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Small-angle X-ray scattering study on the microstructure evolution of zirconia nanoparticles during calcination

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Abstract

Zirconia nanoparticles have been synthesized from zirconium hydroxide precipitates followed by a supercritical CO₂ extraction. The microstructure evolution of these zirconia nanoparticles during the calcination at the moderate temperature has been investigated. Assisted by the analyses of TEM and XRD, small-angle X-ray scattering (SAXS) study offers possibilities to a comprehensive and quantitative characterization of the structural evolution on the nanometer scales. The as-synthesized zirconia sample exhibits a mass fractal structure constructed by the surface fractal particles. Such a structure can be preserved up to 300 °C. After calcination at 400 °C, considerable structural rearrangement occurs. In the interior of nanoparticles zirconia nanocrystallites emerge. It is the scattering from such zirconia nanoparticles that give rise to the broadened crossover in the $\ln[J(q)]$ vs. $\ln q$ plot and the scattering peak in the $\ln[q^3 J(q)]$ vs. q^2 plot. With a further increase in the calcination temperature, the power-law region at large-q in $\ln J(q)$ vs. $\ln q$ plot expands, and the peak in $\ln[q^3 J(q)]$ vs. q^2 plot shifts towards lower q values, indicating size increases in both the nanocrystallites and nanoparticles. Besides, the mass fractal structure constructed by zirconia nanoparticles can be largely preserved during the moderate temperature calcination.

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Keywords: Zirconia oxide; Nanoparticle; Small-angle X-ray scattering; Calcination

1. Introduction

Recent research progress in zirconia has greatly enhanced the prospects for various industrial applications such as solid electrolytes in solid oxide fuel cells and sensors, catalyst/catalyst support, optical films, protective coating, membranes and dispersed phase in composite materials [1–4]. For practical applications, it will be advantageous to precisely control the precessing parameters to produce zirconia with proper microstructures.

The simplest and most common preparation method begins with dissolving a soluble zirconium salt in water and forming zirconium hydroxide gelatinous precipitates by increasing the pH value. The precipitates are then dried and calcined to form crystalline polymorphs of zirconia. It has been demonstrated that the microstructures of zirconia strongly depend on the calcination conditions, which partially determine the particle size distribution, phase construction, crystal size, and so on [5,6]. Hence, it is of great importance to investigate the microstructure evolution during calcination of zirconia precipitates.

Many excellent studies on the calcination process of zirconia have been reported, which characterize the microstructure evolution by means of electron microscopy

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(TEM or SEM), X-ray diffraction (XRD), XRD line broadening analysis, extended X-ray absorption fine structure (EXAFS) and UV Raman spectroscopy, and yield much valuable information on the size, shape of the nanoparticles and the long-range order of the atoms [5–8]. However, due to the complexity of zirconia phase transformation and the restriction of experimental techniques, the microstructure evolution mechanism during the calcination of zirconia nanoparticles have not been completely elucidated.

To probe the structures in the nanometer range, smallangle X-ray scattering (SAXS) that arises from the spatial fluctuations of electronic density within a material, has proved to be a powerful tool. It can provide valuable information on length scales between approximately 1 and 100 nm. Up to now, SAXS technique has been used to study the fractal features of materials directly from the logarithmic form of the scattering intensity curves [9–12]. SAXS can also be employed to study the interfacial characteristics between two phases or the density fluctuations within the matrix according to a negative or positive deviation from Porod's law [13-15]. In analysis of the particle size distribution in colloidal system or the pore size distribution in porous materials, SAXS can yield statistically more evident information about the scatterers' dimension by giving an average over all particles within the illuminated sample volume [10,16]. More recently, with the rapid development in the experimental techniques, SAXS has been widely used to characterize materials such as alloys [17], polymers [18], silica [9,11–15], amorphous zirconia [19-21] and so forth. However, to the best of our knowledge, the microstructure evolution of zirconia nanoparticles during calcination has not been studied by SAXS until now.

In the present work, zirconia nanoparticles were synthesized from zirconium hydroxide precipitates followed by a supercritical CO_2 extraction. The microstructure evolution of so-prepared zirconia particles was investigated by SAXS, TEM, XRD, and N₂ adsorption as a function of the calcination temperature up to 600 °C.

2. Experimental section

2.1. Sample synthesis

Zirconium hydroxide gelatinous precipitate was obtained by adding the aqueous ammonia dropwise to the solution of zirconium oxychloride at room temperature with continuous stirring until pH value reached 10. After an overnight aging, the precipitate was washed thoroughly with distilled water until chloride ions could not be detected, and then washed with anhydrous ethanol to obtain alcogels. To alleviate the hard agglomeration of particles during the drying process, the solvent entrapped in the alcogels was removed by supercritical extraction of CO_2 , which was carried out at 50 °C and 15 Mpa. The assynthesized zirconia powder was calcined in air at different temperatures for 2h. For the sake of clarity, the assynthesized and calcined samples were named hereafter "S050 and SX", respectively, where X denotes the calcination temperature in $^{\circ}$ C.

2.2. Characterization

All zirconia samples were examined with a Hitachi H-800 transmission electron microscope (TEM) to obtain information on the size and morphology of zirconia particles. The crystalline phases present in the as-synthesized and calcined powders were determined on a Rigaku D Max III VC diffractometer equipped with a rotating anode. Line traces were obtained over 2θ values ranging from 20° to 70° . Narrow scan analysis was conducted in the 2θ range of 16–33°, as it contained the strong lines for the tetragonal $(111)_t$ phase, the monoclinic $(11\overline{1})_m$ and $(111)_{m}$ phase. These three peaks were curve fitted using a special peak-fit software equipped on the diffractometer to obtain the full-width at half-maximum intensity (FWHM). The average crystallite size of either the monoclinic phase or the tetragonal phase was then calculated using Scherrer's equation [8]. N₂ physical adsorption analysis was carried out on a Tristar 3000 Sorptometer using the static adsorption procedures. BET surface area was calculated from the linear part of the BET plot according to IUPAC recommendations.

The SAXS experiments were carried out with a long-slit collimation system on 4B9A beamline at the Beijing Synchrotron Radiation Facility, China. A detailed description of the scattering facility was given elsewhere [22]. The incident X-ray wavelength λ was 0.154 nm, the scattering angle 2θ was approximately $0-3^{\circ}$, and the scattering vector was denoted as q, $q = 4\pi \sin \theta / \lambda$. The scattered X-ray intensities were recorded using the imagery plate technology. The background scattering and absorption of the samples were corrected to obtain J(q)-q curves, where J(q) is the slit-smeared scattering intensity. And the data analysis was directly based on the smeared scattering intensity.

3. Theoretical background of SAXS

Since the SAXS phenomenon was experimentally observed, rapid progress has been made on both the theory and the experimental technique. Among the established theoretical system, three basic theories, namely Porod's law [23–25], Debye's theory [26,27], and Guinier's theory [28], have been widely accepted and have become the groundwork for extracting the structural information by processing the SAXS data. These basic theories describe the different aspects of the same object coming from their different approximation to the real electronic structure. Porod's theory describes the asymptotic dependence of the SAXS intensity on the scattering vector at the large scattering vector. Debye's theory reflects the correlation between the scatterers. And Guinier's theory mainly focuses on the shape and size distribution of the scatterers. Thus, the consistency of the results derived from different theories provides good estimation on the validity of the SAXS analysis.

Our SAXS data interpretation was mainly based on the three basic theories. A detailed description of the concerning SAXS theories is as follows.

The general theory about the scattering of a two-phase system is known as [26]:

$$I(q) = I_{\rm e} \langle (\Delta \rho)^2 \rangle V \int_0^\infty \gamma(r) \frac{\sin(qr)}{qr} 4\pi r^2 {\rm d}r, \tag{1}$$

where I(q) is the total scattering intensity, I_e is the scattering intensity of the single electron, $\Delta \rho$ is the electron density contrast between two phases, V is the irradiated volume by X-ray, $\gamma(r)$ is the spatial correlation function of the electron density.

For an ideal two-phase system having sharply defined phase boundaries and a constant but different electron density in each phase, the scattering intensity in the region, where q sufficiently far from zero, will take the form of Porod's law [23]

 $q^4 I(q) = K_{\rm p0} = I_{\rm e} 2\pi (\Delta \rho)^2 S_{\rm p} V$ for pinhole-collimation, and

$$q^{3}J(q) = K_{\rm p} = I_{\rm e}\pi^{2}(\Delta\rho)^{2}S_{\rm p}V \text{ for slit-collimation}, \qquad (2)$$

where K_p is the Porod constant, which is proportional to the total interfacial area, S_pV in the scattering volume. Obviously, according to Porod's law, the $\ln[q^3J(q)]$ vs. q^2 plot will tend progressively to be a straight line with slope of zero at large q value. Moreover, for slit-collimation, the formula to evaluate the surface area per volume unit, S_p can be expressed as follows [24,29,30]:

$$S_{\rm p} = 4w(1-w)K_{\rm p}/Q,$$
 (3)

where *w* is the volume fraction of the scatterers and *Q* is the integrated invariant. The evaluation of *Q* requires carefully using the Guinier approximation [28] and the Porod's approximation [24] for intensity extrapolation at the unmeasurable small and large angles, respectively. The corresponding expression is given by [23-25,30]

$$Q = \int_0^\infty q J(q) \mathrm{d}q = \int_0^{q_{\min}} q J(q) \mathrm{d}q + \int_{q_{\min}}^{q_{\max}} q J(q) \mathrm{d}q + \int_{q_{\min}}^\infty q J(q) \mathrm{d}q$$

$$+ \int_{q_{\max}}^\infty q J(q) \mathrm{d}q. \tag{4}$$

The volume fraction w can either be calculated from the bulk density and skeletal density of the sample or be estimated from the measurement of the absolute intensity of the primary beam, I_0 according to the following equation [30,31]:

$$w = Q/4\pi^2 I_e = QL^2 (m^2 c^4 / e^4) / 4\pi^2 I_0,$$
(5)

where m and e are the mass and electrical charge of an electron, respectively, c is the velocity of light, L is the distance from the sample to the detector.

Different from the Porod's law, Debye considered more about the correlation between the scatterers. For an ideal two-phase system, according to Debye's theory, the slitsmeared scattering intensity is given as [27,32]

$$J(q)^{-2/3} = A^{-2/3} + A^{-2/3} A_{\rm c}^2 q^2,$$
(6)

where A is a constant, A_c is the correlation distance. The parameters, A and A_c can be derived from the slope and intercept of the linear region of $J(q)^{-2/3}$ vs. q^2 plot. From the correlation distance, many valuable structural parameters can be calculated such as the specific surface area S_d , the mean chord length in the solid phase, L_s and that in the pores, L_p of the porous material. The involved equations are listed as follows [30]:

$$S_{\rm d} = 4w(1-w)/A_{\rm c},$$
 (7)

$$L_{\rm p} = A_{\rm c}/w,\tag{8}$$

$$L_{\rm s} = A_{\rm c}/(1-w),$$
 (9)

where w is the volume fraction of the scatterers as mentioned previously.

For a practical, non-ideal system, where there is either a diffuse interface layer or electron density fluctuation within any phase, the deviation from Porod's law will be observed [33–36]. It is the additive scattering derived from the interface layer or the density fluctuation that makes the large-q region of the $\ln[q^3J(q)]$ vs. q^2 plot no longer constant. In this case, the Porod constant, K_p can be obtained by linearly fitting the large-q region of the $\ln[q^3J(q)]$ vs. q^2 plot using the following equations [14,36,37]:

$$\ln[q^3 J(q)] = \ln K_{\rm P} \pm \sigma^2 q^2, \tag{10}$$

where σ is a parameter related to either the thickness of the interfacial layer or the electron density inhomogeneity.

Besides the forementioned applications, the SAXS analysis can also be employed to study the fractal structures. As all known, the typical property of a fractal structure is its self-similarity, i.e., irrespective of length scales or magnification the repetition of disorder within the structure takes place. To describe such a structural property, the fractal dimension D is employed, which quantifies how the mass, M in mass-fractals or the surface area, A in surface-fractals changes with the radius R. In a real system, however, the fractal character can only be observed within a limited range of size. Hence, it is equally important to determine the corresponding length scale region. One approach to obtain the fractal dimension and the corresponding length scales is based on the power-law regions in the SAXS curves [38]. Generally, in the powerlaw regime $(qR_g \gg 1 \gg qa_0, R_g \text{ and } a_0 \text{ corresponding to the}$ radius of gyration of particles and the chemical length of the monomeric units, respectively), the SAXS intensity J(q)may show an exponential dependence on q and can be described as [38]

$$J(q) = Cq^{-\alpha},\tag{11}$$

where *C* is a constant. The exponent $-\alpha$ can be estimated by plotting $\ln J(q)$ vs. $\ln q$, which is related to the mass fractal dimension $D_{\rm m}$ or the surface fractal dimension $D_{\rm s}$ as follows [30,38]:

$$1 \leq \alpha + 1 < 3$$
 for mass fractal, $D_{\rm m} = \alpha + 1$, (12)

$$3 \leq \alpha + 1 < 4$$
 for surface fractal, $D_s = 6 - (\alpha + 1)$, (13)

$$\alpha + 1 \ge 4 \text{ for nonfractal.}$$
(14)

4. Results

4.1. TEM analysis

Fig. 1 shows the TEM images of all samples. It is expected that the sample S050 retain the network structure of the original alcogel on the whole. Calcination at 300 °C can hardly bring any perceptible difference in TEM image, implying no significant changes in size, shape and interaction of particles. As the calcination temperature is gradually elevated up to 600 °C, a monotonic increase in particle size from ~ 10 to ~ 30 nm can be observed. However, the network structure constructed by nanoparticles can be preserved even in sample after calcination at 600 °C.



Fig. 2. X-ray diffraction of zirconia sample: (a) S050, (b) S300, (c) S400, (d) S500, (e) S600.



Fig. 1. TEM images of Zirconia samples: (a) S050, (b) S300, (c) S400, (d) S500, (e) S600.

Table 1 The average crystallite size of the tetragonal and monoclinic phases in ZrO₂ nanoparticles calculated from X-ray diffraction^a

| Sample | D_{t} , (111) (nm) | D _{m,(111)} (nm) | $D_{\rm m}, _{(111)} ({\rm nm})$ |
|--------|----------------------|---------------------------|----------------------------------|
| S400 | 6.4 | 5.1 | 5.7 |
| S500 | 6.9 | 5.8 | 6.8 |
| S600 | 10.7 | 8.9 | 10.4 |

SX denotes the sample calcined at X °C. D_t , (111), D_m , (11 $\overline{1}$) and D_m , (111) are the average crystallite size calculated from the diffraction lines of the tetragonal (111)_t phase, monoclinic (11 $\overline{1}$)_m and (111)_m phase.

^aUncertainty on the calculated values is ± 0.5 nm.

4.2. XRD analysis

Fig. 2 displays the XRD patterns of the samples. Both S050 and S300 are X-ray amorphous. For S400, the diffraction peaks of the tetragonal phase $(t-ZrO_2)$ are predominant, while those of the monoclinic phase (m-ZrO₂) are relatively weak. Besides, small fraction of ZrO₂ may still be existed as amorphous phase because the XRD peaks are somewhat broad. With the further increase in calcination temperature, the diffraction peaks of t-ZrO₂ decline and those of m-ZrO₂ increase, corresponding to the $t \rightarrow m$ phase transformation. However, some t-ZrO₂ phase still exist even after the powder is calcined at 600 °C. In addition, heat treatment at the increasing temperature gives rise to narrower diffraction peaks, indicating an increase in crystallinity. From the strong lines of the tetragonal (111)_t phase, monoclinic $(11\overline{1})_m$ and $(111)_m$ phase, the average crystallite size can be estimated, as shown in Table 1.

4.3. SAXS analysis

Fig. 3 shows the $\ln[q^3 J(q)]$ vs. q^2 plots of all samples. Due to the fluctuation of the incident X-ray intensity, the oscillation of the scattering intensity is unavoidable in the whole q range. For the scattering curves of S050 and S300 (Figs. 3(a) and (b)), no visible deviation from the Porod's law can be observed, revealing systems with nearly homogeneous matrices and sharp interface. However, with a distinct peak emerging in mid-q range, the $\ln[q^3 J(q)]$ vs. q^2 plot gives a thoroughly different appearance after the powder is calcined at 400-600 °C (Figs. 3(c)-(e)). As mentioned above, due to the additive scattering, the scattering character from a non-ideal system may show a negative or positive deviation from Porod's law at large qrange. But in our case, the additive scattering occurs in mid-q region, so it is unreasonable to consider such a phenomenon to be any of the conventional deviations from Porod's law [14,15,34]. Hence, for samples S400, S500 and S600, it is comparatively difficult from the SAXS data to obtain some structural information such as the specific surface area, the correlation distance, or the mean chord length in the solid particles and in the pores. Through Eqs. (2)–(10), only these structural parameters for S050 and S300 can be calculated. With no significant deviation from Porod's law and Debye's theory makes it easy to obtain the Porod constant K_p (Eq. (2) or (10)) and the correlation distance, A_c (Eq. (6)) from the SAXS curves. The integrated invariant Q can be calculated from Eq. (4) by using the Guinier approximation and the Porod's law. The volume fraction, w can be deduced from the absolute intensity of the primary beam I_0 according to the Eq. (5). And then, using Eqs. (3) and (7)–(9), the specific surface areas S_p and S_d and the mean lengths of the chords in two phases L_s and L_p can be obtained. The calculation results are summarized in Table 2. For comparison, the specific surface

As mentioned previously, different from the scattering charater of S050 and S300, the $\ln[q^3 J(q)]$ vs. q^2 plot of the scattering intensity shows a visible peak in the mid-q range after the sample is calcined at 400 °C. And a further increase in the calcination temperature causes a gradual shift of this peak towards lower q value (Figs. 3(c)–(e)). As all known, the SAXS originates from the spatial fluctuation



Fig. 3. $\ln[q^3 J(q)]$ vs. q^2 plots of the scattering intensity of zirconia samples: (a) S050, (b) S300, (c) S400, (d) S500, (e) S600. For sake of clarity, curves (b)–(d) are shifted upwards. The code q_{max} denotes the upper limit of the qrange corresponding to the scattering peak.

| Table 2 | | | | | | | | |
|-----------|------------|------|-----------|--------------------|---------|------|-----|----------|
| Textural | parameters | of | zirconia | samples | derived | from | the | extended |
| Porod's l | aw and Deb | ve's | theory [] | 4.371 ^a | | | | |

| | | 2 | 2 | | | | |
|--------------|--------------|------------------------|------------------------|------------------------|------------------------------------|--|------------------------------------|
| Sample | w | A _c (nm) | L _s (nm) | L _p (nm) | ${S_{ m p}} ({ m m}^2/{ m cm}^3)$ | $\frac{S_{ m d}}{ m cm^{3}}$ (m ² / | $S_{\rm BET} \ ({\rm m}^2/{ m g})$ |
| S050 S300 | 0.29 0.31 | 9.2 8.6 | 13.2 12.6 | 30.8 26.8 | 75.1 82.1 | 91.0 101.6 | 279.6 256.6 |

S050 and S300 denote the samples as-synthesized and calcined at 300 °C. *w* is the volume fraction of the scatterers. A_c is the correlation distance. L_s and L_p denote the mean length of chords in the solid phase and in the pores. S_p and S_d denote the specific surface area derived from Porod's law and Debye's theory, respectively. S_{BET} is the specific area determined by N₂ physical adsorption.

^aThe upper error limit for all derived values is between 5% and 10%.

of electronic density in the investigated system. Hence, these considerable changes in SAXS intensity must be related to significant structure rearrangements. To get a better understanding of the involved structure changes, it is necessary to ascertain the position of these peaks. For sake of clarity, we introduce here q_{\min} and q_{\max} to denote the lower and upper limits of the q range on which the peak existed. In Figs. 3(c)–(e), q_{\max} can be readily estimated from the beginning of the linear trend at high-q region. When q larger than q_{\max} , the plot of $\ln[q^3 J(q)]$ vs. q^2 can be fitted into a straight line with slope of zero. On the contrary, extracting q_{\min} from these curves will give more errors. So we look for another method to ascertain the value of q_{\min} .

The $\ln[J(q)]$ vs. $\ln q$ plots of the scattering intensity are shown in Fig. 4. All scattering curves present, in general, two power-law regions (region I and III), in which the intensity shows an exponential dependence on *q* according to Eq. (11), and a curved crossover region (region II) between them. The $\ln[J(q)]$ vs. $\ln q$ plots of S050 and S300 (Figs. 4(a) and (b)) show features of the mass fractal clusters composed of surface fractals, such as zirconia xerogels [19], silica aerogels [9], and carbon blacks [10]. After the calcination at 400-600 °C, however, the scattering curves are heavily distorted with a much broader crossover region and a suppressed power-law region at large q value (Figs. 4(c)-(e)). It can be demonstrated that the broadened crossovers have a one-to-one correspondence to the peaks presented in the $\ln[q^3 J(q)]$ vs. q^2 plots (Figs. 3(c)–(e)) from both their position and changing tendency with the increase in the calcination temperature. Thus, the q range corresponding to either the peak or the curved crossover region, $q_{\min} < q < q_{\max}$, can be well defined. Using Bragg's law, the corresponding length scale is expressed as $2\pi/q_{\text{max}} < L < 2\pi/q_{\text{min}}$. As to the two power-law regions, the exponents, $-\alpha$ are extracted by linear fitting the data over the q-regions shown in Fig. 4. And the fractal dimensions, $D_{\rm m}$ and $D_{\rm s}$, are obtained through Eqs. (12)-(14). The fractal dimensions and the involved characteristic length scales are summarized in Table 3. A detailed description of the scattering features in Fig. 4 is as follows:

| Table 3 | | | |
|------------------------|--------------------|------------------|---------------------|
| Fractal dimensions and | the characteristic | length scales in | Fig. 5 ^a |

(a) The power law appears at high q (region I), $q_{\rm max} < q < \sim 1.4 \, {\rm nm}^{-1}$, which corresponds to short length scales and shows an exponent of $-\alpha_1$. For samples S050 and S300, this power-law region is between approximately 0.4 and 1.4 nm^{-1} . The values of exponent are found to be -2.92 and -2.89, which correspond to scatterings by surface fractals with D_s as 2.08 and 2.11, respectively. According to the researches of Vollet [9] and Rieker [10], this power-law region should correspond to the surface scattering from the primary scatterers, i.e., zirconia nanoparticles. Moreover, the average size of these nanoparticles can be roughly estimated as $3.5/q_c$ [9], where q_c corresponds to the approximate situation of the crossover region, and their maximum size can be estimated as $2\pi/q_{\text{max}}$. Thus, in sample S050 and S300, zirconia nanoparticles are surface fractals with an average size of about 13.0 nm



Fig. 4. $\ln J(q)$ vs. $\ln q$ plots of the scattering intensity of zirconia samples: (a) S050, (b) S300, (c) S400, (d) S500, (e) S600. For sake of clarity, curves (b)–(d) were shifted upwards. The scattering regions: I is the power-law region at high q, II is the curved crossover region at intermediate q, III is the power-law region at low q. The code q_c corresponds to the approximate situation of the crossover region. The codes q_{\min} and q_{\max} denote the lower and upper limits of the q range corresponding to the extended crossover region.

| | 6 | e | | |
|--------|-------------------|--------------------------|--|-------------|
| Sample | High-q region (I) | Mid-q region (II) | Low-q region (III) | |
| | $D_{ m s}$ | $L_{\min}-L_{\max}$ (nm) | $\Delta L = L_{\rm max} - L_{\rm min} \; (\rm nm)$ | $D_{\rm m}$ |
| S050 | 2.08 | 20.9-26.2 | 5.3 | 2.38 |
| S300 | 2.11 | 19.6-25.1 | 5.5 | 2.40 |
| S400 | Nonfractal | 5.5-18.5 | 13.0 | 2.39 |
| S500 | Nonfractal | 6.5–19.6 | 13.1 | 2.40 |
| S600 | Nonfractal | 10.6-31.4 | 20.8 | 2.32 |

S050 and SX denote the samples as-synthesized and calcined at X° C. D_{s} and D_{m} are the surface fractal dimension and the mass fractal dimension, respectively. L_{\min} is the lower limit of the mid-q region and the maximum size of the primary scatterers. L_{\max} is the upper limit of the mid-q region and the minimum size of the mass fractal clusters. L_{\min} and L_{\max} are defined as $2\pi/q_{\min}$, respectively.

^aUncertainty on the value of the fractal exponents is estimated to be ± 0.05 .

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 $(3.5/0.27 \text{ nm}^{-1})$ and 12.1 nm $(3.5/0.29 \text{ nm}^{-1})$. Their maximum sizes are approximate by 20.9 nm (2π) (0.30 nm^{-1}) and $(19.6 \text{ nm} (2\pi/0.32 \text{ nm}^{-1}))$, respectively. After calcination at 400-600 °C, this power-law region is first suppressed and then expanded gradually towards the small-q region, with q_{max} of about 1.2, 1.0, and 0.6 nm^{-1} (Fig. 4). The exponents approximate to -4.0, suggesting scattering from non-fractal scatterers (Eq. (14)). Using again Bragg's law, the maximum size of the primary scatterers for S400. S500, and S600 can be estimated as 5.5, 6.5, and 10.6 nm, respectively. Obviously, calcination at 400 °C induces a considerable decrease in the size of the primary scatterers from \sim 19.6 to \sim 5.6 nm. Although it has been widely accepted that heat-treatment at a higher temperature may lead to decrease in both the particle size and surface fractal dimension due to the nature of the sintering process, such a decrease is too large to be ascribed to sintering densification. It must be more convincing to relate it to the emergence of a new scatterer population during the structural rearrangement. Combined with XRD results (Fig. 2 and Table 1), the new scatterer population with maximum size of \sim 5.5 nm is believed to be zirconia nanocrystallites. As the calcination temperature is elevated to 500 and 600 °C, the maximum size of these nanocrystallites increases from 5.5 to 6.5 and 10.6 nm, in good agreement with the average size of the nanocrystallites derived from the XRD line broadening analysis (Table 1).

- (b) The power law applies at low q (region III), $\sim 0.1 < q < q_{\min}$. This power law corresponds to long length scales and for all samples, demonstrates an exponent between -1.40 and -1.32, which indicates scattering from mass fractals with fractal dimension of $2.32 < D_{\rm m} < 2.40$ (Eq. (12)). It is obvious that these mass fractals are zirconia clusters constructed by nanoparticles.
- (c) The curved crossover region appears at intermediate q (region II). For S400, S500, and S600, the crossover regions are broadened. The corresponding length scale is between the maximum size of the nanocrystallites and the minimum size of the mass fractal clusters, and is very close to the size of the nanoparticles. Hence, the scattering occurred at this region can be considered as the scattering from zirconia nanoparticles.

5. Discussion

The SAXS data, complemented by TEM, XRD, and N_2 physical adsorption analysis, provide abundant information on the microstructure evolution of zirconia nanoparticles. The set of experimental data can be explained based on the model sketched in Fig. 5, where the structure is sketched as a function of the length scale represented by



Fig. 5. The sketched model for the structural evolution as a function of calcination temperature probed by SAXS: (a) S050 and S300, (b) S400, (c) S500, (d) S600.

circles. The representation is just intended to analyze the structural evolution during the heat treatments.

SAXS results indicate that the as-synthesized zirconia sample consists of mass fractal aggregates constructed by primary particles with nearly uniform interior structure. Such a structural characteristics might derive from both the inheritance of the original wet gel and the slight modification in drying process. According to the recent research of Southon [20] and Chen [39], the formation of zirconia wet gel involved in our case can be generally described as follows: with the high pH value of ~ 10 and slow addition of ammonia, the predominant zirconium coordination monomers in the present system can be regarded as a tetragonal bipyramid, in which hydroxyl ions fully occupy the six acmes of the bipyramid. Based on these monomers, zirconium tetramers with a short-range structure are formed, in which four zirconium atoms are arranged in a two-dimensional square lattice, each connected by double hydroxyl bridges, giving an ideal stoichiometry of Zr(OH)₄. Moreover, the mean bond length of Zr–OH in the tetramer is close to that of Zr–O in bulk tetragonal zirconia [20,39]. Hence, further polymerization between these tetramer precursors mainly forms the netlike ordered tetragonal precursor structure, as well as some local disorders probably due to the defects in lattice, any oxo bridges and incomplete hydroxyl ions substitution [40]. With the subsequent liquid CO_2 exchange and supercritical CO_2 extraction, the boundary of a new particle (primary particle) is formed. However, different from the conventional drying process, removal of liquid phase at the supercritical conditions makes it possible for the assynthesized powder to largely preserve the structure of the original wet gel. Such an inheritance might explain the mass fractal character of the as-synthesized powder. Besides, the interior of thus-obtained primary particles is nearly uniform with only slight electronic density fluctuations that might originate from the local disorder in the original network structure and the imperfect solvent exchange. The slight interior electronic density fluctuation gives an additive contribution to the scattering from the surface boundary of the particles, thus resulting in a little deviation from the scattering exponent -3 of Porod's law, giving the power-law region with exponent of -2.92(Fig. 4(a)), and endowing the particles with surface fractal characteristics.

From the crossover in Fig. 4(a), the average dimension of these new-formed particles has been roughly estimated as ~13.0 nm $(3.5/q_c)$, consistent with the mean chord length in the solid phase L_s of 13.2 nm (in Table 2). And the fractal dimension of the mass fractal clusters has been determined as about 2.38. Both the small particle size of about 13.0 nm and the low mass fractal dimension of 2.38 predict that the as-synthesized powder is a loose-packed material with high specific area, consistent with the results (Table 2) from not only SAXS but also N₂ adsorption analysis.

Such a structure can be essentially preserved after calcination at 300 °C. Indeed, there is no perceptible changes in TEM diagrams and XRD patterns. And the fractal characteristics are very similar to those of the assynthesized powder (Fig. 4). However, due to the advantages of SAXS analysis, the information on the fine structural changes can be detected. As can be seen in Table 2, calcination at 300 °C leads to a little decrease in the average chord length L_s and L_p . This fact can be related to the removal of the small amount of water entrapped in the gel matrix [20,41].

Calcination at 400 °C will lead to the emergence of a new scatterer population. Based on the SAXS and XRD results, this new scatterer population has been assigned to ZrO_2 nanocrystallites due to the phase transformation from amorphous $Zr(OH)_4$ to crystalline ZrO_2 . And an involved phase transformation can be presented as follows. During calcination at 400 °C, the ordered tetragonal precursor structures in the interior of the particles begin to crystallize into tetragonal phase accompanied by the small fraction of monoclinic phase, which might directly come from the locally disordered structure. This phase transformation may involve several steps, including the loss of the terminal hydroxyl groups, oxolation of hydroxyl bridges to form embryonic oxide nuclei and growth of the nuclei to form observable crystallites, and

a perfect phase transformation cannot be achieved at such a low temperature. Therefore, the nanoparticle becomes a complex of tetragonal nanocrystallites, small fraction of monoclinic nanocrystallites and amorphous phase. Such a phase transformation process is supported by our SAXS results in three aspects. First, after calcination at 400 °C, zirconia nanocrystallites become the main scatterers at high-q region. Scattering from the surface of crystallites (non-fractal) might account for the presence of power-law region with exponent $-\alpha_1$ approximate to -4.0 (Fig. 4(c)). Second, when the scattering from the particles comes into consideration, the small fraction of monoclinic and amorphous phase, as well as the grain boundary, may function as the electronic density fluctuation and give an additive contribution to the scattering from the surface boundary of the particles. The electronic density fluctuation in our case occurs at a larger dimension. Thus, instead of giving rise to the conventional positive deviation from Porod's law at large-q value, the additive scattering occurrs at mid-q region and results in the distinct peak in $\ln[q^3 J(q)]$ vs. q^2 plot (Fig. 3(c)). Finally, the scattering from zirconia nanoparticles, which comprise the nanocrystallites and construct the mass fractal clusters, would be responsible for the broadened crossover region in $\ln J(q)$ vs. $\ln q$ plot (Fig. 4(c)).

With a further increase in calcination temperature to 500–600 °C, the average crystallite size increases and t \rightarrow m phase transformation occurs (Fig. 2). According to the researches of Li [6] and Shukla [8], in an agglomerate-free system such as our case, the metastable tetragonal phase can exist only when the crystallite size is less than the critical size, $\sim 6 \text{ nm}$. This is confirmed again by our XRD line broadening analysis (Table 1). Our SAXS analysis shows that the maximum size of the new scatterers increased from 5.5 nm (400 °C) to 6.5 nm (500 °C) and then 10.6 nm (600 °C) (L_{\min} in Table 3), suggesting again that the new scatterers are no other than zirconia nanocrystallites. Moreover, it can predicted that, in these cases, the small fraction of tetragonal phase and the grain boundary may act as the electronic density fluctuation and give rise to the peaks in $\ln[q^3 J(q)]$ vs. q^2 plot. And the expanding of the large-q power-law region (region I) in $\ln J(q)$ vs. $\ln q$ plot and the peak shifting in $\ln[q^3 J(q)]$ vs. q^2 plot towards lower q values can be correlated with the size increase in both nanocrystallites and particles, which arises as a consequence of mass transfer process within and between particles due to the elevated calcination temperature. In addition, as shown in Table 3, the length scale range related to the crossover (ΔL) extends from 13.0 to 20.8 nm as the calcination temperature increases from 400 to 600 °C, indicating a gradual increase in the polydispersity of zirconia nanoparticles.

It is also worth noting that all samples exhibit the mass fractal behavior at low-q region. This suggests that the mass fractal structure constructed by nanoparticles can be largely preserved during the calcination up to 600 °C.

6. Conclusion

In our study, SAXS technique was employed to investigate the microstructure evolution of zirconia nanoparticles during the calcination at moderate temperature. Assisted by the analyses of TEM and XRD, the SAXS study offers opportunities to a comprehensive and quantitative characterization of the structural evolution on the nanometer scales. The detailed description of the involved structural changes is as follows. The as-synthesized zirconia sample has a typical mass fractal structure with fractal dimension $D_{\rm m}$ of 2.38, constructed by the surface fractal particles with an average size of about 13.2 nm and a fractal dimension D_s of 2.08. Such a structure can be largely preserved up to 300 °C. After calcination at 400 °C, considerable structural rearrangement occurs. In the interior of zirconia nanoparticles emerge zirconia nanocrystallites with the maximum size of 5.5 nm. It is the scattering from such zirconia nanoparticles that give rise to the broadened crossover in the $\ln[J(q)]$ vs. $\ln q$ plot and the scattering peak in the $\ln[q^3 J(q)]$ vs. q^2 plot. Further increasing the calcination temperature to 500 °C and then 600 °C, the maximum size of the nanocrystallites increases to 6.5 nm and then 10.6 nm. Simultaneously, the maximum size of the zirconia nanoparticles increases from 18.5 to 19.6 and 31.4 nm due to the mass transfer within and between particles at the elevated temperature. It is also noticeable that the mass fractal structure constructed by zirconia nanoparticles could be largely preserved during the moderate temperature calcination.

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