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Continuous synthesis of nickel nanopowders: Characterization, process optimization, and catalytic properties

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ABSTRACT

The preparation of nanoparticles with tailored properties and in quantities in the order of 10–100 g prepared with laboratory-scale equipment is a target of great interest. In this study, Ni nanoparticles with different sizes, surface morphologies, magnetic, and catalytic properties were obtained from $NiCl_2$, N_2H_4, NaOH, and ethylene glycol as solvent by tuning the synthesis parameters. Preliminary syntheses were done in batch reactors and then the continuous synthesis carried out in the Segmented Flow Tubular Reactor (SFTR). For the first time a SFTR system was applied to a non-aqueous system. By combining SEM, HRTEM, XRD, TGA, XPS, FTIR, specific surface area, SQUID, and catalytic tests, the complete structural, morphological, and functional characterization of the produced nanoparticles were performed. The continuous production of 2.1 g h^{-1} of Ni nanoparticles was carried out up to 6 h without product properties deterioration. The results allow estimating a production >300 g d^{-1} in an *ad-hoc* low-cost single-tube SFTR system. Catalytic tests of CO methanation showed good activity at 769 K with stable methane yield of 83%. The results presented in this study demonstrate that reliable and reproducible synthesis of relatively high amounts of metal nanoparticles with lab-scale equipment can be achieved. This approach opens new opportunities for reliable and controlled preparation of advanced materials in quantities suitable for a full functional characterization.

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1. Introduction

Metal nanoparticles (NPs) have attracted much interest in the last years due to their unique properties and applications in several areas such as microelectronics, catalysis, and biomedicine [1,2]. Specifically, magnetic nanoparticles have potential applications as ferrofluids [3], magnetic retrievable catalysts [4–6] and photocatalysts [7], magnetic carriers for drug targeting [8,9] and hyperthermia [10].

Pure and supported Ni NPs have promising catalytic properties. Double bond hydrogenation, carbon dioxide hydration, CO methanation [11,12], and ethanol steam reforming reactions were reported [13–17]. Moreover, the interest in massive production of fine nickel powders as substitute for noble metals in

microelectronics, such as in the base–metal–electrode multilayer ceramic capacitors (BME-MLCCs), is rapidly growing. In these miniaturized devices, since materials prepared by top-down techniques are approaching the technical limitations, bottom-up methods are more and more attractive [18,19].

Most physical and chemical properties of nanoparticles strongly depend on their size and shape. Several synthesis methods were developed to obtain Ni NPs with well-defined dimension, narrow size distribution, and limited particle aggregation. Solvothermal reduction [20], thermal decomposition [21,22], microwave assisted reduction [23,24], laser ablation [25], irradiation [26], aqueous [27–29] and polyol synthesis routes [30–32] are some of the possible methods.

Although the aforementioned methods allow obtaining satisfying products, the reported productions are often limited to few milligrams and are carried out in lab-scale batch reactors. Laboratory prepared powders are often very difficult to scale-up maintaining the product quality. Thus, the reproducible synthesis

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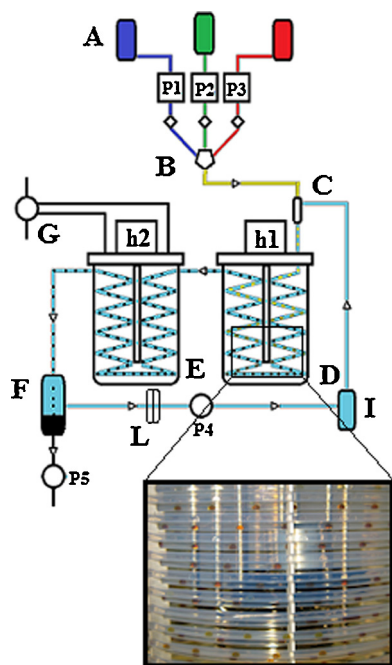
Scheme 1. Sketch of the SFTR reactor. A: pumping system composed by three HPLC pumps (P1, P2, P3) pulsation dumpers and back pressure valves; B: mixer; C: segmenter; D: thermostatic bath equipped with heating head (H1) and mechanical stirrer; E: cooling bath equipped with heating head (H2) and mechanical stirrer and connected to the chiller (G); F: decanter connected to the pump P5; I: reservoir; L: filter; P4: circulating pump.

of nanopowders with desired shape, particle size distributions, stoichiometry, crystalline phase, and in a considerable amount is still a major concern.

In general, chemical solution methods have shown the capability to control composition, size and shape, and are suitable for up-scaling. Among the solution methods, the reduction of inorganic Ni^{2+} salts by hydrazine, with NaOH as promoting agent, in absence of polymeric additives, and using ethylene glycol (EG) as solvent, is a convenient method for Ni NPs preparation. Moreover, according to this method (i) pure Ni is directly produced; (ii) the product has high surface area due to the small primary particle size and particle surface roughness; (iii) the particles surface is not polymer-coated and suitable for catalytic processes without additional thermal treatments; (iv) it does not require expensive chemicals; (v) it is scalable; (vi) has no byproducts difficult to remove or hazardous, (vii) it is rather fast; (viii) it is possible to use high metal salts concentration; (ix) to a certain extent size and morphological control is achievable [33–35]. Only few papers report on continuous methods [36] or larger quantities but in batch reactors [37].

Over recent years a new type of tubular plug flow reactor – the Segmented Flow Tubular Reactor (SFTR) – has been conceived and used in powder synthesis [38]. This type of reactor has shown excellent performances, versatility and robustness through the preparation of different products: $CaCO_3$ [39], $BaTiO_3$ [40], copper oxalate, calcium and nickel-manganese oxalates [41,42] with a high powder quality (chemical and phase composition, narrow particle size distribution, and controlled shape) and reproducibility [43]. The SFTR was developed to overcome the classical problems of up-scaling powder production from batch processes, which are mainly linked with mixing, homogeneity, and heat transfer. A schematic view of the SFTR is given in Scheme 1. The SFTR is composed of three distinct parts: (i) a micromixer which ensures that the reactants are efficiently mixed, (ii) a segmenter, and (iii)

a tubular reactor, placed in a thermostatic bath. Small suspension volumes (about $0.2\,cm^3$) are thus created, producing microdroplets or microreactors in an immiscible fluid, where the reaction – in this case Ni^{2+} reduction and Ni precipitation – takes place. These small volumes ensure a high homogeneity inside each droplet, all circulating through the tube with an identical *history* (e.g., residence time and heat exchange). The reaction or the precipitation occurs in the mixing chamber and/or is induced by the rapid temperature change when the microreactors are heated in the thermostatic bath. According to fluid dynamic modeling, the temperature of the droplets reaches 95% and 99% of the bath temperature within 6 and 10 s, respectively [44]. Fouling on the inner tubular reactor wall is avoided due to the immiscible fluid by forming a thin film on the tube surface [45] and thus allowing long continuous process times (>12 h). The residence time is determined by the pump flow rates and the tube length and adjusted according to the specific reaction kinetics. This is a steady-state process in which each step, mixing and reaction, is well separated, leading to a better control and reproducibility. If needed, after the tubular reactor, in the process line, a heat-exchanger can be placed to cool down the reacting mixture and quench the reaction. Finally, a separation unit or decanter allows the separation of the product by the immiscible fluid; the product – particle in suspension – is collected, while the immiscible fluid is recycled in the process for environmental and cost concerns. To increase productivity for commercial application, the SFTR can be "scaled-out" by multiplying the number of tubes running in parallel instead of scaling-up by increasing their size. The production of calcium carbonate with a scaling-out factor of 5000 with no change in product quality and the robustness of the process in the production of high quality ultrafine barium titanate powders were already demonstrated [46].

This work reports the continuous synthesis of Ni NPs in the SFTR reactor. For the first time, a polyol synthesis was studied and successfully carried out in the SFTR reactor, extending the portfolio of possible applications towards non-aqueous systems and up to the EG boiling temperature. Systematic investigation of the synthesis parameters for Ni NPs preparation such as precursor concentration, temperature, reaction time, for both small batch and continuous SFTR processes are presented. Selected batch samples and the most relevant SFTR products were morphologically, spectroscopically and magnetically characterized. Moreover, thermal and catalytic properties of selected pure Ni samples are presented. With a single tube SFTR reactor, the continuous production of Ni NPs up to $2.1\,g\,h^{-1}$ has been achieved with constant product properties over the time frame tested (6 h), proving the potential of the SFTR not only at laboratory scale.

2. Experimental

2.1. Materials

Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, >98%), hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 65%, reagent grade 98%), sodium hydroxide (NaOH, >98%), ethylene glycol (EG, puriss. p.a. >99.5%), *n*-dodecane (*n*-C_{12}, reagent grade, >99%), and Ni nanopowders – named A01 in the following text – as benchmark (Ni, #577995, declared particle size <100 nm, >99%) were obtained from Sigma–Aldrich and used as received without further purification. Ethanol and acetone used for powder washing purpose were reagent grade and obtained from VWR. γ-Al_2O_3 (Sasol Puralox) was used to dilute Ni particles for catalytic tests.

Few tests were carried out with polymeric additives: Na-polyacrylate (Na-PA, Sigma–Aldrich, AMW = 8k) and polyvinylpirrolidone (PVP, Sigma–Aldrich, AMW = 40k).