

# Environmentally Friendly Pathways for Synthesis of Titanium Dioxide Nano-particles

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## ABSTRACT

Titanium dioxide nano-particles were synthesized via the sol-gel method using titanium butoxide as the precursor. Acid catalyzed and aged gels were dried under air to produce xerogels and under supercritical conditions to produce aerogels. Porous nano-particles obtained were characterized using X-ray diffraction, SEM and BET analysis. Aerogel powder was found to have more favorable properties compared to xerogel powder. Aerogel particles were more porous with more profound anatase crystal structure.

**Keywords:** supercritical carbon dioxide, aerogel, nanostructures, sol-gel, titanium dioxide

## 1 INTRODUCTION

Titanium dioxide is the most widely used photo-catalyst. It is preferred due to its non-toxicity, availability and relatively high activity. The catalytic properties of titanium dioxide that dictate its activity as photo-catalyst are its surface area, pore size, particle size, and crystallographic structure.

In heterogeneous catalysis, reaction takes place at the active surface of the solid catalyst. For effective use of the catalyst, the solid catalyst needs to provide high active area. Sol-gel process ensures production of high surface area gels. Also, pore size and its distribution are critical in effective use of the solid catalysts. Large pores may be essential for some applications. In other cases, smaller pores may be more desirable because they provide higher surface area. Sol-gel process also provides narrow distribution of pore size. However, during drying of the gel, pores shrink due to capillary action and as a result, pore size of the larger pores decreases and smaller pores collapse resulting also in loss of surface area. In order to prevent the destruction in the pore structure during drying, the solvent can be removed from the wet gel under supercritical conditions [1].

Aerogels are prepared through sol-gel process followed by supercritical drying. Supercritical drying eliminates capillary forces exerted on the walls of the pores and results in highly porous materials. Consequently, aerogel catalysts have desired properties of catalysts such as high surface area [2]. Use of templates during the sol-gel process results in uniform, tailored pore size distribution. Large pore size facilitates easier diffusion of large molecules into the pores and results in effective use of the catalyst. Conventionally,

surfactants are removed from the gel by either Soxhlet extraction or by heat treatment. Also, more effective route for removal of the template from the catalyst can be enabled by extraction with supercritical fluids. Supercritical fluid extraction is less time consuming and environmentally friendly compares to solvent extraction. Furthermore, the template can be removed without disturbing the pore structure of the catalyst as opposed to thermal decomposition of the template at high temperatures. [3]

Particle size is another important property of titanium dioxide that needs to be attuned during the synthesis. Sol-gel synthesis results in small nano-particles, where else precipitation results in particles of large size [4].

In photo-catalysis, another issue to be addressed is the crystallographic structure of the metal oxide that is related to its photo-activity. Metal oxides prepared through sol-gel synthesis are basically amorphous. On the other hand, photo-activity of the titanium dioxide is directly related to its crystal structure. Titanium dioxide in the anatase form is found to be the most active photo-catalyst. Although sol-gel derived titanium dioxide is amorphous, when calcined at relatively low temperatures, it can be transformed into the desired crystalline form.

In the present work, titanium dioxide nano-particles are prepared through sol-gel synthesis and dried using supercritical carbon dioxide. The procedure for supercritical drying is explained and effect of solvent removal step (air drying versus supercritical drying) on the properties of the end material is investigated.

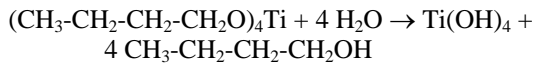
## 2 EXPERIMENTAL

Titanium dioxide particles were synthesized through sol-gel process. They were dried under air or supercritical conditions to produce xerogel and aerogel samples respectively. After drying they were calcined and characterized in order to determine their pore and crystallographic structure. Preparation of the titanium dioxide particles is summarized in Figure 1.

### 2.1 Sol-gel Preparation

Titanium butoxide (Supplier: Aldrich) was dissolved in ethanol (Supplier: Aldrich), stirring for ten minutes. Nitric acid (Supplier: Aldrich) was added to the mixture dropwise. The solution was then mixed with the required amount of distilled water, while stirring continuously at

room temperature. Titanium hydroxide gel was formed according to the following hydrolysis reaction:



Subsequently, the gel was stored at room temperature for two days to age. The molar ratio of the chemicals  $\text{Ti}(\text{O}i\text{Bu})_4$  : ethanol :  $\text{H}_2\text{O}$  :  $\text{HNO}_3$  is 1 : 20 : 6 : 0.8.

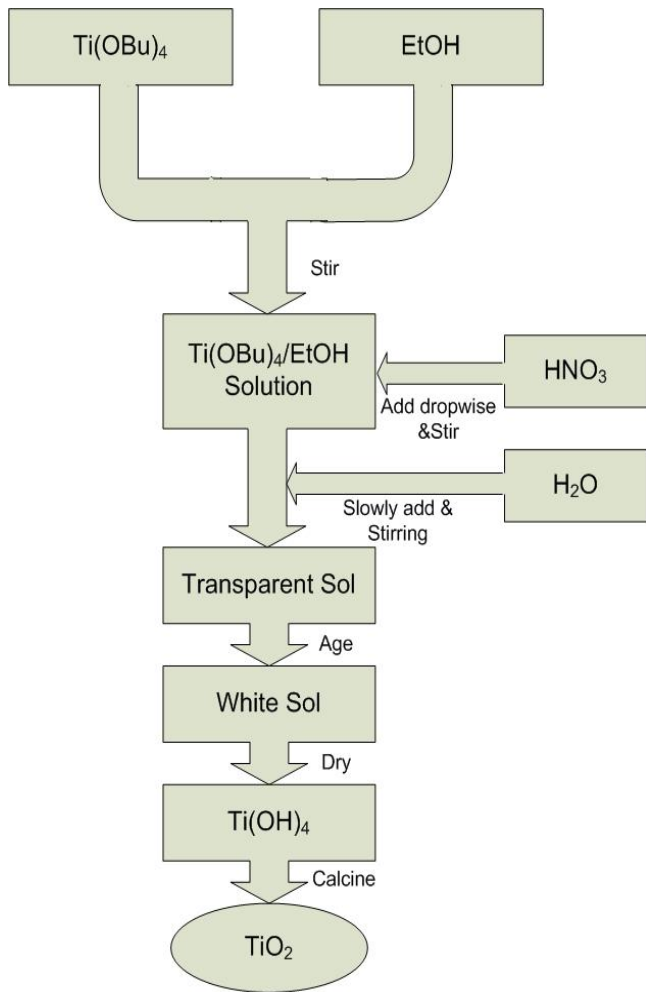


Figure 1. Preparation of titanium dioxide

## 2.2 Drying of the Xerogels and Aerogels

In order to produce titanium dioxide xerogels, the wet gels were dried under air at atmospheric pressure and 373K for 24 hours. Aerogels were produced through supercritical drying. The supercritical fluid (SCF) apparatus used for supercritical extraction and drying is shown in Figure 2. The SCF extraction and drying apparatus can be divided into three main sections; feeding section, drying section and gas-liquid separation and collection section.

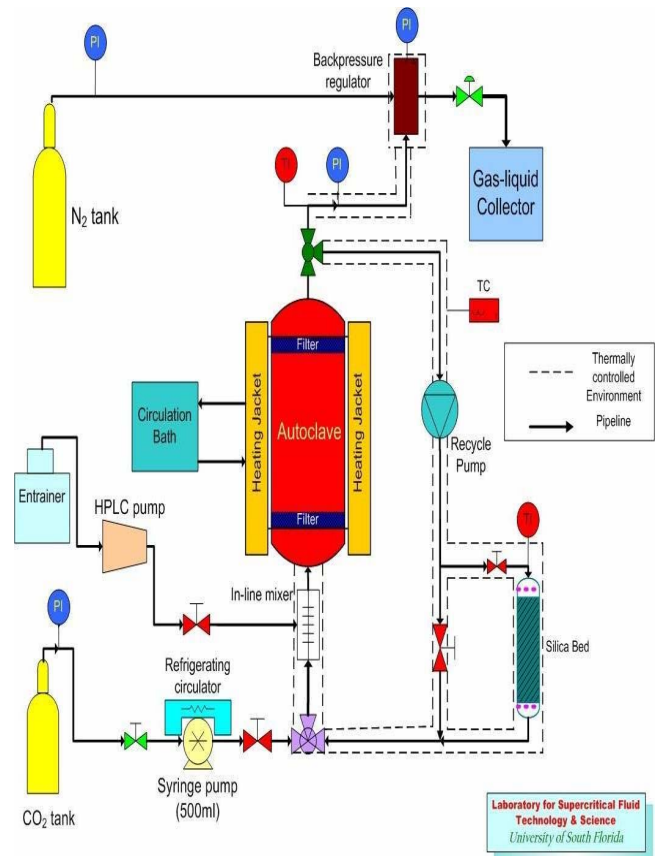


Figure 2. Set-up for supercritical drying

All parts, tubing and *Swagelock*<sup>®</sup> fittings are made of stainless steel, (SS-316). The tubing used in the main fabrication of the SCF setup is mainly 1/4 inch diameter and in some places 1/8 inch diameter. The feeding section consists of compressed carbon dioxide tank (AIRGAS, CD-50), Pressure regulator (Matheson), Refrigerating circulator (Ecoline RE120, Lauda, Brinkmann), HPLC pump (Waters, model 600E), Entrainer container, Syringe pump (ISCO model 500DX), in-line mixer, magnetic pump (*Ruska*, model 2330-802), and number of plug valves and needle valves. The drying section consists of a 100ml controlled heat-jacketed autoclave (Autoclave Engineer), water circular bath (HAKKE, model B81), several electrical heating tapes (Omega), Pressure gauge (Matheson), Thermocouple Probe (Omega, K-type). The gas-liquid separation and collection consists of Compress Nitrogen tank (AIRGAS, NI200), backpressure regulator, and low-pressure gas-liquid separator and venting system.

The drying procedure was as follows: The alcogel sample was placed into a heat-jacketed autoclave which had been pre-heated to setting temperature at 60°C. The autoclave was then closed tightly and purged with carbon dioxide gas. All the vents and outlet valves were then securely closed and the system pressure was initially raised

to 850psi. Meanwhile, backpressure system was turned on and set at 1800 psi.

Carbon dioxide was compressed and cooled down to  $-4^{\circ}\text{C}$  passing through syringe pump, and pressure in the system was kept increasing until it reached the desired set point pressure which was determined and entered into the backpressure regulator at the start of each experimental run. The designed processing pressure for this section was 1800 psi. Carbon dioxide went to an in-line mixer unit just before it was introduced to the autoclave from the bottom section. When the setting pressure was achieved, the feeding flow rate of  $\text{CO}_2$  was kept at 10 ml/min for 2 hours.

Recycle pump was then engaged between the input (bottom) and the output (top) of the autoclave. At the beginning of the run, the recycled fluid was passed through the adsorption bed, which contained silica gel particles as the adsorbent. The mixture of carbon dioxide, part of solvents and residual template was evacuated from the SCF experimental setup through the backpressure regulator. Electrical heating element was used to keep the effluent supercritical mixture from getting frozen, hence preventing blocking the system. Fluid leaving the backpressure regulator went to an ambient pressure vessel inside which the effluent mixture separated into gas and liquid mixture phases.

### 2.3 Calcination of the Xerogels and Aerogels

Samples were calcined at 773K under air-flow in a tubular furnace for three hours.

### 2.4 Characterization of the Catalysts

Nitrogen adsorption-desorption experiments were carried out in order to study the total surface area, total pore volume, average pore size, and pore size distribution for meso-pores, and the micro porosity of the gels. A Nova 2200 series machine along with Enhanced Data Reduction Software from Quantochrome Corp was used for routine pore structure information. BET method was used in order to determine total surface area. Pore size distribution and average pore size of the meso-pores were determined using BJH method. X-ray powder diffraction (XRD) patterns were collected using  $\text{CuK}\alpha$  radiation on a Philips Expert System with a 45 KW and 40 mA in order to determine the crystallinity and phase of the samples. Surface images were collected by a Hitachi 800 Scanning Electron Microscope (SEM).

## 3 RESULTS AND DISCUSSION

Xerogel and aerogel samples were characterized in order to compare their porous and crystallographic structures.

In order to study the crystalline structure, X-Ray diffraction patterns were taken (Figure 3). For both aerogels and xerogels, peaks were observed at  $2\theta$  equal to  $25.2^{\circ}$ ,  $37.8^{\circ}$  and  $48.0^{\circ}$ . These are diffractions of the anatase form corresponding to (1 0 1), (0 0 4) and (2 0 0) respectively. X-Ray diffraction of the aerogels shows higher intensities than the ones of the xerogels that implies larger crystal size for aerogels.

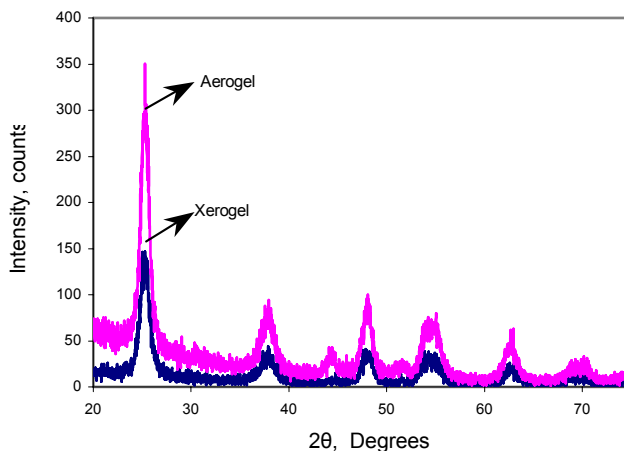


Figure 3: XRD Patterns of aerogels and xerogels.

Comparison of the pore structure of the aerogels and xerogels shows that the aerogels have higher total surface area and pore volume. Also, aerogels have larger average pore diameter than the xerogels. All of these results are indicative of the superior conditions achieved during supercritical drying when compared with evaporation of the solvent.

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