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Controlled chemical precipitation of titania for membrane applications—effect of heat treatment and fabrication conditions on its performance

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Controlled chemical precipitation method was used to obtain nanosized titania (TiO_2) powders. XRD, DTA/TGA/DTG techniques were employed for phase analysis and to know the thermal changes taking place in precipitated precursor during heating. The effect of processing and fabrication conditions viz. calcination temperature, mold pressure and sintering temperature/time on membranes prepared from this titania powder was studied using permeability measurements. The bulk porosity, average pore size and permeability were found to decrease with increase in the molding pressure. However, an increase in the sintering period increases the bubble point and brings the diameter of the larger pores nearer to that of the average pore.

1. Introduction

The development and commercialization of ceramic membranes employed in separation applications have tremendously increased during recent years [1]. These membranes possess some inherent advantages over the organic ones such as thermal and mechanical stability, chemical and microbiological resistance and long life. Many inorganic oxide materials e.g. TiO_2, ZrO_2, Al_2O_3, SiO_2 and zeolite based materials have been tried so far for the fabrication of supported/unsupported membranes [2–4]. They are widely used for ultra/micro filtration because of their high porosity and as supports for depositing thin oxide layers for use in the nanofiltration range. Generally, for titania membranes, the TiO_2 powders are prepared by chemical synthesis routes, namely, sol-gel, sol-precipitation and peptization of hydrated titania in acidic medium [5, 6]. It was observed [5] that the porosity and surface area decreased and pore size increased several times during heat treatment in the temperature range 450°–800°C. Recent studies [7] on TiO_2 membranes revealed that the unpeptized precursor showed comparatively more resistance to porosity reduction during thermal treatment as against peptized samples [7]. Therefore, in the present work, a protocol based on a simple and easier method utilizing the controlled hydrolysis of titanium tetrabutoxide in the presence of acetone, acetic acid and water is used to precipitate nano-sized titania precursor. The nano-sized precursor was precipitated under ambient conditions rather than in dry nitrogen [8, 9]. The results related to the synthesis, the influence of fabrication conditions and thermal treatment on the characteristics and performance of titania membranes made from this nano-sized TiO_2 powder obtained by pyrolysis of titania precursor are reported.

2. Experimental procedure

Monomeric titanium tetra butoxide (BTM, $\geq$99.5% pure, Synthochem, India), acetone (AR grade, SD's, India), acetic acid (99.5% pure, SD's, India) and deionised water were used as starting chemicals during the synthesis of nano-sized titania powder.

2.1. Powder synthesis

Nano-size titania (TiO_2) powder required for the fabrication of disk type membranes was synthesized by the controlled hydrolysis of BTM in the presence of acetone and acetic acid. Anhydrous acetone was used as solvent and acetic acid as catalyst for hydrolysis reaction. BTM was added to a solution ($pH \approx 4$) containing acetone, acetic acid and water. The hydrolysis of BTM was carried out at room temperature using molar ratios, $H_2O/BTM = 10$, acetic acid/BTM = 0.285 and acetone/BTM = 20 (V/V). The titania precursor was synthesized by rapidly adding BTM ($\approx$2 min.) to a solution containing (acetone + acetic acid + water) in proportions mentioned above with continuous stirring. The condition leading to an instantaneous precipitation of the precursor was optimized by systematically varying the H_2O/BTM ratio and the sequence of mixing of the solutions thereafter while stirring. The white hydrated titania precursor was aged for about

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28 h, filtered, washed several times with acetone and finally air-dried. The as-dried precursor was calcined in static air for 2 h at two different temperatures (350° and 700 °C), and characterized further before making membranes.

2.2. Preparation of membrane disks

Titania membranes in the form of disks were fabricated from the powder precursor prepared by the above method to examine the effect of i) sintering temperature and time and ii) disk molding pressure.

The nano-sized TiO_2 powder obtained by the pyrolysis of as-dried titania precursor at 350° and 700°C (period: 2 h) were further cold-pressed into flat circular disks of 19 mm diameter and thickness = 1.5–2.6 mm using 2% (wt.) PVA binder. Green membrane disks were made at a molding pressure of 13.8 MPa and sintered for 2 h at different temperatures, to find out the effect of sintering temperature. The disks made from nano-sized titania powder obtained by calcination at 350°C were sintered at 450°, 550° and 700 °C, whereas those made from the powder calcined at 700 °C were sintered at 900 °C.

Disks were made at molding pressure varying from 13.8 to 34.4 MPa and were sintered at 700 °C in static air for 2 or 7 h to study the effect of molding pressure and sintering time.

2.3. Characterization

The thermal analysis of the as-dried precursor was carried out by DTA/TGA/DTG (Setaram, TG/DTA 92) in air (heating rate: 10 °C/min) to obtain information about the formation temperature and to decide the temperature range of heat treatment. The structure and phase identification of the calcined/sintered, pellet/powder was done using XRD (Cu k_α radiation with Nickel filter, Philips model PW 1730 X-ray diffractometer). The surface area was measured using a Monosorb surface area analyser (Quantachrome Corporation, USA). The density of the porous membranes was determined from their weight and geometrical volume. The membrane porosity was estimated by comparing the measured bulk density with that of the true phase density. The membrane permeability was tested by measuring the flux of isopropyl alcohol (IPA) at 0.152 MPa at 30 °C. The open pore size distribution of the membrane was estimated by the measurements of air diffusion through IPA-wetted membranes at a pressure in the range of 0.02–0.304 MPa. The pore radius was correlated with air pressure using Washburn's equation [10]

$$\mathrm{pr} = -2\tau \cos\theta$$

where 'r' is the pore radius, 'τ' is the surface tension of IPA and 'θ' is the contact angle for IPA/titania. In our calculations $\cos\theta$ is taken as unity which is equivalent to the assumption that IPA completely wets the membrane surface. The lowest pressure at which the airflow appears known as the bubble point is an estimate of the largest pore in the membrane. The presence of the smaller pores can be seen by conducting the air flux measurements at the higher pressure, and average pore size for the measured flux can be calculated [11]. The IPA technique used measures only open-ended pores down to the pore radius of 0.29 μm due to the equipment pressure limitations. The pore size and its distribution in T4 sample were also measured by mercury porosimetry (Autoscan 60, Quantachrome Corporation, USA). The mercury intrusion technique gives information about the total pores in the sample including both open and close-ended pores.

3. Results and discussion

The intention of the present work was to look for the possibility of formation of active nano-sized.TiO_2 powder at room temperature with the help of certain modifications during the hydrolysis of BTM and use it further for membrane fabrication. Some of the important modifications attempted during the titania precursor synthesis are highlighted in Table I. It is clear from this table, that the conditions described in Experiment 2 only lead to instantaneous precipitation of very fine particles of titania precursor. Two competitive reactions occur when alkoxide is added to a stirred solution of acetone, acetic acid and water: i) hydrolysis of −OR groups to give −OH groups and ii) condensation between non hydrolyzed −OR groups and −OH groups to form oxygen (-O-) bridge bond. However, the acidity and rate of hydrolysis vary depending on the experimental conditions, i.e. water/alkoxide ratio, dilution of the medium (Table I). Conditions in Experiment 2 (Table I) led to

TABLE I Modifications in synthesis conditions

Expt. No.	BTM (cm^3) A	Acetone (cm^3) B	Acetic acid (cm^3) C	Water (cm^3) D	Addition sequence	Remark
1	17	200	10	25	[BCA] + D	Very thick gel immediately formed.
2 (Present work)	17	350	5	9	[BCD] + A	Very fine precipitate formed immediately
3	17	350	5	5	[BCA] + D	Gel + Precipitate
4	17	175	20	4.5	[BCA] + D	Initially clear sol, converted to gel after 10 min.

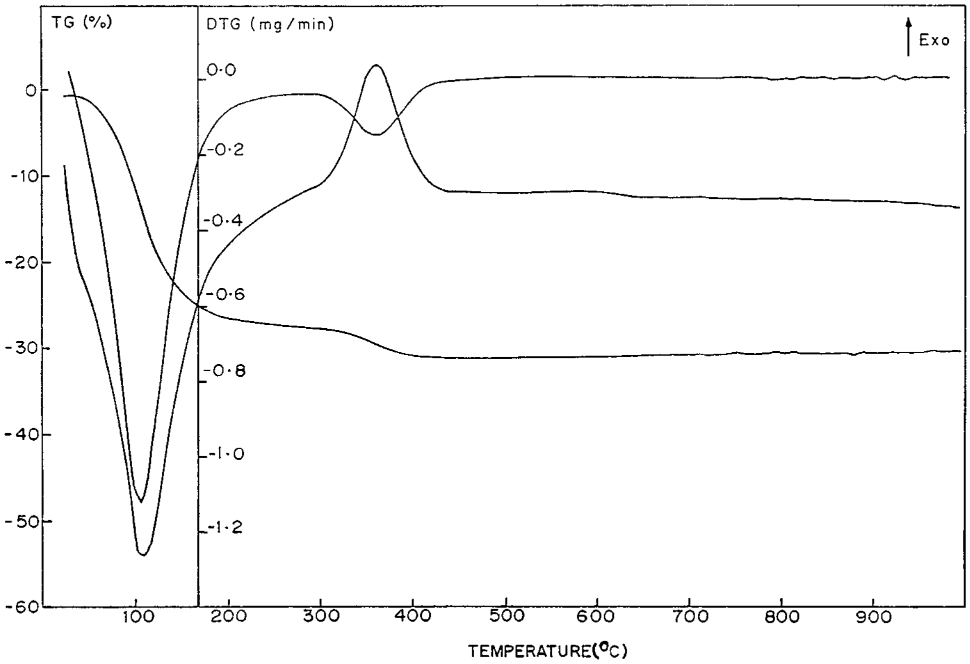

Figure 1 DTA/TG/DTG plots of precipitated TiO_2 powder.

instantaneous precipitation of homogeneous and finer particles of hydrated titania as reaction (i) is dominant. All these results seem to indicate that the use of acetone as a solvent promotes the supersaturating condition for titania precursor by reducing its solubility [12] in organic solvent. Discrete titania precursor particles form agglomerates of the fine nanometer scaled particles by aggregation during drying.

To confirm the composition of the as dried precursor formed by the reaction (i), it was subjected to DTA/TGA/DTG analysis in air. Fig. 1 shows DTA/TGA/DTG curves up to a temperature range of 900 °C. The TGA plot shows a total weight loss of 31.3% in two steps, with DTA recording an endothermic peak at 115 °C and exothermic peak at about 340 °C. The endothermic peak at 115 °C corresponding to major weight loss of 27.2% in the TGA is attributed to the removal of adsorbed/hydrated water from the precursor particles. The minor weight loss of 4.1% shown in TGA curve accompanied with an exotherm at 340°C in DTA curve is related to the decomposition of residual organic species such as butoxy groups ($-OC_4H_9$) and occluded butanol/acetone and their further oxidation in air. After 450°C there is no change in DTA/TGA/DTG curves up to 900°C. If titanium tetrabutoxide was completely hydrolyzed, the experimentally observed weight loss (31.3%) would have been in agreement with that calculated for the oxidation of hydrous titania [$Ti(OH)_4/TiO_2{\cdot}2H_2O$]. In that case no exotherm at 340°C would have appeared in DTA. However, in Fig. 1, a minor weight loss of 4.1% is observed with an exotherm at 340°C in DTA. If this was due to the oxidation of occluded/adsorbed butanol/acetone etc., the observed total weight loss in TG curve would have been greater than 31.3%. Hence it is reasonable to conclude that the precursor formed by hydrolysis may have a composition $Ti(OH)_{4-x}(OR)_x$, $x \leq 0.1$ [13], instead of completely hydrous titania. This is consistent with the observations reported by Rubio *et al.* [14] and Hague *et al.* [15].

This conclusion is further supported by IR studies on vacuum dried precursor which showed clearly the presence of peaks corresponding to H-OH stretching and bending vibrations around 3400 and 1635 cm^{-1} respectively. The peaks corresponding to $-CH$ groups [13] are also seen around 2924 cm^{-1}, and between 1415 and 1358 cm^{-1} respectively, indicating thereby the presence of some unhydrolyzed groups associated with the precursor. Rubio *et al.* [14] and Hague *et al.* [15] have separately reported similar observations about the formation of complex precursor between titanium and organic constituents like ethoxy/butoxy groups, during hydrolysis in acid medium.

To further substantiate these results, XRD studies on as dried precursor and TiO_2 powder obtained by its pyrolysis at two different temperatures (350 °C and 700 °C/2 h) were carried out. The XRD patterns obtained for the same are shown in Fig. 2a–c respectively. It is interesting to note that the as-dried precursor (Fig. 2a) shows broad low intensity peaks corresponding to anatase phase which indicates nano-size nature of the primary particles (5–8 nm). This observation is consistent with Gopal *et al.* [16] where they have reported the synthesis of TiO_2 powder either in rutile or in anatase form from aqueous solutions at lower temperatures (≤100 °C) and atmospheric pressure. Further calcination at 350 °C and 700 °C/2 h showed enhanced crystallinity in anatase phase with crystallite size 10–13 nm and 15–20 nm respectively. No reflections corresponding to rutile phase is observed in TiO_2 powders (Fig. 2b and c). This indicates that although a small broad exotherm near 600 °C is seen in DTA, the phase transformation from anatase to rutile could be too sluggish to be observed. The estimated crystallite sizes are comparable with those reported by Ding *et al.* [8] using sol-gel method utilizing BTM, HCl/HNO_3 and

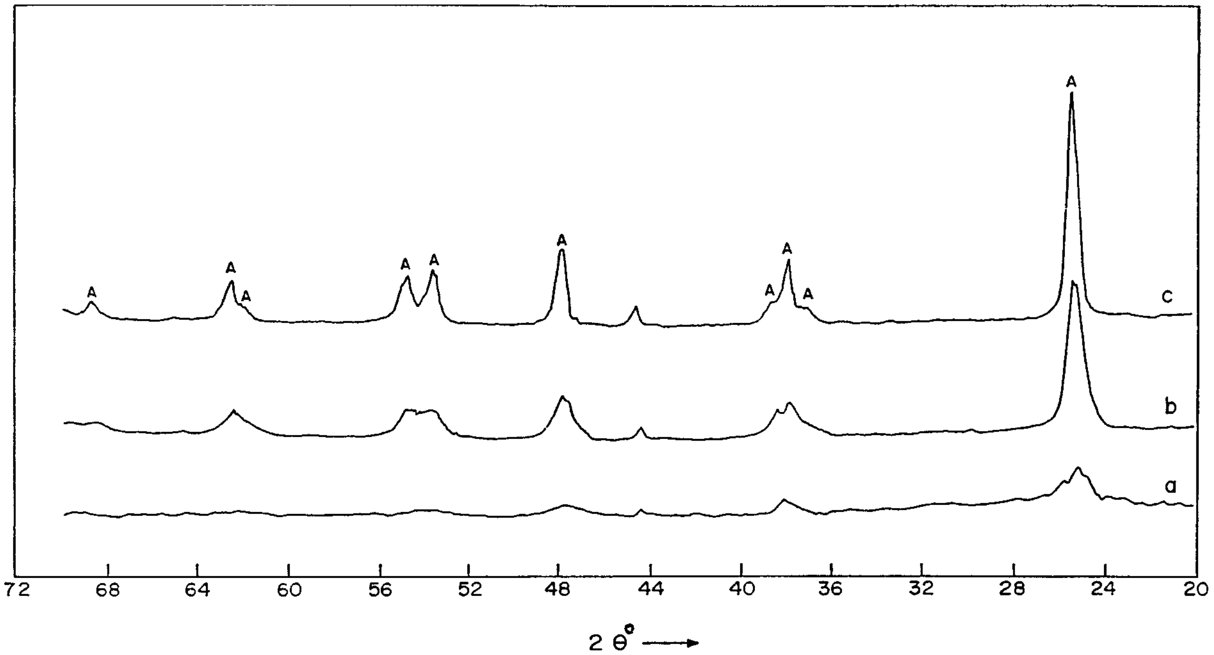

Figure 2 XRD spectra of TiO_2 powder—a) dried in air, b) calcined at 350 °C, c) calcined at 700 °C.

butanol as starting chemicals. The surface area of these two powders were found to be 105 and 28 m^2/g. The particle size estimated by using an equation [14]:

$$D = \frac{6 \times 10^3}{\rho S_{\mathrm{BET}}}$$

is 14.6 nm ('ρ' is theoretical density (3900 kg/m^3) of anatase phase and 'S_{BET}' is measured surface area in m^2/kg) in 350 °C calcined material. The above results show that the powder surface and the particle size are affected by the increase in the calcination temperature. Lower calcination temperature produced reactive anatase TiO_2 powder with large surface area. This means that during the calcination process at 700 °C, the sintering process started [6, 14], which decreased the surface area due to changes in primary particle size and packing density. Although DTA/TGA/DTG results suggested the formation temperature ≈400 °C, the XRD showed clearly the formation of anatase phase at 350 °C. Therefore we have chosen to use a calcination temperature of 350 °C and have given sufficient time (2 h) to get rid of the organic part by oxidative reactions in air and maintain the reactivity of finer titania particles.

It has been established that heat treatment during sintering can cause changes in X-ray structure, porosity, pore size and its distribution [4, 5]. Therefore, to get information about the changes in the structure during heat treatment, X-ray diffraction was carried out by systematically varying the sintering temperature to 450 °C, 550 °C and 700 °C (sintering time: 2 h). Fig. 3 shows the corresponding XRD patterns. It is clear from this figure that the membranes sintered at 450° and 550°C show reflections corresponding to anatase phase indicating thereby the absence of any phase transformation in the membrane up to a sintering temperature of 550 °C. However, the membranes sintered at 700 °C showed characteristic reflections corresponding to anatase ($2\theta = 25.5°$) and rutile ($2\theta = 27.6°$) phases with comparable concentrations. The anatase to rutile transformation is of the nucleation and growth type [4, 7]. The actual temperature and rate at which it occurs depends on how fast the primary particles of the anatase phase sinter together to reach the critical nucleus size. The critical nucleus size is at least three times larger than the crystallites present in the anatase phase [7]. In the present case, therefore, during sintering up to 550 °C the anatase phase is observed whereas in the 350 °C calcined material when sintered at 700 °C/2 h in air the crystallites surpass the critical crystallite size and get transformed into rutile phase (≈40 nm). It has been established that the rate of the transformation and its temperature are dependent on processing conditions as well as on the starting precursor [5, 8, 17–20]. In the present case this transformation occurs around 700 °C during the sintering cycle of the pellets made from 350 °C calcined material (Fig. 3c).

As the precursor calcined at 350 °C showed higher surface area compared to the 700 °C calcined powder, some preliminary experiments were performed to get some idea about the optimization of sintering temperature. For this purpose, 350 °C calcined powder were processed in the form of pellets and sintered at various temperatures e.g. 450°, 550° and 700 °C, for 2 h in air as described earlier whereas the 700 °C calcined TiO_2 powders were sintered at 900 °C/2 h. In these experiments the molding pressure (13.8 MPa) was kept constant. The results obtained on water flux measurements are shown in Table II. It is clear from this table that the porosity is reduced from 60 to 49% and flux has increased from 0.121 to 0.853 $m^3 \cdot m^{-2} \cdot h^{-1}$. On the other hand 700°C calcined powder in the form of pellets sintered at 900 °C/2 h, the porosity was found to reduce drastically to 35% affecting the distilled water flux as 0.07 $m^3 \cdot m^{-2} \cdot h^{-1}$. Therefore, these sintered membranes were not used for further characterization.

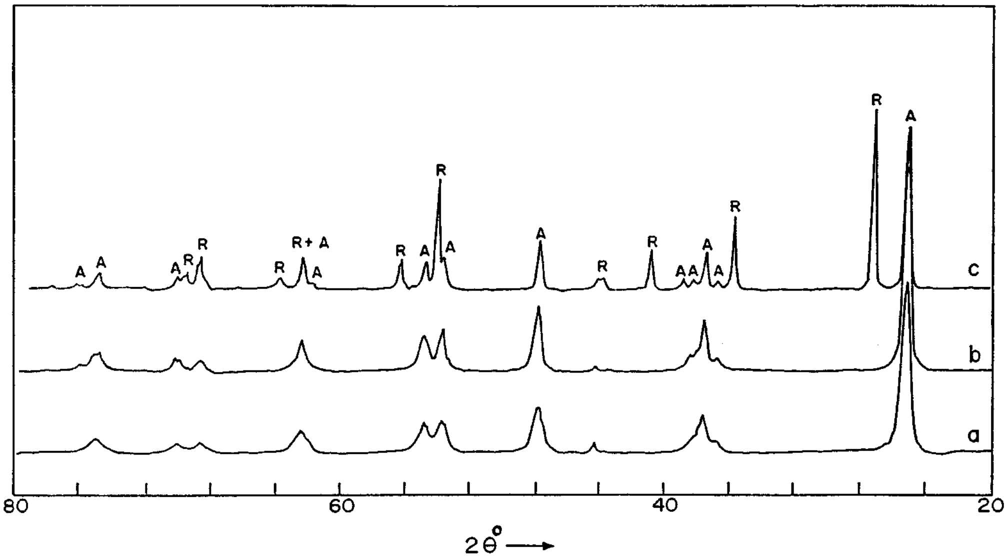

Figure 3 XRD spectra of TiO_2 membranes fabricated from powder calcined at 350 °C and sintered at a) 450°C, b) 550 °C and c) 700 °C for 2 hours.

TABLE II Effect of sintering on water flux of titania membranes

No.	Calcination Temp./Time (°C)	Sintering Temp./Time (°C)	Molding pressure (MPa)	Porosity (%)	Water flux $(m^3 \cdot m^{-2} \cdot h^{-1})$
1	350	450	13.8	60	0.121
		550	13.8	57	0.268
		700	13.8	49	0.853
2	700	900	13.8	35	0.070

Calcination time: 2 h
Sintering time: 2 h

Subsequently, to see the effect of the molding pressure and sintering time the powder calcined at 350 °C was used. It is interesting to note that the sintered pellets at 450°, 550° and 700 °C/2 h showed better mechanical strength and did not break during water flux measurements. This result indicated that high surface energy associated with 350 °C calcined material (because of its nano-sized nature) helped the disks to posses better mechanical strength. Furthermore, the XRD of the same showed the presence of anatase phase up to 550 °C in the sintered sample whereas the 700 °C sintered sample clearly indicated the presence of anatase and rutile phases in comparable concentrations (Fig. 3c). As the anatase to rutile transformation is nucleation and grain growth type, it is expected that 350 °C calcined material may surpass the critical crystallite size and get transformed into rutile phase at a sintering temperature of 700 °C. The structural transformation [5] also brings changes in pore structure and helps to give maximum distilled water flux compared to 450° and 550 °C sintered pellets. After optimizing the sintering temperature (∼700 °C), molding pressure and sintering time were varied systematically. The results obtained on IPA permeability measurements are summarized in Table III. It is evident from this table that the bulk porosity is mildly affected by sintering time except at higher molding pressure. In general, porosity decreases with increase in molding pressure and the decrease is more pronounced at higher sintering time. The average pore diameter of the membrane decreases with increase in both molding pressure and sintering time. However, the membranes fabricated at molding pressure of 20.7 MPa and sintered at 700 °C/2 h showed a bimodal type of pore size distribution with average pore sizes of $\leq$0.49 and 0.60 μm. The IPA permeability is dependent upon both the molding pressure and sintering time. It decreases with increase in molding pressure for the same sintering time. But at constant molding pressure the permeability increases with increase in sintering time. In general, the bulk porosity, average pore size and permeability decreased with increase in molding pressure. This observation is explained on the

TABLE III Effect of fabrication conditions on performance of titania membranes

Sample code	Molding pressure (MPa)	Sintering Temp./Time (°C/h)	Porosity (%)	Bubble point (kPa)	Pore diameter at bubble point (μm)	Average pore size (μm)	IPA permeability $(m \cdot sec^{-1} Pa^{-1}) \times 10^{10}$
T1	13.8	700/2	45.4	18.75	4.78	1.5	5.8
T2	13.8	700/2	47.4	18.44	4.86	1.5	8.9
T3	13.8	700/7	46.2	39.52	4.27	1.2	9.5
T4	20.7	700/2	40.0	23.31	3.78	<0.49 0.63	1.0
T5	20.7	700/7	40.3	25.33	3.54	1.1	3.9
T6	20.7	700/7	39.5	20.27	4.42	1.1	4.3
T7	34.4	700/2	39.2	13.17	6.81	0.9	0.3
T8	34.4	700/7	36.2	60.80	1.47	0.6	1.8

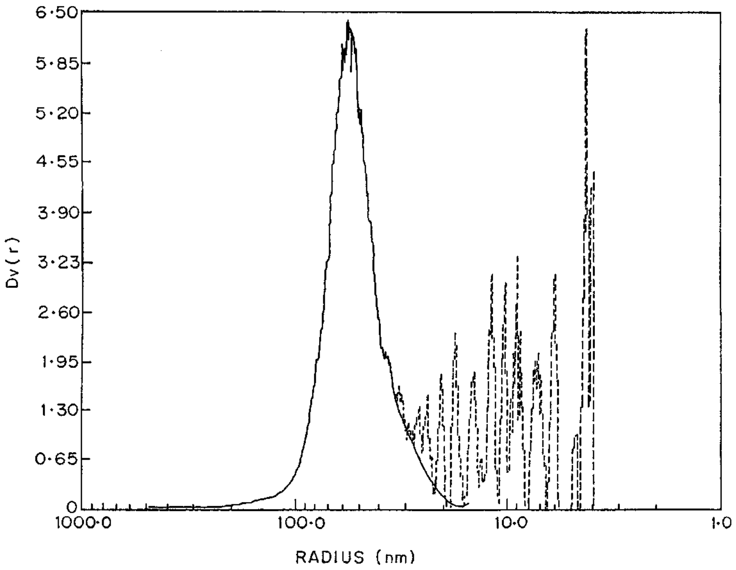

Figure 4 Pore size and its distribution in TiO_2 membrane (sample T4), measured by mercury porosimetry.

basis that on increasing the molding pressure the titania particles are more closely packed influencing thereby sub-coordination leading to high densification rate. On increasing the sintering period from 2 to 7 hrs, there is a decrease in the diameter of the largest pore (pore diameter at bubble point) and average pore diameter. This longer sintering period may help to adjust the microstructure in such a way as to bring down the diameter of the larger pores closer to that of the average pores because of the role of the phase transformation i.e. extent of conversion from anatase to rutile. However, the IPA permeability is found to increase with increase in sintering period pointing to the possibility of increase in effective pore number due to changes in microstructure because of the phase transformation as the atoms are mobile [21]. Comparison of the results shown in Table III gave the T4 sample having promising membrane properties for the microfiltration application. In order to confirm this the pore distribution in sample T4 was also measured by mercury porosimetry. The pore size and its distribution obtained in the sample T4 is shown in Fig. 4 which show pores with radius between 0.02–0.1 μm with maximum number of pores of size 0.055 μm. This pore radius is one fifth of the average pore size estimated from the flux measurements. This is because the data from the flux measurements gave information on the pores open at both the ends and the air pressure <0.405 MPa is not sufficient to open the smaller pores having diameter <0.29 μm which may be present in the membrane.

4. Conclusion

The controlled hydrolysis of titanium tetrabutoxide in a solution of acetone, acetic acid and water gave conditions leading to supersaturation and homogeneous precipitation of nano-sized hydrated crystalline titania precursor. The precursor gave nano-sized anatase titania powder with high surface area after its calcination at 350 °C/2 h. This active powder gave mechanically stable TiO_2 membranes for microfiltration range applications when processed at intermediate pressure and sintered at 700 °C for 2 h. The phase transformation occurring during the sintering cycle controls the microstructure in such a way to make them suitable for microfiltration application.

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