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Nanostructured particles by controlled precipitation techniques Example of nickel and cobalt hydroxides

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Abstract

By controlling the conditions of homogeneous precipitation reactions, it is possible to obtain more and more complex structures from individualized nanoparticles to multi-scale micrometric particles. This is shown in the case of nickel and cobalt hydroxide. Precipitation using the combination of ammonia decomplexation and dodecylsulfate templating leads to nanostructured nickel hydroxide submicronic cylinders and flower-like cobalt hydroxide. After calcination, surfactant is removed and their respective oxides keep the original shapes. NiO nanostructured cylinders exhibit a relatively high specific surface area around 130 m^2/g and a pore size around 4 nm, consistent with the observed nanostructure.
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1. Introduction

The controlled obtention of multi-scale submicronic or micrometric particles is expected to be of interest for catalyst or support preparation since a multi-scale porosity opens the door to optimized diffusion of reactive species between the catalyst surface and the medium. Besides, such particles may develop a large specific surface area without some drawbacks generally exhibited by nanoparticles as far as their production or handling are concerned: complexity of washing and retrieval processes, toxicity by inhalation of powders.

Precipitation techniques are well-known to allow production of homogeneous and relatively monodisperse particles in the micrometric range, but the focus on their multi-scale features is still relatively rare in spite of the common occurence of the phenomenon and intriguing issues about mechanisms leading to size and shape monodispersity. Precipitation of metallic salts aqueous solutions by a base may lead to homogeneous nanoparticles or nanostructured submicronic (hydr)oxide particles on condition that physico-chemical parameters impacting the supersaturation and hence the reactivity of the system are well-controlled. Two main categories of techniques are used. The first strategy consists in controlling the mixing of reactants inducing precipitation. Separated jets are known to produce in some systems well-calibrated and homogeneous particles [1], because reactants may be diluted in the bulk volume before reacting. The second one consists in homogeneous precipitation, avoiding mixing issues. Homogeneous precipitation is generally triggered by heating, inducing for example the decomposition of a molecule (as urea, thioacetamide) that releases a reactant (OH^- or H_2S, respectively) homogeneously in the bulk volume. The technique of urea decomposition [2–4] generally leads to amorphous hydroxycarbonate spherical particles, that can be calcined into oxides keeping the shape and exhibiting nanostructures, whereas thioacetamide decomposition [5–8] usually leads to spherical multi-scale sulfide particles. Urea decomposition was coupled to mesophase templating to produce nano or microtubes, as exhibited with dodecylsulfate for alumina [9], rare-earth oxides [10] and nickel oxide [11]. We have recently developed another kind of homogeneous precipitation taking benefit from decomplexation of ammoniated metallic species at moderate temperature (60–80 °C) [12,13]. Ammonia plays a double role as a ligand and as a base, which generally implies antagonic effects to manage for the precipitation of hydroxide. This technique is very versatile and allows playing with complexation equilibria just by rising temperature in closed

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systems, by working in open systems in order to enhance the reactivity by ammonia removal, and even by bubbling gas to increase the liquid–gas interface. The basicity and reactivity of the system may also be increased by using hydroxide metallic precursors instead of salts. Ammonia decomplexation can also be coupled with templates, giving birth to new features as far as particle morphologies and nanostructures are concerned [12].

Here we show the results of applying homogeneous precipitation by ammonia decomplexation to obtain nickel, cobalt and mixed nickel–cobalt hydroxides, which may be calcined into oxides keeping the morphological and nanostructure features.

2. Experimental

Nickel and cobalt hydroxides were synthesized according to protocols described elsewhere [12]. Briefly, ammonia complexation/decomplexation on nickel (or cobalt) di-dodecylsulfate (DS) was performed as follows: 1.2 mol NH_3 was added slowly to 0.05 mol $Ni(DS)_2$ (respectively $Co(DS)_2$) dissolved in distilled water at 25 °C and the reactor was heated at 60 °C for 23 h. In the case of nickel we operated under air, in the case of cobalt under argon.

3. Characterization

Nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP2010 model. Specific surface area and pore size distribution were calculated applying the Brunauer–Emmet–Teller (BET) model and Barett–Joyner–Halenda (BJH) method on the desorption branch. Scanning electron micrographs (SEM) were obtained using a field effect gun ZEISS DSM 982 LEO Gemini apparatus. Powder samples were fixed on carbon tape and coated with 3 nm of gold–palladium. Transmission electron microscopy (TEM) was performed employing a Phillips EM430 apparatus. Powders were dispersed in distilled water using ultrasonic device and dried in air on carbon-coated copper grids. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer in θ–θ configuration, using cobalt $K\alpha_1$ radiation ($\lambda = 1.789$ Å) and equipped with a position sensitive detector.

4. Results

4.1. Ammonia decomplexation of nickel and cobalt dodecylsulfate

In the case of nickel, a purple solid $Ni(DS)_2(NH_3)_6$ was formed when ammonia was added to $Ni(DS)_2$ solution. It was isolated then transformed in open air at 60 °C during 23 h in (1) ammonia solutions, (2) distilled water, (3) soda solution with stoichiometric quantity of OH^- as compared to nickel, we observe features directly linked to the increasing reactivity: the system with ammonia produces nanostructured cylinders as published elsewhere [12], the system with distilled water gives flat particles still exhibiting some organization by oriented attachment as confirmed by electron diffraction, the system with soda leads within a few minutes to individualized platelets (Fig. 1). The reactions may be written as follows:

- as a first step the transformation of the poorly soluble purple solid into a more soluble blue penta-ammoniated compound.

$$Ni(DS)_2(NH_3)_6 = Ni(DS)_2(NH_3)_5 + NH_3$$

- and as a second step the reaction producing the hydroxide, that may be written

$$Ni(DS)_2(NH_3)_5 = Ni(OH)_2 + 2DS^- + 3NH_3 + 2NH_4^+$$

under low basicity conditions or

$$Ni(DS)_2(NH_3)_5 + 2OH^- = Ni(OH)_2 + 2DS^- + 5NH_3$$

if basicity is high.

In conditions (1) the release of soluble species from the purple solid is very slow and controlled by the equilibrium shift due to ammonia removal, and the second step is also slow due to

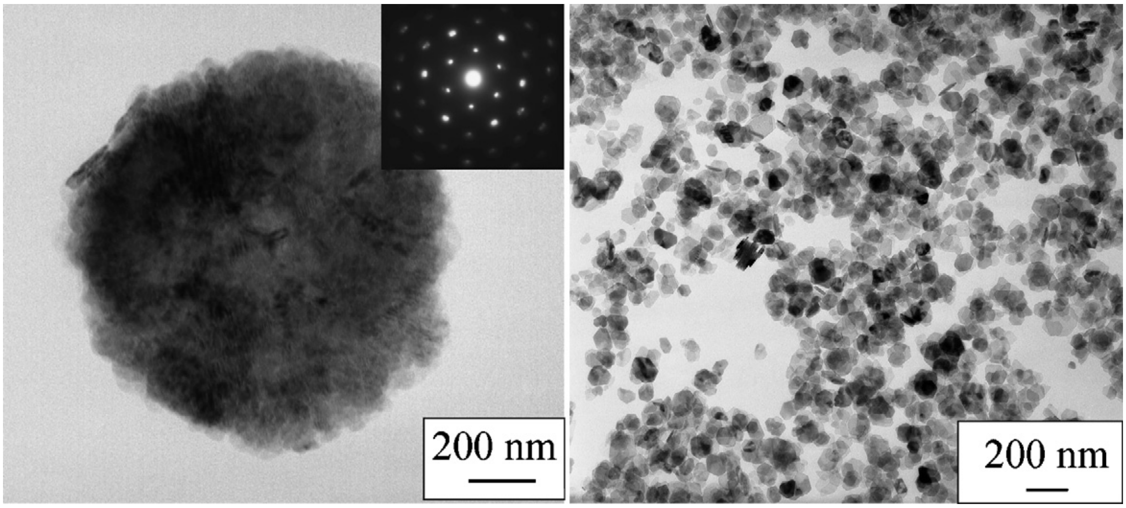

Fig. 1. TEM image of nickel hydroxide particles obtained by ripening of the purple solid $Ni(DS)_2(NH_3)_6$ in water (left) and diluted soda (right).

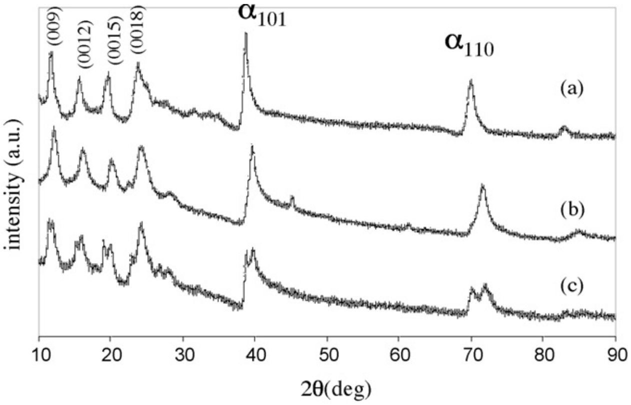

Fig. 2. X-Ray diffractograms of hydroxides obtained by ammonia decomplexation of $x\mathrm{Co(DS)_2} + (1 - x)\mathrm{Ni(DS)_2}$ mixtures. (a) $x = 1$; (b) $x = 0.20$; (c) $x = 0.50$.

the relatively low basicity: the complexing (and stabilizing) effect of ammonia is stronger than its basic power (antagonic effects). In conditions (2) the equilibrium is strongly shifted towards ammonia release and the first step is fast, whereas the kinetics of the second step is moderated by the fact hydroxyls are only produced by ammonia released from the solid. Finally in conditions (3) both steps are fast, the second one being drastically accelerated by the pre-existence of hydroxyls in the solution: in this last case the role of ammonia as a base is no more effective.

These results illustrate that the obtention of multi-scale objects requires low reactivity with OH^- shortage in the case of nickel hydroxides, which facilitates oriented attachment. It is also noteworthy that if we perform the experiment in ammonia solutions in a closed vessel, the purple solid is not transformed, which means the driving force induced by thermal effect is not strong enough and ammonia removal is necessary to shift the first equilibrium and get nickel hydroxide. On the contrary, with distilled water or soda solutions nickel hydroxide is obtained in closed vessels, since the lack of ammonia in the solution was enough to shift the equilibria.

Such particles result from a specific chemistry of Ni^{2+} ammoniated complexes and the existence of a solid hybrid precursor for the hydroxide. Since the chemistry of $Co(OH)_2$ precipitation is close to $Ni(OH)_2$, we performed a synthesis in the same conditions that produced the cylinders, replacing $Ni(DS)_2$ by $Co(DS)_2$. Due to the easy oxidation of Co^{2+} in ammonia solutions, we degassed solutions and maintained an argon atmosphere during reaction. The surfactant stabilized the metastable phase that precipitated during ammonia injection and did not redissolve entirely, contrary to the case of nickel where the alpha phase progressively redissolved to form the purple solid $Ni(NH_3)_6(DS)_2$. In fact α-$Co(OH)_2$ was so stable

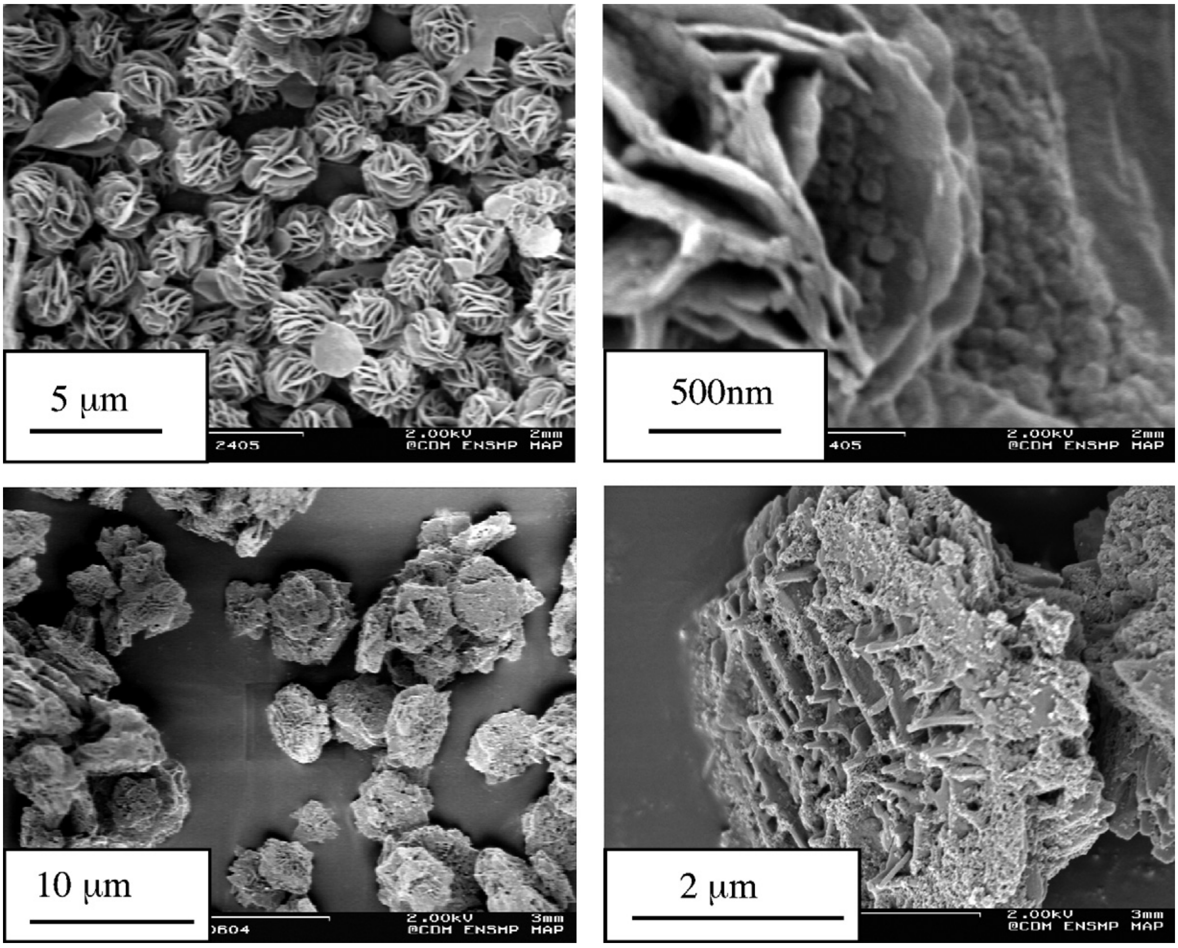

Fig. 3. SEM images of cobalt hydroxide particles resulting from ammonia decomplexation of $Co(DS)_2$ (top) and $Co(NO_3)_2$ (bottom).

that it was the only crystallized phase obtained after 23 h, with no trace of β phase (Fig. 2a). The adsorption of dodecylsulfate was verified by IR spectroscopy, and the peaks observed in XRD between 10° and 20° result from the intercalation of DS as in layered double hydroxides [14]. This phenomenon was also observed in one of our previous work in nickel hydroxide with double jet precipitation, but very marginally [15]. Here the peaks corresponding to the ''mesostructure'' are very intense and give an average interlayer spacing of 26.1 Å, perfectly consistent with deep interpenetration of opposite dodecylsulfate tails the same way as CLIPO® toys. In such a case a partial oxidation of cobalt could explain this significant incorporation, as well as the green color of the precipitate since α-$Co(OH)_2$ is supposed to be blue, which was indeed the color of the suspension only at the beginning of the process. So a more realistic formula for the product is α-$Co(OH)_z(DS)_{1-z}$. The final particles observed by SEM reveal a flower-like structure (Fig. 3, top): particles are much bigger than in the case of nickel, around 2 μm diameter, and there is no stacking of platelets but on the contrary a rather isotropic distribution of the platelets orientations. The platelets constitutive of the ''petals'' seem also relatively flexible. If we consider particles obtained just at the end of ammonia injection ($t = 1$ h), platelets of α-$Co(OH)_2$ are polydisperse (over 5 μm for the biggest ones) and are not self-organized into flowers. That suggests flowers are the result of a ripening that re-shaped the particles without inducing the transformation from α to β phase. To exhibit the role played by the surfactant, the same experiment was performed with cobalt nitrate instead of dodecylsulfate. In this case, cobalt was first precipitated during ammonia addition then entirely solubilized by complexation at room temperature, and the final product after 23 h heating was well-crystallized β-$Co(OH)_2$. Particles are irregularly shaped, but interestingly they have an inner organization resulting from platelets intertwining as exhibited after 3 h experiments (Fig. 3, bottom) this architecture being totally concealed after 23 h by a shell of packed nanoparticles. As for the case of nickel, there is a benefit from a solid precursor that slowly transforms into the final product to get monodisperse multi-scale particles, and we demonstrate in both systems a coupled effect of ammonia and surfactant.

To go further with this system, we performed ammonia decomplexation on mixtures of nickel and cobalt dodecylsulfate in conditions that produced nanostructured cylinders for pure nickel. With 5% or 10% cobalt, the system behaves as in the case of pure nickel: nanostructured cylinders of β mixed hydroxide were still obtained, even if significantly smaller than with pure nickel (Fig. 4). With increasing the cobalt quantity

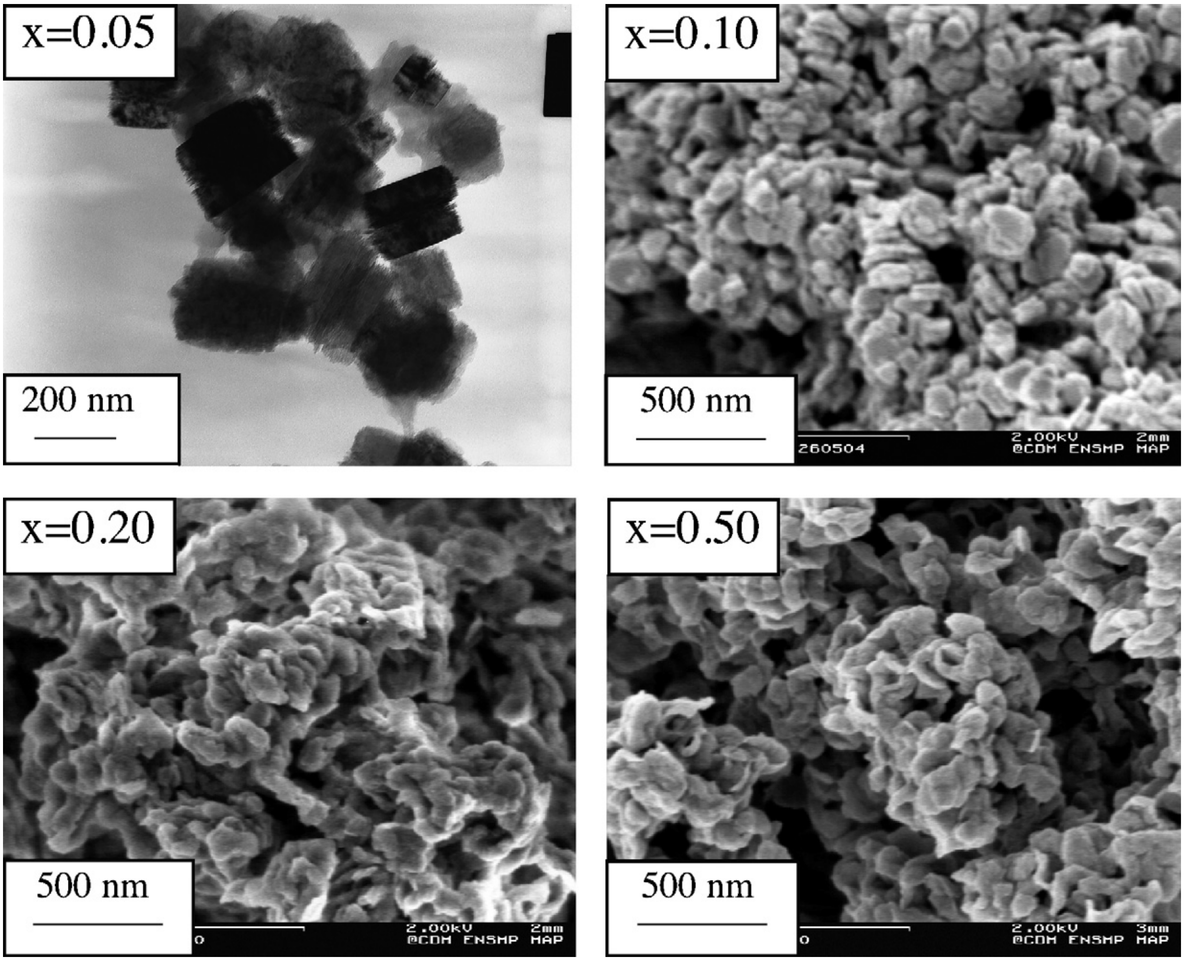

Fig. 4. TEM and SEM images of mixed nickel and cobalt hydroxide particles resulting from ammonia decomplexation of $(1 - x)Ni(DS)_2 + xCo(DS)_2$.

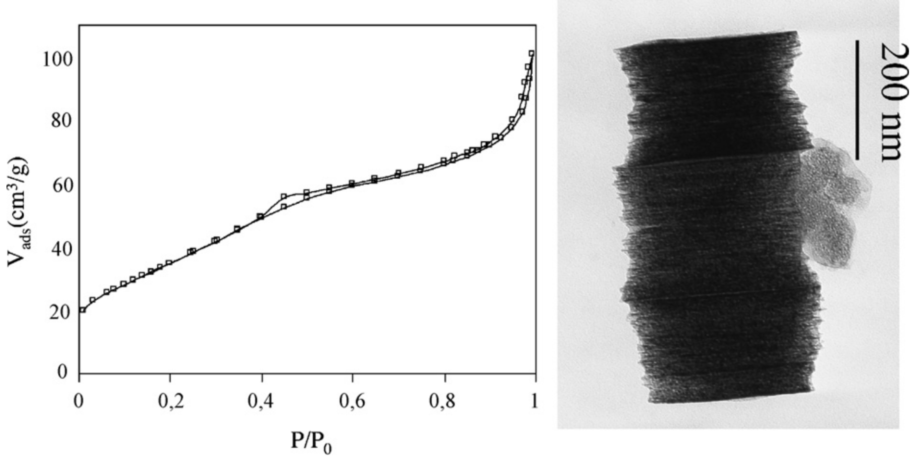

Fig. 5. Nitrogen gas adsorption (left) and TEM image (right) of nickel oxide nanostructured cylinders resulting from calcination of nickel hydroxide.

(20% and 50%) particle got ill-shaped, and crystallized into alpha phase with interlayered surfactant. For 20% cobalt, we got a single alpha phase supposed to be α-$Ni_{0.8}Co_{0.2}(OH)_{2-y}DS_y$ (Fig. 2). This phase with a significant interlayered dodecylsulfate content (seen at low diffraction angles) is all the more intriguing that the same conditions with less than 10% cobalt produce nanostructured β cylinders free from intercalated surfactant. So a ratio between 10% and 20% cobalt totally changes the reactivity of the system by stabilizing the alpha phase that precipitates first during ammonia addition. This stabilization is in correlation with the incorporation of interlayered surfactant. Surfactant incorporation is clearly exacerbated by cobalt as observed in the pure cobalt case, and the stabilization against dissolution after further ammonia addition is probably due to surfactant anchored on the external surfaces, protecting against the attack of ammonia. A mixture α-$Ni_{1-x}Co_x(OH)_{2-y}DS_y$ with x close to 0.2 and pure α-$Co(OH)_{2-z}DS_z$ was evidenced for 50% cobalt (Fig. 2). That means the solubility of cobalt in nickel hydroxide is rather high but limited, and cobalt in excess seems to react alone. The fact that this excess cobalt hydroxide phase does not lead to flowers as for pure cobalt is intriguing but not too surprising considering the delicate and complex mechanisms reshaping cobalt hydroxide sheets into flowers. Hence there was no new feature by using a mixture of cobalt and nickel as far as multi-scale objects are concerned, on the contrary homogeneous multi-scale particles were more easily obtained for pure nickel or cobalt hydroxides. The study of mixed compounds rather revealed interesting new features about the crystallization of surfactant-interlayered α phases.

4.2. *Calcination of nickel hydroxide nanostructured cylinders*

Considering nanostructured nickel hydroxide cylinders obtained with dodecylsulphate and ammonia decomplexation, the lamellar structure is not altered by calcination. The adsorption cycle reveals a mixture of E and B type porosity, and exhibits a rather high specific surface area for NiO: 128 m^2/g, a porous volume of 0.127 cm^3/g and average pore diameter of 4.0 nm (Fig. 5). These values suggests that the exposed surface and porosity are mainly interlamellar: the surface value would correspond to 3 nm thin 2D lamellae, which is close to TEM observations. If we consider only pore diameter inferior to 10 nm, the total pore volume is around 0.09 cm^3/g. Since 1 g of NiO corresponds to a dense volume of 0.147 cm^3, we can evaluate that the pore volume corresponding to interlamellar space is around 1/3 of the cylinder volume. The nanostructure may therefore be described as monodisperse submicronic particles, with confined and regular interlamellar space of a few nanometers easily accessible thanks to the reduced diameter of the cylinders. It is noteworthy that the equivalent lateral plain surface of typical cylinders of 300 nm diameter is 2 m^2/g for NiO. As a consequence, we obtain two scales for the produced particles, each one having a specific interest: the submicronic size of the particles and their monodispersity induce large pores by random packing in powder form, whereas the nanostructure offers homogeneous porosity at the nanometer level and a high specific surface area.

5. Conclusion

Multi-scale nickel or cobalt hydroxide particles can be obtained by homogeneous precipitation via ammonia decomplexation. The use of an anionic surfactant allows obtention of highly monodisperse particles with original nanostructures, that result from the slow transformation of a solid and poorly soluble precursor in both cases: $Ni(DS)_2(NH_3)_6$ or α-$Co(OH)_2$ with intercalated DS. The growth of such structures is controlled by a combination of slow release of reactants and interactions between the anionic surfactant and ammoniated cationic metallic species and/or positively charged surfaces. It is possible to progressively increase reactivity so that multi-scale features disappear, replaced by more common nanoparticles similar to those obtained in double-jet precipitation. These particles and nanostructures can be calcined into nickel or cobalt oxide keeping the morphological features.This technique is expected to be applicable to other transition metal elements to produce pure or mixed nanostructured (hydr)oxides.

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