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Reference:

Herregods Sebastiaan, Wyns Kenny, Mertens Myrjam, Kemps Raymond, Buekenhoudt Anita, Meynen Vera.- From template-assisted mesoporous titania powders to thin films : differences and similarities

Thin solid films: an international journal on the science and technology of thin and thick films - ISSN 0040-6090 - 593(2015), p. 17-25

Full text (Publishers DOI): <http://dx.doi.org/doi:10.1016/j.tsf.2015.09.039>

To cite this reference: <http://hdl.handle.net/10067/1294900151162165141>

From Template-assisted Mesoporous Titania Powders to Thin Films: Differences and Similarities

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ABSTRACT

A huge variety of template-assisted mesoporous powder syntheses are known in literature, but the conditions are not directly transferable to thin films. The present study discusses the differences and similarities between the titania powder and thin film synthesis for the preparation of mesoporous titania materials by means of evaporation induced self-assembly. Kr adsorption at -186 °C is a sufficient method to analyze the porosity of thin films and is traceable to the N₂ adsorption porosity data obtained at -196 °C. Next, problems concerning the macroscopic homogeneity of the thin film are discussed as well as the deposition of the porous layer. Finally, the thermal stabilization and calcination process are compared. In contrast to the powder sample, no nanocrystal formation is observed during the thermal stabilization of the thin film. And thus the average pore size of the thin film is independent of the thermal stabilization in the here investigated range and is in all cases 3,4 nm. Furthermore, the thin film synthesis leads to a better organized and more uniform pore structure as compared to the powder synthesis. Similar to the powder synthesis, uncontrolled crystallization during calcination may lead to a structural collapse of the mesostructure. Although the crystal size after calcination is much smaller for thin films, it seems that the critical crystal size for a structural collapse is smaller for the thin films as compared to the powders. The present study facilitates the transition from optimal powder to optimal thin film synthesis conditions, which could be useful for example in the synthesis of membranes with uniform pores starting from much more extended literature on solid powders certainly with respect to synthesis-structural property correlation.

KEYWORDS: mesoporous titania, Evaporation Induced Self-Assembly, powders, thin films, membranes, Kr adsorption, thermal stabilization, calcination

1. Introduction

Since the development of template-assisted mesoporous powders[1,2], research has extended to template assisted mesoporous thin films on dense[3] and even porous supports[4]. The impact of the support on the thin film properties has however not been studied in much detail in case of porous supports. In comparison to thin films, mesoporous powders provide a much wider range of possible synthesis and characterization techniques since there are fewer restrictions related to sample preparation, amount of sample, possible preferential orientations, etc. Furthermore, the powder literature is much more elaborate as compared to the thin film literature. This makes them attractive as research subject. Also the development of mesoporous thin films gains growing interest due to their applications in dye-sensitized solar cells, smart coatings, membranes etc[5-7]. In contrast to the powder samples, thin films are much more complex to analyze[8] because they generally consist of a thin porous top layer (typically a few hundred nanometers thick) on a thick dense support (typically a few hundred micrometers thick). Therefore, the contribution of the mesoporous top layer is only a fraction of the whole sample, although its impact can be very explicit as it is often the direct contact layer with the environment in the application. Consequently, adjustments to the characterization techniques need to be done in order to analyze mesoporous thin films: e.g. from N₂ adsorption at -196 °C for powders to Kr adsorption at -186 °C for thin films. Much less mass is deposited as a thin, thus the overall surface area is low (layer plus support) which complicates the analysis. Besides the substrate contribution and the very low amount of matter deposited, also structural anisotropy can make the analysis of thin films more complex[9]. Furthermore, next to the differences in characterization techniques needed, there are also differences in the formation mechanism. For a full discussion of the template mechanisms is referred to literature[6,10-13] but some general considerations should be kept in mind. The mesoporous powders made by evaporation induced self-assembly (EISA) are formed by gradual evaporation of the reaction solution from a petridish in which the initial

solution forms a liquid layer in order of magnitude of millimeters thick. Whereas thin films evaporate from much thinner liquid layers (a few 100 nanometers range) influencing the evaporation rates of the volatiles from the system, which has an impact on the self-assembly and hydrolysis/condensation reactions[14]. Due to this, also the air-liquid and air-substrate interfaces can play a more dominant role in thin films. It is well known that a water-surfactant rich liquid-air interface is formed during EISA[15] that subsequently increases progressively in concentration of non-volatile species (surfactant and inorganic oligomers) upon aging of the film at the air-liquid interface. This induces a concentration gradient between the air-liquid and liquid-substrate interface[16,17]. This concentration gradient, which is larger in thick films, can lead to several differently organized phases in the same film[15,18]. Since the powder synthesis can be regarded as a very thick film, the above mentioned concentration gradient could have a more pronounced effect on the powder synthesis. In addition specific attention needs to be given to thin films as they need to be macroscopically homogeneous. Processes like phase segregation or crack formation during thermal treatment could lead to large defects in the thin film, which is detrimental for their performance in the aimed application (e.g. in membrane top layers for high selective separation). Furthermore, not all synthesis processes known for powders can be applied on thin films as they could for example lead to detaching of the thin film from the substrate. Finally, due to the porosity of the support capillary suction of the dipping solution into the support can have a pronounced effect on the deposition and drying of the thin film[19].

Even though literature can be found on controlling the porous properties and formation mechanisms for titania powders[13,20,21] as well as for titania thin films on dense supports[12,14,21], little is described in literature about the differences and similarities in synthesis control mechanisms when going from powders to thin films. Nevertheless, from a development point of view, it is very interesting to know whether optimized powder synthesis

can be transferred to thin films directly without loss of the desired structural control and properties. The present research discusses the differences and similarities between the powder and thin film synthesis by means of EISA. Furthermore, it is of particular importance to understand also the differences in transferring this knowledge to porous supports such as in ceramic membrane development. Ceramic membrane development aiming at narrow pore size distributions (sharp cut offs and thus high selectivity) could largely benefit from the already existing literature on porous titania powders and thin films. However, for this purpose, it is necessary to understand the differences in mechanisms for structural control when transferring knowledge and procedures/mechanisms from powder synthesis to thin films on dense supports and further to transferring it to porous supports (membranes). We have selected titania as the model material to study these mechanistic differences in their synthesis with respect to the nature of the support and final material properties as titania is largely studied and known for powders and thin solid films on dense supports and widely applied as top layer for ceramic membranes. The focus is thus on the impact of support on the differences in formation mechanisms while the synthesis conditions are equal. This correlation would greatly advance and accelerate porous ceramic membrane development. The specific advantages of identifying the specific differences in mechanisms when transferring a synthesis to thin films exist to some extent for thin solid films on dense supports and largely for membrane development, due to the much more elaborated non-destructive characterization techniques existing on powders and solid thin films on dense supports giving much more insights in their synthesis-property correlation and in addition the much larger synthesis mechanistic insights existing in these fields of research.

2. Experimental details

Two different synthesis routes have been investigated:

The first synthesis route was based on the work of the Sanchez group[22-24]. The initial solutions were prepared as described in our previous publication[20] by dissolving 3,44 g surfactant (Brij 58, $C_{16}H_{33}(OCH_2CH_2)_{20}OH$, purchased from Aldrich), 10,2 mL hydrochloric acid (37%, purchased from Merck) and then the inorganic source (18,6 mL titanium tetraisopropoxide 98+%, TTIP, purchased from Acros Organics) into 140 mL isopropanol (IPA, 99,8+%, purchased from Merck). After 15 minutes stirring, an IPA solution with controlled water content was added dropwise. The final molar ratio of the solution was TTIP:1; Brij 58:0,05; IPA:40; H_2O :10 and HCl:2. Prior to deposition, the supports were cleaned by rinsing them three times with IPA. Immediately after the final rinse, the supports were blow dried from the top down using dry compressed nitrogen from the liquid nitrogen tank directed at an angle of about 45 ° from the vertical for dense supports and from above for tubular porous supports. After 30 minutes stirring at room temperature, thin films were dip coated from the solution on a 500 μm thick <100> silicon wafer with a 10 cm diameter (purchased from Si-Mat) or on a 10 cm long tubular TiO_2 membrane support (mean pore size of the top layer is 5 nm, purchased from Inopor (IKTS)) at a constant withdrawal rate of 2-5 mm/s and at a controlled relative humidity (RH) of 40-50%. After the drying line reached the bottom of the film, the films were placed in a controlled atmosphere for 24 h (RH=75 % + IPA vapor) at room temperature. All the samples underwent the same treatment under controlled atmosphere unless stated otherwise. Subsequently, the thin films were transferred to an oven and heated at 1 °C/min. Thermal stabilizations (80-140 °C) were applied for 24 h at different temperatures. The formed thin films were calcined at 360 or 440 °C (2 h, 30°C/h, ambient atmosphere), also a isothermal period of 12 h at 300 °C (plateau) was executed.

The second synthesis route was based on the so-called nanoparticle route[25,26], namely with Brij/Ti ratio of 0,083. The initial solution was prepared by dissolving 4,72g surfactant (Brij

58, $\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$, purchased from Aldrich) into isopropanol (IPA, 99,8+%, purchased from Merck) and then the inorganic source (titanium tetraisopropoxide 98+%, TTIP, purchased from Acros Organics) was added. Afterwards, a solution of hydrochloric acid (37%, purchased from Merck) in isopropanol was added drop wise to the initial solution. The final molar ratio of the solution was TTIP:1; Brij 58:0,083; IPA:25; H_2O :1 and HCl:0,29. After 20 minutes of stirring at room temperature, the white nontransparent solution was aged at 60 °C for 2 h leading to a transparent colorless solution. From this solution thin films were dip coated and treated as described in the above synthesis route based on the work of the Sanchez group.

An additional alkaline treatment [27-30] by means of NH_3 (g) was carried out on two thin films made by synthesis method 1. A solution of NH_4OH (l) was placed for at least 24 h in a small dessicator cabinet in order to obtain a saturated NH_3 (g) atmosphere. Then the thin film was placed for 48 h in the saturated NH_3 (g) atmosphere. In one case the alkaline treatment was performed after 24 h aging under controlled atmosphere ($\text{RH} = 75\% + \text{IPA vapour}$) and prior to the thermal stabilization at 120 °C for 24 h. In the other case the alkaline treatment was performed during a 48 h aging under controlled atmosphere ($\text{RH} = 75\% + \text{IPA vapour} + \text{NH}_3$ (g)) followed by the thermal stabilization at 120 °C for 24 h.

Powders were made by pouring the dipping solution in a 20 cm petridish immediately after the supports were coated and treating them in the same manner as the thin films.

The powder porosity characteristics were determined by performing N_2 sorption measurements at -196 °C using a Quantachrome Quadrasorb SI and a Quantachrome Autosorb-1-MP automated gas system. Prior to the measurements, the samples were outgassed under vacuum during 16 hours at a temperature of 120 °C. The Barret-Joyner-Halenda (BJH) method applied to the adsorption branch of the isotherm was utilized to

determine the pore size distribution or if stated otherwise the non-local density functional theory (NLDFT) model was applied. The Brunauer-Emmet-Teller (BET) method was applied to calculate the specific surface area. The total pore volume was determined at P/P_0 0,98.

The thin film porosity characteristics were determined by performing Kr adsorption measurements at -186 °C using a Quantachrome Autosorb-iQ-C automated gas system as described by Thommes and coworkers[31-33]. Film-on-support samples were cut into square pieces of about 8 by 8 mm with a silicon carbide scribe. Then, the pieces were transferred to a 12 mm diameter glass sample bulb. The used sample mass is that of the entire sample (i.e. deposited layer plus dense support). Prior to measurements, the samples were degassed at 120 °C for 16 h under vacuum. The krypton adsorption isotherms at -186 °C were analyzed using the Quantachrome software (ASiQwin version 3.0). The Brunauer-Emmet-Teller method was applied to calculate the specific surface area. The total pore volume was determined at $P/P_0 = 0,73$ which corresponds to pores smaller than 14,5 nm in order to avoid unwanted solidification of Kr. The conventional methods for pore size analysis based on the Kelvin equation (BJH method) are not applicable for the pore size analysis with Kr adsorption since drastic assumptions concerning the thermophysical properties (e.g. surface tension, contact angle, density) need to be made. Also methods like NLDFT or Grand Canonical Monte Carlo are not yet developed for Kr adsorption at -186 or -196 °C[31]. Therefore, the unique krypton calibration curve at -186 °C developed by Quantachrome instruments is applied to determine the PSD. The krypton calibration curve is traceable to NLDFT pore size analysis[33]. A log-normal fit was made to the PSD as advised by the manufacturer.

Retention and Molecular Weight Cut-Off (MWCO) of the membranes were determined by cross flow filtration experiments conducted on the membranes with an aqueous feed containing polyethylene glycols of different molecular weight (Molecular Weight (MW) = 600, 1500, 3000, and 10000 Da). The retentate and permeate samples were analyzed by gel

permeation chromatography. The applied unit consisted of a High-performance liquid chromatography pump (Waters 510, 1 mL / min), an auto sampler (Waters 717), two in series coupled columns (Ultrahydrogel 500 and 200) and a refractive index detector (Waters 2414). From the chromatography data the retention was calculated by the following equation $R_i [\%] = (1 - (C_{p,i}/C_{r,i})) \cdot 100$, where $C_{p,i}$ is the concentration of the permeate and $C_{r,i}$ is the concentration of the retentate for a given compound i. A retention or cut-off curve is obtained by plotting the retention against molecular weight. The MWCO of a membrane is defined as the MW above which molecules are at least 90 % retained by the membrane.

Scanning electron microscopy (SEM) was performed with a Jeol JSM6340F microscope, which was operated at an acceleration voltage of 5 kV.

X-Ray Diffraction (XRD) analysis was performed to determine the long range organization, i.e. crystallinity (wide angles), and/or the mesoporous (low angles) ordering of the synthesized materials. The measurements were carried out on a PANalytical X'PERT PRO MPD diffractometer with Cu K α -radiation. Also a bracket stage, a monochromator and soller slits were applied. The measurements were performed in the 2 θ -mode using a monocrystal with a scanning speed of 0.04° / 4s and measuring in continuous mode. The crystal size was determined by means of the Scherrer equation: $d = (K \cdot \lambda) / (\beta \cdot \cos\theta)$ where d is the mean crystal size, K is the Scherrer constant which is a dimensionless shape factor (K was 0,9 in the present paper), λ is the X-ray wavelength (Cu-K α radiation was used), β is the width of the peak (i.e. the full-width at half-maximum of the intensity of the anatase (101) peak) and θ is the is the Bragg angle[34,35]. The (101) peak around $2\theta = 25^\circ$ was utilized to determine the mean crystal size since it does not overlap with neighboring peaks.

3. Results and Discussion

3.1 Comparison of N₂ adsorption at -196 °C and Kr adsorption at -186 °C

The analysis techniques used to analyze the porosity of the powder samples (N₂ adsorption at -196 °C) and the porosity of the thin films (Kr adsorption at -186 °C) are compared by measuring the same powder sample (made by the first synthesis method, thermally stabilized at 80 °C (24 h) and calcined at 360 °C (2 h)) with both techniques.

Figure 1 displays the nitrogen adsorption-desorption isotherm (-196 °C) and the krypton adsorption isotherm (-186 °C) of the measured sample. Obviously, the sample is mesoporous since both isotherms exhibit the characteristic type IV isotherm. The nitrogen isotherm exhibits a type H2 hysteresis loop, which is typical for ink-bottle pores (IUPAC classification[36]). The isotherms show a sudden increase in adsorbed volume as a result of capillary condensation in the mesopores. Despite the fact that krypton at -186 °C is well below its bulk triple point (i.e. -157,2°C [37]) capillary condensation in the pores is observed. It appears that at -186 °C only gas-liquid phase transitions are observed in the measured range and the adsorbed krypton is in a super cooled liquid state[31]. This is a requirement in order to obtain a clearly defined relationship between pore filling pressure and pore size, since the adsorbate density needs to be independent of the pore size. Similarly, in literature[38] a shift of the argon triple point to lower temperatures is observed and pore condensation of argon still occurs at -196 °C (i.e. ca. 6,5 °C below the bulk triple point) when confined in pores with a diameter smaller than 8 nm. Although capillary condensation appears in the same relative pressure range and follows a similar slope, at high P/P_0 both isotherms deviate (i.e. the krypton isotherm does not reach a plateau). The reason is unclear but might originate from the pore size being close to 8 nm which is near the limit of the Kr adsorption analysis[31]. Figure 1 (inset) shows the pore size distributions (PSDs) of the sample. There is a good agreement between the NLDFT nitrogen adsorption PSD and the krypton adsorption PSD with the maxima of the PSD at respectively 5,0 nm for nitrogen and 4,8 nm for krypton. Furthermore,

also the width of the PSD (Full Width at Half Maximum (FWHM)) obtained by the NLDFT method applied to the nitrogen adsorption branch of the isotherm is very similar to the width of the PSD (FWHM) obtained by calculating it from the krypton adsorption (2,1 nm and 2,3 nm respectively). This confirms that the pore size data obtained by the krypton method at -186 °C are traceable to NLDFT pore size data obtained from nitrogen adsorption at -196 °C, as stated by the manufacturer[33]. Applying the commonly used BJH method to the adsorption branch of the nitrogen isotherm leads to a broader PSD with the maximum located approximately 1 nm lower than the maxima obtained by the NLDFT method. It is known in literature that the BJH method underestimates the pore size with approximately 1 nm[39-41]. The porosity data is summarized in table 1. The total pore volume obtained by the krypton method is slightly higher than the total pore volume obtained by nitrogen sorption (0,125 mL/g and 0,114 mL/g respectively). Also the specific surface area obtained by the krypton method is higher than the surface area obtained by the nitrogen method (147 m²/g and 113 m²/g respectively).

3.2. Problems concerning macroscopic homogeneity of thin films

The macroscopic integrity of thin films is of utmost importance when synthesizing top layers for high selective membranes. Large defects and/or inhomogeneous top layers will be detrimental for the performance of the membrane. The uniformity and integrity of the macroscopic thin films is determined by many variable parameters of the dip coating process as well as by the composition and properties of the sols utilized. Figure 2A shows a thin film made by synthesis method 1 during aging under controlled atmosphere. The thin film was dip coated under a current of air, which leads to non-uniform evaporation of the solvent, disturbing the evaporation induced self-assembly process. This leads to a non-uniform thin film, thus a steady atmosphere is a necessity in order to achieve a homogeneous thin film of uniform thickness. Figure 2B displays a thin film made by synthesis method 2 during 24 h

aging under controlled atmosphere ($RH = 75\% + \text{IPA vapor}$). The initial sol is a white nontransparent solution due to incomplete dissolving of the template Brij 58 under the given conditions. The sol becomes a colorless transparent solution during heating at $60\text{ }^{\circ}\text{C}$ (2 h) due to increased solubility at higher temperatures. Thin films were dipped from this solution. Consequently, phase segregation occurred during aging under controlled atmosphere at room temperature as a result of the lower solubility of the template Brij 58 at room temperature in the high concentrated solution used in method 2. Therefore, a non-uniform film with large defects appeared although a mesostructured material was observed by SEM (figure 3). The problem of phase segregation could be overcome by aging the thin film under controlled atmosphere at elevated temperature or by increasing the amount of solvent. It has also been empirically determined that higher amounts of water in the reaction mixture significantly increase the solubility of Brij 58 in the solvent but this could complicate the controlled condensation of the titania source. The problems related to phase segregation observed in method 2 are not present when applying method 1 as it consists of a reduced Brij 58 and increased solvent and water content. Furthermore, also the acidity of the reaction solution has been raised in method 1 in order to control the reactivity of the titania source in presence of the elevated water content. Consequently, figures 2C and 2D show non calcined homogeneous thin films made by synthesis method 1 after 24 h aging under controlled atmosphere ($RH = 75\% + \text{IPA vapor}$) and after 24 h thermal stabilization at $80\text{ }^{\circ}\text{C}$ or $120\text{ }^{\circ}\text{C}$. It needs to be pointed out that uncontrolled crystallization can disrupt the template self-assembly process or can induce a pore collapse [20]. Both phenomena lead to an increase in pore size and are detrimental for the uniformity of the pores. Thus, with the application of high selective membranes in mind, uncontrolled crystallization needs to be avoided for applications such as high selective ceramic membranes.

It is shown in literature [27-30] that an alkaline post-modification by refluxing a non-calcined mesoporous titania powder in NH_3 (aq) can lead to nanocrystalline titania walls prior to the template removal. So in that case, a controlled crystallization occurs, leading to an intact mesostructure upon template removal at higher temperatures. The results of these experiments will are not discussed in the present paper. But, it is interesting to point out that upon immersing a thermal stabilized thin film (24 h at 120 °C) into NH_3 (aq) the titania top layer detached almost immediately from the substrate. Therefore, the post-modification method using aqueous NH_3 is not suitable for thin films. Furthermore, a post-modification by means of gaseous NH_3 was executed in order to overcome the detaching of the film. Applying the post-modification before the thermal stabilization leads also to detachment of the titania film from the substrate. Thus the integrity of the thin films is lost. Figure 2E and 2F show inhomogeneous thin films made by synthesis method 1. The thin films were post-modified with NH_3 (g) for 48 h during (figure 2E) and after (figure 2F) aging under controlled atmosphere ($\text{RH} = 75 \% + \text{IPA vapor}$) after which they have been thermally stabilized at 120 °C. However, the integrity of the thin films remained intact when applying the post-modification by means of NH_3 (g) after the thermal stabilization.

3.3. The influence of the dipping speed

A great difference between the powder and thin film synthesis is of course the deposition of the thin film. As a result, there are extra synthesis parameters that control the final properties of the porosity like the dipping speed in the thin film synthesis. Cross section SEM images (not shown) were taken of titania thin films (synthesis method 1, $T_{\text{stab}} = 120 \text{ }^\circ\text{C}$, $T_{\text{cal}} = 360 \text{ }^\circ\text{C}$) deposited with different dipping speeds on a silicon wafer. The SEM images show no observable cracks, indicating that the thin film is defect free in all cases. As known, the film thickness of the deposited titania increases with the dipping speed and is summarized in table 2.

Figure 4 shows the Kr adsorption isotherms and pore size distributions (inset) of the titania thin films (synthesis method 1, $T_{\text{stab}} = 120\text{ }^{\circ}\text{C}$ and $T_{\text{cal}} = 360\text{ }^{\circ}\text{C}$) deposited with variable dipping speed. The porosity data is summarized in table 2. It is noteworthy to mention that the used mass in Kr adsorption (in the specific surface area and total pore volume) refers to the sum of the masses of the porous thin film and the dense support. Clearly all the isotherms exhibit the type IV isotherm characteristics for a mesoporous material. All the isotherms exhibit a steep capillary condensation step between $0 \leq P/P_0 \leq 0,4$ due to the presence of mesopores. Consequently, all the thin films have a narrow PSD around 3,0 – 3,1 nm. The apparent specific surface area and the total pore volume of the thin films increase linear with the dipping speed although not linear to the increase in thickness. Figure 5 shows the retention cut-off curves of the membranes synthesized by depositing a titania thin film on a porous support at 2 or 5 mm/s (synthesis method 1, thermally stabilized at 120 °C (24 h) and calcined at 360 °C (2 h)). The retention curves of both membranes are very similar independent of the applied dipping speed indicating a similar pore size. So, both membranes have a similar MWCO of 4444 Da and 4420 Da for the membranes deposited at 2 and 5 mm/s respectively. Furthermore, both membranes have a similar flux under the same applied conditions: 36,5 and 37,5 L/(h.m²) at a trans membrane pressure of 100000 Pa for the membranes deposited at 2 and 5 mm/s respectively.

The film thickness can be adjusted by altering the dipping speed, which is in good agreement with literature[42]. Higher dipping speeds lead to thicker thin films since the deposited liquid layer has less time to flow back down as a result of gravitational draining. Furthermore, the pore size and pore uniformity is not affected by the difference in dipping speed. This is of utmost importance to warrant reproducible synthesis of e.g. high selective membranes. The apparent specific surface area and total pore volume seems to increase with the dipping speed. But this is misleading, in fact the porosity of the entire thin film remains the same

independent of the dipping speed. The observed increase is a result of the increased film thickness. The values of the apparent specific surface area and total pore volume listed in table 2 are per gram of sample. The sample mainly consist of a non-porous support with thereon a very thin porous layer with negligible mass. It is only this very thin porous layer that contributes to the Kr adsorption isotherm. Therefore, the 5 mm/s sample has an increased apparent specific surface area and total pore volume since it has a thicker porous layer as compared to a 2 mm/s sample with similar mass. But, the porosity of the actual deposited layer is similar in both cases. The independence of the porosity of the dipping speed is confirmed by the retention curves of the membranes, which are in fact almost identical indicating the high reproducibility of the template-assisted synthesis (in contrast to sol-gel synthesis). Furthermore, the increased film thickness seems to be negligible for the performance of the membrane with respect to flux behavior and MWCO.

3.4. The Thermal stabilization

The thermal stabilization is crucial in the template-assisted synthesis of titania mesostructured materials as shown in our previous publication for powders [20]. The thermal stabilization consolidates the inorganic framework prior to template removal in order to avoid a pore collapse, which is detrimental for the uniformity of the pores. Figure 6 shows the Kr adsorption isotherms at -186 °C and the pore size distributions (inset) of titania thin films made by synthesis method 1 and thermally stabilized at different temperatures for a period of 24 hours and subsequently calcined at 360 °C (2 h), the porosity data is summarized in table 3 and compared to the porosity data of the powders under the same conditions. Clearly all the samples exhibit the characteristic type IV isotherm (IUPAC classification[36]) typical for a mesoporous material. The specific surface area and total pore volume reaches a maximum at 120 °C, indicating that 120 °C is the most favorable for the template self-assembly in our thin

film samples. In addition, the 120 °C has the most narrow pore size distribution (smallest FWHM) and thus the most uniform pores.

It has to be noted that the pores of the thin films are more uniform as compared to the powder samples as can be observed by their smaller FWHMs (table 3). Furthermore, in contrast to the powders, the average pore diameter of the thin films is independent of the thermal stabilization temperature and is in all cases around 3,4 nm. Moreover, also the variation in FWHMs is much less variable in case of the thin films as compared to the powders upon changes in the stabilization temperature.

The optimum for thin films at 120 °C is in contrast to the powder samples where at 80 °C the self-assembly is the most optimal and at higher temperatures a pore size increase is observed, accompanied by the formation of less uniform pores (higher FWHM). As discussed in our previous paper [20], this phenomenon in the powder samples is due to the formation of a limited amount of anatase nanocrystals in the mainly amorphous structure, which disrupt the template self-assembly process leading to enlarged and less uniform pores. This low temperature nanocrystal growth seems to be absent in the thin films, which is beneficial for the uniformity of the pores since no disruption of the template self-assembly occurs. This is confirmed by wide angle XRD on a non-calcined thin film thermally stabilized at 120 °C where no characteristic peaks of the anatase crystal phase are observed (not shown), whereas the corresponding powder sample clearly exhibit anatase nanocrystals as proven by wide angle XRD, Raman spectroscopy and TEM [20]. It is known in literature that the presence of water is critical for the crystallization of titania at low temperature[43]. Therefore, the different crystallization behavior of the powder and thin film samples could be the result of the altered drying conditions between the two due to their large difference in deposited liquid layer thickness. Consequently, the altered drying conditions could result in a different liquid layer composition during thermal stabilization which favors the formation of anatase

nanocrystals in the powder samples whereas no crystals are formed in the thin film during the thermal stabilization. Moreover, the thin film samples exhibit a small angle XRD pattern with sharper peaks as compared to the powder samples (figure 7), indicating that the thin film samples exhibit a better organized mesostructure. This can be explained as follows: since the solvent evaporates at the air-liquid interface, the concentration of the surfactant is higher at the air-liquid interface. And so a concentration gradient is formed from the air-liquid interface to the film substrate. This concentration gradient is larger in thicker films and therefore could lead to multiple mesophases in the same film. As the powder synthesis can be regarded as a very thick film, this phenomenon has a larger impact on the powder synthesis leading to an overlap of different peaks and so a XRD pattern with less sharp peaks and broader pore size distribution (larger FWHM).

In addition, figure 7 compares also both thin films which exhibit a distinct different diffraction pattern. It is clear that changing the aging atmosphere in the thin film synthesis from RH = 75 % to RH = 75 % + IPA vapor leads to a change in the mesophase of the thin films since a different d-value is observed. Similar as in silica-CTAB thin film systems [14], this can be due to a co-surfactant effect of IPA. The IPA molecules arrange themselves between the Brij-58 molecules, with the OH groups located at the micelle's surface and the alkyl chain being directed towards the micelle's center. This explains the higher d value (lower angle 2θ) of the thin films aged under RH = 75% + IPA vapor atmosphere due to swelling of the micelle ($d = 77,4 \text{ \AA}$ for RH = 75% +IPA vapor and $d = 57,3 \text{ \AA}$ for RH = 75 %). The exact mesophase is difficult to determine, especially since preferential orientation in the thin film can lead to absence of certain Bragg diffraction peaks (as compared to powder samples) when using a standard powder diffractometer as used in the present paper. Indeed, only the crystallographic planes that are parallel to the surface are typically observed in powder 1D XRD [44]. The use of 2D GISAXS diffractograms can make it possible to

measure Bragg peaks that appear at angles away from the specular plane. However, in some cases[45] a small ‘2D window’ is also visible in 1D powder XRD resulting in additional fingerprint off-specular Bragg peaks. This only occurs if the lattice constants of the mesostructure are small enough and the Soller slit spacing of the XRD setup is large enough.

In conclusion, the thin film synthesis leads to a better organized and more uniform pore structure as compared to the powder synthesis. Moreover, in contrast to the powder synthesis the porosity of the thin film is independent of the thermal stabilization temperature in the investigated range.

3.5. Template removal by means of calcination

The organic template needs to be removed from the titania material by means of e.g. calcination in order to obtain a porous structure. Figure 8 shows the Kr adsorption isotherms at -186 °C and pore size distributions of titania thin films made by synthesis method 1, aged under controlled atmosphere for 24 h (RH=75 % + IPA vapor), thermally stabilized at 80 °C (24 h) and calcined at 360 °C or 440 °C (2 h). The porosity data of the films are summarized in table 4 and compared to the porosity data of the corresponding powder sample. Obviously the thin film calcined at 360°C has a characteristic type IV isotherm (IUPAC classification[36]) typical for a mesoporous material. The thin film has a small pore diameter of 3,5 nm, which is smaller than the corresponding powder sample. Upon calcination of the thin film at 440 °C the capillary condensation shifts to a higher and broader P/P_0 range due to the formation of larger and less uniform pores. Similarly, the pores of the powder sample become less uniform and larger upon calcination at higher temperature. Furthermore, the specific surface area of the thin film decreases drastically after calcination at 440 °C compared to calcination of the thin film at 360 °C, while the total pore volume remains constant and the pore diameter increases. In the same way the specific surface area of the

powder sample also decreases upon calcination at higher temperature, while the pore size increases and the total pore volume of the powder remains constant.

The small angle X-ray diffractograms (figure not shown) of all the calcined samples show no clear signals, indicating that a large part of the organization is lost during calcination. This is in agreement with the mesostructured material observed by SEM (figure 3). Figure 9 shows the wide angle XRD patterns of the titania thin films calcined at 360 or 440 °C (2 h). Both thin films exhibit the characteristic diffraction pattern of an anatase crystal structure. The crystal sizes of the thin films are shown in table 5 and compared to the corresponding powder samples. Thin films have smaller crystals compared to the corresponding powder sample independent of the calcination temperature. The difference in crystal size between the powder and the thin film is larger for samples calcined at 360 °C (Δ crystal size = 3,2 nm) as compared to the samples calcined at 440 °C (Δ crystal size = 1,7 nm). The non calcined thin films exhibit no diffraction peaks whereas the non calcined powder samples consist of small nanoparticles in a mainly amorphous structure (as discussed in our previous paper [20]). This confirms the statement that crystal growth occurs in an earlier stage during the powder synthesis as compared to the thin film synthesis. Therefore, it seems that control of the crystal growth is more crucial in the powder synthesis although it is also of utmost importance in the thin film synthesis as exemplified by the loss in uniform porosity upon calcination at 440°C and coinciding substantial crystal growth. Similar as in the powder sample, the crystal size of the titania thin film increases with the calcination temperature from 4,0 nm at 360 °C to 7,1 nm at 440 °C.

During calcination the same phenomenon occurs in the thin films as in the powders. With the temperature the crystal size of the calcined structure increases as expected. The increase in crystal size leads to an explicit increase in pore size in the thin film calcined at 440 °C, accompanied by a broader pore size distribution (i.e. less uniform pores) and a drastic

decrease in specific surface area while the total pore volume remains constant. Indeed, a structural collapse occurs due to uncontrolled crystallization which is harmful for the formed pore structure, as discussed in literature [20,28,46-48]. In other words, to maintain the pore size as directed by the template, the calcination temperature should be kept below 440 °C in order to avoid uncontrolled crystallization, unless the crystal size is controlled by other methods[27,48-50]. It is worthy of mentioning that, although the crystal growth in the thin films occurs in a later stage of the formation process, it seems that the thin film are more sensitive to the presence of larger crystals and the crystal growth is more substantial upon calcination. Indeed, a pore collapse occurs in the thin film in the presence of 7,1 nm anatase crystals, whereas in the powder sample no pore collapse occurred at crystal sizes of 7,2 nm crystals (table 5). The more substantial crystal growth visible in thin films could be due to the absence of pre-formed crystal nuclei in the films before calcination in contrast to the powders, leading to a less controlled growth and a higher chance of structural collapse.

4. Conclusions

Kr adsorption at -186 °C is a sufficient method to analyze the porosity of titania thin films and is NLDFT traceable to the porosity data obtained by N₂ adsorption at -196 °C. In some cases, the titania thin films synthesis needs to be adjusted in order to form homogeneous crack free thin films, which is a necessity for some applications e.g. high selective membranes. The dipping speed has no influence on the porosity of the titania thin films. Therefore, thicker thin films can be deposited in a reproducible manner by increasing the dipping speed. In contrast to the powder synthesis, no nanocrystal formation is observed during the thermal stabilization of the thin film. Therefore, the porosity of the titania thin film synthesis is independent of the thermal stabilization temperature but more sensitive to calcination in a later step. This is in

contrast to the powder synthesis, where anatase nanocrystal formation during the thermal stabilization leads to disruption of the template self-assembly. In general, the titania thin film synthesis leads to better organized and more uniform mesostructures probably due to the presence of smaller concentration gradient in the thin film. Similar to the powder synthesis, uncontrolled crystallization during template removal (calcination) may lead to a structural collapse of the mesostructure. Although the crystal size after calcination is much smaller for titania thin films, it seems that the critical crystal size for a structural collapse is smaller for the thin films as compared to the powders. Nevertheless, the same calcination regime can be applied for the thin films and the powder without a structural collapse due to uncontrolled crystallization.

Acknowledgements

The authors thank the FWO Flanders (Fund for scientific research, project G0237.09) for financial support. The authors also thank M. Maesen for the gel permeation chromatography measurements.

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List of Figure and Table Captions

Figure 1: N₂ sorption isotherm (at -196 °C), Kr adsorption isotherm (at -186 °C) and the corresponding adsorption pore size distributions (inset) of the same powder synthesized by the first synthesis method ($T_{\text{stab}} = 80$ °C and $T_{\text{cal}} = 360$ °C). The Kr adsorption PSDs are calculated with both the BJH and NLDFT method.

Figure 2: Pictures of various thin films, reflection of the surrounding is visible in some cases. The scale bars represent 1 cm. (A) inhomogeneous thin film due to air current during dip coating. The picture was taken during aging under controlled atmosphere and the thin film was made by synthesis method 1 (B) phase segregation after 24 h aging under controlled atmosphere in a thin film made by synthesis method 2 (C) homogeneous non calcined thin

film after 24 h aging under controlled atmosphere and thermal stabilization at 80 °C for 24 h made by synthesis method 1 (D) homogeneous non calcined thin film after 24 h aging under controlled atmosphere and thermal stabilization at 120 °C for 24 h made by synthesis method 1 (E) detaching of the titania thin film from the substrate after 48 h aging under controlled atmosphere (RH = 75 % + IPA vapor + NH₃ (g)) and thermal stabilization at 120 °C for 24 h made by synthesis method 1 (F) detaching of the titania thin film from the substrate after 24 h aging under controlled atmosphere (RH = 75 % + IPA vapor) followed by a 48 h treatment with NH₃ (g) and subsequent thermal stabilization at 120 °C for 24 h made by synthesis method 1.

Figure 3: Top view SEM image of a titania thin film synthesized by method 2 ($T_{\text{stab}} = 80\text{ °C}$ and $T_{\text{cal}} = 360\text{ °C}$).

Figure 4: Kr adsorption isotherms and adsorption pore size distributions (inset) at -186 °C of titania thin films made with synthesis method 1 and deposited with different dipping speeds ($T_{\text{stab}} = 120\text{ °C}$ and $T_{\text{cal}} = 360\text{ °C}$).

Figure 5: Retention curves of titania membranes made with synthesis method 1 and deposited with different dipping speeds ($T_{\text{stab}} = 120\text{ °C}$ and $T_{\text{cal}} = 360\text{ °C}$).

Figure 6: Kr adsorption isotherm and adsorption pore size distributions (inset) at -186 °C of titania thin films made with synthesis method 1 and thermally stabilized at different temperatures for 24 h ($T_{\text{cal}} = 360$ °C).

Figure 7: Small angle XRD patterns of non-calcined titania thin films and powders (inset) made with synthesis method 1 and aged under different atmospheres ($T_{\text{stab}} = 120$ °C).

Figure 8: Kr adsorption isotherms and adsorption pore size distributions (inset) at -186 °C of titania thin films made with synthesis method 1 and calcined at 360 or 440 °C for 2 h ($T_{\text{stab}} = 80$ °C).

Figure 9: Wide angle XRD patterns of titania thin films and powders made with synthesis method 1 and calcined at 360 or 440 °C for 2 h ($T_{\text{stab}} = 80$ °C).

Table 1: Porosity data obtained by N_2 sorption at -196 °C and Kr adsorption at -186 °C of a titania powder made by synthesis method 1 ($T_{\text{stab}} = 80$ °C and $T_{\text{cal}} = 360$ °C).

Table 2: Porosity data obtained by Kr adsorption at -186 °C (thin films) and film thickness obtained by SEM of titania mesoporous structures deposited with different dipping speeds (made by synthesis method 1, $T_{\text{stab}} = 120$ °C and $T_{\text{cal}} = 360$ °C).

Table 3: Porosity data obtained by Kr adsorption at -186 °C (thin films) and N_2 sorption at -196 °C (powders) of titania mesoporous structures made by synthesis method 1, aged under controlled atmosphere (RH = 75% + IPA (g) for 24 h), thermally stabilized at different temperatures (24 h), and calcined at 360 °C (2 h).

Table 4: Porosity data obtained by Kr adsorption at -186 °C (thin films) and N_2 sorption at -196 °C (powders) of titania mesoporous structures made by synthesis method 1, thermally stabilized at 80 °C for 24 h and calcined at different temperatures for 2 h.

Table 5: The crystal size (obtained from wide angle XRD) of the calcined samples at different temperature and for 2 h. (made by synthesis method 1, thermally stabilized at 80°C for 24h.)