การสังเคราะห์ไทเทเนียมไดออกไซด์ที่มีรูพรุนโดยใช้เรโซซินอล/ฟอร์มัลดีไฮด์เจลช่วย

นางสาว มนันญา โทวิชา

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2553

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Fabrication of porous titanium dioxide assisted by Resorcinol/Formaldehyde gel

Miss Mananya Thovicha

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
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Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering

(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

....Chairman

(Assistant Professor Anongnat Somwangthanaroj, Ph.D.)

....Thesis Advisor

(Assistant Professor Varong Pavarajarn, Ph.D.)

....Examiner

(Associate Professor Tawatchai Charinpanitkul, D.Eng.)

....External Examiner

(Chanchana Thanachayanont, Ph.D.)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

มนันญา โทวิชา : การสังเคราะห์ไทเทเนียมไดออกไซด์ที่มีรูพรุนโดยใช้เรโซซินอล/ฟอร์มัลดีไฮด์ช่วย (FABRICATION OF POROUS TITANIUM DIOXIDE ASSISTED BY RESORCINOL/FORMALDEHYDE GEL)
อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.วรงค์ ปวราจารย์, 73 หน้า.

งานวิจัยนี้ศึกษาการผสานไทเทเนียมไดออกไซด์หรือไทเทเนียเข้าไปในอาร์เอฟเจลซึ่งเตรียมด้วยเทคนิคโซล-เจล โพลีคอนเดนเซชั่นของเรโซซินอลกับฟอร์มัลดีไฮด์ โดยใช้กรดอะซิติกเป็นตัวเร่งปฏิกิริยา ไทเทเนียม เตตระไอโซโพรพรอกไซด์ (ทีทีไอพี) ถูกใช้เป็นสารตั้งต้นของไทเทเนีย ซึ่งปฏิกิริยาระหว่างสารตั้งต้นของไทเทเนียกับสารละลายอาร์เอฟนั้นเกิดค่อนข้างรุนแรง และคายความร้อนเป็นอย่างมาก ดังนั้นไทเทเนียโซลจึงถูกเตรียมขึ้นต่างหากเพื่อชะลอการเกิดปฏิกิริยาเมื่อเติมลงไปในสารละลายอาร์เอฟ ไทเทเนียโซลถูกเตรียมด้วยวิธีโซลเจลของทีทีไอพีที่เวลาบ่มต่างๆ และถูกเติมลงในสารละลายอาร์เอฟ ซึ่งถูกบ่มที่เวลาต่างๆด้วย หลังจากนั้นสารผสมจะถูกบ่มไว้อีก 36 ชั่วโมงก่อนที่นำไปอบที่อุณหภูมิ 80 องศาเซลเซียส และนำไปเผาที่อุณหภูมิ 500 องศาเซลเซียสเป็นเวลา 4 ชั่วโมง เพื่อกำจัดโครงสร้างอาร์เอฟออก จากการทดลองพบว่าไทเทเนียโซลทำปฏิกิริยากับสารละลายอาร์เอฟที่เกิดเป็นกลุ่มก้อนอาร์เอฟ โดยดูได้จากสัญญาณของพันธะของไทเทเนียมต่อกับออกซิเจนและคาร์บอนที่เพิ่มขึ้น ผลิตภัณฑ์ที่ได้สามารถมีโครงสร้างรูพรุนแบบเมโซพอร์จากการใช้อาร์เอฟเจล อย่างไรก็ตามอัตราส่วนโดยโมลของเรโซซินอลต่อฟอร์มัลดีไฮด์และอัตราส่วนโดยโมลของเรโซซินอลต่อตัวเร่งปฏิกิริยาที่มีค่าสูงจะส่งผลต่อปฏิกิริยาระหว่าอาร์เอฟเจลและไทเทเนียโซลทำให้ได้พื้นที่ผิวของผลิตภัณฑ์ที่มาก ส่วนปริมาณไทเทเนียโซลที่ใช้มีผลต่อการเกิดพื้นที่ผิวอย่างมากและทำให้ผลิตภัณฑ์มีความเป็นรูพรุนแบบเมโซพอร์ ระยะเวลาการบ่มของอาร์เอฟเจลและไทเทเนียโซลทำให้เกิดโครงร่างตาข่ายและการเกิดโครงร่างตาข่ายนี้ทำให้ปฏิกิริยาของสารละลายอาร์เอฟกับไทเทเนียโซลเกิดอย่างไม่สมบูรณ์ อย่างไรก็ตามปฏิกิริยาของอาร์เอฟกับไทเทเนียจะเกิดขึ้นโดยที่อาร์เอฟเจลและไทเทเนียโซลเกิดเป็นโครงร่างตาข่ายเชื่อมขวางกันและเกิดโครงร่างตาข่ายของไทเทเนียขึ้นพร้อมกันด้วย

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต มนันญา โทวิชา
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2553

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MANANYA THOVICHA: FABRICATION OF POROUS TITANIUM
DIOXIDE ASSISTED BY RESORCINOL/FORMALDEHYDE GEL.
ADVISOR: ASST. PROF. VARONG PAVARAJARN, Ph.D., 73 pp.

Incorporation of titania into RF solution, which was prepared via the sol-gel polycondensation of resorcinol and formaldehyde using acetic acid as catalyst, was investigated. Titanium tetraisopropoxide (TTIP) was used as precursor for titania. The reaction between titania precursor and RF solution is quite violent and strongly exothermic therefore titania sol wass separately prepared for slowing down the reaction. Titania sol was firstly prepared from TTIP via sol-gel process. After certain period of aging time, the titania sol was added into RF mixture, which had been aged for predetermined period of time as well. After that, the mixture was further aged for another 36 hours before being dried at 80°C. Finally, the dried gel was calcined at 500°C for 4 hours to remove the RF template. From the results, when titania sol is added into RF solution, titania sol reacts with RF solution to form clusters. This reaction is witnessed by the increase in the signal of Ti-O-C. The product is developed from micropore to mesopore by using RF template. In addition, higher of R/F and R/C ratio is affected on the reaction between RF gel and titania sol and then, the final product is high surface area. Amount of titania also affects on surface area and mesoporousity of the product. The period of RF and titania aging time results in the formation of network, which prohibits complete reaction between titania sol and RF solution. However, reaction between RF/titania takes place while RF gel and titania sol are formed into cross-linking of RF gel as well as the cross-linking of titania sol.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Department: Chemical Engineering Student's Signature: มนัญญา โถวิชา

Field of Study: Chemical Engineering Advisor's Signature:

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CHAPTER I

INTRODUCTION

Porous ceramics are essential for many industries where high permeability, high surface area, and insulating characteristics are required [3]. Nanocrystalline titanium dioxide (TiO_2 or titania), as one of the most important oxide semiconductor materials, has been extensively researched during recent years for its superior physical and chemical properties (e.g., catalytic and photocatalytic activity, good stability toward adverse environment, sensitivity to humidity, dielectric character, photo-electrochemical conversion, nonlinear optics, and photoluminescence) [4, 5].

The crystal of titania exists in three different forms, namely rutile, anatase, and brookite. Anatase and brookite are thermodynamically metastable and can be transformed irreversibly to the most stable and condensed rutile phase at high temperatures. Anatase titania has been used as catalyst for photodecomposition and solar energy conversion because of its high photoactivity, whereas rutile titania has been used as white pigment materials for ultraviolet light protection because of its good scattering effect. Brookite titania has a structure belonging to the orthorhombic crystal system, which is formed only under hydrothermal conditions and usually found only in minerals.

It has been demonstrated that the final properties of this material depend on size, morphology and crystalline phase of the prepared TiO_2. In order to prepare nanostructured titanium dioxide with unique properties, several processes have been developed over the last decade, such as liquid processes (e.g., sol–gel, solvothermal and hydrothermal techniques), solid state processing routes (mechanical-alloying/milling, mechanochemical), radio-frequency or thermal-plasma and other routes such as laser ablation [6-10].

Nanocrystalline material, characterized by an ultra fine grain size (<50 nm), is a subject of current interest because of the unusual chemical magnetic, optical and electronic properties. It has been reported that nanometer-sized particles have different physical and chemical properties from bulk materials. Their catalytic activity is expected to be enhanced

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not only because of their increased surface area, but also because of the change of surface properties such as surface defect.

The sol-gel process involves the formation of sol followed by gelation. Sol, which is suspension of solid particles with size ranging from 1 nm to 1 micron in liquid, can be obtained by hydrolysis and partial condensation of a precursor such as inorganic salt or metal alkoxide. Further condensation of sol particles into a three-dimensional network produces gel, which is a diphasic material with solids encapsulating solvent. Alternatively, gel can be produced by destabilizing the solution of preformed sols. In either case, the materials are referred as aquasol (or aquagel) if water is used as a solvent, and alcosol (or alcogel) if alcohol is used. The encapsulated liquid can be removed from gel by either evaporative drying or drying with supercritical extraction (supercritical drying in short).

Resorcinol-formaldehyde (RF) gel is typed of sol-gel processes and formed from polymerization of resorcinol (R) with formaldehyde (F). RF gel can be further processed into carbon aerogel which is a special class of aerogels with many common characteristics such as a tortuous open-cell structure, ultrafine pore size (< 50 nm) and high surface area (400-1000 m^2g^{-1}) [11]. The synthesis of RF aerogels consists of a polycondensation reaction between resorcinol and formaldehyde which is analogous to the sol-gel process for the synthesis of inorganic compound like silica- or titanium- based systems [12].

In this study, porosity of RF-gel will be employed as template for the fabrication of porous titanium dioxide. Effects of many parameters in resorcinol/formaldehyde gel synthesis and titania-sol preparation were investigated in detail to understand the correlation between condition for resorcinol/formaldehyde and properties of the synthesized titania nanoparticles, including morphology and phase stability of titania nanoparticles. This work focuses on the fabrication of porous titanium dioxide assisted by resorcinol/formaldehyde gel and studies its mechanism.

This thesis is divided into five chapters. The first three chapters describe general information about the study, while the following two chapters emphasize on the results and discussion from the present study. Chapter I is the introduction of this work. Chapter II describes basic theory about titania such the general properties of titania, sol-gel process and resorcinol–formaldehyde (RF) gel. Chapter III shows materials and experimental systems.

Chapter IV presents the experimental results and discussion. In the last chapter, the overall conclusion from the results and recommendation for future work are presented.

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CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Physical and chemical properties of titanium (IV) oxide

Titanium dioxide (TiO_2 or titania) is one of the most widely used and promising materials in photocatalytic applications due to strong oxidizing power of its holes, its redox selectivity, high photostability, and easy preparation. An important requirement for high TiO_2 photocatalytic efficiency is a large surface area which increases both amount of photon generated electron/hole pairs and surface-adsorbates [13].

Titania exists in the three polymorphs, including anatase, rutile and brookite. Of the three naturally occurring forms of titania, anatase and brookite are thermodynamically metastable with respect to rutile. All three crystal structures consist of TiO_6 octahedra connected variously by corners and edges, as presented in Figure 2.1. In rutile, two opposing edges of each octahedral are shared to form linear chains along [001]. These TiO_6 chains are linked to each other through corner connection. Anatase has no corner sharing, but has four edges shared per octahedron. The anatase structure can be viewed as zigzag chains of octahedral, linked to each other through shared edges. The density of rutile and anatase is 4.26 and 3.84 g/cm^3 respectively. In brookite, the octahedra share both edges and corners, forming an orthorhombic structure with a density of 4.11 g/cm^3. It is generally accepted that anatase is the most active photocatalyst, and that a combination of high crystallinity and large specific surface area improves photocatalytic performance [2]. Physical properties of all three phases are summarized in Table 2.1

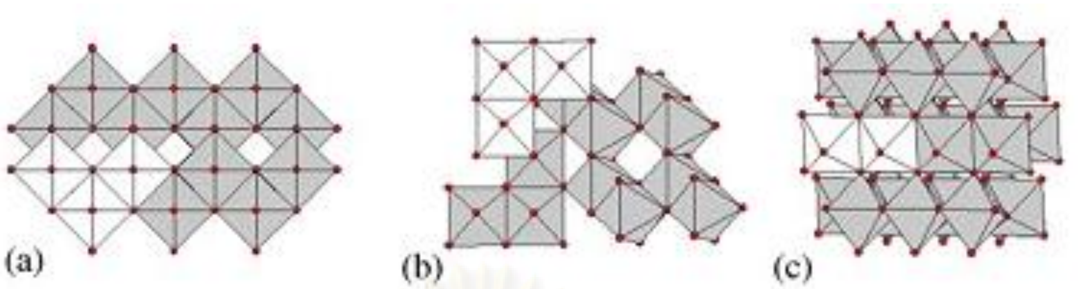

Figure 2.1 Crystal structure of TiO_2; (a) Anatase, (b) Brookite, (c) Rutile [2].

Table 2.1 Crystallographic properties of anatase, brookite, and rutile.

	Anatase	**Brookite**	**Rutile**
Crystal Structure	Tetragonal	Orthorhombic	Tetragonal
Optical	Uniaxial, negative	Biaxial, positive	Uniaxial, negative
Density, g/cm^3	3.84	4.11	4.26
Hardness, Mohs scale	$5\frac{1}{2}$ - 6	$5\frac{1}{2}$ - 6	7 - $7\frac{1}{2}$
Unit cell	$D_4a^{19}.4TiO_2$	$D_2h^{15}.8TiO_2$	$D_4h^{12}.3TiO_2$
Lattice parameters, nm			
a	0.3758	0.9166	0.4584
b		0.5436	
c	0.9514	0.5135	2.953

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2.2 Sol-gel process

Porous titania can be synthesized by various methods such as thermal decomposition of a precipitated from a precursor solution of titanium isopropoxide (IV) and isopropyl alcohol [14]. However, one of the simplest techniques is the sol-gel process.

The sol-gel process is a wet-chemical technique for the fabrication of materials starting either from chemical solution or colloidal particles to produce an integrated network, which undergoes hydrolysis and polycondensation reactions to form colloid, and subsegnenthy form gel according to Equations 2.1 to 2.3.

$$\text{M-O-R} + H_2O \longrightarrow \text{M-OH} + \text{R-OH} \quad \text{(hydrolysis)} \qquad (2.1)$$

$$\text{M-OH} + \text{HO-M} \longrightarrow \text{M-O-M} + H_2O \quad \text{(water condensation)} \qquad (2.2)$$

$$\text{M-O-R} + \text{HO-M} \longrightarrow \text{M-O-M} + \text{R-OH} \quad \text{(alcohol condensation)} \qquad (2.3)$$

where M and R are metal atom and alkyl group, respectively. In general, the sol-gel process involves the transition of a system from liquid “sol” into solid “gel” phase. By applying the sol-gel process, it is possible to fabricate advanced materials in a wide variety of forms, e.g. ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and extremely porous aerogel materials.

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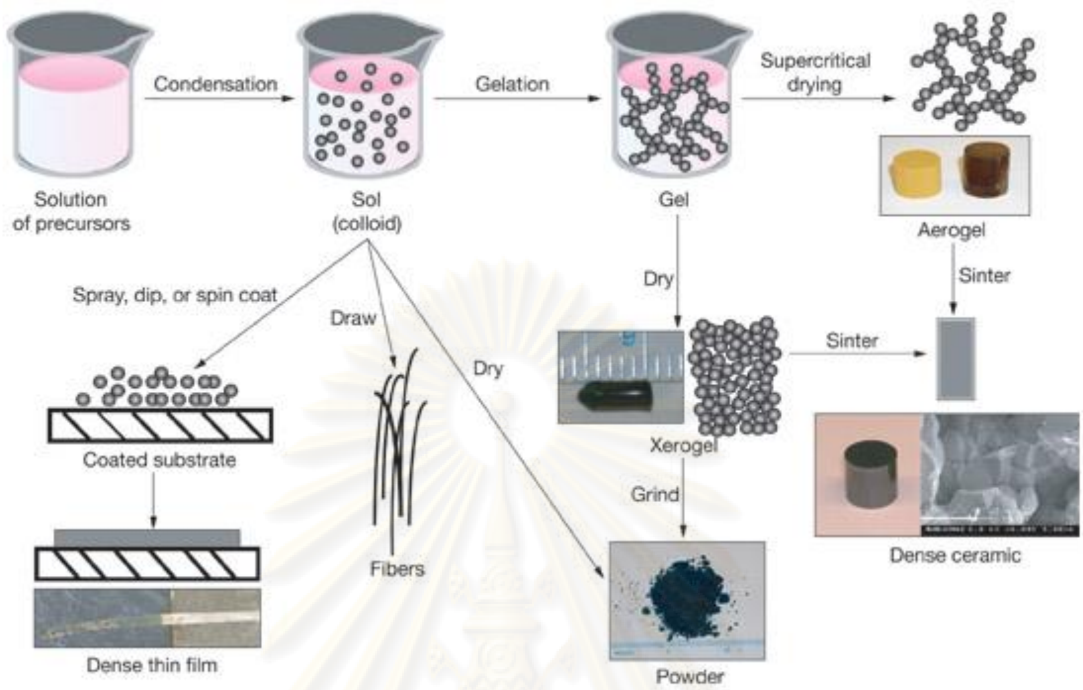

Figure 2.2 Diagram of sol-gel process [1].

2.2.1 Titanium (IV) dioxide synthesis by sol-gel process

The preparation of the TiO_2 colloid can be effectively conducted through the hydrolysis and condenation of titanium alkoxides in aqueous media. In the presence of water, alkoxides are hydrolyzed and subsequently polymerized to form a three dimensional oxide network. These reactions can be schematically represented as follows:

$$\text{Hydrolysis}: \ Ti(OR)_4 + 4H_2O \longrightarrow Ti(OH) + 4ROH \qquad (2.4)$$

$$\text{Condensation}: \ Ti(OH)_4 \longrightarrow TiO_2xH_2O + (2\text{-}x)H_2O \qquad (2.5)$$

where R is alkyl group such as ethyl, *i*-propyl, *n*-butyl, etc [15]. It is well known that the tetravalent cations are too much acidic so that the nucleation of stable hydroxide $Ti(OH)_4$ cannot occur. Water molecules formed according to reaction (2.5) always bear a partial positive charge. Therefore, oxolation and olation can proceed simultaneously during the

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nucleation and growth leading to amorphous hydrous oxide (TiO_2nH_2O) where the number *n* of water molecules depends on experimental conditions. Depending on the experimental procedure, the precipitation of TiO_2 can lead to rutile or anatase phases [30, 31]. The formation of such structures from aqueous molecular precursors can be described as follows. When deoxolation (O=Ti–OH_2 $\longrightarrow$ HO–Ti–Ti–OH) does not occur during the nucleation, olation leads to a linear growth along one of the two equivalent directions in the equatorial plan of $[TiO_2O_2(OH)_4(OH_2)_4]^0$ dimers. Then, oxolation between the resulting $TiO(OH)_2(OH)_2$ linear chains after internal proton transfer leads to corner-sharing octahedral chains (Ti_3O bridges) characteristics of the rutile structure. The formation of rutile may then be associated to the metastability of Ti=O bonds within monomers or dimmers [5].

The titanium dioxide was synthesis by the sol-gel process has been frequenthy reported because the method was favorite, non toxic and easy. Moreover, titanium dioxide synthesized by the sol-gel method is usually anatase phase with high surface area. Titanium (IV) isopropoxide is commonly used as a precursor for titanium dioxide. For example, Khalil and coworkers prepared anatase crystallites and 67-73 m^2/g of specific surface area from calcination of base hydrolysis products of titanium (IV) isopropoxide at 400°C for 3 h [16]. This specific surface area was higher than the commercial titania powders (~ 50 m^2/g). Venkatachalam and coworkers prepared nanocrystalline TiO_2 with 110 m^2/g of specific surface area and 8.1 nm of anatase crystalline size by sol-gel technique using titanium(IV) isopropoxide as the precursor [17].

The variation of sol-gel parameters has significant effect on properties of synthesized TiO_2. Li and coworkers showed that anatase phase could be controlled by adjusting the aging time of the dry gel while rutile phase could be controlled by adjusting the wet gel aging time [2]. The effects of acid addition on sol-gel process have been reported by many researchers. Lee and Liu observed, the effect of the amount of hydrochloric acid on condensation reaction and crystal growth of titanium dioxide [18]. Phonthammachai and coworkers various suggested that the gelation time increased with the increase of the HCl:H_2O volume ratio which consequently leaded to a less dense but stronger network structure [19]. Kashyout and coworkers reported an increase in the fraction of nanosized TiO_2 crystals when acetic acid concentration was increased [20].

2.2.2 Formation of resorcinol/formaldehyde gel

RF gel is an interesting porous material with moderately high surface area and large mesopore volume. Carbon gel derived by pyrolysis of the RF gel is suitable for many applications such as column packing materials for high-performance liquid chromatography, electrode materials for electric double layer capacitors and materials for catalyst supports [21].

The first resorcinol-formaldehyde (RF) gel was produced by Pekala via the sol-gel polycondensation of resorcinol (R) and formaldehyde (F) with sodium carbonate (C) as basic catalyst [22]. The intermediates formed during the reaction further react to form a cross-linked polymer network. The two major reactions include: (a) the formation of hydroxymethyl ($-CH_2OH$) derivatives of resorcinol, and (b) the condensation of the hydroxymethyl derivatives to form methylene ($-CH_2-$) and methylene ether ($-CH_2OCH_2-$) bridged compounds [23].

In general, porosity of the final products depends on the structure of their parent hydrogel, which is mostly formed during the sol-gel transition. A catalyst used in the sol-gel polycondensation usually plays the most important role for the formation of the porous structure of the hydrogel. For the RF gel, the catalyst initially promotes the generation of resorcinol anions. These anions are subsequently transformed into substituted resorcinols, which form RF clusters through polycondensation. Then RF clusters react with each other and grow into colloidal particles, which finally form a RF hydrogel as shown in a schematic diagram in Figure 2.3 [24].

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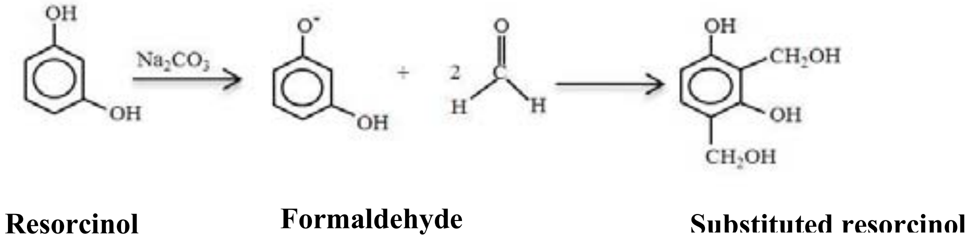
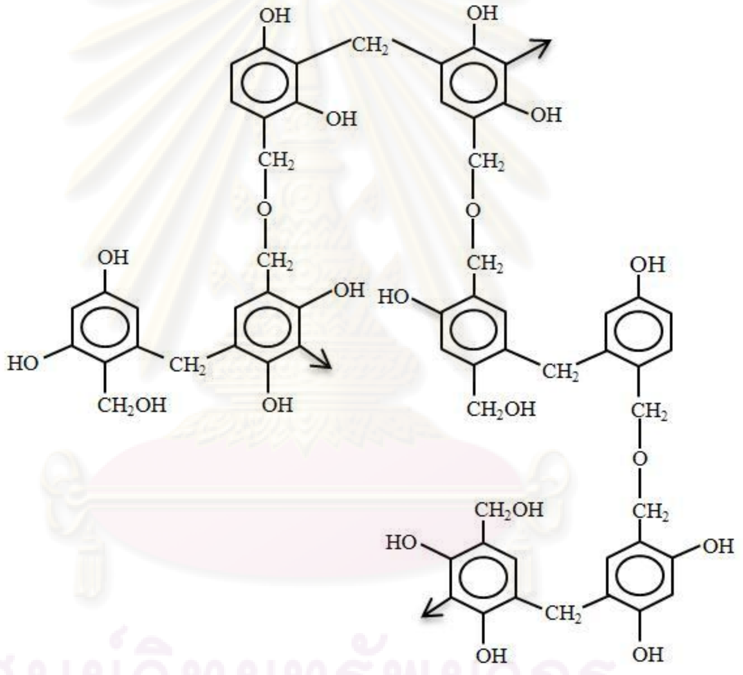


(a) Addition Reaction



Condensation product

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Figure 2.3 Schematic diagram of the sol-gel polycondensation of a RF solution (a) Addition Reaction, (b) Condensation Reaction [24].

Cluster **Colloidal particles** **RF hydrogel**

(b) Condensation Reaction

Figure 2.3 (Continued)

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Properties of RF-gel depend on various synthesis parameters such as R/F ratio, R/C ratio, aging time, temperature and density of solution. Many researchers have explained about these effects. For examples, Shaheen and coworkers suggested that increasing the density of the reactants in the initial solution caused a decrease in the surface area and total pore volume of RF carbon xerogel. Furthermore, the addition of these metal-oxide increases the meso- and macropore volumes [25]. Mulik and coworker various R/F mol ratio (from 1:2 to 1:10) and aging time (at 0, 1, 5 days) for synthesized RF-aerogel which R/F 1:2 had high particle diameter (13.8 nm) at 1 day of aging time. And high surface area was 512 m^2/g at 5 days of aging time. Therefore aging time and R/F ratio was effect to pore structure and surface area of product [26]. Job and coworkers used sodium carbonate as catalyst for polycondensation of resorcinol with formaldehyde and found the pore size tended to decrease when the temperature increased, especially when R/C ratio was high [27]. On the oyher hand, Brandt and coworkers found that acetic acid and base catalyzed carbon aerogels exhibited almost the same properties when R/C ratio was greater than 1000 [28].

2.2.3 Carbon composite and template

TiO_2 was synthesized by many methods that composite carbon and using of template were interested in this research.The research reported that synthesized Carbon composite. For example, Maldonado and coworker (2000) prepared TiO_2/Carbon composites (aerogels and xerogels) to obtain a material with a well developed meso- and macroporosity, in which well dispersed fine TiO_2 particles were located inside the pores. The composite aerogel with the lower TiO_2 content (30%) and its carbonized derivatives had the more developed meso- and macroporosity, indicative of the importance of both the supercritical drying process of these materials and of the TiO_2 content. The composite aerogel carbonized at 500 ^{o}C had the highest activity of propene production and therefore, the highest surface acidity [29]. And many research reported that synthesis of carbon material had been use template. These templates were promoted the property of product. Lukens and Stucky reported the synthesis of Polystyrene/ RF mesocomposites and their pyrolysis to yield mesoporous carbon. The pyrolyzed pellets have large mesopore volumes and considerable microporosity [30]. The template had many types that one of type was using of RF gel template. Example, Tao and coworker reported that zeolite A with mesoporous channels (meso-NaA) could be synthesized by using resorcinol-formaldehyde (RF) aerogels as templates. The surface area of meso-NaA was 472 m^2/g that RF aerogels have predominant mesopores (889 m^2/g). Accordingly, RF aerogels could supply mesoporous structures suitable for the template synthesis [31]. In this study, we interested in RF template for fabrication of titania powder. Du and coworker fabricated titania bead by using different sized agarose beads as templates. The average diameter of titania beads were 15 mm. The pore structure of the titania beads may come from two sources: one was the pore left by the template upon calcinations and the other was the pore accumulated by titania nanocrystals [32]. However, this research was use agarose gel that was type of polymer and use for bioengineering. And then research report the fabrication of titanium dioxide from resorcinol-formaldehyde template. Wang and coworker reported on the first preparation of the TiO_2-carbon composites by mixing a TiO_2 sol with the semi-cured resorcinol and formaldehyde gel. The RF polymers were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using an initial R:F molar ratio 1:2. Deionized water (W) and titanium isoproxide (T) using was 1:170, n-Hexadecyltrimethy-lammonium bromide (CTAB) and Na_2CO_3 were used as surfactant and the basic catalyst. Then, the mixture was dried to 85 ^{o}C and pyrolysis in an inert atmosphere. The TiO_2 contents of the composites were 6.4, 12.2, 17.7, 34.1, 50.0, 54.7%, respectively. The composites with a low TiO_2 content had the similar pore size distribution (PSD) and crystallographic structure to that of the carbon derived from the RF polymer, but the high content TiO_2 in the composites effectively resulted in an increase in mesoporosity and a crystallographic structure of dominant rutile TiO_2 in the TiO_2-carbon nanocomposites. The surface of high content was 542.58 m^2/g for microspores [33]. This thesis was different my work that the surface area of their research would be from carbon. Because of that experiment of pyrolysis would come to residue carbon while my work

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calcined in a box furnace. Therefore the surface area of my work would be from titaniaum dioxide product.

2.3 Drying of gel

As previously mentioned, the structure of hydrogels is affected by the amounts of reactants, catalyst and diluents used in sol-gel polycondensation, gelling temperature, and aging condition. If the solvent is removed from the structure of hydrogels without stress, the structure of hydrogels is maintained [34]. Consequently highly porous dried gels can be obtained. In general, several drying techniques have been applied.

2.3.1 Supercritical drying

Solvent can be removed from RF hydrogel under CO_2 supercritical conditions. Supercritical carbon dioxide (CO_2) can replace water in the gel structure, resulting in what is called RF aerogel. Since water is poorly soluble in CO_2, skeletons of the gel are preserved and highly porous organic gels can be obtained [35].

2.3.2 Freeze drying

During freeze drying, the solvent inside the pores is removed by sublimation after the solvent is pre-frozen. Such removal of the solvent can avoid capillary force occurring in the conventional drying, which may cause the shrinkage of pore structure [35].

2.3.3 Air drying

This conventional technique uses atmospheric convective drying to remove the solvent, without any preliminary treatment. Indeed, when synthesis conditions are adequate, the mechanical strength of the gel network is high enough to withstand capillary pressure, avoiding the collapse of the structure. By drying the gel by means of low temperature treatment (25-100 ^{o}C), it is possible to obtain porous solid matrices called RF xerogels [36, 37].

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CHAPTER III

EXPERIMANTAL

3.1 Chenical agents

The list of chemical agents used in this research are shown in Table 3.1, while their chemical structures are shown in Table 3.2

Table 3.1 List of chemical agents used in the research.

Chemical agents	Using for	Manufacturer/Grade
1. Resorcinol ($C_6H_4(OH)_2$)	Synthesis of Resorcinol-Formaldehyde (RF) solution	Fluka 99.8%
2. Formaldehyde (HCHO)	Synthesis of Resorcinol-Formaldehyde (RF) solution	Ajax Fine Chemical 37%
3. Acetic acid (CH_3COOH)	Synthesis of Resorcinol-Formaldehyde (RF) solution	QRëc / grade AR
4. Ethyl alcohol (C_2H_5OH)	Synthesis of Resorcinol-Formaldehyde (RF) and titania solution	Baker Analyzed 98%
5. Titanium tetraisopropoxide (TTIP)	Synthesis of titania	Sigma-Aldich Chemical 97%
6. Hydrochloric acid (HCl)	Synthesis of titania	Baker Analyzed 36.5-38.0%

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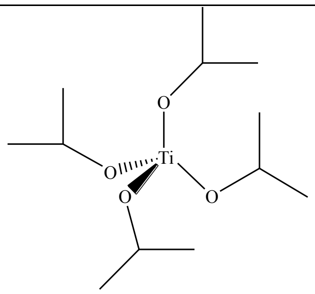
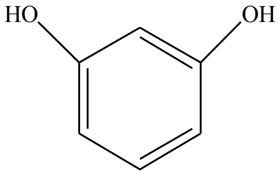
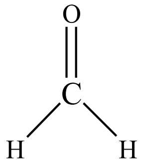
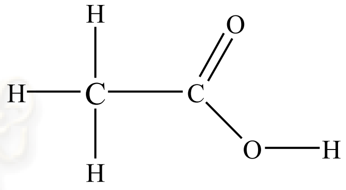
Table 3.2 Chemicals structure of reagents used in this research.

Chemical name	Designation	Chemical structure
Titanium tetraisopropoxide	TTIP	
Resorcinol	R	
Formaldehyde	F	
Acetic acid	Ac	
Hydrocloric acid	C	H—Cl

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3.2 Preparation of RF/TiO$_2$ gel

RF solution was firstly prepared by dissolving resorcinol (99.8%, Fluka) in ethanol under magnetic stirring, with the addition acetic acid. After dissolution, formaldehyde solution (37% in water, stabilized by 10-15% wt. methanol, Ajax Finechem) that was previously mixed with titanium tetraisopropoxide (TTIP 97%, Aldrich) in ethanol was added to the solution and catalyst as hydrochloric acid. The molar ratio of TTIP-to-ethanol-to-hydrochloric acid was 1:9:0.1. The mixture was stirred for another 15 min at room temperature. Then, it was poured into a cup and aged at room temperature for 36 hours in a closed system to obtain RF/TiO$_2$ hydrogels. After that, the obtained gel was dried for 3 hours at 80°C. The dried sample was calcined at 500°C for 4 hours in a box furnace to remove residual organic compound as well as RF gel from titania.

3.3 Characterization of the products

The obtain products were characterized by using various techniques, as following:

3.3.1 X-ray Diffraction Analysis (XRD)

The crystalline phase of TiO$_2$ nanoparticles were identified by a Siemens D5000 X-ray diffractometer using Ni-filtered CuKα radiation. The measurements were carried out in the 2θ range of 20-80 degree at the scan step of 0.04 degree.

3.3.2 Scanning Electron Microscopy (SEM)

Morphology of the obtained products was studied using scanning electron microscope (SEM) model JSM-6400 at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University. Size of the products was then measured from the micrographs, using image processing software (JEOL Semafore 5.0).

3.3.3 Brunauer-Emmett-Teller (BET)and Barrett-Joyner-Halenda method (BJH)

The surface area, pore volume and pore size were measured by an BELSORP-mini adsorption analyzer at the Center of Excellence on Particle Technology, Chulalongkorn University. The operating conditions are as follows:

Sample weight	~ 0.1- 0.2 g.
Degas temperature	200°C
Vacuum pressure	< 10 mmHg

3.3.4 Fourier Transform Infrared Spectroscopy (FT-IR)

Function groups of samples were identified by using Fourier transform infrared spectrophotometer (FT-IR) Model Spectrum One (Perkin Elmer). Infrared spectra were recorded between wavenumber of 400 and 4000 cm^{-1}.

3.3.5 Thermogravimetric Analysis (TGA)

The residual carbon content and thermal behavior of the samples were determined by using thermogravimetric analysis on a SDT Q600 instrument. The analysis was performed from temperature of 50 to 1,000 °C under a heating rate of 10 °C/min in 100 ml/min of oxygen.

3.3.6 Transmission electron microscope (TEM)

The morphology of an individual grain in the sample was observed on a JEOL JEM-2100 Analytical Transmission Electron Microscope, operated at 80-200 keV at Scientific and Technological Research Equipment Centre Foundation, Thailand. The crystallographic information was also obtained from the selected area electron diffraction (SAED) analysis performed in the same instrument.

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CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, titania powders synthesized by an assistant of RF-gel are investigated in detail. General characteristics of the products, effects of RF gel composition on properties of the products synthesized using TTIP or titania sol as the source for titania, as well as effect of aging time of both RF gel and titania sol, are presented.

4.1 General characteristics of the products

For the titania product synthesized by adding the titania precursor (i.e, TTIP solution) into RF gel that was prepared using R/F molar ratio of 0.5 and then calcined at 500°C, the BET analysis revealed type IV adsorption isotherm (see Figure 1a), which suggests the presence of mesopores within the product. By comparing with the adsorption isotherm obtained from the calcined titania sol (i.e., the product formed without the assistance of RF gel), it is clearly indicated that the use of RF gel could introduce meso-porosity into titania. Generally, RF gel that is dried in an oven does not have porosity because of wall collapsing. For the product contains RF gel and TTIP, when RF gel reacts with TTIP, the network is form that the RF network and titania network. Then, when carbon is removed by calcination, the final product becomes porous titania powder. The specific surface area of titania formed using RF gel template, in this case, was found to be 33 m^2/g, which is significantly higher than that of the calcined titania sol, as shown in Table 1.

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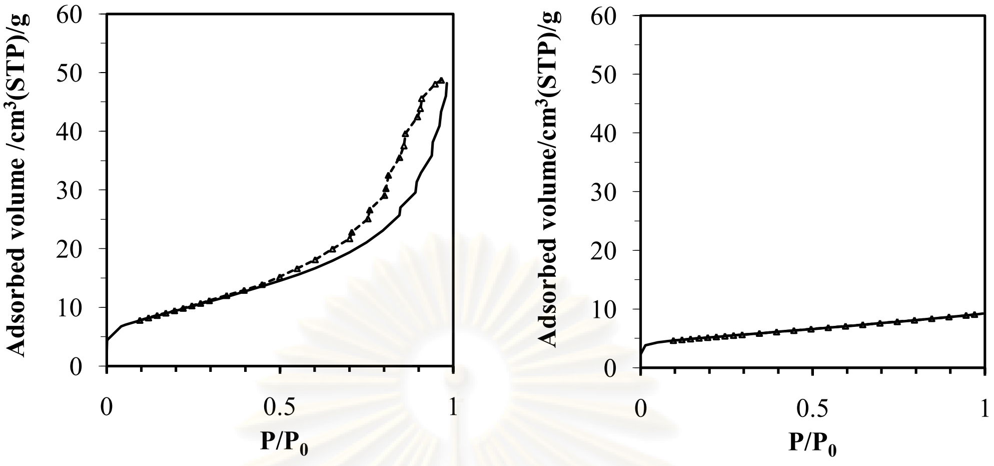

(a) (b)

Figure 4.1 N_2 adsorption/desorption isotherm of titania synthesized with (a) and without (b) the assistance of RF gel.

Table 4.1 Surface area and average pore diameter of products formed with and without the use of RF gel.

Condition	Surface area (m^2/g)	Average pore diameter(nm)
TiO_2	18.5	3.1
RF/TiO_2	33.5	8.9

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Representative XRD pattern of titania products is shown in Figure 4.2. The broad diffraction line of the sample is relating to the nanocrystalline anatase phase and rutile phase.

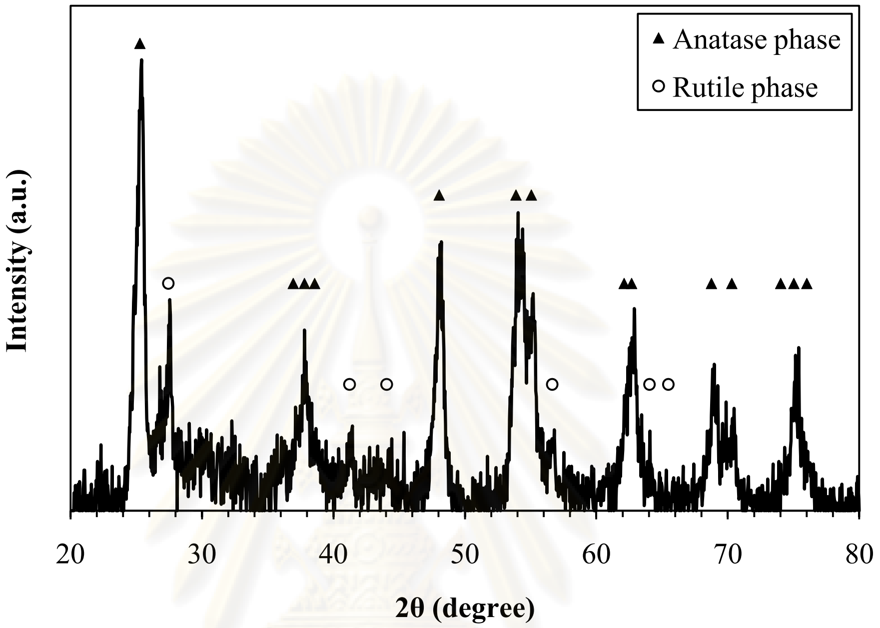

Figure 4.2 The representative XRD pattern of titania product.

Figure 4.3 shows FTIR spectra of the RF/TiO_2 composite prior to the calcination, comparing with those of dried titania sol and neat RF gel. It should be noted that the RF gel employed was aged for 36 h and the R/Ti molar ratio in the RF/TiO_2 composite was 0.35. All samples show the absorption bands at 1375, 1090, 1045, 880 and 800 cm^{-1}, which are results from residual ethanol within the samples [38]. The RF/TiO_2 composite shows similar IR absorption bands as that of the neat RF gel, e.g., at wavenumber of 1612, 1473 and 1443 cm^{-1} for aromatic ether bonds; at 1508 cm^{-1} for C=C in aromatic rings; and at 1218 and 1220 cm^{-1} for C-C-O asymmetric stretching [39]. However, the intensity of some bands are changed. Moreover, besides the broad band at 500-600 cm^{-1} corresponding to Ti-O-Ti bonds, additional signals such as the bands at 1070, 1040, 930 and 880 cm^{-1}, which are corresponding to titanium ethoxide functional groups [38], are also observed. These results suggest the interaction between TTIP and RF network. The fact that the signals for aromatic ether bonds at 1473 and 1443 cm^{-1} [39] are significantly increased also suggest the increased network of resorcinol/formaldehyde assisted by TTIP. When RF gel reacts with TTIP, the interaction results in Ti-O-C bonding. Then, they form into gel. After carbon is removed by calcination in a box furnace, that product becomes TiO_2 powder. The Ti-O-C bond decomposes and forms into Ti-O-Ti bond. After calcination, titania powder shows high signal of Ti-O-Ti and O-Ti-O bonds while signal of Ti-O-C is lost because carbon was removed at 500 °C in the box furnace [38].

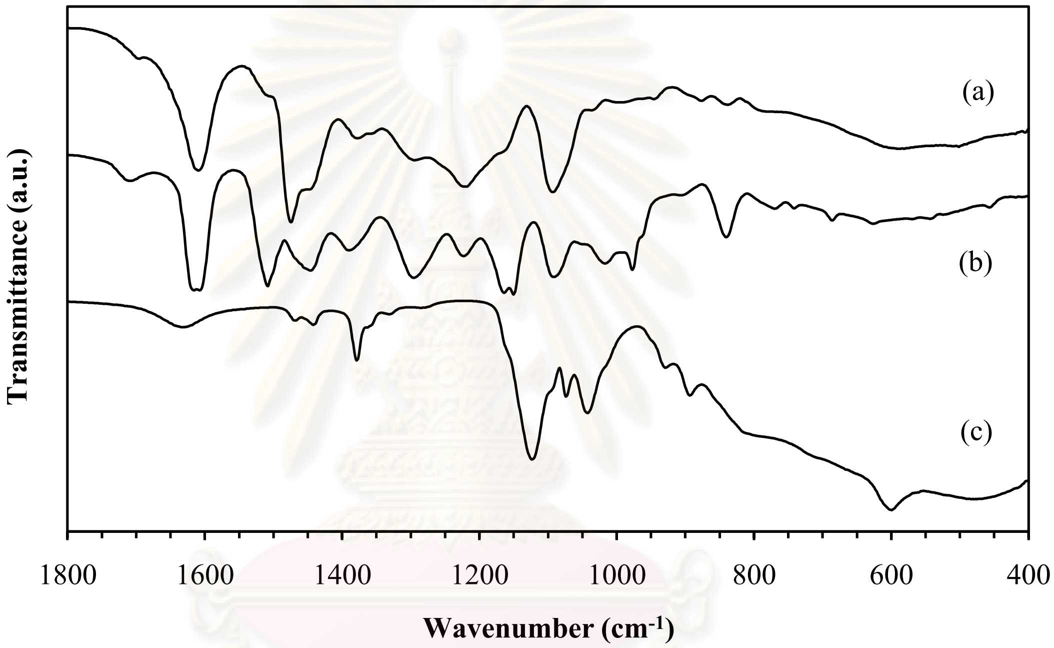

Figure 4.3 FTIR spectra of titania sol (a), neat RF gel (b) and RF/TiO_2 composite before being calcined (c).

4.2 Synthesis of porous titania using TTIP as souce: Effect of RF composition

In the preliminary experiments, titania powders were prepared assisted by RF gel process. TTIP was used as the precursor for titania. Effects of RF composition toward the formation of titania porous structure were investigated by varying R/F ratio (from 0.25, 0.5, 1.0, 1.5 and 2.0) and R/C ratio (from 0.18, 0.3, 1.3, 2 and 5), respectively. All products were calcined at 500 ^oC in a box furnace. The obtain product was TiO_2 powder without residual carbon as confirm by TGA analysis (Appendix D). The calcinations temperature of 500 ^oC is enough to remove carbon from TiO_2 powder.

The surface area and pore diameter of titania product samples were determined. Results for the effects of R/F ratio are shown in Figure 4.5 and 4.6. It can be seen that mesopore surface area of the samples increases with the increase in the R/F ratio while the average pore diameter increases for high R/F ratio. Too much of formaldehyde is used in the sol-gel polycondensation of RF gel can induce collapse of mesopore structure. The surface area of the sample changes slightly and irregularly with the change of R/F ratio. However, the average pore diameter of the sample increases with the increase in R/F ratio especially at high R/F ratio of 2.0. The maximum surface area is obtained when the R/F ratio is about 0.25. The maximum average pore diameter is 6 nm at the R/F ratio of 2.0. Tamon et al. reported that microporosity, micropore area (S_{mic}) and volume of micropore (V_{mic}) are independent of R/F ratio, while total specific surface area (S_{BET}) and volume of mesopore (V_{meso}) are decreased with the increasing R/F ratio [40].

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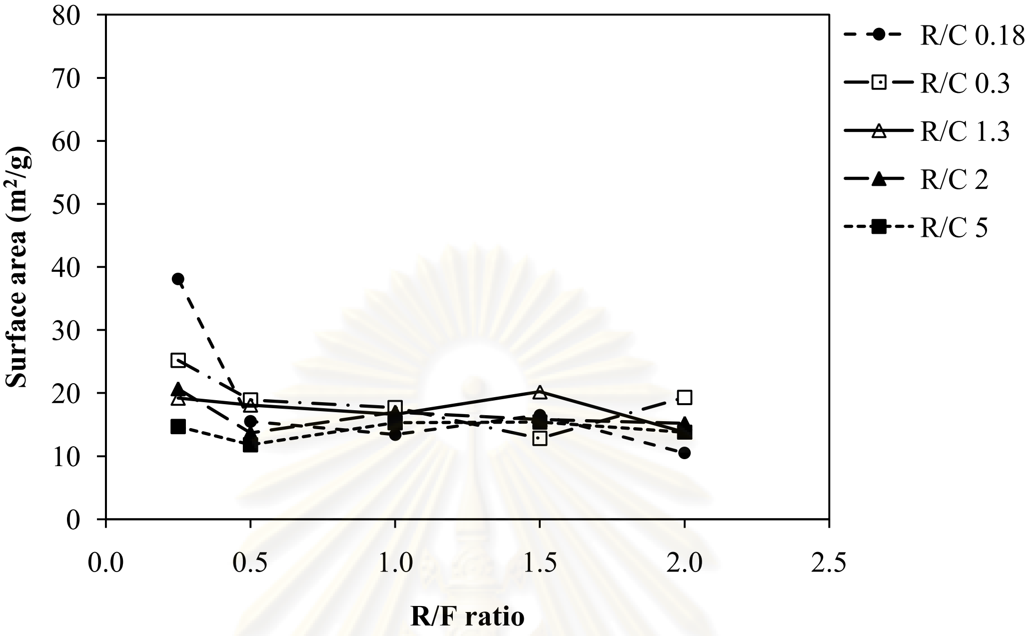

Figure 4.5 Relationship between R/F ratio within the RF gel and BET surface area of titania product prepared using different values of R/C ratio.

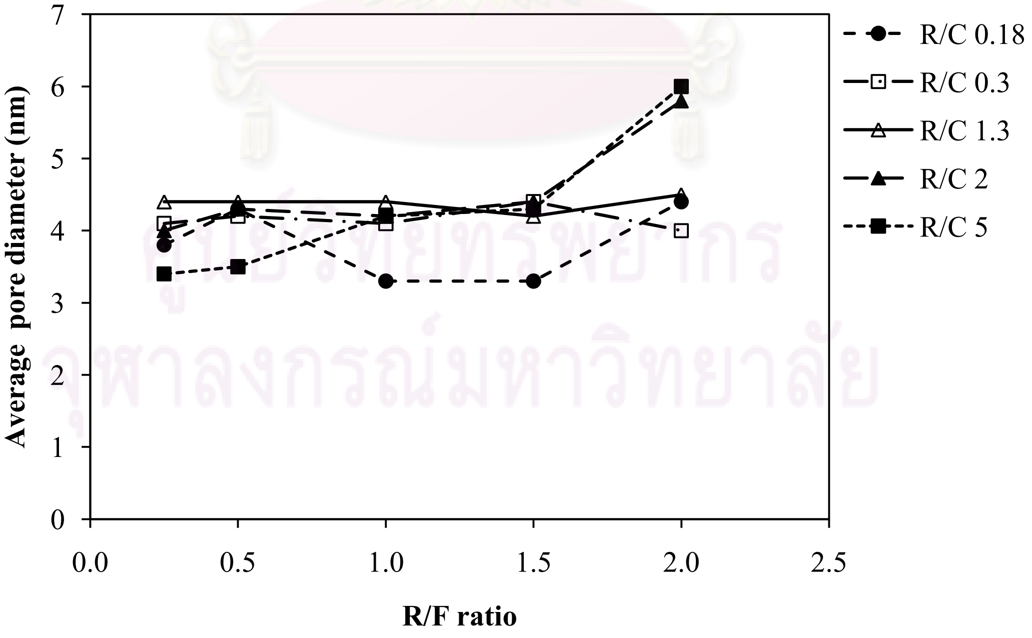

Figure 4.6 Relationship between R/F ratio within the RF gel and average pore diameter of titania product prepared using different values of R/C ratio.

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Figure 4.7 and 4.8 show the effect of R/C ratio for the preparation of RF gel on properties of the titania product. The experimental results indicate that the R/C ratio does not distinctly affect the pore structure of the samples since the surface areas of the products are about 15-20 m^2/g for all samples. In another word, acetic acid does not affect porosity of the product.

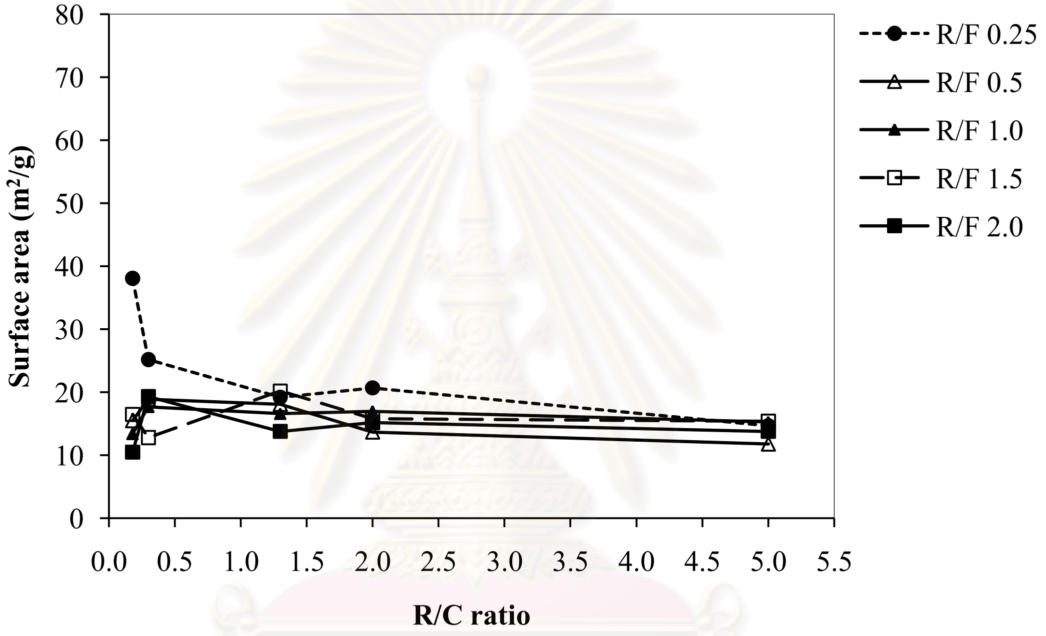

Figure 4.7 Relationship between R/C ratio within the RF gel and BET surface area of titania product prepared using different values of R/F ratio.

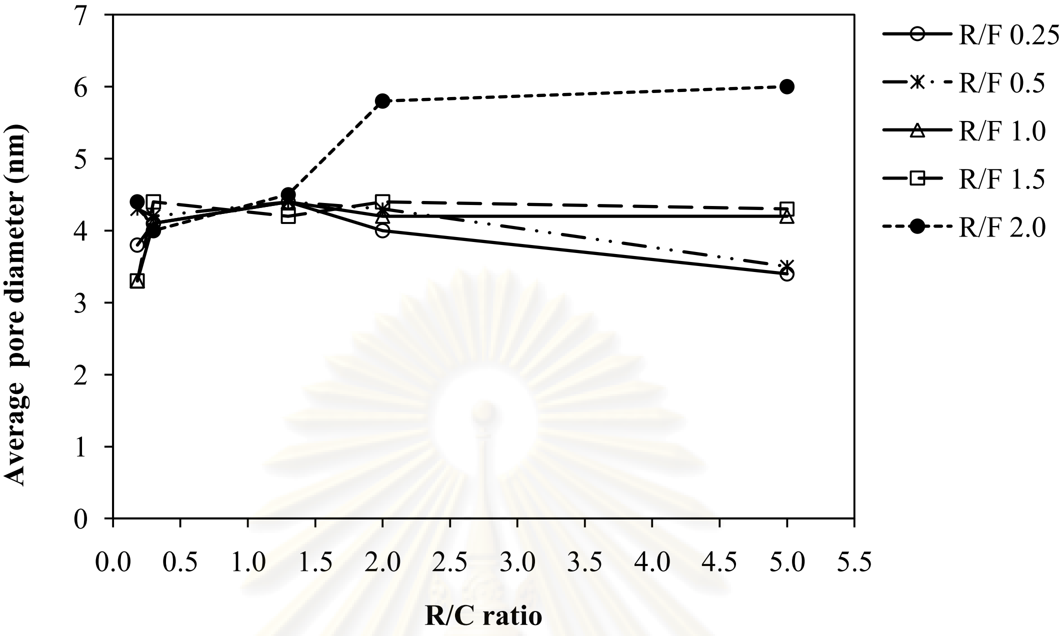

Figure 4.8 Relationship between R/C ratio within the RF gel and average pore diameter of titania product prepared using different values of R/F ratio.

Although the interaction between TTIP and RF gel has been presented by the FTIR spectra in Figure 4.3, it should be noted that the reaction can be witnessed visually. The RF mixture changes its color right after it is mixed with TTIP solution. In some cases, the reaction takes place so rapidly that it causes instantaneous solidification of the gel. This TTIP-RF interaction was investigated further by examining intensities of signal in FTIR spectra. However, in order to eliminate the effect of sample amount that also affects the intensity of the signals, the signal ratio, which is intensity of the interested FTIR band divided by that of the reference signal within the same sample was employed. In this study, the signal from aromatic rings was used as the reference. Moreover, the Fourier Self-Deconvolution (FSD) algorithm was performed on the obtained FTIR spectra to get more defined band.

Figure 4.9 to 4.13 show signal ratios of RF/titania composite prepared using R/C ratio of 0.18 to 5. The R/F ratio is also varied in the range of 0.25 to 2.0. When the R/F ratio is increased, the signal for methylene bridge (i.e., at wave number of 1450 cm^{-1}) increases because RF solution forms cross-linking network. Methylene ether bridge (i.e., at wave number of 1220 cm^{-1}) is also form to network but amount of network is less than methylene bridge that appears for all R/F ratio. At higher R/F ratios (e.g., 1.5 and 2.0) and lower R/C ratios (e.g., 0.18, 0.3 and 1.3), it is found that signal of methylene ether bridge is decreased. It means that there is a few of formaldehyde in the solution so that it is not enough to form methylene ether bridge and amount of acetic acid is much more active with resorcinol. Some of the results showed that the signal for O-Ti-O bonding (or bending vibration of O-Ti-O appearing at 600 cm^{-1}) is decreased because it would form into Ti-O-Ti (wavenumber of 500 cm^{-1}) or Ti-O-C (wavenumber of 1090 cm^{-1}) bondings. The Ti-O-Ti bond is present in titanium oxo-polymers that is a part of network of TiO_2 sol. The Ti-O-C bond confirms the reaction between RF gel and TiO_2 sol. Increased signal from Ti-O-C bond indicates high network between RF gel and TiO_2 sol. In addition, increasing of the Ti-O-C signal is derived from excess resorcinol in the solution that reacts with TTIP solution at high R/F ratio. The signals for Ti-O-C, O-Ti-O and methylene ether bridge remain roughly unaffect by the R/F ratio. This means that as the R/F ratio is increased, network of RF gel increases.

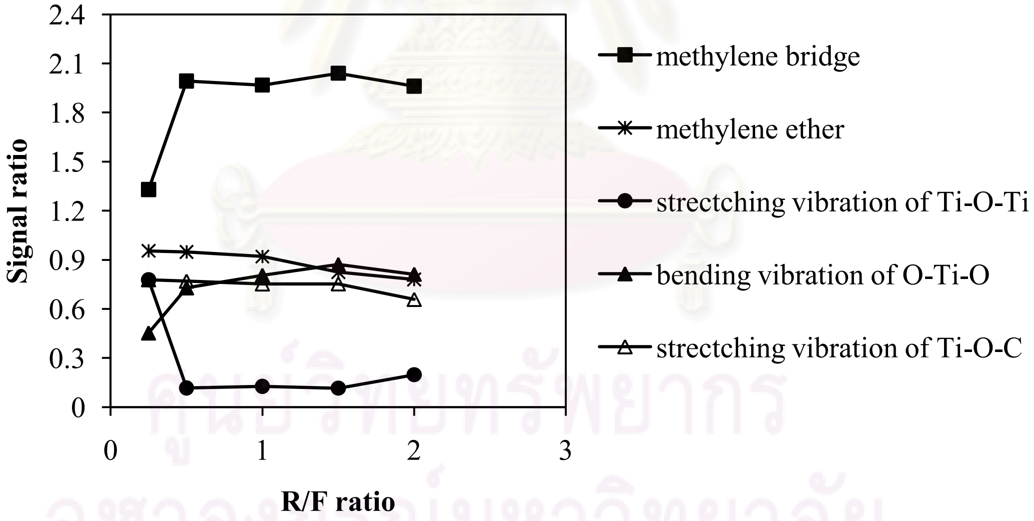

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Figure 4.9 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/C ratio of 0.18. For all signals, signal from aromatic ring was used as the reference signal.

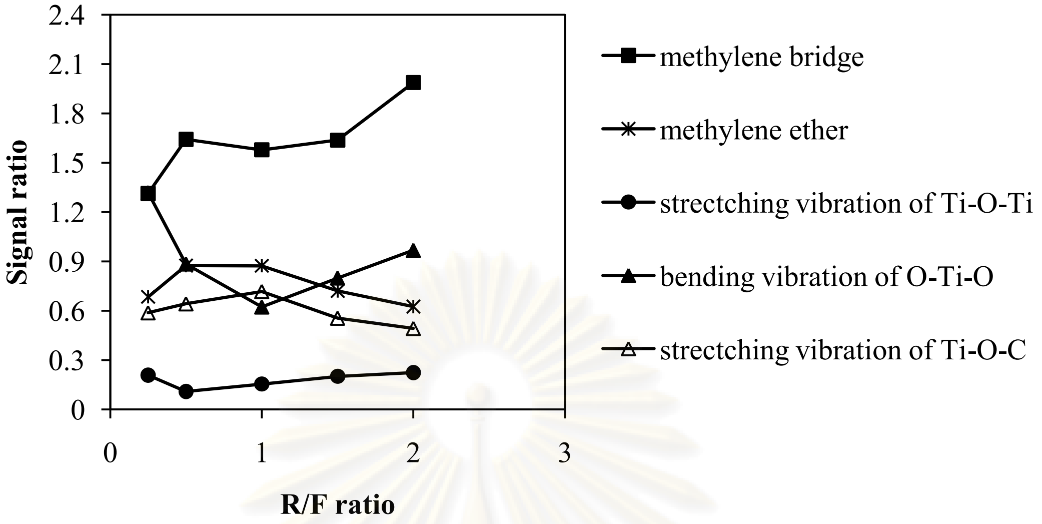

Figure 4.10 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/C ratio of 0.3. For all signals, signal from aromatic ring was used as the reference signal.

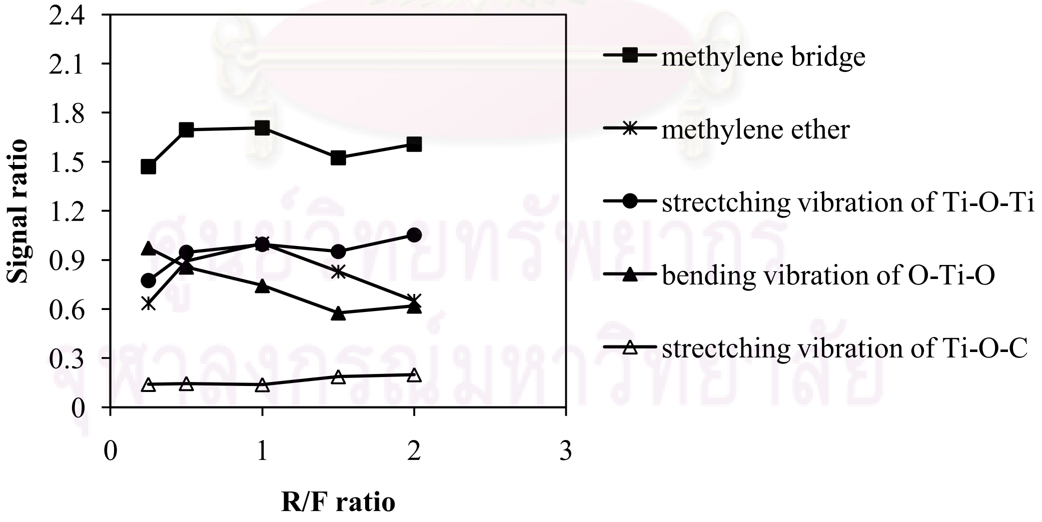

Figure 4.11 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/C ratio of 1.3. For all signals, signal from aromatic ring was used as the reference signal.

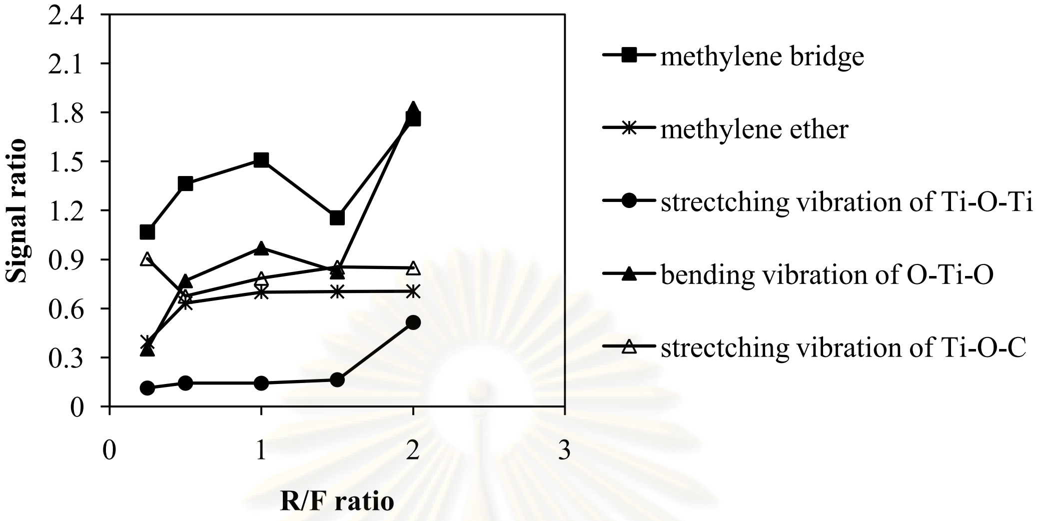

Figure 4.12 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/C ratio of 2.0. For all signals, signal from aromatic ring was used as the reference signal.

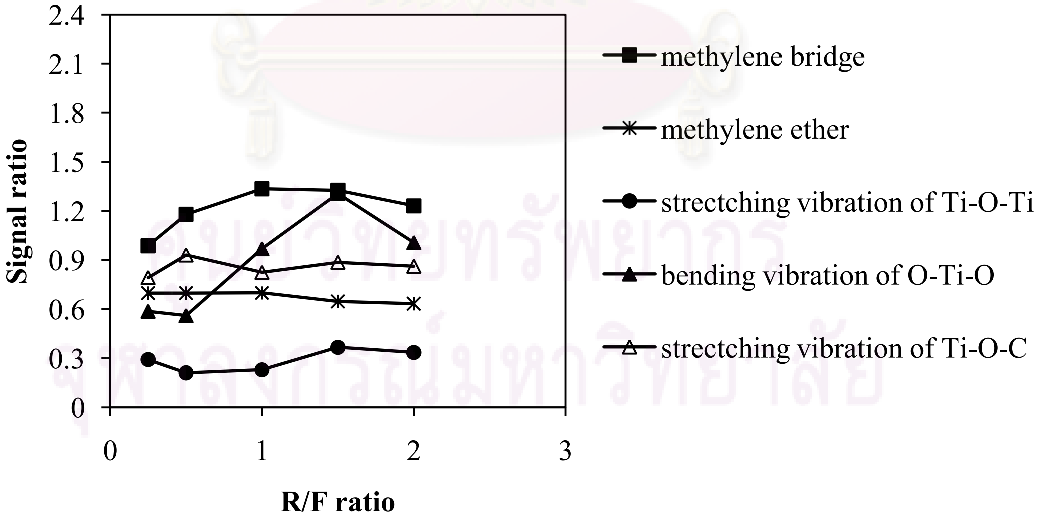

Figure 4.13 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/C ratio of 5.0. For all signals, signal from aromatic ring was used as the reference signal.

SEM micrographs of titania products obtained after calcination of RF/TiO_2 composites are shown in Figure 4.14. The composites were prepared with various R/F ratios. It could be seen that the particles were, in fact, aggregates of nanosized particles.

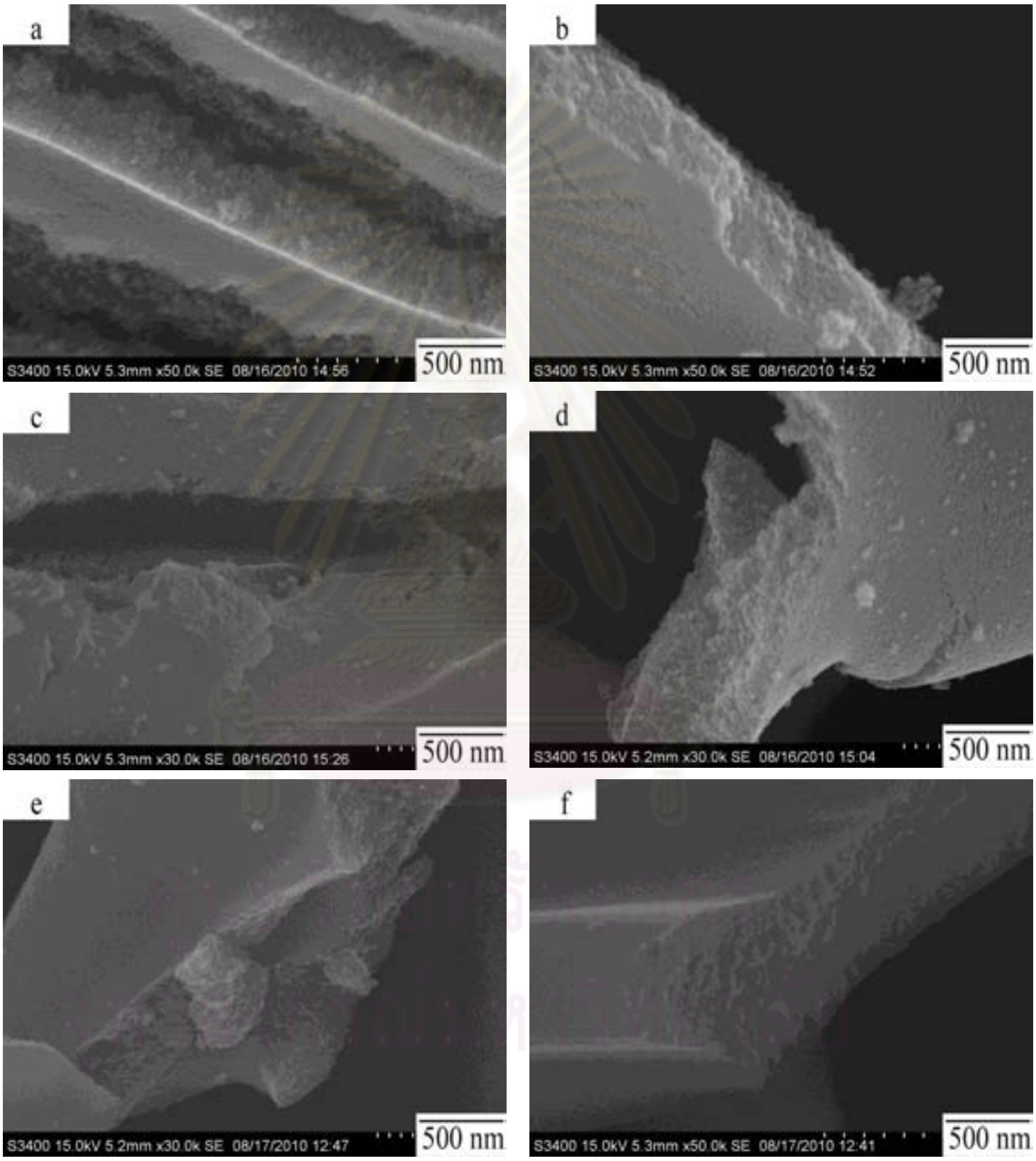

Figure 4.14 SEM images of titania products obtained from the calcination of RF/TiO_2 composites that were prepared using R/F ratio of 0.5 (a-b), 1.0 (c-d) and 1.5 (e-f).

4.3 Synthesis of porous using titania sol as source

As motional earlier, TTIP often interacts with RF gel instantaneously, resulting in rapid solidification of the gel, which also prevents addition of titania precursor in large quantity into RF gel. Therefore, in this section, the reactivity of the titania precursor was lowered by converting the precursor into preformed titania sol. Unless mentioned otherwise, titania sol was formed by aging TTIP solution at room temperature for 6 h prior to the addition into RF gel. Effects of various parameters on porous structure of titania are presented.

TiO_2 sol was form by hydrolysis of TTIP, in which active molecules can interact in condensation process. After that, clusters were formed and cross-linking into network that is called sol and gel respectively. Byproduct of this process is water. Formation of TiO_2 sol as colloidal suspension in the solution can be visually tested by Tyndall effect.

4.3.1 Effect of RF composition

In this section, RF solution was prepared using the R/F ratio of 0.25, 0.5, 1.0, 1.5 and 2.0 and using the R/C ratio of 0.18, 0.3, 1.3, 2 and 5, respectively. Then, the titania sol was added to the mixture in the amount corresponding to the R/TiO_2 ratio of 0.07. The mixture was stirred for 15 min and aged at room temperature for 36 hours.

BET surface area and average pore diameter of titania products prepared with various values of R/F ratio are shown in Figure 4.15 and 4.17, respectively. The representations corresponding to R/C ratio are shown in Figure 4.16, 4.18.

The experiment results from Fig. 4.15 indicate that the R/F ratio does not distinctly affect the surface area of the product. The results are similar to those obtained when TTIP was use as precursor to synthesize the products. When the R/F ratio is increased, the surface area of the product generally decrease, except for the case when R/C ratio is 5.0. However, the surface area of the product is in range of 30-40 m^2/g. The average pore diameter is 3-4 nm corresponding mesoporous structure.

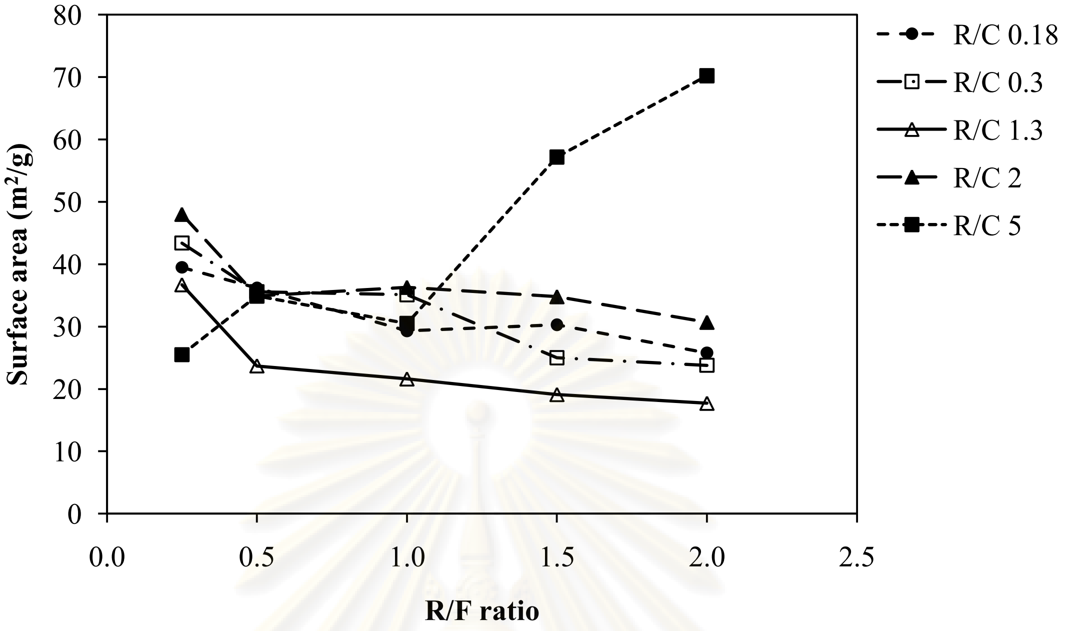

Figure 4.15 Relationship between R/F ratio within the RF gel and BET surface area of titania product prepared using different values of R/C ratio.

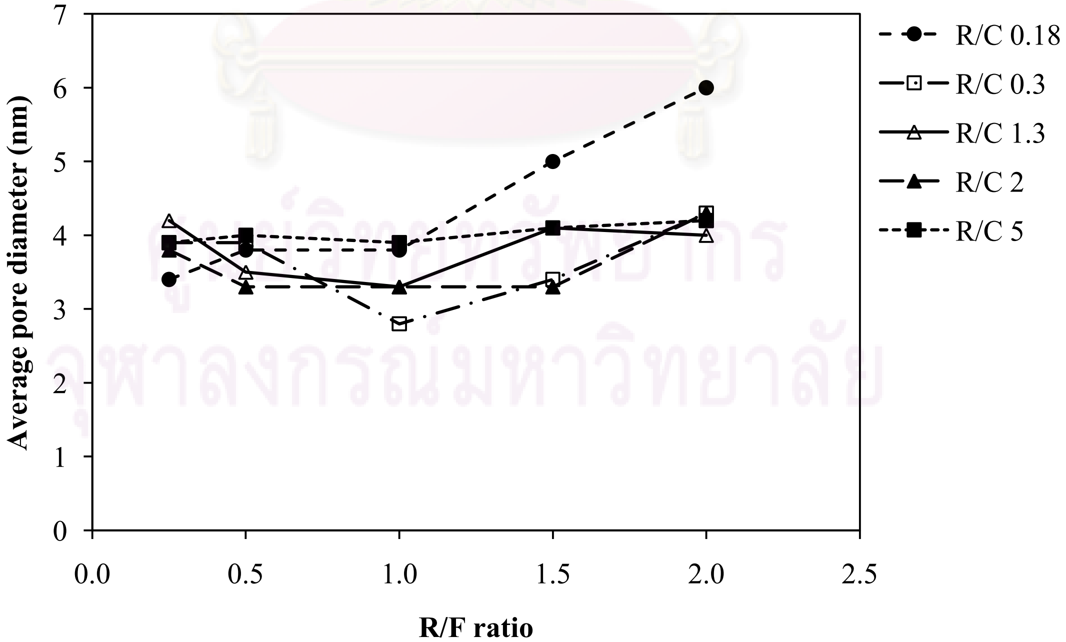

Figure 4.16 Relationship between R/F ratio within the RF gel and average pore diameter of titania product prepared using different values of R/C ratio.

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Figure 4.17 and 4.18 show relationship between the R/C ratio and BET surface area of titania product and relationship between R/C ratio and average pore diameter of titania product, respectively. The surface area becomes high when the R/C ratio is 5. Brandt et al. reported that acetic acid at low content (i.e., at R/C ratio of 5.0) behaved in the same manner as the base catalyst such as sodium carbonate [28]. However, the use of acetic acid for resorcinol-formaldehyde gel formation usually causes the surface area of the RF product to be lower than when sodium carbonate is use as catalyst. In this study, high surface area of 70 m^2/g was obtained when the highest value of the R/C ratio (i.e., 5.0) was used with the highest value of R/F ratio (i.e., 2.0). Because higher of amount acetic acid will react with excess resorcinol and cannot react with titania sol. Therefore excess resorcinol in higher R/F ratio can form network with titania sol for higher R/C ratio. The gel can easily shrink or collapse with an increase in the amount of acetic acid used, thereby causing a increase in the surface area of the products [41]. The average pore diameter is around 4 nm when the RF gel used is prepared with R/C ratio of 5.0. In general, all samples show the average pore size around 3-4 nm, which are considered to be mesoporous.

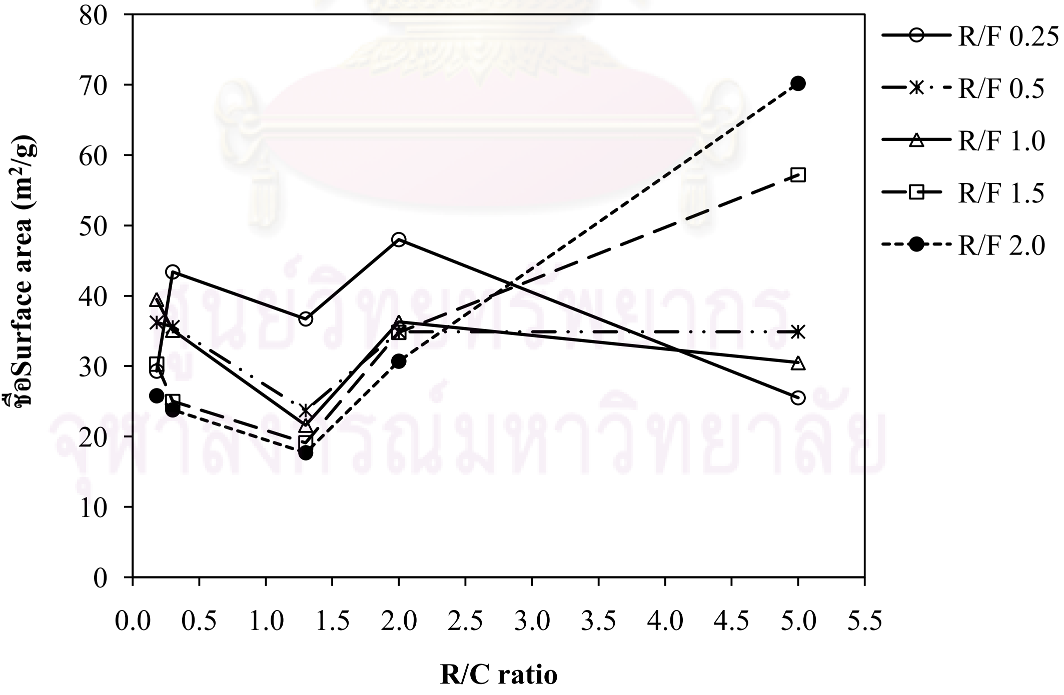

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Figure 4.17 Relationship between R/C ratio within the RF gel and BET surface area of titania product prepared using different values of R/F ratio.

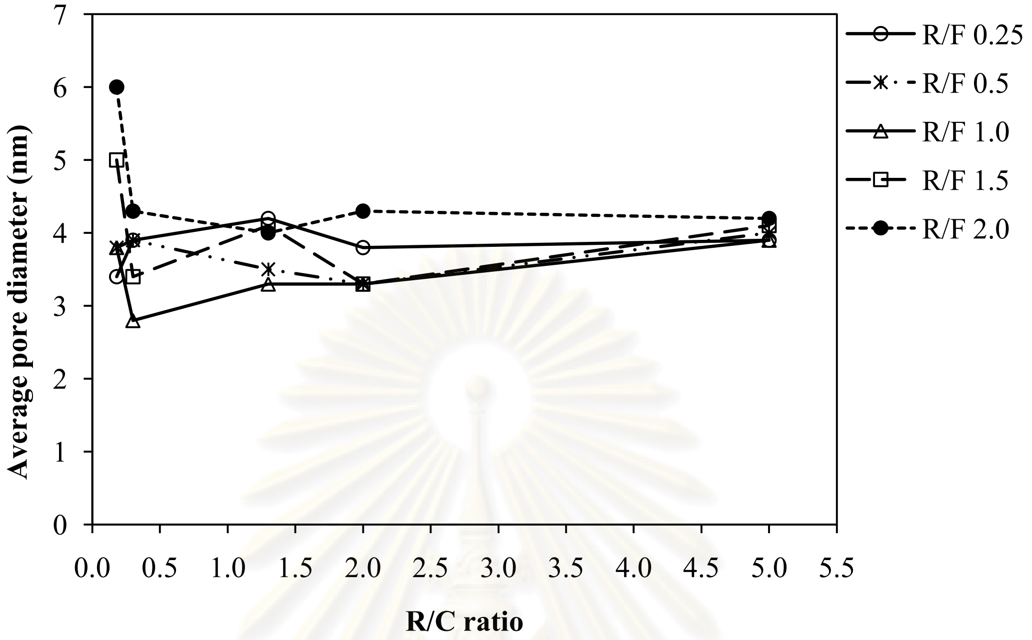

Figure 4.18 Relationship between R/C ratio within the RF gel and average pore diameter of titania product prepared using different values of R/F ratio.

Figure 4.19 to 4.23 show effects of R/C ratio and R/F ratios on the signal ratios of RF/titania composite synthesized by using TiO_2 sol in similar manner as those presented in Figure 4.9-4.13. As the R/F ratio is increased, the signal from Ti-O-C bonding increases as both of methylene and methylene ether bridges of the RF-gel are formed, which suggests that the porosity of the titania is controlled by the growth of RF-network, since the structure of RF/titania is a cross-linking network. Because Ti-O-C bonding can connect to cross-link of RF gel (see Figure 4.23) that RF gel can modify porous structure. Figure 4.23 confirm bonding of Ti-O-C increases, the increasing of surface area at R/C and R/F ratio is 5.0 and 2.0, respectively. The signal ratios of methylene bridge and methylene ether bridge are in the same trend for all of R/C ratios that means RF gel was form to network. Higher value of R/C ratio (e.g., 2 and 5) effects the methylene bridge such that more bridge is formed while the lower R/C ratios do not show significant effect because catalyst react with resorcinol so that formaldehyde cannot react with resorcinol. This effect show in both methylene and methylene ether bridge.

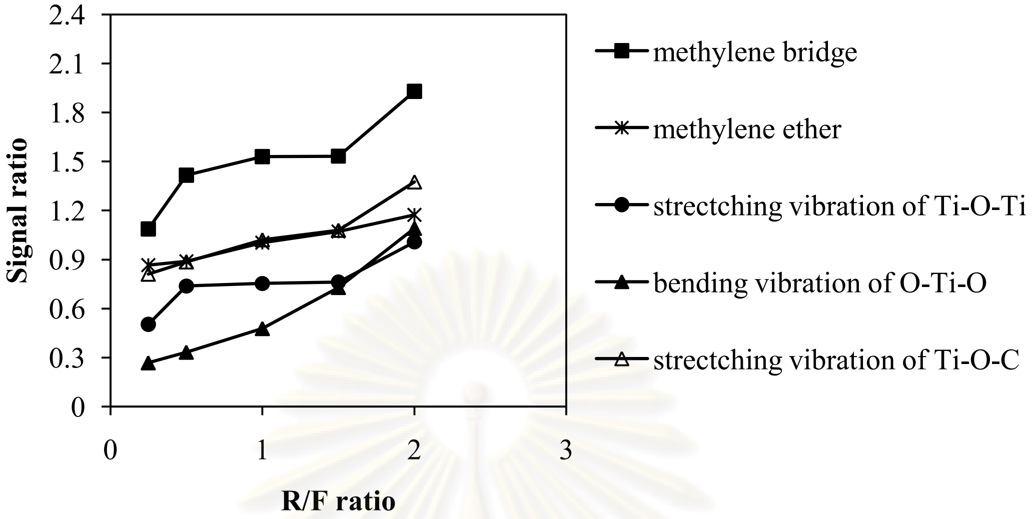

Figure 4.19 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using titania sol with R/C ratio of 0.18. For all signals, signal from aromatic ring was used as the reference signal.

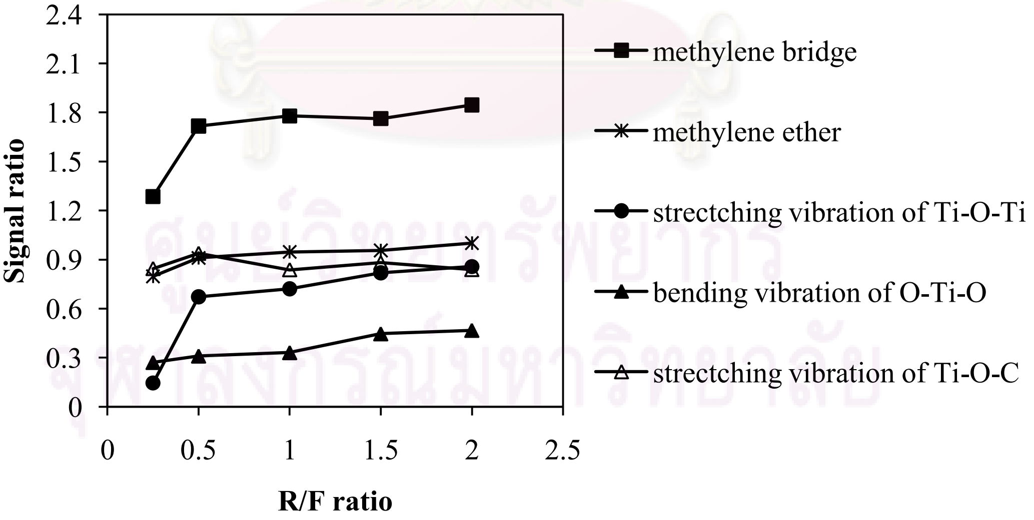

Figure 4.20 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using titania sol with R/C ratio of 0.3. For all signals, signal from aromatic ring was used as the reference signal.

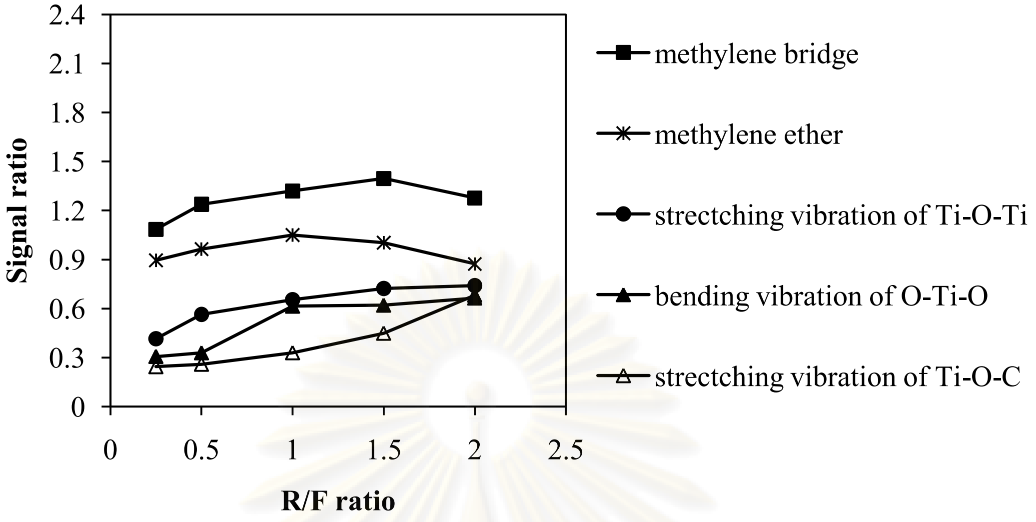

Figure 4.21 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO$_2$ composite prepared using titani a sol with R/C ratio of 1.3. For all signals, signal from aromatic ring was used as the reference signal.

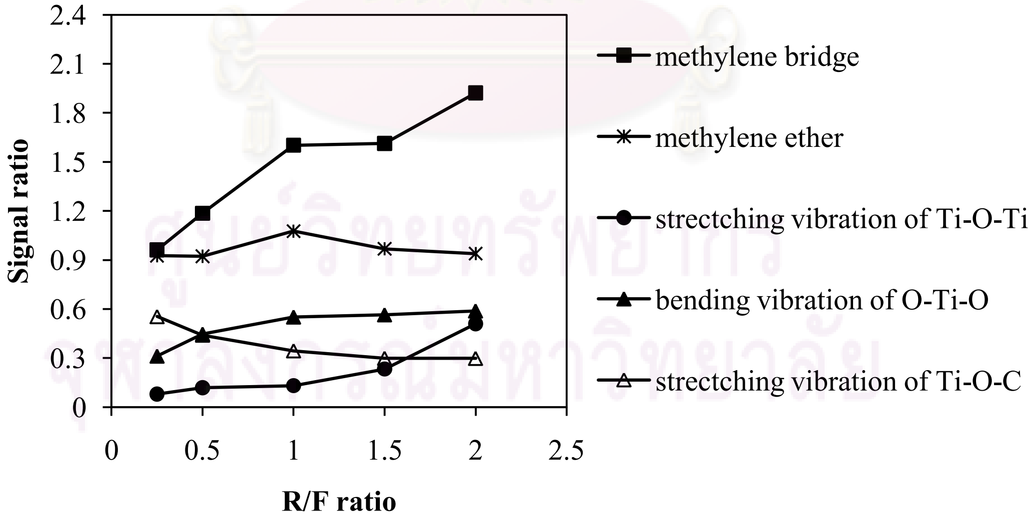

Figure 4.22 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO$_2$ composite prepared using titania sol with R/C ratio of 2.0. For all signals, signal from aromatic ring was used as the reference signal.

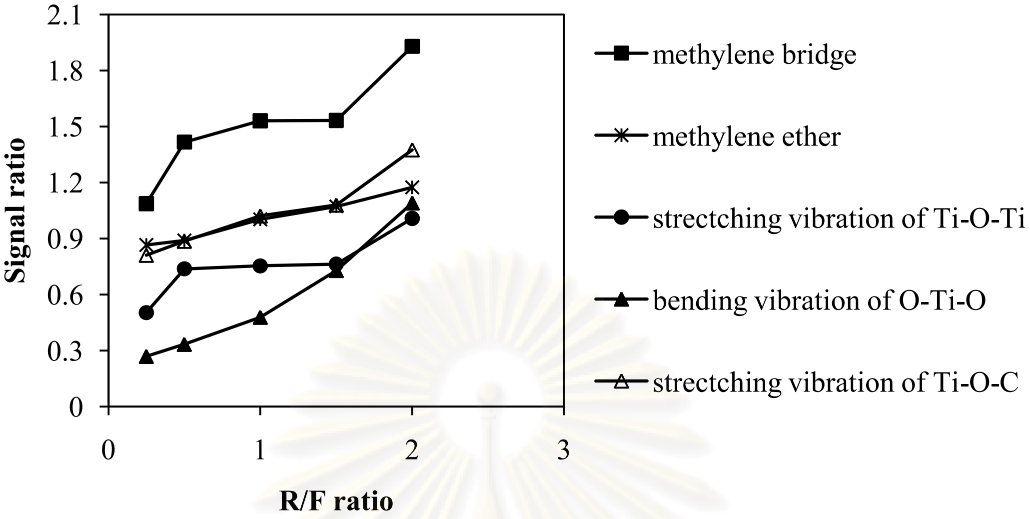

Figure 4.23 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using titania sol with R/C ratio of 5.0. For all signals, signal from aromatic ring was used as the reference signal.

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SEM micrographs of titania products obtained after calcination of RF/TiO_2 composites are shown in Figure 4.24. The composites were prepared with various R/C ratios. It could be seen that the particles were, in fact, aggregates of nanosized particles.

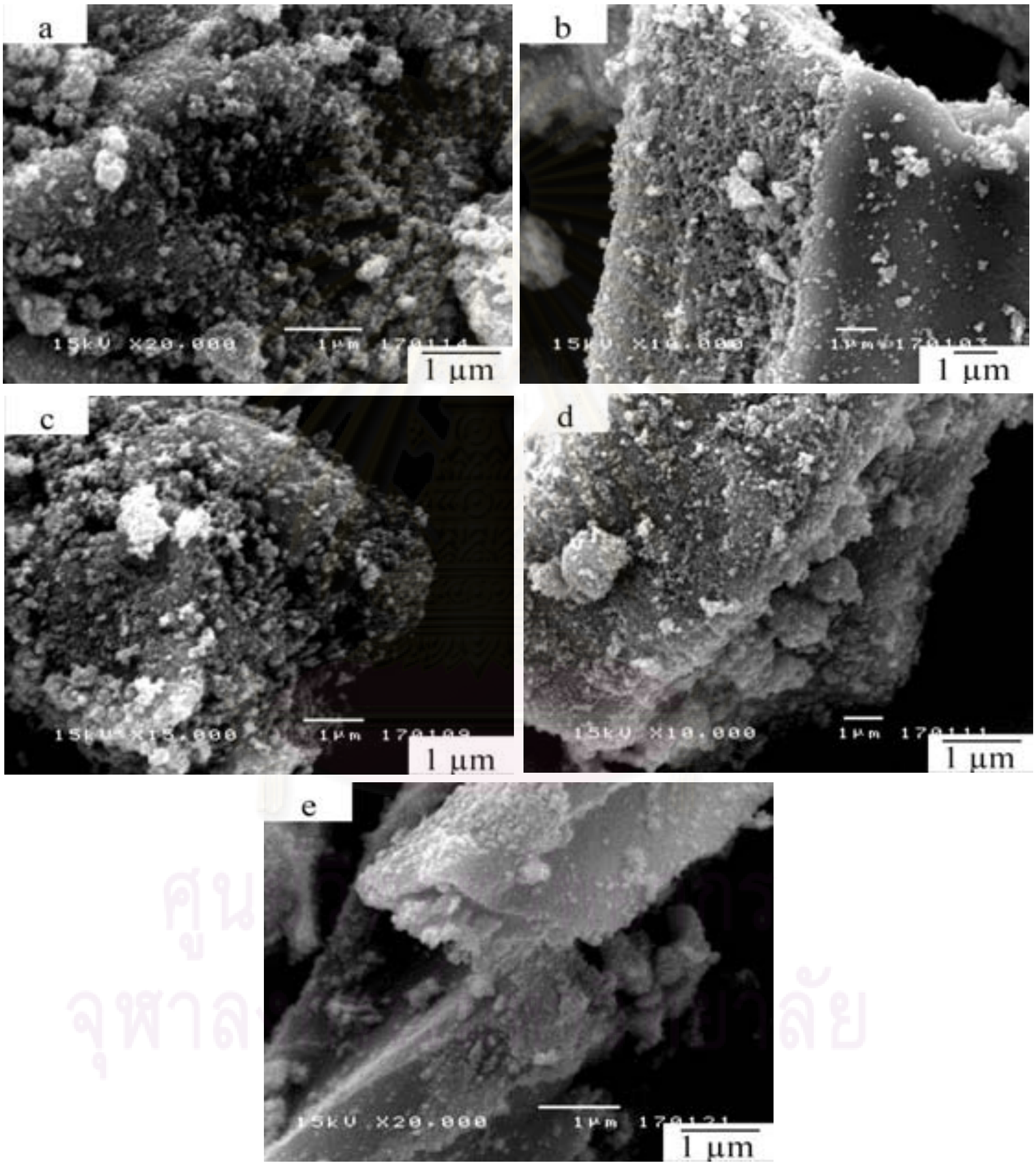

Figure 4.24 SEM micrographs of titania product after calcination. The products were prepared using RF gel and titania sol with R/F ratio of 2.0 and R/C ratio of : (a) 0.18, (b) 0.3, (c) 1.3, (d) 2.0 and (e) 5.0.

4.3.2 Effect of R/TiO_2 ratio

In this section, RF solution was prepared using various of the ratio of R/F (i.e., 0.25, 0.5, 1.0, 1.5 and 2.0) and the R/C ratio of 5.0. Then, the titania sol were added in the various based on the R/TiO_2 molar ratio of 0.06, 0.07, 0.09, 0.11 and 0.13, respectively. Finally, the products were dried and subsequently calcined at 500 ^oC in a box furnace.

Figure 4.25 and 4.26 illustrate the nitrogen adsorption-desorption isotherms and pore size distributions of the calcined products when they were prepared using the R/F ratio of 2.0. All products show classical IV type isotherm with hysteresis loop, which is typical for mesoporous material. The occurrence of a narrow pore size distribution obtained by the BJH method confirms the micro- and mesopores structure (Figure 4.26). The mesopore is about 2-50 nm in range.

At the R/TiO_2 ratio of 0.06, the sample shows mesopores with broader pore size distributions, which is in accordance with its broad hysteresis loops centering at higher relative pressure. Moreover, it has the largest specific surface area among all samples (164.3 m^2/g) with the average pore diameter of 3 nm. At high value of R/TiO_2 ratio, the adsorption-desorption isotherm shows lower faction of mesopore than that of micropores and the surface area decreases (see Figure 4.26). The average pore diameter of product is about 2-5 nm. The pore size distribution becomes broaden of as a result of the addition of greater amount of TiO_2 sol. That means more TiO_2 can react with RF solution and form in greater extent of cross-linking in the network.

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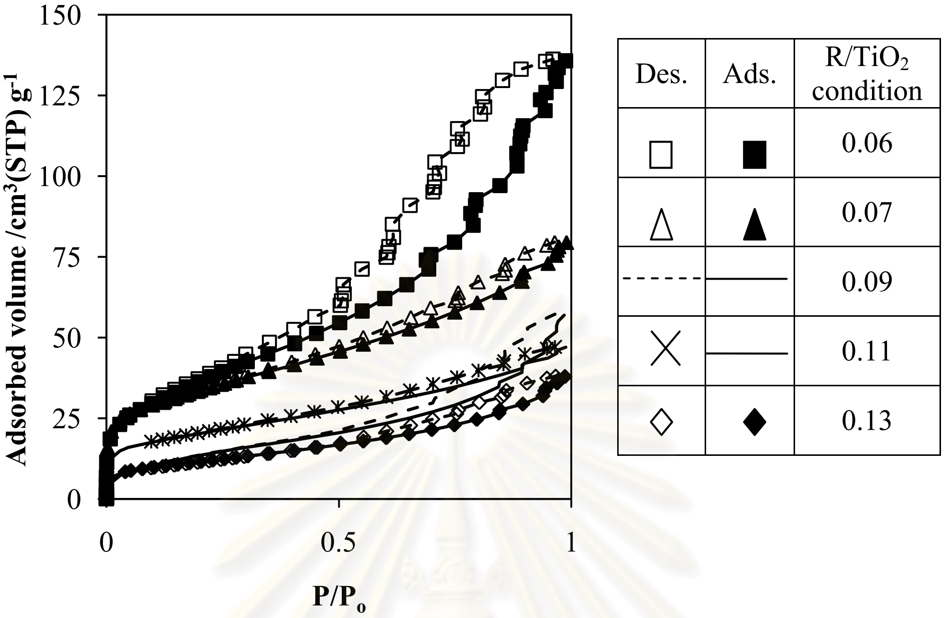

Figure 4.25 Adsorption-desorption isotherms of TiO_2 products prepared by using RF gel with R/F ratio of 2.0, R/C ratio of 5.0 and different value of R/TiO_2 ratio.

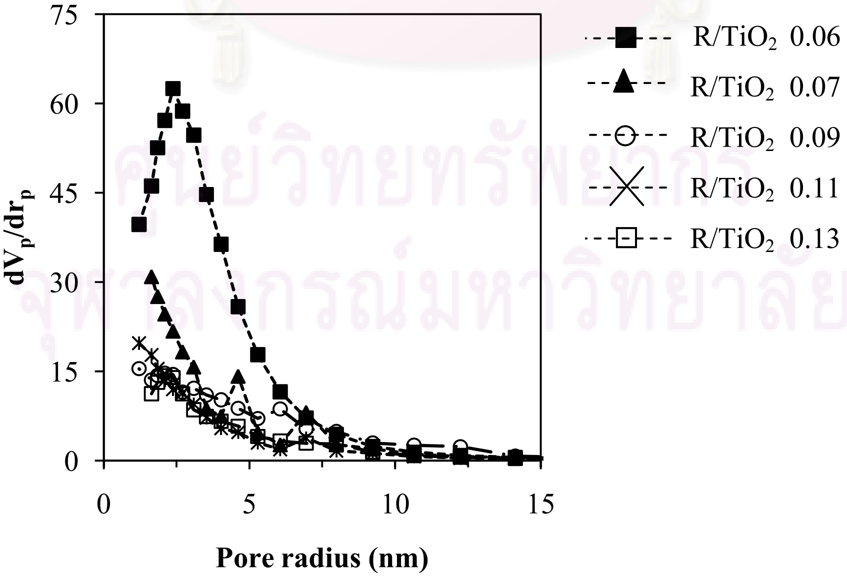

Figure 4.26 Pore size distribution of samples of TiO_2 products prepared by using RF gel with R/F ratio of 2.0, R/C ratio of 5.0 and different value of R/TiO_2 ratio.

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According to Figure 4.27, when R/TiO_2 ratio is decreased, the surface area also decreases such that the R/TiO_2 ratio of 0.06 yields the highest surface area. Higher R/F ratio (2.0) and lower R/TiO_2 (0.06) is completely reaction between RF solution and titania sol. The reaction between the both of them is two processes. One is reactin between RF cluster and titania sol. The other one is interreaction of titania sol so that this condition is high surface area by about 164.3 m^2/g. Generally, when the R/F ratio is increased, the surface area of the product is also increase.

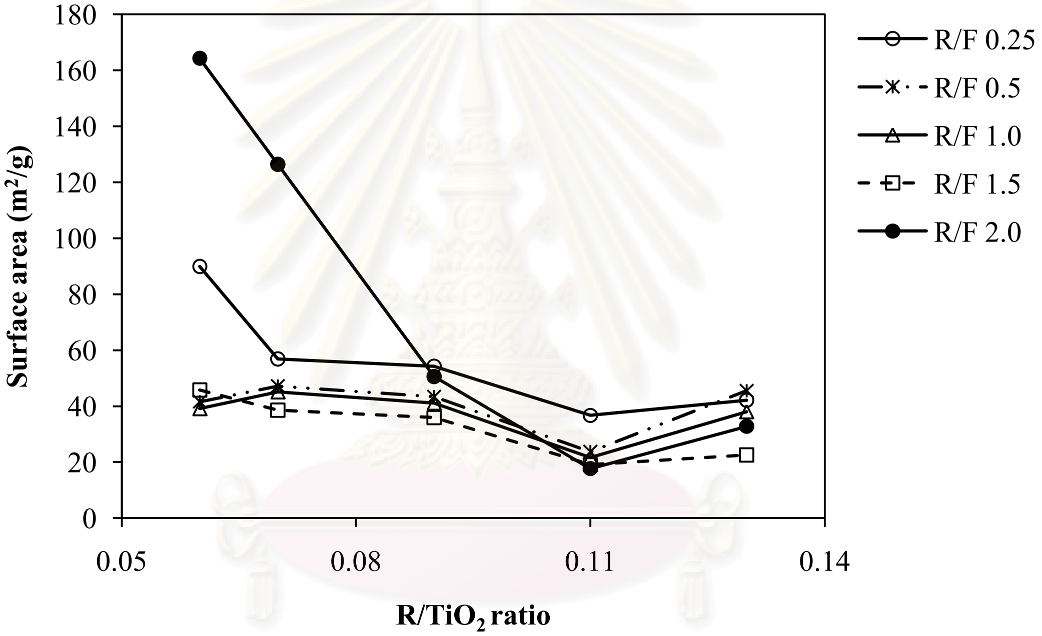

Figure 4.27 Relationship between R/TiO_2 ratio within the RF gel and surface area of titania product prepared using different values of R/F ratio.

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Figure 4.28 shows relationship between FTIR signal ratio of various functional groups within the RF/titania composite prepared by using R/C ratio of 5.0 and R/F ratio of 2.0, as a function of R/TiO_2 ratio. This is the representation the R/TiO_2 ratio is increased from 0.06 to 0.13. Signal of Ti-O-C is high at R/TiO_2 ratio of 0.06 and then it decrease when R/TiO_2 increase. Signal of Ti-O-Ti also increase for the same R/TiO_2 ratio. It means that RF gel reacts with TiO_2 sol and TiO_2 sol form into gel network at the moment. Furthermore, reaction between RF gel and TiO_2 sol is more than reaction of TiO_2 sol that show signal ratio of Ti-O-C is higher than signal of Ti-O-Ti. Additional, signal of Ti-O-C is nearby signal of methylene bridge so that network of Ti-O-C is much as well as cross-linking network of RF gel. When R/TiO_2 ratios increase from 0.06 to 0.13, signal of Ti-O-C decrease because amount of TiO_2 sol is low so that it react a few with RF gel.

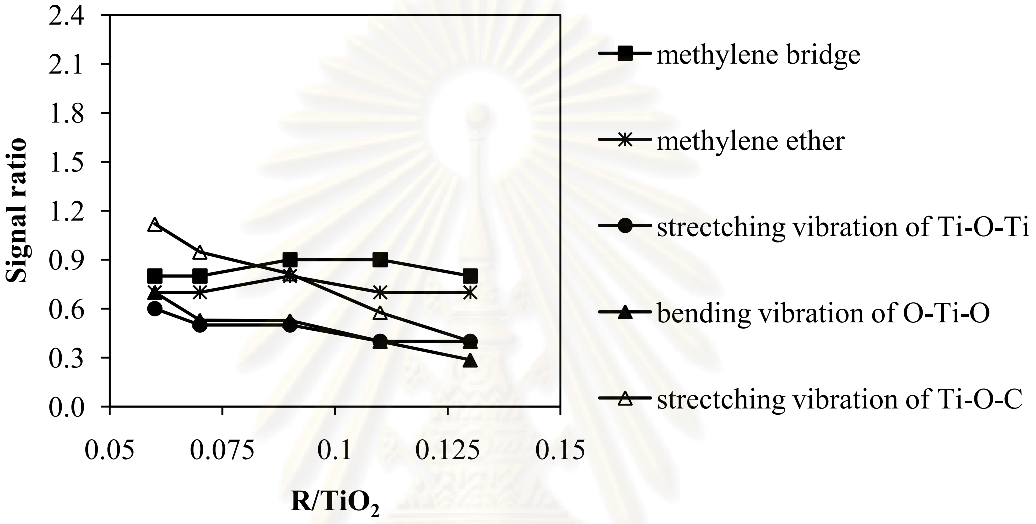

Figure 4.28 Relationship between R/F ratio within the RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/C ratio of 0.5 and R/TiO_2 ratio of 0.06. For all signals, signal from aromatic ring was used as the reference signal.

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4.3.3 Effect of aging time for RF gel

In this part, the effect of aging time for RF gel is investigated. The RF/TiO_2 mixture was prepared by using TiO_2 sol added into RF solution that has been aged for 0, 6, 12,18 and 24 hours, respectively.

Figure 4.29 shows the adsorption-desorption isotherm of titania products prepared by using RF gel that has been aged for 6 hours compared with that prepared from RF gel without aging. The results confirm that aging time could modify pore structure of the product. When aging time is increased from 0 to 6 hours, the pore structure of the final product would changes from microporous to mesoporous. It shows the classical IV-type of isotherm with a hysteresis loop, revealing the presence of mesoporoud structure according to the IUPAC classification of porous material.

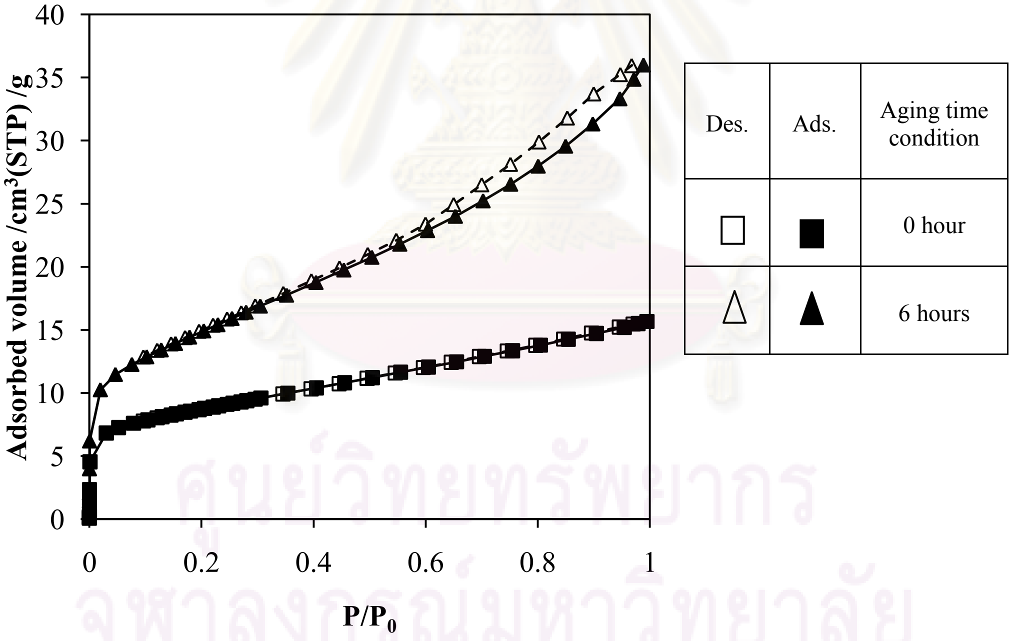

Figure 4.29 Adsorption-desorption isotherms of TiO_2 products prepared by using that has been aged for 0 and 6 hours.

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Figure 4.30 shows relationship between surface area of the product and aging time of RF gel used. When the aging time is increased, the surface area decrease, such that see at R/F ratio of 2.0 for 18 and 24 hours of RF-gel because the RF solution was completly formed into gel before titania sol was put into them so that they could not react together. The surface area of the obtain product would come from titania sol at prolong aging time due to surface area more than the short aging time. For the relationship between aging time aand R/F ratio, the surface area of product at R/F ratio of 2.0 was higher than the other ratios. Because of excessed resorcinol would react with titania sol and titania sol could be form into gel or titania sol would form the interreaction of sol. Figure 4.31 shows relationship between average pore diameter of the product and aging time of RF gel used. The average pore diameter of the products is about 3-4 nm that confirms that the products have mesoporous structure.

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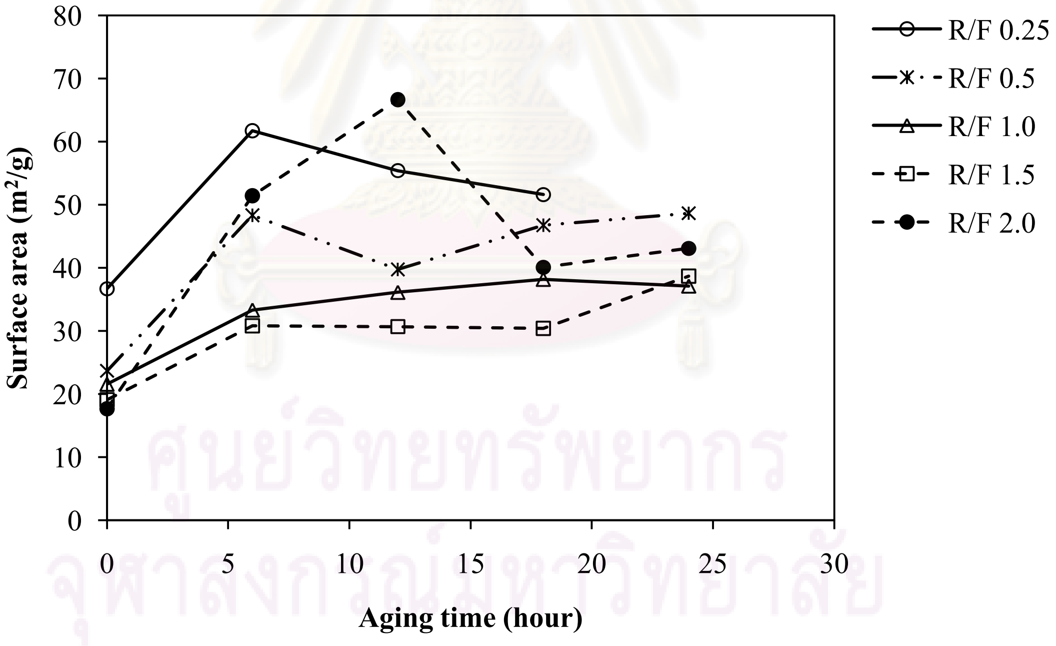

Figure 4.30 Relationship between aging time of RF gel and surface area of titania product prepared using different values of R/F ratio.

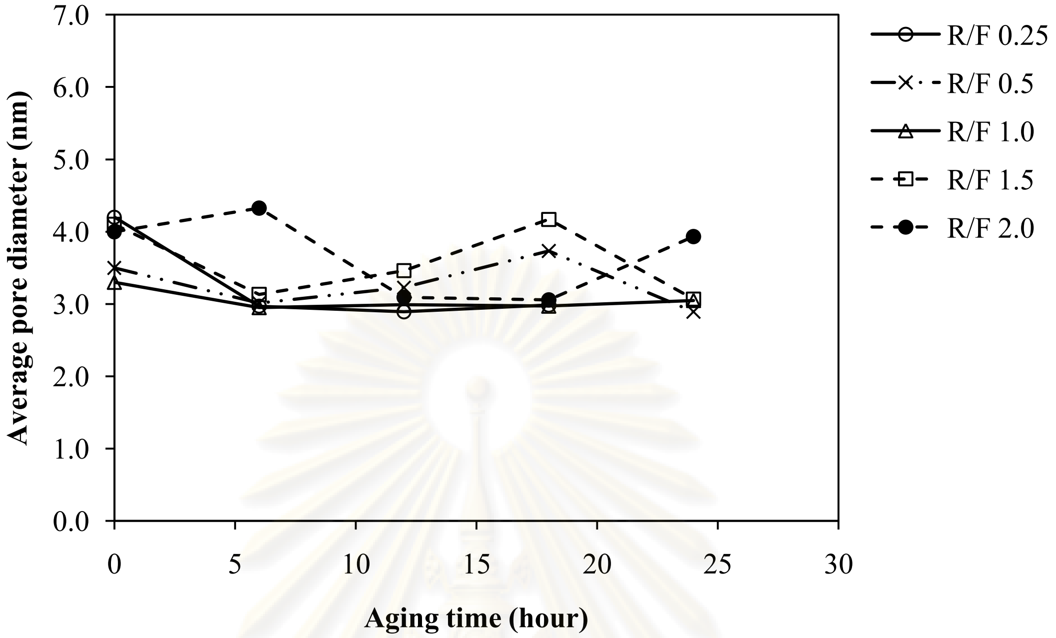

Figure 4.31 Relationship between aging time of RF gel and average pore diameter of titania product prepared using different values of R/F ratio.

RF solution was completely formed to gel at 24 hours of aging time. So that this condition could not put titania sol into the RF gel. When aging time of RF was increased, methylene bridge and methylene ether bridge were increased because of prolong aging time was caused the cross-link network and solution form to gel. Some of sample at the longer aging time, such as 18 and 24 hours, Ti-O-C was decreased. That mean, RF solution would formed to network and titania sol could not react with them thus titania sol would formed to cluster and cross-link to network that showed signal ratio of Ti-O-Ti was increased. For short-term of aging time, titania sol could react with RF solution so that Ti-O-C was increased while Ti-O-Ti signal was also increased. Because of titania sol could react into 2 parts at the moment. One was reaction between RF solution and titania sol and the other one was reaction in internal of them. For relationship of aging time and R/F ratio, see in Figure 4.32-4.36.

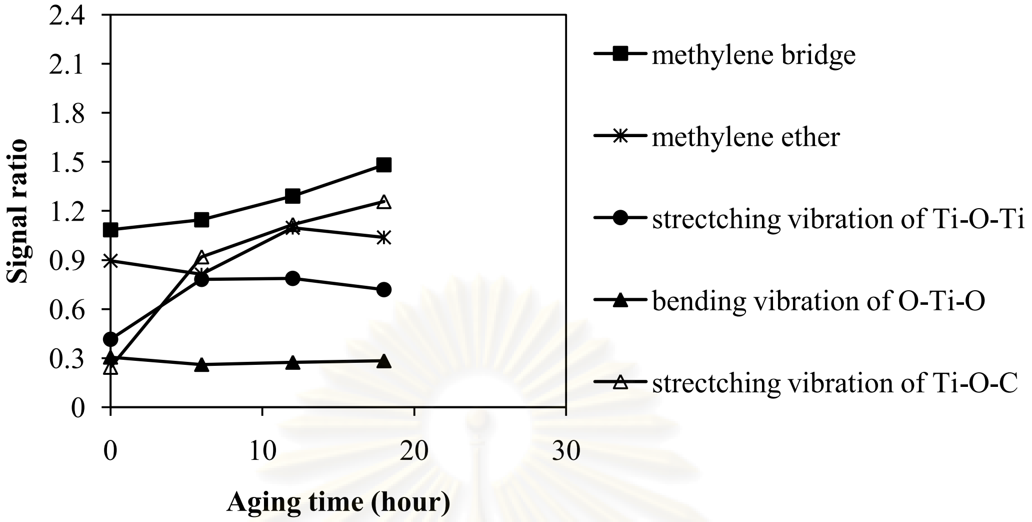

Figure 4.32 Relationship between aging time of RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 0.25. For all signals, signal from aromatic ring was used as the reference signal.

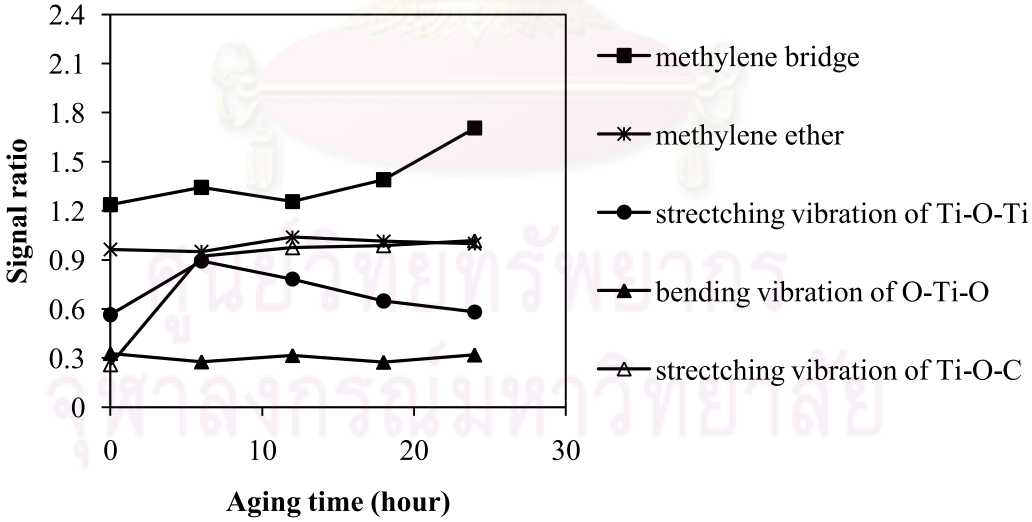

Figure 4.33 Relationship between aging time of RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 0.5. For all signals, signal from aromatic ring was used as the reference signal.

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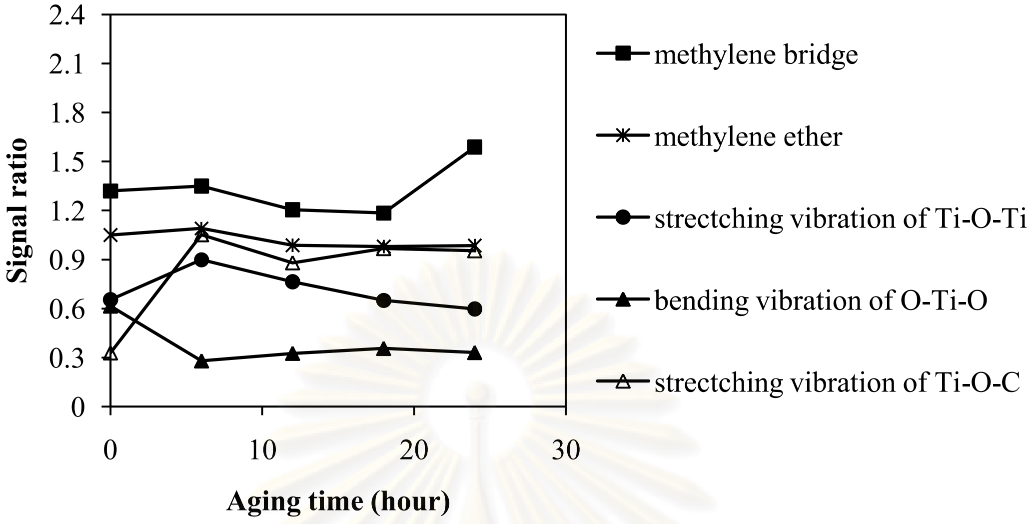


Figure 4.34 Relationship between aging time of RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 1.0. For all signals, signal from aromatic ring was used as the reference signal.

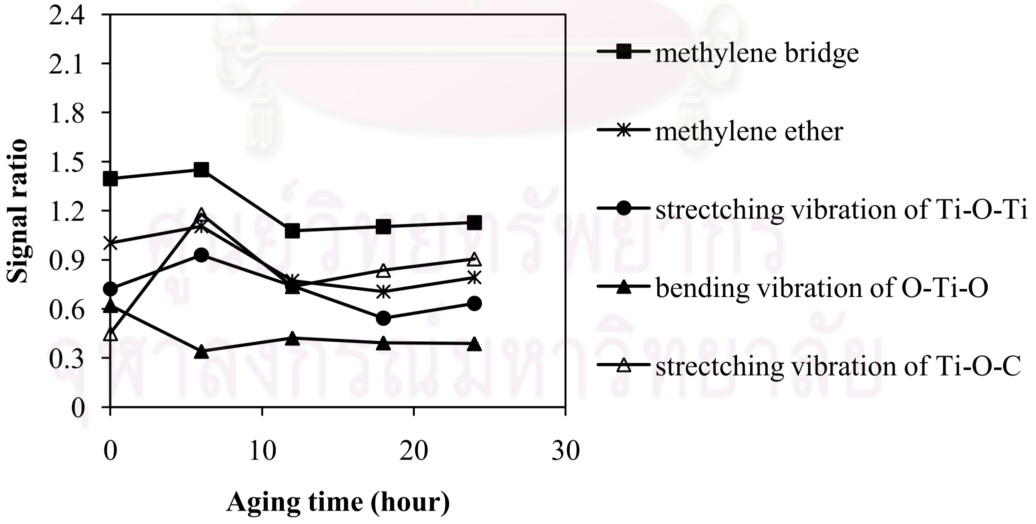


Figure 4.35 Relationship between aging time of RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 1.5. For all signals, signal from aromatic ring was used as the reference signal.

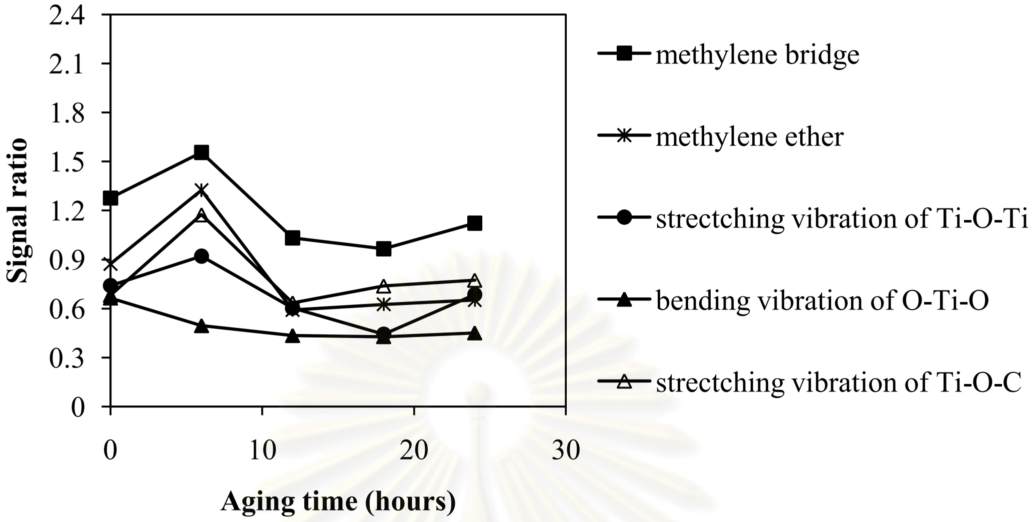
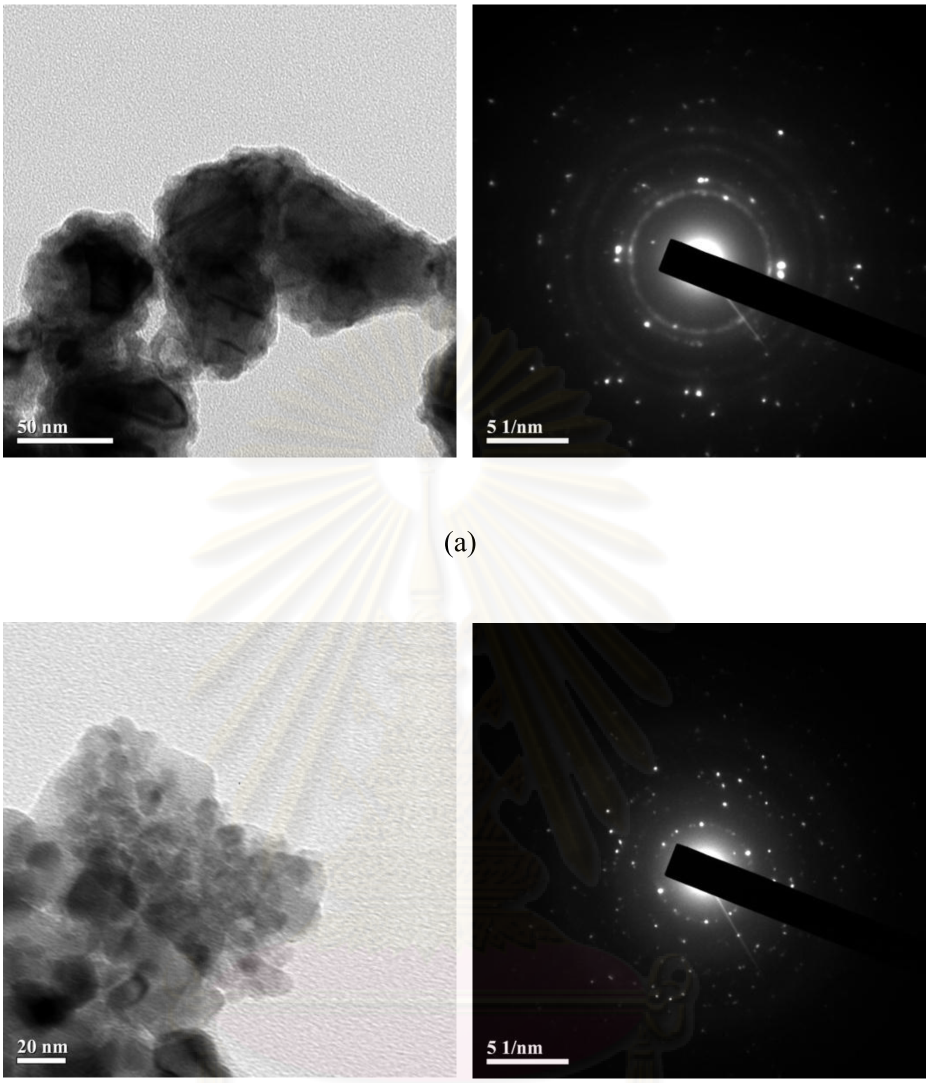


Figure 4.36 Relationship between aging time of RF gel and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 2.0. For all signals, signal from aromatic ring was used as the reference signal.

Figure 4.37 compares TEM images of titania products prepared by an assistance of RF gel that was aged for different period of time. All powders were calcined 500 °C. The selected area electron diffraction (SAED) patterns of both samples show five rings indexed to the (101), (004), (200), (211), and (213) diffraction planes of the hexagonal structure of anatase TiO_2 in agreement with that of bulk crystal data. It is clear from the TEM images that samples are consisting of numerous TiO_2 nanocrystallites. SAED patterns also reveal the polycrystalline nature for both samples. However, the sample shown in Figure 4.38 (a) is more crystalline more than the one shown in Figure (b) because long aging time of RF solution would result in the formation of gel that prohibits interaction with titania sol. The reaction between RF gel and titania sol was agglomerated of particle that see in Figure 4.38 (a). The crystallite are subsequently converted to titania in anatase and rutile phases during the calcination, hence the greater number of titania crystallite as observed in Figure 4.38(b). This result suggests that aging time of RF-gel affects the shape of the crystallite of product.



(a)

(b)

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Figure 4.37 TEM micrographs and their corresponding SAED patterns of titania product prepared by the assistance of RF gel with the R/F ratio of 2.0 that was aged for: 18 and (b) 24 hours.

4.3.4 Effect of aging time of titania sol

In this part, the effect of aging time for titania sol is investigated. The RF/TiO_2 mixture was prepared by using TiO_2 sol added into RF solution (without aging time) that has been aged for 0, 6, 12,18 and 24 hours, respectively.

Figure 4.38 shows the adsorption-desorption isotherm of titania product prepared by using titania sol that has been aged for 24 hours. A broad hysteresis loop is obviously presented in the isotherm curve that confirms the mesoporous structure of the product.

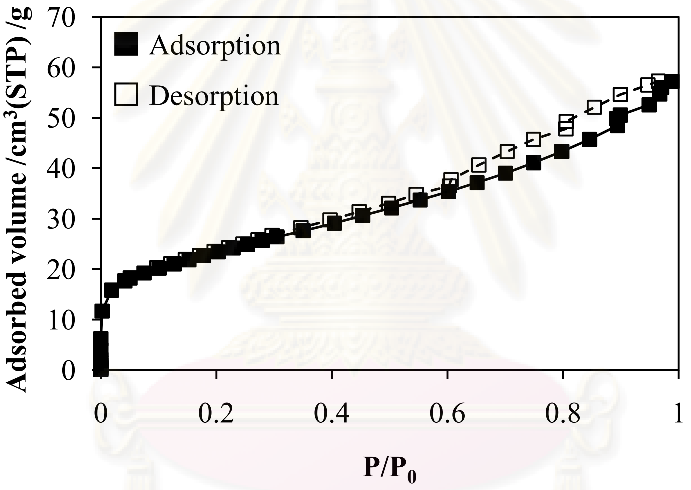

Figure 4.38 Adsorption-desorption isotherm of TiO_2 products prepared by using titania sol that has been aged for 24 hours and RF gel.

Figure 4.39 shows pore size distribution of the product calculated by BJH method. The sample is consisted of micropores (the pore size less than 2 nm) and mesopores (the pore size in the range of 2-50 nm).

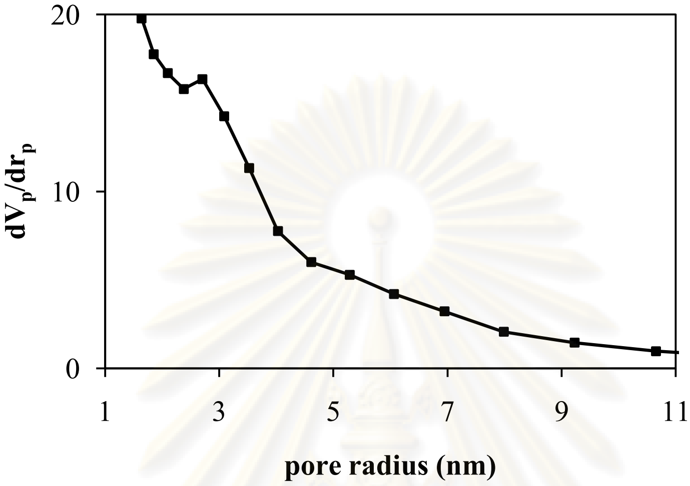

Figure 4.39 Pore size distributions of TiO_2 nanoparticles at 24 hours of titania solution.

Figure 4.40 showed relationship between surface area of the product and aging time of titania sol used. When the aging time of titania sol is increased, the surface area is changed in the range around 30-50 m^2/g. The results show that the surface area is low when the aging time of titania sol is between 6 and 18 hours because titania sol forms into gel before they react with RF solution. And 24 hours of aging time was high surface area because titania sol was form to gel and then, RF solution was unable to react with them. The surface area would come from aging time of titania sol more than reaction between RF solution and titania sol. Effect of aging time of titania sol on surface area can explain to 6 hours and without aging time (see Figure 4.40). When titania sol is aged in before being added into RF solution, the surface area of the product is increased for higher of R/F ratios (e.g., 1.5 and 2.0). Figure 4.41 shows relationship between average pore diameter of the product and aging time of titania sol. Average pore diameter of product is about 3.5-4 nm in range that confirms the mesoporous structure of the product.

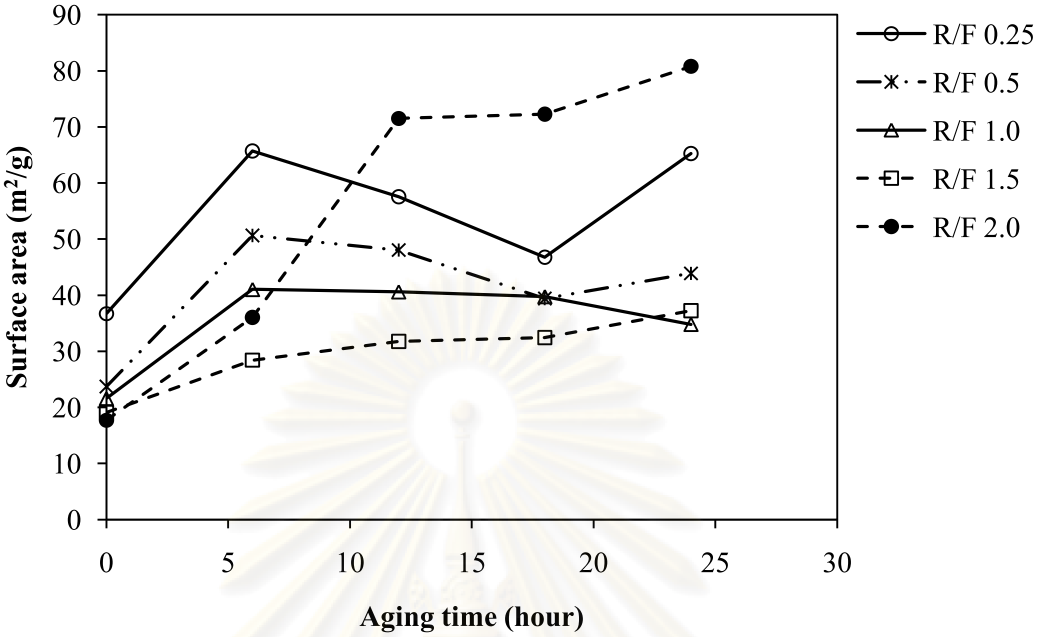

Figure 4.40 Relationship between aging time of titania sol and surface area of titania product prepared using different values of R/F ratio.

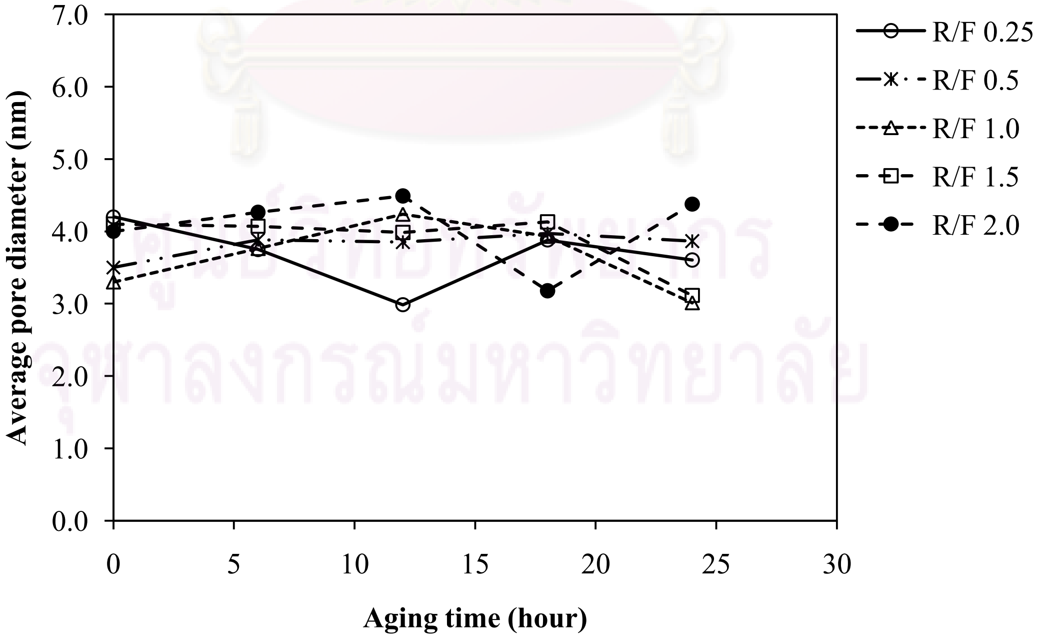

Figure 4.41 Relationship between aging time of titania sol and average pore diameter of titania product prepared using different values of R/F ratio.

According to Figure 4.42-4.46, which show FTIR signal ratio with respect to aging time of titania sol, the Ti-O-C signal increases significantly as the aging time is increased from 0 to 6 hours. This confirms that the aging time of titania sol affects bondings between titania sol and RF solution. When aging time of titania sol is increased, the signal of Ti-O-C is also increased, but the signal becomes unchanged after prolonged aging time, because titania sol form crossed-linking network before being put into the RF solution. Signal Ti-O-Ti confirms the formation of titania network. The increase of aging time titania barely results in any change in the signal ratio of all kinds of bonding when the R/F ratio is 2.0 because the excess amount of resorcinol in the solution and titania sol was formed to network. It means that titania sol could not react with excess resorcinol in the RF solution.

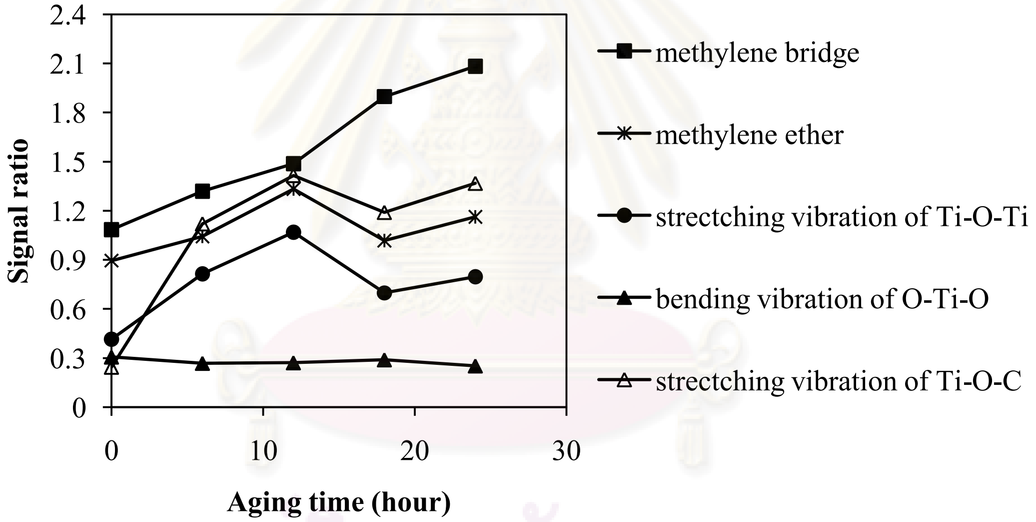

Figure 4.42 Relationship between aging time of titania sol and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 0.25. For all signals, signal from aromatic ring was used as the reference signal.

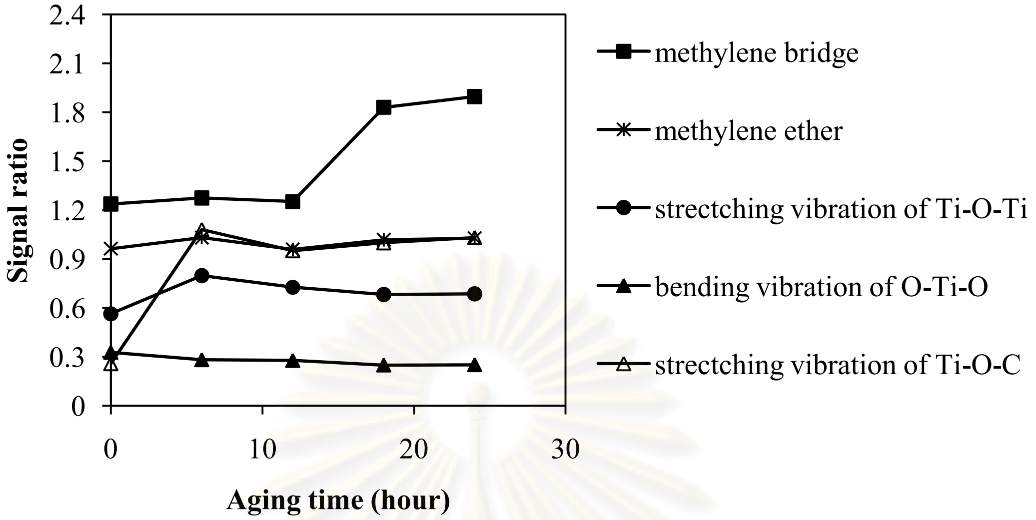

Figure 4.43 Relationship between aging time of titania sol and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 0.5. For all signals, signal from aromatic ring was used as the reference signal.

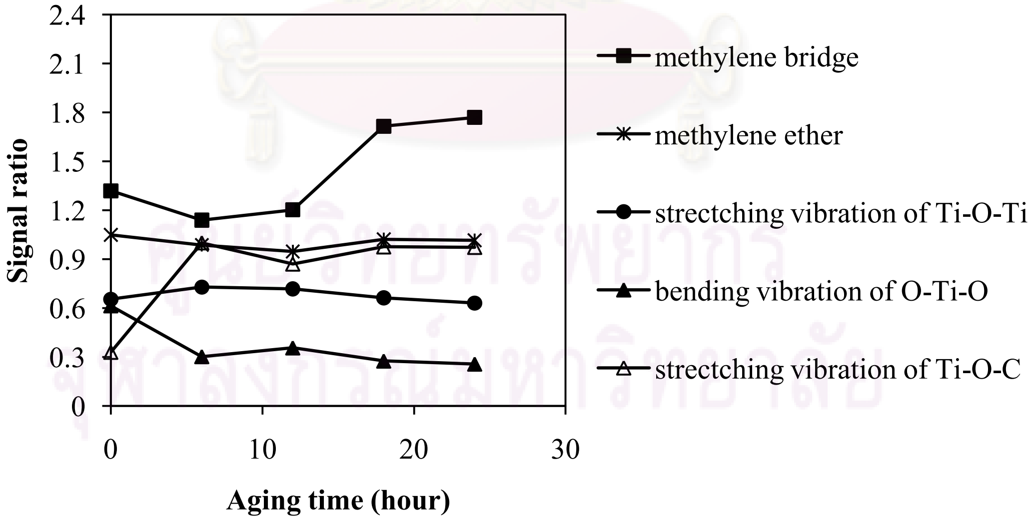

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Figure 4.44 Relationship between aging time of titania sol and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 1.0. For all signals, signal from aromatic ring was used as the reference signal.

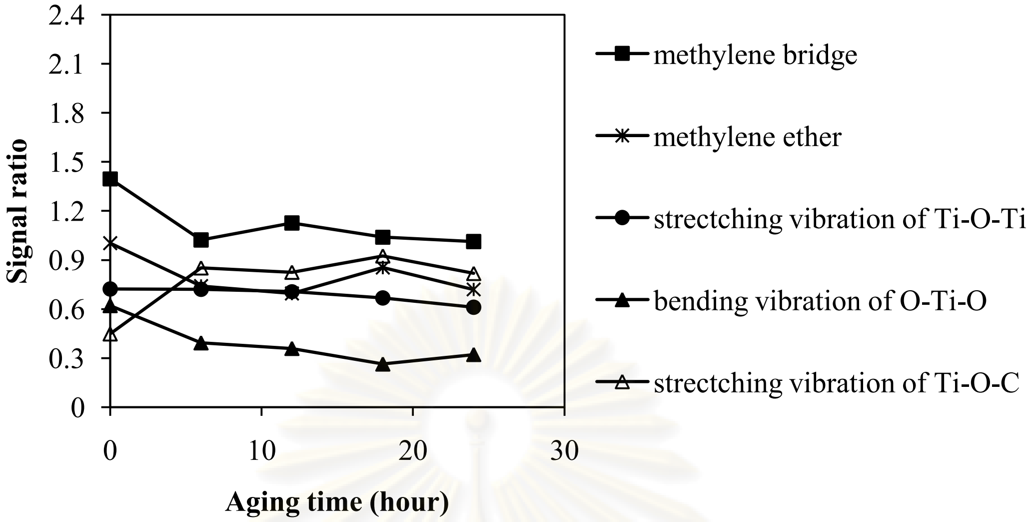

Figure 4.45 Relationship between aging time of titania sol and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 1.5. For all signals, signal from aromatic ring was used as the reference signal.

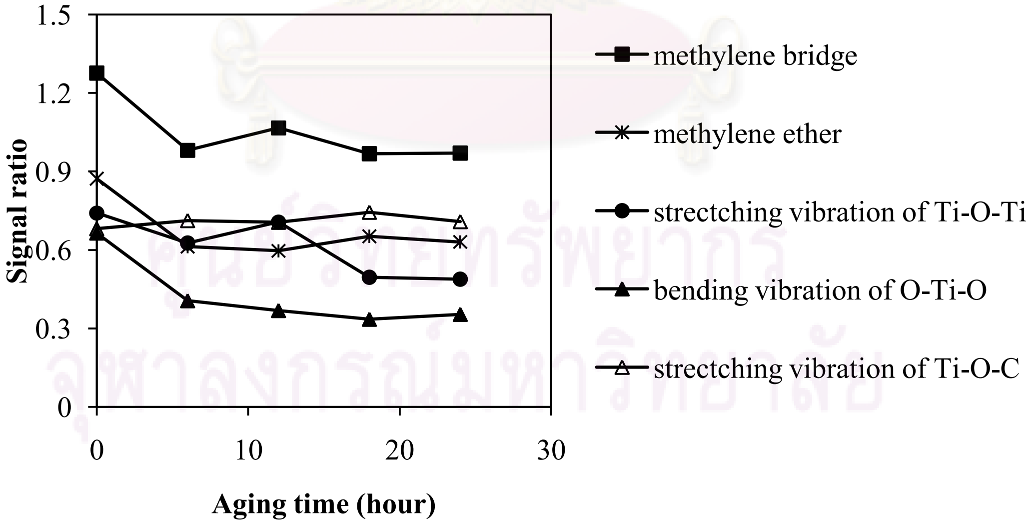

Figure 4.46 Relationship between aging time of titania sol and FTIR signal ratio of various functional groups within the RF/TiO_2 composite prepared using R/F ratio of 2.0. For all signals, signal from aromatic ring was used as the reference signal.

The TEM micrographs of samples, presented in Figure 4.47, confirmed the nanoscale size of the titania powder. Aging time of titania sol is affected the particle size and the number of crystallite of product as same aging time of RF gel. In addition, the trend of surface area is the same as aging time of RF gel that surface area increases from R/F ratio 2.0, 0.25, 0.5, 1.0 and 1.5, respectively. It means that aging time of titania sol and RF gel is unaffected on particles.

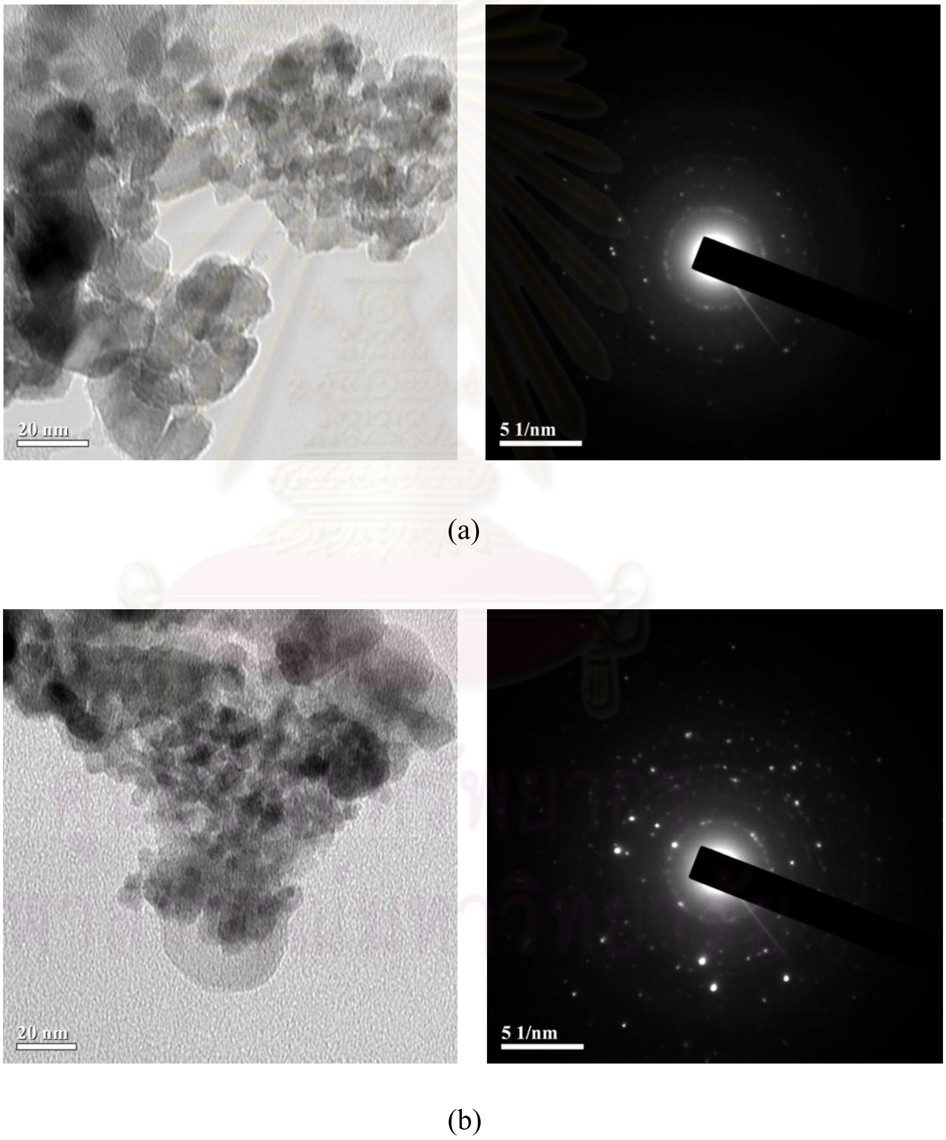

Figure 4.47 TEM micrographs and their corresponding SAED patterns of titania product prepared by the assistance of RF gel with the R/F ratio of 2.0 that was aged for; 18 and (b) 24 hours**.**

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, the formation of porous titania by the aid of RF clusters via the sol-gel polycondensation is investigated. The conclusions of the present research are the following:

1. RF template can produce mesoporousity for titania product.

2. Reaction between TTIP and RF solution is strongly exothermic that results in low surface area of the product.

3. Titania sol can react with RF solution and form to network. Higher of R/F ratio yields high surface area and modifies mesoporous structure of the final product.

4. Amount of acetic acid has effect on reaction between RF gel and titania sol because acetic acid reacts with resorcinol and then, formaldehyde cannot react with them.

5. Cross-linking between titania sol and RF gel affects surface area of the final product.

6. Both aging time of RF gel and titania sol affect mesoporousity of the product. For prolonged aging time, the surface area of the product is increased from cross-linked of RF gel with titania sol.

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5.2 Recommendations for Future Work

In this study, effects of various factors, such as general characteristics of the product, Rf gel composition, type of titania precursor (i.e., TTIP solution and titania sol), R/TiO_2 ratio of TiO_2 sol, aging time of RF gel, aging time of titania sol, on the synthesis of titania powder by RF template have been investigated. Some recommendations for future work are listed as follows: (i) type of titania precursor on property of product, (ii) the pH of prepared titania sol has affected on final size of titania nanoparticle, (iii) the control of humidity of gel for aged gel, (iv) the applications of titania powders should be investigated.

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APPENDICES

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APPENDIX A

DATA OF SURFACE AREA AND AVG. PORE DIAMETER

Table A.1 Data of surface area of synthesized titania product at R/F and R/C different ratio by TTIP solution put into RF solution.

R/F ratio	Surface area (m^2/g)				
	R/C 0.18	R/C 0.3	R/C 1.3	R/C 2	R/C 5
0.25	38.1	25.2	19.2	20.7	14.7
0.50	15.5	18.9	18.1	13.7	11.8
1.00	13.4	17.7	16.6	17.0	15.3
1.50	16.5	12.8	20.2	15.8	15.4
2.00	10.5	19.3	13.8	15.2	13.8

Table A.2 Data of average pore diameter of synthesized titania product at R/F and R/C different ratio by TTIP solution put into RF solution.

R/F ratio	Average pore diameter (nm)				
	R/C 0.18	R/C 0.3	R/C 1.3	R/C 2	R/C 5
0.25	3.8	4.1	4.4	4.0	3.4
0.50	4.3	4.2	4.4	4.3	3.5
1.00	3.3	4.1	4.4	4.2	4.2
1.50	3.3	4.4	4.2	4.4	4.3
2.00	4.4	4.0	4.5	5.8	6.0

Table A.3 Data of surface area of synthesized titania product at R/F and R/C different ratio by TTIP solution put into RF solution.

R/C ratio	Surface area (m^2/g)				
	RF 0.25	RF 0.5	RF 1.0	RF 1.5	RF 2.0
0.18	38.1	15.5	13.4	16.5	10.5
0.3	25.2	18.9	17.7	12.8	19.3
1.3	19.2	18.1	16.6	20.2	13.8
2.0	20.7	13.7	17.0	15.8	15.2
5.0	14.7	11.8	15.3	15.4	13.8

Table A.4 Data of average pore diameter of synthesized titania product at R/F and R/C different ratio by TTIP solution put into RF solution.

R/C ratio	Average pore diameter (nm)				
	RF 0.25	RF 0.5	RF 1.0	RF 1.5	RF 2.0
0.18	3.8	4.3	3.3	3.3	4.4
0.3	4.1	4.2	4.1	4.4	4.0
1.3	4.4	4.4	4.4	4.2	4.5
2.0	4.0	4.3	4.2	4.4	5.8
5.0	3.4	3.5	4.2	4.3	6.0

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Table A.5 Data of surface area of synthesized titania product at R/F and R/C different ratio by titaniasol put into RF solution.

R/F ratio	Surface area (m^2/g)				
	RC 0.18	RC 0.3	RC 1.3	RC 2	RC 5
0.25	39.5	43.4	36.7	48.0	25.5
0.50	36.2	35.6	23.7	34.9	34.9
1.00	29.3	35.1	21.6	36.3	30.5
1.50	30.3	25.0	19.1	34.8	57.2
2.00	25.8	23.8	17.7	30.7	70.2

Table A.6 Data of average pore diameter of synthesized titania product at R/F and R/C different ratio by titania sol put into RF solution.

R/F ratio	Average pore diameter (nm)				
	RC 0.18	RC 0.3	RC 1.3	RC 2	RC 5
0.25	3.4	3.9	4.2	3.8	3.9
0.50	3.8	3.9	3.5	3.3	4.0
1.00	3.8	2.8	3.3	3.3	3.9
1.50	5.0	3.4	4.1	3.3	4.1
2.00	6.0	4.3	4.0	4.3	4.2

Table A.7 Data of surface area of synthesized titania product at R/F and R/C different ratio by titaniasol put into RF solution.

R/C ratio	Surface area (m^2/g)				
	RF 0.25	RF 0.5	RF 1.0	RF 1.5	RF 2.0
0.18	29.3	36.2	39.5	30.3	25.8
0.3	43.4	35.6	35.1	25.0	23.8
1.3	36.7	23.7	21.6	19.1	17.7
2.0	48.0	34.9	36.3	34.8	30.7
5.0	25.5	34.9	30.5	57.2	70.2

Table A.8 Data of average pore diameter of synthesized titania product at R/F and R/C different ratio by titania sol put into RF solution.

R/C ratio	Average pore diameter (nm)				
	RF 0.25	RF 0.5	RF 1.0	RF 1.5	RF 2.0
0.18	3.4	3.8	3.8	5.0	6.0
0.3	3.9	3.9	2.8	3.4	4.3
1.3	4.2	3.5	3.3	4.1	4.0
2.0	3.8	3.3	3.3	3.3	4.3
5.0	3.9	4.0	3.9	4.1	4.2

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Table A.9 Data of surface area of synthesized titania product at different ratio of R/TiO_2.

R/TiO_2 ratio	Surface area (m^2/g)				
	R/F 0.25	R/F 0.5	R/F 1.0	R/F 1.5	R/F 2.0
0.06	42.1	45.5	38.0	22.6	32.8
0.07	36.7	23.7	21.6	19.1	17.7
0.09	54.3	43.4	41.4	35.9	50.6
0.11	56.9	47.2	45.1	38.6	126.4
0.13	89.9	41.6	39.1	45.8	164.3

Table A.10 Data of average pore diameter of synthesized titania product at different ratio of R/TiO_2.

R/F ratio	Average pore diameter (nm)				
	T3.5	T4.5	T5.5	T6.5	T8
0.25	3.7	8.4	4.0	3.9	4.2
0.50	3.0	5.5	3.8	3.1	4.1
1.00	2.9	5.0	3.3	3.1	4.1
1.50	3.4	4.4	4.0	4.0	4.0
2.00	3.5	4.1	3.1	4.2	3.0

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Table A.11 Surface area of synthesized titania product at different aging time of RF gel**.**

Aging time, hour	Surface area (m^2/g)				
	R/F 0.25	R/F 0.5	R/F 1.0	R/F 1.5	R/F 2.0
0	36.7	23.7	21.6	19.1	17.7
6	61.7	48.3	33.3	30.8	51.5
12	55.4	39.8	36.2	30.7	66.7
18	51.6	46.8	38.2	30.4	40.1
24		48.7	37.1	38.7	43.1

Table A.12 Data of average pore diameter of synthesized titania product different aging time of RF gel.

Aging time, hour	Average pore diameter				
	R/F 0.25	R/F 0.5	R/F 1.0	R/F 1.5	R/F 2.0
0	4.2	3.5	3.3	4.1	4.0
6	3.0	3.0	3.0	3.1	4.3
12	2.9	3.2	3.0	3.5	3.1
18	3.0	3.7	3.0	4.2	3.1
24		2.9	3.0	3.1	3.9

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Table A.13 Surface area of synthesized titania product at different aging time of titania sol.

Aging time, hour	Surface area (m^2/g)				
	R/F 0.25	R/F 0.5	R/F 1.0	R/F 1.5	R/F 2.0
0	36.7	23.7	21.6	19.1	17.7
6	65.7	50.7	41.0	28.4	36.0
12	57.6	48.1	40.6	31.8	71.5
18	46.8	39.4	39.8	32.5	72.3
24	65.2	43.9	34.8	37.2	80.8

Table A.14 Data of average pore diameter of synthesized titania product different aging time of titania sol.

Aging time, hour	Average pore diameter (nm)				
	R/F 0.25	R/F 0.5	R/F 1.0	R/F 1.5	R/F 2.0
0	4.2	3.5	3.3	4.1	4.0
6	3.7	3.9	3.8	4.1	4.3
12	3.0	3.9	4.2	4.0	4.5
18	3.9	4.0	3.9	4.1	3.2
24	3.6	3.9	3.0	3.1	4.4

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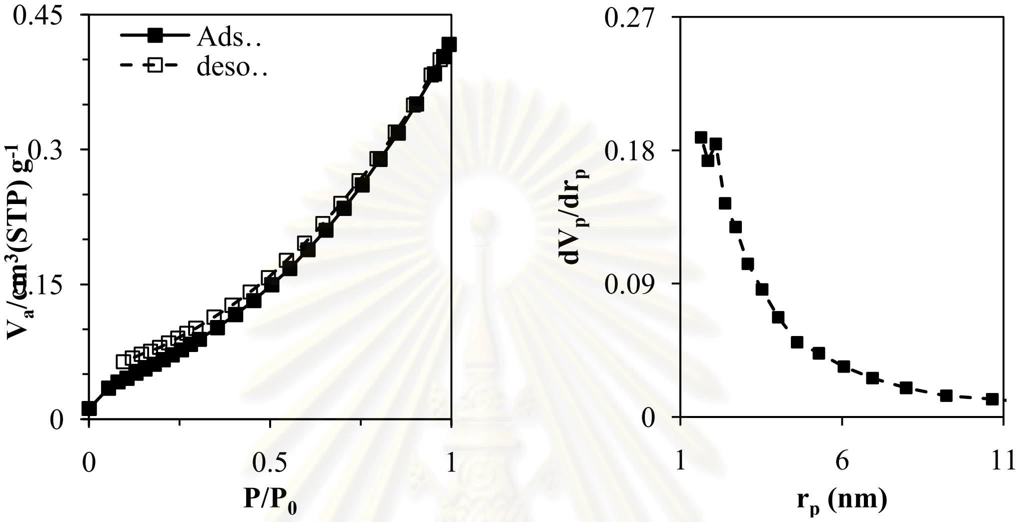
APPENDIX B

CHARACTERISTIC OF RF GEL



(a) (b)

Figure B.1 Adsorption-desorption isotherm(a) and pore size distribution (b) of RF gel product.

Table B.1 Property of RF gel product.

Sample	Surface area (m2/g)	Average pore diameter (nm)	Total pore volume (cm^3(STP)/g)
RF-gel	0.36	7.06	0.08

APPENDIX C

DATA OF TGA ANALYSIS

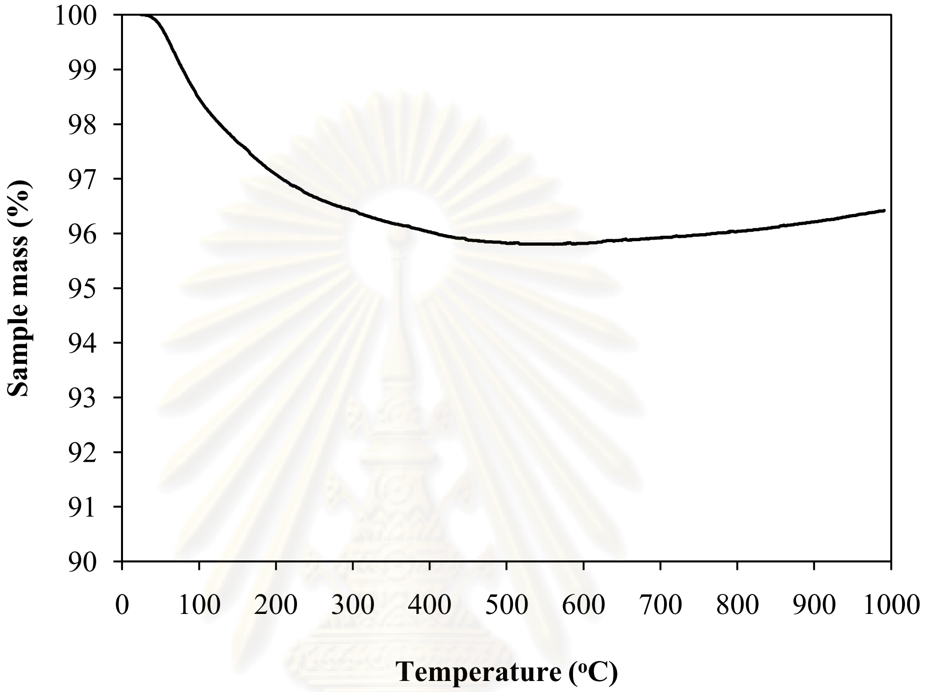


Figure C.1 TGA analysis in oxygen atmosphere of the products after calcinations, was prepared from titania/RF gel formed

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APPENDIX D
DATA OF XRD ANALYSIS

Figure D.1 shows XRD patterns of RF/titania composite after being calcined at 500°C. The samples were prepared using different preparation details. The first sample, i.e., T001, was prepared by slowly adding 4.5 ml TTIP solution into RF solution. It took 2 min to complete the addition process. The second sample (T002) was prepared in similar manner to that of T001, but the TTIP solution was added to the RF solution within 5 second. For the last sample (T003), TTIP was poured into RF solution within 5 second as well, but no acetic acid was used in the preparation of RF gel. The XRD results show that T001 and T003 samples were titania in anatase phase, while T002 was mainly rutile. The result clearly indicated that the rate of TTIP addition significantly influenced the phase of the final product. The increased TTIP addition rate favored the formation of titania in rutile phase. On the other hand, the presence of acetic acid in RF gel did not affect phase formation of titania.

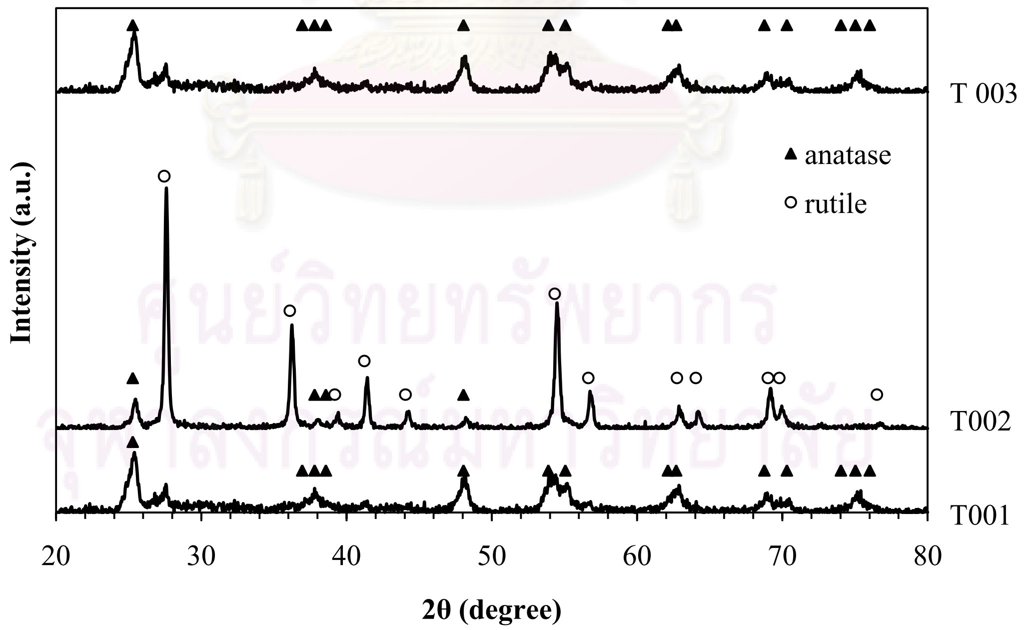

Figure D.1 XRD patterns of titania powders prepared by using different rate of TTIP addition.

VITA

Miss. Mananya Thovicha was born on 11 November, 1986, in Bangkok, Thailand. She received the Bachelor's Degree of Engineering with a major in Chemical Engineering from Mahidol University, *Nakornpathom* in March 2009. She entered the Master of Engineering in Chemical Enguneering at Chulalongkorn University, Bangkok, Thailand in May 2009.

List of publication

1. Mananya Thovicha, Varong Pavarajarn, "Fabrication of mesoporous titanium dioxide assisted by Resorcinol/Formaldehyde gel", the 17th Regional Symposium on Chemical Engineering, Bangkok, Thailand, November 22-23, 2010.

2. Mananya Thovicha, Varong Pavarajarn, "Effects of Gel Network on the Formation of Mesoporous Titania Assisted by Resorcinol/Formaldehyde Gel", the 7th Asian Aerosol Conference, Xi'an, china, on August 17-20, 2011.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย