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Design of Cobalt Nanoparticles with Tailored Structural and Morphological Properties via O/W and W/O Microemulsions and Their Deposition onto Silica

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Abstract: Cobalt nanostructures with different size and morphology, *i.e.*, spherical nanoparticles, nanorods, and particles arranged into elongated structures, were prepared using micelles and microemulsions as confined reaction media. The syntheses were carried out using three types of systems: aqueous surfactant solutions, oil-in water (O/W), and water-in-oil (W/O) microemulsions. The influence of the surfactant and the precipitating agent used for synthesis was also investigated. For this purpose, cobalt nanostructures were prepared using different non-ionic surfactants, namely Synperonic® 10/6, Pluronic® P123

and a mixture of SPAN 20–TWEEN 80. Three different precipitating agents were used: sodium borohydride, sodium hydroxide, and oxalic acid. Our findings revealed that by changing the type of reaction media as well as the precipitating agent it is possible to modify the shape and size of the cobalt nanostructures. Moreover, the use of O/W microemulsion generates better results in terms of colloidal stability and uniformity of particle size with respect to W/O microemulsion. The different cobalt nanostructures were supported on commercial and mesoporous silica; transmission electron microscopy (TEM) images showed that after deposition the Co nanocrystals remain well dispersed on the silica supports. This behavior suggests their great potential in catalytic applications.

Keywords: cobalt nanoparticles; cobalt oxide; microemulsions; nano-reactor; silica support

1. Introduction

Over the past decades, nanomaterials have received considerable interest because of their unique optical, electrical, magnetic, and mechanical properties, which are due to the quantum size effect, high surface area and lower amount of structural defects. The size and shape of nano-sized materials and their large surface area can greatly affect their properties and reactivity. In particular, the synthesis of cobalt nanoparticles with tailored morphology has attracted much attention for their potential applications in many fields, such as heterogeneous catalysis [1,2], gas sensors [3], and magnetic devices [4]. Among various cobalt-based nanoparticles, both Co^0 and Co_3O_4 have received great interest [5–9].

Cobalt nanoparticles (Co^0), are very promising for electronic and information storage devices because of their large magnetic susceptibility as compared to other metallic nanomaterials [6]. Moreover, it is well known that supported cobalt nanostructures present a high activity and selectivity in the Fisher-Tropsch (FT) reaction, in which syngas (a mixture of CO and H_2), is converted into liquid fuel via catalytic surface polymerization which leads to a large variety of products such as paraffins, olefins, alcohols, and aldehydes [2]. Cobalt catalysts are the best candidates for converting syngas to clean liquid fuels because of lower deactivation rates, low water-gas shift activity, and high chain growth probability [10]. On the other hand, Co_3O_4, an oxide with a spinel crystalline structure has also received great consideration for its potential applications in heterogeneous catalysis [1,2,8], solid-state sensors [3], and electrochemical devices [5]. Furthermore, Co_3O_4 nanoparticles have also been used as catalysts for the FT reaction, since this material can be reduced to active Co by thermal treatment under a flow of hydrogen; cobalt catalysts with a mesoporous silica shell and a high selectivity towards the C_5-C_{18} fraction have been prepared in this way from $Co_3O_4@m\text{-}SiO_2$ [11].

Many synthetic strategies have been developed for the synthesis of nanoparticles; among them, the microemulsion reaction method involving reverse micelles has been demonstrated as a versatile approach for the preparation of a great variety of nanomaterials [12–16]. Microemulsions are transparent and thermodynamically stable colloidal dispersions in which two liquids initially immiscible (typically water and oil) coexist in one phase due to the presence of a monolayer of surfactant molecules [17]. Depending on the ratio of oil and water and on the hydrophilic-lipophilic

balance (HLB) of the surfactant, a microemulsion can exist as oil-swollen micelles dispersed in water (O/W microemulsion), or water-swollen inverse micelles dispersed in oil (W/O microemulsion); at intermediate compositions and HLBs, bicontinuous microemulsions with a sponge-like structure can exist; in these systems, both water and oil phases form continuous channels separated by a monolayer of surfactant. Since first reported in 1982 [18], the W/O microemulsion reaction method has received increasing attention for the synthesis of a great variety of nano-sized materials. Microemulsion droplets act as a reaction media that is confined to the nanoscale, allowing the production of nanoparticles with a controlled size under soft reaction conditions [13,15].

According to the literature [6], surfactant/polymer-encapsulated cobalt nanocrystals with an average diameter of ~3.5 nm were recently prepared using W/O microemulsions. Porous cobalt oxide (Co_3O_4) nanorods were obtained by a microemulsion-based method in combination with a subsequent calcination process [5]. Rod-shaped nanostructures of cobalt oxalate dihydrate were synthesized at room temperature through a reverse micellar route using cetyltrimethylammonium bromide (CTAB) [19]. Recently, an investigation was focused on the comparison of the microemulsion method with the incipient wetness impregnation technique for the preparation of cobalt metal nanoparticles with controlled size using carbon nanotubes as catalyst support; the materials synthesized using W/O microemulsions showed a CO conversion 15% higher than the materials prepared by incipient wetness impregnation, demonstrating the potential of the W/O microemulsion method for the synthesis of active catalysts for the FT reaction [20]. Moreover, besides the use of microemulsions, the synthesis of cobalt nanoparticles was recently carried out in alcoholic solution by reduction with sodium borohydride using a triblock copolymer Pluronic® P123 as stabilizing agent [21].

However, in spite of its versatility and advantages, the W/O microemulsion reaction method has certain drawbacks such as the use of large amounts of organic solvent. With this motivation, we developed in recent years the oil-in-water (O/W) microemulsion reaction method [22], which is more environmentally friendly since it uses water as the main component. This method consists of the use of organometallic precursors, dissolved in nanometer scale oil droplets of O/W microemulsions, and stabilized by a monolayer of hydrophilic surfactant. Normally, water-soluble precipitating agents are directly added to the microemulsions as aqueous solutions, without compromising microemulsion stability. This method has been successfully used to prepare a variety of metal and metal oxide nanoparticles, resulting in small nanoparticles with a narrow size distribution, good crystallinity, and high specific surface area [22–26].

Nowadays, the development of facile and environmentally friendly procedures for the synthesis of cobalt nanoparticles with a tailored morphology is still an important challenge, with particular interest in the use of aqueous solutions and non-toxic reagents. In the present work, different synthetic routes for the preparation of nanostructured cobalt-based materials were compared in order to investigate the role of the composition of the system, as well as the nature of the surfactant and precipitating agent on the morphological and structural properties. In particular, three types of system were used for the synthesis of cobalt nanostructures: (a) O/W microemulsions; (b) W/O microemulsions and (c) aqueous surfactant solution.

The attention was mainly focused on O/W microemulsions, which is a more environmental friendly procedure. To the best of our knowledge, the use of O/W microemulsions for the preparation of cobalt nanostructures has not been reported so far. The as-prepared cobalt-based nanostructures were

supported onto silica, in order to establish if it was possible to prevent the agglomeration of cobalt nanocrystals during the deposition and the subsequent calcination process, since this feature is key for catalytic applications.

2. Results

Cobalt nanostructures prepared using different synthetic procedures were compared in order to investigate the role of the composition of the system, as well as the nature of the surfactant and precipitating agent on their size, morphology, and structural properties. The synthesis was carried out using three types of systems: (a) O/W microemulsions; (b) W/O microemulsions and (c) aqueous surfactant solution (direct micelles). Moreover, different nonionic surfactants, namely Synperonic® 10/6 (hexaethyleneglycol isodecyl ether), Pluronic® P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), SPAN® 20 (sorbitan monolaurate) and TWEEN® 80 (polyethylene glycol sorbitan monolaurate) were used in the formulations, thus testing the suitability of these different nonionic surfactant systems as stabilizers for cobalt nanostructures.

With Synperonic® 10/6, both O/W and W/O microemulsions were formulated. The former were prepared by using hexane and cobalt (II) 2-ethylhexanaote (Co(II)2EH) as the oil phase and water as the continuous phase; the latter were formed by using isooctane as the oil phase and solutions of cobalt (II) nitrate ($Co(NO_3)_2$) as the aqueous phase. These microemulsions were labeled as CoME1 and CoME2, respectively. This particular strategy was implemented in order to investigate the role of the type of microemulsion (O/W or W/O) whilst using the same surfactant system. With Span® 20–Tween® 80 (Span-Tween), an O/W microemulsion was formulated, based on previous work carried out with the synthesis of Pt NPs [23]. Thus, the precursor Co(II)2EH was dissolved in both the oil phase (ethyl oleate) and the cosurfactant (1,2-hexanediol), in order to boost Co content in the microemulsion. This system was labeled as CoME3. Aqueous micellar solutions were prepared with Pluronic® P123, which was labeled CoME4; this system corresponds to direct micelles of triblock copolymer surfactant. With these four systems, Co nanoparticles were prepared by reduction of cobalt (II) precursor with solutions of sodium borohydride ($NaBH_4$) under an inert atmosphere (N_2). The composition and reaction conditions for the different samples are shown in Table 1. All systems were processed at 25 °C, as care was taken to formulate microemulsions that were formed at this temperature.

The influence of the precipitating agent on the morphological properties of cobalt-based nanostructures was also investigated. To this purpose, O/W microemulsions with Synperonic® 10/6 (with the same composition as CoME1) were used as reaction media. The formation of cobalt nanostructures was achieved using $NaBH_4$ for cobalt reduction under an inert atmosphere (N_2) in CoME1; using NaOH for cobalt precipitation as cobalt hydroxide in CoME5; and finally, oxalic acid (($COOH)_2$) was used for cobalt precipitation as oxalate in CoME6.

The formation of cobalt nanoparticles in O/W and W/O microemulsions (CoME1 and CoME2) presented some interesting differences on the basis of the first optical observations. In both cases cobalt nanoparticles were formed quickly upon addition of $NaBH_4$, which was indicated by the change of microemulsion appearance, from transparent-bluish (due to the color of the Co(II) precursor) to black. Nonetheless, nanoparticles formed in the W/O microemulsion (CoME2) started to agglomerate

and precipitate after a few minutes, whilst nanoparticles prepared in the O/W microemulsions (CoME1, CoME3) remained very well dispersed for a longer time. Thus, even though the surfactant used was exactly the same (Synperonic® 10/6) in both types of microemulsions CoME1 and CoME2 (O/W and W/O), it was observed that the synthesis in O/W microemulsions promoted the formation of much more stable nanoparticle dispersions, which is key for the homogeneous and well dispersed deposition of metallic NPs onto catalyst supports. The nanoparticles prepared in aqueous Pluronic® P123 direct micelles (CoME2), also remained very stable. On the other hand, nanoparticles prepared using the other precipitating agents behaved very differently: when using NaOH the color of the dispersion became brown (indication of $Co(OH)_3$ or $CoO(OH)$ formation), whilst with oxalic acid the formation of micron-sized pink needles (typical of cobalt (II) oxalate) was observed.

The as-prepared cobalt nanostructures were deposited onto commercial silica and mesoporous SBA-15 supports and all the samples were subsequently calcined at 400 °C. The morphology and dispersion of supported cobalt nanostructures were investigated by transmission electron microscopy (TEM) analysis in order to evaluate if it was possible to prevent the agglomeration of cobalt nanocrystals during their deposition and calcination. The preparation of highly dispersed cobalt nanostructures supported onto commercial silica and mesoporous SBA-15 is very important for various catalytic applications [27].

Table 1. Experimental conditions (composition, type of system, precipitating agent) used for the synthesis of cobalt-based nanostructures.

Sample ID	Composition (weight ratio)	Type of System	$[Co^{2+}]$ in final system/(wt.%)	Surfactant/Co^{2+} (weight ratio)	Precipitating agent
CoME1	Water/Synperonic® 10/6/(Hexane + Co(II)2EH) 67.5/22.5/10	O/W microemulsion	0.20	112.5	NaBH$_4$
CoME2	(Water + Co(NO$_3$)$_2$)/ Synperonic®10/6/Isooctane 2/29.4/68.6	W/O microemulsion	0.26	112.5	NaBH$_4$
CoME3	Water/Tween®80/Span®20/(1,2-hexanediol + Co(II)2EH)/(Ethyl oleate + Co(II)2EH) 70/10.5/7/7.5/5	O/W microemulsion	0.25	100.0 *	NaBH$_4$
CoME4	(Water + Co(NO$_3$)$_2$)/ Pluronic® P123 92.6/7.4	Direct micelles	1.18	6.3	NaBH$_4$
CoME5	Water/Synperonic® 10/6/(Hexane + Co(II) 2EH) 67.5/22.5/10	O/W microemulsion	0.20	112.5	NaOH
CoME6	Water/Synperonic® 10/6/(Hexane + Co(II) 2EH) 67.5/22.5/10	O/W microemulsion	0.20	112.5	(COOH)$_2$

* For this particular system, the Surfactant/Co^{2+} ratio was calculated taking into account Tween® 80, Span® 20 and 1,2-hexanediol as surfactants; the former is a surfactant and the last two species are cosurfactants.

The morphology, size and dispersion of cobalt nanoparticles prepared in O/W and W/O microemulsion (CoME1 and CoME2) were compared with the corresponding samples supported onto silica (CoME1S and CoME2S,) shown in Figures 1a,b and 2a,b, respectively. The micrograph in Figure 1a shows that Co NPs prepared in O/W microemulsion CoME1 were very small and spherical, and their particle size distribution was uniform (~3 nm). NP agglomeration was not detected in the TEM micrographs, in agreement with the good colloidal stability detected visually in the dispersions. Furthermore, nanoparticles obtained using O/W microemulsion (CoME1) had a smaller size than those obtained in W/O microemulsion (CoME2). The latter sample was also more polydisperse (Figure 1b, 5–10 nm), even though the W/O microemulsion used for synthesis had a lower content of internal phase (2 wt.% aqueous phase for W/O microemulsion *versus* 10 wt.% oil phase for O/W microemulsion), which in principle would be responsible for smaller microemulsion droplets [12].

After deposition onto silica and calcination at 400 °C over 4 h in air, Co NPs remained highly dispersed on the support in the sample prepared using O/W microemulsion (CoME1S), as shown by TEM (Figure 2a). Whilst the sample prepared in W/O microemulsion (CoME2S) presented mostly well-dispersed Co NPs, in addition, slight agglomeration was detected as observed in Figure 2b. The average diameter of Co NPs remained around 3 nm for CoME1S and between 5–10 nm for CoME2S. Furthermore, diffraction peaks from crystalline cobalt-based phases were not detected by X-ray diffraction measurements (Figure 3b), which is also an indication that Co NPs were small and very well dispersed on the silica support. On the other hand, the particles prepared using the O/W microemulsion based on Span$^®$20–Tween$^®$80 as stabilizers, deposited onto silica and calcined (CoME3S), resulted in small (3–10 nm) and well dispersed nanoparticles, with very slight agglomeration as shown in Figure 2c. The analysis of CoME3S by X-ray diffraction (XRD) does not show characteristic peaks either, another indication of the good dispersion and small size of these nanomaterials.
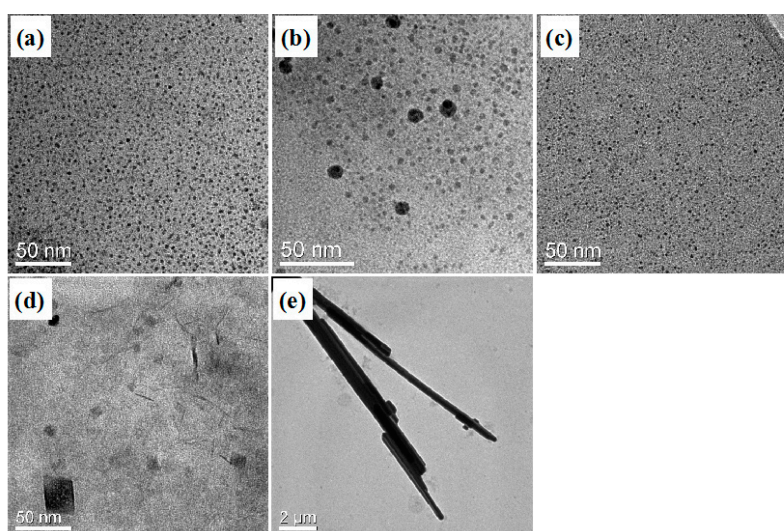
Figure 1. Transmission electron microscopy (TEM) results obtained using different surfactant systems and precipitating agents. Co NPs prepared with NaBH$_4$: (**a**) CoME1 (O/W microemulsion, Synperonic$^®$ 10/6); (**b**) CoME2 (W/O microemulsion, Synperonic$^®$ 10/6); (**c**) CoME4 (direct micelles, Pluronic P123). (**d**) CoO(OH) prepared with NaOH CoME5 (O/W microemulsion, Synperonic$^®$ 10/6); (**e**) Cobalt oxalate prepared with oxalic acid CoME6 (O/W microemulsion, Synperonic$^®$ 10/6).

In order to compare the formation of Co NPs by reduction with NaBH$_4$ using a more conventional system, an experiment was carried out using direct micelles of Pluronic® P123 as reaction media. In this case, since the continuous phase is water and the precursor used, cobalt (II) nitrate, is water-soluble, it implies that the Co^{2+} ions to be reduced are located in the continuous phase, as opposed to being confined inside the droplet or at the interface, which would be the case in microemulsion systems. From TEM analysis it can be observed that small particles in the order of 3 nm were formed (Figure 1c), and these are very well dispersed, which means that Pluronic® P123 was very good for stabilizing Co NPs in aqueous media, as no agglomerates were detected. However, when these particles were supported onto commercial silica, it was observed that a great number of the nanoparticles were only loosely bound to the support, as numerous unsupported Co NPs were detected by TEM (Figure 2d).

The precipitation of cobalt with NaOH (CoME5) significantly affects the morphological and structural properties of the nanoparticles. Nanoneedles and highly facetted nanoparticles (probably nanocubes) were observed by TEM (Figure 1d). The nanoneedles had a thickness from 1.5–3.5 nm and a length from 20–40 nm; the facetted particles had a length of 8–35 nm. XRD analysis of this sample (Figure 3a) was consistent with the formation of CoO(OH), which has a rhombohedral structure (JCPDS No. 01-073-1213), and a crystallite size of 7 nm, estimated using the Scherrer equation. On the other hand, the precipitation with oxalic acid (CoME6) produced much larger needles, with a thickness in the order of 0.4–0.8 micrometers and a length of 5–15 micrometers (Figure 1d). These findings are in agreement with the literature, which reported the formation of rod-shaped nanostructures for cobalt oxalate [19,28].
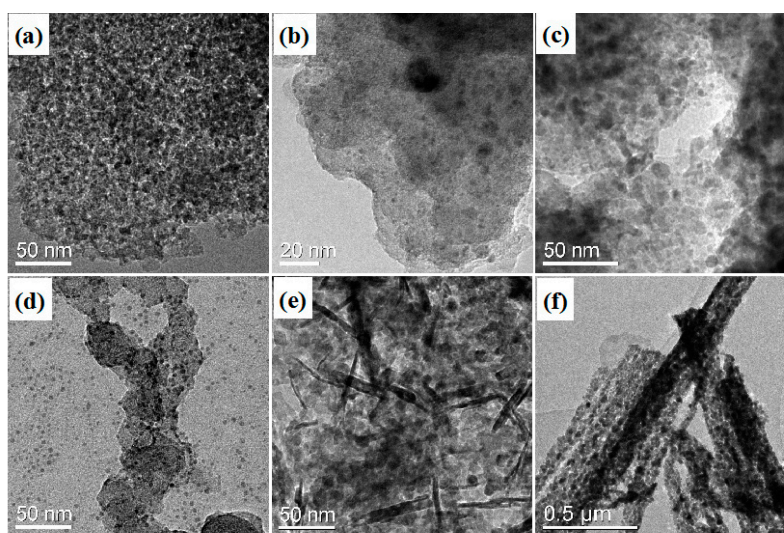
Figure 2. TEM images of Co-based NPs supported onto commercial silica and calcined at 400 °C. Supported Co NPs prepared with NaBH$_4$: (**a**) CoME1S (O/W microemulsion, Synperonic® 10/6); (**b**) CoME2S (W/O microemulsion, Synperonic® 10/6); (**c**) CoME3S (O/W microemulsion, Span–Tween), (**d**) Co ME4S (direct micelles, Pluronic® P123). Supported Co$_3$O$_4$ NPs: (**e**) CoME5S (prepared with NaOH, O/W microemulsion, Synperonic® 10/6); (**f**) CoME6S (prepared with oxalic acid, O/W microemulsion, Synperonic® 10/6).

Upon deposition onto silica and calcination, the size and shape of the nanoneedles and faceted particles from CoME5 were retained (CoME5S shown in Figure 2e). On the contrary, CoME6 changed significantly upon deposition and calcination (CoME6S shown in Figure 2f). The long needles were transformed into nanoparticles (~30 nm), which were self-assembled into elongated structures resembling the original micron-sized needles. However these aggregates shrank to a certain extent and were smaller (around 200 nm width and 1–3 microns in length). Additional TEM images of these two samples are shown in Figure 4, in order to demonstrate more clearly the morphology and crystallinity of the particles; the latter can be observed in the lattice fringes of Figure 4c,f (for samples CoME5S and CoME6S, respectively).
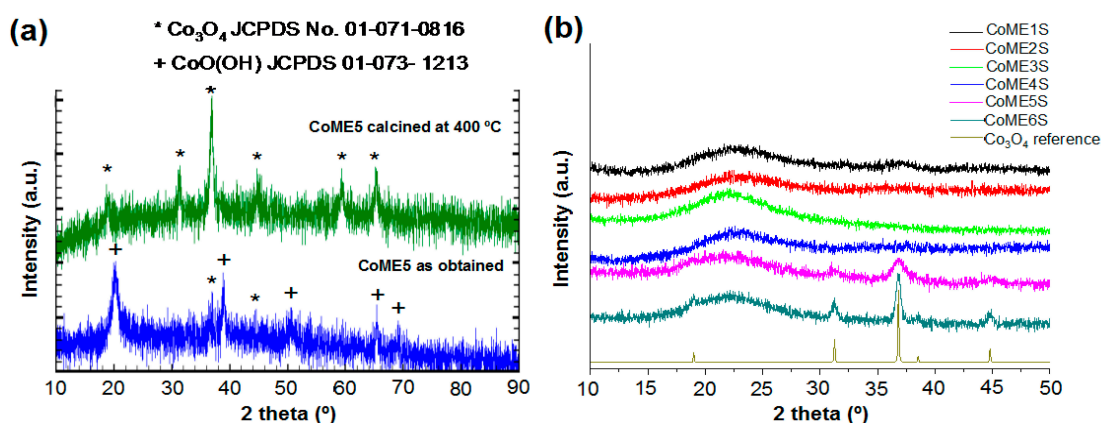

Figure 3. (**a**) X-ray diffraction (XRD) patterns of CoME5, prepared with NaOH, O/W microemulsion, Synperonic$^{®}$ 10/6 (as obtained and calcined at 400 °C); (**b**) XRD patterns of Co-based NPs supported onto commercial silica and calcined at 400 °C. Supported Co NPs prepared with NaBH$_4$: CoME1S (O/W microemulsion, Synperonic$^{®}$ 10/6); CoME2S (W/O microemulsion, Synperonic$^{®}$ 10/6); CoME3S (O/W microemulsion, Span–Tween), CoME4S (direct micelles, Pluronic P123). Supported Co$_3$O$_4$ NPs: CoME5S (prepared with NaOH, O/W microemulsion, Synperonic$^{®}$ 10/6); CoME6S (prepared with oxalic acid, O/W microemulsion, Synperonic$^{®}$ 10/6).

XRD profiles showed that calcined CoME5S was made up of Co$_3$O$_4$ with a cubic crystalline structure and average crystallite size of 8 nm (Figure 3b), whereas the crystallite size of unsupported Co$_3$O$_4$ obtained from calcination of CoME5 was 17 nm (Figure 3a). The assignment of the Co$_3$O$_4$ crystalline phase was based on the JCPDS database (JCPDS 01-071-0816). For CoME6S the same phase was observed, but with a crystallite size of 20 nm (Figure 3b). Thus, both cobalt oxyhydroxide (CoO(OH)) and cobalt oxalate, formed by precipitation with NaOH and (COOH)$_2$, respectively, were transformed into Co$_3$O$_4$ upon calcination at 400ºC without the formation of other phases.

Selected microemulsion procedures were used for the deposition of cobalt-based nanoparticles onto SBA-15, a well-known mesoporous silica with a high surface area and a well-ordered hexagonal pore structure [29]. These features make this material a promising candidate as support for active nanoparticles with the aim of confining the supported species into the pore structure enhancing their dispersion and slowing down their agglomeration. A scheme of the pore structure in SBA-15 and the TEM image of the obtained support are shown in Figure 5; the material was synthesized in this

investigation following the method reported by Zhao *et al.* [29]. High-resolution TEM images of bare mesoporous SBA-15 were recorded in order to corroborate the long range order of the pore structure. The high resolution transmission electron microscopy (HRTEM) result, which is reported in Figure 5b,c, allows the detection of a highly ordered hexagonal porosity, such as the fringes observed in Figure 5b and the ordered pores observed directly in Figure 5c.
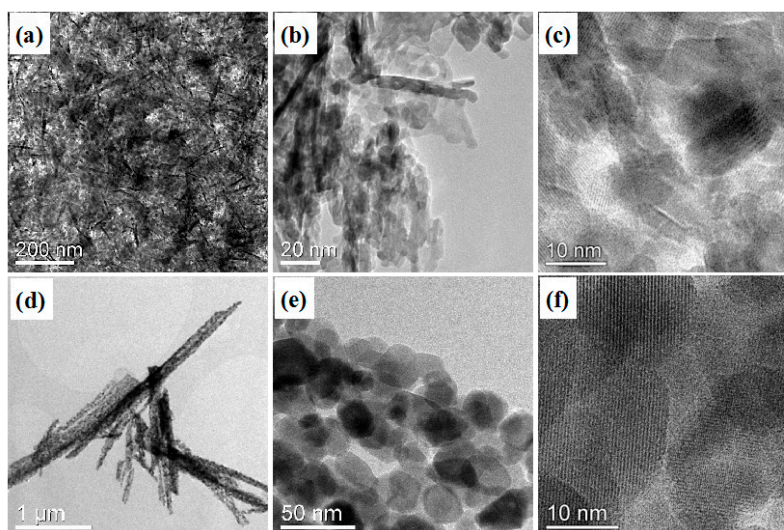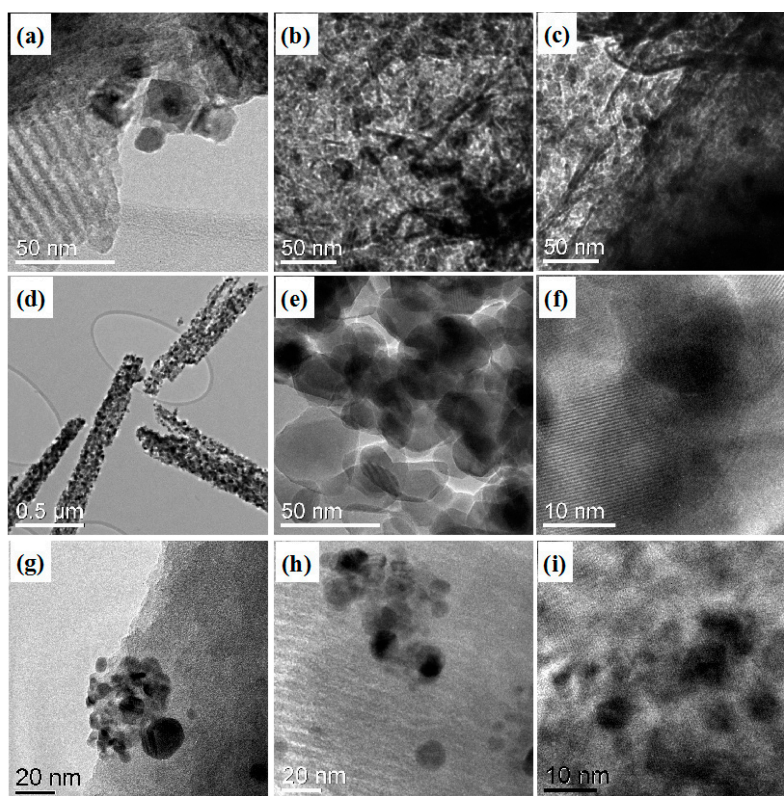

Figure 4. TEM images of Co_3O_4 NPs supported onto commercial silica. (**a–c**) CoME5S (prepared with NaOH, O/W microemulsion, Synperonic® 10/6); (**d–f**) CoME6S (prepared with oxalic acid, O/W microemulsion, Synperonic® 10/6).
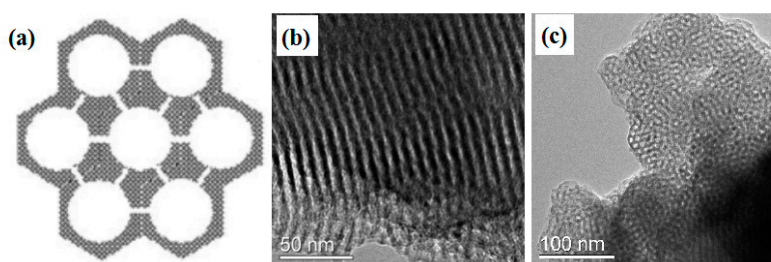
Figure 5. A scheme of the pore structure (**a**) and high resolution TEM images (**b**), (**c**) of mesoporous silica SBA-15 prepared in this study.

Cobalt-based nanostructures, prepared according to CoME5 and CoME6 procedures, were deposited onto mesoporous SBA-15. The obtained materials were characterized by XRD measurements and showed structural properties similar to the ones supported onto commercial silica. The morphology of the cobalt nanostructures supported onto SBA-15 was also investigated by TEM analyses; for comparison purposes, a sample prepared by incipient wetness impregnation of SBA-15 with a cobalt precursor solution was also investigated (CoSBA). For CoME5SBA the images (Figure 6a–c) show the formation of supported cobalt nanorods and facetted nanoparticles onto SBA-15, in agreement with results for particles supported onto commercial silica (CoME5S) and unsupported particles (CoME5). HRTEM reveals the retention of the highly ordered pore structure of SBA (Figure 6a). For CoME6SBA, a very similar morphology to CoME6S was observed (Figure 6d–f), that is, globular particles in the order of 30 nm, arranged into elongated structures. A highly ordered hexagonal pore structure of SBA

is also visible from HRTEM (Figure 6e). In comparison, the sample prepared by incipient wetness impregnation presented a wide size distribution of quasi-spherical particles, which were mostly agglomerated as clusters of particles (Figure 6g–i).

Figure 6. TEM images of Co_3O_4 NPs supported onto mesoporous silica SBA15 and calcined at 400 °C (**a–c**): CoME5SBA (prepared with NaOH, O/W microemulsion, Synperonic® 10/6); (**d–f**): CoME6SBA (prepared with oxalic acid, O/W microemulsion, Synperonic® 10/6). (**g–i**) Co NPs supported onto mesoporous silica SBA-15 prepared by incipient wetness impregnation followed by calcination at 400 °C (CoSBA).

3. Discussion

At first sight, the different results obtained with the samples prepared with O/W and W/O microemulsions based on Synperonic® 10/6 (CoME1 and CoME2) may be attributed to the higher cobalt loading attained in the internal phase of the W/O microemulsion (13.06 wt.% of Co in the aqueous phase of W/O microemulsion *versus* 2 wt.% Co in the oil phase of the O/W microemulsion). Nonetheless, the overall Co loading was in the same order of magnitude for both samples (0.26 wt.% Co in the W/O microemulsion *versus* 0.2 wt.% Co in the O/W microemulsion, Table 1). Furthermore, the surfactant/Co^{2+} weight ratio was the same in both samples (112.5, Table 1). Taking into account these similarities, the high HLB of the surfactant (12.6) must be taken into account. A surfactant with such an HLB value is more suitable for systems with an aqueous continuous phase, and hence, it should be more efficient for stabilizing nanoparticles in aqueous-based, O/W microemulsion systems (CoME1) than in oil-based, W/O microemulsion systems (CoME2). With nonionic surfactant systems, this is particularly valid when working at relatively low temperatures, such as the conditions used in

this study (25 °C). Thus, the smaller and more uniform particle size and the better dispersion obtained with the sample synthesized in O/W microemulsions (CoME1), as compared to the sample prepared in the W/O microemulsion (CoME2), may be explained by the better suitability of the surfactant to stabilize species such as nanoparticles in water-based systems.

A similar explanation may hold for the results obtained with CoME3, which was also obtained in O/W microemulsions. This sample was formulated with a mixture of Tween® 80, Span® 20 and 1,2-hexanediol (HLBs of 15, 8.6 and 7.95, respectively), in weight ratios 10/7/7.5. The combined HLB of this surfactant system was ~11.1, and several scenarios are possible for the stabilization of the Co NPs that are formed in this microemulsion after reduction with $NaBH_4$. Since Tween® 80 is the surfactant with the highest HLB of the system, it is likely that the Co NPs are mainly stabilized with this surfactant, although certain contribution from the lower HLB surfactants could explain the slight agglomeration detected in the supported sample (CoME3S).

On the other hand, as mentioned in the Results section, the sample synthesized in direct micelles of Pluronic® P123 produces very small nanoparticles and these remain were very well dispersed in the reaction media as shown in the TEM micrograph (Figure 1c). Although the HLB of this surfactant is not very high (HLB value 7–9), the hydrophilic parts of the molecule are rather large (20 ethylene oxide units which comprise the outside blocks of the triblock copolymer), thus providing a good environment for stabilization in water based systems, forming a corona of chemisorbed triblock copolymer on the surface of Co NPs, as shown by Chen *et al.* [21]. However, when these well-dispersed Co NPs are supported onto silica, it turns out that the particles are extremely stabilized by Pluronic® P123, causing a weak adhesion between the particles and the support. Thus, unsupported Co NPs were observed on the TEM grid (Figure 2b), which means that these particles were detached from the support upon preparation of the sample for TEM (that is, dispersion of the calcined powder in isopropanol and sonication for 30 s). It must be highlighted that for all the other samples (prepared either in W/O or O/W microemulsions), this behavior (detachment from the support) was not observed. This means that in the latter cases the deposited cobalt-based particles were strongly bound to the surface of the support, even though they were very well dispersed prior to deposition. This feature is key for a material that is going to be used as a catalyst, in order to obtain stable materials in which the concentration of the active phase is constant. Loosely bound particles imply that the cobalt nanoparticles can be easily lost during processing.

The results obtained with CoME5, carried out with sodium hydroxide, illustrate the advantages of using O/W microemulsions as compared to conventional aqueous solution methods. According to the literature, in order to form CoO(OH) in aqueous media, it is necessary to form first $Co(OH)_2$ which can be formed under relatively mild conditions (45 °C), followed by additional treatment with H_2O_2 under alkaline conditions [30]. Furthermore, the crystallite size obtained by Yang *et al.* by such a method was significantly larger (40 nm *versus* 7 nm obtained in the present investigation). Other works report the formation of CoO(OH) by heating $Co(OH)_2$ at 100–110 °C [31]. In our case, CoO(OH) was formed directly in one step, by using only NaOH as precipitating agent at 25 °C, without the need for additional steps, oxidizing agents or thermal treatment. Thus, it appears that oxygen in the air atmosphere was sufficient to form CoO(OH) in the alkaline O/W microemulsion environment. When this material was calcined at 400 °C, Co_3O_4 with a cubic spinel structure (JCPDS 01-071-0816) was formed, as indicated by the XRD results (Figure 3a). The crystallite size was estimated as 17 nm

(Scherrer equation), which is smaller than the crystallite size obtained from calcination of $Co(OH)_2$ nanoparticles by Yang *et al.* (30 nm) [30]. Thus, the O/W microemulsion method for the formation of $CoO(OH)$ and Co_3O_4 offers advantages *versus* other water-based methods, since smaller particles are obtained under milder conditions. On the other hand, the fact that the crystallite size of Co_3O_4 was smaller for the sample supported onto silica CoME5S as compared to the unsupported sample CoME5 (8 nm and 17 nm, respectively), is a consequence of the excellent dispersion of the nanoneedles and nanocubes onto the silica support. The high dispersion protected the crystals against growth and sintering, thus maintaining almost the same crystallite size for the non-calcined sample ($CoO(OH)$, non-calcined CoME5, 7 nm), and the calcined sample (Co_3O_4, calcined CoME5S, 8 nm).

Some interesting findings regarding the samples CoME6S and CoME6SBA should be noted. According to the literature [19,28,32], cobalt oxalate microrods decompose into Co_3O_4 nanoparticles and carbon monoxide/carbon dioxide during calcination. In this work, the elongated, micron sized cobalt oxalate needles were converted into much smaller (around 30 nm), globular, and highly crystalline Co_3O_4 nanoparticles. An important difference with respect to other works is that the needle morphology was retained in the present study, since Co_3O_4 nanoparticles were self-assembled into elongated structures (Figures 2f, 4d and 6d). On the contrary, in other investigations[19,28] the needle shape was lost, and instead of an ordered arrangement of Co_3O_4 NPs into elongated structures, random aggregation of NPs without a particular shape was reported. A possible explanation for the results obtained in this study is that the presence of the support and its interaction with the cobalt oxalate precursor permitted the retention of the elongated shape upon calcination, improving the mechanical resistance of the assembly.

It must be highlighted that the d-spacings from lattice fringes of CoME5S, CoME5SBA, CoME6S, and CoME6SBA observed by HRTEM were in agreement with the XRD results, as the most frequent d-spacings found were 0.467nm, 0.286 nm, and 0.244 nm, consistent with the Miller indexes (hkl) 111, 220 and 311 respectively, of the cubic Co_3O_4 with normal spinel structure. On the other hand, the sample prepared by incipient wetness, CoSBA, consists of spherical Co particles, more polydisperse and agglomerated than the samples prepared as Co nanoparticles supported onto commercial silica and prepared from O/W and W/O microemulsions (CoME1S, CoME2S, and CoME3S).

Thus, it can be inferred that the best systems for producing highly dispersed cobalt-based nanoparticles onto silica supports are CoME1, CoME2, CoME3, and CoME5. CoME4 may be discarded due to insufficient binding of the nanoparticles to the support, even though the dispersion is very good. CoME6 produces self-assembled Co_3O_4 structures and thus proper dispersion onto silica may be lost. Table 2 summarizes the different results obtained in this study, in order to facilitate their comparison.

Table 2. Summary of results (particle size, shape, and dispersion onto silica) for the Co-based nanostructures supported onto commercial silica, obtained with the different systems and precipitating agents.

Sample ID	Surfactant	Type of System	Precipitating agent	Product	Shape and size	Dispersion onto silica support
CoME1S	Synperonic® 10/6	O/W ME	NaBH₄	Co	Spherical ~ 3 nm	Very good
CoME2S	Synperonic® 10/6	W/O ME	NaBH₄	Co	Spherical ~ 5-10 nm	Good, slight agglomeration
CoME3S	Tween®80/ Span®20/ (1,2-hexanediol)	O/W ME	NaBH₄	Co	Spherical ~3–10 nm	Good, slight agglomeration
CoME4S	Pluronic® P123	Direct micelles	NaBH₄	Co	Spherical ~3 nm	Very good, but poor adhesion
CoME5S	Synperonic® 10/6	O/W ME	NaOH	Co₃O₄	Needles (~1.5 nm to 3.5 nm thickness, 20–40 nm length); faceted particles (cubes, ~8–35 nm length)	Good, slight agglomeration
CoME6S	Synperonic® 10/6	O/W ME	(COOH)₂	Co₃O₄	Globular, slightly faceted, ~30 nm, self-assembled into elongated structures (~200 nm width, 1–3 microns length)	Particles are self-assembled, thus, dispersion is not good

4. Experimental Section

4.1. Materials

Synperonic® 10/6 was a gift from Croda. Cobalt (II) 2-ethylhexanoate (65 wt.% in mineral spirits), cobalt (II) nitrate hexahydrate (≥99%), oxalic acid (≥99%), Pluronic® P123 (EO20PO70EO20, average M_n ~5800 g/mol), sodium hydroxide and 1,2-hexanediol were purchased from Sigma-Aldrich (Stockholm, Sweden). Tween® 80, ethyl oleate, sodium borohydride (NaBH₄), hexane (Suprasolv, for gas chromatography) and isooctane (Suprasolv, for gas chromatography), were purchased from Merck (Stockholm, Sweden) Span 20® was purchased from Roig Farma (Barcelona, Spain).

4.2. Synthesis of Cobalt Nanostructures

Cobalt nanoparticles were prepared using different nonionic systems, such as (1) water/Synperonic® 10/6/hexane (O/W microemulsions); (2) water/Synperonic® 10/6/isooctane (W/O microemulsions); (3) water/SPAN® 20/TWEEN® 80/1,2-hexanediol/ethyl oleate (O/W microemulsions) and (4) water/Pluronic® P123 (direct micelles). All systems were processed at 25 °C. For O/W

microemulsions with Synperonic ® 10/6 (CoME1), the oil phase contained the precursor cobalt (II) 2-ethylhexanoate dissolved in hexane, in a concentration equivalent to 2 wt.% of cobalt. For W/O microemulsion with Synperonic ® 10/6 (CoME2), the precursor cobalt (II) nitrate was dissolved in the aqueous phase in a concentration equivalent to 13.06 wt.% of cobalt. For the O/W microemulsion with SPAN® 20/TWEEN® 80 (CoME3), the oil phase contained the precursor cobalt (II) 2-ethylhexanoate dissolved in ethyl oleate, in a concentration equivalent to 2 wt.% of cobalt, and additionally, the precursor was also added to 1,2-hexanediol in a concentration equivalent to 2 wt.% of cobalt. The system of direct micelles of Pluronic® P123 (CoME4), contained cobalt (II) nitrate precursor with a concentration equivalent to 1.18 wt.% of Co. The precipitation of nanoparticles was carried out by adding the precipitating agent as an aqueous solution. Hence, one-microemulsion approach was followed. For these four samples (CoME1, CoME2, CoME3, and CoME4), the nanoparticles were prepared by reduction of the cobalt precursor with sodium borohydride ($NaBH_4$), using a Co: $NaBH_4$ molar ratio of 1:2 and a nitrogen atmosphere in all cases. The microemulsion compositions and reaction conditions used for the synthesis of cobalt samples are reported in Table 1.

The O/W microemulsion with Synperonic® 10/6 was also selected in order to investigate the influence of the precipitating agent. Besides the use of $NaBH_4$ for cobalt reduction under inert atmosphere (CoME1) as described above, NaOH and $(COOH)_2$ were also used for cobalt precipitation as oxyhydroxide and oxalate in CoME5 and CoME6, respectively; the O/W microemulsion compositions used for synthesis with these samples were identical to CoME1. The molar ratio Co:Oxalic acid was 1:1.2. The synthesis with NaOH was carried out by adding sufficient NaOH solution (10%) to reach pH 12.

4.3. Deposition of Cobalt Nanostructures onto Commercial Silica

Commercial silica (Merck) was added under stirring to the as-prepared microemulsions containing cobalt nanostructures, which were destabilized by adding an appropriate amount of water and/or acetone. The concentration of Co in the Co/Silica system was kept at 12 wt.%. The system was kept under stirring for 2 h, and then the powder was recovered by centrifugation and washed several times with an ethanol/acetone mixture with volume ratio 1/1. All the samples were dried at 120 °C for 5 h and calcined in air at 400 °C during 4 h using a ramp rate of 1 °C/min. The cobalt nanostructures supported onto silica were labeled as CoME*x*S with *x* being between 1 and 6 depending on the procedure of synthesis as indicated in Table 1.

4.4. Synthesis of Ordered Mesoporous Silica and Subsequent Deposition of Cobalt Nanostructures

According to the process reported by Zhao *et al.* [29], SBA-15 was prepared using triblock copolymer Pluronic® P123 as templating agent and tetraethoxysilane (TEOS) as precursor. The use of a structure-directing agent during the synthesis leads to materials with high surface area, narrow pore size distribution, and a well-ordered 2D hexagonal structure.

Selected cobalt-based materials were deposited onto mesoporous SBA-15 using the same procedure, previously described for commercial silica. All the samples were dried at 120 °C for 5 h and calcined in air at 400 °C over 4 h using a ramp rate of 1 °C/min. The cobalt nanostructures supported onto SBA-15 were labeled as CoME*x*SBA with *x* being between 1 and 6 depending on the

procedure of synthesis as indicated in Table 1. CoSBA, prepared by incipient wetness impregnation, was prepared according to Lualdi *et al.* [27].

4.5. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a X-ray diffraction (XRD; Siemens D5000, using Cu Kα radiation of wavelength; λ = 0.1540 nm).

Particle size and morphology were investigated by High Resolution Transmission Electron Microscopy (HRTEM). The sample was prepared as follows: 0.5 mg of powder were suspended in isopropanol (2 mL) and sonicated during 30 s. For analysis a drop of this dispersion was deposited onto a holey formvar/carbon copper grid. Observation was carried out using a HRTEM 200 KV JEOL 2100 LAB6 (objective polar piece with a resolution of 2.3 Å).

5. Conclusions

On the basis of our findings, it has been established that the shape and size of supported cobalt nanoparticles are strongly dependent on the nature of the surfactant, the type of system, and the precipitating agent used. The nature of the surfactant mainly affects the dispersion of cobalt nanoparticles. In particular, the use of Synperonic® 10/6 was responsible for a better dispersion and narrower particle size distribution and for this reason our attention was focused on this surfactant. Furthermore, O/W microemulsion with Synperonic® 10/6 lead to superior results as compared to W/O microemulsion in terms of particle size and dispersion onto a silica support. It is worth noting that the use of O/W microemulsion for the synthesis of cobalt nanoparticles has not been reported so far. This novel route seems quite promising, since, besides producing a more uniform particle size, it is a more environmental friendly procedure than the W/O microemulsion method. Moreover, the nature of the precipitating agent strongly affects the shape of the nanoparticles. In particular, spherical nanoparticles, nanorods, and nanocubes have been obtained by using $NaBH_4$ and NaOH. Furthermore, the good interaction between deposited particles and the silica support allowed the formation of self-assembled Co_3O_4 NPs arranged into elongated structures, in the case of the sample prepared via microneedles of cobalt oxalate precursor (using $(COOH)_2$ as precipitating agent). These findings demonstrate that the size and morphology of cobalt nanostructures can be easily tuned by changing the type of system, the surfactant, and the precipitating agents. It is worth noting that the presence of an appropriate stabilizing agent prevents the agglomeration of cobalt nanocrystals after their deposition onto both commercial and mesoporous silica and in the subsequent calcination process. This behavior suggests their great potential in catalytic applications.

Acknowledgments

Author Contributions

Conflicts of Interest

The authors declare no conflict of interest.

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