# CHAPTER II
LITERATURE SURVEY
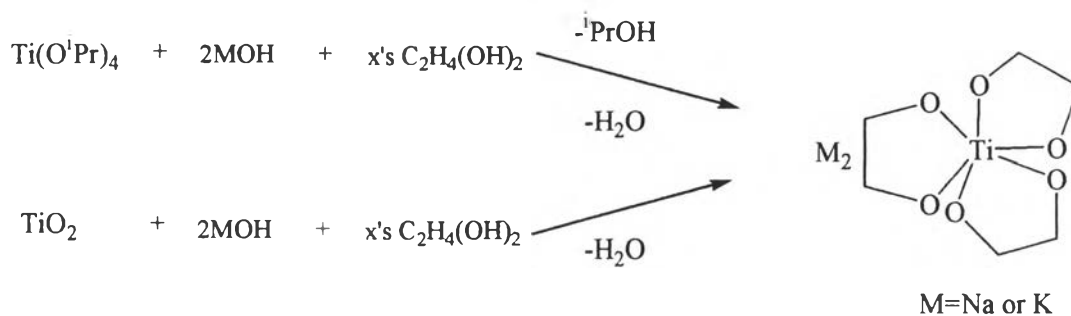
2.1 Synthesis of Metal Alkoxides

Fundamentally the uses of metal alkoxides depend on their chemical reactivity coupled with their volatility and solubility in common organic solvents. The chemical reactivity is manifest in the variety of catalytic applications of the alkoxides, ranging from redox catalyst (aluminium alkoxides in Meerwein-Ponndorf-Verly reactions with those used to synthesize primary alcohol from aldehyde), olefin polymerization catalysts (titanium and vanadium alkoxides as components of Ziegler-Natta catalysts) to accelerators for drying paints and inks. Ultimately the alkoxides are valuable precursors to the metal oxides through hydrolysis, pyrolysis or combustion. Where high purity is at stake and the metal alkoxides offer considerable advantages as starting materials for the preparation of high purity oxides. Therefore, the alkoxide chemistry has been investigated up to now.

Laine *et al.* (1991) investigated a straightforward and low-cost route to produce alkoxide precursors by direct reactions of a stoichiometric mixture of silica and group I metal hydroxide with ethylene glycol. This route, termed the "oxide one pot synthesis" (OOPS) process, provides processable precursors, as shown in Scheme I.
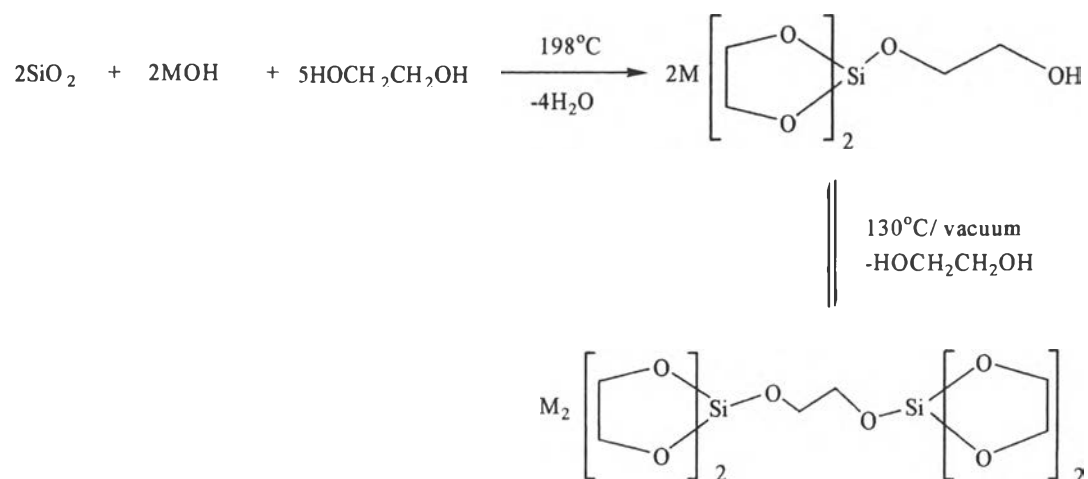
Scheme I

Gainsford *et al.* (1995) synthesized potassium and sodium tris(glycotitanate) complexes from the reaction of titanium dioxide or titanium tetraisopropoxide with two equivalent of sodium or potassium hydroxide in an excess ethylene glycol (Scheme II).

$$Ti(O^iPr)_4 \; + \; 2MOH \; + \; x's \; C_2H_4(OH)_2 \xrightarrow[\; -H_2O \;]{\; -^iPrOH \;}$$

$$TiO_2 \; + \; 2MOH \; + \; x's \; C_2H_4(OH)_2 \xrightarrow[\; -H_2O \;]{}$$

M=Na or K

Scheme II

Suzuki *et al.* (1997) synthesized titanium tetraethoxide ($Ti(OEt)_4$) and titanium tetrapropoxide ($Ti(OPr^n)_4$) by the reaction of hydrous titanium dioxide ($TiO_2.nH_2O$, n=0.15-1.23) and dialkyl carbonates using varied alkali-metal hydroxides catalyst (LiOH, NaOH, KOH and CsOH). The reaction was carried out in autoclave at a heating rate of 90 Kh^{-1}. They reported that use of sodium hydroxide gave the highest yield compared to the others (Scheme III).

$$TiO_2.nH_2O \; + \; (2+n)R'OC(=O)OR' \longrightarrow Ti(OR')_4 + (2+n)CO_2 \; + \; 2nR'OH$$

(when R' = Et, Pr^n)

Scheme III

Wang *et al.* (1999) synthesized titanium glycolate complex by the reaction of titanium tetraethoxide, n-butylamine and ethylene glycol. The reaction was carried out in autoclave at 180 °C for 5 days. The product exhibited outstanding high stability not only in alcohol but also in water, as shown in Scheme IV.

$$Ti(OC_2H_5)_4 \; + \; x's \; HOCH_2CH_2OH \; + \; CH_3(CH_2)_3NH_2 \longrightarrow$$
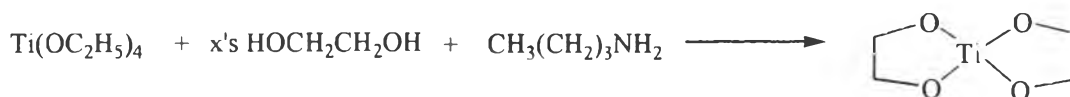
Scheme IV

2.2 Synthesis of Titania

The interest in titania stems from its wide applications, either as a raw material used in electronic and structural ceramics, or as material used in the catalyst industry. The increasing number of applications for TiO_2 nano-particles in this fields of catalysts, photo-catalysts or sensors has been imposing strict requirement on synthesis processing. Many different methods were used to prepare titania nanoparticles including a new route for preparation of inorganic precursors.

Ding (1997) synthesized nanocrystalline titania via a sol-gel process using tetrabutyl titanate (Ti (O-Bu)$_4$) as a precursor. Acetyl acetone ($C_5H_8O_2$) and hydrochloric acid (HCl) used as catalyst of hydrolysis reaction. In comparison with the $C_5H_8O_2$- catalyzed titania gel, the HCl-catalyzed one crystallized into anatase at a much lower temperature, and the crystallite size is smaller after the same heat treatment, on the other hand, pure rutile phase can be more easily obtained in the $C_5H_8O_2$-catalyzed gel. In the lower hydrolysis water content (H_2O/ Ti (O-Bu)$_4$) samples, the grain size is smaller, and the starting temperature of the anatase-to-rutile (A→R) transformation is a little lower, in comparison with those higher hydrolysis water content samples.

Izutsu *et al.* (1997) prepared anatase titania nanoparticles by the hydrolysis of titanium tetraisopropoxide (TTIP) and used freeze-dry method to increase surface area of the particles. After calcinations at 700 °C for 8 h, the freeze-dried particles showed more than 97 % anatase phase with a surface area of 29 m^2g^{-1}. The starting transformation temperature of the particles from anatase to rutile was about 700 °C.

Wei *et al.* (1999) prepared nanosized monodispersed TiO_2 by forced hydrolysis of Ti(SO$_4$)$_2$ in the deionized water and 98 % H_2SO_4 for 5 h. As the inhibition of H_2SO_4 to phase transformation causes the nucleation rate to slow down, however when the concentration of H_2SO_4 continues to rise, the particles size not only increases, but also the production of TiO_2 powder is reduced. In addition, they successfully prepared titania with an average particle size of 80 nm.

Kim (2001) synthesized ultrafine titania particles by hydrolysis of titanium tetraisopropoxide (TTIP) in the nanodroplets of water/NP-5/cyclohexane microemulsion. TiO_2 particles did not form at a water/surfactant molar ratio below

0.53 since water was mostly bound to the surfactant molecules. The particles grew largely by intra-agglomerate densification below 700 °C, whereas, they grew by inter-agglomerate densification above 700 °C. With raising calcination temperature, the specific surface area of TiO_2 particles decreased rapidly, whereas their average pore radius increased considerably due to shrinkage and densification of the agglomerates.

Sun *et al.* (2001) prepared nanocrystalline anatase titania by MOCVD (metal oxide chemical vapor deposition) method using titanium tetrabutoxide (TTB) as starting precursor in oxygen containing atmosphere. Anatase titania nanoparticles with average grain sizes ranging from 7.4 to 15.2 nm were prepared at an optimum temperature of about 700 °C and the anatase-rutile transformation temperature as high as 700-1000 °C, which is about 200 °C higher than that of the particles prepared by spray hydrolysis method.

Yang (2001) prepared highly crystallized anatase TiO_2 by hydrothermally treating the titania sols at 240 °C for 2 h after peptization with three types of tetraalkylammonium hydroxides (TANOHS), i.e. tetramethyl, ethyl, and butyl ammonium hydroxides refered as TMNOH, TENOH and TBNOH, respectively. All three peptizers enhance the growth of anatase particles. However, TMNOH-derived powders showed the largest particle size, whereas TBNOH-derived sample exhibited the smallest particle size. By increasing the peptizer concentrations, elongated structure was obtained in TMNOH-derived samples, while no significant changes in particle shape was observed for the samples peptized with different amounts of TBNOH.

Zhang *et al.* (2002) prepared nanocrystalline titania by using sol-gel technique. Butanediol mixed with tetrapropylorthotitanate was used as precursors. They found that aging time for the synthesis has an evident influence on the phase transition of titania. When the aging time increased, the beginning of anatase-to-rutile temperature decreased. Following the early evolution of anatase and rutile, the end of phase transition of anatase-to-rutile terminated at low temperatures as well. They also reported that the surface area of titania increased when calcined the samples at lower temperature.

From all of the literatures, many method can be used to prepare high surface area titania. But most of these methods require high costs and are very complicated to give satisfied results. Therefore, sol-gel process could be the appropriate method for preparation of titania due to many applications, such as films and monoliths. Moreover, this process can give satisfied results in surface area, homogeneity and porosity, but the precursors in sol-gel process are very expensive and extremely moisture sensitive. Therefore, it is challenging to study sol-gel processing of glycolato titanium precursor prepared under mild conditions and inexpensive method.