

CHAPTER IV
OXIDE ONE POT SYNTHESIS OF A NOVEL TITANIUM GLYCOLATE
AND ITS PYROLYSIS

Abstract

A much milder, simpler and more straightforward reaction to titanium glycolate product was successfully investigated by the reaction of titanium dioxide, ethylene glycol and triethylenetetramine using the oxide one pot synthesis (OOPS) process. FT-IR spectrum demonstrates the characteristics of titanium glycolate at 619 and 1080 cm^{-1} assigned to Ti-O stretching and C-O-Ti stretching vibration, respectively. ^{13}C -solid state NMR spectrum gives two peaks at 75.9 and 79.8 ppm due to the relaxation of the crystalline spiro titanate product. The percentage of carbon and hydrogen from elemental analysis are 28.6 and 4.8, respectively. Thermal analysis study from TGA exhibits one sharp transition at 340 °C, corresponding to the decomposition transition of organic ligand, and giving a ceramic yield, titanium glycolate, of 46.95% which is close to the theoretical yield of 47.5%. XRD patterns show the morphology change of its pyrolyzed product from anatase to rutile as increasing calcining temperatures from 500° to 1100 °C while at 300 °C the amorphous phase is formed.

Keywords: Titanium Dioxide, Titanium Glycolate, Oxide One Pot Synthesis, Pyrolysis, Phase Transformation

Introduction

Titania is a very useful material and has received a great attention in recent years for its humidity- and gas-sensitive behavior, excellent dielectric property, as well as catalysis applications.¹ The important factor to produce titania with good properties is the purity of titanium alkoxide precursor. However, the synthesis of titanium alkoxides is greatly challenging to scientists due to their extreme moisture sensitivity and very expensive starting materials. In this work the great interest in titanium glycolate, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$, is owing to its difference from most crystalline titanium alkoxides, generally having low polymeric O-dimensional molecular. Nevertheless, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ is a novel crystalline complex with infinite one-dimensional chains, and exhibits outstanding high stability not only in alcohol but also in water.²

The method required for the synthesis of alkoxy derivatives of an element generally depends on its electronegativity. In the case of comparatively less active metals, a catalyst is generally employed for successful synthesis of metal alkoxides. Wang *et al.*² synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ from very expensive starting material, tetraethyl orthotitanate to react with ethylene glycol using n-butylamine as a catalyst. The reaction took place under a very vigorous condition. It occurred in a Teflon-lined stainless steel autoclave at 160°-180 °C for 5 days. The alkalinity of the initial reaction mixture is a dominant factor of the product. The ethylene glycol served as both a solvent and a bidentate chelate occupying sites on titanium coordination sphere so as to bridge adjacent titanium atoms and formed the one-dimensional structure.

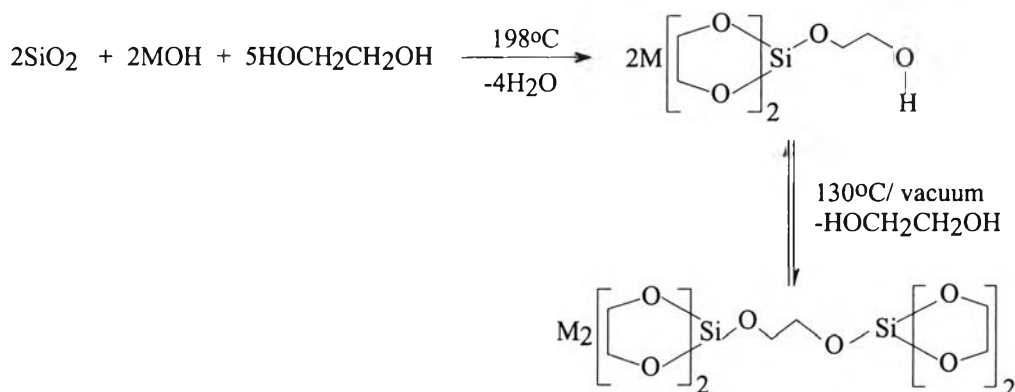
Gainsford *et al.*³⁻⁴ studied the synthesis and characterization of the soluble titanium glycolate complexes obtained from the reaction of titanium dioxide or titanium isopropoxide with glycol in the presence of alkali metal hydroxides. The reaction of $\text{Ti}(\text{O-}i\text{-Pr})_4$ with 2 equivalent of sodium or potassium hydroxides provided tris(glycolate) salts, which were highly crystalline, hygroscopic materials, crystallized as salts and solvated with varying numbers of glycol molecules.

Suzuki *et al.*⁵ synthesized titanium tetraalkoxides from hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) and dialkyl carbonates in an autoclave at a heating rate of 90K h^{-1} . The effect of reaction temperature was studied. At temperature range of 495-

533 K, practically completed conversion of hydrous titanium dioxide to $\text{Ti}(\text{OEt})_4$ could be attained. LiOH , NaOH , KOH , and CsOH were used as catalysts which NaOH gave highest yield of $\text{Ti}(\text{OEt})_4$. The effect of the molar ratios of diethyl carbonate/hydrous titanium dioxide was studied. As high molar ratio of 10 was required to obtain a high yield of $\text{Ti}(\text{OEt})_4$.

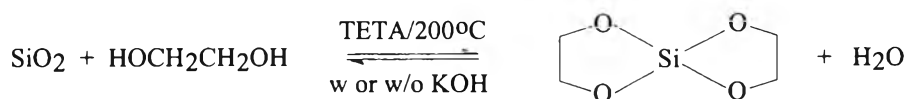
Related metalglycolates formed from alkaline glycol were reported for aluminium and titanium⁶⁻¹¹. Potassium and sodium tris(glycotitanate) complexes were obtained from the reaction of titanium dioxide or titanium tetraisopropoxide with ethylene glycol in the presence of alkali metal hydroxides.³⁻⁴

Laine *et al.* investigated a straightforward, low-cost route to 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 1.¹²⁻¹⁴



Scheme 1.

Recently, Jitchum *et al.* synthesized neutral alkoxy silanes, tetracoordinated spiro silicates, directly from silica and ethylene glycol or ethylene glycol derivatives, using triethylenetetramine as catalyst, in the absence or presence of potassium hydroxide as co-catalyst (Scheme 2).¹⁵



Scheme 2.

The OOPS method is simple, low-cost and can produce new chemicals in only one step. Thus, the objective of this work is to use the OOPS process to synthesize titanium glycolate. The phase transformation of its pyrolyzed product will be studied, as well.

Experimental

Materials

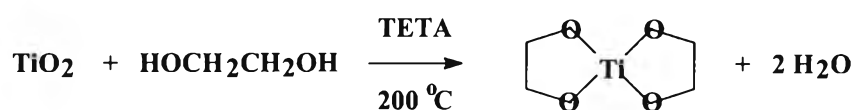
UHP grade nitrogen; 99.99% purity was obtained from Thai Industrial Gases Public Company Limited (TIG). Titanium dioxide was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG), purchased from Malinckrodt Baker, Inc. (USA), purified by fractional distillation under nitrogen at atmospheric pressure, 200°C before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile were purchased from Lab-Scan Company Co. Ltd. and purified by standard techniques. Acetonitrile was distilled over calcium hydride powder.

Instrumental

Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm⁻¹ using transparent KBr pellets, 0.001 g of the sample was ground and mixed with 0.06 g of KBr. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10 °C/min over 30°-800 °C temperature range. Mass spectrum using the positive fast atom bombardment mode (FAB⁺-MS) was measured on a Fison Instrument (VG Autospec-ultima 707E) with VG data system using glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration. ¹³C- solid state NMR spectroscopy modeled Bruker AVANCE DPX-300 MAS-NMR was used to determine peak position of carbon containing in the product. Elemental analysis (EA) was carried out on a C/H/O Analyser (Perkin Elmer PE2400 series II). X-ray diffraction patterns were analyzed using a D/MAX-2200H Rigaku equipped with Cu X-ray generator.

Methodology

The titanium glycolate was synthesized by the OOPS method, see Scheme 3. A mixture of TiO_2 (2g, 0.025 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm^3) and heated at the boiling point of EG under N_2 atmosphere. After heating for 24 h the solution was centrifuged to separate the unreacted TiO_2 from the solution part. The excess EG and TETA were removed by vacuum distillation to obtain crude precipitate. The white solid product was washed with acetonitrile and dried in a vacuum desiccator.



Scheme 3.

Results and Discussion

Synthesis

The reaction of titanium dioxide, triethylenetetramine catalyst and ethylene glycol used as both solvent and reactant was achieved by heating in a simple distillation apparatus. The glycol was slowly distilled off along with water generated during the condensation reaction to drive the reaction forward. The resulting product was isolated by distilling off glycol, followed by addition of acetonitrile to remove residual glycol and TETA. The final product, titanium glycolate, was moisture-stable.

Characterization

The FT-IR spectrum of titanium glycolate is shown in Figure 1. As compared with the work done by Wang², the result clearly shows the characteristics of titanium alkoxide at the 1080 and 619 cm^{-1} bands, corresponding to C-O-Ti and Ti-O stretching, respectively. Moreover, the band at 2927-2855 cm^{-1} is assigned to the C-H stretching of ethylene glycol ligand.

Due to the insolubility of the product in organic solvent, ^{13}C -solid state NMR was employed. The obtained spectrum, see Figure 2, gives two peaks at 74.8 and 79.2 ppm. It is due to the crystalline phase of titanium glycolate, causing the peak to split during relaxation time of nuclei, as discussed by Wang.²

To confirm the structure of the desired product, both elemental analysis and mass spectroscopy techniques are carried out. The results are shown in Tables 1 and 2, respectively. The obtained C/H percentages are close to those calculated theoretically. The proposed fragmentation and structures presented in Table 2 also confirms the expected structure of the titanium glycolate.

As for its thermal stability, Figure 3 shows the same TGA thermogram as obtained by Wang.² The result exhibits one sharp transition at 340°C, corresponding to the decomposition transition of the glycol ligand. The final ceramic yield obtained is 46.95% that is close to the theoretical yield, 47.5%.

Phase transformation

The TGA result indicating the oxidation of organic compound at 340 °C, and the crystallization at 500 °C. The crystalline titanium glycolate decomposed and changed to an amorphous phase at 300 °C (Figure 4). As increasing the calcination temperature, the XRD pattern gives anatase phase at 500 °C to 900 °C and completely changes to rutile phase at 1100°C.

Conclusions

Titanium glycolate is successfully synthesized using low cost starting materials, and a much simpler and milder reaction condition. The product shows good property in moisture stability. The results from spectroscopy, namely, FT-IR, EA, Solid state NMR, and TGA, confirm the product structure. The transformation from anatase to rutile phase indicates the anatase stability up to 900°C. The stability of the synthesized product provides researchers to make use in many applications.

Acknowledgement

This research work is supported by the Thailand Research Fund (TRF).

References

1. Ding, X.Z., and Liu, X.H. *Materials Science and Engineering A224*. 1997, 210-215
2. Wang, D., Yu, R., Kumada, N. *Chem. Mater.* 1999, 11, 2008-2012.
3. Gainsford, G.J., Kemmitt, T., Lensink, C., and Milestone, N.B. *Inorg. Chem.* 1995, 34, 746-748.
4. Gainsford, J.G., Kemmitt, T., and Milestone, B.N. *Inorg. Chem.* 1995, 34, 5244-5251.
5. Suzuki, E., Kusano, S., Hatayama, H., Okamoto, M., and Ono, Y. *J.Mater.Chem* 1997, 7(10), 2049-2051.
6. Bickmore, C.R., Waldner, K.F., Baranwal, R., Hinklin, T., Freadwell, D.R., and Laine, R.M. *Journal of the European ceramic Society*. 1998, 18, 287-297.
7. Yang, J., MEI, S., and Ferreira, J.M.F. *Materials Science and Engineering C* 2001, 15, 183-185.
8. Laine, R.M.; Youngdahl, K.A.; Nardi, P. Washington Research Foundation, U.S. Pat. No. 5,099,052, 1992.
9. Laine, R.M.; Youngdahl, K.A. Washington Research Foundation, U.S. Pat. No. 5,216,155, 1993.
10. Day, V.W., Eberspacher, .A., Frey, M.H., Klemperer, W.G., Liang, S. and Payne, D.A. *Chem Mater* 1996, 8, 330-332.
11. Duan, Z., Thomas, L.M., and Verkade, J.G. *Polyhedron* 1997, 16, 635-641.
12. Laine, R.M.; Blohowiak, K.Y.; Robinson, T.R.; Hoppe, M.L.; Nardi, P.; Kampf, J.: Uhm, J. *Nature* 1991, 353, 642.
13. Blohowiak, K.Y.; Laine, R.M.; Robinson, T.R.; Hope, M,L.; Kampf, J.I. *Inorganic and Organometallic Polymers with Special Properites*; ACS: Netherland, 1992.
14. Bickmore, C.;Hoppe, M.L.; Laine, R.M. *Mat.Res.Soc.Symp.Proc.* 1992, 249, 81.
15. Jitchum, V.; Chivin, S.; Wongkasemjit S.; Ishida, H. *Tetrahedron* 2001, 57, 3997

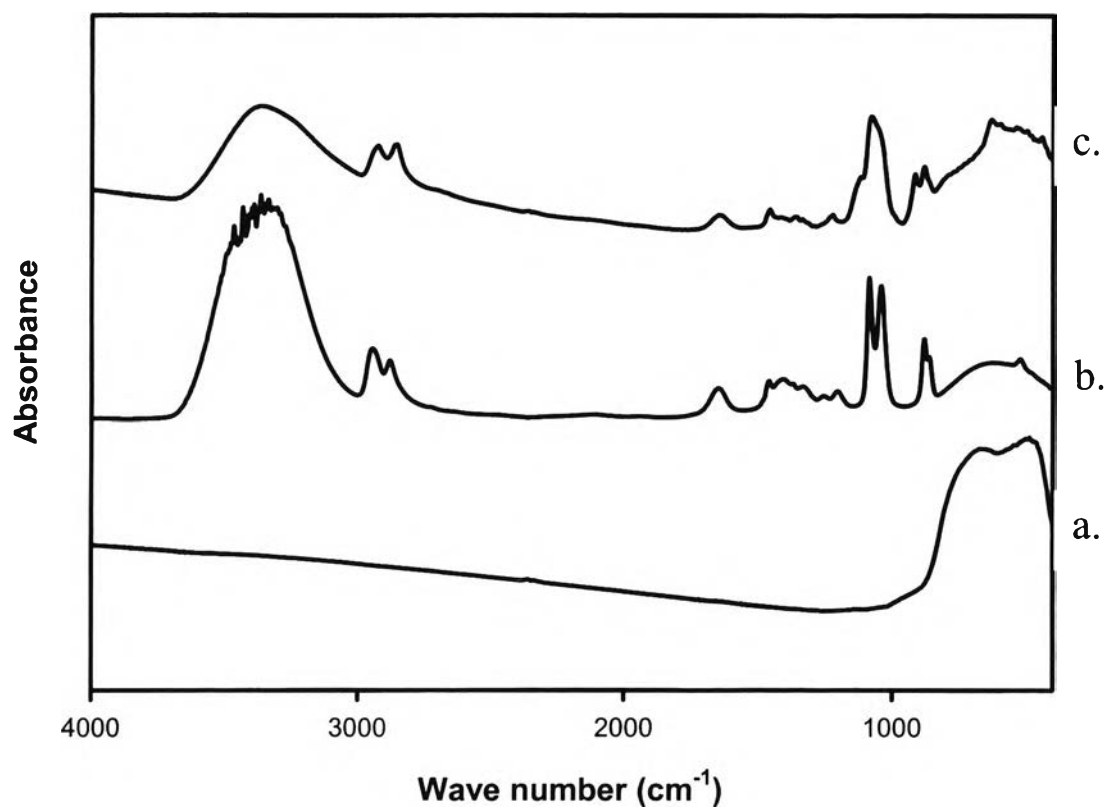


Figure 4.1 FT-IR spectra of (a). TiO_2 ; (b). $\text{HOCH}_2\text{CH}_2\text{OH}$ and (c). $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$.

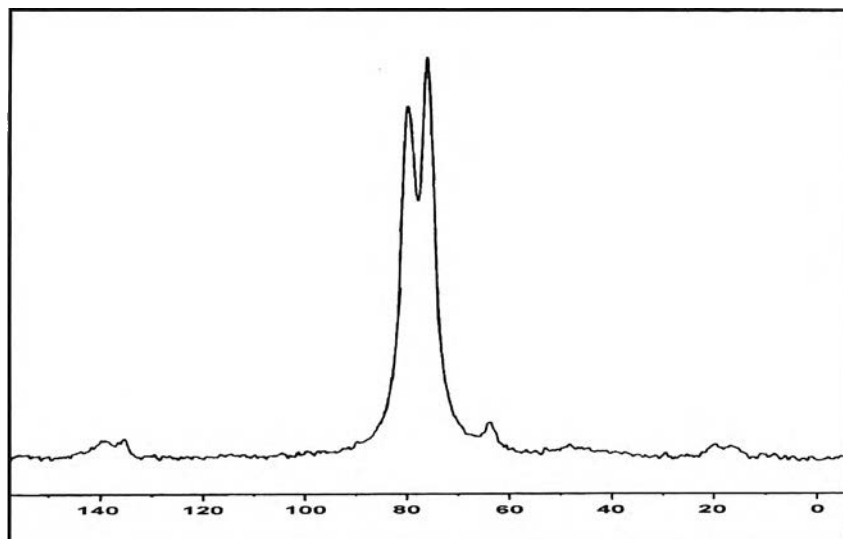


Figure 4.2 ^{13}C -Solid state NMR spectrum of the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$.

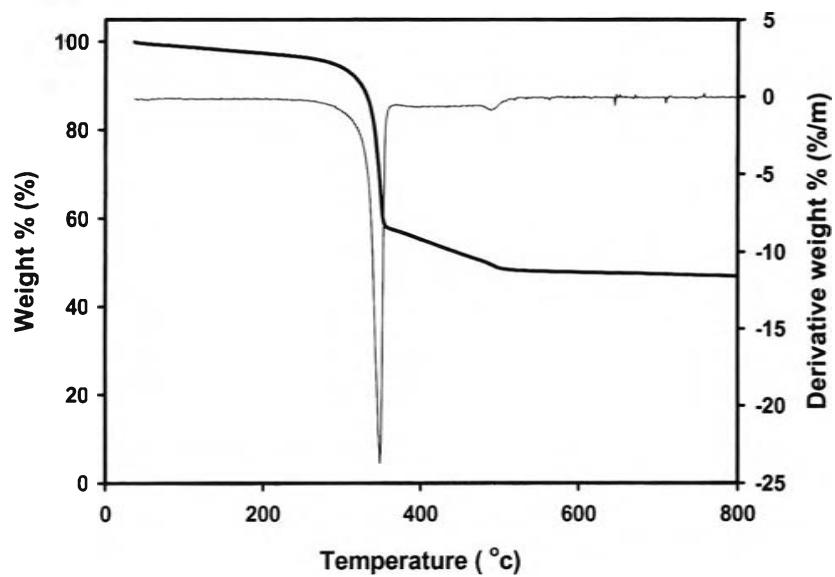


Figure 4.3 TGA curve of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$.

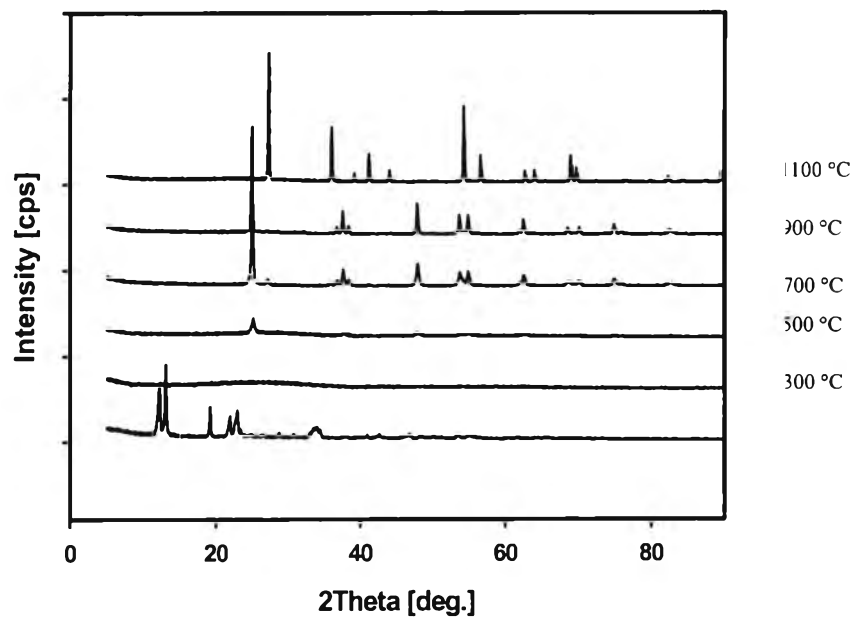
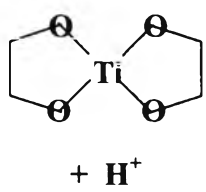


Figure 4.4 XRD patterns of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ at different temperatures: a.) titanium glycolate without calcinations, b.) 300°C, amorphous, c.) 500°C, anatase, d.) 700°C, anatase, e.) 900°C, anatase and f.) 1100°C, rutile.

Table 4.1 Percentages of C and H presented in the synthesized $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

Element (%)	Theoretical	Experimental
C	27.9	28.6
H	5.6	4.8

Table 4.2 Proposed fragmentation and product structures of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$

M/e	%intensity	Proposed structure
169	8.5	 + H ⁺
94	73.5	O-Ti-OCH ₂
45	63.5	CH ₂ CH ₂ OH