Synthesis of Inorganic Compounds (Metal, Oxide and Hydroxide) in Polyol Medium: A Versatile Route Related to the Sol-Gel Process

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Abstract. A new route for the preparation of powdery metal, oxide and hydroxide materials is presented as a chimie douce alternative to the sol-gel method. It consists in the reduction or the hydrolysis of a metal salt dissolved and heated in a polyol medium. It appears through zinc and cobalt examples that the use of acetate precursors contrarily to chloride or sulfate ones leads to the precipitation of a solid (metal, oxide, hydroxide) whose nature depends on two main factors: the hydrolysis ratio, defined by the water to metal molar ratio, and the reaction temperature. As in the sol-gel method, acetate leads to the formation of intermediate alkoxyacetate complex. The absence of water favors metal formation while its presence favors oxide or hydroxyacetate formation.

Keywords: hydrolysis, reduction, polyol, sol-gel, precursor

Introduction

The work of Figlarz et al. published twenty years ago opened up an attractive new route for preparing metals with controlled morphology [1]. It consists in the reduction of a metal cation in a polyol medium. Over the past few years, polyols have also been used to elaborate a great variety of oxides [2–7] and layered hydroxy-salts [8] by means of hydrolysis and inorganic polymerization. All these compounds have been obtained starting from an ionic salt dissolved in a polyol and heated at a fixed temperature. The chemical reactions involved (reduction, hydrolysis, polymerization) are made possible by several properties of polyols, including high boiling point, dissolving, complexing, reducing and protective properties in addition to their amphiprotic character.

These works show that the formation of an inorganic compound in such a medium depends on the nature of the anion in the precursor salt. Nitrate will not be considered in the present study since this anion is an oxidant which interferes with the reducing property of the polyol. For the chloride and sulfate salts, the solution remains limpid after dissolution of the precursor and no precipitation is observed upon heating. Under otherwise identical conditions, if acetate is employed an inorganic compound precipitates and its nature (metal, oxide, hydroxide) depends on two main factors: the hydrolysis ratio (defined by the water to metal molar ratio) and the reaction temperature. This paper studies in detail the role of these factors on the reactions occurring in polyols, namely reduction and hydrolysis. Two cations with different electronegativities (Zn and Co) have been chosen to illustrate this point.

Experimental

Precursor salt $MX_2 \cdot nH_2O$ (M = Zn or Co, X = Cl, $0.5SO_4$ or CH_3CO_2) was dispersed in 250 mL of

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diethyleneglycol (DEG) or ethyleneglycol (EG) with a metal concentration of 0.05–0.6 M. The mixture was then heated, under stirring, to a fixed temperature which may reach the boiling point of the polyol. Water can be added to the mixture after salt dissolution. A wide range of hydrolysis ratios (H = 0–300) was tested.

XANES and EXAFS measurements at the Zn and the Co K edges were performed in the transmission mode at the French facility (LURE, Orsay) on the XAS 13 beamline of the DCI storage ring. XANES and EXAFS spectra were recorded using a Si (331) and Si (111) channel-cut monochromator respectively. The data were analyzed using the "EXAFS pour le MAC" software package [9] with tabulated McKale amplitude and phase shift functions [10].

Powder morphology was examined by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) using JEOL-100 CX II and LEICA-STEREOSCAN 440 microscopes, respectively.

Results

Influence of the Anion

X-Ray absorption measurements, performed on a solution of chloride dissolved in a polyol, clearly show that chloride anion remains in the first shell of the cation. The XANES spectrum of the zinc chloride dissolved in polyol is shown along with those of two references: solid $ZnCl_2$ and its solution in water (Fig. 1). In solid $ZnCl_2$, the Zn ion is coordinated to four chloride anions forming a tetrahedron [11]. In the aqueous solution, the chloride acts as a counter-ion and the first shell of the cation is an octahedron of water molecules [12]. The in-
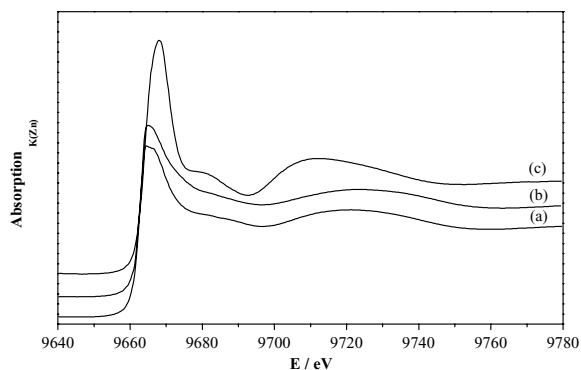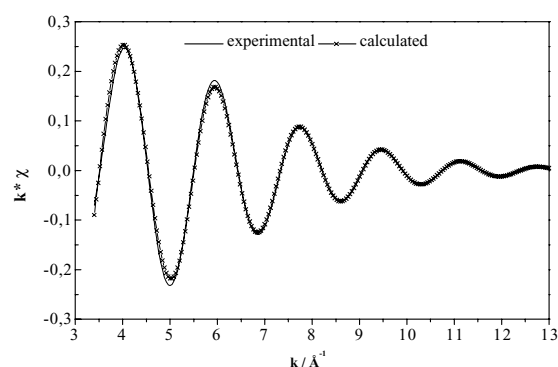

Figure 2. Experimental and calculated EXAFS spectra of zinc chloride dissolved in DEG for the first neighbor shell.

tensity and shape of the absorption spectrum of the zinc chloride dissolved in DEG are very similar to those of the spectrum of the solid. EXAFS calculations confirm this similarity. Fits of the data show that Zn^{2+} is coordinated to two chloride and two oxygen atoms at 2.23 and 2.08 Å, respectively (Fig. 2). The presence of chloride in the first shell of cobalt is also established. The XANES spectrum of the polyol solution is very close to that of solid $CoCl_2 \cdot 6H_2O$ (Fig. 3) and EXAFS calculations show that Co^{2+} is coordinated, as in the solid [13], to two chloride and four oxygen atoms at 2.28 and 2.09 Å, respectively (Fig. 4).

The comparison of the XANES spectra of the zinc and cobalt acetate polyol solutions with the corresponding solid acetate hydrate brings interesting results. According to structural characterization, the acetate anion chelates the cation in the solid $Zn(CH_3CO_2)_2 \cdot 2H_2O$ [14], whereas it appears as an unidentate ligand in $Co(CH_3CO_2)_2 \cdot 4H_2O$ solid [15]; this is characterized in the XANES spectrum of the former by a shoulder in

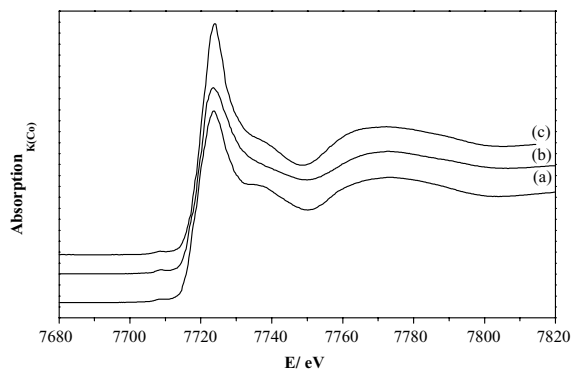*Figure 1.* XANES spectra of zinc chloride solid (a), dissolved in DEG (b) and in water (c).

Figure 3. XANES spectra of cobalt chloride solid (a), dissolved in DEG (b) and in water (c).
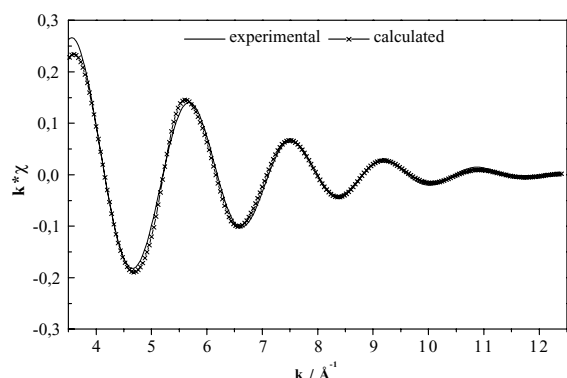
Figure 4. Experimental and calculated EXAFS spectra of chloride cobalt dissolved in DEG for the first neighbor shell.
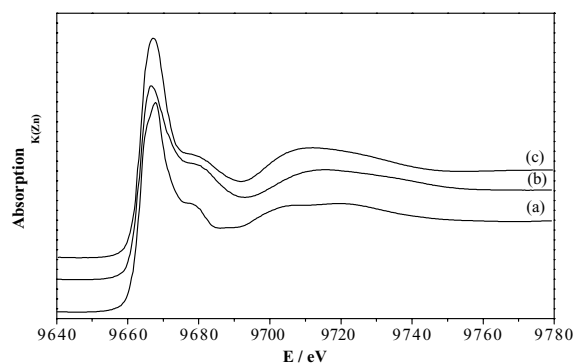

Figure 5. XANES spectra of zinc acetate solid (a), dissolved in DEG (b) and in water (c).
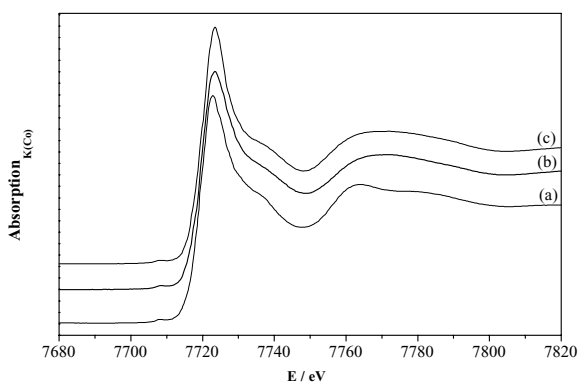

Figure 6. XANES spectra of cobalt acetate solid (a), dissolved in EG (b) and in water (c).

the edge structure (Fig. 5(a)) not observed for the later (Fig. 6(a)). Such a shoulder is not observed as well in the polyol solution spectra in both cases (Figs. 5(b) and 6(b)); if acetate is still bonded to the cation, that suggests it acts probably as an unidentate ligand.

In the case of zinc acetate solution in DEG or EG, single crystals of intermediate complexes are observed if the solution is kept at room temperature for a few hours for DEG or several months for EG. Structural determination on mono crystal showed that the two complexes have a lamellar structure in which Zn ions are linked to both polyol and acetate anions [16, 17]. Furthermore, acetate acts as a bridging ligand allowing polymerization to occur.

Influence of the Hydrolysis Ratio and the Reaction Temperature

Starting from an acetate dissolved in polyol, the nature of the material (metal, oxide or hydroxide) which precipitates upon heating depends mainly on the amount of water present in the solution. However, it should be noted that in a first step the formation of an intermediate solid phase was always observed. The composition of this phase varies from case to case. For zinc, it consists of a layered hydroxyacetate with the chemical formula $Zn(OH)_{1.5}(CH_3CO_2)_{0.5},0.5H_2O$ [8]. For cobalt, the composition depends on the nature of the polyol. For a non-zero hydrolysis ratio, DEG leads to a hydroxyacetate with chemical formula close to that of the Zn analogue. EG gives rise to the formation of an alkoxyacetate for relatively low hydrolysis ratios ($H < 50$) [18]. This alkoxyacetate is stable towards reduction. Raising the temperature leads to the progressive dissolution of the intermediate phase which acts then as a reservoir for the cation complex species. When water is distilled off and the temperature reaches the boiling point of the polyol, this then acts as a reducing agent leading to the formation of metal. It should be noted that, because of their mild reducing power, polyols are unable to reduce a cation of an electropositive metal such as zinc. In this case an unknown phase precipitates. A less electropositive metal such as cobalt is reduced [19]. When water remains in the solution, the reduction is inhibited. One can observe stabilization of the intermediate solid phase or oxide precipitation depending on the amount of water and the reaction temperature. High hydrolysis ratios (typically, $H > 25$ in DEG and $H > 50$ in EG) and low reaction temperature ($T < 60°C$ in DEG and $T < 130°C$ in EG) favor the formation of the hydroxyacetate [8]. Decreasing the hydrolysis ratio and increasing the reacting temperature leads to the formation of oxides [3, 7] preceded by the dissolution of the intermediate phase. The mechanism of formation of oxide or metal particles consists
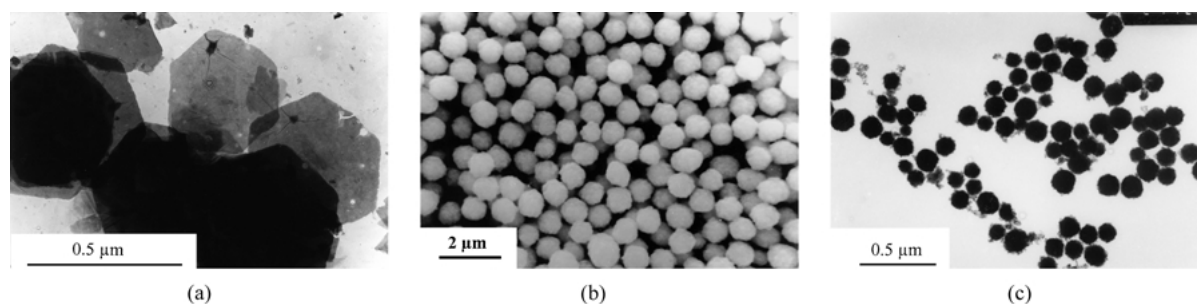
Figure 7. TEM images of different inorganic compounds obtained from $Co(CH_3CO_2)_2 \cdot 4H_2O$: cobalt hydroxyacetate (DEG, $H = 26$, $T = 60°C$) [8] (a), cobalt metal (EG/DEG, $H = 0$, $T = 200°C$) [19] (b) and cobalt(II) oxide (DEG, $H = 4$, $T = 185°C$) [7] (c).

of two separate steps: dissolution of the intermediate phase and then nucleation and growth of particles from the solution. This mechanism is inferred from the morphological characteristics for the different phases involved. Indeed while the intermediate phases appear as aggregates of thin platelets, thin crumpled sheets or micrometer polyhedra, metals and oxides so obtained present significantly different morphologies. They consist of spherical, monodispersed, non-agglomerated particles in the submicrometer or nanometer size range (Fig. 7).

Discussion

Polyols have successfully been used in the past two decades to prepare a great variety of inorganic compounds (metal, oxide, hydroxyacetate) obtained via reduction or hydrolysis.

As discussed above, the nature of the anion present in the precursor plays a decisive role. Inorganic compounds can be prepared only with acetate, not with chloride or sulfate. The present work is, to the best of our knowledge, the first attempt to understand this role. It also highlights the advantages of this novel route compared to the well-known sol-gel method. The results discussed above show clearly that chloride anion remains coordinated to the cation. This chemical bond appears to be very stable in polyol medium towards chemical reactions such as hydrolysis and inorganic polymerization. EXAFS and structural characterization show that acetate plays two main roles. In polyol medium, this anion deprotonates partially the polyol leading to an alkoxy group, and also acts as a complexing (unidentate or bridging) agent towards the cation. This leads to the formation of solid alkoxyacetate complexes. According to previous works on alkoxide precursors in sol-gel chemistry [20], it is assumed that

the nature of the molecular complexes still dissolved is similar.

It is interesting to note that alkoxyacetate complexes are also obtained in the sol-gel alkoxide method when an alkoxide precursor $M(OR)_n$ is dissolved in alcohol in the presence of acetic acid [21]. As in the sol-gel method, oxides or hydroxyacetates are obtained in polyol via hydrolysis and inorganic polymerization of such intermediate precursors (alkoxyacetates). These species control hydrolysis and polymerization because of the different electronegativity of alkoxy and acetate anions. As observed in the sol-gel method [22], less electronegative ligands (alkoxy) are first hydrolyzed and rather quickly removed from the cation coordination sphere upon hydrolysis, while more electronegative anions (acetate) may remain, thus leading to hydroxyacetate. At higher temperature, forced hydrolysis and inorganic polymerization remove the acetate anion and oxides are obtained.

The new method discussed here may be considered as an intermediate route between the two sol-gel methods described in the literature: hydrolysis of an inorganic salt dissolved in aqueous solution and hydrolysis of an alkoxide in an organic solvent (alcohol). Indeed, in this novel route, an ionic salt (acetate) is dissolved in an organic medium (polyol). To our knowledge, the sol-gel alkoxide route has never been employed to prepare oxides or hydroxides of 3d metals like Zn, Ni, Co and Fe. This is due to the fact that the corresponding alkoxides are polymeric, insoluble and therefore commercially unavailable. The novel method studied here overcomes these difficulties. It offers several advantages: the use of common ionic salts instead of alkoxide, a wide operating temperature range making it possible to obtain oxides and metals with good crystallinity. It allows also a certain control of the morphological characteristics that is useful for several applications.

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