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Solvent effect in the nonaqueous synthesis of ZrO₂ nanoparticles under alkaline conditions

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ABSTRACT

This work deals with the synthesis of zirconium dioxide (ZrO₂) nanoparticles (NPs) in different solvents and their structural characterization for better understanding the oxygen donor solvent/zirconium precursor/NPs structure relationships. By selecting solvents over their capacity to produce different crystalline states from alkalized zirconium alkoxide, spherical nanoparticles with a size of about 1.3 to 3 nm and a narrow size distribution were elaborated using a nonaqueous solvothermal sol-gel route. Conventional X-ray diffraction (XRD) was used to determine the average structure and crystallite size of the nanoparticles. Well crystallized and single-phased nanoparticles with average monoclinic and tetragonal structure were obtained with benzaldehyde and benzyl alcohol respectively, and a much distorted structure was observed for the synthesis in anisole. The atomic pair distribution functions (PDF) of the samples were also analyzed to access the local structure of the nanoparticles. The PDF of the benzaldehyde-prepared sample is consistent with the monoclinic structure. However, the local structure of nanoparticles synthesized with benzyl alcohol does not fully conform to the tetragonal structure observed by XRD but exhibits monoclinic-like distortions. Lastly, the anisole-prepared nanoparticles present large structural distortions at the medium-range and monoclinic local structural features. The restructuring of this last sample was studied by post-treatments in different solvents and leads to the expression of the tetragonal polymorph. Moreover, it seems that the main structural features are obtained in the early stages of the nanoparticles' formation.

Keywords: Zirconium dioxide; Nanoparticles, Solvothermal synthesis; Atomic Pair Distribution Function; X-ray diffraction; Rietveld refinement

1. Introduction

Zirconia (ZrO_2) is a remarkable ceramic material with great technological applications such as catalysis [1, 2], gas sensing [3, 4], fuel cell technology [5, 6], and high performance materials [7]. From a structural point of view, it also possesses a complex polymorphism and can be obtained at the nanoscale in crystalline forms which are not stable at standard pressure and ambient temperature [8]. The nanocrystalline state provides new properties induced by quantum confinement effect [9, 10, 11, 12]. The reduction of size also makes the nanoparticle structure different from the perfect single crystal [13], which in turn affects its final properties. The main difficulties in understanding nanocrystal structures rely on the complexity in synthesizing stable objects of less than 5 nm in size with different structures and to characterize them [14].

Chemical solution routes, especially solvothermal routes [15], are usually chosen when synthesizing nano-sized particles. They offer a versatile way to form particles of various sizes, and in principle dramatically reduces the lower limit of size that can be formed. Based on the consequent research conducted on the titanium dioxide system and involving metal halides, or metalorganic precursors [16, 17], zirconium (IV) isopropoxide-isopropanol adduct ($\text{Zr}(\text{O}^i\text{Pr})_4 \cdot (\text{HO}^i\text{Pr})$) is a good candidate for such syntheses and was previously selected by other research groups [18, 19, 20, 21]. In solvothermal syntheses, the choice of solvent affects the formation of metal oxide bridges as it is also used as the source of oxygen during the condensation reaction [22, 23]. Typically, three main families of solvents are expected to behave differently, namely alcohols, aldehydes and ethers. The use of benzyl alcohol is relatively well documented, in particular in the work done by Garnweitner *et al.* and De Keukeleere *et al.*. In their results, the authors proposed that the formation of the zirconium oxide bridges was initiated by the partial ligand exchange of the isopropoxide groups with benzoxide ones, accompanied by an alcohol elimination as shown in equation (1). The benzoxide-modified zirconium precursor could then proceed with the condensation reaction forming the zirconium oxide bridge accompanied by the release of various ethers (diisopropylether, dibenzyl ether or mixed ether) as shown for the case of a mixed ether in equation 2 [17, 18, 21].



The use of benzaldehyde was not investigated so heavily, but it is however expected to offer an alternative reaction pathway for the formation of zirconium oxide bridges, as shown by Garnweitner *et al.* [17] for the synthesis of TiO_2 nanocrystals. Finally, ethers were used as

solvents in the synthesis of titania nanoparticles, and in some cases excellent yields were obtained at moderate temperatures [16].

In these circumstances it is surprising to note that the systematic study of the sole effect of solvent on the structure of the nanoparticles was never conducted, and the previous authors never concluded about this fact. Different alcohols were indeed investigated by Anandan *et al.* [24], but the obtained samples were all monoclinic. The aim of the present work is thus to determinate if the solvent is a valid synthesis parameter with the same importance as temperature or the nature of the metal precursor or its concentration [25].

Many research groups investigated the catalytic effect of acidic medium onto the formation mechanism of nanoparticles. In the literature, the most encountered syntheses indeed take place in acidic media, or in a medium where the acidity is brought either by the metal precursor or by the solvent [21, 26]. However other syntheses routes are possible. In addition, we observed that the presence of water produced by the dehydration of the alcoholic reagents is detrimental to the phase purity of tetragonal ZrO₂ nanocrystals [27]. This effect of *in-situ* water, generally overlooked, can be averted by the use of sodium metal in the solution in order to promote a strong base activation of the global process. This dehydrating effect can also be achieved by sodium hydroxide (NaOH), with similar results. The present paper will thus focus on the effect of different solvents in alkaline conditions.

Hence, this work was devoted to the determination of a reproducible way to synthesize nanoparticles with selectable phase and tunable size. Then, having control over these parameters, the structural features of the samples were studied. Finally, complementary experiments helped understanding the restructuring effect of the solvent by retreating previously formed nanoparticles in solvents of similar or different chemistry than the original one.

2. Experimental details

2.1 Synthesis

The synthesis of ZrO₂ nanoparticles was conducted by a solvothermal nonaqueous route from zirconium isopropoxide-isopropanol adduct (Zr(OⁱPr)₄·(HOⁱPr), CAS No 14717-56-7, STREM, 99.9%), sodium hydroxide (NaOH, CAS No 1310-73-2, Alfa Aesar ACS 97% min) and an oxygen donor solvent. The list of the used solvents is given in Table 1. Two main studies

were conducted in this work. The first one aimed at determining the effect of solvents (alcohol, ether and aldehyde) with different chemical properties on the ZrO₂ polymorph selection and size control. The second one focused on three of these solvents to conduct the structural study of the freshly synthesized samples and their sensitivity towards restructuring in a solvothermal post-treatment.

The reagents were mixed into a Teflon[®] insert and then heated in an autoclave at 210°C for 3 days. The concentration of the metal precursor was set to 0.3 mol.L⁻¹ in all the experiments, the concentration of NaOH was 0.2 mol.L⁻¹ and the total volume of the reaction mixture was 15 mL. All the syntheses were carried out under autogenous pressure. During the autoclave treatment the solution was mixed with a magnetic stirrer set at 350 rpm. Due to the sensitivity of the anhydrous reagents, and to prevent the accidental introduction of water during the treatments, the syntheses were conducted inside a glovebox under a continuous flow of dry air.

After the solvothermal treatment, the turbid suspensions were centrifuged, washed with 15 mL of anhydrous ethanol (CH₃CH₂OH, CAS No 64-17-5, Alfa Aesar 96%) and centrifuged again at 10000 rpm for 10 min. This process was repeated until the supernatant liquid became clear. Finally, the obtained powders were dispersed into 20 mL of dichloromethane (CH₂Cl₂, CAS No 75-09-2, Alfa Aesar, 99.5%) and dried in ambient conditions.

Table 1: List of solvents used in the nonaqueous sol-gel solvothermal syntheses of zirconia nanoparticles.

Used in study	Name	Chemical formula	Provider	Purity	CAS No
1	Dibenzyl ether	(C ₆ H ₅ CH ₂) ₂ O	Sigma Aldrich	98%	103-50-4
1	Diisopropyl ether	((CH ₃) ₂ CH) ₂ O	Sigma Aldrich	99%	108-20-3
1	Isopropyl alcohol	(CH ₃) ₂ CHOH	Sigma Aldrich	99.7%	67-63-0
1 & 2	Anisole	C ₆ H ₅ OCH ₃	Alfa Aesar	99%	100-66-3
1 & 2	Benzaldehyde	C ₆ H ₅ CHO	Alfa Aesar	99%	100-52-7
1 & 2	Benzyl alcohol	C ₆ H ₅ CH ₂ OH	Sigma Aldrich	99.8%	100-51-6

2.2 Morphological and structural characterization

The morphological characteristics and crystalline state of the samples were characterized via high resolution transmission electron microscopy (TEM - JEOL JEM 2100f). The samples were prepared by first diluting one drop of the washed suspension into 20 mL of dichloromethane and 2 drops of oleic acid ($C_{18}H_{34}O_2$, CAS No 112-80-1, Sigma Aldrich, 90%) and then laying one drop of this diluted solution onto an ultrathin carbon-A holey 400 mesh copper grid. Due to the characteristics of the suspension (as described in the results part), the preparation of the samples synthesized in benzaldehyde was different. In this case, the dried powder was dispersed in ethanol and then deposited on the grid.

The average structural characteristics of the samples were determined by X-ray powder diffraction using a Bruker D8 Advance equipped with a Lynxeye detector. Measurements were performed with wavelength $\lambda_{CuK\alpha 1} = 1.5406 \text{ \AA}$ over the range of 10 to 110° with a step size of 0.02° and an equivalent time per step of 1567 s. The XRD diagrams were analyzed by the Rietveld method using the FullProf suite program [28]. The scale factor, background, unit cell parameters, atomic positions and thermal displacements were refined, as well as the peak widths in order to obtain the average diameter and microstrains of the nanoparticles. Line profile were modelled by the modified Thompson-Cox-Hastings formulation of the pseudo-Voigt function [29].

The atomic pair distribution function (PDF) of the sample were obtained from X-ray total scattering experiments using a home-made setup equipped with a molybdenum source ($\lambda = 0.709 \text{ \AA}$) and a scintillator point detector. Data were measured from 0 to 147.29° (2θ) with counting time of 240 s per step such as to reach a maximum scattering vector length (Q) of 17.2 \AA^{-1} with a constant step size of 0.02 \AA^{-1} . The zirconia powders were sealed into a 0.7 mm borosilicate glass capillary. Raw data were corrected for capillary and empty environment scattering, Compton scattering, fluorescence, absorption, polarization and normalized before Fourier transformation. Both acquisitions and data corrections and normalization were performed with homemade software [30,31]. More details on the experimental setup and software are given elsewhere [32].

3. Results and discussion

3.1 Effect of the type of solvent

The aim of the first set of experiments was to determine the effect of different alkalized solvents on the synthesis of ZrO_2 nanoparticles. For this, syntheses were carried out using alcohols (isopropanol and benzyl alcohol), reactive ethers (diisopropyl ether and dibenzyl ether), anisole as an inert ether, and benzaldehyde. This should help to investigate whether the formation of single phased nanoparticles is exclusively limited to some solvents. The crystallization process indeed involves a good interplay of the forward and reverse reactions of the sol-gel process in order to allow an effective restructuring as the particles grow, which is the reason why solvents with different chemical properties and reactivity were selected. The XRD diagrams of the washed and dried samples are presented in Figure 1.

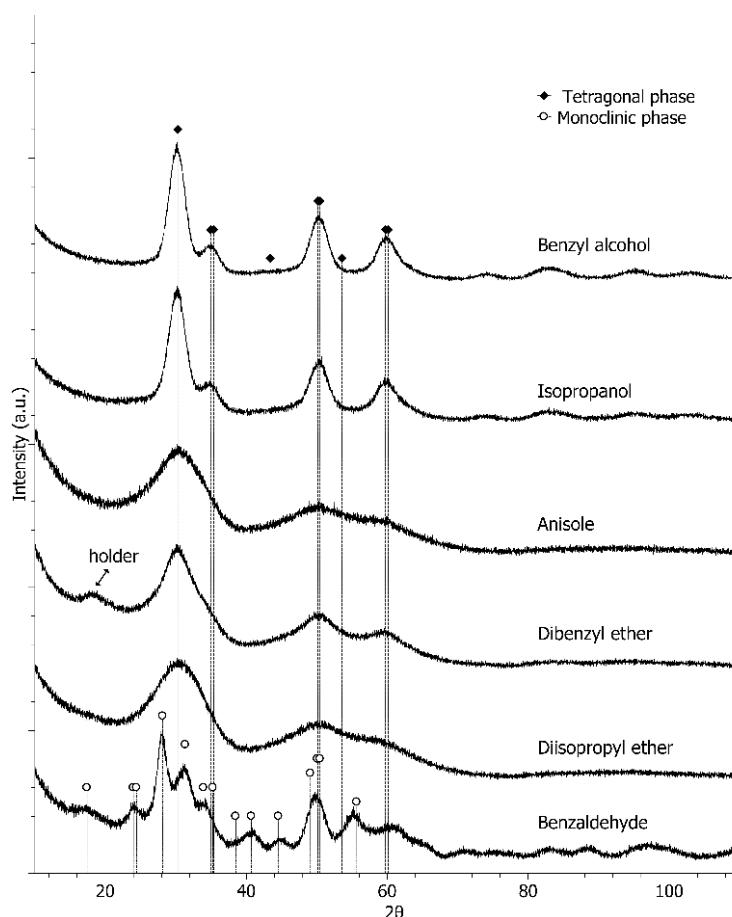


Figure 1: XRD patterns of zirconia samples prepared via a solvothermal synthesis in different solvents. Note: the sample holder's contribution visible in the pattern synthesized in dibenzyl ether is due to the very low amount of powder produced, thus requiring the use of a specific holder.

All the reaction mixtures led to the formation of zirconia. The diffraction peaks are broad and can be attributed to its different polymorphs. Firstly, the samples prepared in alkalized alcohols were composed of tetragonal-like ZrO_2 nanoparticles (t- ZrO_2). This suggests that the condensation and decondensation of the oxidic network during the synthesis is not limited to benzyl alcohol or alcohols having an aromatic and primary alcohol class but also works similarly with aliphatic secondary alcohols. One can note that previous experiments using $Zr(O^iPr)_4 \cdot (HO^iPr)$ were conducted by Garnweitner *et al.* [18]. With a lower concentration of metallic precursor in benzyl alcohol, they successfully obtained metastable cubic-type zirconia in a neutral medium. The differences in the synthesis parameters (concentration, pH) do not seem to have a strong influence on the synthesized polymorph in this specific case and the chosen reagents may prevail.

Then, for the samples prepared in alkalized ethers, we observed only some minor differences in their characteristic peaks, while their very broad nature lead to a difficult direct phase identification. Only the sample prepared in dibenzyl ether revealed more distinctly the features of t- ZrO_2 . Compared to alcohols, ethers are definitively less effective and lead to a lowest degree of restructuring, suggesting that alcoholysis is more competitive than etherolysis in the process. Finally, we can distinguish some slight differences in the efficiency of the ethers. Anisole is ineffective to promote restructuring since etherolysis is not possible, and only the eventual presence of byproducts (e.g. isopropanol from the precursor or diisopropyl ether issued from ether-elimination of isopropoxide groups) in the reaction medium is able to initiate a restructuring. Only diisopropyl ether and dibenzyl ether used as solvents in large amount can cleave and promote etherolysis and it seems that dibenzyl ether is more effective than diisopropyl ether probably due to the strong mesomeric effect promoted by the aromatic ring.

The alcoholysis occurring in the sample prepared in abundant alcohol seems to be efficient in achieving a larger ordering of the oxidic network, while the sample prepared in abundant inert ether remains highly disordered. The use of reactive ethers however showed that the etherolysis enables the ripening of the oxidic network during the synthesis. To illustrate this point, by using the sample prepared in alkalized anisole with zirconium isopropoxide isopropanol adduct (containing at least 1 equivalent of isopropanol for 1 equivalent of zirconium) as a standard, we can establish the relative and qualitative scale of efficiency for the restructuring process promoted by the reaction medium as it is schematically represented in Figure 2.

Finally, the sample prepared in benzaldehyde showed the distinct features of the monoclinic polymorph of ZrO_2 (m- ZrO_2) with a relatively good crystallinity, comparable to the one obtained in alcohols.

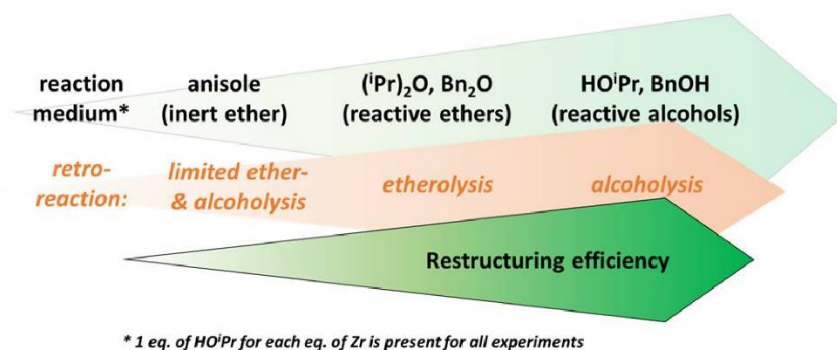


Figure 2: Restructuring efficiency represented for a selection of alcohols and ethers in the presence of sodium hydroxide.

In this set of experiments, from the point of view of the oxidic conversion of the metallic precursor, the use of $Zr(O^iPr)_4 \cdot (HO^iPr)$ allowed to form nanocrystallites under the action of a large panel of alkalinized solvents. The phase control to obtain a sample exclusively composed of tetragonal or monoclinic nanocrystals was also successfully obtained. However, further analyses, such as Rietveld refinements of the XRD patterns and PDF analysis based on total scattering experiments are necessary, in particular to unambiguously identify which polymorph is present in the case of disordered samples. They will thus be presented in the next parts of this work for selected samples, representing three very different crystallization status. They are the following: *i.* a well crystallized tetragonal sample (synthesized in benzyl alcohol), *ii.* a well crystallized monoclinic sample (synthesized in benzaldehyde), *iii.* a highly disordered sample (synthesized in anisole).

3.2 Structural analysis of the samples

3.2.1 Rietveld analysis

The Rietveld refinements obtained for the three samples are illustrated in Figure 3, with their corresponding TEM images. The refined parameters are given in Table 2 for the best structure model except for the sample prepared in anisole, for which all tested models are presented.

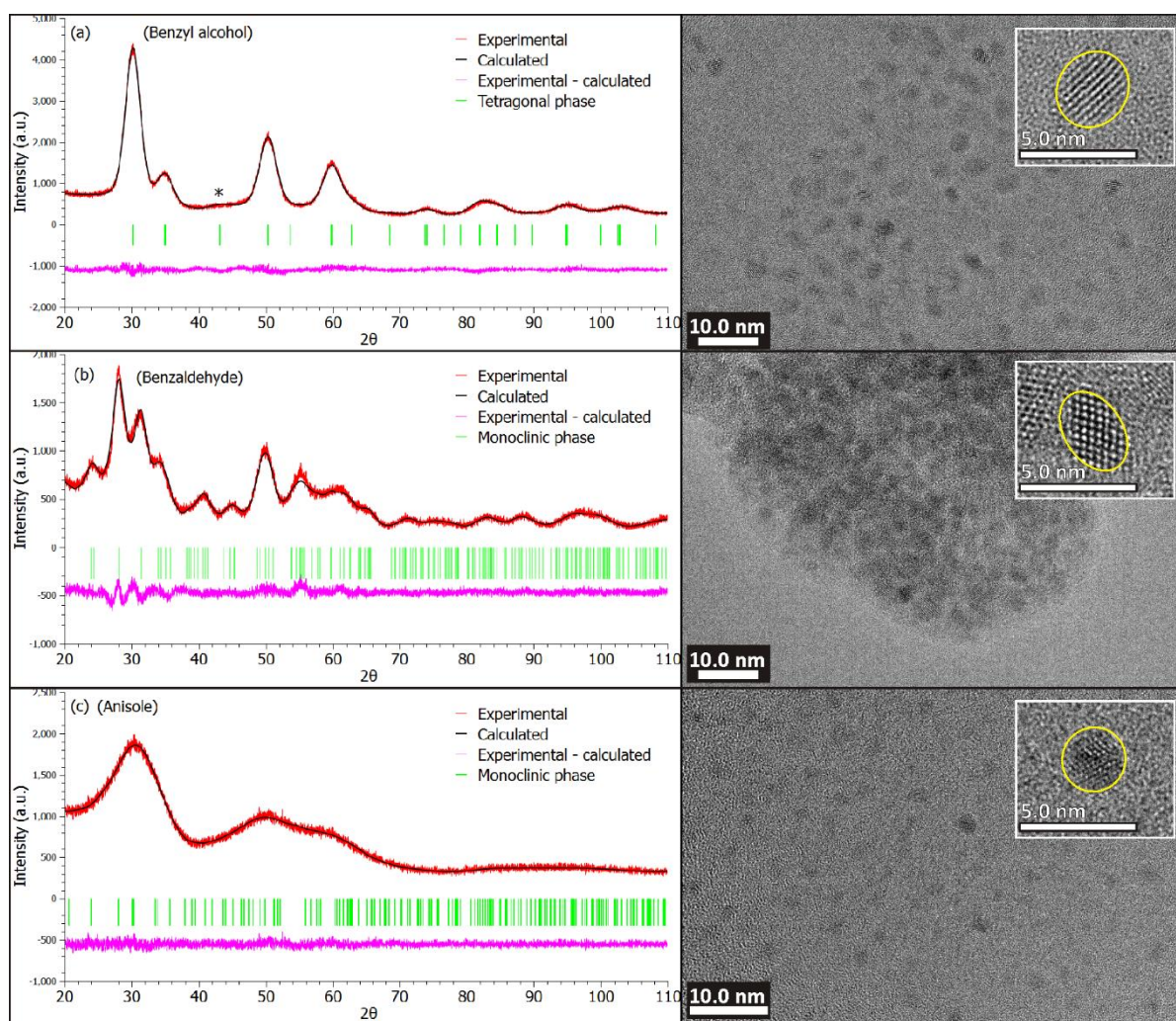


Figure 3: left: Rietveld refinement of the XRD diagram of the zirconia sample prepared in (a) benzyl alcohol, (b), benzaldehyde and (c) anisole. Right: TEM images of the corresponding samples, general view and single nanoparticle. (*) position of the tetragonal phase 102 peak.

Table 2: Rietveld refinement results of the zirconia samples prepared in benzyl alcohol, benzaldehyde and anisole (* fixed parameter).

Solvent	Model	χ^2 , average diameter (ϕ_{av}) and microstrain (ϵ_{av})	Unit cell parameters
Benzyl alcohol	Tetragonal	$\chi^2 = 1.48$ $\phi_{av} = 3.0$ nm $\epsilon_{av} = 0.98$ %	$a = b = 3.617(3)\text{\AA}$ $c = 5.136(6)\text{\AA}$ $R_t = \frac{c}{a\sqrt{2}} = 1.004$
Bezaldehyde	Monoclinic	$\chi^2 = 1.59$ $\phi_{av} = 2.7$ nm $\epsilon_{av} \sim 0$	$a = 5.168(3)\text{\AA}$ $b = 5.214(3)\text{\AA}$ $c = 5.337(3)\text{\AA}$ $\beta = 99.20(3)^\circ$
Anisole	Monoclinic	$\chi^2 = 1.05$ $\phi_{av} = 1.4$ nm $\epsilon_{av} = 2.76$ %	$a = 4.35(1)\text{\AA}$ $b = 4.73(1)\text{\AA}$ $c = 6.02(2)\text{\AA}$ $\beta = 99.1(2)^\circ$
Anisole	Cubic	$\chi^2 = 1.15$ $\phi_{av} = 1.3$ nm $\epsilon_{av} = 8.17$ %	$a = 5.104^*\text{\AA}$
Anisole	Tetragonal	$\chi^2 = 1.09$ $\phi_{av} = 1.2$ nm $\epsilon_{av} = 7.09$ %	$a = b = 3.619^*\text{\AA}$ $c = 5.126^*\text{\AA}$ $R_t = 1.001$
Anisole	Orthorhombic	$\chi^2 = 1.09$ $\phi_{av} = 1.4$ nm $\epsilon_{av} = 5.14$ %	$a = 9.70(6)\text{\AA}$ $b = 5.2(2)\text{\AA}$ $c = 5.2(2)\text{\AA}$

For the sample prepared in benzyl alcohol (Figure 3a), the peaks located at the positions $2\theta = 30^\circ, 35^\circ, 50^\circ$, and 60° are consistent with both the tetragonal and cubic phases of zirconia. The tetragonal zirconia can be differentiated by the presence of the low intensity 102 peak located at $2\theta = 43^\circ$, which is detected on the diagram. The tetragonal model is confirmed with the Rietveld refinement, which gives the best fit. It is interesting to note that the tetragonality of the particle $R_t = \frac{c}{a\sqrt{2}} = 1.004$ is much less than that of the perfect tetragonal phase ($R_t = 1.023$

[33]), so that the metric is almost cubic. The refined average diameter and microstrains are 3.0 nm and 0.98%, respectively. Based on the TEM images of the sample shown in the right part of Figure 3a, the samples are mainly composed of spherical-like particles with an average diameter of 3.2 nm, which is consistent with XRD.

The Rietveld refinement of the sample prepared in benzaldehyde using a monoclinic structure model is shown in Figure 3b. The agreement with experiment is overall good even if some discrepancies between the model and experiment remain. The lattice parameters (see Table 2) also compare well with those of the monoclinic zirconia [34]. The refined microstructural parameters give an average particle diameter of 2.8 nm with almost zero microstrain. The TEM images support well the description of the sample, with particles of about 3 nm. For this sample, the synthesized suspension was highly organic and very difficult to wash. It was thus not possible to obtain images from it and the measurement was done using dried powders dispersed in ethanol. Due to its aggregated state in this form, the estimated size of the nanoparticles obtained by TEM image analysis was more difficult to measure; it is however clearly in the same range as the value obtained by XRD.

As already stated, the experimental pattern of the sample prepared in anisole lacks any distinguishable features to attribute to one particular polymorph. The Rietveld refined parameters are given in Table 2 for the four fluorite-derived zirconia polymorphs and the fit obtained with a monoclinic model is shown in Figure 3c, the others are not presented. All models gave a reasonable fit of the data making it difficult to determine what type of zirconia phase is the sample. The particle diameter vary between 1.2 and 1.4 nm for the four models. The amount of refined microstrains varies from ~3% to 8% which is very large and reflect that the particles have large structural distortions. However, the lowest microstrains value is obtained for the monoclinic model, which favors this particular model for describing the average structure. TEM measurements (Figure 3c, right) clearly reveal resolved atomic planes, which confirm that the sample is crystallized with an average diameter of 2 nm.

For all the samples, the refinements confirm the very small size of the particles, well below 4 nm. It is interesting to note that they are also largely below the critical size of 10 nm initially estimated by Garvie [8, 35, 36], below which the tetragonal phase is assumed to be favored over the thermodynamically stable monoclinic bulk phase due to surface energy considerations. Our results suggest that very small sized monoclinic particles, well below the critical size, can be obtained. This fact has been observed in few other cases. For example, De

Keukeleere *et al.* [21] managed to obtain in an acidic reaction mixture stable monoclinic nanoparticles of 6.5 nm. Dippel *et al.* [37], also observed monoclinic nanoparticles with a 5 nm diameter obtained by *in situ* solvothermal synthesis.

3.2.2 The local structure of the nanoparticles

The experimental PDFs of the samples prepared in benzyl alcohol, benzaldehyde and anisole are shown in Figure 4. They are characterized by intense and narrow peaks in the short-range order region and a strong decrease of peak intensity at higher distances, which is mainly due to the finite particle size and possibly to structural disorder within the particles. The structural coherence lengths of the nanoparticles, estimated from Figure 4, are tabulated in Table 3. For the syntheses in benzyl alcohol (Figure 4a) and benzaldehyde (Figure 4b), they are found to be about 3.0 nm with estimated uncertainty of about 0.2 nm. They compare relatively well with XRD and TEM measurements. For the sample prepared in anisole (Figure 4c), the coherent length is of about 1.1 nm, which is consistent with XRD and clearly smaller than the TEM values. The difference suggests that the particles lose structural coherency because of large structural disorder, which agrees with the large strain values obtained from XRD analysis.

Table 3: Average crystallite diameter measurements for zirconia particles.

Measurement method \ Solvent	TEM	XRD	PDF
Benzyl alcohol	3.2 nm	3.0 nm	3.0 nm
Benzaldehyde	3 nm	2.7 nm	3.0 nm
Anisole	2 nm	1.3 nm	1.1 nm

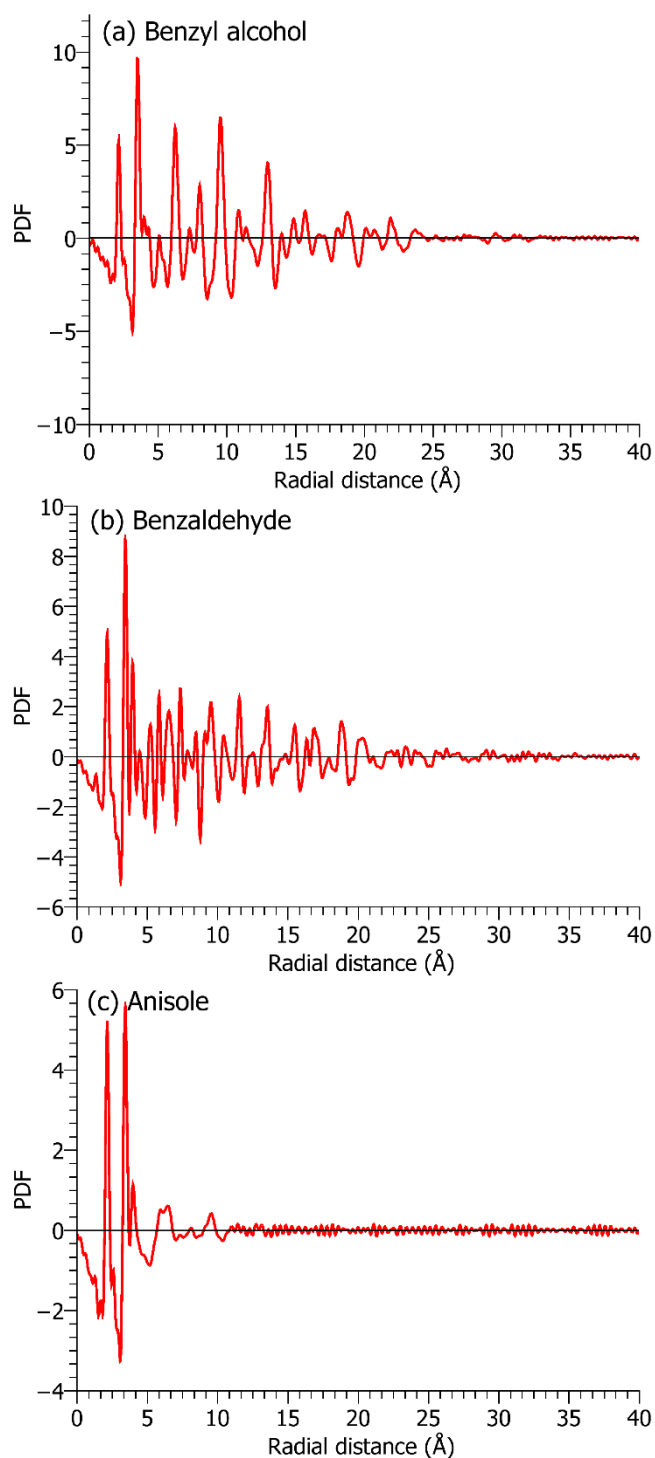


Figure 4: Experimental PDFs of the zirconia particles produced in (a) benzyl alcohol (b) benzaldehyde and (c) anisole.

The low-r region of the PDF (1.5 to 5 Å) are presented in Figure 5. The region from 1.5 to 3.0 Å is similar for all samples. It contains an intense peak at 2.15 Å, which corresponds to the typical Zr-O bond length found in zirconia polymorphs. Differences are clearly visible after

3.0 Å. The second intense peak at about 3.5 Å, which corresponds to the shortest Zr-Zr distances, changes in position from one sample to another. For both the samples prepared in benzaldehyde and anisole, the peak is located at 3.44 Å, corresponding to the Zr-Zr distance found in the monoclinic polymorph. This analogy with the monoclinic structure is also confirmed with the next peak at 3.93 Å also typically found in the monoclinic phase and corresponding both to Zr-Zr and Zr-O distances. Thus, the nanoparticle local structure for these two samples is typical of the monoclinic polymorph. For the sample prepared in benzyl alcohol, things are different. The intense peak is found at 3.52 Å, being the average value of 3.44 Å (monoclinic) and 3.60 Å of the tetragonal structure, thus favoring neither phase clearly. The second peak at 3.98 Å is rather weak and better matches with that of the tetragonal phase. The nanoparticles of this sample thus presents a structure with a medium-range order similar to the tetragonal phase, as evidenced by XRD, but certainly with local monoclinic-like distortions.

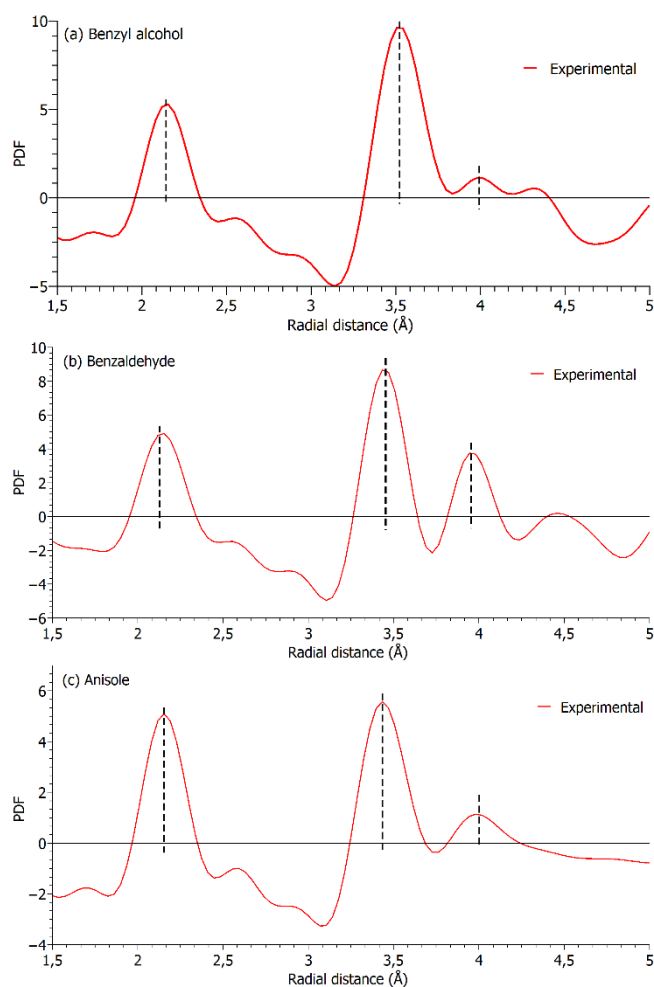


Figure 5: Experimental PDF of the nanoparticles produced in (a) benzyl alcohol, (b) benzaldehyde and (c) anisole and compared with the interatomic distances found in tetragonal [33] and monoclinic [34] zirconia polymorphs.

One question remains concerning the sample prepared in anisole. Its local structure can be described as a monoclinic-like one but no clear information was gathered for its medium-range structure due to its high degree of disorder. The samples synthesized in reactive ethers tend to express some tetragonal-like features and it would be interesting to verify whether it is the same for anisole-based nanoparticles. A dual stage synthesis in different conditions (longer time and/or more reactive solvent) was thus applied on the disordered particles prepared in anisole in order to increase their crystallinity and see which zirconia polymorph would prevail in their average structure.

3.3 Influence of a dual stage solvothermal synthesis on the average structure

In order to test how the initial synthesis conditions influence both the final structure of the nanoparticles, especially their medium-range order, and the nanoparticles growth, a dual stage solvothermal synthesis was experimented. This dual stage solvothermal synthesis consisted in applying to the product obtained after the original synthesis (stage 1) a second solvothermal treatment with a different solvent without the presence of an alkali precursor. The use of a sole solvent in the second step was chosen to ensure that its effect would not be overridden by the alkaline's.

For this experiment, both the relatively well crystallized sample synthesized in benzyl alcohol and the highly disordered sample prepared in anisole were used. On the one hand, the crystallized t-ZrO₂ sample was used to verify whether a second treatment in a similar reactive solvent would induce a dramatic particles' size increase. On the other hand, the dual stage synthesis applied to disordered nanoparticles (*i.e.* initially prepared in anisole) was devoted to the better understanding of the restructuring effect of the solvent on particles with no specific long range order. All the samples sustained identical second stage syntheses, *i.e.* a solvothermal treatment at 210°C for 3 days in the selected solvent of the freshly centrifuged nanoparticles without any washing or purification. The parameters of the dual stage solvothermal syntheses are listed in Table 4.

Table 4: Synthesis parameters of the dual stage solvothermal syntheses.

Sample	Stage	NaOH (mol.L ⁻¹)	Zr-source (mol.L ⁻¹)	Solvent	Solvothermal treatment (days)	Temperature (°C)
(a)	1	0.2	0.3	Benzyl alcohol	3	210
	2	0	0	Benzyl alcohol	3	210
(b)	1	0.2	0.3	Anisole	3	210
	2	0	0	Anisole	3	210
(c)	1	0.2	0.3	Anisole	3	210
	2	0	0	Benzal dehyde	3	210
(d)	1	0.2	0.3	Anisole	3	210
	2	0	0	Benzyl alcohol	3	210

The XRD patterns and refined crystallite sizes of the resulting samples are given in Figure 6 and Table 5 respectively. Note that in the figure, as samples (b₁), (c₁) and (d₁) are actually the same, only (b₁) was represented. No effect is visible in the sample (a); indeed, the sample (a₂) remains tetragonal-like in nature and the apparent crystallite size is still 3.0 nm after the second solvothermal treatment. The absence of any change in the case of a second solvothermal step performed in benzyl alcohol indicates the robust feature of the synthesis achieved in the initial one. Thus, such a reaction mixture does not allow the sample to undergo a phase conversion from the tetragonal-like state to the monoclinic one nor an excessive crystallite growth.

In the case of the samples treated in anisole, the very disordered nature of the sample after the first solvothermal treatment suggested that a restructuring was more likely to occur. Firstly, the sample (b₂) retreated in anisole, which is an inert solvent, did not lead to any modification in terms of phase identification or crystallite size. Then, in the case of a retreatment in benzaldehyde (c₂), the broadening of the peaks is less prominent, and the characteristic peaks of the tetragonal polymorph of ZrO₂ are clearly visible. The crystallite size increased from

1.2 nm to 2.6 nm, which is still low. After the retreatment in benzaldehyde, the sample was difficult to wash while keeping a reasonable amount of powder for characterization, its XRD diagram is thus a little less clear although the same parameters were used for the measurement. Finally, after a retreatment in benzyl alcohol (d_2), the crystallite size increased from 1.2 nm to 2.3 nm. This grain growth allowed the XRD expression of the tetragonal-like polymorph of zirconia in the sample. It seems that the sample issued from the alkalized anisole route is highly sensitive towards retreatment in reactive solvents (benzaldehyde or benzyl alcohol) and that this retreatment reveals a tetragonal-like structure in the medium range in both cases, although benzaldehyde-synthesized samples are monoclinic. The anisole-based sample might thus be seen as an early stage in the growth of tetragonal nanoparticles. This goes well with the previous experiments showing that synthesizing nanoparticles in reactive ethers led to the formation of t-ZrO₂.

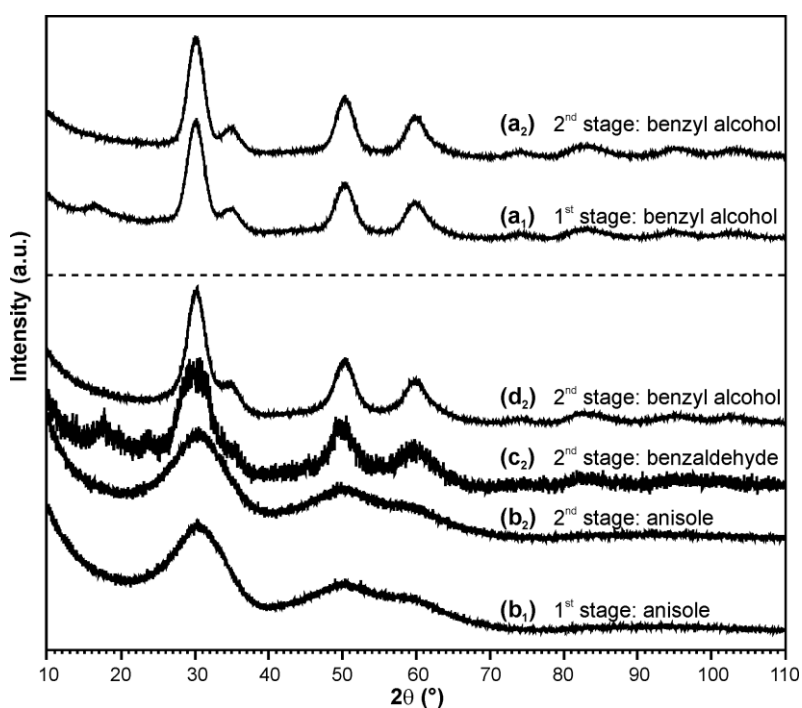


Figure 6: XRD patterns of the samples prepared by dual stage synthesis.

Table 5: Average size of the samples prepared by dual stage synthesis measured after the first and second stage.

Sample	Solvent (stage 1)	Size (nm)	Solvent (stage 2)	Size (nm)
(a)	Benzyl alcohol (a ₁)	3.0	Benzyl alcohol (a ₂)	3.0
(b)	Anisole (b ₁)	1.2	Anisole (b ₂)	1.2
(c)	Anisole (c ₁)	1.2	Benzaldehyde (c ₂)	2.6
(d)	Anisole (d ₁)	1.2	Benzyl alcohol (d ₂)	2.3

Retreating previously formed and crystallized nanoparticles in a post synthesis treatment was not able to promote the transformation into a phase with a different symmetry, whatever the used solvent. One can note that during this study, trials to modify the polymorphic distribution (originally monoclinic, tetragonal or a mixture of both) in a synthesized sample by applying second treatments in different solvents systematically failed to modify the phase distribution of the samples. Retreating in an inert ether, such as anisole, also never modified the original sample. It seems that the formation of the particle from the organic precursor, by forward and reverse alcoholysis or in a lesser extent etherolysis, prevails on the expression of its polymorph.

4. Conclusion

In conclusion, the effect of different solvents on the synthesis of nanosized zirconia was investigated. The syntheses were conducted via a nonaqueous solvothermal strategy in an adapted environment (alkalinized mixture, use of an alkoxide precursor). X-ray diffraction and total scattering were used for analyzing the average and local structural of the nanoparticles.

The effectiveness of the reaction medium governing the crystallization has been observed. It shows a hierarchical reactivity order which is strongly related to the reverse sol-gel reactions (etherolysis or alcoholysis) occurring during the synthesis. Moreover, it seems that the use of alcohol is not necessarily restricted to alcohols having an aromatic ring and primary level since similar samples have been produced using isopropanol. Also, the use of other types of alcohols and ethers suggests that the effect brought about by benzyl alcohol is not exclusive. This confirms the possibility of using alternative reagents for the synthesis of zirconia nanoparticles in alkalinized medium.

The use of benzyl alcohol as a solvent lead to relatively well-crystallized spherical nanoparticles of about 3.0 nm in diameter and with low amount of microstrain. Their average structure is tetragonal with monoclinic distortion of the local structure. In benzaldehyde, strain-free nanoparticles of 2.7 nm were synthesized with and an unambiguous monoclinic structure. Finally, the sample prepared in anisole was highly disordered with a large amount of strain and a coherent size of about 1.3 nm. The local structure of this sample was attributed to the monoclinic polymorph. It also seems that a second stage restructuring step can later transform zirconia having large structural distortions towards a better crystallized tetragonal-like zirconia with a limited size of 2.3 nm to 2.6 nm in reactive solvents, while retreatment in anisole does not alter the sample.

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