Cobalt-based Nanoparticles Synthesis in Organic Solvents with Environmentally Sound Processes

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A process for the synthesis of cobalt-based nanoparticles is proposed, where standard reducing agent like hydrazine, alkali metal borohydrides, hypophosphites or other toxic reducing agents have not been employed. The solvothermal reaction is carried out in organic solvents and the dimension of the nanoparticles thus obtained have been analyzed by dynamic light scattering. Cobalt nitrate proved to be an efficient precursor, in agreement with previous literature works where its suitability for analogous processes has been tested and compared with the efficiency typical of other precursors routinely used. The soundness of this method, in terms of process safety, has been checked by analyzing the formation of toxic by-products that could be formed by side-reactions between the precursor and the solvent. This work may add some more details to a discussion pertaining to the accidental formation of N-nitroso derivatives of aliphatic compounds in the presence of alkanolamines and oxides of nitrogen.

1. Introduction

Metal nanoparticles (MNPs) are widely recognized as a basic material for many applications, including catalysis (Han et al., 2016) biomedical science (Long et al., 2015), magnetic separations (Aseri et al., 2015) and composite material engineering (Pascariu et al., 2013). In particular, nanoparticulate dispersions in liquids are very promising in place of traditional fluids in heat exchangers for cooling devices, where a high efficiency is needed to damp steep thermal gradients often associated with sudden heating processes described by thermal waves (Reverberi et al, 2008). Chemical methods for MNP synthesis represent a valid alternative to physical methods owing to their greater cost effectiveness with respect to complex apparatuses as required, for example, by plasma or laser methods (Reverberi et al., 2014). A novel wet-chemical technique for MNP synthesis in non-aqueous media, relying upon an atypical inorganic reductant, was recently proposed (Reverberi et al., 2016). The beneficial effects of comminution of the phases by nebulization of reagents represents a safer and more inexpensive technique, compared with conventional spray processes followed by high-temperature pyrolysis (Chiarioni et al., 2006). The paper of Lai et al. (2015) is an extensive survey on the other methods and we refer the reader to the references quoted therein. In the specific context of cobalt nanoparticles (Co-NPs), chemical methods comprise different techniques having many aspects in common with the ones typical of other ferromagnetic metals. As a rough classification, these schemes are essentially based on bottom-up processes relying upon two main families,that is thermolysis of metal precursors and chemical reduction. In the former, cobalt carbonyls are the most commonly used precursors undergoing thermal decompositions in organic solvents, generally carried out in the absence of air to avoid a fast surface oxidation. Robinson et al. (2009) obtained Co-NPs by laser irradiation of a solution of cobalt carbonyl, using the wavelength of light as a tuning parameter to control the nanoparticles dimension. These methods, when transferred to a large scale production pose some emerging safety challenges to be carefully considered (De

Rademaeker et al., 2014), as they require the use of costly and toxic metal precursors and stabilizing agents, like aliphatic amines or phosphine oxides. The latter are still object of intense investigations, as they show a wide choice of variants according to the type of cobalt precursor, solvent and surfactant. The selection of the more appropriate metal precursor, despite it could seem a secondary problem at first glance, is considerably important for many aspects. For example, cobalt nitrate proved to be reduced to zerovalent cobalt more easily than other inorganic salt of the same cation (Shin et al., 2010), allowing safer operative conditions in terms of temperature (Reverberi et al., 2013). This intriguing aspect will be reconsidered in the following. As for solvents, polyol methods still represent a cornerstone in wet chemical methods for Co-NPs synthesis, owing to their great versatility and to the possibility of exploiting both the capping and the reducing properties of the solvent itself. A crucial drawback is given by the need of using high reaction temperatures, owing to the slow reduction kinetics and the unfavorable thermodynamics related to mild reducing properties of polyols toward an element being much more electropositive than noble metals as Au and Ag. In many cases, to promote the nucleation process, salts of less electropositive cations are added to the solvent, as in the study proposed by Liu et al. (2015). They added iridium salts (H_2IrCl_6) catalyzing the synthesis of cobalt nanostructures, and they proved that the Ir/Co ratio is a valid tuning parameter to control the shape of the nanophase thus obtained. In the absence of external cations, the particles are spherical, while their shape shifts to a rod-like and even to multi-pods for increasing values of the aforementioned parameter. Whatever the solvent in which the metal precursor is dissolved, a reductant is generally adopted, and this rule of thumb is generally valid also in case of cobalt nanoparticles synthesis. However, despite some exceptions can be found in literature, papers dealing with cobalt nanostructures produced by reduction carried out by the sole solvent are rather uncommon. In the present study, we describe some experimental techniques aiming at synthesizing Co/CoO-NPs in different solvents avoiding the use of toxic or noxious reducing agents as hydrazine or alkali metal borohydrides, which have long been considered as a first choice in the synthesis of non-noble metallic nanophases. As amply known, the very essence of green and sustainable chemistry from one side is to "… reduce or eliminate the use or generation of hazardous substances", from the other side is to adopt alternative renewable energy forms, possibly substituting conventional energies of fossil origin (e.g. Palazzi et al., 2002). These commitments are intrinsically connected to route design and process safety. The elimination of these hazards fits with the application of the "substitution" guideword, by developing an inherently safer method, in the early stages of process development. The as-prepared Co-NPs are characterized for size by dynamic light scattering (DLS), while the relevant composition is investigated by standard analysis techniques. The role of different reductants and the effects of their combination are discussed in the context of the specific solvent and of the corresponding operative conditions. Finally, the solvents have been analysed to check for the presence of noxious and potentially carcinogenic chemical species that could be incidentally formed by side-reactions between a solvent and some products of precursor dissociation.

2. Materials and Methods

2.1 Experimental set-up

The process has been carried out in two different solvents, namely pure triethanolamine (TEA) and a mix 50%-50% TEA with anhydrous propylene glycol (PG), where cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), has been dissolved with a concentration of 0.1 M. No reductant has been intentionally added in any solution, in order to check the sole action of TEA and TEA+PG.

The reactions have been carried out at 200°C in pure TEA and at 150°C in case of mixed solvents TEA+PG, both in an electrically heated Erlenmeyer flask with a reflux condenser and a trap for vapors. The process is stopped 30 min after its beginning.

2.2 Analytical methods

The composition of the solid phase is determined by standard analytical techniques. All results are expressed as the mean of three replicates. The solid phase is separated from the supernatant after dilution with ethanol and further centrifugation. Subsequently, it is dried at moderate temperature (110°C) under argon atmosphere to protect the nanoparticle surface from further oxidation, until a stable weight is attained. Furthermore, a weighted solid is dissolved in nitric acid and the relevant solution is analysed in order to estimate its content in elemental cobalt by atomic adsorption spectrometry (AAS) carried out by an instrument AA240FS (Varian Instruments, USA). The particle size distribution is investigated by a DLS analyzer Zetasizer Nano ZS (Malvern Instruments, UK). A sample containing each solid phase dispersion was diluted by a factor of 3 and transferred in suitable cuvettes of polymethyl-methacrylate. The presence of N-nitroso-dietanolamine (NDELA) together with other ten non-oxydrilated N-nitrosamines indicated in Table 1, has been throughly determined by two different analytical methods.

Table 1: *List of ten non-hydroxylated N-nitrosamines whose concentration has been checked in the samples obtained by the present method.*

Chemical species	CAS Number	Abbreviation
N-nitrosodimethylamine	62-75-9	NDMA
N-nitrosodiethylamine	55-18-5	NDEA
N-nitrosodipropylamine	621-64-7	NDPA
N-nitrosodibutylamine	924-16-3	NDBA
N-nitrosodiisononylamine	1207995-62-7	NDiNA
N-nitrosomorpholine	59-89-2	NMOR
N-nitrosopiperidine	100-75-4	NPIP
N-nitrosodibenzylamine	5336-53-8	NDBzA
N-nitroso-N-methyl-N-phenylamine	614-00-6	NMPhA
N-nitroso-N-ethyl-N-phenylamine	612-64-6	NEPhA

The concentrations of non-oxydrilated nitrosamines have been measured according to the standard UNI EN 71-12:2013, requiring an analysis by high-performance liquid chromatography-mass spectrometry (HPLC-MS). The analysis of NDELA has been carried out following the criteria enforced by European Pharmacopoeia for Trolamine. The analytical method consists of a dissolution of the sample in a mix of chloroform and acetone, followed by its purification on two different glass columns. The first column contains a packed beds of kieselguhr and potassium carbonate, while the second one contains silica gel mixed with sodium sulfate. N-nitrosodiisopropanolamine has been used as inner standard, which is added to each sample before each preparation process. The analysis has been carried out by gas chromatography-nitrogen chemiluminescence detector (GC-NCD), used in specific mode to maximize selectivity and specificity toward N-nitrosoalkanolamines. A fused silica column of 30 m length and 0.25 mm diameter has been used, with helium as carrier gas and at a flow rate of 2 mL/min. The temperature of the column, starting from 180°C, has been progressively brought to 280°C after 5 minutes and it is kept at this value until the completion of the analysis.

3. Results and discussion

3.1 The solid reaction products

At the start, the solutions in pure TEA and in TEA+PG are purple-red owing to the formation of a coordinate complex that, according to the studies of Hughes and Rutt (1968), corresponds to the following expression:

$$Co(N(CH_2CH_2OH)_3)_2 \, (NO_3)_2 = Co(TEA)_2 \, (NO_3)_2 \tag{1}$$

During the process, the color shifts progressively to brown indicating the onset of precursor dissociation. At the reaction end, the solutions are visually transparent by light transmission and opaque at the reflecting light. They are further diluted in ethanol and analysed by DLS. The results are reported in Figure 1. The samples obtained in pure TEA show a population of particles whose average diameter (2.2 ± 0.5 nm) is considerably smaller than the one obtained in mixed solvents (14.6 ± 0.5 nm), probably owing to the stronger capping activity and to a higher viscosity of TEA with respect to PG. Another possible explanation can be qualitatively ascribed to the role of different temperatures adopted in different solvents: in pure TEA, at higher temperature, the reaction kinetics are enhanced with a fast generation of nanoparticles nuclei, whose growth and aggregation are hindered by the stabilizing role of pure TEA, as previously stated. These aspects are consistent with the observations reported by Alagiri et al. (2013), who obtained spherical-like superparamagnetic Co-NPS of similar diameter by a solvothermal method using $CoCl_2$ as precursor in mixed solvents, with hydrazine hydrate and TEA, as reducing and stabilizing agent, respectively.

As previously detailed, the solid phase was separated and accurately characterized for the content in elemental cobalt. Assuming that cobalt oxide is present only as CoO, we estimated a solid composition made of $68\pm5\%$ elemental Co with TEA as reductant and of $41\pm5\%$ elemental Co with TEA+PG as reductant, reasonably proving that pure TEA has a higher reducing power with respect to a mix of TEA+PG.
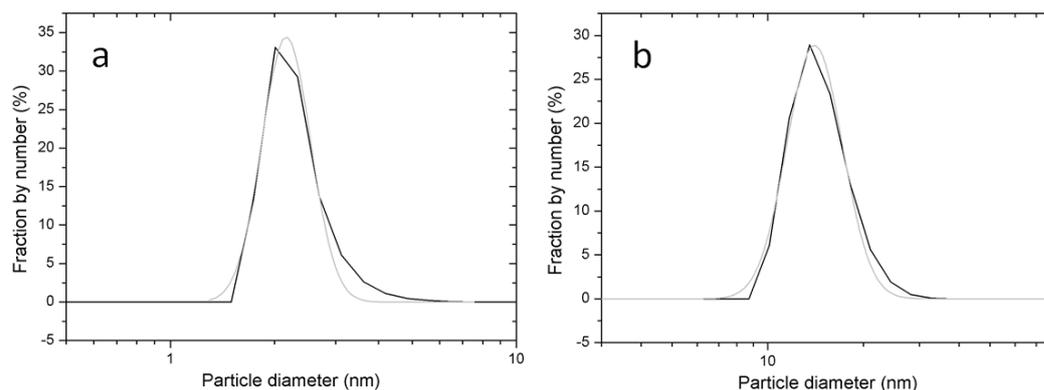
Figure 1: Populations of particle diameters obtained by DLS (black lines) with respective log-normal best fitting curves (gray lines). (a): sample obtained using pure TEA; average diameter=2.2 nm. (b): sample obtained using 50-50% TEA-PG; average diameter=14.6 nm.

These results are not surprising at all when taking into account that we have used a cobalt salt that has a higher affinity to electrons, and hence a greater tendency to be chemically reduced, with respect to many other precursors of the same cation. In fact, Raj and Viswanathan (2011) calculated different enthalpies of reaction in case of reductions of different salts like cobalt nitrate, chloride and acetate as precursors for the preparation of Co-NPs with glucose as reductant in mixed solvents. These authors concluded that, in most cases, $Co(NO_3)_2$ requires an energy many times lesser that needed by other cobalt salts.

3.2 A detailed insight into the synthesis of N-nitroso ethanolamines as reaction by-products

A second notable aspect of this work concerns the discussion about an incidental production of N-nitrosamines resulting from side reactions when TEA is the embedding solvent. The issue of side reactions leading to unwanted toxic compounds represents a hazard well relevant in the process sector, as highlighted by a large number of events. Among them, Seveso represents one of the best known of all chemical plant disasters, contributing to a huge legislative fall-out and a major shift in the way that industry faces and deals with process safety (Fabiano et al., 2016). It is well known that the thermal decomposition of metal nitrates may give rise to nitrites, in case of alkali cations, or to lower nitrogen oxides and metal oxides in case of less electropositive cations. It has been questioned whether, in the case here presented, the presence of $Co(NO_3)_2$ and its thermal dissociation might have produced nitrogen oxides having a potential role in the production of highly toxic and charcinogenic N-nitroso ethanolamines like NDELA (N-nitroso diethanolamine). The formation of N-nitroso compounds is a process typically occurring when a secondary amine reacts with the nitrite ion in acidic environment. This phenomenon has been accurately studied to monitor the health of operators working in contact with cutting fluids, where mixed alkanolamines comes in contact with sodium nitrite at higher temperatures.
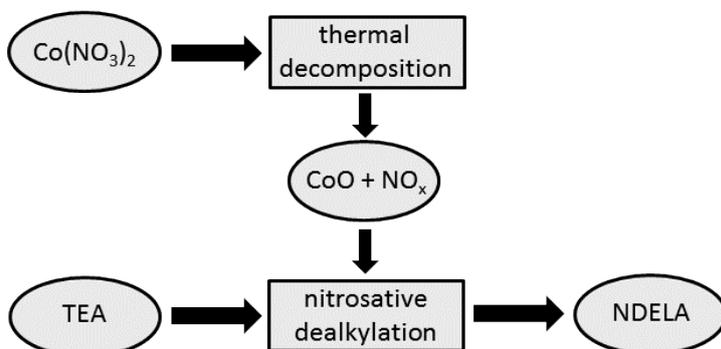

Figure 2: Scheme of a possible sequence of reactions for the synthesis of NDELA from TEA.
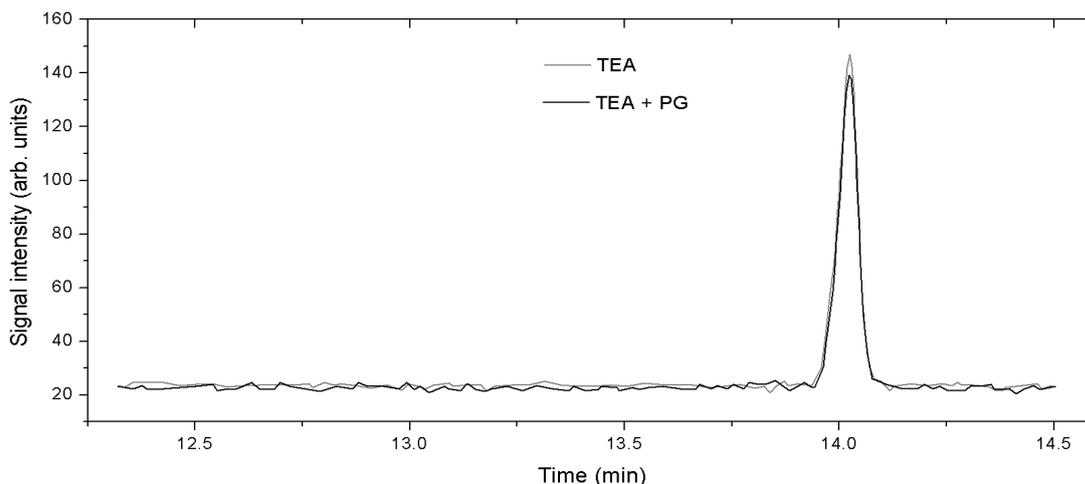
Figure 3: Plot of the GC-NCD response to the samples obtained using pure TEA and TEA+PG as the solvents. The response curves overlap almost completely.

According to IARC (1987), it has been ascertained that the temperature and the presence of transition metal complexes may increase considerably the kinetics of formation of N-nitroso derivatives of alkanolamines. As an example, the concentration of NDELA in cutting fluids is subject to wide variations, ranging in the interval [200-30,000] ppm for metalworking fluids used in the Unites States (IARC, 1987).

Moreover, the possibility that not only nitrites, but also nitrates in certain conditions may act on triethanolamine to form N-nitroso derivatives, even for neutral or moderately low pH values, is still an open question. Gowenlock et al. (1978) studied the kinetics of dealkylation of tertiary amines up to 80°C, in the presence of nitrites, and concluded that the concentration of hydrogen ions plays a basic role in determining the formation of N-nitrosoamines in acidic medium. For these reasons, we have investigated a NDELA synthesis according to a hypothesized reaction scheme described in Figure 2.

The concentrations of each of the ten non-hydroxylated nitrosamines reported in Table 1, determined by HPLC-MS was lower than 3 ppb both for pure TEA solvent and for TEA+PG. The concentrations of NDELA determined by GC-NCD is lower than 25 ppb both for pure TEA solvent and for TEA+PG, according to the plot reported in Figure 3.

4. Conclusions

We have investigated the synthesis of cobalt-based nanoparticles by a solvothermal method where $Co(NO_3)_2$ as a precursor is heated in non-aqueous solvents at different temperatures. The results can be summarized as follows:

- TEA proved to be a satisfactory reducing agent toward the cobalt precursor in the absence of other reductants that are commonly adopted in typical solvothermal methods; its role as electro-donor has been exploited in many different contexts (Pellegrin and Odobel, 2016).
- The average diameter of the particles obtained with the present technique are smaller for growing TEA concentration. This result confirms the excellent properties of TEA as capping agent, in agreement with the previous literature works.
- Incidentally, this work may add some further information about the puzzling problem of N-nitrosoalkanolamines formation like NDELA from triethanolamine. Despite the high process temperatures and the simultaneous presence of coordinate compounds of transition metals as possible catalyst, the yield in NDELA is particularly and unexpectedly low. A possible explanation can be found in unfavourable conditions related to the lacking protonation, the low yield in nitrite ions from the nitrate ion contained in the precursor and the short reaction time.
- Due to environmental concerns, there is an up-to-date research trend towards the elimination or reduction of the use of conventional organic solvents, as these are environmentally harmful (Primerano et al., 2016). Even if organic solvents are not fully eliminated, the results here outlined proves that, in the process conditions adopted relying upon pure organic solvents in the absence of water and reductants, the process can be considered relatively safe with respect to unwanted side reactions leading to hazardous N-nitroso derivatives.

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