

CHAPTER I

INTRODUCTION

1.1 Background

Titanium dioxide (TiO₂) or titania is generally considered to be “unreactive” and not a particularly suitable starting material for further titanium chemistry. However, titania is a very useful material and widely used in various branches of industry, such as electronic materials due to its photocatalytic activity, high-performance ceramics and microelectronic components. In recent years it has received great attention for its gas-sensitive behaviour, excellent dielectric property (Fukushima *et al.*, 1989), as well as catalytic applications.

Naturally titania has three polymorphs: brookite (orthorhombic, Pcab), anatase (tetragonal, I4₁/amd), and rutile (tetragonal, P4₂/mnm). Rutile is the only stable phase, whereas anatase and brookite are both metastable at all temperatures. Anatase and rutile are most commonly utilized. Anatase modification of titania is an important material for water purification, catalyst supports, gas sensor and inorganic membrane. However, anatase is metastable phase and it will transform irreversibly to the stable rutile phase at temperatures above 915 °C. The transformation temperature will decrease with the increase in surface area (Kumar *et al.*, 1993). For many applications the transformation is not favored, for two main reasons (Izutsu *et al.*, 1997): first, anatase has distinctly better catalytic properties than rutile, and second, this transformation always results in a dense (non-porous) rutile phase, which is not useful as a catalyst or as a ceramic membrane material. Therefore, it is important to prepare titania with a high surface area as well as high anatase-rutile transformation temperature.

1.2 Sol-Gel Process

Basically the sol-gel process means the synthesis of an inorganic network by a chemical reaction in solution at low temperature. The most obvious feature of this

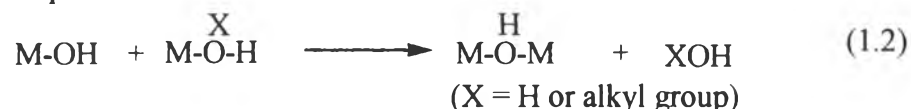
reaction is the transition from a liquid (solution or colloidal solution) into a solid (di- or multiphase gel) led to the expression of “sol-gel process”.

Sol-gel chemistry is based on inorganic polymerization reactions starting from molecular precursors, such as metal alkoxides, an oxide network is obtained via inorganic polymerization reactions. Initiation is performed through the hydroxylation of metal alkoxides which occurs upon the hydrolysis of alkoxy groups, as in the following in equation 1.1.



As soon as hydroxyl groups are generated, propagation occurs through a polycondensation process. Depending on experimental conditions, two competitive mechanisms have to be considered. They can be described as follows:

1. **Olation** : formation of hydroxo bridges through the elimination of solvent molecules, see equation 1.2.



2. **Oxolation** : formation of oxygen bridges through the elimination of H₂O or XOH, as shown in equation 1.3.



These three reactions (hydrolysis, olation and oxolation) can be involved in the transformation a metal alkoxide precursor into an oxide network. The structure and the morphology of the resulting network strongly depend on the relative contribution of them. These reactions can be described as nucleophilic substitutions which depend on the nucleophilic group (H₂O, OH⁻, HO-M), the leaving group (ROH, H₂O) and the metal atom (Si, Ti, Zr, etc.).

The chemical reactivity of metal alkoxides toward hydrolysis and condensation mainly depends on the positive charge of the metal atom $\delta(\text{M})$ (electrophilic character of the metal) and its ability to increase its coordination number N (degree of insaturation of the metal is expressed by the difference between N-Z where N is the coordination number usually found in the oxide, and Z is the oxidation state). For a given oxidation state (Z), both δ and N-Z increase with increasing atomic number, as shown in table 1.1. Thus, silicon alkoxides are not very reactive. Its gelation occurs within several days after water has been added.

Titanium alkoxides are highly sensitive to moisture. They must be handled with great care in a dry glove box. Precipitation occurs as soon as some water is present. Therefore, for study of sol-gel processing of titanium alkoxide precursors, it is necessary to prepare titanium alkoxide that has low hydrolytic reactivity.

Table 1.1 Partial charge $\delta(M)$ and maximum coordination number (N) of some tetravalent metal alkoxides ($Z = 4$)

Alkoxide	$\delta(M)$	N	Z	N-Z
Si(OPr ⁱ) ₄	+0.32	4	+4	0
Ti(OPr ⁱ) ₄	+0.60	6	+4	2
Zr(OPr ⁱ) ₄	+0.64	7	+4	3
Ce(OPr ⁱ) ₄	+0.75	8	+4	4

One property of the sol-gel process is the ability to control the process all the way, from the molecular precursor to the product. Sol-gel chemistry offers many advantages, such as a lower processing temperature allowing the synthesis of metastable oxides phases and opening a field of opportunity for the synthesis of new materials including both organic and inorganic components. The rheological properties of sols and gels allow fibers or films to be processed by techniques, such as spin-drawing, dip-coating or screen-printing.

Generally, sol-gel process relatively involves 4 following steps:

1. Solution chemistry (gel formation)
2. Aging
3. Drying
4. Calcination/Sintering

Solution chemistry step: Starting materials (metal salt or metal alkoxides) are dissolved in an appropriate solvent to form a solution. The gel is hereafter formed in the gelation process, involving simultaneous hydrolysis and polycondensation of metal alkoxide precursor. At this step, the most important parameters are types of precursor, solvent, precursor concentration and temperature.

Aging step: This step represents the time between the formation of a gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel can undergo many transformations. This step can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle.

Drying step: It is a process of evaporating solvent from a gel network. Similarly to aging, a gel is not static during drying and, for that reason, drying can be viewed as part of the overall aging process. The properties of product are thus dependent on the drying method and condition.

Calcination/Sintering: It often is done in the presence of a reactive gas (e.g. flowing air, oxygen) in order to burn off any residue organics or to oxidize the sample. Exposing the sample to a high temperature over an extended period of time leads to sintering and consequently a decrease in surface area. The process also causes the material to crystallize into different structure forms. Thus, the physical characteristics of the product depend on parameters, such as temperature, heating rate and gaseous environment.