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Articles

Peptization Process in the Sol–Gel Preparation of Porous Anatase (TiO_2)

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The process variables were studied for the peptization of titania in the production of anatase membranes. The original precipitate formed by the hydrolysis of titanium ethoxide does not gel without addition of acid. An acidified (nitric or hydrochloric acid) sol peptized at room temperature leads to the formation of rutile. Under refluxing at elevated temperatures, the result is a gel that is essentially 100% anatase. Both hot and room-temperature acid peptization yield stable sols and well-crystallized systems. Less than 15 min is required for the high-temperature peptization of titania with nitric acid and increasing that time results in only the growth of the anatase particles.

Introduction

A common element in many industrial processes is the necessity to separate the products from the reactants and waste components. Membranes are becoming attractive separators because they offer several advantages relative to other processes. Specifically, gas separations with membranes are of increasing interest to the chemical industry because they permit energy savings relative to conventional separation techniques (e.g., distillation). Processes involving the separation of gases by membranes are generally considered to operate via one of four mechanisms: (i) molecular sieving, (ii) gas separation via Knudsen diffusion, (iii) surface diffusion, and (iv) capillary condensation.[1] Regardless of which mechanism is controlling the separation, the membrane needs to have a stable pore structure.

While most emphasis has been placed on organic membranes,[2] increased interest is being shown for utilizing inorganic membranes for gas separations[1,3–15] because inorganic membranes have a higher chemical, thermal, and mechanical stability than do organic polymeric membranes, allowing inorganic membranes to perform under conditions where organic membranes would fail. However, commercial applications of ceramic membranes have been limited to date because of the difficulties encountered in producing crack-free membranes having a pore size on the molecular scale and narrow pore size distributions. This situation can be remedied by using the sol–gel process, which first came into significant commercial use some 20 years ago for preparing uranium dioxide pellets.

The sol–gel process involves the low temperature synthesis of an inorganic network by a chemical reaction in solution. For a thorough review of this process, one should refer to the text of "*Sol–Gel Science*" by Brinker and Scherer.[16] Advantages of the sol–gel process include the ability to form well-defined multicomponent oxides, to selectively dope a material with extreme purity, and to synthesize monoliths at lower temperatures than conventional ceramic processes.[17]

While the sol–gel process may appear to be a simple operation, many variables can influence the quality of the final product.[18] These variables include the choice of solvent,[19] whether acid or base catalysis is employed,[20] and use of stabilizing agents.[21,22] Although the

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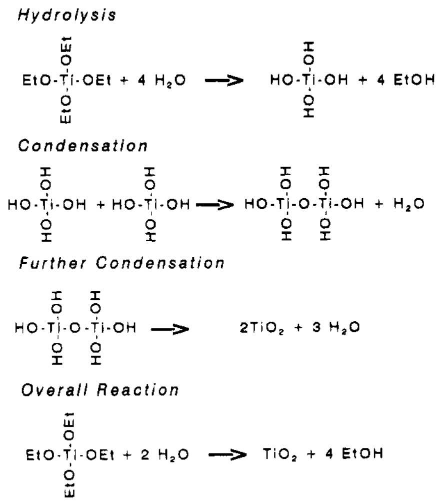

Figure 1. Hydrolysis reaction of titanium ethoxide.

sol–gel process has historically been used to prepare nonporous materials by eliminating pores at low temperatures, porous membranes can be prepared by careful control of these preparation conditions. Yoldas[23,24] found electrolytes influenced the sol–gel transformation and the ability of the gel to retain its integrity while preparing porous transparent alumina. Yoldas also discovered that the rate of peptization drops dramatically below 80 °C[23] and that peptizing with strong acids with noncomplexing anions (e.g., HNO_3, HCl, $HClO_4$) formed stable sols, while with HF and H_2SO_4 they did not.

Leenaars et al.[4–7] also prepared ceramic alumina membranes using sol–gel techniques. Bayerite suspensions do not gel easily whereas boehmite suspensions are easy to gel.[25] Hydrolyzing aluminum tri-*sec*-butoxide above 80 °C results in a sol comprised of crystalline boehmite which transforms to γ-Al_2O_3 when fired above 390 °C.[4] Room-temperature hydrolysis results in the formation of the amorphous monohydroxide which upon aging converts to the undesirable trihydroxide bayerite.

We have shown previously in this laboratory that titanium oxide membranes can be prepared by the sol–gel process.[26,27] The overall hydrolysis and condensation reactions are illustrated in Figure 1. For illustration purposes the hydrolysis and condensation reactions are shown to proceed to completion in the figure. However, it is understood that OR groups could persist due to incomplete hydrolysis, and the resultant particles being amorphous hydrous titania would also have surface OH groups and not be TiO_2. The hydrolysis of titanium isopropoxide or titanium ethoxide in excess water followed by peptization with nitric acid at refluxing temperatures yields a sol comprised of titania particles. Gelation of the sol and firing of the subsequent gel produces an anatase membrane. Membranes and porous materials comprised of titanium dioxide are desirable not only as separators but also because of their catalytic and photocatalytic properties.[28] To have high catalytic activity, though, a high surface area material is needed. Also the membranes must be composed of small particles (<30 nm) in order for the pore diameter to be under 45 Å.

Anatase and rutile are the two forms of titanium dioxide produced most easily in the laboratory at atmospheric pressure. Because the change in Gibbs free energy (ΔG) for the transformation of anatase to rutile is less than zero under all conditions of temperature and pressure (ΔG estimated to be −1.27 kcal/mol at 25 °C and −1.04 kcal/mol at 695 °C), anatase is said to be metastable with respect to rutile.[29] The transformation has been reported in the literature to occur at temperatures from 400 to 1100 °C.[30–32] Previous work in our laboratory found that TiO_2 gels transformed to rutile when fired to a temperature of 600 °C for 3 h[28] resulting in a drastic loss of surface area and porosity. Suzuki and Tukuda[33] transformed anatase particles of 0.05–0.3 μm into 0.5–0.7 μm rutile particles at 1050 °C. This indicates an important need to prepare membranes composed of anatase particles if small pores are desired. Unfortunately, this imposes an upper limit on the temperature where TiO_2 membranes can be utilized for separation reactions. One method to overcome this apparent temperature limit would be to produce membranes composed of small rutile particles. This is the approach undertaken by Kumar and co-workers,[34] where they crystallized small rutile crystallites (<20 nm) by precipitation of titania on SnO_2 nuclei. This avoids the phase transformation step and increases thermal stability. However, for this study we are interested only in what facets of the sol–gel process aid in the production of anatase membranes.

Giannelis and co-workers[35] hydrolyzed titanium isopropoxide under acidic, neutral, and basic conditions. Acid- and base-catalyzed systems produced amorphous titania, while the neutral hydrolysis resulted in a mixture of anatase and brookite. Heating to 650 °C resulted in anatase from acid hydrolysis and sodium titanate from base hydrolysis. A mixture of anatase, brookite, and rutile resulted when the titania from the neutral hydrolysis was heated to 650 °C. Larbot and co-workers[3] also hydrolyzed titanium isopropoxide and obtained an amorphous titania which crystallized to anatase upon heating above 180 °C. Matijević[36] found rutile was formed by the slow hydrolysis of acidic titanium solutions containing sulfate ions, while amorphous titania is produced by the hydrolysis of aerosol droplets of titanium ethoxide, titanium isopropoxide, or titanium tetrachloride.

As stated above, anatase membranes can be formed from sols produced by the hydrolysis of titanium alkox-

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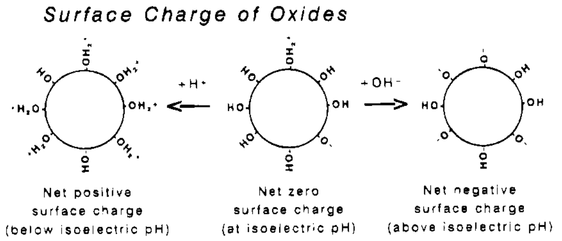

Figure 2. Effect of pH on surface charge of an oxide.

ides followed by peptization with nitric acid.[26,27] Schaefer found that charged particles have a low sticking probability due to electrostatic repulsive forces between particles that counteract the natural attractive van der Waals forces between particles (Figure 2) producing smaller aggregates.[37] These aggregates would be made up of densely packed particles because the smaller net attractive forces allow for the rearrangement of particles until an efficient packing is achieved. These weaker interactions can be overcome by the forces in the gelation process, and thus these aggregates would be the building blocks for a gel having relatively low porosity. Avery and Ramsay studied the gels produced from aggregated and nonaggregated sols[38] by varying the amount of acid used for peptization. Nonaggregated sols produced gels with an efficient packing of particles, while aggregated sols produced gels with a much more open structure, higher porosity, and larger pore size. Anatase has been found to have an isoelectric point (pH_{IEP}) ranging from 4.7 to 6.7.[39] At a pH well below the pH_{IEP} (e.g., pH = 1−2), the surface of TiO_2 would have a net positive charge yielding a nonaggregated sol.

To ensure that the membrane we produce contains particles of anatase, we must understand under what conditions small particulate anatase is formed. If rutile is crystallized during any step in this process, resulting membranes likely will be composed of large particles and possess larger pores. To fully understand the whole process of preparing anatase membranes, we need to know at which stage the material crystallizes to the anatase phase. Does this occur during the hydrolysis and the formation of the initial precipitate? Or does the crystallization occur because of the heating? Yoldas[40] found titanium ethoxide hydrolyzed forming amorphous titania which transformed to anatase and brookite under certain calcination conditions. Is the crystal phase dependent on the acid used (nitric, sulfuric, hydrochloric)? Or is it a combination of heating and acid choice? These questions will be addressed in this paper. In addition, this paper investigates the effect of peptization parameters on the properties of titania and its ability to form a gel. Specifically, this paper addresses the influence of processing temperature and nature of the counterion of the inorganic acid on both the crystal structure and physical properties of the resulting gels.

Experimental Section

Titanium oxide was prepared in a manner similar to Anderson et al.[26] Titanium ethoxide (Aldrich Co.), used without further purification, was diluted with an equal volume of ethanol. The mixture was added slowly to enough MilliQ (Millipore Corp.) filtered water to yield a mole ratio of water to titanium in the starting material of 200. The resulting precipitate was stirred for 2−3 days and provides the base material for these experiments. An aliquot, sample A, having undergone no peptization, was removed at this point. The remaining precipitate was split into 40−60 mL aliquots and peptized according to Table 1. The major variables considered for investigation were (i) whether or not acid is employed, (ii) peptizing at room temperature or at the boiling point, and (iii) if the alcohol is removed. It should be pointed out that the conditions for samples A−H were selected based on a factorial analysis of these three major peptization variables. The remaining samples all were peptized with acid and heat and with removal of the alcohol. However, the acid concentration and type were varied. Samples J and K (along with sample H) have varying concentrations of nitric acid (H^+/Ti from 0.1 to 0.5) and samples L, M, and N employed hydrochloric acid and two concentrations of sulfuric acid. Because sulfuric acid is diprotic, it can dissociate twice yielding sulfate anions having a charge of −2. The ionic strength contribution from sulfate ions is 4 times as great as that from monovalent nitrate and chloride ions. Therefore, two concentrations of sulfuric acid were included in order to eliminate possible ionic strength problems.

Where heat is indicated in the table, the suspension was heated to reflux (>80 °C) for 6−8 h. Alcohol was either removed by distillation (for heated samples) or by stirring in an open flask in a fume hood overnight. The amount of water lost to evaporation was determined gravimetrically and replaced. Concentrated nitric, sulfuric, and hydrochloric acids were added to the aliquots of the starting precipitate to give the mole ratios of hydrogen ion to titanium shown in Table 1. For acid peptizing, the acid was added followed by either refluxing or stirring (for samples where no heat is applied). Samples A−D were stirred for 48 h, but no heat was applied. The resulting sols or precipitates were poured into polystyrene weighing boats. Each sol was evaporated at 56% relative humidity requiring 3−5 weeks for complete gelation or drying.

In addition to the above experiments, the effects of aging and peptization time were also studied. A precipitate was prepared exactly as above. Samples were stirred at room temperature in order to study the effect of aging time. In the peptization time study, an aliquot was removed immediately after the nitric acid (H^+/Ti = 0.45) was added (PT0). The remaining material was then heated and the remaining samples were removed at the times indicated in Table 2. All times were measured from the time the suspension reached 80 °C. Samples for both of these studies were evaporated quickly overnight in a fume hood in order to quench any further reactions.

The crystal phase of these gels (or powders where gelation did not occur) were determined using a Scintag automated diffractometer. Crystal structure identification and crystal-size quantification were made using *d* spacings at 3.52 Å (101) for anatase, 3.25 Å (110) for rutile, and 2.90 Å (121) for brookite. For quantification of anatase and rutile, the ratios of the integrated areas under the above peaks were compared with those of premeasured standards. Crystal-size determinations employed peak-broadening analysis utilizing the Scherrer equation

$$L = \frac{\lambda k}{B \cos \theta} \qquad (1)$$

where θ is the Bragg's angle of diffraction for the peak, B is the broadening of the peak at half the maximum height (full width at half-maximum or fwhm) measured in radians, L is the length of the crystal in the direction of the d spacing, λ is the wavelength of the radiation used, and k is a constant usually equal to about 0.94.

Specific surface areas were determined using an automated N_2 adsorption manifold. Adsorption and desorption of samples was performed at 77 K to a relative pressure (P/P_0) of approximately 0.95. This limit was chosen because as pres-

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Table 1. Sample Preparation Conditions and Results

sample	heat	alcohol removal	acid	H^+/Ti	forms gel	crystal structure	crystal size (nm)	BET a^s (m^2/g)^a	calc particle diam (nm)	porosity (%)
A	no	no	none		no	anatase and brookite	n/a	216	7.2	52.7
B	no	no	HNO_3	0.5	yes	anatase (51%) rutile (49%)	5.3 (a) 12.5 (r)	153	10.0	32.1
C	no	yes	none		no	anatase (70%) brookite (30%)	n/a^1	263	5.9	56.6
D	no	yes	HNO_3	0.5	yes	anatase (69%) rutile (31%)	4.6 (a) 13.3 (r)	165	9.5	27.6
E	yes	yes	none		no	anatase and tr. brookite	6.3	248	6.3	52.4
F	yes	no	none		no	anatase and tr. brookite	6.5	254	6.2	54.7
G	yes	no	HNO_3	0.5	yes	anatase and tr. brookite	5.3	202	7.7	31.8
H	yes	yes	HNO_3	0.5	yes	anatase and tr. brookite	5.4	16.5	9.5	29.7
J	yes	yes	HNO_3	0.2	yes	anatase and tr. brookite	6.3	149	10.0	30.4
K	yes	yes	HNO_3	0.1	yes	anatase and tr. brookite	6.0	192	8.1	32.0
L	yes	yes	HCl	0.5	yes	anatase and tr. brookite	5.6	211	7.4	33.2
M	yes	yes	H_2SO_4	0.5	yes	anatase and tr. brookite	4.9	10	153	10.8
N	yes	yes	H_2SO_4	0.125	yes	anatase and tr. brookite	5.7	229	6.8	36.9

[1] Brookite peaks overlap with anatase and exact proportions were not determined. [a] a_s: specific surface area.

Table 2. Results of X-ray Diffraction Measurements for Samples at Different Peptization Times[a]

sample	time (h)	crystal structure	peak area	anatase fwhm	anatase size (nm)
PT0	0	amorphous	N/A	N/A	N/A
PT1	0.25	anatase + tr. brookite	7564 (A) 266 (B)	1.93	4.7
PT2	0.67	anatase + tr. brookite	8030 (A) 232 (B)	1.74	5.2
PT3	1.25	anatase + tr. brookite	6256 (A) 411 (B)	1.72	5.3
PT4	2.5	anatase + tr. brookite	5488 (A) 430 (B)	1.73	5.2
PT5	11	anatase + tr. brookite	7897 (A) 483 (B)	1.62	5.5

[a] All times (except PT0) were measured from time sol reached 80 °C. Sample PT0 was removed at room temperature and sol reached 80 °C in 10 min.

sures approach saturation, homogeneous condensation of N_2 occurs. This pressure limit also imposes a maximum on the size of mesopores that can be determined of about 500 Å. Samples were pretreated by heating at 80–100 °C under vacuum for 6 h to remove water of gelation. Standard procedures for this outgassing step usually require holding samples in a vacuum at 200 °C for about 4 h. This ensures the removal of not only bulk water but also water adsorbed on the surface of the oxides and trapped in the pores between the particles. Heating these materials to 200 °C could cause coarsening of these crystals and change the measured specific surface area, but the interest of this study was to determine the properties of as-prepared particles of titania. Therefore, it was decided that the possible inability to fully remove all the pore water was outweighed by the need to maintain particle size.

Results

Results of gel properties and X-ray diffraction measurements are summarized in Table 1. Figure 3 presents the results of gelation properties and polymorph identification in a flowchart. Gelation occurs in all samples containing acid. When no acid is added, the result is not a gel but a precipitate.

It is apparent that the peptizing conditions greatly affect the crystal structure of the resulting particles. From X-ray diffraction measurements, it was found that the material stirred without heat or acid, sample A, is a mixture of anatase and brookite. Both anatase and brookite are metastable polymorphs of TiO_2. When nitric acid was added but no heat was applied to the sol, the product was a mixture of anatase and rutile.

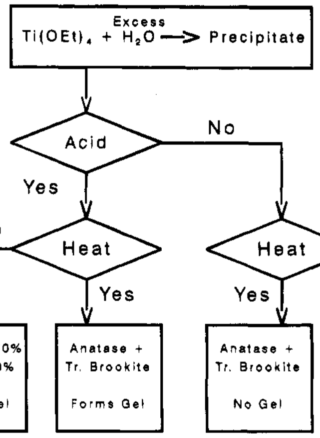

Figure 3. Flowchart illustrating the properties of TiO_2 obtained by adding acid or heating during peptization.

All samples where both acid was added and the sol was refluxed were mainly anatase with just a trace of brookite. It also appears from the results that the removal of the alcohol does not seem to influence the crystallization during the peptization process.

X-ray peak broadening was used to determine crystal sizes. Note that this technique weights the larger particles more heavily in determining the average particle size of the sample. fwhm values ranged from 1.46 to 1.96 for anatase and 0.74 to 0.76 for rutile. The Scherrer equation (eq 1) was applied to these data to compare the crystal sizes to particle sizes determined from specific surface area data. Where both anatase and a significant amount of brookite are present in the sample, the fwhm for anatase could not be determined. Brookite has 2 separate *d* spacings close to the anatase (101) spacing so that the peaks could not be deconvoluted. This makes it difficult to quantify the relative abundances of each.

Table 1 summarizes the results of N_2 adsorption measurements. An assumption of spherical particles was used to convert the BET specific surface areas to particle diameters. The porosity of the resulting gels was calculated using the volume of N_2 at the adsorption maximum. The volume of N_2 adsorbed at a relative pressure (P/P_0) of 0.95 was chosen as the adsorption maximum. For the porosity calculations, 0.808 g/cm^3 was employed for the density of adsorbed N_2 while the density of the solid was assumed to be that of anatase (3.84 g/cm^3) in all the calculations.

The measured specific surface areas were between 150 and 230 m^2/g for all samples, reflecting an average particle diameter of between 6 and 11 nm, except for the material peptized with a high concentration of sulfuric acid. For sample M (high H_2SO_4), the specific surface area was determined to be around 10 m^2/g yielding an average particle size around 150 nm. This value is in complete disagreement with the results of the crystal size from X-ray peak broadening measurements, which was 4 nm.

Table 2 summarizes the results obtained by varying the time of the high temperature peptization of titania. The original precipitate was found to be amorphous by X-ray diffraction. The aging study showed no crystallization occurred in the precipitate by stirring in water for several days. When acid was added and heat applied, the titania crystallized into anatase after only 15 min. Longer peptization time resulted in an increase in the size of the anatase but had no effect on gelation as all the samples gelled overnight.

Discussion

From the study investigating the peptization conditions, it was thought that the initial hydrolysis and condensation product was a mixture of anatase and brookite. However, it was determined in the second set of experiments using X-ray diffraction that amorphous titania is formed originally. When this amorphous titania was aged and dried over a period of 3–5 weeks, the result was a mixture of anatase and brookite. Drying this titania overnight caused no change in the structure of the material. Why this slow aging causes the formation of a mixture of metastable polymorphs is unclear. One possibility is that the originally formed titania is crystalline but the crystallites are too small to be detected by X-ray diffraction as crystalline. After a small growth (which takes a long time at neutral pH) these particles are identified to be anatase and brookite.

When either heat is applied or acid is added, the results indicate a change in structure of the titania. One possible explanation for this observation is that dissolution of titania is followed by crystallization to anatase or rutile. Newly precipitated amorphous titania will have a higher solubility than crystalline titanium oxide.[41] The order of thermodynamic stability of the three polymorphs produced in these studies are brookite (least stable), anatase, and rutile (most stable). At low temperatures the dissolution of the titania would be slower and lead to slower crystallization. This crystallization would be governed by thermodynamics and not kinetics and result in the most stable crystal form, rutile. At higher temperatures dissolution of titania would be increased which could lead to a more rapid precipitation, resulting in the metastable anatase or brookite.

Titanium ethoxide reacts very quickly with water especially in the presence of a very large stoichiometric excess of water. The very rapid initial hydrolysis results in a solution with a high degree of supersaturation of hydroxylated titanium. This leads to a high rate of nucleation and the formation of small particles or crystallites.[42] Because of the rapid nucleation rate, the particle growth may be governed by kinetics and not thermodynamics, leading to the formation of amorphous titania or a metastable polymorph. This may explain why the first material formed is amorphous.

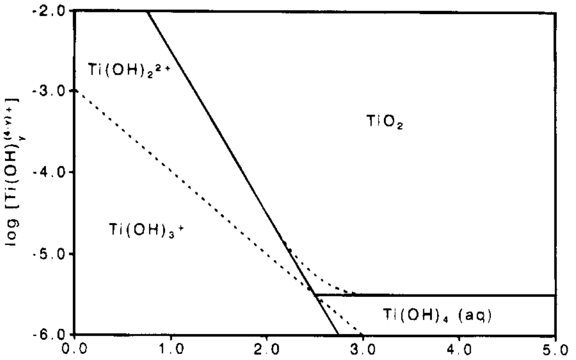

Figure 4. Solubility of hydrous TiO_2. Calculated using constants from ref 41.

The addition of acid for peptization results in an increase in the solubility of titania (Figure 4). In fact, the acid decreases the pH of the sol to between 1.0 and 1.3. At this pH nearly 1% of the titania would be dissolved. The most likely material to dissolve is the amorphous titania. Matijević found that raising the temperature of an acidified solution containing metal ions could lead to a forced hydrolysis.[36] The first step in this process is a rapid nucleation. Therefore, crystallization could result in the formation of a metastable polymorph. Samples B and D have acid added but have not been heated. In both cases the product is a mixture of anatase and rutile. The acid increases the solubility of titania, but the slow crystallization at room temperature yields the more stable rutile form. Samples G and H also had acid added and were also heated. The results were the formation of the metastable forms anatase and brookite.

It was originally believed that the only result of peptization with acid would be the breakup of large aggregates into smaller aggregates by the electrostatic repulsion of the charged particles. However, now it is clear that the addition of acid and heat has a great influence not only on the ability of the particles to gel but also on the crystal structure of the TiO_2. Yoldas has stated that heat reduces the time required for peptization.[23] One would also believe that it would be impossible to overpeptize a sol. Nevertheless, there is no need to peptize a sol for several days when only several hours is needed. The results in Table 2 show that very little time is required for peptization in order to obtain an unsupported TiO_2 gel. Also, it was observed that a stable sol was obtained after only 75 min of peptizing at reflux temperatures. However, the table displays one disturbing fact. As the time of peptization is increased, the diameter of the anatase particle is increased. In fact, the particles in sample PT0 are believed to be amorphous because they are too small to contain enough unit cells to be detected by X-ray diffraction. The anatase may be formed by Matijević's forced hydrolysis process[36] described above and the growth can be attributed to a dissolution–growth

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(41) Baes, C. F., Jr.; Mesmer, R. E. *Hydrolysis of Cations*; Wiley-Interscience: New York, 1976.

(42) Stumm, W.; Morgan, J. J. *Aquatic Chemistry,* 2nd ed.; Wiley: New York, 1981.

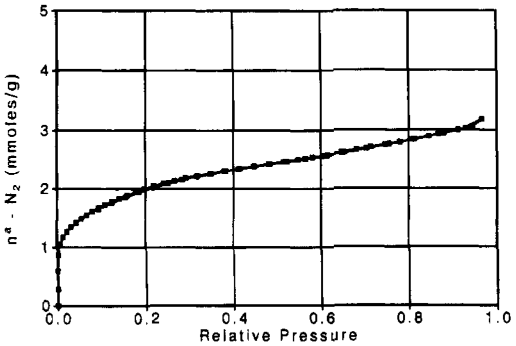

Figure 5. Adsorption–desorption isotherm of sample H using N_2 at 77 K.

process similar to Ostwald Ripening caused by the increased acidity. From this work, it can be concluded that a length of peptization should be selected that stabilizes the sol but minimizes the growth of the anatase particles.

Since membranes are fabricated from gels, it is extremely important to define the conditions required to form a gel. It is evident that where acid was added, a gel formed upon evaporation of the water. If no acid was added, a stable sol was not obtained and would subsequently not gel. In this case, only a powder remained upon drying which precludes the formation of a membrane. However, it should also be pointed out that a gel with efficient packing was prepared with the lowest acid-to-titanium ratio investigated (0.1:1).

The values of the percent porosity of the gels produced in this study varied from about 10% to about 57%. For all the materials peptized with either nitric or hydrochloric acid, the porosity was between 27.6 and 33.2 percent. This suggests that the acids produce efficient packing by raising the surface charge of the particles and breaking up large aggregates. If no acid is employed, porosity is high indicating a low packing density due to the presence of large aggregates that are not broken up during gelation. When sulfuric acid was used, the result was either a fairly efficient packing when the concentration of acid was low or an almost non-porous material with a higher concentration of acid.

The sorption curves for N_2 also demonstrate the packing density for the various peptization regimes. Figure 5 is the adsorption–desorption curve for sample H which has been peptized in nitric acid under reflux. The curve has the shape of a type I (IUPAC classification scheme) isotherm[43] typical of activated carbons or zeolites. The initially high adsorption at very low pressures indicates the presence of micropores (pore diameter less than 20 Å). This is followed by a linear sloped portion up to the adsorption maximum that differs from a standard type I isotherm. Because zeolites have a relatively low external surface, a normal type I isotherm plateaus above the initial micropore filling. The desorption branch lies directly on top of the adsorption branch with no hysteresis, indicating absence of mesopores. The isotherms for all samples where nitric (B, D, G, H, J, and K), hydrochloric (L), or a low concentration of sulfuric acid (N) was employed were all of similar shape. Relationships of packing density, particle size and pore size with each other indicate sample H should contain particles with diameters below 13 nm. [The particle size is equal to the pore size (<2 nm) divided by 0.155 (ratio of pore diameter to particle diameter of a close-packed material) or less than 13 nm.] This is consistent with the particle size determined from X-ray peak broadening and specific surface area measurements.

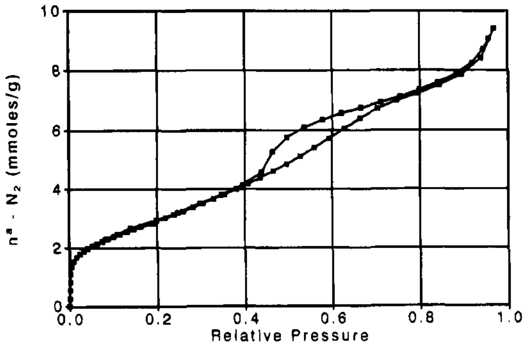

Figure 6. Adsorption–desorption isotherm of sample F using N_2 at 77 K.

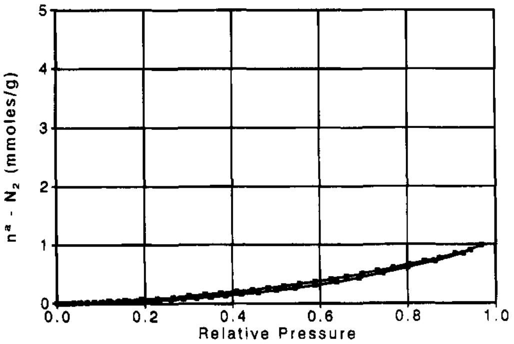

Figure 7. Adsorption–desorption isotherm of sample M using N_2 at 77 K.

The sorption isotherm for sample F (no acid with heat) presented in Figure 6 seems to fit a classic type IV isotherm.[43] But careful inspection shows that the isotherm is a combination of a type I and a type IV. This curve has two very distinct regions. At very low pressures, the curve exhibits high adsorption indicating the sample contains micropores and thus very small particles (type I). However, at relative pressure between 0.4 and 0.8, the curve exhibits a hysteresis loop (which does not really fit the standard loop shapes) indicating the presence of mesopores. This is confirmed by pore-size analysis. Using a model employing the Kelvin equation based on the filling of cylindrically shaped pores, the average diameter of the mesopores was determined to be between about 20 and 60 Å using the desorption curve. The existence of mesopores would suggest either the presence of larger particles or the formation of larger pores as a result of a less efficient packing of the small particles. The latter hypothesis is supported by the small crystal size and high porosity measured. All samples without acid (A, C, and E) gave adsorption–desorption curves very similar to sample F.

Figure 7 the isotherm for sample M containing a high concentration of sulfuric acid, most closely resembles a type III isotherm.[43] This isotherm shape generally indicates important adsorbate–adsorbent interactions.

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(43) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.*, **1985**, *57 (4)*, 603–619.

(44) Matijević, E. *Pure Appl. Chem.* **1978**, *50*, 1193.

The curve gives no indication of the existence of either micropores or mesopores. The specific surface area of this sample was determined to be very low, suggesting that the average particle size is very large. But this is in contrast to the crystal size measured by X-ray diffraction.

Sulfuric acid has properties very different from those of the other acids in this study. Given the amount of acid added in the acid-peptized sols, the concentration of dissolved titanium would be relatively high. Sulfate ions can complex with the dissolved titanium and may be instrumental in the growth of the anatase particles. Matijević found that, in highly acidic solutions containing titanium ions, sulfate ions bind with the titanium ions and slowly decompose on heating.[44] Ostwald ripening may be promoted by this complexation of dissolved titanium by sulfate and thus shifting the dissolution farther toward completion. This type of growth could cause the low specific surface area and porosity measured, but the crystal size determination reflects the presence of small anatase particles. Therefore, the most likely explanations for this anomaly are (1) that the low specific surface area and porosity may be due to the presence of a sulfur compound, possibly titanium sulfate precipitated in the pores or (2) that sulfate ions promoted the formation of large polycrystalline particles made up of small crystallites.

In summary, particles originally formed are believed to be amorphous because of the extremely fast hydrolysis of the titanium ethoxide. Extremely rapid precipitation can result in formation of a less thermodynamically stable material that is less dense than the stable rutile crystalline state. When acid is added to reduce pH, the solubility of titania is increased and the amorphous titania will dissolve. Where heat is applied, the crystallization is fast, most likely resulting in the formation of anatase. Where no heating is employed, the recrystallization is slow and this results in the formation of a more stable rutile structure. The results of this study support this hypothesis.

Conclusion

A fundamental understanding of how varying the peptization conditions can influence the gel formation is the main goal of this study. Because the original hydrolysis of titanium ethoxide is fast, a high degree of supersaturation of hydroxylated titanium yields an amorphous titania. This original precipitate does not gel without addition of acid. Because the addition of acid decreases the pH, it also increases the solubility of the titania. If the acidified (nitric or hydrochloric acid) sol is peptized at room temperature, a slow dissolution–crystallization leads to the formation of rutile. Under refluxing, the crystallization rate is accelerated and the result is a gel that is essentially 100% anatase. Both hot and room-temperature acid peptization yield stable sols and well-crystallized systems. Peptization with sulfuric acid is more complicated. A low concentration of H_2SO_4 yields a stable sol and porous gel, while increasing the acid concentration produces a nonporous material. Finally, very little time is required for the high-temperature peptization of titania with nitric acid and increasing that time only results in the continued growth of the anatase particles.

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