample. Conditions: Total flow rate 40 (\blacksquare) and 80 (\square) ml min^{-1} , Feed gas composition 500 ppm NO + 500 ppm CO with balance He, Catalyst weight 80 mg, GHSV 30000 (\blacksquare) and 60000 (\square) h^{-1} .