Controlled formation of amine-templated mesostructured zirconia with remarkably high thermal stability

Kristof Cassiers,*a Thierry Linssen,a Katrien Aerts,b Pegie Cool,a Oleg Lebedev,c Gustaaf Van Tendeloo,c René Van Griekenb and Etienne F. Vansant*a

aLaboratory of Adsorption and Catalysis, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium. E-mail: kristof.cassiers@ua.ac.be;
Fax: 32-3-820.23.74; Tel: 32-3-820.23.80
bMicro & Trace Analysis Centre, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium
cCentre for Electron Microscopy and Materials Science, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

Received 27th August 2003, Accepted 8th October 2003
First published as an Advance Article on the web 28th October 2003

In order to control the reactivity of the inorganic precursor and the hybrid formation, the evaporation induced self-assembly procedure (EISA) has been applied to direct alkyl amines into zirconia hybrid composites. It is demonstrated that, with controlled water amounts, a mesostructured wormhole-like high-surface-area zirconia can be formed but the mesostructure collapses due to massive crystallisation of the zirconia walls into tetragonal zirconia as the calcination temperature rises to 400 °C. To overcome the lack in thermal stability, zirconia hybrids are treated in aqueous ammonia to protect the primary particles in the zirconia walls against uncontrolled particle growth and crystallisation. The growth of the initially amorphous zirconia particles in the walls is limited by increasing the condensation degree upon ammonia treatment resulting in mesostructured zirconia consisting of nanosized ‘tetragonal’ particles at higher temperatures. It is shown that the alkaline-treated zirconias have a remarkable thermal stability with retention of most physical characteristics such as high surface area, pore volume and mesoporosity up to a temperature of 800 °C.

Introduction

Many attempts to synthesise mesostructured transition metal oxides have been reported since the first examples of stable transition metal oxide mesoporous molecular sieves appeared in 1996.1,2 Due to the large field of applications ranging from (photo)catalysis to ceramics, zirconia is of particular interest among the non-silica mesoporous oxides. Zirconium oxide has been found to have applications in the field of redox and acid catalysis.3,4 It contains both weakly acidic and basic surface sites, providing for high activity in reactions requiring bifunctional acid–base catalysts.5,6 Porous zirconia with surface areas up to 500 m² g⁻¹ can be prepared by chemical methods and supercritical drying of zirconia gels.7–10 However, an inherent drawback of these materials is the facile loss of surface area with increasing temperature, especially at temperatures higher than 400 °C. The major thermodynamic driving force is the crystalline transformation of these zirconia materials into dense, low-surface-area monoclinic and metastable tetragonal phases.11 The low thermal stability of pure zirconia can be improved by introducing dopants, such as phosphates12 and sulfates.13

One of the fundamental problems in the synthesis of mesostructured transition metal oxides is to control the formation of the organic/inorganic hybrid network. Inorganic hydrolysis and condensation of the metal precursor have to be mastered, to avoid the instantaneous formation of an extended inorganic network that would irreversibly freeze into an ill-organised mesostructure. Second, redox reactions or phase transitions accompanied by thermal breakdown of the structural integrity make it difficult to remove the templates in order to create porous materials.

The synthesis of zirconium-based mesoporous materials was first achieved by Hudson and Knowles.14,15 They suggested that the synthesis of mesoporous ZrO₂ in the presence of cationic surfactants occurs through a scaffolding rather than a templating mechanism. After calcination at 500 °C, pure mesostructured zirconia was obtained with surface areas ranging from 240 to 330 m² g⁻¹ but no regular pore system was observed.

Almost simultaneously, Pacheco et al.16,17 and Larsen et al.18 reinvestigated the preparation of mesoporous zirconium oxide using anionic surfactants, where Pacheco et al. concluded on the same scaffolding mechanism. In their syntheses, the fixation of phosphate or sulfate in the walls helped to preserve the porous structure at 500 °C. In a later study, Pacheco et al.19 showed that sulfate stabilises the tetragonal phase while phosphate delays the crystallisation from amorphous to the tetragonal phase, thereby shifting collapse upon phase transformation to higher temperatures. Huang et al.20 also found that sialation of the precursor formed using primary amines, and subsequent calcination, led to a stable mesoporous material. The mesostructure in this case consists of amorphous sulftated zirconia up to 600 °C in contrast to the results on sulfated zirconia of Pacheco et al.19 consisting of tetragonal zirconia walls.

Schüth et al.21,22 have synthesised for the first time highly ordered hexagonal mesoporous zirconium oxide with thermal stability up to 500 °C, but also in this case, phosphate groups preclude collapse upon crystallisation. Ying et al.23 confirmed that phosphate groups remaining on the inorganic wall appeared necessary for thermal stability in this case.

Since the introduction of nonionic poly(ethylene oxide) based surfactants as templates for the synthesis of mesostructured materials, the evaporation induced self-assembly (EISA) technique is a synthesis method that has been proven to be especially well-adapted to the design of transition metal oxide based mesoporous materials. As solvent is removed, a
mesoporous material around the voids of a meso-organised liquid-crystalline phase, so presenting a segregation of organic and mineral domains at the nanoscale. By using this procedure, Stucky et al. prepared pure phosphate- and sulfate-free mesoporous zirconia with surface area of 150 m² g⁻¹ and a thermal stability of at least 400 °C. Sanchez et al. recently showed that these zirconia mesostructures are stable to 450 °C and collapse at higher temperature upon massive crystallisation to tetragonal zirconia.

In this paper, we report for the first time on the controlled formation of pure mesostructured zirconia hybrids synthesised by the EISA procedure with other neutral templates, in particular alkyl amines. In order to increase the thermal stability of the template-, phosphate- and sulfate-free mesostructured zirconia, a new post-synthesis treatment procedure has been developed.

**Experimental**

**Synthesis**

For the syntheses of mesoporous zirconia, two kinds of amine templates were used, in particular dodecylamine (DDA) and N,N-dimethyldodecylamine (NNDDA). Zirconium propoxide 70 wt% solution in 1-propanol was used as the zirconium source.

**Evaporation induced self assembly**

In a typical synthesis, the amine template was dissolved in absolute ethanol. To this solution, the zirconium propoxide was added and stirred at ambient temperature. After a dropwise addition of water to this mixture, a white suspension was formed and the solution was stirred for 15 minutes. Additionally, the solution was aged at room temperature in a closed system to avoid evaporation. The molar gel composition was Zr/amine/H₂O/Ethanol = 1/0.33/x/90 with x = 2 or 30. After 24 hours ageing, the mixture was transferred into a Petri dish to evaporate the solvent in open air at room temperature. Zirconia mesostructures synthesised by this EISA technique are further named as Zr-DDA-EISA(x) or Zr-NNDDA-EISA(x) where x is the H₂O/Zr molar ratio.

**Post-treatment with NH₃**

NH₃ treatment was carried out in a reflux system. NH₃OH was added to pure water until a pH of 9 to 10 was reached. Before evaporation of the solvent in open air in the EISA synthesis, a part of the mixture after ageing for 24 hours was filtered, the wet solid was added to the water and the pH was again brought to a value between 9 and 10. For 1 g of wet solid, 50 ml of basic water was used. The solution was refluxed for 48 h and the pH was kept between 9 and 10. Zirconia hybrids synthesised by this procedure are further denoted as Zr-DDA-NH₃ or Zr-NNDDA-NH₃.

**Characterisation**

X-Ray diffractogram patterns were recorded on a Philips PW1840 powder diffractometer, using Ni-filtered Cu Kα radiation. Porosity and surface area studies were performed on a Quantachrome Autosorb-1-MP automated gas adsorption system. All samples were outgassed for 16 h at 200 °C prior to adsorption. Gas adsorption occurred using nitrogen as the adsorbate at liquid nitrogen temperature (77 K). The SEM image was recorded using a JEOL-JSM-6300 scanning electron microscope operating at an accelerating voltage of 20–30 kV. The sample was sputtered with a thin film of gold. The TEM image was recorded using a JEOL-4000-EX microscope operated at 400 kV to analyse the framework structure of the developed material. The thermogravimetric analysis (TGA) experiments were performed on a Mettler TG 50/TA 3000 thermobalance controlled by a TC10A microprocessor. Samples were heated at a rate of 5 °C min⁻¹ or under a flow of air (TGA) at a flow rate of 50 cm³ min⁻¹.

**Thermal stability**

To assess thermal stability, the samples were calcined in air starting from end temperature of 300 °C. The end temperature was each time increased by 100 °C as long as no complete collapse of the zirconia mesostructure had occurred. All the sample precursors were calcined with a heating rate of 2 °C min⁻¹ and kept at the end temperature for 2 h.

**Results and discussion**

**a. Strategies toward zirconia hybrids**

To control the reactivity of the zirconia source and mesostructure formation, we used an ageing procedure where two major steps are separated. In a first step, DDA or NNDDA was dissolved in absolute ethanol followed by the addition of the zirconium source. Similar to the synthesis of mesoporous zirconia with block copolymer templates described by Stucky et al., the formation of rod-like micelles takes place by a mechanism that combines amine self-assembly with complexation of these amines with the zirconium propoxide. In the second step, a quantity of water with a molar ratio H₂O/Zr = 2 or 30 is slowly added to condense the network to a low-condensed zirconia–amine complex micellar system. After this ageing procedure, two different strategies are applied to extend further hydrolysis and polymerisation of the low-condensed zirconia walls into the final amine–zirconia hybrids. In the first pathway we make use of the so-called evaporation-induced self-assembly (EISA) technique, which has recently been successfully applied to the syntheses of mesostructured zirconia and other transition metal oxides with poly(ethylene)-based surfactants. The amine–zirconia hybrid formation and the inorganic polymerisation of the zirconia walls are continued during a solvent evaporation process in open air in combination with the uptake of water provided by moisture in the air. The second route is a completely new method where the aged product is transferred into an excess of water containing ammonia to condense the walls.

**b. Evaporation induced self assembled zirconia**

Fig.1 shows the X-ray diffraction patterns of DDA and NNDDA-templated zirconia hybrids prepared with a low amount of water (H₂O/Zr = 2) and Zr-NNDDA-EISA aged with H₂O/Zr = 30. A relatively intense broad single Bragg peak can be observed in the range 2θ = 2° to 6° for both surfactants when using low amounts of water, suggesting that the respective zirconia meso-ordered hybrids are well formed by the EISA method. On the other hand, no diffraction peak can be seen for Zr-NNDDA-EISA(30). The pioneering work on the interaction between amines and metal precursors has been done by Antonelli et al. who studied the formation mechanism of amine–niobium hybrids from the first stages of the synthesis. Depending on the amount of water, the template can interact with the metal precursor via H-bonding interactions or via a tighter covalent bond. They proposed two hypothetical reaction paths, depending on the stability of the N–Nb bond. In the first pathway, the N–Nb bond is kept along all the steps that lead to the mesostructured material, without completely being hydrolysed. Some ‘small’ amounts of water permit the remaining alkoxy groups to be hydrolysed, triggering the condensation of the metal atoms fixed on the amine polar heads and further helping the micellisation process (a sort of co-assembly process). Due to a strong N–Nb bond,
no residual hydrolysed alkoxy groups or water exchange with the co-ordinated amine. This pathway leads to hexagonally ordered Nb materials. On the other hand, if hydrolysis and condensation of metal alkoxides is very fast (excess of water), a great fraction of the amine complex is destroyed. Hydrolysis produces hydrophilic Nb–oxo oligomers. In contrast to the first pathway, these species can in turn associate with the surfactant heads via H-bonding interactions. 'Excess' of water induces a more extended condensation of the mineral network and simultaneously encourages the segregation of the amine chains into micellar domains. Upon drying, residual solvent is eliminated, and certain metal sites that are not coordinatively saturated may interact with the surfactant polar heads. This pathway leads to wormlike Nb materials. A similar formation mechanism was observed in the case of tantalum. However, no residual hydrolysed alkoxy groups or water exchange with the co-ordinated amine. This pathway leads to hexagonally ordered Nb materials. A similar formation mechanism was observed in the case of tantalum. However, it was shown that no initial covalent bond can only be formed upon evaporation of ethanol after the combination of amine and tantalum. In case the covalent bond cannot form, a different pathway leads to wormlike Nb materials. A similar formation mechanism was observed in the case of tantalum.

Because no diffraction line can be seen with large amounts of added water, it seems to be more likely that Zr–amine hybrids follow the interaction mechanism of Ti–amine instead of Nb or Ta–amine. Therefore, it can be expected that a Zr(O-Prop)₄[H₂N(CH₂)₁₁CH₃] complex is formed between the metal center and the amine at the first stage of the synthesis, before addition of water. After addition of a small quantity of water, controlled hydrolysis and condensation without destabilisation of the template-zirconium complex leads to a meso-ordered hybrid. H₂O/Zr = 2 is just sufficient to hydrolyse zirconium propoxide groups with a relatively slow rate. On average, one Zr(O-Prop)₄[H₂N(CH₂)₁₁CH₃] group is hydrolysed to Zr(OH)₃(O-Prop)₃[H₂N(CH₂)₁₁CH₃] Condensation between two such entities leads to the release of one or two water molecules, which can take part in further hydrolysis of the propoxide groups. Under such conditions, only a few nuclei are formed and particle growth occurs by attachment of unhydrolysed Zr(OR)₄ entities to Zr–OH groups of the growing nuclei or by condensation of two Zr–OH groups. In the presence of excess water, the initially formed Zr(O-Prop)₄[H₂N(CH₂)₁₁CH₃] complex immediately hydrolyses to Zr(OH)₄ entities, so the amine-zirconium complex is completely destroyed upon water attack. This rapid hydrolysis leads to the formation of many small nuclei and condensation in this case is much faster because many more OH groups are available to condense. No meso-ordered hybrid is formed due to the absence of zirconium-template interactions on the one hand and fast polymerisation of the zirconium source on the other hand.

Based on thermogravimetric measurements (not shown), Zr-DDA-EISA and Zr-NNDDA-EISA show a total weight loss between 50 and 260 °C of around 40% corresponding to the loss of volatile species such as water, ethanol, propanol. Steep weight losses at 230 and 255 °C are caused by the decomposition of DDA and NNDDA, respectively. To release the pores, samples were therefore calcined to 300 °C. For samples prepared with H₂O/Zr = 2, both template-free zirconias display a well-defined step in the isotherms at P/P₀ = 0.2–0.4 and, similar to the diffractograms of the corresponding hybrid materials, one broad reflection can be observed in their X-ray patterns. Similar N₂ sorption and diffraction properties were also observed for ‘amine’-templated silica assembled by Sºººº and (Sºººº)ₓ(X⁻¹)ₓ pathways and amine-templated titania and have been found to exist in wormhole like channel systems where the regular separation between single channel walls gives rise to the broad XRD reflection.

The physical characteristics derived from XRD and N₂ sorption measurements are listed in Table 1. The two samples prepared with H₂O/Zr = 2 possess relatively high pore volumes and surface areas up to 0.16 cm³ g⁻¹ and 316 m² g⁻¹, respectively. The thickness of the pore walls is estimated by the difference between the d-spacing, corresponding to the pore-to-pore distance, and the BJH diameter. Both zirconias prepared

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>S BET/m² g⁻¹</th>
<th>Vₚ cm³ g⁻¹</th>
<th>dÅ</th>
<th>Dₜ₁₀ Å</th>
<th>Dₜ₂₀ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-DDA-EISA-2</td>
<td>179</td>
<td>0.10</td>
<td>31.8</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>Zr-NNDDA-EISA-2</td>
<td>316</td>
<td>0.16</td>
<td>35.4</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>Zr-NNDDA-EISA-30</td>
<td>92</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

*No mesoporosity could be detected.*
with $\text{H}_2\text{O}/\text{Zr} \approx 2$ have pore sizes near the micro-mesopore border and the estimated wall thickness is around 15 Å. The $d$-spacing and pore diameter for the mesoporous zirconia prepared with NNDDA are somewhat larger compared to the DDA-prepared sample due to the more bulky head group of the NNDDA template. On the other hand, the quality of the $\text{N}_2$ isotherm and the surface area of the zirconia sample prepared with $\text{H}_2\text{O}/\text{Zr} \approx 30$ are much lower and, similar to the corresponding non-calcined sample, no diffraction peak can be seen in the X-ray diffractogram. This confirms that no mesostructure was formed during ageing in excess water. From this point, all samples further discussed in this paper were synthesised with $\text{H}_2\text{O}/\text{Zr} = 2$.

In order to assess the thermal stability, the EISA-prepared samples were calcined at 400 °C for 2 h. At this temperature, the structure appears to collapse and the mesophase is completely lost as indicated by the absence of the steep increase in the isotherms between $P/P_0 \approx 0.2$ to 0.4 and the disappearance of the small angle XRD reflection (not shown). Furthermore, the surface areas are drastically decreased to around 5 m$^2$ g$^{-1}$. Fig. 3 shows the XRD powder patterns of samples. If the calcination temperature increases from 300 to 400 °C, new diffraction lines arise at $2\theta \approx 30.4^\circ$ and $35.4^\circ$, characteristic of tetragonal crystalline zirconia.$^{32}$ Apparently, the crystallisation from amorphous to tetragonal zirconia goes along with the degradation of the mesostructural ordering.

c. NH$_3$-treated zirconia

The EISA technique can be successfully extended to pure, mesoporous zirconia oxides prepared with amine templates. Template-free zirconia phases are stable to a calcination temperature of 300 °C but, similar to many other synthesis pathways to mesostructured zirconia, these materials are unstable to calcination at 400 °C or higher due to the uncontrolled crystallisation and aggregation into tetragonal zirconia of very low surface area without meso-organisation.

Typical powder X-ray diffraction patterns are shown in Fig. 4 for the as-synthesised NH$_3$-treated zirconia hybrids. For both NH$_3$-treated hybrids, analogous single peak patterns as for the corresponding EISA-prepared zirconia samples can be observed. This indicates that the treatment for 48 h with NH$_3$ has no disadvantageous influence on the zirconia hybrid formed during ageing. Moreover, the reflections for the NH$_3$-prepared hybrids are narrower and sharper, signifying a greater degree of structural ordering. Fig. 5 shows the $N_2$ isotherms and X-ray diffraction patterns of Zr-DDA-NH$_3$ and Zr-NNDDA-NH$_3$ calcined to 300 °C for 2 h while Table 2 shows their physical characteristics. The shape of the isotherms and the X-ray patterns look very similar to the EISA samples calcined to 300 °C. However, it can be concluded that the NH$_3$-treated mesostructures have better physical characteristics. The pore volumes are drastically increased, very high surface areas

![Fig. 3 X-Ray diffraction patterns of Zr-DDA-EISA (a) and Zr-NNDDA-EISA (b) calcined at 400 °C for 2 h.](image)

![Fig. 4 X-Ray diffraction patterns of as-synthesised (a) Zr-DDA-NH$_3$ and (b) Zr-NNDDA-NH$_3$.](image)

![Fig. 5 N$_2$ adsorption-desorption isotherms and X-ray diffraction patterns (inset) of Zr-DDA-NH$_3$ (a) and Zr-NNDDA-NH$_3$ (b) calcined at 300 °C for 2 h. The isotherm of Zr-NNDDA-NH$_3$ is offset by 100 cm$^3$ g$^{-1}$ for clarity.](image)

<table>
<thead>
<tr>
<th>Table 2 Physical characteristics of NH$_3$-treated zirconia samples calcined at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>Zr-DDA-NH$_3$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Zr-NNDDA-NH$_3$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

*No diffraction line could be detected.*
of more than 400 m² g⁻¹ can be calculated whereas the BJH diameters are also increased. This indicates that the ammonia treatment has a beneficial influence on the mesoporosity of the mesostructure. The wormhole like pore channel, which was already suggested above, is evidenced by the representative transmission electron microscopic (TEM) image of the NH₃-treated DDA-templated zirconia sample (Fig. 6). The wormhole-like channels, though more or less regular in diameter, have no discernible long-range order. Furthermore, a scanning electron microscopic image (SEM) in Fig. 7 shows that the NH₃-treated samples consist of spherical particles with a size of approximately 1 μm.

Meso-ordered zirconia hybrids that were treated for 48 hours in ammonia solution followed by calcination at high temperature show an unusual stabilisation of the mesostructure. In contrast to the EISA-prepared samples, a broad reflection can be observed for both templates in the small angle XRD pattern up to a calcination temperature of 700 °C (Fig. 8A). Moreover, the shapes of the N₂ adsorption–desorption isotherms of the NH₃-treated samples remain the same to at least 700 °C for both templates (Fig. 9). Also, as shown in Table 2, the BET surface area and mesopore volume appear to have relatively high values up to 800 °C. Despite the serious decline in surface area and mesopore volume above a temperature of 600 °C, still a surface area and pore volume of >180 m² g⁻¹ and 0.12 cm³ g⁻¹, respectively, can be observed while mesoporosity is still present at 800 °C. It should be emphasised here that, when considering mesoporous transition-metal oxides such as zirconia, on first glance one might not be too impressed with the relatively low specific surface areas compared to those of silica materials. However, one has to keep in mind that the density of the oxide wall enters the calculation of specific surface areas and pore volumes. Assuming an identical oxide wall thickness density as in the crystalline bulk (which is a reasonable approximation for this comparison, the real wall thickness density is probably somewhat lower than the bulk), 1000 m² g⁻¹ for silica (density of quartz 2.6 g cm⁻³) corresponds to 440 m² g⁻¹ for zirconia (density of zirconia 5.9 g cm⁻³).

These observations clearly show that the ammonia-treated mesostructured hybrids have a much higher thermal stability with retention of all the physical properties up to 700 °C. In agreement with the X-ray diffraction patterns between 2θ = 10 and 40° (Fig. 8B), this increased stability goes together with a visible delay of crystal phase formation (from 600 °C), compared to the EISA-prepared samples (400 °C). Furthermore, it should be emphasised that, in contrast to the EISA samples, the phase transformation did not cause a complete collapse of the mesostructure.

Since extended condensation in the initial stage of the synthesis leads to uncontrolled phase separation of the inorganic and organic phase (e.g. upon addition of excess water), the addition of ‘low water amounts’ slowly hydrolys the zirconium–amine complex. Subsequently, different zirconium–amine entities combine and a mesostructured hybrid is nicely formed. However, due to the low amount of water, the inorganic phase of the final hybrid has a relatively low condensation degree. Upon solvent evaporation by the EISA technique, the uptake of moisture from the air is not enough to further condense the hybrid and no other condensation-promoting steps were introduced. Therefore, the inorganic ZrO₂ phase is still hydrous for samples prepared by the EISA procedure.

Chuah33 studied the effect of pH at increased temperatures on pre-formed hydrous ZrO₂. The authors found that, independent of the pH, the condensation degree of the initially formed hydrous primary ZrO₂ particles increases with increasing temperature, which results in a strengthened porous inorganic network. The mechanism causing the increased condensation however depends on the pH. They found that refluxing hydrous ZrO₂ at alkaline pH of 9 or above leads to limited particle growth. In this pH region, the solubility of ZrO₂ is very low and the condensation degree of the pre-formed primary particles will increase. In contrast, at low pH, where the solubility is appreciable, particle growth occurs due to the continuous dissolution–recrystallization of the hydrous ZrO₂. This recrystallisation allows the hydrous ZrO₂ to become crystalline after sufficiently long treatment.

Similar to the observations of Chuah, the primary particles formed during the initial stage of the synthesis (aging) are further condensed in basic solution in such a way that no particle growth appears. Due to the higher condensation degree upon ammonia treatment, defects, which are believed to be responsible for surface diffusion leading to particle growth, are eliminated.34 The more condensed amorphous primary particles are therefore discouraged to grow upon temperature increase.

When the NH₃-treated samples are thermally treated to 400 °C, no crystalline phase could be seen in the corresponding X-ray diffractogram. It is however more likely that the highly condensed primary particles are transformed from amorphous to nanosized crystallised tetragonal particles at the same temperature as the massive crystallisation of the EISA-prepared zirconia samples, with the major differences that the nanosized particles formed between 300 and 400 °C are very small and therefore X-ray amorphous. Upon further temperature
increment, these nanosized X-ray amorphous particles do not grow extensively and the mesostructure is preserved. From 600 °C, the mesostructure is still preserved but the tetragonal phase shows up in the X-ray pattern. These observations are in agreement with the results of Garvie and Goss, 35 who showed that for highly dispersed zirconia systems, surface energies rather than bulk energies would determine the stable phase. Surface energy effects become important in crystallites below 300 Å. As primary particles of diameter smaller than 30–40 Å are X-ray amorphous, no reflections can be seen in the X-ray pattern up to 500 °C. When the temperature further increases to 600 °C, these particles grow very slowly and become larger than 40 Å, which occurs together with the appearance of reflections characteristic of the tetragonal phase. It should be mentioned that the particle growth is controlled, as the materials are still mesoporous at this temperature. The mesostructure is lost when particles become too large (especially above 300 Å when bulk energies are dominant) or when a phase transformation from tetragonal to the monoclinic phase occurs (which is not observed).

In case of the EISA-prepared samples, unlimited growth of the hydrous ZrO₂ inorganic network will take place when the temperature increases. Between 300 and 400 °C, the large secondary formed amorphous particles will transform into large tetragonal crystals with total loss of mesoporosity.

Conclusions

In this report, the controlled synthesis of mesostructured amine-templated zirconia according to the evaporation induced self-assembly technique has been described. It has been shown that, when using controlled water amounts, a mesostructured hybrid can be formed which is stable upon template removal to 300 °C. However, these pure template-free EISA-prepared mesostructures were completely collapsed due to the massive crystallisation of the amorphous zirconia walls into tetragonal crystals between 300 and 400 °C.

It has been demonstrated that this low thermal stability is caused by the absence of a locking step, which should transform the hydrous ZrO₂ into highly condensed grains before removal of the template. By treating the aged samples in a refluxing alkaline solution, the condensation degree of the primary particles has increased. This higher cross-linking degree is accompanied by a decrease in particle growth due to fewer defects in the zirconia lattice as the temperature rises. Calcination removes the amine template and leaves stable mesosstructures with walls consisting of very small particles of X-ray amorphous tetragonal zirconia originating from the nicely transformed amorphous primary particles. It was further shown that the alkaline-treated zirconias have an outstanding thermal stability with retention of most physical characteristics such as high surface area, pore volume, mesoporosity up to 800 °C, and a low angle X-ray reflection up to 700 °C, which is remarkably high for pure mesostructured zirconia. In contrast to EISA-prepared zirconia, it thus appeared that for calcined alkali-treated amine-templated zirconia, there exists a temperature window from 400 to 800 °C in which the pore walls are crystalline, while these nanosized crystallites are still predominantly meso-organised.
Acknowledgements

P. C. thanks the FWO (Fund for Scientific Research, Flanders, Belgium) for a position as senior research assistant. T.L. is indebted to the IWT-Flanders-Belgium for a Ph.D. grant. This work has been performed within the framework of IUAP V-1 of the Belgian government.

References


Fig. 9 N2 adsorption-desorption isotherms of (A) Zr-DDA-NH3 and (B) Zr-NNDDA-NH3 calcined at different temperatures.