

CHAPTER III

THEORY

In the previous chapter, reviews of recent research on titania catalysts, and titania-supported cobalt catalysts. They present knowledge and understanding of influencing parameters on the performance of titania catalysts for photocatalytic, and Co-based catalysts for CO hydrogenation system. This chapter focuses on the fundamental theory of titanium (IV) oxide, method for synthesis catalysts, photocatalytic process, and Fischer-Tropsch Synthesis (FTS) which is well known as one type of carbon monoxide (CO) hydrogenation using Co-based catalysts.

3.1 Titanium (Ti) (Sornnarong Theinkeaw, 2000)

Titanium (atomic number 22; ionization potentials: first 6.83 eV, second 13.67 eV, third 27.47 eV, fourth 43.24 eV) is the first member of Group IVB of the periodic chart. It has four valence electrons, and Ti (IV) is most stable valence state. The lower valence states Ti (II) and Ti (III) exist, but these are readily oxidized to the tetravalent state by air, water, and other oxidizing agent. The ionization potentials indicate that the Ti^{4+} ion would not be expected to exist and, indeed, Ti (IV) compounds are generally covalent. Titanium is able to expand its outer group of electrons and can form a large number of addition compounds by coordination other substances having donor atom, e.g., oxygen or sulfur. The most important commercial forms are titanium (IV) oxide and titanium metal.

Thermochemical data

Thermochemical data of titanium (IV) oxide and other titanium compounds are described. Data relating to changes of state of selected titanium compounds are listed in Table 3.1. Table 3.2 gives values for heat of formation, free energy of formation, and entropy of a number of titanium compound at two temperature, 298 K and 1300K.

Table 3.1 Thermal data for changes of state of titanium compounds

Compound	Properties	Temperature,K	$\Delta H, \text{kJ/mol}$
TiCl ₄	melting point	249.05	9.966
	Boiling point	409	35.77
TiCl ₃	sublimation temperature	1104.1	166.15
TiCl ₂	sublimation temperature	1591.5	248.5
TiI ₄	melting point	428	19.23±0.63
	Boiling point	652.6	56.48±2.09
TiF ₄	sublimation temperature	558.6	97.78±0.42
TiBr ₄	melting point	311.4	12.89
	Boiling point	504.1	45.19
TiO ₂	phase change (anatase to rutile)		ca-12.6

3.2 Titanium (IV) oxide (Sornnarong Theinkeaw, 2000 and Fujishima *et al.*, 1999)

Physical and chemical properties

Titanium dioxide may take on any of the following three crystal structures: rutile, which tends to be more stable at high temperatures and thus is sometimes found in igneous rocks, anatase, which tends to be more stable at lower temperatures (both belonging to the tetragonal crystal system), and brookite, which is usually found only in minerals and has a structure belonging to the orthorhombic crystal system. The titanium dioxide use in industrial products, such as paint, is almost a rutile type. These crystals are substantially pure titanium dioxide but usually amount of impurities, e.g., iron, chromium, or vanadium, which darken them. A summary of the crystallographic properties of the three varieties is given in Table 3.3.

Although anatase and rutile are both tetragonal, they are not isomorphous (Figure 3.1). The two tetragonal crystal types are more common because they are easy to make. Anatase occurs usually in near-regular octahedral, and rutile forms slender prismatic crystal, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titanium.

The three allotropic forms of titanium dioxide have been prepared artificially but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystal. The transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol), but the rate of transformation is greatly affected by temperature and by the presence of other substance which may either catalyze or inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is ca. 973 K, but this is not a transition temperature. The change is not reversible; ΔG for the change from anatase to rutile is always negative (see Table 3.1 and 3.2 for thermodynamic data).

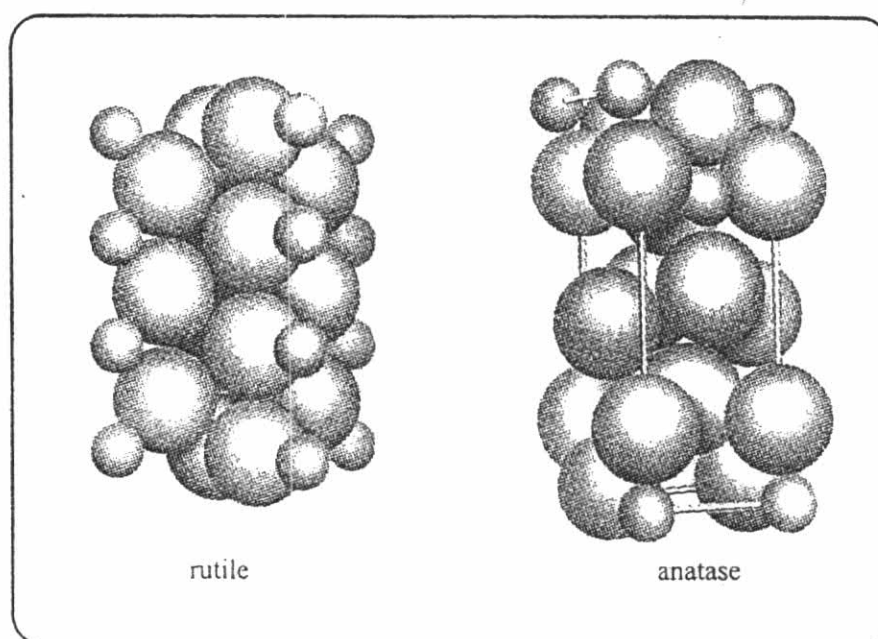


Figure 3.1 Crystal structure of TiO₂. (Fujishima *et al.*, 1999)

Heating amorphous titanium (IV) oxide, prepared from alkyl titanates of sodium titanate with sodium or potassium hydroxide in an autoclave at 200 to 600°C for several days has produced brookite. The important commercial forms of titanium dioxide are anatase and rutile, and these can readily be distinguished by X-ray diffraction spectrometry.

Since both anatase and rutile are tetragonal, they are both anisotropic, and their physical properties, e.g. refractive index, vary according to the direction relative to the crystal axes. In most applications of these substances, the distinction between

crystallographic directions is lost because of the random orientation of large numbers of small particles, and it is mean value of the property that is significant.

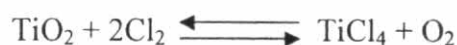
Table 3.2 Crystallographic properties of anatase, brookite, and rutile.

<i>Properties</i>	Anatase	Brookite	Rutile
Crystal structure	Tetragonal	Orthorhombic	Tetragonal
Optical	Uniaxial, negative	Biaxial, positive	Uniaxial, negative
Density, g/cm ³	3.9	4.0	4.23
Harness, Mohs scale	5 ^{1/2} – 6	5 ^{1/2} – 6	7 – 7 ^{1/2}
Unit cell	D _{4a} ¹⁹ .4TiO ₂	D _{2h} ¹⁵ .8TiO ₂	D _{4h} ¹² .3TiO ₂
Dimension, nm			
a	0.3758	0.9166	0.4584
b		0.5436	
c	0.9514	0.5135	2.953

Measurement of physical properties, in which the crystallographic directions are taken into account, may be made of both natural and synthetic rutile, natural anatase crystals, and natural brookite crystals. Measurements of the refractive index of titanium dioxide must be made by using a crystal that is suitably orientated with respect to the crystallographic axis as a prism in a spectrometer. Crystals of suitable size of all three modifications occur naturally and have been studied. However, rutile is the only form that can be obtained in large artificial crystals from melts. The refractive index of rutile is 2.75. The dielectric constant of rutile varies with direction in the crystal and with any variation from the stoichiometric formula, TiO₂; an average value for rutile in powder form is 114. The dielectric constant of anatase powder is 48.

Titanium dioxide is thermally stable (mp 2128 K) and very resistant to chemical attack. When it is heated strongly under vacuum, there is a slight loss of oxygen corresponding to a change in composition to TiO_{1.97}. The product is dark blue but reverts to the original white color when it is heated in air.

Hydrogen and carbon monoxide reduce it only partially at high temperatures, yielding lower oxides or mixtures of carbide and lower oxides. At ca. 2273 K and under vacuum, carbon reduces it to titanium carbide. Reduction by metal, e.g., Na, K, Ca, and Mg, is not complete. Chlorination is only possible if a reducing agent is present; the position of equilibrium in the system is



The reactivity of titanium dioxide towards acids is very dependent on the temperature to which it has been heated. For example, titanium dioxide that has been prepared by precipitation from a titanium (IV) solution and gently heated to remove water is soluble in concentrated hydrochloric acid. If the titanium dioxide is heated to ca. 1173 K, then its solubility in acids is considerably reduced. It is slowly dissolved by hot concentrate sulfuric acid, the rate of salvation being increased by the addition of ammonium sulfate, which raises the boiling point of the acid. The only other acid in which it is soluble is hydrofluoric acid, which is used extensively in the analysis of titanium dioxide for trace elements. Aqueous alkalies have virtually no effect, but molten sodium and potassium hydroxides, carbonates, and borates dissolve titanium dioxide readily. An equimolar molten mixture of sodium carbonate and sodium borate is particularly effective as is molten potassium pyrosulfate.

3.3 Preparation procedure

Large surface area titanium dioxide powders have been prepared by several methods. The physical and chemical properties of titanium dioxides are quite different by the process of preparation.

3.3.1 Precipitation method

Precipitation method involves the growth of crystals from a solvent of different composition to the crystal. The solvent may be one of the constituents of the desired crystals, e.g., crystallization of salt hydrate crystals using water as the solvent, or the solvent may be entirely separate liquid element or compound in which the crystals of interest are partially soluble, e.g., SiO_2 and various high melting silicates

may be precipitated from low melting borate or halide melts. In these cases, the solvent melts are sometimes referred to as fluxed since they effectively reduce the melting point of the crystals by a considerable amount.

The method has recently been used to grow crystals of titanium (IV) oxide using titanium tetrachloride as starting material. Titanium (IV) oxide which, after washing and drying at 383 K, can be calcined at 1073 K to remove combined water and chloride, according to the stoichiometric relation as follows:



This method used involves precipitation from titanium tetrachloride as hydrated titanium (IV) oxide conversion of the precipitate to the double oxalate, recrystallization of this from methanol and subsequent calcinations.

3.3.2 Sol-gel method

To prepare a solid using the sol-gel method, a sol is first prepared from suitable reactants in a suitable liquid. Sol preparation can either be simply the dispersal of an insoluble solid or addition of a precursor which reacts with the solvent to form a colloid product. A typical example of the first is the dispersal of oxides or hydroxides in water with the pH adjusted so that the solid particles remain in suspension rather than precipitate out. A typical example of the second method is the addition of metal alkoxides to water. The alkoxides are hydrolyzed giving the oxide as a colloidal product. The sol is then either treated or simply left to form a gel. To obtain a final product, the gel is heated. This heating serves several purposes—it removes the solvent, it decomposes anions such as alkoxides or carbonates to give oxides, it allows rearrangement of the structure of the solid and it allows crystallization to occur.

3.3.3 Hydrothermal method (West, 1997)

The method involves heating the reactants in water/steam at high pressures and temperatures. The water performs two roles, as a pressure-transmitting medium

and as a solvent, in which the solubility of the reactants is P, T-dependent. In addition, some or all of the reactance are partially soluble in the water under pressure and this enables reaction to take place in, or with the aid of, liquid and/or vapor phases. Under these conditions, reactions may occur that, in the absence of water, would occur only at much high temperatures. The method is therefore particularly suited for the synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

The design of hydrothermal equipment is basically a tube, usually of steel, closed at one end. The other end has a screw cap with a gasket of soft copper to provide a seal. Alternatively, the 'bomb' may be connected directly to an independent pressure source, such as a hydraulic ram; this is known as the 'cold seal' method. The reaction mixture and an appropriate amount of water are placed inside the bomb, which then sealed and placed inside an oven at the required temperature, usually at a temperature in the range 100-500°C. Pressure is controlled either externally or by the degree of filling in a sealed bomb. By making use of the P/T 'phase diagram', Figure 3.3(a); curve AB is the saturated steam curve and separates water (above) from steam (below); at temperatures above 374°C, point B, the water is in the supercritical condition and there is no distinction between liquid and vapor states.

The applications of the hydrothermal method are:

(a) Synthesis of new phases: calcium silicate hydrate.

Hydrothermal methods have been used successfully for the synthesis of many materials. A good example is the family of calcium silicate hydrates, many of which are important components of set cement and concrete. Typically, lime, CaO and quartz, SiO₂, are heated with water at temperatures in the range 150 to 500°C and pressure of 0.1 to 2 kbar. Each calcium silicate hydrate has, for its synthesis, optimum preferred conditions of composition of starting mix, temperature, pressure and time. For example, xonolite, Ca₆Si₆O₁₇(OH)₂, may be prepared by heating equimolar mixtures of CaO and SiO₂ at saturated steam pressures in the range 423 K to 623 K.

(b) Growth of single crystals.

For the growth of single crystals by hydrothermal methods it is often necessary to add a mineralizer. A mineralizer is any compound added to the aqueous solution that speeds up its crystallization. It usually operates by increasing the solubility of the solute through the formation of soluble species that would not usually be present in the water. For instance, the solubility of quartz in water at 673 K and 2 kbar is too small to permit the recrystallization of quartz, in a temperature gradient, within a reasonable space of time. On addition of NaOH as a mineralizer, however, large quartz crystals may be readily grown. Using the following conditions, crystals of kilogram size have been grown: quartz and 1.0 M NaOH solution are held at 673 K and 1.7 kbar; at this temperature some of the quartz dissolves. A temperature gradient is arranged to exist in the reaction vessel and at 633 K the solution is supersaturated with respect to quartz, which precipitates onto a seed crystal. In summary, therefore, quartz dissolves in the hottest part of the reaction vessel, is transported throughout the vessel via convection currents and is precipitated in cooler parts of the vessel where its solubility in water is lower. Quartz single crystals are used in many devices in radar and sonar, as piezoelectric transducers, as monochromators in X-ray diffraction, etc. Annual world production of quartz single crystals, using hydrothermal and other methods, is currently a staggering 600 tons.

Using similar methods, many substances have been prepared as high quality single crystals, e.g. corundum (Al_2O_3) and ruby (Al_2O_3 doped with Cr^{3+}).

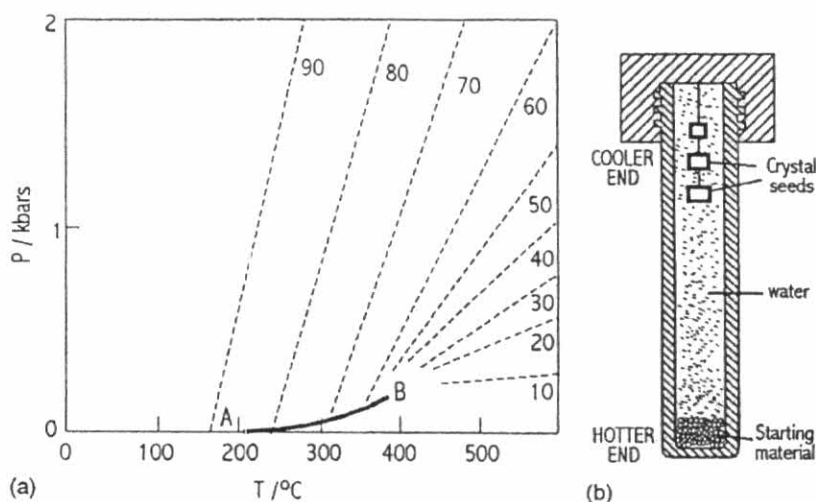


Figure 3.2 (a) Pressure-temperature relations for water at constant volume, dashed curves represent pressures developed inside a close vessel; numbers represent the percentage degree of filling of the vessel by water at ordinary P, T. (b) Schematic hydrothermal bomb used for crystal growth.

3.3.4 Glycothermal and solvothermal method

Glycothermal method and solvothermal method have been developed for synthesis of metal oxide and binary metal oxide by using glycol and solvent as the reaction medium, respectively. The use of glycol or solvent instead of water in the hydrothermal method produced the different form of intermediate phase and the stability of such intermediate phase was not strong. Instability of the intermediate phase gives a large driving force to the formation of product under quite mild condition. The preparation method is described in the experimental section, Chapter IV.

3.4 Single crystal (McGraw-Hill encyclopedia of science & technology, 1997)

In crystalline solids the atoms or molecules are stacked in a regular manner, forming a three-dimensional pattern, which may be obtained by a three-dimensional repetition of a certain pattern unit called a unit cell. When the periodicity of the pattern extends throughout the certain piece of material, one speaks of a single crystal.

A single crystal is formed by the growth of a crystal nucleus without secondary nucleation or impingement on other crystal.

3.4.1 Growth techniques

Among the most common methods of growing single crystals are those of P. Bridgeman and J. Czochralski. In the Bridgeman method the material is melted in a vertical cylindrical vessel, which tapers conically to a point at the bottom. The vessel then is lowered slowly into a cold zone. Crystallization begins in the tip and continues usually by growth from the first formed nucleus. In the Czochralski method a small single crystal (seed) is introduced into the surface of the melt and then drawn slowly upward into a cold zone. Single crystals of ultrahigh purity have been grown by zone melting. Single crystals are also often grown by bathing a seed with a supersaturated solution, the supersaturation being kept lower than necessary for sensible nucleation.

When grown from a melt, single crystals usually take the form of their container. Crystals grown from solution (gas, liquid, or solid) often have a well-defined form, which reflects the symmetry of the unit cell. For example, rock salt or ammonium chloride crystals often grow from solutions in the form of cubes with faces parallel to the 100 planes of the crystal, or in the form of octahedrons with faces parallel to the 111 planes. The growth form of crystals is usually dictated by kinetic factors and does not correspond necessarily to the equilibrium form.

3.4.2 Physical properties

Ideally, single crystals are free from internal boundaries. They give rise to a characteristic x-ray diffraction pattern. For example, the Laue pattern of a single crystal consists of a single characteristic set of sharp intensity maxima. Many types of single crystal exhibit anisotropy, that is, a variation of some of their physical properties according to the direction along which they are measured. For example, the electrical resistivity of a randomly oriented aggregate of graphite crystallites is the same in all directions. The resistivity of a graphite single crystal is different, however, when measured along crystal axes. This anisotropy exist both for structure-sensitive properties, which are strongly affected by crystal imperfections (such as cleavage and

crystal growth rate), and structure-insensitive properties, which are not affected by imperfections (such as elastic coefficients).

Anisotropy of a structure-insensitive property is described by a characteristic set of coefficients, which can be combined to give the macroscopic property along any particular direction in the crystal. The number of necessary coefficients can often be reduced substantially by consideration of the crystal symmetry, whether anisotropy, with respect to a given property, exists depends on crystal symmetry. The structure-sensitive properties of crystals (for example, strength and diffusion coefficients) seem governed by internal defects, often on an atomic scale.

3.5 Photocatalytic process [Fujishima *et al.*, (1999)]

The primary photocatalytic process occurring upon irradiation of a semiconductor catalyst. A semiconductor (SC) is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB), and the lower empty band called conduction band (CB), are separated by a band gap. The magnitude of the fixed energy gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band in its intrinsic state. The band gap also defines the wavelength sensitivity of the semiconductor to irradiation [Fox and Dulay (1993)]. When a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the valence band is promoted to the conduction band with simultaneous generation of an electronic vacancy or "hole" (h⁺) in the valence band. Figure 3.3 shows the photocatalytic process occurring on an illuminated semiconductor particle.

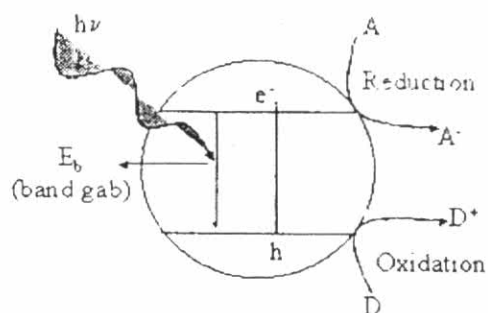
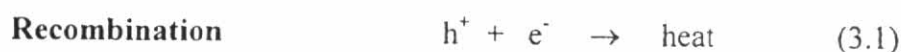


Figure 3.3 The photocatalytic process occurring on an illuminated semiconductor particle [Litter (1999)].

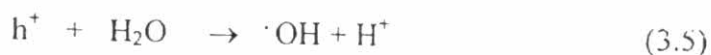
In most materials that are electrically conductive, i.e. metals, two types of carriers - electrons (e^-) and holes (h^+) - immediately recombine on the surface or the bulk of particle in a few nanoseconds and the energy dissipated as heat (equation (3.1)). On semiconductor such as titanium dioxide, however, they survive for longer periods of time to allow these carriers can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle (equations (3.2), (3.3), (3.4)) [Litter (1999)].



Thereby, subsequent oxidation and reduction can be initiated.

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

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



The hydroxyl radicals can then react with organic components, initially producing free radicals (unstable molecules that have one unpaired electron). When molecular oxygen is present (reactions always occur in the presence of oxygen from the air in the use of the photocatalyst for environment), because it also has unpaired electrons, it likes to react with these free radicals producing organic peroxy radicals, which, in addition to containing an unpaired electron, also now contain two oxygens. These radicals can then take part in chain reactions. In a short time, organic compounds are completely degraded, i.e. converted into carbon dioxide and water.

Meanwhile, the electrons that are produced in the electron-hole pairs are also put to work. These electrons are used to reduce (i.e., add electrons) to oxygen in air. Because oxygen is easier to reduce than water, it will tend to be reduced, producing the superoxide radical anion (O_2^-) (equation 3.7).



The superoxide anion attaches itself to the peroxy radicals mentioned in the previous paragraph. The resulting unstable product now contains at least four oxygens and can decompose to produce a carbondioxide molecule. On the molecular scale, superoxide acts like a "supercharge", greatly increasing the oxidation process, which is in fact a form of combustion. In addition to this mechanism, another interpretation proposed recently is that the formation in air of so-called atomic oxygen (O), which is extremely reactive, directly acts on the carbon bonds in organic material

3.6 The main factors involved in photocatalytic process

There are two main factors involved in photocatalytic process. Photocatalysis is the combination of photochemistry and catalysis, it implies that light and catalyst are the main factors, which initiate the chemical transformation, oxidation and

reduction reaction. Light is not only one, which can work effectively, but it, can work effectively when teamed up with catalyst especially titanium dioxide catalyst.

3.6.1 Photocatalyst [Fujishima *et al.* (1999)]

Catalyst that used in photocatalytic process usually called "photocatalyst". In the previous section, photochemical process involves in electronic structure of photocatalyst.

Atoms have discrete energy levels for their electrons. Molecules often contain like atoms but the Pauli exclusion principle forbids identical quantum numbers in all respects, resulting in the "splitting" of a given atomic energy level into a set of closely spaced levels typically of order of the numbers of atoms involves energy levels split so finely that a so-called "band" structure of allowed energies (quantum states) emerges, with infinitesimal or virtually continual distribution of energy levels within a given "orbital". For a semiconductor such as titanium dioxide (TiO_2), the highest filled band is termed the valence band, and the lowest unoccupied level is the conduction band. The separation of the valence band top from the conduction band bottom is termed the band gap [Ollis (1998)].

As already mentioned, the reaction starts with the exposure of photocatalyst to light. After light is absorbed by photocatalyst, two types of carriers - electron (e^-) and holes (h^+) - are generated. Unlike metals oxide, a semiconductor oxide is good photocatalyst because of the long live both of these carriers. For this reason semiconductor oxides are used in photocatalytic process such as TiO_2 , ZnO , SrTiO_3 , K_4NbO_2 , Fe_2O_3 and SnO_2 .

Especially titanium dioxide (TiO_2), titanium dioxide is one of the most basic materials in our daily life. It also has been used widely in photocatalytic process because of its radiation stability, non-toxicity and good reactivity [Alberici (1997)]. Naturally, the type of titanium dioxide that used as a pigment is different from that used as a photocatalyst. Might say that titanium dioxide has two aspects but one set of

properties. Titanium dioxide is a semiconductor and is chemically activated by light energy. Its photoactivity tends to decompose organic materials that come in contact with it.

One of the reasons for the anatase type titanium dioxide is more photoactive than the rutile type may lie in the differences in their so-called energy band structures.

The band gap energy of a semiconductor is the minimum energy of light required to make the material electrically conductive or in the other words, to get the electrons excited enough to get moving. For anatase -type titanium dioxide this energy is 3.2 electron volts (eV), which corresponds to UV light (388 nanometers), while the band gap energy for the rutile type is 3.0 eV, corresponding to violet light (413 nanometers). In more technical terminology, the band gap energy for a semiconductor indicates the minimum energy of light necessary to produce conduction band (CB) electrons, which, for example, can give rise to electrical conductivity (photoconductivity) and valence band (VB) "holes," which are actually the absence of electron. These holes can react with water to produce the highly reactivity hydroxyl radical (OH^\cdot). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials. The level of the CB for anatase turns out to be 0.2 eV higher than that for rutile (figure 3.4).

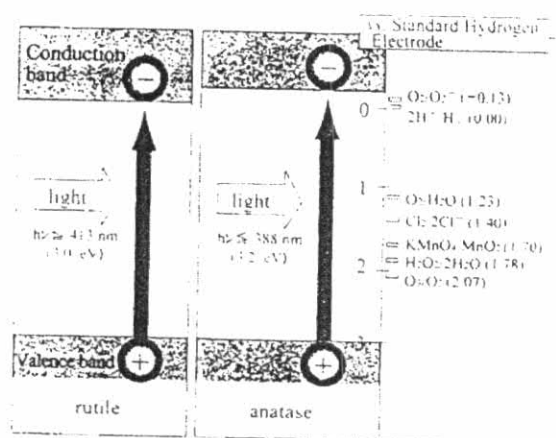


Figure 3.4 Energy diagram for TiO_2 and relevant redox potentials [Fujishima *et al.* (1999)].

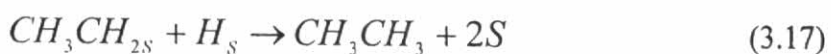
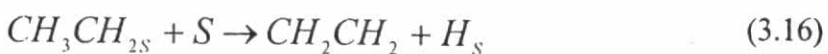
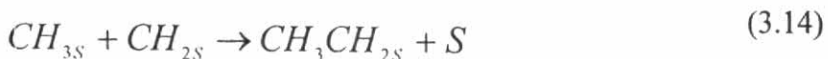
3.7 Fischer-Tropsch synthesis (FTS)

Fischer-Tropsch synthesis (FTS) that discovered by Fischer and Tropsch over 80 years ago, as an alternate process, can convert the synthesis gas (H_2/CO) derived from carbon sources such as coal, peat, biomass and natural gas, into hydrocarbons and oxygenates. During the past decades, FTS has been developed continuously by many researchers, although the rise and fall in research intensity on this process has been highly related to the demands for liquid fuels and relative economics. This synthesis is basically the reductive polymerization (oligomerization) of carbon monoxide by hydrogen to form organic products containing mainly hydrocarbons and some oxygenated products in lesser amounts. The main reactions of FTS are:



Equation (3.1) is the formation of hydrocarbons higher than C1, and the equation (3.2) is methanation. The water-gas shift reaction, which is undesirable for natural gas conversion, is shown in equation (3.3). The Boudouard reaction, which results in carbon deposition on the catalyst surface, is shown in equation (3.4).

The mechanism consists of surface steps in five categories: (1) the adsorption of reactants (H_2 and CO); (2) chain initiation; (3) chain propagation; (4) chain termination and desorption of products; (5) readsorption and secondary reaction of olefins. Depending upon the type of catalyst used, promoters, reaction conditions (pressure, temperature and H_2/CO ratios), and type of reactors, the distribution of the molecular weight of the hydrocarbon products can be noticeably varied.



Normally, catalysts used for this synthesis are group VIII metals. By nature, the hydrogenation activity increases in order of $Fe < Co < Ni < Ru$. Ru is the most active. Ni forms predominantly methane, while Co yields much higher ratios of paraffins to olefins and much less oxygenated products such as alcohols and aldehydes than Fe does. The reaction mechanism of FTS on Co, Fe and Ru catalysts has been reviewed by Bell (1091). A general and reasonably widely accepted

mechanism for FTS on Group VIII metals from his review is show below. This mechanism involves: (1) the adsorption and dissociation of CO (equation 3.5 and 3.6) and the dissociative adsorption of H₂ (equation 3.7) all in a quasi-equilibrium; (2) surface reactions of O and H_{atoms} to form water and of O atoms and CO to form CO₂ (equation 3.8 and 3.9); (3) reaction of adsorbed carbon and hydrogen atoms to form adsorbed CH_x species (reactions 3.10 and 3.12); (4) the hydrogenation of adsorbed methyl radicals to form methane (equation 3.13); (5) chain growth through the addition of methylene groups to methyl and ethyl radicals (equations 3.14 and 3.15); and (6) the termination of an ethyl radical to form ethylene or hydrogenation to form ethane (equations 3.16 and 3.17).

With regards to the operating conditions, usually higher pressures will result in higher rates. There are basically three reactor types used for FTS: (1) fixed bed, (2) fluid bed, and (3) slurry bed. Because of the high exothermicity of the reaction (142 kJ mol⁻¹ of reacted carbon), all three reactor types are carefully designed for rapid heat removal using a combination of various techniques including heat exchange, recycle, fluidized and slurry beds, and stage systems. The attributes, advantages and limitations of each of these reactors is different as summarized below.

Fixed-bed reactor: In a typical fixed bed reactor heat is removed by heat exchangers or by production steam. To facilitate temperature control while maximizing conversion and linear gas velocity, a portion of the tail gas is recycle, typically with a recycle: fresh volume ratio of about 2. Since the heat exchanger design favors lower temperatures of operation (220-250°C), predominantly higher hydrocarbons including gasoline, diesel fuel and waxes are produced. *Fluid-bed reactors:* Fluid beds are of generally two types, fixed and circulating. This reactor has better heat removal (near isothermal operation), higher reaction temperature (exit temperature of 340°C) and hence higher selectivities for lighter products, alkenes, branched products and aromatics, and higher throughput per volume of reactor relative to the fixed bed. With on-line catalyst removal and addition, process runs are much longer than for the fixed bed. Nevertheless, the fluid-bed reactor is a more complex system requiring an attrition-resistant catalyst and grater system maintenance. Moreover, process conditions and temperature must be adjusted to limit production of heavy hydrocarbons which would condense on the catalyst and

defluidize the bed. *Slurry-bed reactor*: slurry-bed reactor, in which a finely divided catalyst is suspended in a heavy oil by gas bubbling up through the slurry, have been investigated fairly for FTS by Koelber, Sasol and Rheinpreussen-Koppers. This reactor type has the advantages of (1) capability of operating at low $H_2:CO$ ratios without problems with carbon deposition, (2) very efficient heat transfer and uniform temperature, (3) high catalyst efficiency/performance, and (4) simple construction. Although some of the operating problems in using a slurry bed reactor FTS are daunting, such as high slurry viscosities, particle settling, catalyst liquid-separation and possible gas-liquid mass transport limitations. Slurry-bed reactors are better than fixed-bed reactors for FTS since they can remove heat from this exothermic synthesis, allowing better temperature control.

The current main goal in using FTS is to obtain high molecular weight, straight chain hydrocarbons. However, methane and other light hydrocarbons are always present as less desirable products from the synthesis. According to the Anderson-Schulz-Flory (ASF) product distribution, typically 10 to 20% of products from the synthesis are usually light hydrocarbon (C_1-C_4) these light alkanes have low boiling points and exist in the gas phase at room temperature, which is inconvenient for transportation. Many attempts have been made to minimize these byproducts and increase the yield of long chain liquid hydrocarbons by improving chain growth probability. It would be more efficient to be able to convert these less desirable products into more useful forms, rather than re-reforming them into syngas and recycling them.

3.8 Cobalt (Young 1960; Othmer, 1991)

3.8.1 General

Cobalt, a transition series metallic element having atomic number 27, is similar to silver in appearance.

Cobalt and cobalt compounds have expanded from use colorants in glasses and ground coat frits for pottery to drying agents in paints and lacquers, animal and human nutrients, electroplating materials, high temperature alloys, hard facing alloys,

high speed tools, magnetic alloys, alloys used for prosthetics, and used in radiology. Cobalt is also as a catalyst for hydrocarbon refining from crude oil for the synthesis of heating fuel.

3.8.2 Physical Properties

The electronic structure of cobalt is $[\text{Ar}] 3d^7 4s^2$. At room temperature the crystalline structure of the α (or ϵ) form, is close-packed hexagonal (cph) and lattice parameters are $a = 0.2501$ nm and $c = 0.4066$ nm. Above approximately 690 K, a face-centered cubic (fcc) allotrope, the γ (or β) form, having a lattice parameter $a = 0.3544$ nm, becomes the stable crystalline form. Physical properties of cobalt are listed in Table 3.3.

The scale formed on unalloyed cobalt during exposure to air or oxygen at high temperature is double-layered. In the range of 573-1173 K, the scale consists of a thin layer of mixed cobalt oxide, Co_3O_4 , on the outside and cobalt (II) oxide, CoO , layer next to metal. Cobalt (III) oxide, Co_2O_3 , may be formed at temperatures below 573 K. Above 1173 K, Co_3O_4 decomposes and both layers, although of different appearance, are composed of CoO only. Scales formed below 873 K and above 1023 K appear to be stable to cracking on cooling, whereas those produced at 873-1023 K crack and flake off the surface.

Cobalt forms numerous compounds and complexes of industrial importance. Cobalt, atomic weight 58.933, is one of the three members of the first transition series of Group 9 (VIII B). There are thirteen known isotopes, but only three are significant: ^{59}Co is the only stable and naturally occurring isotope; ^{60}Co has a half-life of 5.3 years and is a common source of γ -radioactivity; and ^{57}Co has a 270-d half-life and provides the γ -source for Mössbauer spectroscopy.

Table 3.3 Physical properties of cobalt (Othmer, 1991)

Property	Value
atomic number	27
atomic weight	58.93
transformation temperature, °C	417
heat of transformation, J/g ^a	251
melting point, °C	1493
latent heat of fusion, ΔH_{fus} J/g ^a	395
boiling point, °C	3100
latent heat of vaporization at bp, ΔH_{vap} kJ/g ^a	6276
specific heat, J/(g·°C) ^a	
15-100°C	0.442
molten metal	0.560
coefficient of thermal expansion, °C ⁻¹	
cph at room temperature	12.5
fcc at 417°C	14.2
thermal conductivity at 25 °C, W/(m·K)	69.16
thermal neutron absorption, Bohr atom	34.8
resistivity, at 20 °C ^b , 10 ⁻⁸ Ω·m	6.24
Curie temperature, °C	1121
saturation induction, $4\pi I_s$, T ^c	1.870
permeability, μ	
initial	68
max	245
residual induction, T ^c	0.490
coercive force, A/m	708
Young's modulus, Gpac	211
Poisson's ratio	0.32

Table 3.3 Physical properties of cobalt (cont.)

Property	Value		
Hardness ^f , diamond pyramid, of %Co	99.9	99.98 ^c	
At 20 °C	225	253	
At 300 °C	141	145	
At 600 °C	62	43	
At 900 °C	22	17	
strength of 99.99 %cobalt, MPa ^g	as cast	annealed	sintered
tensile	237	588	679
tensile yield	138	193	302
compressive	841	808	
compressive yield	291	387	

^aTo convert J to cal, divided by 4.184.

^bconductivity = 27.6 % of International Annealed Copper Standard.

^cTo convert T to gauss, multiply by 10⁴.

^dTo convert GPa to psi, multiply by 145,000.

^eZone refined.

^fVickers.

^gTo convert MPa to psi, multiply by 145.

Cobalt exists in the +2 or +3 valance states for the major of its compounds and complexes. A multitude of complexes of the cobalt (III) ion exists, but few stable simple salt are known. Octahedral stereochemistries are the most common for cobalt (II) ion as well as for cobalt (III). Cobalt (II) forms numerous simple compounds and complexes, most of which are octahedral or tetrahedral in nature; cobalt (II) forms more tetrahedral complex than other transition-metal ions. Because of the small stability difference between octahedral and tetrahedral complexes of cobalt (II), both can be found equilibrium for a number of complexes. Typically, octahedral cobalt (II) salts and complexes are pink to brownish red; most of the tetrahedral Co (II) species are blue.

3.8.3 Cobalt Oxides

Cobalt has three well-known oxides:

Cobalt (II) oxide, CoO , is an olive green, cubic crystalline material. Cobalt (II) oxide is the final product formed when the carbonate or the other oxides are calcined to a sufficiently high temperature, preferably in a neutral or slightly reducing atmosphere. Pure cobalt (II) oxide is a difficult substance to prepare, since it readily takes up oxygen even at room temperature to re-form a higher oxide. Above about 1123 K, cobalt (II) oxide form is the stable oxide. The product of commerce is usually dark gray and contains 75-78 wt. % cobalt. Cobalt (II) oxide is soluble in water, ammonia solution, and organic solvents, but dissolves in strong mineral acids. It is used in glass decorating and coloring and is a precursor for the production of cobalt chemical.

Cobalt (III) oxide, Co_2O_3 , is formed when cobalt compounds are heated at a low temperature in the presence of an excess of air. Some authorities told that cobalt (III) oxide exists only in the hydrate form. The lower hydrate may be made as a black powder by oxidizing neutral cobalt solutions with substances like sodium hypochlorite. Co_2O_3 or $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is completely converted to Co_3O_4 at temperatures above 533 K. Co_3O_4 will absorb oxygen in a sufficient quantity to correspond to the higher oxide Co_2O_3 .

Cobalt oxide, Co_3O_4 , is formed when cobalt compounds, such as the carbonate or the hydrated sesquioxide, are heated in air at temperatures above approximately 538 K and not exceeding 1073 K.

3.9 Co-based Catalysts

Supported cobalt (CO) catalysts are the preferred catalysts for the synthesis of heavy hydrocarbons from natural gas based syngas (CO and H_2) because of their high Fischer-Tropsch (FT) activity, high selectivity for linear hydrocarbons and low activity for the water-gas shift reaction. It is known that reduced cobalt metal, rather than its oxides or carbides, is the most active phase for CO hydrogenation in such

catalysts. Investigations have been done to determine the nature of cobalt species on various supports such as alumina, silica, titania, magnesia, carbon, and zeolites. The influence of various types of cobalt precursors used was also investigated. It was found that the used of organic precursors such as CO (III) acetyl acetate resulting in an increase of CO conversion compared to that of cobalt nitrate.

3.9.1 Co-Titanate Formation

Cobalt-support compound formation in titania supported Cobalt catalysts was investigated by Jongsomjit *et al.* (2003). It is known that the formation of Cobalt and oxide supports during standard reduction is facilitated by the presence of water vapor and resulted in a less active catalyst. The reduction peaks of cobalt oxides during TPR were shifted to higher temperature as the amount of water vapor increased suggesting an increase in the formation of more difficult to reduced Co-support species. However, the Co-SCF in titania support is in highly dispersed form that could not be detected by XRD due probably to the migration of cobalt into the titania matrix. The Co- SCF in titania is non-reducible at temperatures < 1073 K during TPR.