Combined use of XAFS, XRD and TEM to unravel the microstructural evolution of nanostructured $\text{ZrO}_2\text{--SiO}_2$ binary oxides: from nanometres down to the molecular domain

Fabio Meneghetti,^{ab} Eric Wendel,^b Simone Mascotto,^{ac} Bernd M. Smarsly,^c Eugenio Tondello,^a Helmut Bertagnolli^b and Silvia Gross^{*a}

Received 4th June 2009, Accepted 15th December 2009

First published as an Advance Article on the web 15th January 2010

DOI: 10.1039/b911004f

In this paper, the detailed study of the microstructural evolution under annealing of zirconium-based inorganic–organic hybrid materials to give silica–zirconia mixed oxides was addressed by X-ray absorption fine structure (XAFS) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The silica materials embedding different amounts of ZrO_2 nanoparticles were prepared by copolymerisation of the organically modified oxozirconium cluster ($\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ (OMc = methacrylate)) with methacryloxypropyltrimethoxysilane (MAPTMS). By the free radical copolymerisation of the oxoclusters bearing 12 methacrylate groups with the methacrylate-functionalised siloxanes, a stable anchoring of the clusters to the silica network was achieved. The thermal treatment of these hybrids at high ($\geq 500^\circ\text{C}$) temperatures yielded the $\text{SiO}_2\text{--ZrO}_2$ mixed oxides. The microstructural evolution upon heating was studied at increasing temperatures, namely 500, 600, 700, 900, 1000 and 1300°C . Furthermore, different samples characterised by different Zr : Si atomic ratios and annealed at 1000°C were comparatively analysed to study the effect of the composition on the evolution of the hybrids to give the mixed oxides. In a third experiment, samples characterised by the same composition were annealed at the same temperature by using either a conventional muffle or a microwave oven in order to evidence whether the different processing could also affect the microstructural features of the final oxide materials. Through XRD and XAFS it was demonstrated that at temperatures above 800°C , crystallisation of tetragonal zirconia occurs in the samples of high zirconium concentration treated in muffle, whereas amorphous oxide materials form upon annealing in microwave oven. The presence of zirconia nanoclusters having an average size of 5–10 nm was evidenced by TEM.

1. Introduction

The understanding of the properties of nanocomposite materials requires a careful characterisation not only of their composition and microstructure, but also a deep comprehension of their crystallisation behaviour and of the nucleation and growth steps leading to the formation of the nanostructure. This information is a valuable starting point for the following establishment of structure–property relationships and for a better understanding of their stability. Only once these critical stages of inorganic solid crystallisation and the main phenomena occurring on both the nano- and the microscale have been unraveled, the improvement and the tuning of their properties would become possible. Since these changes occur, at different time domains, over the *molecular* (local coordination, chemical environment), *nanoscopic* (nucleation of primary units) and *microscale* (growth of

crystallites) levels, thus involving different length scales, their investigation by using a single technique can hardly provide all the information on the different size regimes to get an overall insight into the evolution of the system. As a consequence, the key stages of these events can be followed and studied only by combining complementary techniques providing mutually integrating and consistent pieces of information on the system at different size scales.

To this aim, in this study, we addressed the structural investigation of our binary oxide systems by using XAFS, XRD and TEM methods, covering different length scales, which were set to follow the evolution of the mixed oxides from the nucleation of the first seeds to the complete crystallisation of tetragonal zirconia nanoparticles dispersed in the silica matrix.

A combined analytical approach to the study of crystallisation in inorganic solids has been already proposed by several authors and, more recently, Weckhuysen *et al.*¹ have pioneered a combined SAXS–WAXS–XAFS setup to carry out time-resolved studies on the crystallisation path of zinc-substituted aluminiumphosphates.

With respect to these previous studies, we faced the study of the nucleation, growth and crystallisation behaviour of zirconia nanoparticles in a silica matrix also by investigating the effect of

^aCNR–ISTM, Dipartimento di Scienze Chimiche, Università di Padova, and INSTM UdR Padova, via Marzolo, 1, 35131 Padova, Italy. E-mail: silvia.gross@unipd.it

^bInstitut für Physikal. Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

^cPhysikalisch-Chemisches-Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

the different experimental parameters involved ((i) composition, (ii) temperature of annealing and (iii) type of thermal processing) on the evolution of the systems and on their final structural features.

The studied system is a well known one, and the interest devoted to the binary zirconia–silica mixed oxides can be traced back to its unusual thermal, mechanical and chemical properties.² The incorporation of ZrO₂ into glass and ceramic materials strongly improves their properties and addition of few percent of zirconia to silica has been reported to remarkably increase the resistance to alkaline attack.³ Zirconia–silica systems have been envisioned also as catalysts or catalyst supports⁴ as well as structural materials and materials with enhanced physico-chemical properties (high thermal, chemical stability or fracture toughness).⁵ The refractive index,² the chemical resistance to alkaline conditions⁶ as well as the strength and the hardness of these binary systems increase with increasing ZrO₂ amount.² For all these applications, and especially for the catalytic ones, the atomic intermixing of the components and the absence of phase separation are important requirements to be met. These mixed systems are difficult to prepare by conventional melting–quenching methods, due to the very high temperatures required.⁷ Furthermore, as already extensively reported, synthesis and processing affect structure and crystallisation behaviour both in pure metal oxide materials⁸ as well as in binary xerogels.⁹

In many previous works, these binary systems have been obtained by a conventional sol–gel procedure starting from the corresponding alkoxides^{8–10} and by chemical solution deposition.¹¹ A route yielding a strong chemical bond among the components is, however, highly desirable and can instead enable the enhancement of the stability and the control of the composition of the material, the microstructure and the mutual arrangements of the building blocks, and consequently the features, the performances and the stability of the final oxide system.

As already outlined, the investigation at a molecular level of the microstructural evolution of these composite materials and of the mechanisms leading to their crystallisation is of primary concern for the improvement of these materials and of their synthesis routes. In this regard, Mountjoy and co-workers have extensively used XAFS to investigate a wide plethora of binary xerogels based on mixed oxides like zirconia–silica,^{10a,b} tantala–silica,¹² titania–silica¹³ and also ternary systems like zirconia–silica–titania.¹⁴ By using EXAFS, structural comparisons among the atomic structure of different binary oxides (zirconia–silica, hafnia–silica, titania–silica) were also carried out.^{10a} EXAFS has already been extensively used to investigate the local structure,¹⁵ the static and thermal distortions¹⁶ and the effect of doping of different zirconia polymorphs.¹⁷

In this work, inorganic–organic hybrid materials, in which the metal oxide precursor, the zirconium oxocluster Zr₄O₂(OMc)₁₂, is homogeneously polymerised together with a silane (MAPTMS) bearing a methacrylate (OMc) group, were conveniently used as “composite precursors” for the preparation, upon calcination, of binary oxide systems of the type ZrO₂–SiO₂, in which the guest metal oxide is evenly dispersed in the silica matrix, as elsewhere extensively described.^{18,19} In the previous studies, it was evidenced that the properties of these binary systems are strongly affected by the composition, by the

microstructure and by the degree of mixing of the two oxide components.

In particular, in this study, the effect (i) of the temperature of annealing (500–1000 °C), (ii) of the different compositions (Zr : Si = 1 : 1.3, 1 : 2.5, 1 : 5, 1 : 10, 1 : 20, 1 : 40) and (iii) of the type of thermal processing (either conventional or microwave-assisted) on the microstructural features of the hybrid materials and on their structural evolution to give the final binary oxide was thoroughly investigated.

The study of so-obtained materials was addressed by XAFS, TEM and XRD which provide information about the different microstructural features induced by the variation of the experimental parameters at different size ranges.

With respect to our previous studies and in particular to that reported in ref. 18, it should be underlined that the focus of the present paper was mostly on the thorough investigation of the effect of selected experimental parameters (Zr : Si molar ratio, annealing temperature and method of annealing) on the formation of a crystalline nanostructure and on the structural evolution at a molecular and nanosize level. In this regard, XAFS, with respect to TEM and XRD, was intended to fill the gap between the nanometre and atomic domains, and to extend the investigation of the nanostructure formation down to the atomic/molecular level. The effort was here devoted to the combination of the results yielded by the three analytical methods to build a more detailed and reliable picture of the addressed systems. In this framework, XRD and TEM results, although partially already published, were reconsidered here as data to be complemented by XAFS results.

Beyond the practical interest and applications of these mixed oxide materials, which have been discussed in ref. 18,19 and 22, the aim of the present work was, on a more fundamental level, to shed light on the crystallisation and the microstructural behaviour of these nanocomposite systems on different length scales. Nevertheless, this combined study was also carried out to achieve a better understanding of these points in view of their functional application as catalyst support as well as of a possible structural application as ceramic structural materials.

In fact, X-ray absorption fine structure (XAFS) spectroscopy is a useful method for determining the local structure around a specific atom in disordered systems.²⁰ In a XAFS spectrum two regions can be distinguished: the EXAFS (extended X-ray absorption fine structure) region and the XANES (X-ray absorption near edge structure) region. The EXAFS region provides information about the coordination number, the nature of the scattering atoms surrounding a particular absorbing atom, the interatomic distance between the absorbing atom and the backscattering atoms and the Debye–Waller-like factors (structural disorder) of the different shells. This structural determination of the local structure is limited to a distance given by the mean free path of the photoelectron in the condensed matter, which is between 5 and 10 Å radius from the element. The XANES region provides information about the oxidation state and the coordination geometry of the absorbing atom. These characteristics make XAFS a powerful structural local probe, which does not require a long-range order and which effectively complements the longer range XRD investigations.

The complementary and mutually integrating information (from the point of view of the length scale and of the nature of the

delivered information) provided by the different analytical tools allowed us to follow the progressive conversion of the hybrid materials into amorphous solids and eventually into the crystalline oxide. The composition as well as the temperature of annealing were proven to play a major role in determining the microstructural changes in the binary oxide, whereas remarkable differences were pointed out also by comparing microwave- and conventional muffle-treated samples. This combined study was carried out to achieve a better understanding of their functional applications as catalyst support as well as a possible structural application as ceramic structural materials.

2. Experimental

Chemicals

Methacryloxypropyltrimethoxysilane (MAPTMS), anhydrous tetrahydrofuran, and dibenzoylperoxide, all purchased from Aldrich, were used as received. Zirconium butoxide (80 wt% in BuOH) was purchased from ABCR, Karlsruhe, Germany. Methacrylic acid 99%, purchased from Aldrich, was distilled under reduced pressure. All the chemicals were stored under argon, while the solvents were additionally stored on molecular sieves. The cluster $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ was synthesised by reaction of methacrylic acid with zirconium butoxide according to the previously reported procedure.²¹

Preparation of the starting solution

The investigated materials were prepared as elsewhere reported.¹⁸ The preparation of the samples used for the preparation of the gels is schematically sketched in Fig. 1 and involves three different steps. For experimental details, see ref. 22.

Table 1 summarises the different parameters used for the preparation of the samples, according to the nominal composition of the solution.

The 21 samples, as reported in Table 1, were prepared by varying (i) the Zr cluster : methacryloxysilane molar ratio, (ii) the heating source (conventional muffle or microwave oven) and (iii) the annealing temperature (500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1300 °C). In Table 1 and through the text, the labels ZS indicate specimens prepared by using zirconium (Z) and silicon (S) source, the zirconium oxocluster and the methacryloxysilane, respectively; the numbers hereafter indicate the Zr : Si molar ratio (1 : 1.3, 1 : 2.5, 1 : 5, *etc.*). MF means annealing in a muffle oven, whereas MW means that the heating was carried out in a microwave oven. The final number denotes the annealing temperature. After polymerisation the zirconium-based gels were dried under vacuum at 80 °C for 12 h to remove the residual solvent.

Annealing of the samples

The prepared hybrid materials were subsequently thermally annealed in air at different temperatures (500–1300 °C) to promote the pyrolysis of the organic components of the hybrids and their conversion to the corresponding binary oxides. Each sample was annealed only at one temperature, then quenched to room temperature and analysed. The typical annealing procedure in a conventional muffle oven (Linn High Term VMK 1800)

Fig. 1 Flow chart of the synthesis route. (S. Mascotto, O. Tsetsgee, K. Müller, C. Maccato, B. Smarsly, D. Brandhuber, E. Tondello and S. Gross, *J. Mater. Chem.*, 2007, **17**, 4387–4342, Reproduced by permission of The Royal Society of Chemistry (RSC).)

is characterised by a temperature ramp with a heating rate of 5 °C min⁻¹ to the final value, a plateau of 5 h and a temperature decrease to room temperature. The obtained powders were finely ground by using a Retsch MM200 ball mill (Retsch GmbH, Austria) for 20 min at a frequency of 20 Hz.

The microwave-assisted thermal treatments, which were previously optimised as elsewhere reported,¹⁸ were carried out by using a Milestone MLS-1200 Pyro oven operating at a frequency of 2.45 GHz. The treatments were performed in the presence of SiC susceptor bars. The temperature in the chamber was recorded by using a NiCr alloy-based thermocouple coated with a ceramic layer. The experimental details used for the microwave processing are thoroughly described elsewhere.¹⁸

Materials characterisation

X-Ray diffraction. The XRD data were collected with a Bruker D8 Advance Diffractometer equipped with a Göbel mirror. The angular accuracy was 0.001° and the angular resolution was better than 0.01°. The average crystallite sizes were calculated by means of the Scherrer formula from the most intense peaks of each spectrum.

XAFS analysis. The XANES and EXAFS measurements at the Zr K-edge (17 998 eV) were performed at the beamline X1 of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY in Hamburg, Germany. The samples were measured in transmission mode with a Si(311) double crystal monochromator. The

Table 1 Labeling and experimental parameters for the preparation of the analysed samples

Sample name	Zr : Si molar ratio	Annealing temperature/°C	Type of thermal treatment
ZS1:1.3MF500	1 : 1.3	500	Muffle
ZS1:1.3MF700	1 : 1.3	700	Muffle
ZS1:1.3MF900	1 : 1.3	900	Muffle
ZS1:1.3MF1000	1 : 1.3	1000	Muffle
ZS1:2.5MF800	1 : 2.5	800	Muffle
ZS1:2.5MF 900	1 : 2.5	900	Muffle
ZS1:2.5MF1000	1 : 2.5	1000	Muffle
ZS1:2.5MF1300	1 : 2.5	1300	Muffle
ZS1:5MF600	1 : 5	600	Muffle
ZS1:5MF1000	1 : 5	1000	Muffle
ZS1:5MW600	1 : 5	600	Microwave
ZS1:5MW1000	1 : 5	1000	Microwave
ZS1:10MF1000	1 : 10	1000	Muffle
ZS1:20MF600	1 : 20	600	Muffle
ZS1:20MF1000	1 : 20	1000	Muffle
ZS1:20MW600	1 : 20	600	Microwave
ZS1:20MW1000	1 : 20	1000	Microwave
ZS1:40MF500	1 : 40	500	Muffle
ZS1:40MF700	1 : 40	700	Muffle
ZS1:40MF900	1 : 40	900	Muffle
ZS1:40MF1000	1 : 40	1000	Muffle

sample powders were mixed with polyethylene and pressed into pellets. All experiments were carried out under ambient conditions at 21 °C. Energy calibration was performed with a zirconium metal foil.

Data evaluation started with the removal of background absorption from the experimental spectrum by subtraction of a Victoreen-type polynomial which was fitted to the pre-edge region of the spectrum. This step and also the following normalisation of the spectrum were performed with the program WinXAS.²³ After the normalisation, the program AUTOBK²⁴ was used to remove the post-edge background and to isolate the EXAFS function $\chi(k)$. Curve fitting analysis of the EXAFS function, weighted with k^3 , was performed according to the curved wave formalism of the program EXCURV98 with XALPHA phase and amplitude functions.²⁵ EXCURV98 uses an overall energy shift, E_f , to correct the edge energy E_0 . In all fits E_f was iterated. The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI set to -4.00 eV) and the amplitude reduction factor (AFAC) was fixed at 0.8. The quality of a fit is given in terms of the R -factor which is defined by eqn (1) (in our case the parameter n is equal to 3 since k^3 -weighting was used). The errors of the obtained structural parameters can be estimated as follows: $\pm 1\%$ for distances, $\pm 10\%$ for coordination numbers and Debye–Waller-like factors of shells with $r < 2.5$ Å and $\pm 15\%$ for coordination numbers and Debye–Waller-like factors of shells with $r > 2.5$ Å. Linear combination fits of the XANES spectra were carried out with the program ATHENA.^{26,27}

$$R = \frac{\sum_i |\chi^{\text{calc}}(k_i) - \chi^{\text{exp}}(k_i)| k_i^n}{\sum_i |\chi^{\text{exp}}(k_i)| k_i^n} \times 100\% \quad (1)$$

TEM analysis. TEM micrographs were obtained with a Zeiss EM 912 OMEGA operating at an acceleration voltage of 120 kV.

Samples were ground and suspended in acetone. One drop of the suspension was applied to a carbon-coated 400 mesh copper grid and left to dry.

3. Results and discussion

3.1 Reference samples

Monoclinic and tetragonal ZrO_2 , as well as $\text{Zr}(\text{O}^t\text{Bu})_4$ dissolved in toluene, were firstly studied as structural references for the ZrO_2 – SiO_2 mixed oxides. Table 2 summarises the three references and their structural parameters determined by curve fitting analysis of the EXAFS spectra. For monoclinic and tetragonal ZrO_2 the k^3 -weighted EXAFS spectra and Fourier transform plots are shown in Fig. 3. The EXAFS results of monoclinic and tetragonal ZrO_2 are in good agreement with the crystallographic data (Table 2).

In monoclinic ZrO_2 the zirconium atoms have a $\text{Zr}(\text{O})_7$ coordination characterised by a very broad distribution of bond distances (XRD:²⁸ 2.044, 2.064, 2.135, 2.167, 2.169, 2.254 and 2.269 Å). These oxygen neighbours could be fitted with two shells having coordination numbers of 3 and 4 and average Zr–O distances of 2.10 and 2.23 Å, respectively. The first Zr-shell with a coordination number of 7 was fitted at a distance of 3.46 Å. This is in agreement with the average distance of the first seven Zr neighbours known from XRD²⁸ (3.338 , 2×3.447 , 2×3.462 , 3.478 and 3.573 Å). Two additional Zr-shells with coordination numbers of 4 and 1 could be fitted at distances of 4.01 Å (XRD:²⁸ 2×3.926 and 2×4.017 Å) and 4.56 Å. All in all, monoclinic ZrO_2 can be considered a low-symmetry structure.¹⁵

In tetragonal ZrO_2 the zirconium atoms have a $\text{Zr}(\text{O})_8$ coordination with 4 oxygen neighbours at 2.08 Å and another 4 oxygen atoms at 2.36 Å.²⁸ However, the fitted value of the second oxygen shell is only 2.30 Å. This deviation can be explained by the measurement at room temperature, at which the second oxygen shell is much less resolved than at 10 K.¹⁶ Additionally, a Zr-shell with a coordination number of 12 could be fitted at 3.63 Å (XRD:²⁸ 4×3.592 and 8×3.627 Å).

Table 2 Structural parameters of the reference compounds, tetragonal and monoclinic ZrO_2 and $\text{Zr}(\text{O}^t\text{Bu})_4$ dissolved in toluene, determined from the Zr K-edge EXAFS spectra

Sample	A–Bs ^a	N^{be}	$r^c/\text{Å}$	$r^c/\text{Å}$ XRD ^e	$\sigma^d/\text{Å}$	R -Factor, k -range/ Å^{-1}
Monoclinic ZrO_2	Zr–O	3	2.10	2.08 ^f	0.059	34.52
	Zr–O	4	2.23	2.21 ^f	0.071	3.4–14.0
	Zr–Zr	7	3.46	3.46 ^f	0.092	
	Zr–Zr	4	4.01	3.97 ^f	0.102	
	Zr–Zr	1	4.56	4.54	0.077	
Tetragonal ZrO_2	Zr–O	4	2.10	2.08	0.063	31.98
	Zr–O	4	2.30	2.36	0.092	3.2–14.0
	Zr–Zr	12	3.63	3.62 ^f	0.105	
$\text{Zr}(\text{O}^t\text{Bu})_4$ dissolved in toluene	Zr–O	2	1.97	—	0.045	46.38
	Zr–O	2	2.14	—	0.077	3.4–14.0
	Zr–O	2	2.24	—	0.077	
	Zr–C	2.8	3.07	—	0.081	
	Zr–Zr	1	3.54	—	0.063	
	Zr–C	3.3	3.54	—	0.059	

^a Absorber (A)–backscatters (Bs). ^b Coordination number N .

^c Interatomic distance r . ^d Debye–Waller-like factor σ . ^e The fixed coordination numbers and crystallographic distances for monoclinic and tetragonal ZrO_2 were taken from ref. 28. ^f Averaged values, see text.

The structure of $\text{Zr}(\text{O}^i\text{Bu})_4$ dissolved in toluene is characterised by an octahedral $\text{Zr}(\text{O})_6$ coordination.^{29,30} This oxygen environment could be fitted with three separate shells at 1.97 (coordination number $N = 2$), 2.14 ($N = 2$) and 2.24 Å ($N = 2$). The Zr backscatterer ($N = 1$) at 3.54 Å proves that $\text{Zr}(\text{O}^i\text{Bu})_4$ has a dimeric structure in solution. The coordination numbers of the carbon shells at 3.07 and 3.54 Å were iterated because it is not clear how many and which carbon atoms contribute to these shells.²⁹

The XANES spectra of the three references are shown in Fig. 2. All three references have different shapes at the top of the absorption rise. $\text{Zr}(\text{O}^i\text{Bu})_4$ exhibits a plateau-like shape with a positive slope, which is typical for octahedrally coordinated zirconium.^{9,31–33} Monoclinic ZrO_2 with 7-fold coordination has a white line with a strong negative slope and tetragonal ZrO_2 with 8-fold coordination exhibits a narrower white line with a double peak.^{9,15} Additionally, there is a pre-edge feature at about 18 005 eV corresponding to a $1s \rightarrow 4d$ transition which is only allowed if there is some p–d mixing. The intensity of this transition is stronger in compounds that are distorted from centrosymmetry. Since the $\text{Zr}(\text{O})_8$ geometry in tetragonal ZrO_2 consists of two sets of non-equivalent tetrahedra and because tetrahedral geometries are known to enhance p–d mixing (due to the lack of centrosymmetry), the strongest transition is observed in tetragonal ZrO_2 .¹⁵ For centrosymmetric coordination geometries like in $\text{Zr}(\text{O}^i\text{Bu})_4$ the $1s \rightarrow 4d$ transition is very weak. Furthermore, tetragonal ZrO_2 exhibits a prominent shoulder around 18 049 eV which can be attributed to multiple scattering involving second nearest neighbour atoms or higher shells.⁹

3.2 Effect of the variation of the experimental parameters

3.2.1 Effect of temperature. The first part of the study was devoted to investigate, other conditions being equal, the effect of the annealing temperature on the microstructure of the samples. For this purpose, we analysed two sets of samples with Zr : Si

Fig. 2 Normalised Zr K-edge XANES spectra of the references monoclinic ZrO_2 , tetragonal ZrO_2 and $\text{Zr}(\text{O}^i\text{Bu})_4$ dissolved in toluene. Spectra shifted on the y-axis for clarity.

molar ratios of (a) 1 : 1.3 and (b) 1 : 40 (*i.e.* very concentrated and very diluted binary systems, respectively), which were annealed at temperatures ranging from 500 °C to 1000 °C (Table 3).

Since they are characterised by very different concentrations of ZrO_2 , the two sets of samples are discussed below separately.

The EXAFS spectra of the samples with a Zr : Si molar ratio of 1 : 1.3 are shown in Fig. 3. All spectra were fitted with two oxygen shells and one zirconium shell (Table 3). For the low-temperature sample ZS1:1.3MF500 the oxygen shells were found at distances of 2.09 and 2.23 Å. During the fitting procedure the sum of the oxygen coordination numbers was fixed at the value of 6.6, which was obtained from XANES linear combination fits (see below). In Fig. 3b it can be seen that the oxygen peak of sample ZS1:1.3MF500 is broader than the ones of the high-temperature samples ZS1:1.3MF900 and ZS1:1.3MF1000. Also, there is some similarity between the oxygen peaks of ZS1:1.3MF500 and monoclinic ZrO_2 with its broad distribution of Zr–O distances. This implies a disordered oxygen coordination in the low-temperature sample ZS1:1.3MF500.

Additionally, a Zr-shell with a coordination number of 1.1 could be fitted at a distance of 3.41 Å. This distance is similar to the first Zr–Zr distance (3.46 Å) in monoclinic ZrO_2 (Table 2). Therefore, it can be inferred that there is a similar arrangement of Zr–O–Zr units in ZS1:1.3MF500 and monoclinic ZrO_2 . Furthermore, in the fitting procedure of sample ZS1:1.3MF500 we made the assumption that the Debye–Waller-like factor of the Zr-shell has the same value as the one in monoclinic ZrO_2 . The obtained coordination number of 1.1 for the Zr-shell suggests the presence of Zr–O–Zr dimers dispersed in the SiO_2 framework, probably a first nucleus for the formation of the oxide occurring

Table 3 Effect of the temperature of annealing. EXAFS results are shown for two sets of samples (Zr : Si = 1 : 1.3 and 1 : 40) with annealing temperatures of 500 °C, 700 °C, 900 °C and 1000 °C

Sample	A–Bs ^a	N ^b	r ^c /Å	σ ^d /Å	R-Factor, k-range/Å ^{−1}
ZS1:1.3MF500	Zr–O	2.4	2.09	0.063	31.74
	Zr–O	4.2	2.23	0.092	3.4–14.0
	Zr–Zr	1.1	3.41	0.092	
ZS1:1.3MF700	Zr–O	2.0	2.07	0.059	29.49
	Zr–O	4.6	2.22	0.097	3.4–12.0
	Zr–Zr	1.1	3.40	0.092	
ZS1:1.3MF900	Zr–O	4.0	2.11	0.077	34.35
	Zr–O	4.0	2.30	0.100	3.2–14.0
	Zr–Zr	3.8	3.63	0.105	
ZS1:1.3MF1000	Zr–O	4.0	2.09	0.077	31.21
	Zr–O	4.0	2.29	0.110	3.2–14.0
	Zr–Zr	7.5	3.62	0.105	
ZS1:40MF500	Zr–O	4.1	2.02	0.063	39.67
	Zr–O	2.0	2.23	0.074	3.4–14.0
	Zr–Zr	1.2	3.33	0.092	
ZS1:40MF700	Zr–O	4.6	2.02	0.071	39.83
	Zr–O	1.5	2.25	0.059	3.4–14.0
	Zr–Zr	1.2	3.33	0.092	
ZS1:40MF900	Zr–O	3.6	1.99	0.055	39.63
	Zr–O	2.5	2.17	0.110	3.4–14.0
	Zr–Zr	1.4	3.31	0.092	
ZS1:40MF1000	Zr–O	3.7	1.97	0.067	41.20
	Zr–O	2.3	2.13	0.102	3.4–14.0
	Zr–Zr	1.2	3.29	0.092	

^a Absorber (A)–backscatterers (Bs). ^b Coordination number N . ^c Interatomic distance r . ^d Debye–Waller-like factor σ .

Fig. 3 Experimental (solid line) and calculated (dotted line) EXAFS functions (a) and their Fourier transforms (b) of the samples with a Zr : Si molar ratio of 1 : 1.3 along with the references monoclinic and tetragonal ZrO_2 , measured at the Zr K-edge. Spectra shifted on the y-axis for clarity.

at higher temperature. It should be mentioned that, apart from Zr–O–Zr and Zr–O–H bonds, also Zr–O–Si bonds are expected in the mixed oxide materials. However, an additional Si-shell could not be fitted in a reliable way to the second peak in the Fourier transform. This can be explained with the weak back-scattering amplitude of silicon in combination with a broad distribution of Zr–Si distances.⁹ Sample ZS1:1.3MF700 was fitted with the same procedure as sample ZS1:1.3MF500.

The two high-temperature samples ZS1:1.3MF900 and ZS1:1.3MF1000 exhibit a Zr-shell at a distance of about 3.63 Å, which is typical of tetragonal ZrO_2 (Table 3). Accordingly, the Debye–Waller-like factors of the Zr-shells were fixed at the value of the tetragonal reference during fitting. Also, the coordination numbers of the two oxygen shells were kept fixed at 4, according to a local structure similar to tetragonal ZrO_2 . The obtained Zr–O distances are in good agreement with the tetragonal reference. For ZS1:1.3MF900 and ZS1:1.3MF1000 the coordination numbers of the Zr-shells ($N = 3.8$ and 7.5) are smaller than in tetragonal ZrO_2 ($N = 12$) and increase with increasing annealing temperature. This behaviour can be explained with the presence of phase-separated ZrO_2 domains which grow in size and become more crystalline with increasing temperature due to further condensation and to the removal of remaining organic moieties.

The XANES spectra of the samples with a Zr : Si molar ratio of 1 : 1.3 are shown in Fig. 4a. The samples ZS1:1.3MF500 and ZS1:1.3MF700 have a plateau-shaped white line with a slightly negative slope. These XANES spectra were analysed with the empirical model that the zirconium atoms are present in two different coordination sites: one fraction having a $\text{Zr}(\text{O})_7$ coordination similar to monoclinic ZrO_2 and the remainder having a $\text{Zr}(\text{O})_6$ coordination similar to $\text{Zr}(\text{O}^i\text{Bu})_4$. Accordingly, the spectra were fitted with a linear combination of the XANES spectra of monoclinic ZrO_2 and $\text{Zr}(\text{O}^i\text{Bu})_4$ (Fig. 4a). The plots overlay reasonably well. The obtained fractions of zirconium atoms in $\text{Zr}(\text{O})_7$ and $\text{Zr}(\text{O})_6$ coordination sites are reported in Table 4. In the samples ZS1:1.3MF500 and ZS1:1.3MF700

Fig. 4 Normalised Zr K-edge XANES spectra of the samples with a Zr : Si molar ratio of 1 : 1.3 (a) and 1 : 40 (b). The dotted lines depict the results of the XANES linear combination fits. These fits were obtained by fitting the sample spectra with a linear combination of the XANES spectra of monoclinic ZrO_2 and $\text{Zr}(\text{O}^i\text{Bu})_4$. Spectra shifted on the y-axis for clarity.

about 64% of the zirconium atoms have a $\text{Zr}(\text{O})_7$ coordination similar to monoclinic ZrO_2 . The fractions (f) of monoclinic ZrO_2 -like sites and $\text{Zr}(\text{O}^i\text{Bu})_4$ -like sites were also used to calculate the average oxygen coordination numbers N_{LC} (eqn (2), Table 4). These values were used in the EXAFS analysis. For example, the sum of the coordination numbers of the two oxygen shells in sample ZS1:1.3MF500 was kept fixed at 6.6 in the fitting procedure.

$$N_{\text{LC}} = f(\text{m-ZrO}_2) \times 7 + f(\text{Zr}(\text{O}^i\text{Bu})_4) \times 6 \quad (2)$$

For the high-temperature samples ZS1:1.3MF900 and ZS1:1.3MF1000 the EXAFS results proved the presence of tetragonal ZrO_2 domains. This is also confirmed by the XANES spectra. They exhibit a narrower white line, a stronger $1s \rightarrow 4d$ transition than in the low-temperature samples and a shoulder at 18 049 eV in agreement with tetragonal ZrO_2 .

The EXAFS results were also confirmed by XRD and TEM analyses carried out on slightly less concentrated samples (*i.e.* Zr : Si 1 : 2.5) annealed at different temperatures, *i.e.* 800 °C, 900 °C, 1000 °C, and 1300 °C. By comparing the XRD diffractograms

Table 4 Results of the XANES linear combination fits. XANES spectra of the samples were fitted with a linear combination of the XANES spectra of monoclinic ZrO_2 and $\text{Zr}(\text{O}^i\text{Bu})_4$

Sample	$f(\text{m-ZrO}_2)^a$	$f(\text{Zr}(\text{O}^i\text{Bu})_4)^b$	N_{LC}^c
ZS1:1.3MF500	0.65	0.35	6.6
ZS1:1.3MF700	0.62	0.38	6.6
ZS1:5MF600	0.56	0.44	6.6
ZS1:5MW600	0.57	0.43	6.6
ZS1:5MW1000	0.64	0.36	6.6
ZS1:20MF600	0.21	0.79	6.2
ZS1:20MW600	0.23	0.77	6.2
ZS1:20MW1000	0.33	0.67	6.3
ZS1:40MF500	0.11	0.89	6.1
ZS1:40MF700	0.11	0.89	6.1
ZS1:40MF900	0.07	0.93	6.1
ZS1:40MF1000	0.02	0.98	6.0

^a Fraction of Zr in sites with local geometry similar to monoclinic ZrO_2 .

^b Fraction of Zr in sites with local geometry similar to $\text{Zr}(\text{O}^i\text{Bu})_4$.

^c Oxygen coordination number calculated using eqn (2).

(Fig. 5), it can be observed that the samples at lower temperatures (800 °C) show a completely amorphous pattern, whereas as the temperature increases, the features become gradually more defined and sharp. At 1300 °C, the reflections typical of tetragonal zirconia could be well recognised and indexed.

The evolution from a starting amorphous material to finely dispersed zirconia nanoparticles in silica as a function of increasing annealing temperature could also be evidenced by TEM analyses. Fig. 6 shows the TEM micrographs of three Zr : Si 1 : 2.5 samples which were annealed at 800 °C, 900 °C and 1000 °C. There is no evidence of cluster formation for the sample treated at 800 °C, at least in the size regime accessible by electron microscopy. The formation of well dispersed nanoparticles having diameters of about 5–10 nm could be detected in the sample treated at 900 °C, which become more defined and sharper in the same sample after annealing at 1000 °C.

In summary, the structure of the mixed oxides with a high Zr : Si molar ratio (1 : 1.3, 1 : 2.5) depends strongly on the thermal treatment. At annealing temperatures of 500 °C and 700 °C the zirconium atoms are present as Zr–O–Zr dimers dispersed in the SiO₂ framework and their coordination geometry is similar to monoclinic ZrO₂. At annealing temperatures of 900 °C and 1000 °C phase-separated domains of tetragonal ZrO₂ are formed, which become detectable also with TEM and XRD. These domains become bigger and more crystalline with increasing annealing temperature.

It can be inferred that, at lower temperatures, zirconium oxide nuclei start to aggregate, but they do not reach the critical size to crystallise (also due to their dilution in silica), whereas the higher temperatures of annealing promote their mobility inside the silica matrix to give larger aggregates which then crystallise. It is likely that at intermediate temperatures (700 °C < *T* < 900 °C) crystallites are formed, which have, however, a size lower than the detection limits of XRD (about 3–4 nm) and conventional TEM

Fig. 5 Diffraction patterns of the Zr : Si 1 : 2.5 samples annealed at 800, 900, 1000 and 1300 °C. (S. Mascotto, O. Tsetsgee, K. Müller, C. Maccato, B. Smarsly, D. Brandhuber, E. Tondello and S. Gross, *J. Mater. Chem.*, 2007, **17**, 4331–4342, Reproduced by permission of The Royal Society of Chemistry (RSC).)

Fig. 6 TEM micrographs of the Zr : Si 1 : 2.5 samples annealed at 800 (a), 900 (b) and 1000 °C (c).

(1–2 nm). In this intermediate spatial range, in which other methods are “blind”, the contribution of EXAFS in providing short range information becomes pivotal to follow the structural evolution of these systems.

As previously described, formation of tetragonal zirconia instead of the expected monoclinic polymorph was observed,

which can be ascribed to the dispersion of zirconia into a silica matrix. The observed behaviour can be explained by considering the phase diagram of ZrO_2 . Zirconium dioxide (zirconia) occurs in three different modifications, namely monoclinic (stable up to 1000 °C), tetragonal (stable above 1000 °C) and cubic (stable above 2300 °C).³⁴ Under normal conditions, the thermodynamically stable phase up to 1000 °C is the monoclinic one. A metastable tetragonal phase may be present in pure zirconium dioxide when non-equilibrium techniques of synthesis³⁵ are used. Furthermore, “dilution” of zirconia into silica was reported to remarkably increase the crystallisation temperature of tetragonal zirconia and also to increase the temperature at which the transformation from tetragonal to monoclinic zirconia takes place.¹¹ Terry *et al.*^{36a} argued that the initial formation of tetragonal zirconia instead of the thermodynamically expected monoclinic form can be traced back not only to surface and strain energies, but also to a hindered tetragonal to monoclinic transformation which, being slightly displacing (3–5% by volume), can be inhibited whenever zirconia is mixed with silica. As a consequence, this increase in the crystallisation temperature with respect to pure zirconia can in turn be related to the homogeneous distribution of zirconia in the silica network.

In fact the crystallisation of zirconia requires diffusion and grain growth, which is more difficult whenever zirconia is mixed with another oxide, in this case silicon dioxide. This hindered grain growth is particularly evident in more diluted samples. The existence of this correlation seems to be proven by a decrease in the rate of grain growth for tetragonal zirconia with a decreasing ZrO_2 concentration.

A completely different crystallisation behaviour was observed for the samples characterised by a low amount of zirconia, *i.e.* Zr : Si 1 : 40. The XANES spectra of the 1 : 40 samples look different than the 1 : 1.3 ones (Fig. 4b). The white lines exhibit a positive slope and are very similar to the XANES spectrum of $\text{Zr}(\text{O}^t\text{Bu})_4$, indicating a $\text{Zr}(\text{O})_6$ coordination. This was also verified by the XANES linear combination fits which yield average oxygen coordination numbers of about 6.1 (Table 4). The high-temperature samples ZS1:40MF900 and ZS1:40MF1000 show very strong $1s \rightarrow 4d$ transitions which are even more intense than in tetragonal ZrO_2 . This indicates an increasing distortion of the $\text{Zr}(\text{O})_6$ octahedra with increasing annealing temperature.⁹ However, it should also be mentioned that in the literature such a strong $1s \rightarrow 4d$ transition has also been interpreted as an indication for tetrahedral coordination.^{37,38}

In the EXAFS analysis the sum of the oxygen coordination numbers was fixed at the values obtained from the XANES linear combination fits. Additionally, the Debye–Waller-like factors of the Zr-shells were fixed at the value of monoclinic ZrO_2 . This resulted in good fits to the data (Fig. 7). The obtained Zr–O distances of the first oxygen shells have values of 2.02, 1.99 and 1.97 Å and are smaller than the corresponding values of the samples with a Zr : Si ratio of 1 : 1.3. This is in agreement with the reduced 6-fold oxygen coordination in comparison to the 7- or 8-fold coordination of the 1 : 1.3 samples. Similarly, the obtained Zr–Zr distances (3.33, 3.31 and 3.29 Å) are also smaller than the distances found in the samples ZS1:1.3MF500 and ZS1:1.3MF700. For all samples the coordination number of the Zr-shell is about 1.2, which indicates the presence of Zr–O–Zr

Fig. 7 Experimental (solid line) and calculated (dotted line) EXAFS functions (a) and their Fourier transforms (b) of the samples with a Zr : Si molar ratio of 1 : 40, measured at the Zr K-edge. Spectra shifted on the y-axis for clarity.

dimers. There is no formation of phase-separated ZrO_2 domains with increasing annealing temperature. This can be explained with the strong dilution of the zirconium atoms inside the silica due to the Zr : Si molar ratio of 1 : 40.

For these highly diluted samples also XRD and TEM analyses did not show any formation of crystalline zirconia. In agreement with the previously described hypothesis, it can be argued that in this case, due to the high dilution of zirconia nuclei in silica, they do not reach, even at higher temperature, the critical size to produce ordered structure. This is particularly evident in the lower Zr–Zr coordination number observed (1.2) in sample ZS1:40MF1000 with respect to the more concentrated sample ZS1:1.3MF1000 at the same temperature (7.5).

3.2.2 Effect of composition. In order to determine the influence of the composition on the structure of the ZrO_2 – SiO_2 mixed oxides, we analysed six samples with varying Zr : Si molar ratios (1 : 1.3, 1 : 2.5, 1 : 5, 1 : 10, 1 : 20 and 1 : 40) and a common annealing temperature of 1000 °C (Table 5). All these samples, except ZS1:40MF1000, exhibit XANES spectra similar to tetragonal ZrO_2 (Fig. 8), indicating an 8-fold oxygen coordination. However, the typical features of tetragonal ZrO_2 (white line with double peak, shoulder at 18 049 eV) become less pronounced with decreasing zirconium concentration. This is in agreement with the previously reported results (see Section 3.2.1), indicating that, other conditions being equal (high temperature of annealing), the composition and in particular the amount of zirconia dispersed in the silica matrix play a major role in determining the occurrence of crystallisation. Sample ZS1:40MF1000 with the lowest zirconium concentration is not 8-fold coordinated like the other samples but has a distorted octahedral $\text{Zr}(\text{O})_6$ coordination (see above).

The EXAFS fits of the samples with Zr : Si molar ratios ranging from 1 : 1.3 to 1 : 20 yield Zr–Zr distances of about 3.62 Å, which confirms the local structure similar to tetragonal ZrO_2 (Table 5). Also, the coordination numbers of the Zr-shells increase with increasing zirconium content of the samples (Fig. 9). This indicates that the domains of tetragonal ZrO_2 are bigger and more crystalline in the samples with high zirconium content, in agreement with the XANES results. Sample ZS1:40MF1000 contains only Zr–O–Zr dimers and no crystalline ZrO_2 domains.

Table 5 Effect of composition. EXAFS results for samples with Zr : Si molar ratios of 1 : 1.3, 1 : 2.5, 1 : 5, 1 : 10, 1 : 20 and 1 : 40 and with a common annealing temperature of 1000 °C

Sample	A–Bs ^a	N ^b	r ^c /Å	σ ^d /Å	R-Factor, k-range/Å ⁻¹
ZS1:1.3MF1000	Zr–O	4.0	2.09	0.077	31.21
	Zr–O	4.0	2.29	0.110	3.2–14.0
	Zr–Zr	7.5	3.62	0.105	
ZS1:2.5MF1000	Zr–O	4.0	2.09	0.067	31.33
	Zr–O	4.0	2.28	0.100	3.2–14.0
	Zr–Zr	8.6	3.62	0.105	
ZS1:5MF1000	Zr–O	4.0	2.10	0.077	27.27
	Zr–O	4.0	2.29	0.102	3.2–14.0
	Zr–Zr	5.7	3.63	0.105	
ZS1:10MF1000	Zr–O	4.0	2.10	0.084	33.31
	Zr–O	4.0	2.29	0.102	3.2–14.0
	Zr–Zr	2.4	3.62	0.089 ^e	
ZS1:20MF1000	Zr–O	4.0	2.09	0.097	33.70
	Zr–O	4.0	2.28	0.110	3.2–14.0
	Zr–Zr	2.2	3.62	0.105	
ZS1:40MF1000	Zr–O	3.7	1.97	0.067	41.20
	Zr–O	2.3	2.13	0.102	3.4–14.0
	Zr–Zr	1.2	3.29	0.092	

^a Absorber (A)–backscatterers (Bs). ^b Coordination number *N*. ^c Interatomic distance *r*. ^d Debye–Waller-like factor *σ*. ^e *σ* was iterated and not fixed like for the other samples.

Fig. 8 Normalised Zr K-edge XANES spectra of the samples annealed at 1000 °C. Spectra shifted on the y-axis for clarity.

The XRD patterns of these samples (data not shown, see ref. 18) evidence that the samples become more crystalline as the zirconia concentration increases.

3.2.3 Effect of the type of thermal treatment. The effect of microwave annealing was studied by comparing samples which were annealed (at the same temperature) either in a conventional muffle or in a microwave oven. In particular, eight samples with

Fig. 9 Experimental (solid line) and calculated (dotted line) EXAFS functions (a) and their Fourier transforms (b) of the samples annealed at 1000 °C, measured at the Zr K-edge. Spectra shifted on the y-axis for clarity.

Zr : Si molar ratios of 1 : 5 and 1 : 20 and annealing temperatures of 600 °C and 1000 °C were analysed (Table 6). At an annealing temperature of 600 °C, a difference between samples which were annealed in a muffle or in a microwave oven could hardly be recognised. At temperatures lower than 800 °C, as already evidenced in Section 3.2.1, crystallisation of zirconia in silica does not occur. For example, samples ZS1:5MF600 and ZS1:5MW600 exhibit the same coordination numbers and interatomic distances. Therefore, both samples have the same local structure which is very similar to sample ZS1:1.3MF500 (see above). The zirconium atoms are mainly present as Zr–O–Zr dimers with coordination geometries similar to monoclinic ZrO₂. Also, samples ZS1:20MF600 and ZS1:20MW600 have almost identical structural parameters. Due to the stronger dilution of the zirconium atoms in the silica matrix the coordination environment is very similar to sample ZS1:40MF500 (see above).

Table 6 Effect of the type of thermal treatment. EXAFS results are shown for pairs of samples with the same annealing temperature and Zr : Si molar ratio but with different types of thermal treatment (muffle oven or microwave oven)

Muffle oven samples	A–Bs ^a			Microwave oven samples	A–Bs ^a		
	N ^b	r ^c /Å			N ^b	r ^c /Å	
ZS1:5MF600	Zr–O	1.7	2.05	ZS1:5MW600	Zr–O	1.7	2.04
	Zr–O	4.9	2.21		Zr–O	4.9	2.20
	Zr–Zr	0.9	3.40		Zr–Zr	0.9	3.38
ZS1:5MF1000	Zr–O	4.0	2.10	ZS1:5MW1000	Zr–O	2.6	2.07
	Zr–O	4.0	2.29		Zr–O	4.0	2.22
	Zr–Zr	5.7	3.63		Zr–Zr	0.8	3.38
ZS1:20MF600	Zr–O	2.7	2.02	ZS1:20MW600	Zr–O	2.9	2.03
	Zr–O	3.5	2.21		Zr–O	3.3	2.21
	Zr–Zr	1.1	3.34		Zr–Zr	1.1	3.35
ZS1:20MF1000	Zr–O	4.0	2.09	ZS1:20MW1000	Zr–O	3.8	2.04
	Zr–O	4.0	2.28		Zr–O	2.5	2.24
	Zr–Zr	2.2	3.62		Zr–Zr	0.9	3.33

^a Absorber (A)–backscatterers (Bs). ^b Coordination number *N*. ^c Interatomic distance *r*.

However, the muffle and microwave samples differ significantly upon annealing at 1000 °C. The muffle treated samples ZS1:5MF1000 and ZS1:20MF1000 show Zr–Zr distances typical of tetragonal ZrO₂ and also an increase of the zirconium coordination numbers. Thus, as already seen above, the annealing treatment in the muffle oven causes the formation of phase-separated tetragonal ZrO₂ domains. This is not the case for the microwave annealed materials. The local structures of samples ZS1:5MW1000 and ZS1:20MW1000 are hardly different from the corresponding samples annealed at 600 °C. The zirconium atoms remain well dispersed in the silica matrix and there is no formation of tetragonal ZrO₂ domains. Therefore, the annealing treatment in the microwave oven causes a completely different crystallisation behaviour. This result can be explained with both a shorter annealing time of the microwave samples (microwave: 1 h; muffle: 5 h) and with a different mechanism of heat transfer.

Accordingly, the XRD patterns and TEM micrographs (data not shown) of the samples treated by microwaves, irrespective of the temperature, are completely featureless.

Here, the data obtained by XRD and TEM could be effectively strengthened and complemented by the XAFS data.

4. Conclusions

In this work, the crystallisation behaviour of zirconium oxide nanoparticles dispersed in silica matrix was studied as a function of different (i) annealing temperatures, (ii) composition and (iii) thermal processing methods. This study was addressed by the combined use of different analytical tools, namely XAFS, XRD and TEM providing mutually integrating and complementary information on different length scales.

In order to study the effect of the annealing temperature on the final structure of the materials two sets of samples with Zr : Si molar ratios of 1 : 1.3 and 1 : 40 and different annealing temperatures were analysed by means of XAFS spectroscopy.

Also, the influence of the composition on the structure of the mixed oxides was studied. The effect of microwave annealing on the structure of the materials was further investigated by comparing samples which were annealed either in a conventional muffle or in a microwave oven. Here, the muffle treated samples exhibit crystalline tetragonal ZrO₂ domains, whereas the microwave treated samples retain a more disordered local structure similar to the samples annealed at 600 °C. These differences can be explained with both a shorter annealing time of the microwave samples and with a different mechanism of heat transfer, as already extensively discussed.¹⁸

Taken together, these results show that the delayed crystallisation of zirconia in silica requires high temperatures and high amounts of zirconia to start. The starting formation of Zr–O–Zr dimers further evolves, likely through coalescence and aggregation events, to give bigger aggregates which then crystallise. The formation of crystalline zirconia clusters is evidenced by TEM and XRD to occur in the more concentrated samples (1 : 20 < Zr : Si < 1 : 1.3) between 800 °C and 900 °C, and EXAFS does not show any crystalline ordering at 700 °C. This means that the crystallisation occurs at temperatures higher than 700 °C, but it is complete already at 900 °C. The fact that in the case of diluted samples (Zr : Si 1 : 40), even at high temperatures, no formation of crystalline aggregates was observed confirms that the growth

of the nuclei requires diffusion of matter through the host material, which is in this latter case hampered by the low amount of zirconia. In the case of microwave treatment, even for higher amounts of zirconia and high annealing temperatures, no crystallisation was observed.

As already reported,^{18,19} the remarkable different features observed in the microstructure of the samples can be ascribed to the different annealing paths promoted by microwaves.^{39,40}

In this case, it can be argued that the more uniform heating of the hybrid materials enables a different decomposition path for the organic parts of the hybrid to give the final oxides. The increased rate of reaction, leading to the oxide in a much shorter time than in the case of the muffle oven, could also explain the absence of crystalline phases, whose formation requires probably a longer time for the growth of the initially nucleated oxide “seeds”.

In this framework, XAFS allowed us to investigate at a lower length scale (subnanometric range) the formation of the first crystallisation nuclei, to unravel the first ordering steps leading to crystallisation of the material and to follow its evolution up to a size domain which can be investigated by TEM and XRD.

This combined study was also useful to achieve a better understanding of the microstructural behaviour under annealing of these materials, which have already shown their potentialities not only as functional materials (catalysis and catalyst support), but also as structural ceramic materials. In this context, the knowledge of the correlations between experimental parameters and the formation/presence/evolution of a crystalline phase is of pivotal importance to appropriately use these materials.

In a more general perspective, this work has evidenced that the rational combination of different analytical tools, yielding information over different length scales, can represent a powerful approach to the elucidation of structural changes and phenomena occurring at the nano- and even molecular scale, which eventually lead to the occurrence of a “macroscopic” event such as crystallisation. The interplay and complementarities among different analytical methods in the characterisation of crystalline materials have already been the topics of different investigations^{41–43} and here a further proof of an effective combination of different tools was provided. Furthermore, the evolution of the local environment of Zr in inorganic–organic hybrid materials, although investigated with different methods, has been the topic of two further contributions by Ribeiro *et al.*^{44,45}

Acknowledgements

F. Meneghetti gratefully thanks the University of Padova and the European Union for the awarding of a Erasmus-Socrates Grant for a research period at the University of Stuttgart, Germany. The National Research Council (CNR), Italy and the Deutsche Forschungsgemeinschaft (DFG), Germany are acknowledged for their financial support. We thank the Italian Rectors Conference (CRUI) and the Ateneo Italo-Tedesco, Rome, Italy and Deutsche Akademische Austauschdienst (DAAD), Bonn, Germany, for funding of the researchers mobility in the framework of a Vigoni Programme. S. Gross gratefully thanks Mr Antonio Ravazzolo for his skilful technical

support and the Deutsche Akademische Austauschdienst (DAAD), Bonn, Germany, for the awarding of a DAAD grant to finance a research period in Germany. We finally thank HASYLAB at DESY, Hamburg, for the provision of synchrotron radiation for XAFS measurements.

References

- 1 A. M. Beale, A. M. J. van der Eerden, S. D. M. Jacques, O. Leynaud, M. G. O'Brien, F. Meneau, S. Nikitewko, W. Ras and B. M. Weckhuysen, *J. Am. Chem. Soc.*, 2006, **128**, 12386–12387.
- 2 M. Nogami, *J. Non-Cryst. Solids*, 1985, **69**, 415–423.
- 3 A. Paul, *Chemistry of Glasses*, Chapman and Hall, London, 1982.
- 4 (a) M. Itoh, H. Hattori and K. J. Tanabe, *J. Catal.*, 1974, **35**, 225; (b) J. B. Miller and E. I. Ko, *J. Catal.*, 1996, **159**, 58; (c) H. J. M. Bosman, E. C. Kruissink, J. Vanderspoel and F. Vandenbrink, *J. Catal.*, 1994, **148**, 660; (d) Z. Feng, W. S. Postula, C. Erkey, C. V. Philip, A. Akgerman and R. G. Anthony, *J. Catal.*, 1994, **148**, 84.
- 5 R. G. Simhan, *J. Non-Cryst. Solids*, 1983, **54**, 335.
- 6 K. Kamiya, S. Sakka and Y. Tatemichi, *J. Mater. Sci.*, 1980, **15**, 1765.
- 7 A. M. Evans, J. P. H. Williamson and F. P. Glasser, *J. Mater. Sci.*, 1980, **15**, 2325.
- 8 A. V. Chadwick, G. Mountjoy, V. M. Nield, J. F. Poplett, M. E. Smith, J. H. Strange and M. G. Tucker, *Chem. Mater.*, 2001, **13**, 1219.
- 9 G. Mountjoy, D. M. Pickup, R. Anderson, G. Wallidge, M. A. Holland, R. J. Newport and M. E. Smith, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2455.
- 10 (a) G. Mountjoy, M. A. Holland, P. Gunawidjaja, W. D. Wallidge, M. Pickup, R. J. Newport and M. E. Smith, *J. Sol–Gel Sci. Technol.*, 2003, **26**, 161, and references therein; (b) G. Mountjoy, R. Anderson, R. J. Newport and M. E. Smith, *J. Phys.: Condens. Matter*, 2000, **12**, 3505; (c) G. Mountjoy, D. M. Pickup, G. Wallidge, R. Anderson, J. M. Cole, M. E. Smith and R. J. Newport, *Chem. Mater.*, 1999, **11**, 1253; (d) G. Mountjoy, M. A. Holland, G. Wallidge, P. Gunawidjaja, M. E. Smith, D. M. Pickup and R. J. Newport, *J. Phys. Chem. B*, 2003, **107**, 7557; (e) Z. Zhan and H. C. Zeng, *J. Non-Cryst. Solids*, 1999, **243**, 26, and references therein; (f) J. B. Miller and E. I. Ko, *Catal. Today*, 1997, **35**, 269.
- 11 D. A. Neumayer and E. Cartier, *J. Appl. Phys.*, 2001, **90**, 1801.
- 12 G. Mountjoy, M. A. Holland, G. Wallidge, R. J. Newport and M. E. Smith, *J. Mater. Chem.*, 2000, **10**, 1887.
- 13 (a) D. M. Pickup, G. Mountjoy, M. A. Holland, G. Wallidge, R. J. Newport and M. E. Smith, *J. Phys.: Condens. Matter*, 2000, **12**, 9751; (b) R. Anderson, G. Mountjoy, M. E. Smith and R. J. Newport, *J. Non-Cryst. Solids*, 1998, **234**, 72.
- 14 (a) G. Mountjoy, M. A. Holland, G. Wallidge, P. Gunawidjaja, M. E. Smith, D. M. Pickup and R. J. Newport, *J. Phys. Chem. B*, 2003, **107**, 7557; (b) G. Mountjoy, M. A. Holland, P. Gunawidjaja, D. M. Pickup, G. Wallidge, M. E. Smith and R. J. Newport, *J. Sol–Gel Sci. Technol.*, 2003, **26**, 137.
- 15 P. Li, I.-W. Chen and J. E. Penner-Hahn, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 10063.
- 16 P. Li, I.-W. Chen and J. E. Penner-Hahn, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 10082.
- 17 P. Li, I.-W. Chen and J. E. Penner-Hahn, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 10074.
- 18 S. Mascotto, O. Tsetsgee, K. Müller, C. Maccato, B. Smarsly, D. Brandhuber, E. Tondello and S. Gross, *J. Mater. Chem.*, 2007, **17**, 4387–4399.
- 19 M. M. Natile, A. Galenda, A. Glisenti, S. Mascotto and S. Gross, *J. Non-Cryst. Solids*, 2009, **355**, 481–487.
- 20 H. Bertagnolli and T. S. Ertel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 45.
- 21 G. Trimmel, S. Gross, G. Kickelbick and U. Schubert, *Appl. Organomet. Chem.*, 2001, **15**, 410.
- 22 L. Armelao, H. Bertagnolli, S. Gross, V. Krishnan, U. Lavrencic-Stangar, K. Müller, B. Orel, G. Srinivasan, E. Tondello and A. Zattin, *J. Mater. Chem.*, 2005, **15**, 1954–1965; L. Armelao, S. Gross, K. Müller, G. Pace, E. Tondello, O. Tsetsgee and A. Zattin, *Chem. Mater.*, 2006, **18**, 6019–6030.
- 23 T. Ressler, *J. Synchrotron Radiat.*, 1998, **5**, 118–122.
- 24 M. Newville, P. Livins, Y. Yacoby, J. J. Rehr and E. A. Stern, *Phys. Rev. B: Condens. Matter*, 1993, **47**, 14126.
- 25 S. J. Gurman, N. Binsted and I. Ross, *J. Phys. C: Solid State Phys.*, 1986, **19**, 1845.
- 26 B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537–547.
- 27 M. Newville, *J. Synchrotron Radiat.*, 2001, **8**, 322–324.
- 28 B. Bondars, G. Heidemane, J. Grabis, K. Laschke, H. Boysen, J. Schneider and F. Frey, *J. Mater. Sci.*, 1995, **30**, 1621.
- 29 D. Peter, T. S. Ertel and H. Bertagnolli, *J. Sol–Gel Sci. Technol.*, 1994, **3**, 91.
- 30 G. Kickelbick, M. P. Feth, H. Bertagnolli, M. Puchberger, D. Holzinger and S. Gross, *J. Chem. Soc., Dalton Trans.*, 2002, 3892.
- 31 R. B. Gregor, K. Y. Blohowiak, J. H. Osborne, K. A. Krienke, J. T. Cherian and F. W. Lytle, *J. Sol–Gel Sci. Technol.*, 2001, **20**, 35.
- 32 F. Farges, C. W. Ponader and G. E. Brown, *Geochim. Cosmochim. Acta*, 1991, **55**, 1563.
- 33 C. Sanchez and M. In, *J. Non-Cryst. Solids*, 1992, **1**, 147–148.
- 34 L. Gmelin, R. J. Meyer, E. H. E. Pietsch, A. Kotowski and M. Beche-Goehring, *Gmelins Handbuch der anorganischen Chemie*, Zr, Verlag Chemie, Weinheim, 1973.
- 35 R. Suyama, T. Asida and S. Kume, *J. Am. Ceram. Soc.*, 1985, **68**, 314.
- 36 (a) K. W. Terry, C. G. Lugmair and T. D. Tilley, *J. Am. Chem. Soc.*, 1997, **119**, 9745; (b) P. Scardi, L. Lutterotti and R. Di Maggio, *Powder Diffr.*, 1991, **6**, 20, and references therein; (c) R. C. Garvie and M. F. Goss, *J. Mater. Sci.*, 1986, **21**, 1253–1257.
- 37 H. Kanai, Y. Okumura, K. Utani, K. Hamada and S. Imamura, *Catal. Lett.*, 2001, **76**, 207.
- 38 J.-D. Grunwaldt, S. Hannemann, J. Göttlicher, S. Mangold, M. A. Denecke and A. Baiker, *Phys. Scr., T*, 2005, **T115**, 769.
- 39 E. Clark, W. H. Sutton and V. Lewis, *Microwaves: Theory and Application in Materials Processing IV*, *Br. Ceram. Trans.*, 1997, **80**, 731.
- 40 S. H. Jung, J.-H. Lee, P. M. Forster, G. Ferey, A. K. Cheetham and J.-S. Chang, *Chem.–Eur. J.*, 2006, **12**, 7899–7905.
- 41 P. Scardi and M. Leoni, *ECS Trans.*, 2006, **3**, 125–132.
- 42 P. Scardi, M. Leoni, D. G. Lamas and E. D. Cabanillas, *Powder Diffr.*, 2005, **20**, 353.
- 43 M. Leoni, R. Di Maggio, S. Polizzi and P. Scardi, *J. Am. Ceram. Soc.*, 2004, **87**, 1133–1140.
- 44 R. R. Gonçalves, J. J. Guimarães, J. L. Ferrari, L. J. Q. Maia and S. J. L. Ribeiro, *J. Non-Cryst. Solids*, 2008, **354**, 846–851.
- 45 D. C. Oliveira, A. G. Macedo, N. J. O. Silva, C. Molina, R. A. S. Ferreira, P. S. André, K. Dahmouche, V. de Zea Bermudez, Y. Messaddeq, S. J. L. Ribeiro and L. D. Carlos, *Chem. Mater.*, 2008, **20**, 3696–3705.