CHAPTER II

LITERATURE SURVEY

In this research, the versatile properties of surface-active-agent were employed to prepare the thermodynamically stable W/O microemulsion for synthesis of submicron silica particle from the TBOS hydrolysis via an aqueous ammonia based catalyst. The natures of W/O microemulsion system, general roles, and physico-chemical mechanisms of silica particle formation are described briefly in this chapter.

2.1 Characteristics and Properties of Surfactant Molecule

The structure of surfactants or amphiphilic molecules is comprised mainly of hydrophilic (head group) and hydrophobic (tail group). The head group usually contains ionic molecules (e.g., SO_3^-) or high polar group with hetero-atoms (such as nitrogen, oxygen, sulfur and phosphorus) for ionic surfactants. On the other hand, if head groups contain hydrogen-bonding functional groups (e.g., OR, R, alkyl group), it is known as nonionic surfactants. Since hydrophilic portions are polar, they can assimilate in polar media. These functional groups have a physical volume defined by the summation of the atomic volume of their constituent atoms which is typically defined in the terms of van der Waals radii. The polar head groups of amphiphilies can associate with themselves or other polar molecules by physical-chemical interaction, such as electrostatic forces, hydrogen bonding, dipole-dipole interactions, and electron-donor acceptor interactions (Chang and Fogler, 1996). Due to the aqueous components presented in the system, these head groups are attracted

with water molecules by either the electrostatic or hydration forces. Electrostatic repulsion occurs between ionic molecules in aqueous component and ionic head groups those have same sign of charge (i.e., positive or negative). The hydration of the head group layer of surfactants by water also results in the separation of head groups from one another. When the number of functional groups of surfactant increases, the area occupied by surfactant head groups at the oil-water interface will also increase. This phenomenon is occurred due to the repulsive interactions and the actual physical volume of functional groups (Chang and Fogler, 1996). On the other hand, the tail groups are generally contained with long-chain of aliphatic hydrocarbon ($-CH_2-$) in linear or branched structures. Furthermore, it is less composed with halogenated or oxygenated or siloxane in the hydrocarbon chain. These chains assemble into nonpolar media, due to the hydrophobic habit. The tail groups can associate with themselves or other molecules via only weak London van der Waals attractions. Their surfactants encompass of an oil-water interface area those changes throughout its conformation. Due to the effect of this conformational change and the actual physical volume of the aliphatic chains, the area occupied by the tail group of surfactants at the interface also increases with the increasing in length of tail groups (Evans, 1994).

The chemical structure of surfactant molecule can affect the phase behavior of the system containing surfactant, oil, and water. The phase behavior can be reflected by the hydrophile-lipophile balance (HLB). The HLB indicates a number of emulsification behavior and related to the balance between the hydrophilic and hydrophobic portions of the surfactant molecule. The expected surfactant behavior can be characterized from the definition of the HLB value. If the HLB value is low then hydrophilicity will be low or W/O emulsion feature will be easily formed, and vice versa. In this work, nonionic surfactants with polyoxyethylene head groups and alkylbenzene tail groups were used to

prepare the single-phase W/O microemulsion media for silica particle formation. The HLB number for this system was less than 10. Also, the number of carbon atom on the tail group of these surfactants is approximately twice, when compared with the number of combination of oxylene groups in the head group (Rosen, 1989).

2.2 Nature of W/O Microemulsions

In the emulsion formation, one of the two immiscible liquids is generally broken up into droplets and dispersed into the second liquid. The dispersed droplets are in constant motion which causes frequent collisions among them. Regarding to the unlike properties mentioned above of the head and tail groups, the surfactant molecules are used to increase the interfacial free energy of these liquids. The head and tail groups are oriented toward the polar and non-polar liquids, respectively. The head groups are associated themselves at the interface between both liquids with physical-chemical bonding. The surfactant molecules that are adsorbed at the liquid-liquid interface as an oriented interfacial film performs two functions (Solans and Kunieda, 1995):

(1) It reduces the interfacial tension between the two insoluble liquids and consequently the thermodynamic instability of the system is obtained resulting from the increase in the interfacial area between the two phases.

(2) It decreases the rate of coalescence of the dispersed liquid droplets by forming mechanical, steric, and electrical barriers around them.

The steric and electrical barriers inhibit the close approach of one particle to another. The mechanical barrier increases the resistance of the dispersed particles to mechanical shock and prevents them from coalescencing when they do collide.

Microemulsion is the transparent solution containing two immiscible liquids with 10-100 nm in diameter of dispersed media. This solution is generally obtained upon mixing the ingredients gently. Microemulsions may be water-external (O/W) or oil-external (W/O), or both. All of these happen due to the nature of surfactant, additive components (e.g., inorganic molecules, alcohol), type of oil, temperature, and the contained portion of water and oil. Whether one considers a microemulsion to be a solution in one liquid of micelles swollen by solubilized second liquid or a dispersion of tiny droplets of one liquid in a second liquid, the interfacial tension of the microemulsion against both of these liquids must be close to zero. The compartmentalized characteristics and size of microemulsion (droplet radius) can be controlled by changing composition parameters, such temperature, salinity, the types of surfactant and oil media (Chang and Fogler, 1997).

The formation of a single-phase W/O microemulsion solution can be easily started with a nonpolar oil containing surfactants. In this solution, the association of surfactant head groups as called reverse micelle is configured with tiny and polydispersed droplets. These micelle droplets' cores will grow larger and more close-packed aggregate with the gradually addition of water into solution which can be referred as swollen reverse micelles. The adding amount of aqueous solution is limited with the solubility of that surfactant depending on the number of head or tail groups (Evans, 1994).

Reverse transition may arise from the presence of attractive droplet interactions and generally leads to the formation of various structures: flocs coexisting with dilute droplets or gels which consist of a network of connected droplets. As an example, two or more colloidal droplets' particles, generally two, may attract each other when surrounded by smaller ones.

Certain aspects of microemulsions remain controversial, such as the nature of interface (discrete or bicontinuous) between the dispersed particles, the

nature of the continuous phase (swollen micellar solution and hence, one-phase, thermodynamically stable, or emulsion of exceedingly small particle size and hence, two-phase, possibly kinetically stable), and whether they contain one type of dispersed particle or micelle, or more (Evans, 1994).

In this thesis, polyoxyehyl phenylether was used in the formation of W/O microemulsion. This surfactant is composed by the polar head group which is ethoxy (EO) groups, and the tail group generally constitutes from the nonpolar aliphatic of hydrocarbon (-CH2-). Both groups are connected with a benzene ring in the para-position, as illustrated in Figure 2.1.

$$CH_3(CH_2)_n\text{-}\langle\bigcirc\rangle\text{-}(OC_2H_4)_mOH$$

Figure 2.1 Molecular structure of polyoxyethyl phenylether, where n is the number of alkyl groups and m is the number of alkoxyl groups

Once the transparent microemulsion is prepared with the appropriated amount of the surfactant, oil, and water, the droplets having spherical shape with monolayer and monodisperse are presented with the hydrodynamic diameter in the range of 1 - 20 nm. The water solubility is conferred by the ability of the oxygen atoms of head group and hydroxyl groups via hydrogen bonding with water molecules. One molecule of surfactant can not drag a hydrocarbon chain into solution, but 5-10 molecules will be sufficient. The EO head groups also interact each other with the driving force of the dipole-dipole interaction between hydrated groups (Chang and Fogler, 1997). The hydration of head groups layer of surfactant results in the separation of head groups from one another. These repulsive interactions and the actual physical volume of functional groups make the area occupied by the surfactant head group at the

oil-water interface increase with increasing the number of EO groups in the head group. This increase also leads to an increase in potential surfactant monomer attraction at the oil-water interface (Rosens, 1989). The increase of thermodynamically aggregation of polyoxyethylene phenylether head groups causes not only the addition of sufficient water content, but also the using of cosurfactant such as alcohol or aqueous ammonium as catalyst base to stabilize through hydrogen-bonding. The employed amount of water is reached where unbound or free water molecules are present in the hydrophilic parts. On the other side, the hydrocarbon tail group of surfactant molecule encompasses an area at the oil-water interface through the change of its conformation by the tail toward to the oil phase. The turned color of colloid solution to transparent bluish is used to indicate that the increase of aqueous swollen in microemulsion droplets. The water pool of micelles can dynamically exchange with others which leads microemulsion solution to conduct electrical charge. The film durable of microemulsion is shown with the ternary phase diagrams of the surfactant/oil/water system. The nonionic surfactant was studied in the ternary system mixed of polyoxyethylene alkylphenylether ($C_x(OC_2H_4)_y$), heptane, and water (Evans, 1994; Chang and Fogler; 1997; and Esquena et al., 1997). These works also illustrated the evolution of microemulsion configuration and film properties.

2.3 Dynamic Process in Microemulsions

The discretion of aqueous microdroplets are encircled with surfactant molecules in continuously oil media resulting in formation of W/O microemulsions under thermodynamic equilibrium. The stability of dispersions is based on Brownian movement which leads to constant collision between themselves, coalescence as transient dimers, and the mass exchange in the

aqueous cores of microemulsion droplets. The inter-droplets' phenomenon is known as inter-micellar mass exchange. The process is started from the diffusion and collision of a pair of droplets, then uncapping the water-oil interface, follow with interchanging of the mass in the aqueous cores, finally, isolating and recapping interface film (Chang and Fogler, 1997). This dynamic mechanism of inter-micellar mass exchange between microemulsion droplets is illustrated in Figure 2.2
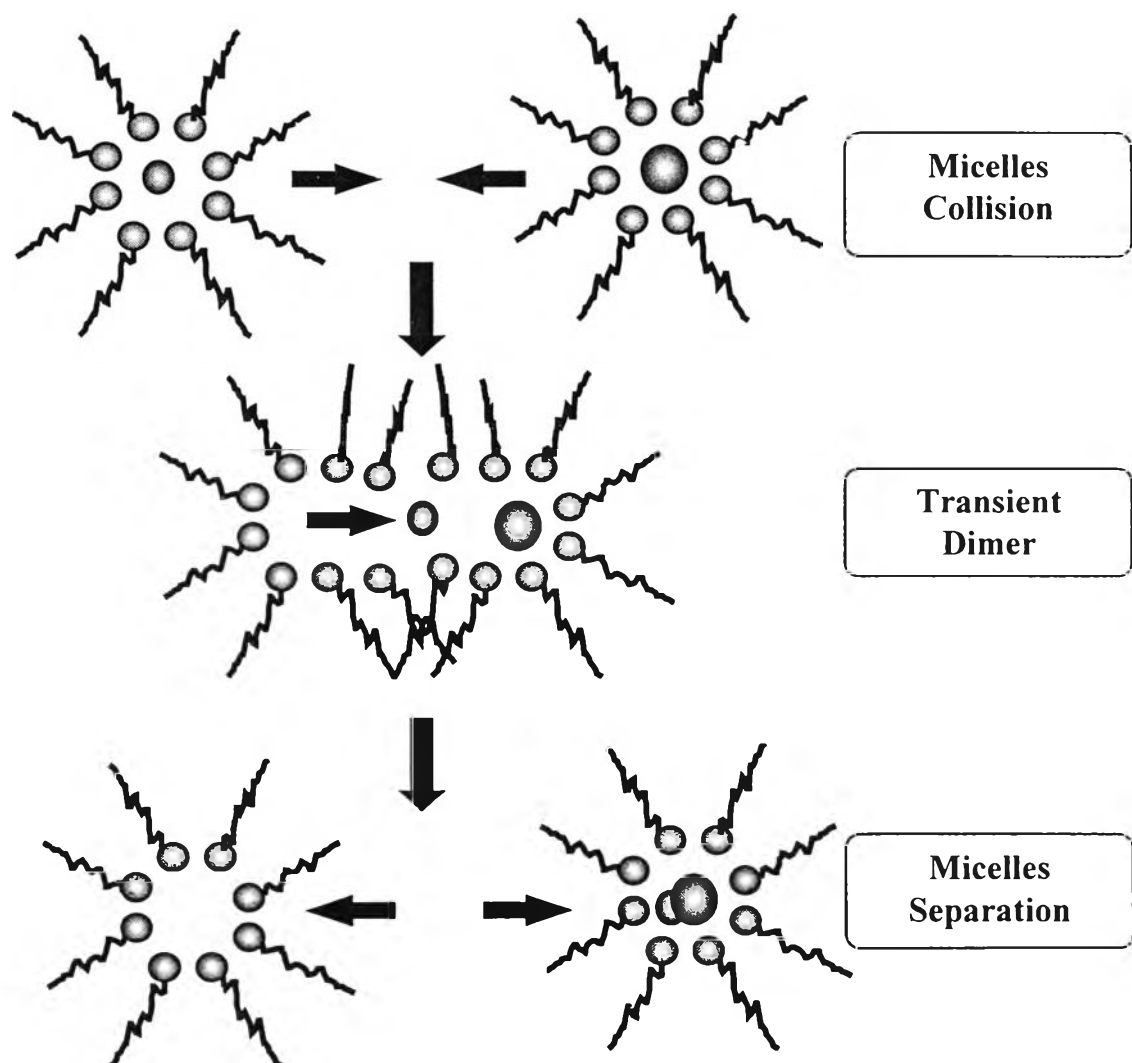
Figure 2.2 Mechanism of inter-micellar mass exchange between microemulsion droplets

The time period of the collision of microemulsion droplets and the inter-micellar mass exchange is extremely short. Increasing the attractive interaction between the droplets can extend the aggregation period and therefore increases the lifetime of the transient dimer. Due to fluid-like feature of surfactant layers can be deformed easily, the coalescence of droplets can create an open water channel through the colliding surfactant film. Therefore, the rate of droplet coalescence is mainly dictated by the fluidity and integrity of surfactant layers (Chang and Fogler, 1996).

Polyoxyethylene head groups of surfactant generate weak associated interaction with themselves which causes the structure of surfactant layer to be ruptured more easily. Therefore, the rigidity of interfacial film will depend on the number of polyoxyethylene. If the oxygen atoms of head groups increase, the hydrogen-bonding among the head groups will also increase. This leads to the reduction of the fluidity of interfacial film which causes the rate of mass exchange among microemulsion droplets decreases. This rate is also influenced by the type of oil or some materials that alter the physical properties of oil (e.g., alcohol), the size of droplets, and the temperature (Clark et al., 1990). The polarity and structure of oil molecules affect the fluidity and permeability of surfactant layers. More polar and smaller oil molecules will swell the surfactant layer to a larger extent and make the surfactant layer more rigid and less permeable. In the contrast, nonpolar and larger oil molecules will increase the lifetime of inter-micellar mass exchange period (Fletcher et al., 1987). Moreover, the other additives (e.g., alcohol) can change the polarity of oil which produces similar results (Arriagada and Osseo-Asare, 1994; and Esquena et al., 1997).

The water-to-surfactant molar ratio can influence the size of microemulsion and the rate of inter-micellar mass exchange. For the system consisting of polyoxyethylene alkylphenylether surfactant, the size of microemulsion

droplets is much larger and the rate of inter-micellar mass exchange increases when the concentrations of each component in the system are far from the phase boundary. On the other hand, the rate of inter-micellar mass exchange can be decreased significantly when it is occurred near the phase boundary due to the stronger attractive interaction among microemulsion droplets. The increase in hydrogen bonding among water and oxygen atoms of head group causes rigidity of interfacial film to increase. The effect of temperature on the rate of inter-micellar mass exchange also depends on the microemulsion systems. For the ternary system of water/hepatane/$C_{12}EO_5$, it has been found that the rate of inter-micellar mass exchange increased when temperature was reduced until it reached the solubility boundary of the system(Clark and Fletcher, 1990). Furthermore, the additional materials (i.e., ionic material, alcohol) can also affect to change the rate of inter-micellar mass exchange (Esquena et al., 1997).

2.4 Formation of Particles in Microemulsions

Since water-in-oil (W/O) microemulsion is thermodynamically soluble and has compartmentalized feature, it will act as a special nanometer reactor that hosts the synthesis of inorganic particles. Microemulsion is occurred by encapsulating the surfactants. The advantages of surfactant are not only to prevent the aggregation with steric barrier of hydrophobic groups, but also to confine the dimension and maintain the stability of precipitated particles during and after their growth period. Many particles have been successfully synthesized in W/O microemulsion, such as metal particles (e.g., Pt, Rh, Ag, and Au), metal sulfide (e.g., CdS, ZnS, and, CuS), metal oxide (e.g., SiO_2, ZrO_2, and Fe_3O_4), metal halide (e.g., AgCl and AgBr), metal boride (e.g.,

Ni_2B, Fe_2B, and Co_2B), and metal carbonate ($CaCO_3$ and $BaCO_3$) (Solans, 1995).

The method for synthesizing inorganic particles in W/O microemulsion system can be classified as three following categories (Arriagada, 1991).

(1) Microemulsion plus trigger: All of reactants are presented inside microemulsion droplets, then reaction is initiated by light or heat.

(2) Two microemulsions: Two reactants reside in the aqueous droplets of two separate microemulsion solutions, and reaction is initiated by mixing these two media.

(3) Microemulsion plus an oil-soluble reactant: One reactant resides in the microemulsion droplets, and reaction is initiated by applying a second reactant (either liquid or gas) in the oil phase.

For the first two methods, all of reactions take place within the core of microemulsion. Therefore the formation of particles is controlled by the rate of the chemical reaction and the rate of inter-micellar mass exchange. In the third method, the reactions transpires at the oil-water interface. The formation of particles depends upon the rate of inter-micellar mass exchange and on the rate of transferring reactions through the interface.

2.5 Mechanisms of Particles Formation in Microemulsions

Once the W/O microemulsion system is utilized to synthesize the inorganic nano-particles, the concentration of each species in the system must be essentially concerned. Many factors, including the type of synthesized particles, the mechanism of formation, and the synthesis method, affect to the colloidal properties and dimension of microemulsion droplet. The importance of these parameters on the particle formation are discussed as follows.

One of significant criteria of forming stable colloidal suspension is the stability of reacted species during the particle formation. The stability of synthesized particles can increase only when the initial matter that called nuclei particles reaches the critical size. The stability of particle size is important to determine the final size distribution of the particles formed. Many inorganic particles synthesized in W/O microemulsion solution reside in the aqueous core of microdroplets. Consequently, the surfactant layer coated on the aqueous droplets assists to reduce the probability of collision among the particles formed with the steric hindrance of tail groups. The collision of particles via inter-micellar mass exchange causes the formation of a larger core of microemulsion. This will only occur if the surfactant layer curvature changes significantly from its equilibrium value (HLB) or there may be a large desorption of surfactant molecules from the colliding surfactant layer area. Due to this highly energetically unfavorable process, the stability of particles in microemulsion droplets increases dramatically with the particle size. An evidence obtained from previous research works can conclude that reactant molecules need to be polymerized to a sufficiently larger particle in order to become a stable nucleus in the droplet (Nagy et al., 1989).

The size distribution of particles formed in microemulsion solution is fundamentally controlled by the competitive rates of two steps as following:

(1) the rate of chemical reaction (i.e., the rate of increasing of total mass of particle, the rate of polymerization of reactant).

(2) the rate of inter-micellar mass exchange of reacting species among microemulsion droplets.

All of the reacting species is definitely polymerized to form particles in the aqueous core of microemulsion droplets before the matter exchange between droplets will be proceeded. The smaller matters usually move to merge with the larger particle during the transient dimer step, since they are less steric

hindrance and involve with thermodynamic driving force between microemulsion droplets (Ward and Friberg, 1989). The rate of chemical reaction is not significantly slower than the rate of inter-micellar mass exchange. Therefore, the number of synthesized particles is comparable to the number of microemulsion droplets. For example, the initial chemical reaction between Cd^+ and S^{2-} to form CdS particle occurs immediately after rapid mixing of the two microemulsion solutions containing Cd^+ and S^{2-}. Due to the extremely fast reaction of both ions, the tiny ultra-fine particles (less than 5 nm.) are immediately formed (Ward anf Friberg, 1989).

On the other hand, if the rate of the polymerization of reacting species is much slower than that of mass exchange among microemulsion droplets, the outcome will be different. The amount of reacting species polymerized in individual droplets is not sufficient to form stable nuclei without the occurrence of the mass exchange among microemulsion droplets. Hence, the mass or dimension of precipitated particles can continuously redistribute the microemulsion droplets until the size reaches the critical mass for forming stable nuclei. Since it is not likely to form a stable nucleus in each microemulsion droplet, the number of synthesized colloidal particles is always significantly lower than that of microemulsion droplets. The synthesis of silica particles (SiO_2) from the hydrolysis of silica-alkoxide precursor (e.g., tetraethyl orthosilicate (TEOS)) in nonionic W/O microemulsion solution is one instance for this case. (Chang and Fogler, 1996). Likewise, this thesis was to study on the synthesis of silica particles in nonionic W/O microemulsion system from tetrabuthyl orthosilicate (TBOS) as an effective precursor.

2.6 Formation of Silica Particles from TBOS Hydrolysis

Several types of nanometer-sized particles have been successfully synthesized from the hydrolysis reaction of alkoxide precursor in aqueous media of W/O microemulsion droplets. The physical-chemical properties of alkoxide reagent and the mechanisms of silica particle formation from this reagent will be discussed in this section.

Metal Alkoxide $(M(OR)_n)$ is one of the versatile molecular precursors for synthesis of organic and inorganic oxide particles. M is usually known as a transition metal (e.g., Ti, Zr) or a semiconductor metal (e.g., Si). R is a saturated or unsaturated organic group. The alkoxyl group (OR) is a hard p-donor and stabilized at the highest oxidation state of the M molecule. Therefore the chemistry of electron rich metal alkoxides has long been restricted by oligomerization reactions which leads to the formation of insoluble polymeric species. Some alkoxides are currently used in industry and commercially available at relatively low costs (e.g. Si, Ti, Al, Zr). Moreover, the transition metal alkoxide precursors have to be prepared in laboratories, with the conventional methods or the synthesis of metal alkoxides. Due to the high electroneffmity of transition metals, their reactivity are extremely higher than the simple metals in the aqueous partition of microemulsion droplet (Livage, 1982).
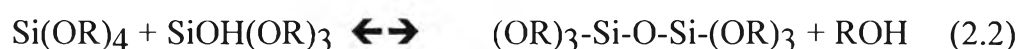
The mechanism of silica particle formation in aqueous media of microemulsion system essentially involves the two fundamental reactions which are hydrolysis and condensation of reactant. In a number of previous works TEOS was commonly used to synthesize the silica particles via these reactions. For this work, tetrabuthyl orthosilicate (TBOS, $Si(OC_4H_9)_4$) was used to produce the nano-scale silica particles by the hydrolysis and condensation reactions in W/O microemulsion system via aqueous ammonium as based catalyst. TBOS is always monomeric and has structure like a

tetrahedral. In general, the reactions involving silica particle formation from TBOS precursor can be described by the following equations (Livage, 1982):
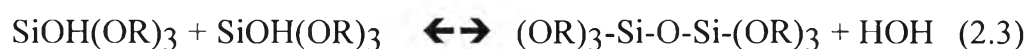
hydrolysis

$$Si(OR)_4 + H_2O \longleftrightarrow SiOH(OR)_3 + ROH \qquad (2.1)$$

alcohol condensation

$$Si(OR)_4 + SiOH(OR)_3 \longleftrightarrow (OR)_3\text{-}Si\text{-}O\text{-}Si\text{-}(OR)_3 + ROH \quad (2.2)$$

water condensation

$$SiOH(OR)_3 + SiOH(OR)_3 \longleftrightarrow (OR)_3\text{-}Si\text{-}O\text{-}Si\text{-}(OR)_3 + HOH \quad (2.3)$$

overall reaction

$$Si(OR)_4 + H_2O \longleftrightarrow \text{-}[Si\text{-}O\text{-}Si]\text{-} \text{(polymer chain)} + 4ROH \quad (2.4)$$

All of the above equations illustrate the formation of silica particles that involves the hydrolysis of buthosilane groups (Si-OR, R is C_4H_9) of TBOS that will become hydroxylsilane (Si-OH) groups. Due to the electronegativity of alkoxy groups (OR) resulting in the silica atom highly prone to nucleophilic attraction, TBOS is, therefore, extremely reactive with water molecules in microemulsion core. This leads to the formation of hydroxides or hydrous oxide's silica. These hydroxide molecules can be reacted with either molecules themselves for water condensation or TBOS molecules for alcohol condensation. Both of condensations proceed cyclically until TBOS precursor is depleted. Later production is a cross-linked silicon dioxide structure that then condensed to silica particle. In the previous studies (Chang and Fogler, 1996 and 1997), TEOS was typically used to form the silica particles. The results lead to a conclusion that the base-catalyzed hydrolysis of TEOS is in pseudo-first order with respect to TEOS and hydroxyl ion (OH^-), since water composition in W/O microemulsion system is larger than the used concentration of TEOS. The rate of second order overall reaction is no longer

depends on water concentration. The reaction involves the displacement of OR^- by OH^-, proceeding through a penta-coordinate transition state. The alkoxide ion, OR^-, is subsequently neutralized by reacting with water regenerating OH^-. The mechanism of this reaction can be identified as S_N2 (in organic chemistry), meaning substitution, nucleophilic, and second order (with inversion of configuration). Due to the statistical depletion of hydrolyzable OR^- groups and the inductive effects (OH^- more electron withdrawing than OR^-), hence the substitution of OH^- for OR^- renders the silica atom to be more susceptible to nucleophilic attack. Therefore, the hydrolysis of the first OR group will be slow but becomes much faster for the following ones. The activity of the alkylsilane group decreases with the increase in the length of the alkyl chain. This should then decrease the sensitivity of the alkoxide towards the rate of hydrolysis. However, the influences of steric hindrance and charge distribution alone cannot explain the hydrolysis rate of silica alkoxides. The rate of the condensation of silicic ($(SiOH)_4$) increases with increasing pH value of the solution. This condensation reaction is also a nucleophilic reaction which involves the neutralization between a silanol group (acid) and an ionized silanol group (base), as shown below:

$$Si(OR)_3\text{-}O^- + OH\text{-}Si(OR)_3 \longleftrightarrow (OR)_3\text{-}Si\text{-}O\text{-}Si\text{-}(OR)_3 + OH^- \quad (2.5)$$
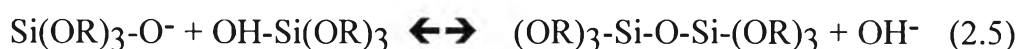
The catalytic effect of the hydroxyl ion on condensation reactions lies in the ionization of the silanol group:

$$Si(OR)_3\text{-}OH + OH^- \longleftrightarrow (OR)_3\text{-}Si\text{-}O^- + HOH \quad (2.6)$$
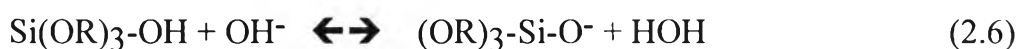
The condensation reaction described in equation 2.5 also implies a configuration inversion (S_N2) of the groups that is attached to the Si atom of Si

(OR)$_3$-OH when the Si-O$^-$ group is substituting for the OH group of Si(OR)$_3$-OH. Therefore, it means that smaller cross-linked groups can undergo inversion to be easier than bulkier ones to a large network of silica polymers. As a result, the addition extensive monomer to existing large cross-linked polymer is much more favorable than the polymer-polymer condensation. One of evident for supporting these mechanisms is the study of the silica particle formation through the TEOS hydrolysis and condensation. The precipitated SiO$_2$ polymers like a very dense cross-linked particle that is supported as the statement above (Ballard et al., 1993).

2.7 Kinetics of Silica Particle Formation

As mentioned before, the kinetics and mechanism of silica particles growth have been extensively studied in alcohol media with the hydrolysis of TEOS via ammonium base catalyst (Aelion et al., 1950, Stober et al., 1968, Van Helden et al., 1981, Brinker and Scherer, 1989, and Bergna, 1994). These studies have provided the valuable insight of the formation of silica particles in microemulsion.

Aelion et al. (1950) investigated the kinetics of TEOS hydrolysis in methanol solutions under the catalysis of dilute sodium hydroxide (NaOH) by Karl-Fischer titration method. They suggested that the base-catalyzed hydrolysis of TEOS had a pseudo-first order reaction with respect to the concentrations of both TEOS and hydroxyl ion (OH$^-$), as shown below:

$$-\frac{d[TEOS]}{dt} = k[TEOS][OH^-] \qquad (2.7)$$

In this study, the base-catalyzed TEOS hydrolysis reaction was proposed as a nucleophilic (S$_N$2) substitution reaction involving with the displacement of

the ethoxide (-OC$_2$H$_5$) group of TEOS by hydroxyl ion (-OH) through a penta-coordinate transition state. Nevertheless, the kinetics of TEOS hydrolysis in alcohol media with aqueous ammonia, as a weak base catalyst, appears to be more complicated. Based on the previous studied, it can be concluded that the rate of TEOS hydrolysis depend upon [H$_2$O] and [NH$_3$] which has reaction orders of 1.5 and 1, respectively (Byers et al., 1987; Bogus and Zukoski, 1991; and Van Blaaderen et al., 1992). Moreover, types of alcohol solvent also influence the rate of TEOS hydrolysis with 1-butanol > methanol > 1-propanol > ethanol > 2-propanol. This order may be induced from the hydrogen-bonding and steric hindrance effects of alcohol molecules (Harrier et al., 1990).

Several studies reported that the rates of silica particle growth and TEOS hydrolysis were first order reaction with closely value of specific rate constant. They suggested that the growth of silica particle to be limited by the hydrolysis of TEOS (Matsoukas and Gulari, 1988). Due to this reaction-controlled growth, the monodisperse of silica particles can be formed in the initial state of particle growth through the addition of monomeric and oligomeric hydrolyzed TEOS species. Silica nuclei were formed with the coagulation of primary hydrolyzed polymeric silica species during the nucleation period. Also, the produced particles were under the control of the surface charge density of these particles and the ionic strength of the alcohol media (Bogush and Zukoski, 1988).

2.8 Control of Silica Particle Formation in W/O Microemulsions

Microemulsion is widely employed for synthesizing the silica particles to shape and size distribution in the needed of using the different types of oil, surfactant, and additive (Arriagada and Osseo-Asare, 1995; Chang and Fogler 1996; Chang and Fogler 1997; and Esquena et al., 1997). Arriagada and Osseo-Asare (1995) studied how to control the size distribution of silica particle in

W/O microemulsion system. They found that benzyl alcohol increased the rigidity of water-oil interface. The inter-micellar matter exchange among typical droplets became to the lowest rate. They also found that the silica particle growth and the particle size were increased according to the increase in concentration of benzyl alcohol to the sodium bis(2-ethylhexyl) sulfosuccinate (AOT) microemulsions system. Chang and Fogler (1996 and 1997) used nonionic W/O microemulsion system to study the influences of types of oil and surfactant and concentrations of water, oil, and surfactant. Their results showed that those parameters could affect to the final size distribution of silica particle. It was concluded that an addition of organic additives (i.e., alcohol) could control the microemulsion droplet and the size of synthesized silica particles. Esquena et al. (1997) produced the silica particles in W/O microemulsion by using nonionic surfactant as block copolymer and polyehtylene glycol alkyl ether. They also investigated the effect of alcohol with different their alkyl chain length and concentration. From the results, they found that increases of alcohol alkyl chain and their concentrations could increase the size of silica particle in W/O microemulsion system. This outcome implied that there was a significant mass transfer between microemulsion droplets due to the increase of water-oil interfacial fluidity.

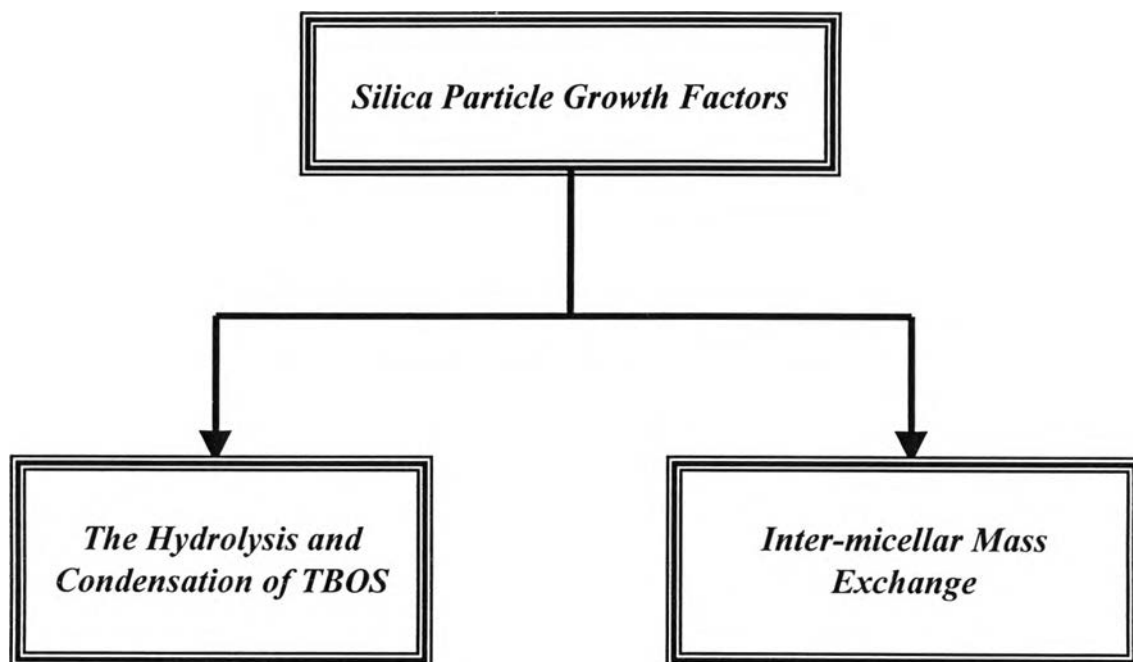## 2.9 Silica Particle Formation in W/O Microemulsions from TBOS

The previous section has shown the overall reaction of silica particle formation from TBOS via the hydrolysis and condensation reactions. When the W/O microemulsion system is used to form the silica particles, some mechanisms involve with the dynamics among microemulsion droplets are comprehended in this section.

The microemulsion reaction media consists of two main phases of a continuous oil phase containing solubilized TBOS molecules, and a discrete aqueous phase containing ammonia and water. TBOS molecules diffuse into the interfacial surfactant layer and are then hydrolyzed rapidly to form silica hydrous oxide species with silianol groups (SiOH). These TBOS molecules are bounded at the oil-water interface and condensed into large polymeric silica molecules which will further grow into silica spheres. The entire silica particle growth process generally lasts for a week, presumably due to the slow rate of TBOS hydrolysis. The diameter of final silica particles is in the range of 30 - 70 nm which is significantly larger than that of microemulsion droplets. The entire process of the formation of silica particles in microemulsion is illustrated schematically in Figure 2.3.

The final size and distribution of synthesized silica particles are affected by various factors such as the concentrations of surfactant, water, and ammonium. The excessive amounts of surfactant, water, and ammonium are essential to establish a rigidity surfactant-water layer on the silica surface. This adjustment is not only to prevent silica particle from aggregating, but also to increase the rigidity of surfactant interface. Furthermore, some aqueous compatible materials (i.e., alcohol) can alter the physical and chemical characteristics of microemulsion droplet. Consequently, the interchange dynamic among microemulsion droplets is increased in the terms of inter-micellar matter exchange, due to the interfacial film becomes more flexible from the adsorption of alcohol molecules on silica surface. A more clearly diagram can be illustrated in Figure2.4, that describes all of silica particle growth mechanisms (Esquena, 1997).
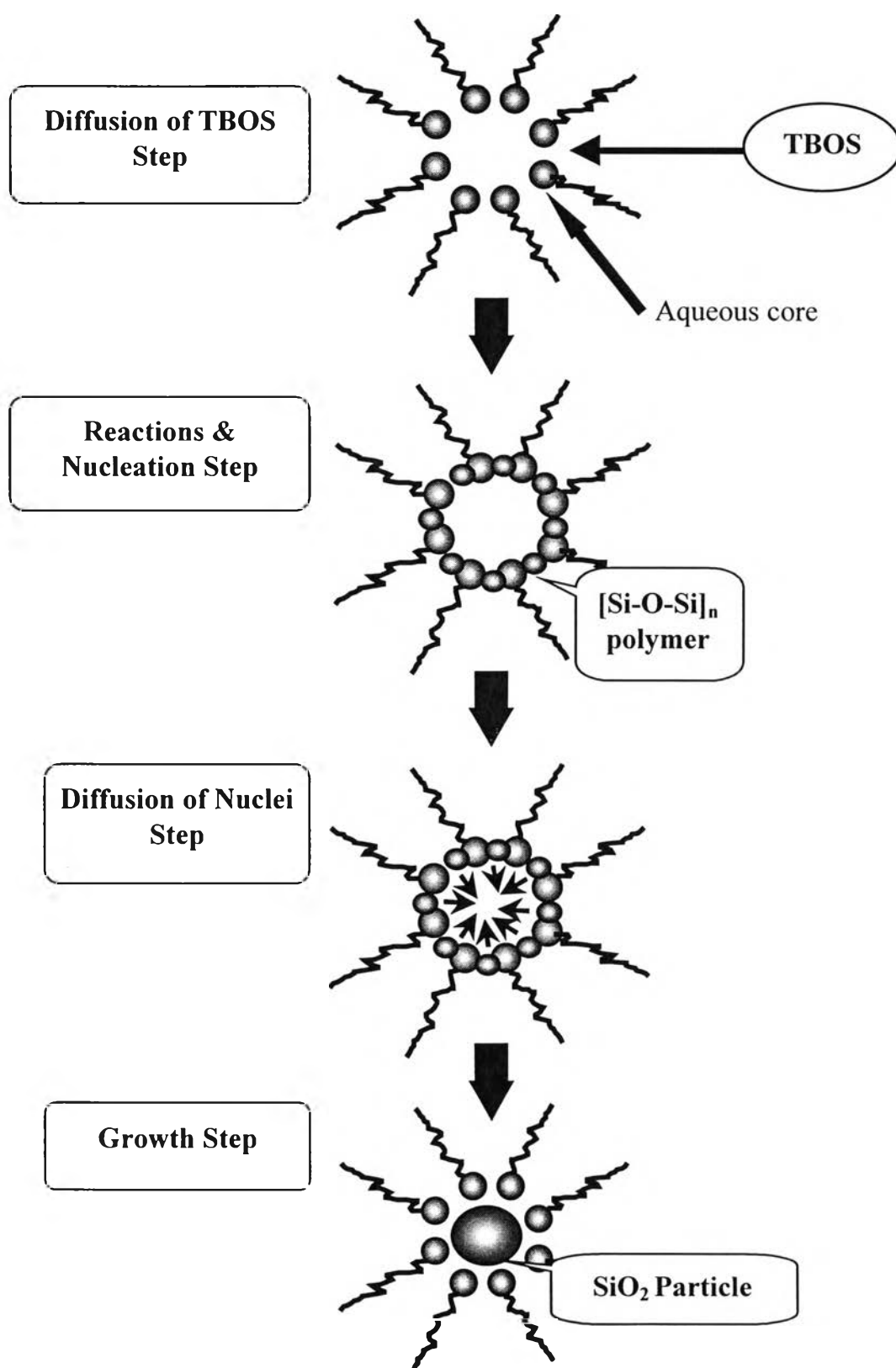
Figure 2.3 Overall mechanisms of silica particle growth from
TBOS hydrolysis (Chang and Fogler, 1997)

Figure 2.4 Categories of silica particle growth in W/O microemulsion system