

## CHAPTER III

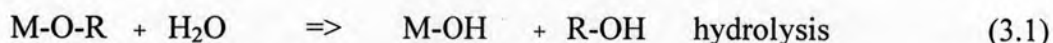
### THEORY

#### 3.1 Aerogel

Aerogel is prepared via a sol-gel method together with removal of the solvent by supercritical drying to prevent the collapse of pores. The resulting powder possesses unique properties such as high surface area, large pore volume, and low density.

##### 3.1.1 *Sol-gel method* [Su et al 2004]

The use of a sol-gel synthesis as a convenient and practical method for the preparation of nanostructured TiO<sub>2</sub> with tailored microstructural properties is well documented in the field of heterogenous catalysis. This method is mainly based on the hydrolysis and condensation of a metal alkoxide, which ultimately yields hydroxide or oxide under certain conditions. The sol-gel synthesis goes through the formation of a sol of colloidal particles in a solution, gelation of the sol by the agglomeration of these particles into a big gel network structure, removal of the solvent, and heat treatment to transfer gel into solid. Depending on reaction conditions, the sol particles may grow further or form gel.



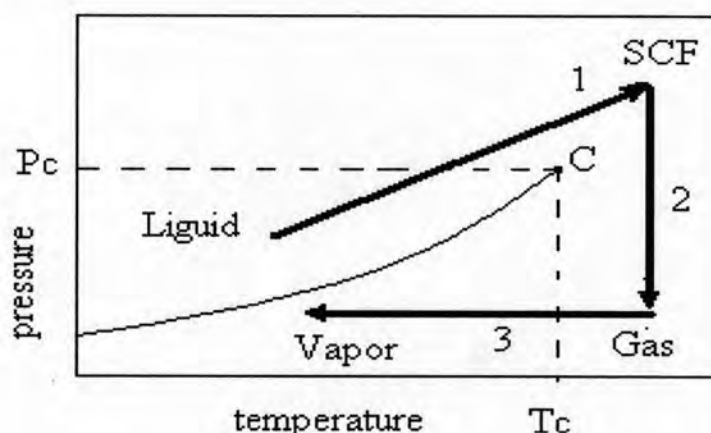
where R represents alkyl group, and M represents metal atom.

The advantage of the sol-gel method is molecular-scale mixing of the component, simple and low cost technology, high purity of the precursor, and

homogeneity of products with high uniformity of physical, morphological, and chemical properties.

### 3.1.2 Supercritical Drying [Pajonk 1997; Scheider and Baiker 1997]

The removal of the solvent by drying causes the shrinking of the gel and significant reduction in the volume due to increasing capillary forces. The high capillary pressure in the pores causes the collapse of the gel network structure and the production of less porous powder (xerogel). Therefore, the resulting powder possesses low porosity and small surface area (xerogel). The problems could be avoided by removing the liquid from the pores above the critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ) of the liquid (aerogel) [Kistler 1931]. In this state, the solvent is above its critical pressure and critical temperature. Therefore, the solvent possesses properties of both liquid and gas and consequently, there is no liquid-vapor interface and no capillary pressure.



**Figure 3.1** Temperature-pressure diagrams for supercritical drying

The present stage of supercritical drying can be divided into high-temperature and low temperature drying processes, based on liquid solvent and  $\text{CO}_2$ , respectively. Both processes circumvent the destructive differential capillary stresses of conventional evaporative drying either by transferring the solvent into its supercritical state (high-temperature drying) or by replacing the solvent mainly with supercritical  $\text{CO}_2$  (low-temperature drying).

### 3.1.2.1 High temperature supercritical drying

In this process, wet gel is placed in an autoclave. The temperature and pressure are increased above the critical point of the solvent. Once the critical point is passed, the solvent is vented at a constant temperature ( $> T_c$ ) and cooled down to room temperature. The solvents currently used include methanol, ethanol, propanol, and acetone. (see Table 3.1). Water cannot be used as the solvent because a number of oxides dissolve in water under supercritical conditions and the oxide peptizes and produces a dense crystallized oxide bulk. Inorganic precursors, in addition to water as solvent, can be selected to make the sol-gel step. The solvent must be exchanged by an organic solvent before undergoing the supercritical drying. However, high critical temperature and pressure of alcohol in combination with its flammability requires strong precautions.

**Table 3.1** Critical properties of various solvents.

Solvent	Molecular weight g/mol	Critical temperature K	Critical pressure Mpa (atm)	Density g/cm <sup>3</sup>
Carbon dioxide (CO <sub>2</sub> )	44.01	304.1	7.38 (72.8)	0.469
Water (H <sub>2</sub> O)	18.02	647.3	22.12 (218.3)	0.348
Methane (CH <sub>4</sub> )	16.04	190.4	4.60 (45.4)	0.162
Ethane (C <sub>2</sub> H <sub>6</sub> )	30.07	305.3	4.87 (48.1)	0.203
Propane (C <sub>3</sub> H <sub>8</sub> )	44.09	369.8	4.25 (41.9)	0.217
Ethylene (C <sub>2</sub> H <sub>2</sub> )	28.05	282.4	5.04 (49.7)	0.215
Propylene (C <sub>2</sub> H <sub>2</sub> )	42.08	364.9	4.60 (45.4)	0.232
Methanol (CH <sub>3</sub> OH)	32.04	512.6	8.09 (79.8)	0.272
Ethanol (C <sub>2</sub> H <sub>5</sub> OH)	46.07	513.9	6.14 (60.6)	0.276
Acetone (C <sub>3</sub> H <sub>6</sub> O)	58.08	508.1	4.70 (46.4)	0.278

### *3.1.2.2 Low temperature supercritical drying*

In this process, solvent is removed from the gel by supercritical CO<sub>2</sub>. This is typically achieved by exchanging solvent for liquid acetone, allowing a better miscibility gradient. Carbon dioxide is fed directly into an autoclave, containing the wet gel and then temperature and pressure are raised above its critical point (> 31.1 °C and > 7.38 MPa). Finally, all liquid is removed from the gel and is replaced with CO<sub>2</sub>, without allowing the gel structure to collapse or lose volume. Also, water cannot be used as a solvent because of its very poor solubility in liquid CO<sub>2</sub>. Thus, a solvent exchange from water to an organic solvent, which is easily soluble in liquid CO<sub>2</sub>, is beneficial.

Although high-temperature supercritical drying via the direct transformation of the solvent into its supercritical stage avoids capillary stresses, other destructive forces arise from expansion of the liquid (permeability), contact with the autoclave linear wall, and an increase in solvent reactivity. The main disadvantage of the high temperature route is the stronger temperature impact. Whereas low-temperature drying is performed at much lower temperature, which saves energy, and very safe since CO<sub>2</sub> is non-flammable, non-explosive, and chemically inert in the condition it is employed. By comparison with high temperature route, the low-temperature one is friendlier, while the high-temperature route implies some chemical reaction beside the pure physical evolution during the drying step.

When compared to low-temperature supercritical drying, high-temperature route leads to thermodynamically more stable aerogel, which is reflected by prominent structural and chemical change. In general, specific surface areas of the aerogels are higher for that prepared at low temperature than that prepared at high temperature. However, when calcination temperature is increased this behavior vanishes or may even be inverted. Anatase is observed in the case of high-temperature drying, whereas low-temperature aerogel remains amorphous.

### 3.2 Titanium dioxide

Titanium dioxide has three crystal structures: anatase, which tends to be more stable at low temperature; brookite, which is usually found only in minerals and has a orthorhombic crystal structure; and rutile, which is the stable form at higher temperatures. Generally, anatase shows a higher photocatalytic activity than other types of titanium dioxide. Comparison of typical physical properties of rutile, brookite, and anatase is displayed in Table 3.2

**Table 3.2** Comparison of properties of rutile, brookite and anatase. [Othmer, 1991 and Fujishima et al., 1999]

Properties	Anatase	Brookite	Rutile
Crystal structure	Tetragonal	Orthorhombic	Tetragonal
Optical	Uniaxial, negative	Biaxial, positive	Uniaxial, negative
Density, g/cm <sup>3</sup>	3.84	4.0	4.26
Hardness, Mohs scale	5 <sup>1/2</sup> -6	5 <sup>1/2</sup> -6	7-7 <sup>1/2</sup>
Unit cell	D <sub>4h</sub> <sup>19</sup> .4TiO <sub>2</sub>	D <sub>2h</sub> <sup>15</sup> .8TiO <sub>2</sub>	D <sub>4h</sub> <sup>12</sup> .3TiO <sub>2</sub>
Dimension, nm			
a	0.3758	0.9166	0.4584
b	-	0.5436	-
c	0.9514	0.5135	2.953
Refractive index	2.490	-	2.903
Permittivity	31	-	114
Melting point	Changes to rutile at high temperature	-	1858°C

Although anatase and rutile are both tetragonal, they do not have the same crystal structures. Anatase exists in near-regular octahedral and rutile forms slender prismatic crystal. Rutile is the thermally stable form and is one of the two most important ores of titanium.



The three forms of titanium (IV) oxide have been prepared in laboratories but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystal. The transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol), but the rate of transformation is greatly affected by temperature and by the presence of other substance which may either catalyze or inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is around 700 °C, but this is not a transition temperature. The change is not reversible since  $\Delta G$  for the change from anatase to rutile is always negative.

Brookite has been produced by heating amorphous titanium (IV) oxide, which is prepared from an alkyl titanate or sodium titanate, with sodium or potassium hydroxide in an autoclave at 200 to 600 °C for several days. The important commercial forms of titanium (IV) oxide are anatase and rutile and they can readily be distinguished by X-ray diffractometry.

Since both anatase and rutile are tetragonal structure, they are both anisotropic, and their physical properties, e.g, refractive index, vary according to the direction relative to the crystal axes. In most applications of these substances, the distinction between crystallographic directions is lost because of the random orientation of large numbers of small particles, and only average values of the properties are significant.

Measurement of physical properties, in which the crystallographic directions are taken into account, may be made for both natural and synthetic rutile, natural anatase crystals, and natural brookite crystals. Measurements of the refractive index of titanium (IV) oxide must be made by using a crystal that is suitably orientated with respect to the crystallographic axis as a prism in a spectrometer. Crystals of suitable size of all three modifications occur naturally and have been studied. However, rutile is the only form that can be obtained in large artificial crystals from melts. The refractive index of rutile is 2.903. The dielectric constant of rutile varies with direction in the crystal and with any variation from the stoichiometric formula,  $TiO_2$ ;

an average value for rutile in powder form is 114. The dielectric constant of anatase powder is 48.

Titanium (IV) oxide is thermally stable (mp. 1855 °C) and very resistant to chemical attack. When it is heated strongly under vacuum, there is a slight loss of oxygen corresponding to a change in composition to  $\text{TiO}_{1.97}$ . The product is dark blue but reverts to the original white color when it is heated in air.

Titanium dioxide is one of the most common materials in our daily life. Titanium dioxide has been widely used in a variety of paints, plastics, paper, inks, fibers, cosmetic, sunscreen, and foodstuffs.

Naturally, the type of titanium dioxide that is used as a pigment is different from that used as a photocatalyst. The photocatalytic technology is becoming more and more attractive to industries today because environmental pollution has been recognized as a serious problem that needs to be addressed immediately. Various applications in which research and development activities involving titanium dioxide have been investigated, such as anti-fogging activity, anti-bacterial activity, anti-viral activity, fungicidal activity, anti-soiling activity, self-cleaning property and self-sterilizing property, deodorizing effect, photocatalytic air purification, cancer therapy, water treatment and water purification, decomposition of organic compounds, and so on.

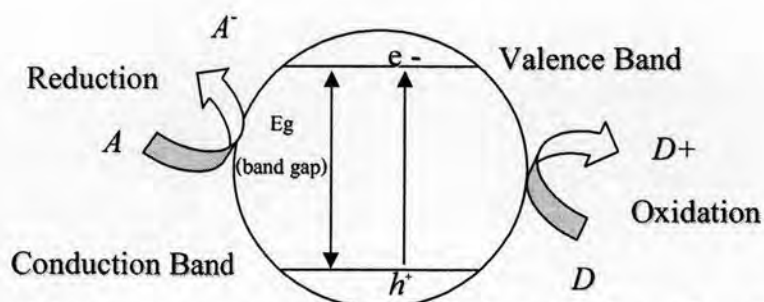
Even though a photocatalyst is not suitable for decomposing a large amount of substance in a short time, it can be effective in controlling bacteria and viruses while they are still relatively small in number, before they start multiplying out of control.

### 3.3 Photocatalytic reaction

The photoinduced water splitting on titanium dioxide electrodes was found by Honda and Fujishima [1972]. This reaction opens new possibilities for the application of semiconductor solid materials for catalysis induced by light irradiation.

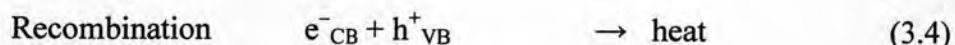
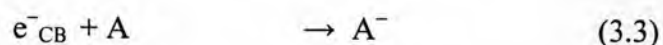
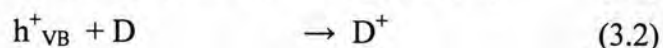
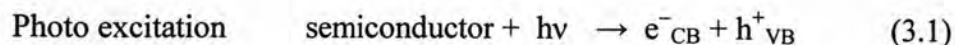
A semiconductor has an electronic and band structure. The highest band occupied energy band (valence band) and the lowest empty band (conduction band) are separated by a band gap. The magnitude of the energy of band gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band in this intrinsic state. The band gap defines the wavelength sensitivity of the semiconductor to irradiation. [Fox and Dulay, 1993].

The popular application of semiconductor under light irradiation was photocatalytic pollution purification. The process occurs on the surface of semiconductor under light irradiation. The UV irradiation of the semiconductor surface causes the separation of electron vacancies or "holes" and electrons by electron migration to the conduction band and holes production in the valence band. The generation of electrons and holes in the conduction and valence bands occurs only when a photon of energy larger than the band gap ( $h\nu \geq E_g$ ) is absorbed on the catalyst (Equation 3.1). A wider band gap requires shorter wavelengths. Figure 3.1 shows the photocatalytic process occurring on an irradiated surface of semiconductor particle.



**Figure 3.2** photocatalytic process occurring on an irradiated surface of semiconductor particle.

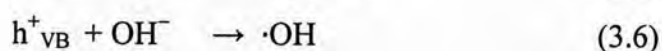
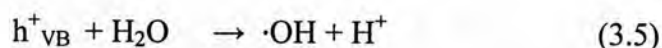




However, the charge carriers survive longer periods of time. These carriers can be trapped in surface states, where they can react with an electron donor (D) or an electron acceptor (A) species adsorbed on or close to the surface of TiO<sub>2</sub> [Litter, 1999] (Equation 3.2 and 3.3). Subsequently, oxidation and reduction can be initiated. Electron and hole recombination process prevent activity of photocatalytic reaction (Equation 3.4).

In aqueous solution, hydroxyl radical ( $\cdot\text{OH}$ ) production is favorable because of the abundance of hydroxyl groups and water molecules on the surface of catalyst. However, in the gas phase, organic substrate can themselves act as adsorbed traps for the photogenerated hole since in the gase phase, water molecule are not the predominant species in contact with the catalyst. Although in the presence of water vapor, hydroxyl groups are presented on the catalyst surface and their contribution to photooxidation cannot be discarded [Alherici et al 1997].

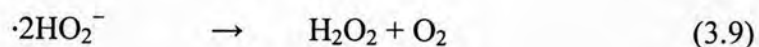
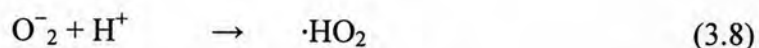
When adsorbed water molecules are oxidized by holes, hydroxyl radicals, which have strong oxidizing power, are formed (Equation 3.5 and 3.6)



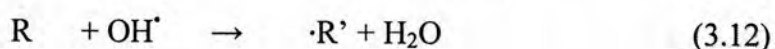
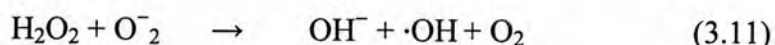
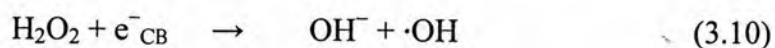
Meanwhile, the electrons in the conduction band reduce oxygen in air. Because oxygen can be reduced more easily than water, it will tend to be reduced, producing the superoxide radical anion ( $\text{O}_2^-$ ) as seen in Equation 3.7



The addition of  $\text{H}_2\text{O}_2$  (Equation 3.8 and 3.9) increases the concentration of  $\cdot\text{OH}$  radical since it inhibits the recombination of electron and hole.



$\text{H}_2\text{O}_2$  is considered to have two functions in the photocatalytic degradation. It accepts a photogenerated conduction band electron thus promoting the charge separation (equation 3.10) and it also forms  $\cdot\text{OH}$  (Equation 3.11).



The hydroxyl radicals can then react with organic components (Equation 3.12), initially producing free radicals. When molecular oxygen is present (reaction always occurs in the presence of oxygen in the air for the use of the photocatalyst for environment), it can react with these free radicals producing organic peroxy. These radicals then take part in chain reactions. In a short time, organic compounds are completely degraded and  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are the products.