

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Mesoporous materials

According to IUPAC notation, porous materials are classified into several kinds by their size. Microporous materials have pore diameters of less than 20 Å. Mesoporous material is material containing pores with diameters between 20-500 Å. Macroporous materials have pore diameter greater than 500 Å. Properties and examples of these materials are shown in Table 2.1.

Especially, mesoporous materials have important applications in a wide variety of fields such as separation, catalysis, adsorption and advanced nanomaterials. Pore size distribution, high surface area and pore volume make periodic mesoporous silicas promising supports for metal and oxide catalysts [19].

Table 2.1 Pore-size systems and representative porous inorganic materials.

Pore size system	Definition	Examples
Macroporous	> 500 Å	- porous glasses
Mesoporous	20 - 500 Å	- aerogels - pillared layered clays - mesoporous silica (MC41S, SBA-15, FSM-16 and HMS)
Microporous	< 20 Å	- zeolite - zeotypes

The synthesis of this family of mesoporous materials is based on the combination of two major sciences, sol-gel science and surfactant (templating) science. The template agent used is no longer a single, solvated organic molecule or metal ion, but rather a self-assembled surfactant molecular array [20]. Mesopores are present in aerogels, and pillared layered clays which show disordered pore systems with broad pore-size distributions. A constant demand has been developed for larger pores with well-defined pore structures. The design and synthesis of



organic, inorganic, and polymeric materials with controlled pore structure are important academic and industrial research projects.

In the early 1990s, Kresge et al. [21] reported the emergence of a new family of so called mesoporous molecular sieves, and in recent years, research in this area has been extended to many metal oxide systems other than silica and also to the novel organic-inorganic hybrid mesoporous materials [22]. These new silicate materials possess extremely high surface areas and narrow pore size distributions [23]. Figure 2.1 shows the different structures of the M41S family [24].



Figure 2.1 Schematic diagram of the M41S materials, MCM-50 (layered), MCM-41 (hexagonal) and MCM-48 (cubic) [20].

The structural phase of mesoporous materials (Figure 2.2) is based on the fact that surfactant molecules are themselves distinct as very active components with variable structures in accordance with increasing concentration [25]. At low concentrations, the surfactants energetically exist as monomolecules. With increasing concentration, surfactant molecules combine together to form micelles in order to decrease the system entropy [25-27]. This phenomenon is rationalized in the following way. Below the initial concentration threshold the monoatomic molecules aggregate to form isotropic micelles which is called the critical micellization concentration (CMC). In the micelle core, which is essentially liquid hydrocarbon, there is greater freedom for movement and so the entropy associated with the hydrocarbon tails also increases [25, 27].

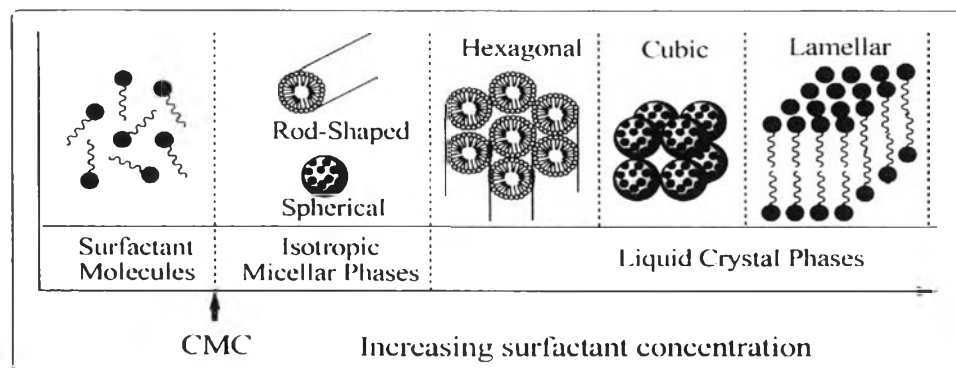


Figure 2.2 Phase sequence of surfactant-water binary system [25].

The mesophases are formed by interaction of the organic parts with inorganic species, and thus both components play a crucial role in the assembly. Interactions between the inorganic species and the head group of the organic template with consideration of the possible synthetic pathway in acidic, basic, or neutral media depend on the synthesis conditions and the silica source or the type of organic template used, many other mesoporous silica materials (HMS, MSU, KIT, SBA) can be prepared with properties different as shown in Table 2.2 [28].

Table 2.2 Possible pathways for the synthesis of mesoporous silicas with hexagonal structure.

Template condition	Interaction		Synthesis condition	Mesoporous materials
	<i>Strong (electrostatic) interactions</i>			
Ionic surfactant	- Direct interaction	S^+I^-	Basic	MCM-41
		S^+I^+	Neutral-basic	
	- Anion mediated interaction	$S^+X^-I^+$ or S^+X^-I	Acidic Basic	SBA-3
Nonionic surfactant	<i>Weak interactions</i>			
	- Hydrogen bonding interaction	S^0I^0	Neutral	HMS
Co-polymer	- Hydrogen bonding interaction	N^0I^0	Acidic	SBA-15

S^- = anionic template, S^+ = cationic template, S^0 = neutral template, N^0 = nonionic species,

I^- = anionic inorganic species, I^+ = cationic inorganic species, I^0 = neutral inorganic species, X^- = Cl^- or Br^-

2.2 Sol-gel process for the synthesis mesoporous silica

The sol-gel process involves transformation of a sol to a gel. A sol is defined as a colloid of small particles that are dispersed into a liquid. A gel, on the other hand, is a rigid non-fluid mass and is usually a substance made up of a continuous network including a continuous liquid phase [29-31]. Therefore, sol-gel reactions involve hydrolysis and condensation reactions of inorganic alkoxide monomers in order to develop colloidal particles (sol) and consequently convert them into a network (gel).

Alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), are extensively used for the production of silica gels. Aluminates, titanates, and zirconates, however, are usually used for the synthesis of alumina, titania, and zirconia gels, respectively. Figure 2.3 displays the involved hydrolysis and condensation reactions of TEOS. The hydrolysis step takes place by the addition of water to the TEOS solution under neutral, acidic, or basic conditions.

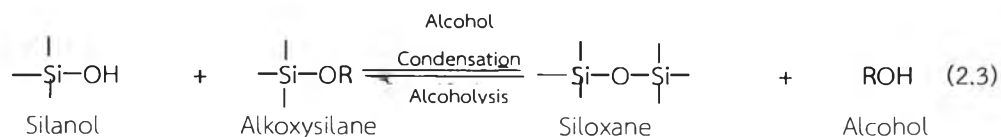
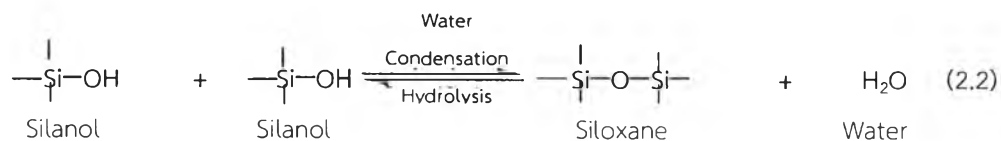
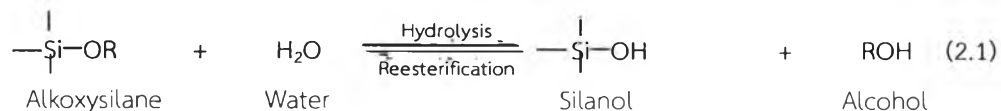


Figure 2.3 Sol-gel general reaction scheme [20].

The hydrolysis step, Equation 2.1, leads to the generation of a silanol group (Si-OH). The mechanism of hydrolysis is catalyst dependent while its rate depends on the pH parameter, the water to alkoxide ratio, and the employed solvent. Since alkoxysilanes are not water-soluble, an organic co-solvent is required to facilitate the hydrolysis step by mixing the alkoxysilane with the water in the reaction mixture [32].



In the second step, the silanol group condensed with either an alkoxide or another silanol group (the forward reactions in Equations 2.2 and 2.3) to build a strong siloxane linkage (Si–O–Si) with the loss of either an alcohol (ROH) or a water molecule. The siloxane hydrolysis and alcoholysis reactions (the reverse reactions in Equations 2.2 and 2.3, respectively) break the siloxane bond, but along with the forward reactions, the stepwise construction of the emerging network is permitted [29, 32]. As the number of Si–O–Si bridges increases, the siloxane particles can aggregate into a sol, which disperses in the solution into small silicate clusters. Condensation of the latter silicate clusters leads to the formation of a network (a gel), trapping the water and the alcohol by-products. Removal of these trapped molecules from the formed gel network by heat treatment under vacuum yields a vitrified, dense glass network. It is noteworthy to mention that hydrolysis and condensation reactions go on concomitantly, so that the full hydrolysis of tetraalkoxysilane to $\text{Si}(\text{OH})_4$ does not necessarily occur before the beginning of the condensation reactions [29, 33].

The hydrolysis of alkoxysilanes is so slow that it necessitates the addition of either an acid or base catalyst, see Figure 2.4. When an acid catalyst is employed, the rate-controlling step is the particle nucleation and the fast step is the hydrolysis. This fact leads to the production of more linear-like networks with less siloxane bonds and a high concentration of silanol groups, and hence, minimally branched polymeric species. On the other hand, alkoxide hydrolysis by base catalyst is faster than acid and prevents the quick aggregation of sol particles resulting in highly dense materials with fewer silanol groups in the overall network. The rates of both of the hydrolysis and condensation reactions depend strongly on the pH parameter as shown in Figure 2.5 [29]. For instance, at $\text{pH} \approx 7$, molecular hydrolysis takes place at a slow rate, while molecular condensation occurs at a fast one. This inverse relationship between the rates of the hydrolysis and condensation reactions controls both the kinetics of the reaction and the ultimate network structure.



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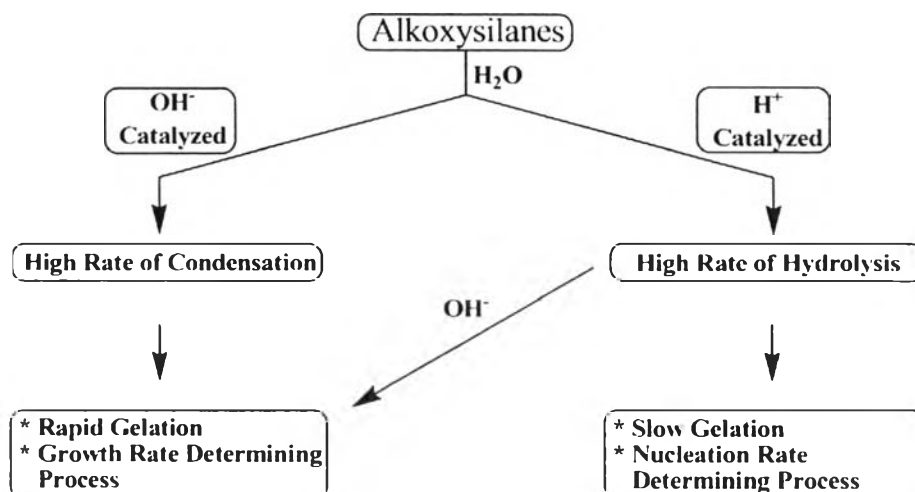


Figure 2.4 Effect of catalyst on hydrolysis and condensation [20].

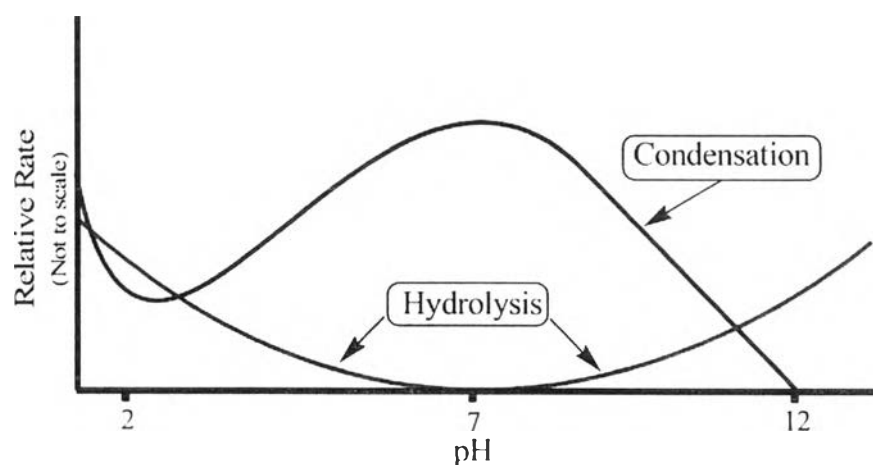


Figure 2.5 Effect of pH on hydrolysis and condensation rates [20].

2.3 Mesoporous silica with hexagonal structure

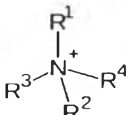
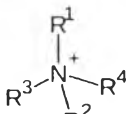
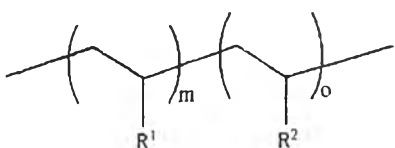
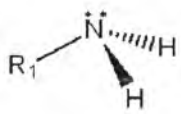
2.3.1 General features of mesoporous silica with hexagonal structure

Mesoporous silicas with hexagonal structure are subset of mesoporous material which were first described in 1992 as a result of the self-assembly of a structure directing agent and the silica source. These material possessed many important characteristics such as large surface area, high mesopore volume, and narrow pore size distribution in the range of mesopores [34-36]. Therefore, they are attracted in many fields such as in the industry as catalysts or catalyst supports in

the pharmaceutical and fine chemical industries, in adsorption and separation process.

Mesoporous silica with hexagonal structure can be classified by using different synthetic procedures, based on the organic template used for separation and the interaction of inorganic species (silica source) and organic surfactant molecule. The interaction of various types of organic template with inorganic species for assembling these materials are different as summarized in Table 2.3, together with the condition typically employed for a synthesis [21, 37, 38].

Table 2.3 Various synthesis conditions of mesoporous silica with hexagonal structure and the types of interaction between templates and inorganic species.

Material	Template	Synthesis pathway	Synthesis condition	Ref.
MCM-41	Quaternary ammonium salt 	Electrostatic	base or acid	[39-41]
FSM-16	Quaternary ammonium salt 	Electrostatic	base	[42-44]
SBA-15	Amphiphilic triblock copolymer 	H- bonding	acid (pH<2)	[45-47]
HMS	Primary amine 	H- bonding	neutral	[48-50]



MCM-41 and FSM-16 can be synthesized using quaternary ammonium salt as a template. In case of SBA-15, amphiphilic triblock copolymer can be modified as a template and must be synthesized in acidic condition of HCl. On the other hand, HMS can be prepared in neutral and environmentally benign condition using primary amine as a template. Although these materials have the same hexagonal structure, some properties are different as shown in Table 2.4.

Table 2.4 Properties of some mesoporous silicas with hexagonal structure.

Material	BET specific surface area (m ² /g)	Pore size (Å)	Pore volume ₃ (cm ³ /g)	Morphology structure	Ref.
MCM-41	>1000	15-100	0.6 – 1.0	Honey comb	[39-41]
FSM-16	680-1000	15-32	0.8 – 1.2	Folded sheet	[42-44]
SBA-15	630-1000	46-300	0.6 – 1.3	Rope-like	[45-47]
HMS	640-1000	29-41	0.5 – 0.9	Wormhole	[48-50]

2.3.2 Synthesis method of mesoporous silica with hexagonal structure

There are three kinds of relevant materials of mesoporous silica with hexagonal structure obtained by using different synthetic procedures. Based on the template used for synthesis and the interaction of inorganic species and organic surfactant molecule, these materials can be grouped as follow:

2.3.2.1 Ionic surfactant and ionic inorganic precursor

Using ionic surfactant (S^+ and S^-), the hydrophilic head mainly binds with inorganic species through electrostatic interactions. There are two possible formation routes. Firstly, direct pathway: surfactant and inorganic species of which charges are opposite interact together directly (S^+I^- and S^-I^+). Another is the indirect pathway, occurring when the charges of surfactant and inorganic species are the same, so the counter ions in solution get involved as charge compensating species for example the $S^+X^-I^+$ path takes place under acidic conditions, in the present of halogenide anions ($X^- = Cl^-$ or Br^-) and the $S^-M^+I^-$ route is the characteristic of basic media, in the existence of alkaline cation ($M^+ = Na^+$ or K^+). Figure 2.6 shows the possible hybrid inorganic-organic interfaces.

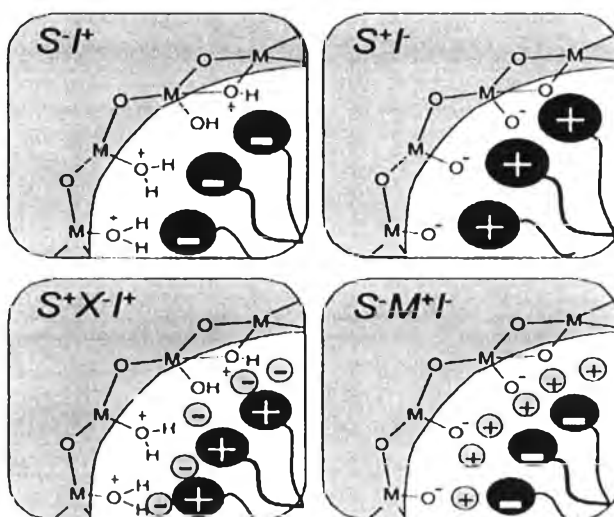


Figure 2.6 Schematic representation of the different types of silica-surfactant interfaces [51].

The preparation of M41S materials is based on charge matching between ionic surfactants and ionic inorganic reagents. The original preparation of the materials involves direct co-condensation of a cationic surfactant (S^+) and anionic species (I^-) to produce assembled ion pairs (S^+I^-). For example, the schematic representation of the mesoporous silica MCM-41 is shown in Figure 2.7. Formation mechanism is that surfactant micelle aggregate into a hexagonal array of rods, followed by interaction of silicate or aluminates anions present in the reaction mixture with the surfactant cationic head groups. Thereafter condensation of the silicate species occurs, leading to the formation of an inorganic polymeric species. After combusting of the surfactant template by calcinations, hexagonally arranged inorganic hollow cylinders are obtained.

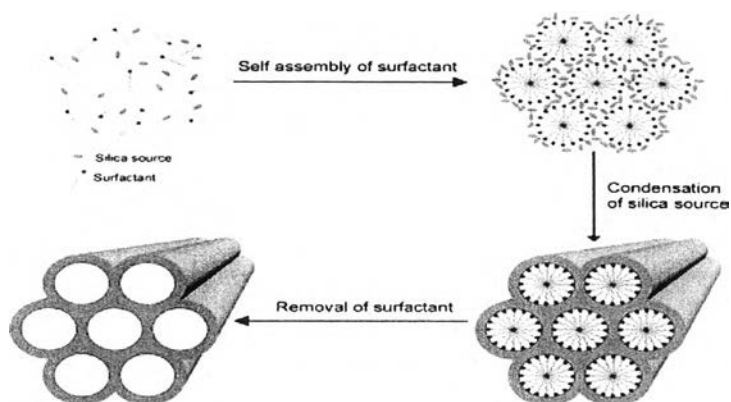


Figure 2.7 Schematic representative of the synthesis of MCM-41

2.3.2.2 Neutral surfactant and inorganic precursor

The second route of mesoporous silicate was introduced by Tanev and coworker by using two neutral routes based on hydrogen bonding and self-assembly between neutral primary amine micelles (S°) (as shown example in Figure 2.8) and neutral or inorganic precursors (I°). This mechanism produces neutral $S^{\circ}I^{\circ}$ templating route. Mesoporous silicas prepared by this technique are hexagonal mesoporous silica (HMS and MSU). These materials are less ordered than mesoporous silicas produced with ionic surfactants. One of the most important advantages of HMS compared with MCM-41 is that the organic phase can be totally removed from as-synthesized samples by solvent extraction.

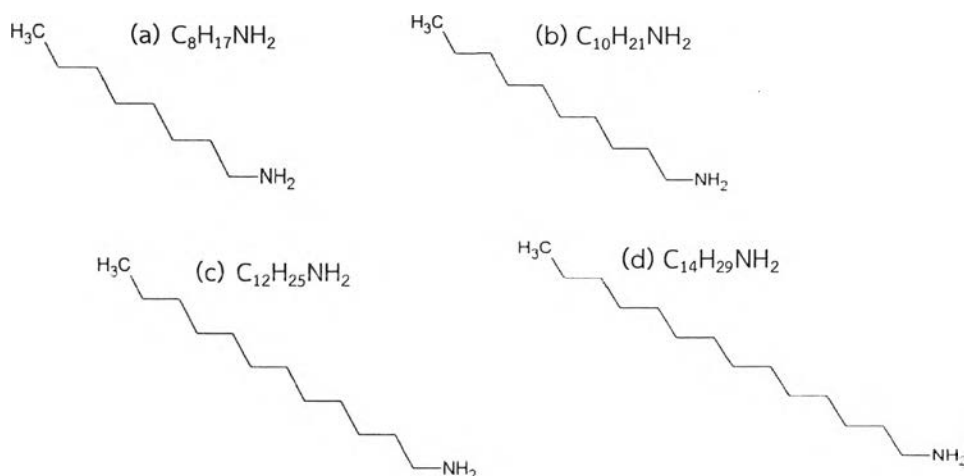


Figure 2.8 Primary amine used in mesostructured generation.

2.3.2.3 Using amphiphilic di- and tri-block copolymer

A new synthesis route involving amphiphilic di- and tri-block copolymers as the organic structure directing agents was introduced by Stucky and co-workers [11]. Poly(ethylene oxide) monoethers were used to form materials showing worm-like disordered or hexagonally ordered mesopores with pore sizes of ca. 5nm. One of the most useful groups of surfactants are the triblock co-polymers consisting of poly(ethylene oxide)_x-poly-(propylene oxide)_y-poly(ethylene oxide)_x, (PEO)_x(PPO)_y(PEO)_x, (trade name: Pluronic) which show the ability to form liquid-crystal structures.

Generally, amphiphilic block copolymer has been used in the field of surfactants, detergent manufacturing, emulsifying, coating, etc. The properties of block copolymer can be continuously tuned by adjusting solvent composition, molecular weight, or type of polymers. Figure 2.9 shows typical block copolymer used as templates.

Mesoporous silica with hexagonal structure formed via this pathway (denoted as SBA-15, Santa Barbara Acid No.15) exhibits a thick wall of 3-7nm thickness and large pore sizes adjustable between 6 and about 15nm. The thick wall of this material significantly improves the thermal and hydrothermal stability compared to mesoporous MCM-41 and related silicates.

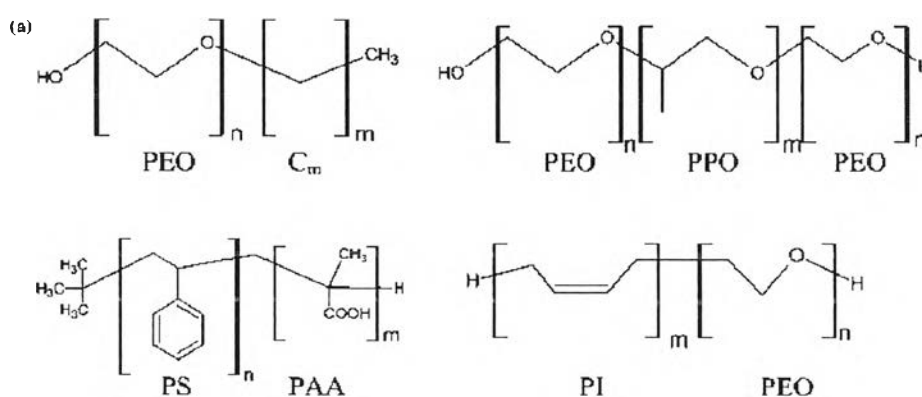


Figure 2.9 Block copolymer used in mesostructured generation [52].

2.4 Hexagonal mesoporous silica (HMS)

Hexagonal mesoporous silicate (HMS) is a kind of mesoporous silicates produced by the neutral synthesis pathway (S^{01}) which was firstly proposed by Tanev and Pinnavaia (1996) [53]. They possessed wormhole-like or sponge-like framework structures as depicted TEM image in Figure 2.10(a), a large surface area, and a narrow pore size distribution, by a neutral assembly pathway between a neutral primary amine surfactant and a neutral inorganic precursor under mild conditions, has been reported [53-58]. In addition, HMS exhibited small spherical aggregates of silica particles as depicted SEM image in Figure 2.10(b). Comparing HMS with other kinds of mesoporous silica with hexagonal framework structures reveals the smaller particle sizes together with the random channel packing of silica molecular sieves that results in a high textural mesoporosity and better transport channels for chemical substances [54]. In addition, it exhibits a thicker silica framework that promotes a high thermal stability. In addition, the primary amine surfactants used as templates are cheaper, and can be simply removed by extraction using a solvent, such as acidified water [55] and ethanol [56]. These advantages make HMS attractive for many applications.

The schematic of synthesis pathway is shown in Figure 2.11. The pore systems of the latter silicas have been shown to have rather worm-like structures than long-range ordered hexagonal arrays which are characteristic for MCM-41. If these nonionic surfactants are used instead of ionic ones, hydrogen bonding is the driving force for the formation of mesophases.

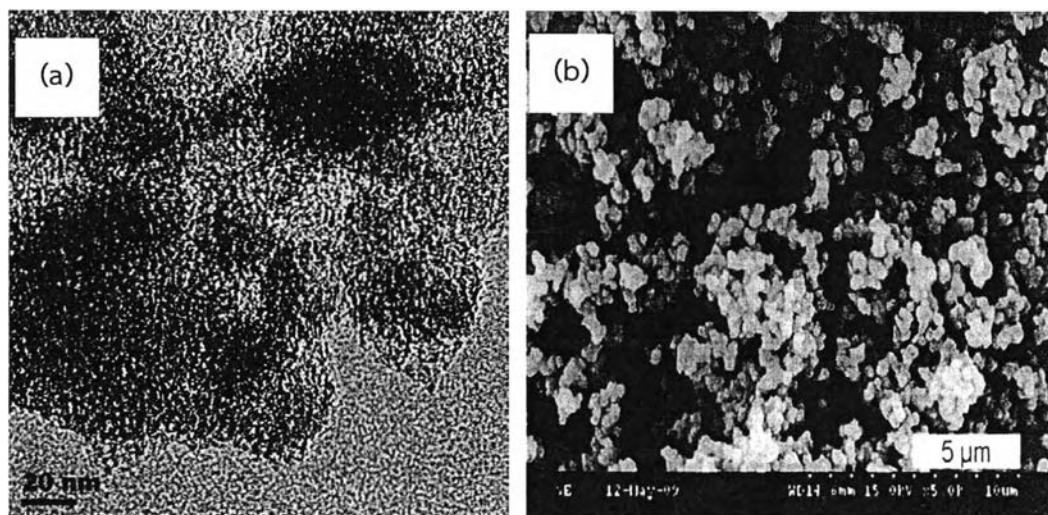


Figure 2.10 TEM image of HMS (a) and SEM image of HMS (b) [59].

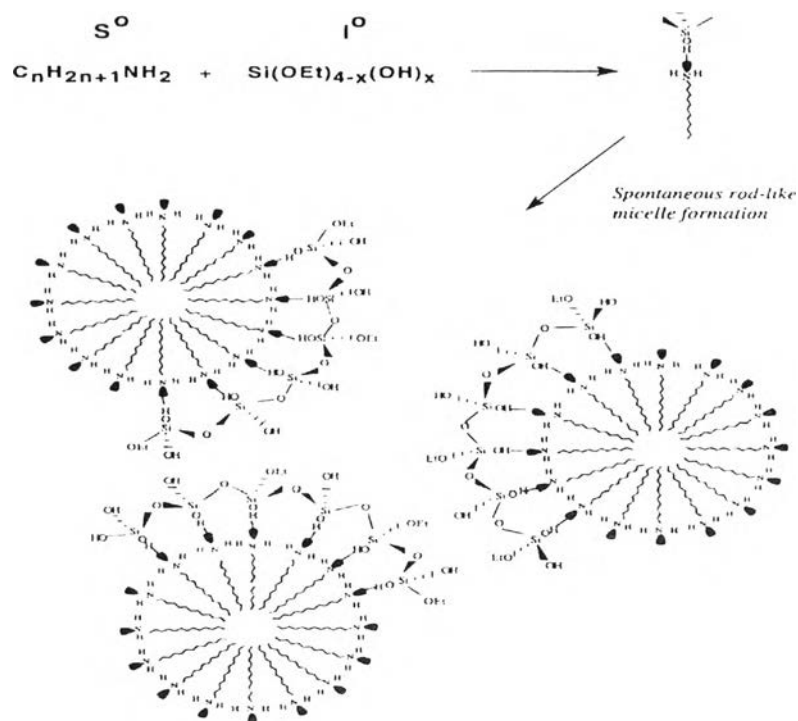


Figure 2.11 Schematic representation of the $S^I I^I$ template mechanism of formation of HMS mesoporous silica [53].

2.5 Surface modification of mesoporous silicas

The application of mesoporous silicas itself is restricted because of the limitations in the active sites. Hence, in order to utilize the unique properties of the mesoporous material for specific applications, such as catalysis and adsorption, reactive functional groups by the incorporation of organic functional group or metal substitution. The advantages of the functionalization of these materials can provide the adjusting of the surface properties (such as hydrophilicity/hydrophobicity), thermal and structural stability. In addition, the organic functional group or metal element can be modified for various specific applications.

Organic functionalized mesoporous silicas have been demonstrated to be a very useful method to prepare materials with unique surface properties for adsorption [60-64] and catalysis [65-67]. To enhance specific characteristic of mesoporous silicas, their surface can be modified with organosilanes by instead of silanol groups ($\equiv Si-OH$) as shown in Figure 2.12. Generally, there are two modification surface method such as post synthesis and direct co-condensation methods.

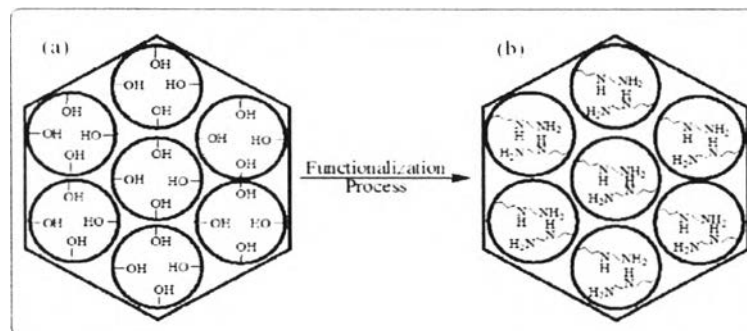


Figure 2.12 Diagram illustrating: (a) unmodified pore wall and (b) the presence of functional group on the pore wall.

2.5.1 Post synthesis method

Grafting procedure based on modification of the silica surface with organic groups through silylation reaction occurring on isolated ($\equiv\text{Si-OH}$) and germinal ($=\text{Si}(\text{OH})_2$) silanol groups using trichloro- or trialkoxyorganosilane and silylamines as organic precursors [68] as shown in Figure 2.13. Typically, this method is accomplished by one of the following procedures:

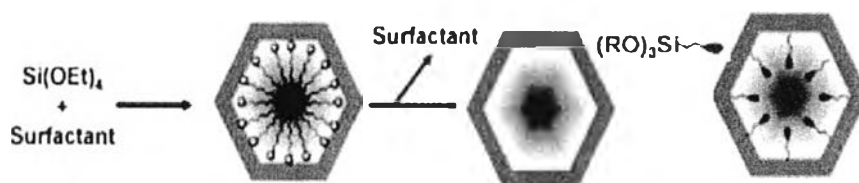


Figure 2.13 Functionalization of inner walls of mesoporous silicas by post synthesis method [69].

The most apparent advantage is good preservation of the mesostructure after post-modification, but decrease of pore volume diameter. This method is suitable for organic and inorganic, which do not include every kind of functional group due to limitation of access to silanol group, and also the heterogeneity of surface functional group. In addition, it often results in non-uniformly distributed organic moieties due to congregation of the organosilane on the channel pore mouth and on the exterior surface of the mesoporous materials [14, 15] and the functionalized materials suffer a loss of surface area, pore size and pore volume [9].

2.5.2 Co-condensation method

The co-condensation method is a one-step procedure and allows a better control of the loading and distribution of organo-functional groups [16]. However, it often produces materials with less ordered mesoporous structures. Typically, this method involves the one-step co-condensation between silica sources with organosilanes through a sol-gel process in presence of an organic template. The advantages of this method are the stability of the inorganic framework even at higher organic loadings, homogenous distribution of the organic groups in the pore channels as well as the single step preparation procedures. The schematic of the direct co-condensation method of mesoporous silica with hexagonal framework is shown in Figure 2.14. Further, the comparison between post synthesis and co-condensation methods is summarized in Table 2.5.



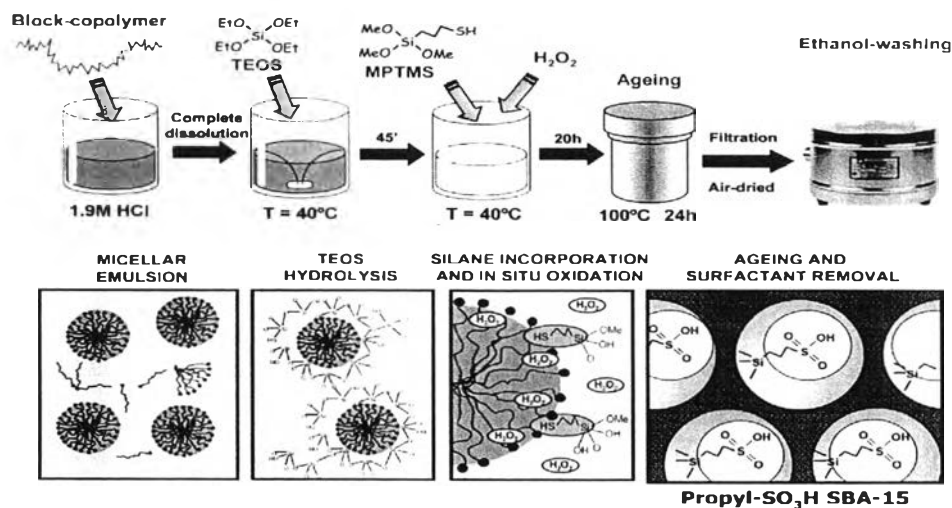


Figure 2.14 *In-situ* oxidation synthesis strategy for the preparation of organo-sulfonic acid group modified hexagonal mesoporous material [14].

Table 2.5 Summary of advantage and disadvantage of two organic functionalized modification methods.

Post synthesis method	Co-condensation method
<p>Advantage:</p> <ul style="list-style-type: none"> ● Good preservation of the mesostructure after post-modification <p>Disadvantage:</p> <ul style="list-style-type: none"> ● Reduce pore size and pore volume ● limited loading level of the functional groups can be grafted because of the limited density of the reactive surface silanols ● Time consuming ● Ineffective due to partial cross-linking of the functional groups with the silica-surface silanol groups ● Obtain low density and non-uniformity of functionality 	<p>Advantage:</p> <ul style="list-style-type: none"> ● Higher and more uniform surface coverage of functionality ● Capable control in surface properties. <p>Disadvantage:</p> <ul style="list-style-type: none"> ● Loss in original structure ordering such as aminopropyltriethoxysilane (APTES) functionalization.

2.6 Organic esters

2.6.1 General features

Esters are chemical compounds comprising of carbonyl group adjacent to an ether linkage. Generally, they are carboxylic acid derivatives in which the hydroxyl group ($-OH$) is replaced by an alkoxy group ($-OR$). The ester is a combination of a carboxylic acid and an alcohol in which a molecule of water is loosed [70]. Figure 2.15 shows the molecules of organic esters with various carboxylic acids and alcohols.

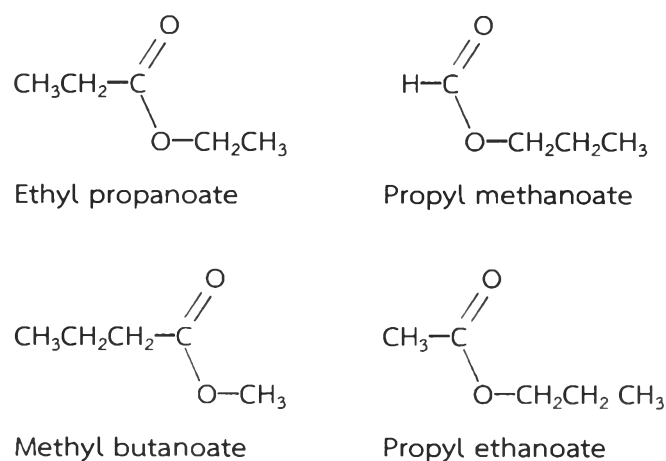
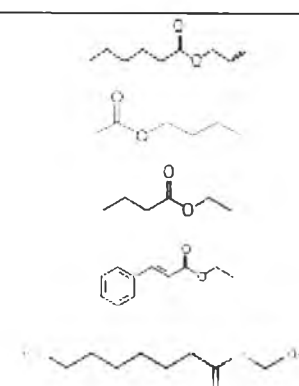
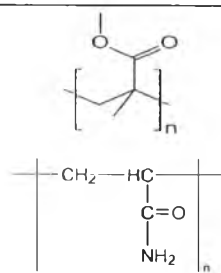
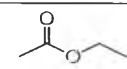


Figure 2.15 Examples of organic ester molecules.

Esters of carboxylic acids are important in various products, ranging from perfumes to biofuels. The organic esters are used widely in the manufacturing of flavors/foods, pharmaceuticals, plasticizers, fuel, and polymerization monomers as shown example in Table 2.6. They are also used as emulsifiers in the food and cosmetic industries [71].

Table 2.6 Examples of organic esters are used in the manufacturing.

Application	Ester Name	Ester molecule	Remarks
Flavor/Foods	- Allyl hexanoate - Butyl acetate - Ethyl butyrate - Ethyl cinnamate - Ethyl octanoate		- Odor of pineapple - Odor of apple, honey bee - Odor of banana - Odor of cinnamon - Volatile ethyl ester found in wine
Pharmaceutical	- Acetylcholine - Methacholine - Carbamoylcholine - Bethanechol	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\beta}{\text{CH}_2}-\overset{\alpha}{\text{CH}_2}-\text{N}^+(\text{CH}_3)_3$ $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{N}^+(\text{CH}_3)_3$ $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{N}^+(\text{CH}_3)_3$ $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}^+(\text{CH}_3)_3$	Cholinergic drugs
Polymer	- Poly(methyl methacrylate) - Polyacrylamide		Plastics
Fuel	- Methyl esters - Polyol ester	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3$ $\text{R}'-\overset{\text{R}'''}{\underset{\text{R}''}{\text{C}}}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	- Biodiesel - Lubricant
Solvent	- Ethyl acetate		- Nail polish remover



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The physicochemical properties of esters can be controlled via an appropriate selection of the raw materials used by which they are mainly dependent on molecular weight, number of ester groups per molecule, and degree of branching in the hydrocarbon chain. The ester linkages exhibit high bond energy, resulting in a good heat resistance [72].

Esters are more polar than ethers, but less so than alcohols. They participate in hydrogen bonds as H-bond acceptors, but cannot act as H-bond donors, unlike their parent alcohols and carboxylic acids. This ability to participate in H bonding confers some H₂O-solubility, depending on the length of the alkyl chains attached. Because they have no labile hydrogens (as alcohols and carboxylic acids do), esters do not self-associate. Consequently esters are more volatile than carboxylic acids of similar molecular weight.

2.6.2 Synthesis of esters

Esters are usually prepared from carboxylic acids by esterification. Thus, carboxylic acids are converted directly into esters by the reaction of a carboxylate ion with a primary alkyl halide or by Fischer esterification of a carboxylic acid with an alcohol in the presence of a mineral acid catalyst. Moreover, acid chlorides are converted into esters by treatment with an alcohol in the presence of base [73]. The preparation routes of organic esters are depicted in Figure 2.16.

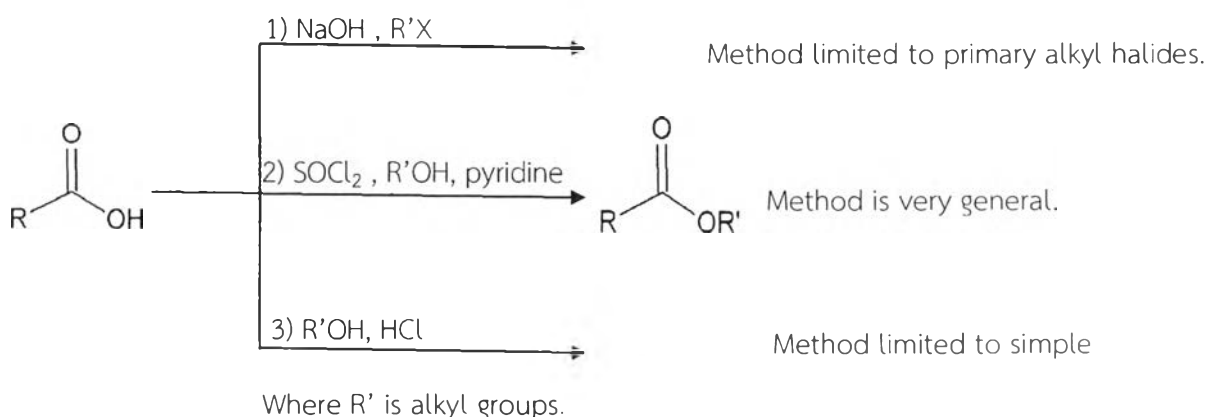


Figure 2.16 Pathway for preparation of organic esters.

2.7 Acid catalyzed esterification

The most usual method for the preparation of esters is the reaction of carboxylic acid and alcohol with elimination of water. Esterification is a reversible reaction (Figure 2.17), but is driven to completion by using of excess alcohol and removal of water [74].

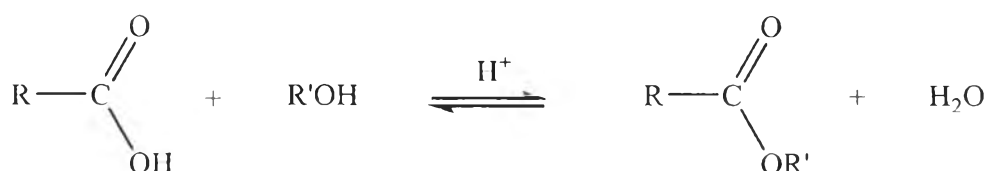


Figure 2.17 Esterification of carboxylic acid with alcohol.

The reaction without catalyst is usually too slow to be useful. The carboxylic acid and alcohol can be reacted thermally, usually in the presence of a catalyst in an esterification reactor. Possible catalysts include sulfuric, *p*-toluene sulfonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulfate, phosphorous oxides and stannous octanoate (Figure 2.18).

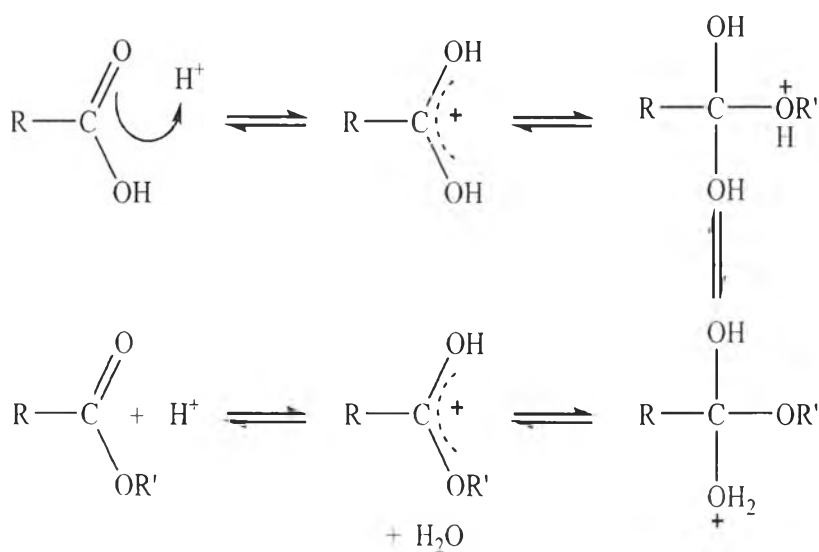


Figure 2.18 Mechanism of acid catalyzed esterification.

Step 1: An acid/base reaction, protonation of the carbonyl makes it more electrophilic.

Step 2: The alcohol O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3: An acid/base reaction, deprotonate the alcoholic oxygen.

Step 4: An acid/base reaction. Need to make an OH leave, it doesn't matter which one, so convert it into a good leaving group by protonation.

Step 5: Use the electrons of adjacent oxygen to help "push out" the leaving group, a neutral water molecule.

Step 6: An acid/base reaction, deprotonation of the oxonium ion reveals the carbonyl in the ester product.

2.7.1 Homogeneous acid catalysts

Homogeneous acid catalyzes reaction in the same phase as the reactants. Most commonly, the homogeneous acid catalyst is dissolved in a solvent with the reactants. Especially, esterification is usually carried out in the presence of strong homogeneous acids, such as H_2SO_4 , *para*-toluenesulfonic acid. Figure 2.19 shows conventional process for synthesis of ester lubricants via esterification by using strong homogeneous acid catalyst. The use of homogeneous acid catalyst is associated with high toxicity, material corrosion, large amount of liquid waste and difficulty of separation from the products [75].



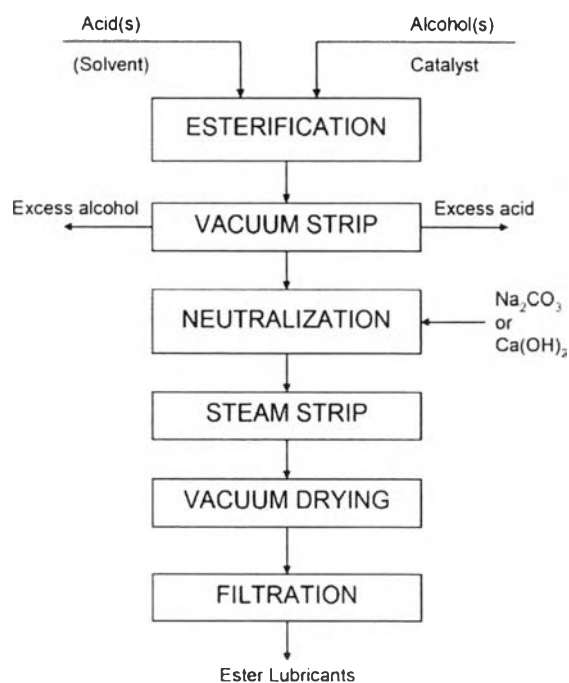


Figure 2.19 Conventional process for synthesis of ester lubricants via esterification [76].

2.7.2 Heterogeneous acid catalysts [75]

Solid acid catalysts have served, as important functional materials, for the chemical process, such as esterification, hydrolysis and cracking, for the production of valuable chemicals. The use of solid acid catalysts has many advantages over the homogeneous counterpart. Heterogeneous acid catalysts can enhance the selectivity to desired product, make the product separation easy, and can be reused. The amount of waste can be reduced also. However, in some cases, the reaction over the solid catalysts has to be performed under relatively severe conditions and subjected to mass transfer limitation.

Heterogeneous acid catalysts can be divided into 2 groups, i.e. supported catalysts and bulk catalysts as shown in Figure 2.20.

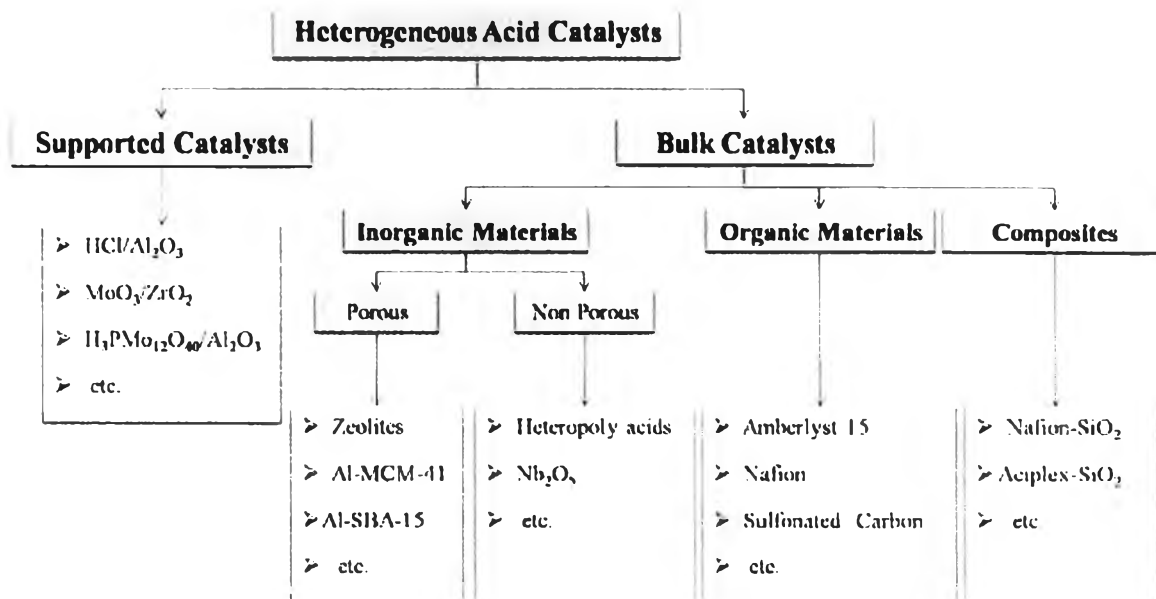


Figure 2.20 Classification of the heterogeneous acid catalysts [75].

2.7.2.1 Supported catalysts

These catalysts are easily prepared by simple impregnation method such as $\text{HCl}/\text{Al}_2\text{O}_3$ and $\text{MoO}_3/\text{ZrO}_2$. Although they are very active in the reactions and high thermal stability, for example using $\text{MoO}_3/\text{ZrO}_2$ report that was highly active in the hydrolysis of ethyl acetate in excess water and esterification of acetic acid with ethanol, they prone to deactivation by leaching of active species [77].

2.7.2.2 Bulk catalysts

These solid catalysts are more commonly used as industrial acid catalysts. They can be divided into inorganic materials, organic materials and composites.

(a) *Inorganic-based catalysts* are mainly the oxides and mixed oxides of metals with or without porosity such as zeolites, Al-MCM-41, heteropoly acids, Nb_2O_5 , etc. The major advantages of the catalysts in this class are high thermal stability and high shape selectivity.

Zeolites are example of porous acidic catalysts that received extensive attention recently. Their acid site formed behaves as a classic Brønsted, proton donating acidic site as shown in Figure 2.21. The highly acidic sites combined with the high selectivity

arising from shape selectivity and large internal surface area makes the zeolite as an ideal industrial catalyst [78].

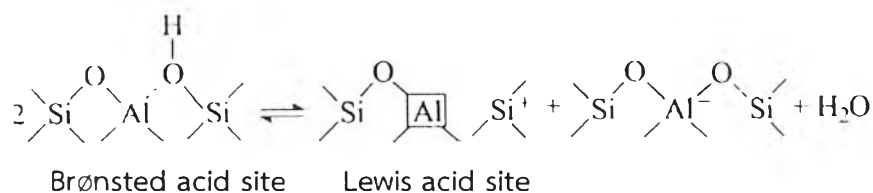


Figure 2.21 Brønsted and Lewis acid sites in zeolites.

Heteropolyacids are non-porous catalyst. They have been commercially utilized for several petrochemical processes. For example, they were used as catalyst in the hydration of propene for the manufacture of 2-propanol, hydration of *n*-butenes and hydration of isobutylene. The heteropolyacid can be regarded as environmentally friendly due to its high selectivity, easy separation, and use of only the reactants and catalyst. Furthermore, the lifetime of a heteropoly catalyst can be >10 years, and the investment for a heteropoly catalyst facility is roughly half that of a sulfuric acid facility [75].

(b) *Organic-based catalysts* are mostly functional polymers and ion-exchange resins such as AmberlystTM resins, Nafion.

AmberlystTM resins have been used in a wide range of acid-catalyzed reaction due to having strong acidity. Moreover, they have high hydrophobic property that reduces poisoning of the acid sites due to water adsorption. So, AmberlystTM resins have been explored as powerful catalysts for various acid-catalyzed organic reaction. The structure of AmberlystTM resins such as Amberlyst-15 is shown in Figure 2.22.

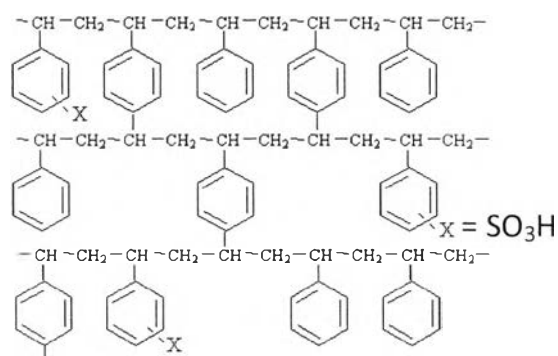


Figure 2.22 The polymer structure of Amberlyst-15.

Nafion is a fluorinated polymer-support sulfonic acid group discovered in the early 1960s by Walther Grot of DuPont. Nafion consists of a polytetrafluoroethylene backbone and regular spaced long perfluorovinyl ether pendant side chains terminated by a sulfonate ionic group. The chemical formula of Nafion shown in Figure 2.23 where M^+ is the counter ion (H^+ , Li^+ or Na^+). One major drawback of Nafion is the low surface area ($0.02 \text{ m}^2 \text{ g}^{-1}$). This property results in low activity.

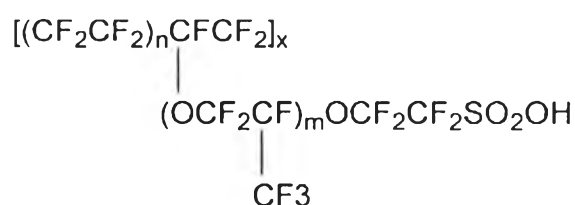


Figure 2.23 Chemical formula of Nafion [79].

(c) *Composite catalysts* are combined good aspects of inorganic and organic materials together in which the organic parts possess strong acidity and the inorganic parts contribute to the catalyst porosity.

Figure 2.24 proposed a classification of the composite material of mesoporous silica with organic components [79]. Type (A) is surface modification using $R\text{-Si}(\text{OR})_3$ compounds and Type (B) is framework modification such as periodic mesoporous organosilicas (PMOs). Type (C) shows composite materials with polymeric

compounds in the pore voids. Composite mesoporous materials with polymers in the framework are named Type (D).

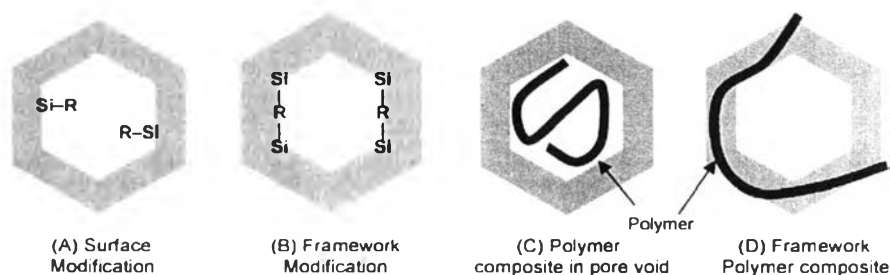


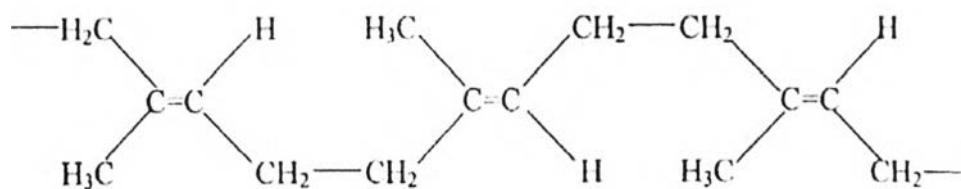
Figure 2.24 Conceptual scheme of composite materials of mesoporous silica with organic components [79].

Silica-supported Nafion[®] catalyst (SAC) is an example of the acidic composite. SAC is composite that Nafion entrapped in a highly porous silica matrix. SAC is solid acid catalysts followed by the Nafion loading, e.g. SAC-13 containing 13 wt.% Nafion in the silica matrix.

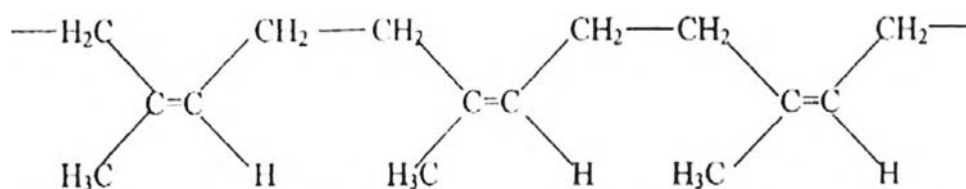
2.7 Natural rubber

Natural rubber (NR) is a hydrophobic polymer of *cis* 1,4- isoprene monomers (Figure 2.25) that obtained from the milky secretion (latex) of various plants. Especially, the important commercial source of natural rubber (sometimes called Para rubber) is the tree *Hevea brasiliensis*. Most of the world's natural rubber are supplied from South East Asia, mainly Thailand, Malaysia and Indonesia [80]. Natural rubber does not dissolve in water, alcohol or acetone but be dissolved as solution in organic solvent such as toluene and/or tetrahydrofuran. In addition, it can swell and disperse in the some organic solvents, such as toluene, benzene. The processed form of natural rubber is also commonly called "latex".





trans-Polyisoprene (repeat unit, $n = 100$; $M_w = 7,000$)



cis-Polyisoprene (repeat unit, $n = 1,500$ to $15,000$; $M_w = 100,000$ to $1,000,000$)

Figure 2.25 Isoprene structure of natural rubber.

2.8 Natural rubber/silica composites

The incorporation of silica fillers into the natural rubber has become of special interest since it imparts many interesting and useful properties to the resultant particle-filled composites obtained, such as enhanced mechanical properties and thermal stability [81-83]. The *in situ* silica filling in rubbers in particular has been focused on since it can be performed by a simple sol-gel reaction and results in a controlled size of silica particles with a high level of dispersion with low level of aggregation in the rubber matrix as depicted SEM image in Figure 2.26.

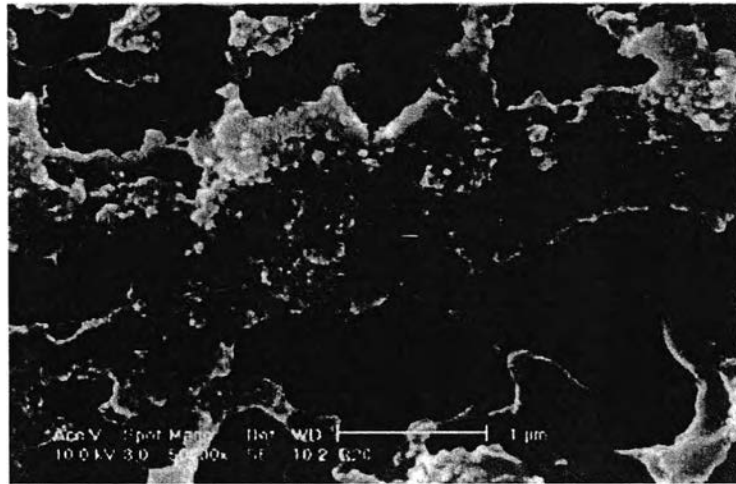


Figure 2.26 SEM image of natural rubber/silica composites [84].

Generally, the generation of *in situ* silica within the rubbery polymer is undertaken in the alkoxy silane such as tetraethoxysilane (TEOS) as the silica precursor [85]. A reaction is the acid- or base-catalyzed hydrolysis of TEOS in Figure 2.27. The base-catalyzed sol-gel reaction by using primary amine performs in two steps. Firstly, TEOS swelling in the rubbery polymer is hydrolyzed by water, followed by condensation of silicate species to form silica particles [29]. In practice, the hydrolysis is carried out in ethanol as a solvent under controlled conditions that allow the solution (sol) to form a formable loosely cross-linked matrix (gel). The important parameters affecting the rates of the sol-gel reaction are the types of polymer [86-88], solvent, silica precursor and base, the water: silica precursor molar ratio, the temperature, and the mixture pH [89].

2.9 Literature reviews

2.9.1 Synthesis of natural rubber/silica composites via *in situ* sol-gel reaction

Kohjiya *et. al.* (2000) [90] prepared the *in situ* silica filling in the rubber matrix before vulcanization by immersing the NR sheet of ca. 1 mm thickness in TEOS and aqueous solution of *n*-butylamine using as base catalyst. The fine and well-dispersed *in situ* silica particles were generated by the sol-gel reaction of TEOS in the rubber matrix before vulcanization and those did not much inhibit the crosslinking reaction of NR compound by sulfur. This result suggested that the amount of silanol groups on the surface of *in situ* silica was much lower than that of conventional silica.

Poompradub *et. al.* (2005) [91] studied on the sol-gel reaction of *in situ* silica in NR matrix. The mechanical properties of conventional silica composites were studied comparing with the *in situ* silica composites. The various primary amines (*n*-butylamine, *n*-hexylamine, *n*-octylamine, dipropylamine, and triethylamine) were used as the base catalyst. The use of *n*-hexylamine as the catalyst in sol-gel reaction generated high *in situ* silica content 71 phr at 40 °C for 72 h.

2.9.2 Functionalization of silica with sulfonic acid group

Suaus *et. al.* (1985) [92] studied the application of benzyl sulfonic acid siloxane for the oligomerization of isobutene. The attachment of organic ion exchangers to silica as a support would produce a catalyst of higher temperature stability. Benzyl sulfonic acid attached to silica by reacting benzyl sulfonic acid silanetriol with silica gel. These catalysts proved to have a much higher thermal stability than ion-exchange resins because they can used as an acidic catalyst for reactions higher than 130°C.

Yang *et. al.* (2005) [93] studied the increasing acidity of SBA-15 by grafting sulfonic acid group on the surface using post-synthesis method. The effects of time and amount of oxidizing agent were investigated. The resultant material showed the highest acidity when oxidized with 30% H₂O₂ for 24 hrs. Moreover, SBA-15-SO₃H exhibited a good long-range order, high specific surface areas (ca. 600 m²/g) and uniform pore sizes (ca. 6 nm).

Long *et. al.* (2011) [94] synthesized polymer-oxide hybrid materials based on non-porous silica-supported sulfonic acid-containing polymer brush materials that proposed here as a new class of potentially water-tolerant solid acid catalyst. The designed to improve the hydrolytic stability of the catalyst, was used to create



poly(styrene) brushes on the surface of fumed silica. The catalysts were evaluated in the hydrolysis of ethyl lactate, with the polymer brush materials having the same activity as a homogeneous catalyst, *p*-toluenesulfonic acid, and being substantially more active than an acidic polymer resin (Amberlyst 15).

2.9.3 Esterification over heterogeneous acid catalysts

Liu *et. al.* (2006) [95] studied the impact of carboxylic acid chain length on the kinetics of liquid-phase acid-catalyzed esterification. Using sulfuric acid and a commercial Nafion/silica composite solid acid catalyst (SAC-13), initial kinetics were measured for the reactions of a series of linear chain carboxylic acids (acetic, propionic, butyric, hexanoic, and caprylic acid) with methanol at 60 °C. It was found that reaction rate decreased as the number of carbons in the linear alkyl chain increased for both H₂SO₄ and SAC-13. The reaction kinetic parameters of SAC-13 catalysis were determined and compared for different carboxylic acids. Moreover, important parameters, such as water deactivation, catalyst reusability, and regeneration, were also affected by the size of the carboxylic acid used. Nafion/SiO₂ nanocomposite catalyst showed good reusability in the esterification of low-molecular-weight acids. However, the catalyst experienced continuous activity loss in consecutive reaction cycles when using caprylic acid as the reactant. Catalyst deactivation was probably due to accumulation of the carboxylic acid molecules/intermediates on or in the nanodomains of the Nafion resin.

Díaz *et. al.* (2005) [96] studied influence of the alkyl chain length of HO₃S-R-MCM-41 (R= different alkyl) on the esterification of glycerol with lauric acid and oleic acid. The catalytic performance of the resulting HSO₃-ethyl-MCM-41, HSO₃-ethyl/methyl-MCM-41 and HSO₃-methyl-MCM-41 new materials is also compared to those of HSO₃-phenyl/methyl-MCM-41 and HSO₃-propyl/methyl-MCM-41. It has been demonstrated that an optimum balance among parameters such as nature of the organic group which support the sulfonic acid, distance between the sulfonic group and the silica surface, average pore size of the material, etc., obtain catalysts with improved activity and selectivity for these reactions. HSO₃-ethyl/methyl-MCM-41 and HSO₃-methyl-MCM-41 catalysts are active and selective in the esterification of glycerol with lauric and oleic acids. An optimum balance among parameters such as nature of the organic group, which support the sulfonic acid (aromatic or alkyl, length of the alkyl chain), distance between the sulfonic group and the silica surface, average pore size of the material, etc., allowed to obtain catalysts with improved activity and selectivity for these reactions.



Altiokka *et. al.* (2009) [97] studied the kinetics of esterification of acrylic acid with propylene glycol in the presence of Amberlyst-15 as a heterogeneous catalyst. The reaction was realized in a batch reactor at different temperatures and initial reactant mol ratios. The simultaneous dimerization/polymerization of acrylic acid and products, in addition to the reversible esterification reaction, was proposed as the reaction mechanism. It was also concluded that the selectivity of hydroxypropyl acrylate is significantly low at high conversion levels of acrylic acid. Therefore, to work at low conversion with a proper recycle of unreacted stream, after product separation, is recommended in industrial usage. Kinetic equations corresponding to the reaction mechanism have also been developed. Temperature dependence of the reaction rates and activation energies was determined.

Miao *et. al.* (2011) [98] investigated the kinetics of acetic acid esterification with methanol using a propylsulfonic acid-functionalized SBA-15 catalyst. To determine whether a different mechanism was applicable for heterogeneous or homogeneous catalyzed esterification, propane sulfonic acid was also examined as this homogeneous acid has the same structure as the functional groups tethered onto SBA-15 as shown in Figure 2.28. The experimental results demonstrated that acetic acid esterification with methanol followed a dual-site Langmuir–Hinshelwood type reaction mechanism, which required both the adsorption of acetic acid and methanol over propylsulfonic acid-functionalized SBA-15. In contrast, esterification reaction with the homogeneous catalyst followed an Eley–Rideal mechanism. The kinetic data were successfully fit with a model in which the surface reaction was the rate-limiting step.



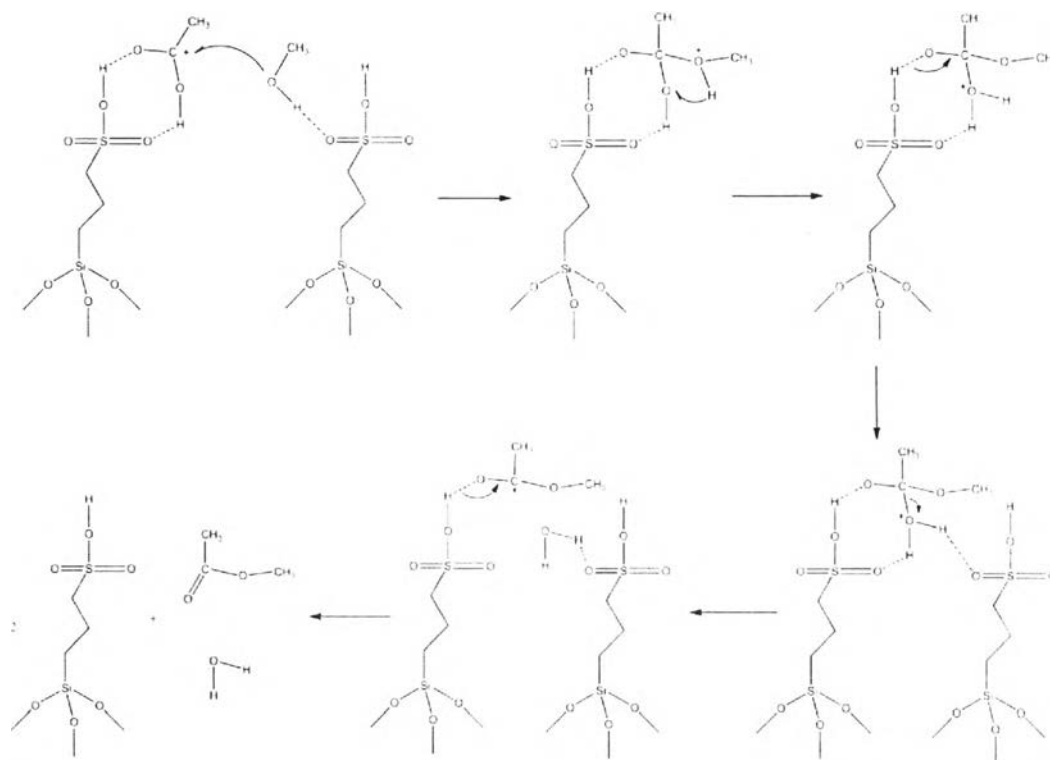


Figure 2.27 Possible reaction mechanism for the acetic acid esterification with methanol over propylsulfonic acid-functionalized SBA-15 [98].

