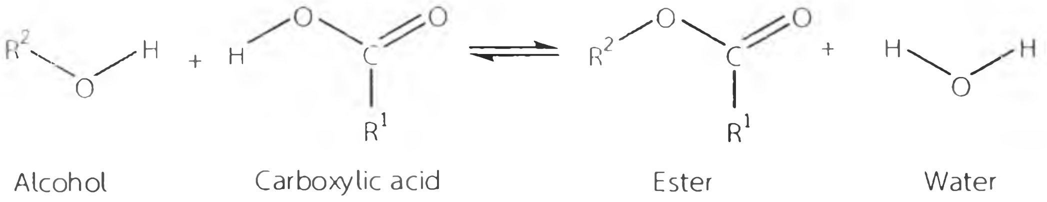
CHAPTER II

THEORY

2.1 The Fischer Esterification

The preparation of ester is the reaction of alcohol (R-OH) and carboxylic acid (R-OOH) with elimination of water, called Fischer Esterification. Replacing the -OH group of a carboxylic acid with -OR group of an alcohol gives a carboxylic ester. Because the esterification is a reversible reaction, available techniques are required to increase yields of ester. Using a large of the alcohol or the acid and a dehydrating agent removing water are the ways to form an ester. The acid and alcohol can be reacted thermally, usually in the presence of a catalyst is an esterification reactor.



The Fischer esterification mechanism, shown in **Figure 2.1**, is nucleophilic acyl substitution using acid catalyst. The carbonyl group of a carboxylic acid is not adequately electrophilic to be attacked by an alcohol. The carbonyl group is protonated and activated toward nucleophilic attack by the acid catalyst. Loss of a proton gives the hydrate of an ester. After that, protonation prepares the good leaving -OH group, a neutral water molecule. The water, as nucleophile, deprotonates at oxonium to form ester product.

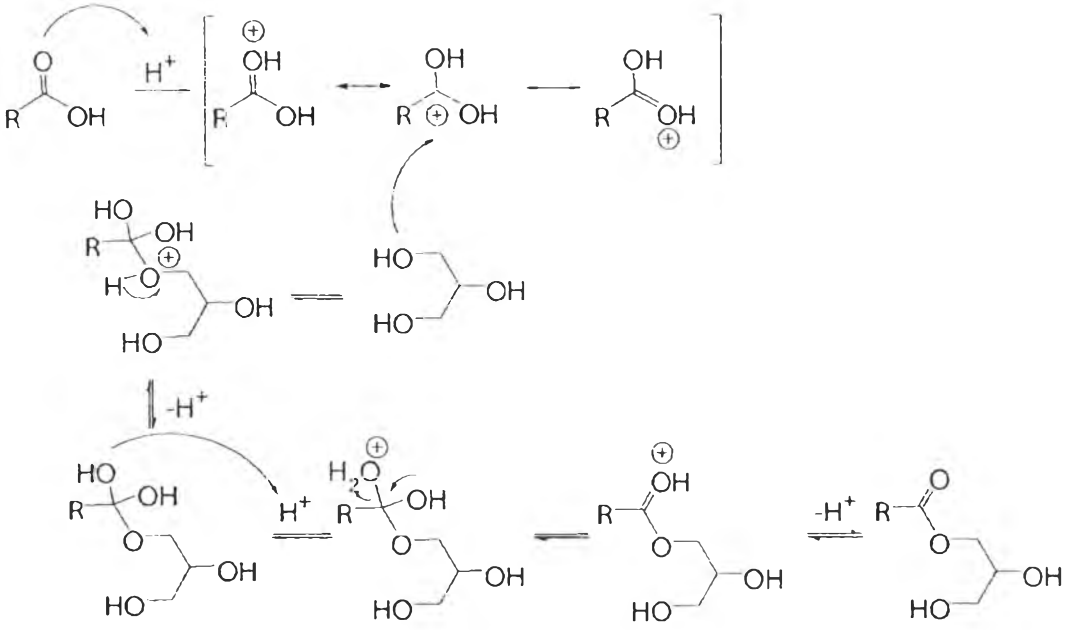


Figure 2.1 The Fisher esterification mechanism [19].

2.2 Free fatty acid

A fatty acid is a long aliphatic chain with a carboxylic acid functional group, which is either saturated or unsaturated, has double bonds on its structure. The natural fatty acids have a chain of an even number of carbon atoms, from 4 to 28. Fatty acid is classified as short to long [20].

- Short-chain fatty acids (SCFA) are fatty acids with aliphatic tails of fewer than six carbons (*i.e.* butyric acid).

- Medium-chain fatty acids (MCFA) are fatty acids with aliphatic tails of 6–12 carbons, which can form medium-chain triglycerides.

- Long-chain fatty acids (LCFA) are fatty acids with aliphatic tails 13 to 21 carbons.

- Very long chain fatty acids (VLCFA) are fatty acids with aliphatic tails longer than 22 carbons.

2.2.1 Unsaturated fatty acid

Unsaturated fatty acids have double bonds in the structure that two carbon atoms in the chain that maybe either *cis* or *trans* configuration, depending in the geometry of double bond.

The differences in geometry between the various types of unsaturated fatty acids, as well as between saturated and unsaturated fatty acids, play an important role in biological processes, and in the construction of biological structures (such as cell membranes).

2.2.1.1 Oleic acid (C_{18})

Oleic acid can be found in many animal and vegetable fats and oils. It is classified as a monosaturated omega-9 fatty acid. One of the chief sources of this acid in foods is olive oil. Moreover, canola and grape seed oil also contain oleic acid, which has less cholesterol levels. Oleic acid is used as moisturizer in cosmetic industries. Furthermore, oleic acid is a key role in warning colony members of death or coming danger in the insect industries [21].

2.2.2 Saturated fatty acid

Saturated fatty acids have no double bonds between individual carbon atoms. It's mean that the chain of carbon atom is fully with hydrogen atoms. In the nature, It can be found the saturated fatty acid from 3 carbon (propionic acid) to 36 (hexatriacontanoic acid).

2.2.2.1 Acetic acid (C_2)

Acetic acid is the main component of vinegar with a distinctive sour taste and pungent smell. It is one of the simplest carboxylic acid. Moreover, it is mainly produced as a precursor to polyvinylacetate for wood glue and cellulose acetate for photographic film. For food industry, acetic acid was used as food additive in code E230 as a acidity regulator.

2.2.2.2 Caproic acid (C_6)

Caproic acid is another name of hexanoic acid, is a colorless liquid with fatty odor. It can be several found naturally in animal fats and oils. It has been used in the esters manufactory for artificial flavors, and in the manufacture of hexyl derivatives, such as hexylphenols. Moreover, It commonly used neat in butter, cream, milk, bread, beer, nut, strawberry and other flavors.

2.2.2.3 Lauric acid (C_{12})

Lauric acid or dodecanoic acid, saturated fatty acid with 12 carbon atom chain, is a white solid at room temperature but easily melts by boiling water. It can be obtained from 45-57% of coconut milk. Laurel oil, milk and palm kernel oils also have high concentrations of around 50%. Used in manufacturing is as an ingredient in soaps and shampoos. Other common uses include the manufacturing of lauryl alcohol, insecticides and cosmetics.

Table 2.1 Properties of varied carbon chain carboxylic acid.

Properties	Acetic acid	Caproic acid	Lauric acid	Oleic acid
Molecular formula	$C_2H_4O_2$	$C_6H_{12}O_2$	$C_{12}H_{24}O_2$	$C_{18}H_{34}O_2$
Molar mass (g/mol)	60.05	116.16	200.32	282.46
Density (g/cm^3)	1.049	0.929	0.880	0.845
Melting point (°C)	16-17	-3.4	43.2	13-14
Boiling point (°C)	118-119	205.8	298.9	360.0
Acidity (pKa)	4.76	4.88	5.78	-

2.3 Catalysts

A catalyst is substance that can reduce the activation energy (E_a) than the corresponding uncatalyzed reaction to increase rate of reaction at the same temperature as shown in **Figure 2.2** [22]. The highest energy is the highest peak position that referred to the transition state. In regularly reaction, the input of energy to go in the transition state is high, while the catalyzed reactions have lower amount of energy to start a reaction. The catalyst stabilizes the transition state more than it stabilizes the starting materials. The chemical and product energy unchanged at the end of the reaction, they have no effect on chemical equilibrium. Moreover, a catalyst enable a chemical process to work more efficiently, more selective manner and often with less waste. Therefore, catalysts are essential in industrial chemistry.

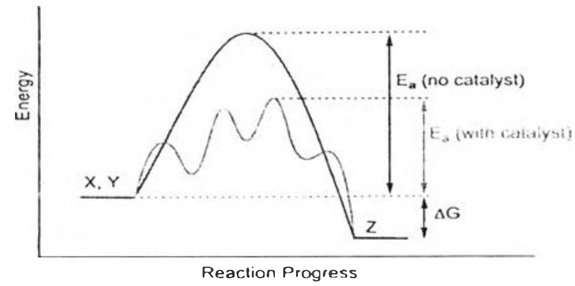


Figure 2.2 The relationship between activation energy (E_a) and enthalpy (ΔH) of the reaction with and without a catalyst [22].

2.3.1 Type of catalyst

Catalyst is classified into two types by identifying the boundaries of the catalyst and the reactant. The different phase reaction between catalyst and reactants is called heterogeneous reaction, while the catalyst in the same phase of reactant is called homogeneous reaction. Heterogeneous catalyst has a lower degree of dispersion than homogeneous catalyst because only the surface atoms are active [23]. Summary of the advantage and disadvantage of two-type catalyst is presented in **Table 2.2**.

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Table 2.2 Comparison of homogeneous and heterogeneous catalysts [24].

Consideration	Homogeneous catalyst	Heterogeneous catalyst
1. Active centers	All metal atoms	Only surface atoms
2. Concentration	Low	High
3. Selectivity	High	Low
4. Diffusion problems	Practically absent	Present (mass-transfer-controlled reaction)
5. Reaction conditions	Mild (50-200°C)	Severe (often >250°C)
6. Applicability	Limited	Wide
7. Activity loss	Irreversible reaction with product (cluster formation), poisoning	Sintering of the metal crystallites, poisoning

Consideration	Homogeneous catalyst	Heterogeneous catalyst
8. Modification possibility	High	Low
9. Thermal stability	Low	High
10. Catalyst separation	Sometimes laborious (chemical decomposition, distillation, extraction)	Fixed-bed: unnecessary Suspension: filtration
11. Catalyst recycling	Possible	Unnecessary (fixed-bed) or easy (suspension)
12. Cost of catalyst	High	Low

The difficulty to separate from reaction mixture has become the main disadvantage of homogeneous catalyst. This is why heterogeneous catalysts are chosen to solve this problem because they are able to either automatically removed in the process (*e.g.* vapor-phase reaction in fixed bed reactor) or separated by simple methods such as filtration or centrifugation. Nevertheless, homogeneous catalysts are necessarily used in more complex processes, distillation, liquid-liquid extraction and ion exchange.

2.4 Porous molecular sieves

The IUPAC defines the porous materials into three main types depending on their pore size that are microporous material, mesoporous material, and macroporous material, as shown in **Table 2.3**. The Porous materials are molecular sieves that exhibit selective adsorption properties [25].

Table 2.3 IUPAC classification of porous materials.

Type of porous molecular sieve	Pore size (Å)	Examples
Microporous materials	< 20	Zeolites, Activated carbon
Mesoporous materials	20 - 500	M41s, SBA-15, Pillared clays
Macroporous materials	> 500	Glasses

2.4.1 Shape Selectivity

Shape selectivity plays a very important role in catalysis. Highly crystalline and regular channel structures are among the principal features that zeolite used as catalysts offer over other materials. Shape selectivity is divided into 3 types: reactant shape selectivity, product shape selectivity and transition-state shape selectivity. These types of selectivities are shown in **Figure 2.3**. Reactant shape selectivity results from the limited diffusivity of some reactants, which cannot effectively enter and diffuse inside the zeolites. Product shape selectivity occurs when diffusing product molecules cannot rapidly escape from the crystal, and undergo secondary reactions. Restricted transition-state shape selectivity is a kinetic effect arising from the local environment around the active site: the rate constant for a certain reaction mechanism is reduced if the necessary transition state is too bulky to form readily.

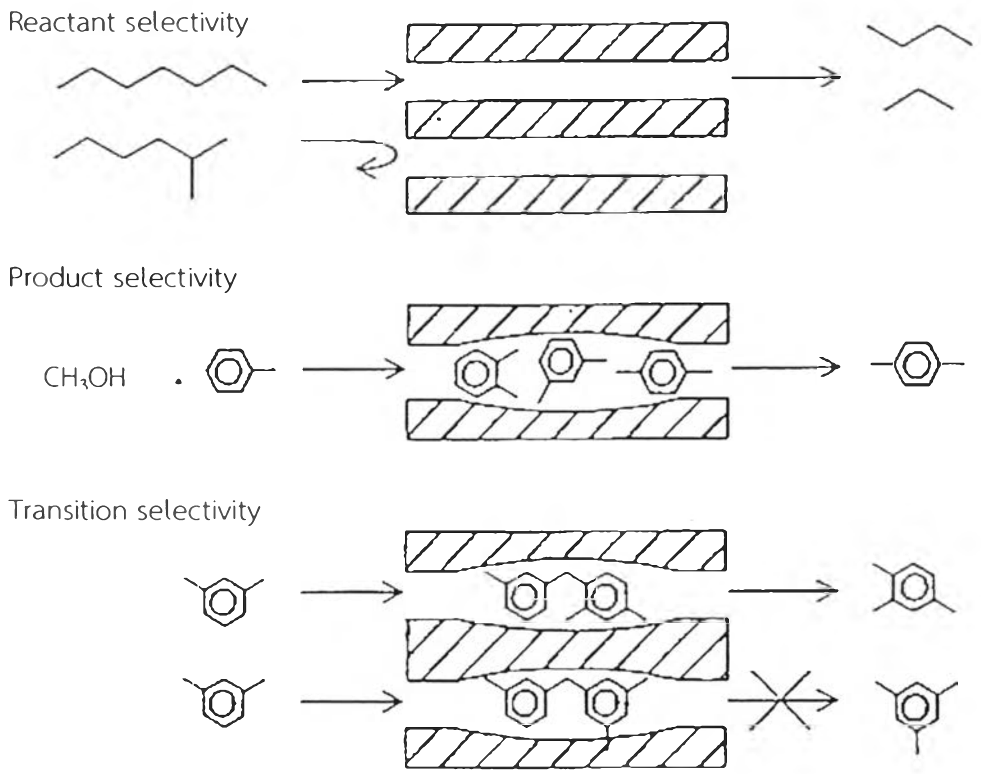

Figure 2.3 Three types of selectivity in zeolites: reactant, product and transition state shape selectivity [20].

2.5 Mesoporous materials

Mesoporous materials are a type of molecular sieves, including silicas or transitional aluminas or modified layered materials such as pillared clays and silicates. Mesoporous silica has uniform pore sizes from 20 to 500 Å and has found great utility as catalysts and sorption media by capillary effect because of the regular arrays of uniform channels. Larger surface area is desired for enhancing of the efficient in the reactions [26].

The silica surface catalyst is composed of reactive silanol (Si-OH) groups easily reacting with organic functionalities (**Figure 2.4**) for allowing to organic/inorganic hybrid material creation. The silica surface comprises a consist of isolated silanols (**Figure 2.4 (a)**), germinal silanols (**Figure 2.4 (b)**), vicinal silanols (**Figure 2.4 (c)**) and siloxane bridge (**Figure 2.4 (d)**). Consequently, preparation of the organic/inorganic hybrid material can be altered from all of silanol species [27].

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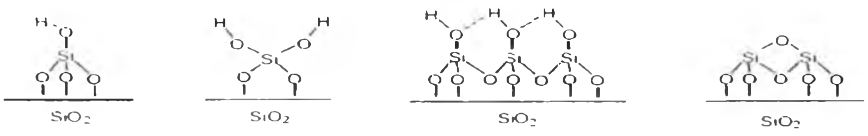

(a) (b) (c) (d)

Figure 2.4 Types of silica surface Si-O species [27].

In 1992, the scientist from Mobil Corporation found out the M41S family of silicate/aluminosilicate mesoporous molecular sieves with large uniform pore structures, which has resulted in a worldwide new study in this area. Three different mesophases in this family have been identified, *i.e.*, lamellar, hexagonal, and cubic phase. MCM-41 [26] has a hexagonally packed array of cylindrical pores. The structure of MCM-48 [28] has a three-dimensional, cubic-ordered pore structure and MCM-50 [29] contains a lamellar structure as illustrated in **Figure 2.5**.

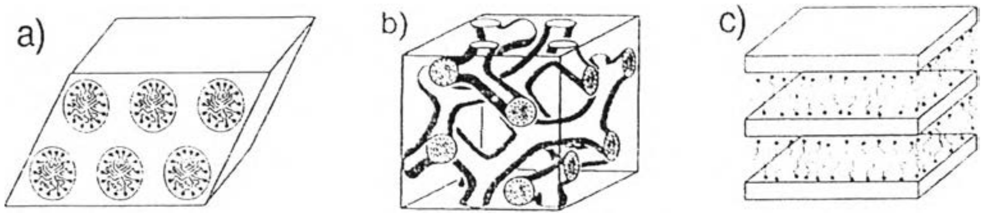

Figure 2.5 A schematic presentation of three inorganic-surfactant mesostructures: (a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase.

Nowadays, many families of mesoporous materials were discovered. Example, a new mesoporous species with hexagonal structure was discovered, such as HMS (Hexagonal Mesoporous Silica) [30], FSM-16 (Folded Sheets Mesoporous Materials) [31] and SBA-15 [32] (Santa Barbara Amorphous). The different types of templates can be used for synthesizing hexagonal mesoporous materials at various pHs of gel, the new hexagonal materials can be obtained. The interactions of various types of template with inorganic species for assembling these materials are different as summarized in **Table 2.4**, together with the condition typically employed for a synthesis.

Table 2.4 Various synthesis conditions of hexagonal mesoporous materials and the type of interaction between template and inorganic species.

Material	Template	Assembly	Media (pH)
MCM-41	Quaternary ammonium salt	Electrostatic	Basic or Acid
FSM-16	Quaternary ammonium salt	Electrostatic	Basic (pH = 8.5)
SBA-15	Amphiphilic triblock copolymer	Hydrogen bonding	Acid (pH = 1-2)
HMS	Primary amine	Hydrogen bonding	Neutral

MCM-41 and FSM-16 can be synthesized using quaternary ammonium salt as a template. In case of SBA-15, amphiphilic tribock copolymer can be modified as a template and must be synthesized in acid condition of hydrochloric acid. 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 2.5**.

Table 2.5 Properties of some hexagonal mesoporous materials [33-36].

Material	Pore size (Å)	Wall thickness (nm)	BET specific surface area (m^2/g)	Framework structure
MCM-41	15-100	1	>1000	Honey comb
FSM-16	15-32	-	680-1000	Folded sheet
SBA-15	46-300	3-6	630-1000	Rope-like
HMS	29-41	1-2	640-1000	Wormhole

2.5.1 Synthesis schemes of mesoporous materials

Crystalline molecular sieves are generally obtained by hydrothermal crystallization. The reaction gel, usually, contains cations (*e.g.* Si^{4+} for silicate materials, Al^{3+} for aluminate materials) to form the framework; anionic species (*e.g.* OH^- and F^-); organic template and solvent (generally water). Typically, the nature of template can be considered into two parts that are hydrophobic tail on the alkyl chain side and hydrophilic head on another side. The examples of used templates are primary, secondary tertiary and quaternary amines, alcohols, crown or linear ethers, and as well as polymers. An understanding of how organic molecules interact with each other and with the inorganic frameworks would increase the ability to design rational routes to molecular sieve materials. The organic templates are frequently occluded in the pores of the synthesized material, contributing to the stability of mineral backbone.

2.5.1.1 The behavior of surfactant molecules in an aqueous solution

In a simple binary system of water-surfactant, surfactant molecules can aggregate to form micelles in various types at a particular concentration. The shapes of micelle depend on the concentrations as shown in **Figure 2.6**.

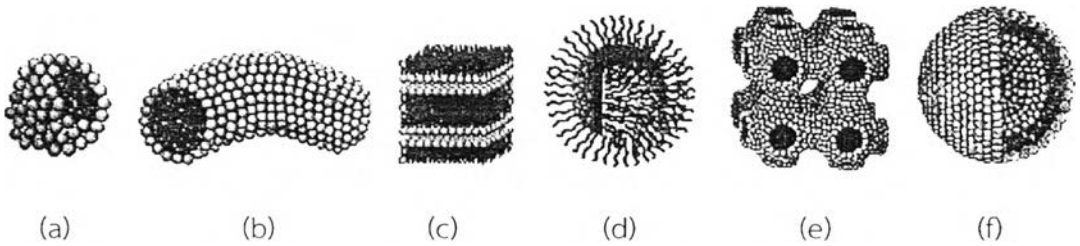

Figure 2.6 Phase sequence of the surfactant-water binary system (a) spherical micelle, (b) rod-shaped micelle, (c) lamellar phase, (d) reverse micelle, (e) bicontinuous phase and (f) liposome [37].

At low concentration, they energetically exist as isolated molecules. With increasing concentration, surfactant molecules aggregate together to form isotropic spherical and rod shaped micelles by directing the hydrophobic tails inside and turning the hydrophilic heads outside in order to decrease the system entropy. The initial concentration threshold at which those molecules aggregate to form isotropic micelle is called critical micelle concentration (CMC). The CMC determines thermodynamic stability of the micelles. When the concentration is continuously increased, the micellar shape changes from sphere or rod shapes to hexagonal, lamellar, and reverse micelles. The particular phase present in a surfactant aqueous solution depends not only on the concentrations but also on the natural of surfactant molecules such as its length of the hydrophobic carbon chain, hydrophilic head group, and counter ion. Besides the ionic strength, pH value, and temperature including other additives are the factors determining the shape of micelles.

2.5.1.2 Interaction between inorganic species and surfactant micelles

A number of models have been proposed to explain the formation of mesoporous materials and to provide a rational basis for synthesis routes [37]. On the common level, these models are predicted upon the presence of surfactants in a solution to direct the formation of inorganic mesostructure from stabilized inorganic precursors. The type of interaction between the surfactant and the inorganic species is significantly different depending on the various synthesis routes as shown in **Table 2.6**.

Table 2.6 Example routes for interactions between the surfactant and the inorganic soluble species.

Surfactant type	Inorganic type	Interaction type	Example materials
Cationic (S^+)	I^-	S^+I^-	MCM-41, MCM-48
	I^+X^-	$S^+X^-I^+$	SBA-1, SBA-2, zinc phosphate
	I^0F^-	$S^+F^-I^0$	silica
Anionic (S^-)	I^+	S^-I^+	Al, Mg, Mn, Ga
	I^-M^+	$S^-M^+I^-$	alumina, zinc oxide
Neutral S^0 or N^0	I^0	S^0I^0 or N^0I^0	HMS, MSU-X, aluminum oxide
	I^+X^-	$S^0X^-I^+$	SBA-15

Where S^x or N^x : surfactant with charge of X

I^x : inorganic species with charge of X

X^- : halogenide anions F^- : fluoride anion

M^{n+} : with charge of X

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 2.7** shows the possible hybrid inorganic-organic interfaces.

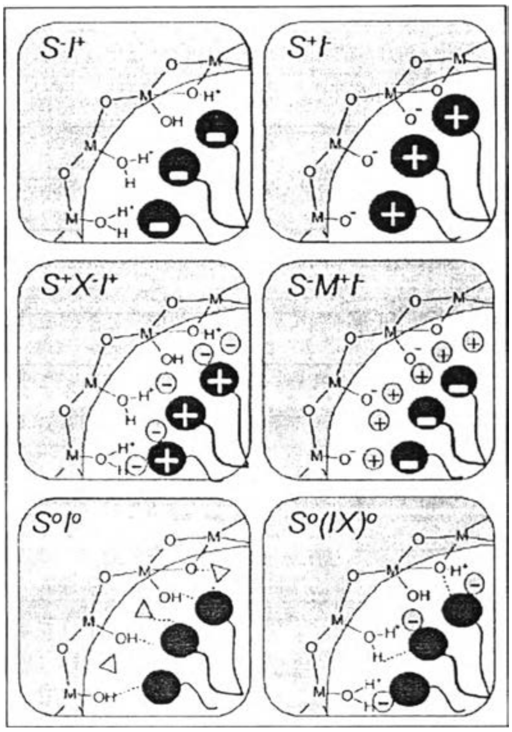

Figure 2.7 Schematic representation of the different types of silica-surfactant interfaces. Dashed line corresponded to H-bonding interactions [37].

In case of non-ionic surfactant (S^0 or N^0), the main interaction between template and inorganic species is hydrogen bonding or dipolar, which is called neutral path *i.e.* S^0I^0 and $S^0F^-I^+$. Nowadays, non-ionic surfactants give important commercial advantages in comparison to ionic surfactants because they are easily removable, nontoxic, biodegradable and relatively cheap.

2.5.1.3 Formation mechanism of mesoporous materials

Mechanism of mesoporous formation can be classified on the basis of synthetic route into three types exhibited in **Figure 2.8**.

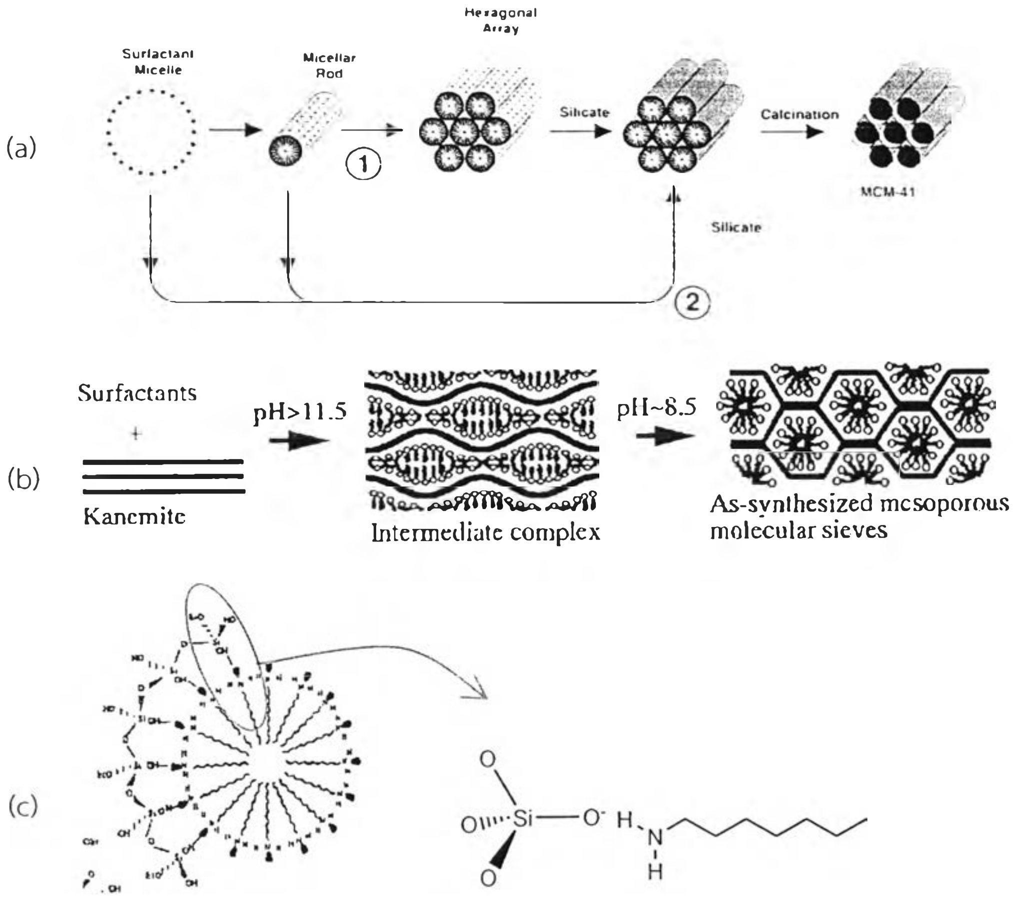

Figure 2.8 Mechanism of **mesoporous** formation (a) LCT of MCM-41 formation, (b) Folding sheet formation of FSM-16 and (c) H-bonding interaction in HMS formation [38, 39].

(a) *Liquid Crystal Templating (LCT) mechanism*: *i.e.* MCM-41. From **Figure 2.8(a)** there are two main pathways; firstly, liquid crystal phase is intact before silicate species are added or another pathway is the addition of the silicate results in the ordering of the subsequent silicate-encased surfactant micelles (pathway 2).

(b) *Folding sheet formation*: *i.e.* FSM-16. The intercalation of ammonium surfactant into hydrate sodium silicate, which composes of single layered silica sheets called "kanemite" (ideal composition $NaHSi_2O_5.3H_2O$), produces the lamellar-to-hexagonal phase in FSM-16. After the surfactants are ion exchanged into layered structure, the silicate sheets are thought to fold around the surfactants and condense into a hexagonal structure.

(c) *Hydrogen-bonding interaction*: The neutral templating produces mesoporous materials with thicker walls and higher thermal stability as compared to the LCT-derived silicates.

2.5.2 Synthesis strategy of mesoporous material using block-copolymer as structure directing agent

In the synthesis of mesoporous materials such as MCM-41, FSM-16, ionic surfactant *i.e.* the cationic, alkyltrimethyl ammonium (C_nTA^+, 8<n<18), and anionic surfactant, tertiary amine ($C_nH_{2n+1}N^+(CH_3)_3$) are used as template, respectively. These syntheses are done in extreme (alkaline) pH condition and the obtained materials have pore size in the range of 15 to 100 Å only. However, by this mean, two limitations occur:

(1) The lower stability of the obtained materials: due to the thinner pore wall of materials (8-13 Å).

(2) Difficult to expanding the pore size: the ionic surfactants give a limited pore size. The only way to expand the pore size is in employing swelling agents such as 1,3,5-trimethyl benzene, involving complicate synthesis.

Thus, the block copolymer has been used to solve these problems. 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.

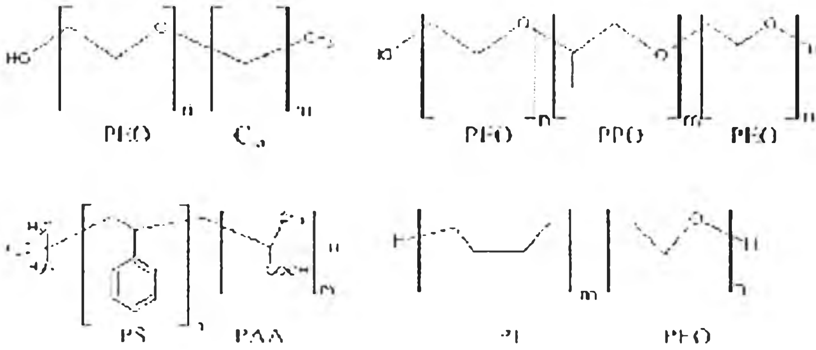

Figure 2.9 Block copolymer used in mesostructured generation [40].

Some advantages of using these block copolymer are:

(1) *The thicker wall thickness* (about 15-40 Å), enhancing hydrothermal and thermal stability of materials.

(2) *Pore diameter can be tuned easier* by varying type or concentration of polymer.

(3) *Easier to remove from mineral framework* by thermal treatment or solvent extraction. Due to the hydrogen bonding interaction between template and inorganic framework, therefore, it should be easier to dissociate as compared to ionic templates (electrostatic interaction).

Interaction between block copolymer template and inorganic species, calls hybrid interphase (HI), is particularly important, especially in PEO-PPO based one. Different possible interactions take place at the HI are schematized in **Figure 2.10**. Most of the fine HI characterization has been performed on PEO-based (di or triblock) templates. For lower polymeric silica ratios, non-ordered gels were formed. This lack of order was due to a relatively strong interaction (probably of H-bonding type) of the (Si-O-Si) polymers forming the inorganic skeleton with both PEO and PPO blocks.

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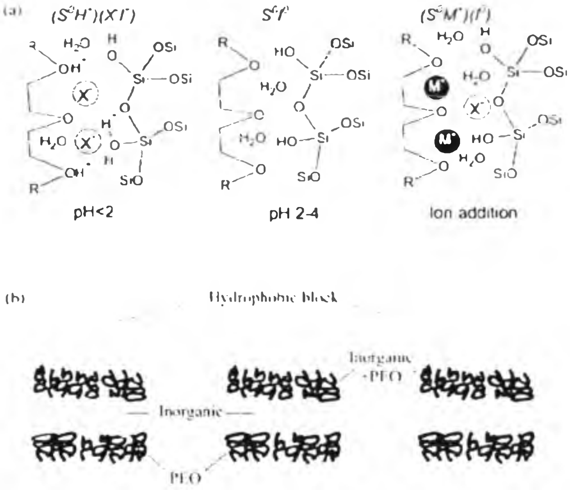
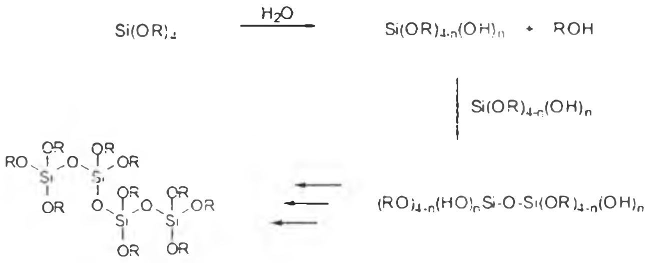


Figure 2.10 (a) Schematic view of the $(S^0H^+)(X^-I^+)$, S^0I^0 , and $(S^0M^+)(X^-I^0)$ hybrid interphases (HIs) (b) Three possible structures of a HI composed by a nonionic polymer and an inorganic framework [41].

2.5.3 Hexagonal mesoporous silica SBA-15

2.5.3.1 Structure and properties

Generally, silica materials was synthesized by the polymerization of $Si(OR)_4$ (tetraalkyl orthosilicate, where R is the alkyl chain) to form a of SiO_2 network (**Scheme 2.1**). The structure and properties of the silica was depending on reaction conditions. The cubic mesoporous silica (MCA) and SBA-15, which are mesoporous material, were prepared by using non-ionic triblock copolymer (Pluronic 123) as a non-ionic triblock copolymer (Pluronic 123), which serves as a structure directing agent [27].



Scheme 2.1 Amorphous SiO_2 framework [27].

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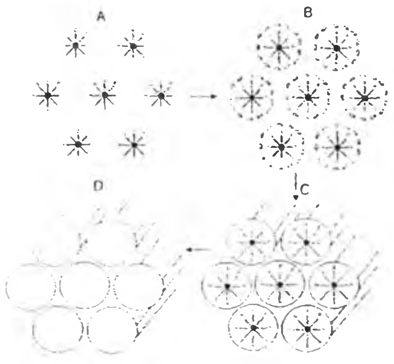
Specially, the micelles were formed by triblock copolymer in acidic aqueous ethanol solution (**Scheme 2.2A**). After the micelles dispersion, tetraethyl orthosilicate was adjusted as the silica source and polymerized surrounding the micelles to appearance the inorganic framework (**Scheme 2.2B and 2.2C**). TEOS was used as the silica source because it could be prevent the contamination of silica material with residual halogen compounds that can be incorporated when used the other silica sources, such as $SiCl_4$. Subsequently, the copolymer was removed from the silica material by calcination in air. Also, the pore size in the silica product was controlled by a triblock copolymer that directed the silica source to form the according size and shape of micelles. Finally, a unidirectional, hexagonally aligned mesoporous silica material was achieved (**Scheme 2.2D**).



Scheme 2.2 Synthesis of SBA-15 [27].

In addition, SBA-15 has shown higher hydrothermal stability as compared to MCM-41 mesoporous material due to its thicker pore walls (3.1-6.4 nm). They also demonstrate uniform and hexagonal-structured channel similar to MCM-41 with larger pore size which make them more desirable to deal with bulky molecule. Some properties of MCM-41 and SBA-15 are compared as described in **Table 2.7**. According to the properties listed in **Table 2.7**, SBA-15 shows a better performance than MCM-41 in almost of properties.

Table 2.7 Comparison of two well-known mesoporous materials, MCM-41 and SBA-15 in their characteristic properties [27], [32].

Properties	MCM-41	SBA-15
Pore size (Å)	20-100	46-300
Pore volume (mL/g)	>0.7	0.8-1.23
Surface area (m^2/g)	>1000	690-1040
Wall thickness (Å)	10-15	31-64

2.5.3.2 Synthesis of SBA-15 and formation mechanism

Many families of mesoporous materials with hexagonal structure were discovered, such as HMS (Hexagonal Mesoporous Silica), FSM-16 (Folded Sheets Mesoporous Materials) and SBA-15 with straight hexagonal structure. Because different types of templates can be used for synthesizing hexagonal mesoporous materials at various pH of gel, the new hexagonal materials can be obtained [42]. The interaction of various types of template with organic or inorganic species for assembling these materials are different as summarized in **Table 2.8**, together with the condition typically employed for a synthesis.

Table 2.8 Various synthesis conditions of hexagonal mesoporous materials and the type of interaction between template and inorganic species.

Material	Template	Assembly	Media (pH)
MCM-41	Quaternary ammonium salt	Electrostatic	Basic or Acid
FSM-16	Quaternary ammonium salt	Electrostatic	Basic (pH = 8.5)
SBA-15	Amphiphilic triblock copolymer	Hydrogen bonding	Acidic (pH = 1-2)
HMS	Primary amine	Hydrogen bonding	Neutral

A number of models have been proposed to explain the formation of mesoporous materials and to provide a rational basis for the various synthesis routes [42]. On the most common level, these models are predicted upon the presence of surfactants in a solution to direct the formation of the inorganic mesostructure from the solubilized inorganic precursors. The type of interaction between the surfactant and the inorganic species is significantly different depending on the various synthesis routes as shown in **Figure 2.11**.

In case of MCM-41 and FSM-16-Pr-SO_3H, the interaction between template and inorganic species is electrostatic interaction while hydrogen bonding interaction occurs in HMS and SBA-15 synthesis [32]. The pore diameters of these materials are controlled by alkyl chain length of surfactant. Mechanisms of mesoporous formation are different depending on synthesis route for each material.

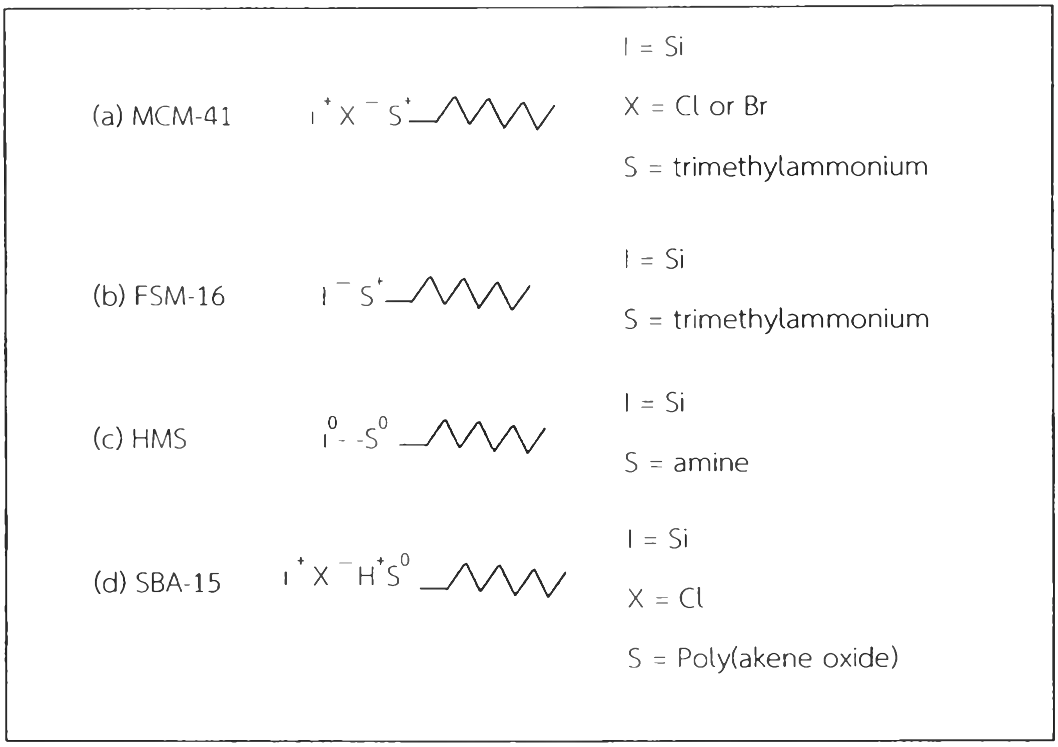
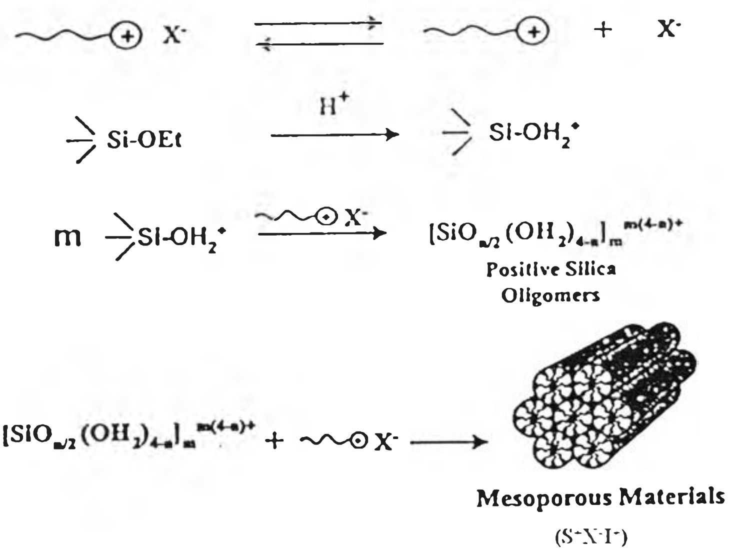


Figure 2.11 Various types of interaction of surfactant head group with inorganic species: electrostatic in MCM-41 (a) $I^+X^-S^+$ and FSM-16 (b) S^+I^-, hydrogen bonding in HMS (c) S^0I^0 and SBA-15 (d) $I^+X^-H^+S^0$.

In SBA-15 synthesis method, amphiphilic tribock copolymer can be modified as a template and must be synthesized in acid condition (**Table 2.8**) of hydrochloric acid. The mechanism of the mesoporous silica formation in acid condition was shown in **Scheme 2.3**. Using tetraethylorthosilicate (TEOS) as a silicon source, the mechanisms include a variety of phenomena: binding of the counter ion and surfactant; the hydrolysis of TEOS; preferred polymerization of silicate species at the surfactant-silicate interface; and charged-matching combination of the surfactant and silicate oligomers. In acid synthesis (pH<1), the dominating cationic silica precursor (I^+) combines with S^+X^- type active sites on the surfactant micelles through a weaker electrostatic interactions. The silica condensation in $S^+X^-I^+$ was promoted without X^- releasing.



Scheme 2.3 The formation process of the mesoporous material in acidic condition [33].

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2.5.4 Cubic *Ia-3d* Mesoporous silica (MCA)

The cubic *Ia-3d* mesoporous silica is Analcime (ANA) framework type with cell parameters 13.567 Å, 90 degree. Secondary building units is 6-2 or 6 or 4-[1,1] or 1-4-1 or 4. It can be built using distorted 6-ring chairs (one in bold in **Figure 2.12**). A one-dimensional Periodic Building Unit (PerBU) is produced when 6-rings are connected through 4-rings into chains along *b* as shown in **Figure 2.12**.

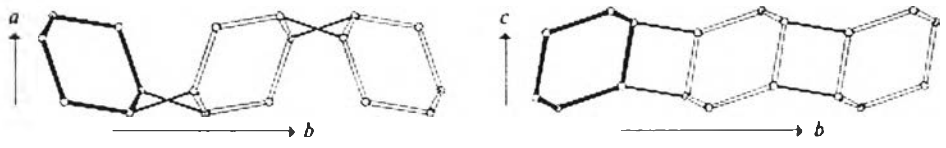

Figure 2.12 PerBU in ANA (chain of 6-rings) viewed along c (left), and along a (right).

Figure 2.13 showed connected chains along [100] and along [001] through 4-rings to form the *ba* and *bc* layers. Neighboring chains in the *ba* layer are related by a 2-fold screw axis parallel to [010] and in the *bc* layer are related by a 2-fold axis parallel to [010]. From the connections of *ba* and *bc*, the projection of cubic *Ia-3d* structure was showed in **Figure 2.14** which seen along *c*. It can see that all three projection are the same [43].

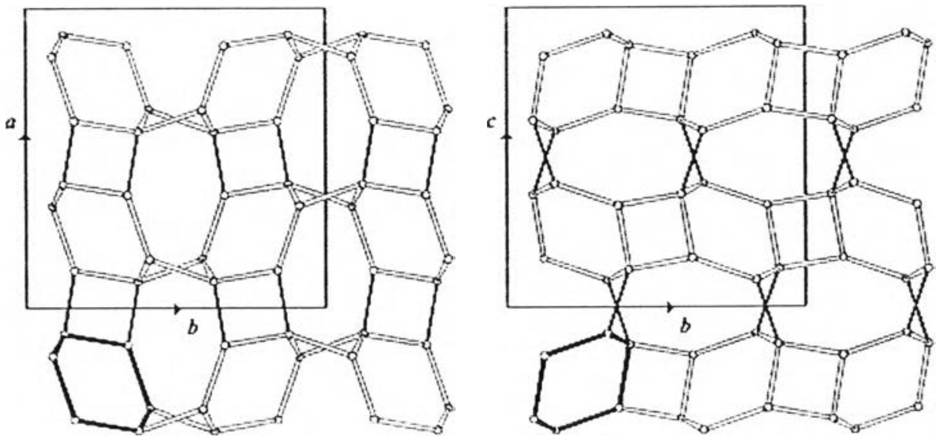

Figure 2.13 Connection modes in ANA which PerBUs are connected into *ba* layers (left) and into *bc* layers (right) through 4-rings.

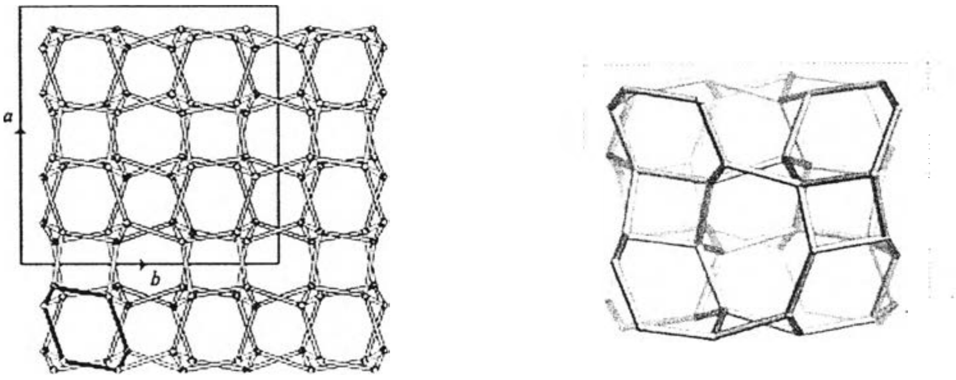

Figure 2.14 Cell content of cubic *Ia-3d* structure was seen along *c*.

The cubic *Ia-3d* mesoporous silica (MCA) was synthesized by using Pluronic P123 as the structure directing agent. This mesopore have higher hydrothermal resistance than MCM-48, which is cubic *Ia-3d* mesoporous silica synthesized by using CTAB. The pore size of MCA is larger than MCM-48 so it can react with larger molecules. Comparison of MCA and MCM-48 surface property was shown in **Table 2.9**.

Table 2.9 Surface properties of MCA and MCM-48.

Properties	MCA [8]	MCM-48 [44]
Pore size (nm)	5.3-7.5	3.3-3.1
Pore volume (cm^3/g)	1.03-1.30	0.53-0.80
Surface area (m^2/g)	1,022-1,152	660-1,010

2.5.5 Modification of catalyst by organic functionalization

Nowadays, the attachment of organic functionalities such as sulfonic acid groups to the surface of catalytic mesoporous material is an interesting research area in heterogeneous catalysis and green chemistry. Basically, two strategies have been generally used to anchor organic groups onto a mesostructured silica surface.

2.5.5.1 Direct synthesis

Direct synthesis consists of the co-condensation of siloxane and organosiloxane precursors in the presence of the corresponding structure-directing agent. The preparation of sulfonic-acid modified mesostructured materials is illustrated in **Figure 2.15**. This method is simplicity, because the incorporation of the organic precursor and the formation of the mesoporous material occur in a single synthetic step. To have a useful catalyst after synthesis, one must be able to extract the template from within the pores to create porosity. Calcination the synthetic material will destroy the incorporated organic functional groups. Extraction technique can be most effectively accomplished by ethanol solution [45-47].

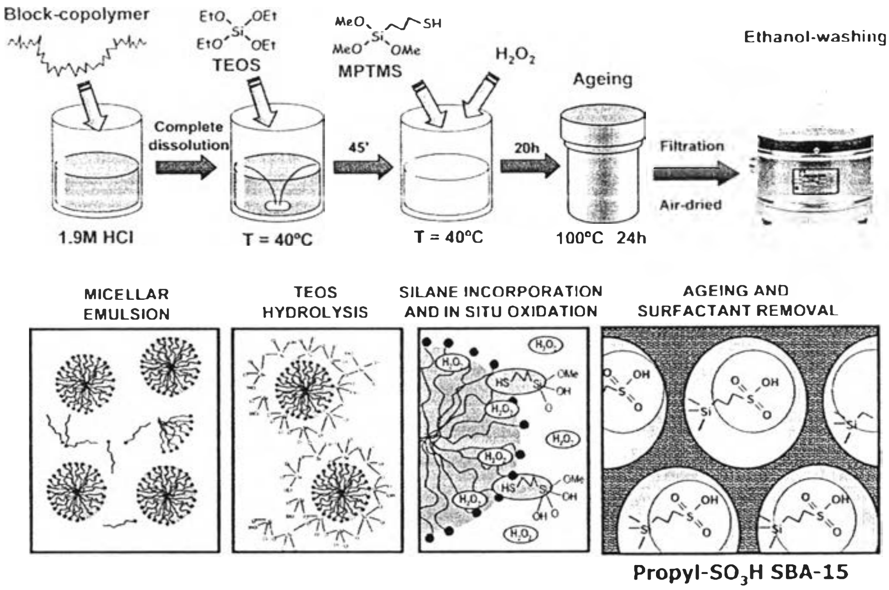

Figure 2.15 In-situ oxidation synthesis strategy for the preparation of sulfonic acid-modified mesostructured materials [46].

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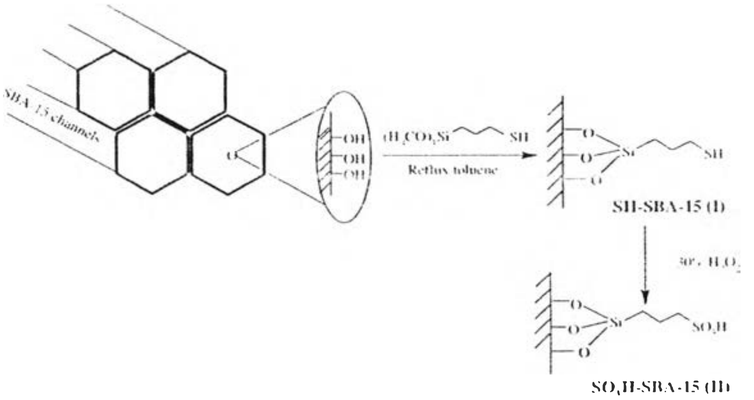
2.5.5.2 Post synthesis

Grafting procedure based on modification of the silica surface with organic groups through silylation reaction occurring on isolated ($\equiv$Si-OH) and germinal (=Si(OH)$_2$) silanol groups using trichloro or trialkoxyorganosilane and silylamines as organic precursors [46].

Synthesis of sulfonic functionalized SBA-15 by post synthesis is shown in **Scheme 2.4**. In typical procedure, calcined SBA-15 is treated with a silating agent like 3-mercaptopropyltrimethoxysilane (MPTMS) in nonpolar solvent (commonly toluene) to immobilize thiol groups on the surface. These thiol functionalities are then oxidized, normally using hydrogen peroxide. The most apparent advantage of this procedure is good preservation of the mesostructure after post-modification.



Scheme 2.4 Post synthesis procedure for the preparation of sulfonic acid modified mesostructured materials [35].

The difference between the two methods mainly involves the location of the organic functional group on the resulting silica material. The co-condensed material contained the groups on the surface and within the walls of the silica framework whereas the functional groups of grafted material only exhibited on the surface (**Figure 2.17**).

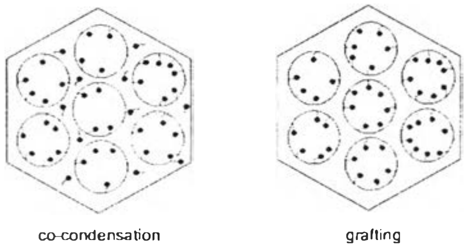


Figure 2.16 Comparison of functionalization via co-condensation or grafting [27].

2.6 Microwaves energy

Microwaves are a form of electromaganetic energy. Microwave, like all electromagnetic radiation, have an electric component as well as a magnetic component. The microwave portion of the electromagnetic spectrum is characterized by wavelengths between 1 mm and 1 m, and corresponds to frequencies between 300 MHz and 300 GHz. Typically, household microwave uses it is important to recognize that the energy delivered by microwave is insufficient for breaking covalent chemical bond. This information can help to narrow speculation on the mechanism for enhancement in specific reaction. The household microwave ovens produce radiation with a fixed frequency of 2,450 MHz (2.45 GHz) [48].

2.6.1 Microwave interaction with matter

One can broadly characterization how bulk materials behave in a microwave field. Materials can absorb the energy (e.g. water, carbon, polar organic molecules), they can reflect the energy (e.g. metal), or they can simply pass the energy (e.g. glass, PP). It should be noted that few materials are either pure absorbers, pure reflectors, or completely transparent to microwaves. The chemical composition of the material, as well as the physical size and shape, will affect how it behaves in a microwave field.

Microwave interaction with matter is characterized by a penetration depth. That is, microwaves can penetrate only a certain distance into a bulk material. Not only the penetration depth is a function of the material composition, but it is also less than sample size; it is considered as a “surface heating”. On the contrary, a “volumetric heating” will occur in a bulk material when the penetration depth is larger than a sample size.

2.6.2 Two principle mechanisms for interaction with matter

There are two specific mechanisms of interaction between materials and microwaves: (1) dipole interactions and (2) ionic conduction. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves.

Dipole interactions occur with polar molecules. The polar ends of a molecule tend to align themselves and oscillate in step with the oscillating electrical field of the microwaves. Collisions and friction between the moving molecules result in heating. Broadly, the more polar a molecule, the more effectively it will couple with (and be influenced by) the microwave field.

Ionic conduction is only minimally different from dipole interactions. Obviously, ions in solution do not have a dipole moment. They are charged species that are distributed and can couple with the oscillating electrical field of the microwaves. The effectiveness or rate of microwave heating of an ionic solution is a function of the concentration of ions in solution.

Materials have physical properties that can be measured and used to predict their behavior in a microwave field. One calculated parameter is the dissipation factor, often called the loss tangent. The dissipation factor is a ratio of the dielectric loss (loss factor) to the dielectric constant. Taken one more step, the dielectric loss is a measure of how well a material absorbs the electromagnetic energy to which it is exposed, while the dielectric constant is a measure of the polarizability of a material, essentially how strongly it resist the movement of either polar molecules or ionic species in the material. Both the dielectric loss and the dielectric constant are measurable properties.

2.7 Microwave and conventional heats

2.7.1 Conventional heating methods

In all conventional means for heating reaction mixtures, heating proceeds from a surface, usually the inside surface of the reaction vessel. Whether one uses a heating mantle, oil bath, steam bath, or even an immersion heater, the mixture must be in physical contact with a surface that is at a higher temperature than the rest of the mixture [12], [48].

In conventional heating, energy is transferred from a surface, to the bulk mixture, and eventually to the reaction species. The energy can either make the reaction thermodynamically allowed or it can increase the reaction kinetics.

In conventional heating, spontaneous mixing of the reaction mixture many occur through convection or mechanical means (stirring) can be employed to homogeneously distribute the reactants and temperature throughout the reaction vessel. Equilibrium temperature conditions can be established and maintained.

Although it is an obvious point, it should be noted here that in all conventional heating of open reaction vessels, the highest temperature that can be achieved is limited by the boiling point of the particular mixture. In order to reach a higher temperature in the open vessel, a higher-boiling solvent must be used.

2.7.2 Microwave heating methods

Microwave heating occurs somewhat differently from conventional heating. First the reaction vessel must be substantially transparent to the passage of microwaves. The selection of vessel materials is limited to fluoropolymers and only a few other engineering plastics such as polypropylene, or glass fiber filled PEEK (poly ether-ether-ketone). Heating of the reaction mixture does not proceed from the surface of the vessel; the vessel wall is almost always at a lower temperature than the reaction mixture. In fact, the vessel wall can be an effective route for heat loss from the reaction mixture. Second, for microwave heating to occur, there must be some component of the reaction mixture that absorbs the penetrating microwaves. Microwaves will penetrate the reaction mixture, and if they are absorbed, the energy will be converted into heat. Just as with conventional heating, mixing of the reaction mixture may occur through convection, or mechanism means (stirring) can be employed to homogeneously distribute the reactants and temperature throughout the reaction vessel.

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Table 2.10 Heating mechanism comparison between conventional and microwave process.

Conventional process	Microwave process
● Radiant heat source: gas burners, electric resistance element ● Heat transfer mechanism: - From heat source to surface: convection and radiation - From surface to center: conduction ● Surface is at higher temperature than center.	● Microwave source: Magnetrons, traveling wave tube, 25 transmission lines ● Heat generation occurs internally. ● Sample is at higher temperature than surrounding. ● Heat loss from surface by conventional and radiation. ● Center is at higher temperature than surface.

2.7.3 Microwave effect

To understand how microwave heating can have effects that are difference from conventional heating techniques, one must focus on what in the reaction mixture is actually absorbing the microwave energy. The simple fact is that materials or component of a reaction mixture can differ in their ability to absorb microwaves.

Differential absorption of microwaves will lead to differential heating and localized thermal in homogeneities that cannot be duplicated by conventional heating techniques.

2.8 Characterization of materials

2.8.1 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) is an instrumental technique used for identification of minerals, as well as other crystalline materials. XRD is a technique in which a collimated beams of nearly monochromatic. X-rays is directed onto the flat surface of a relatively thin layer of finely ground material. XRD can provide additional information beyond basic identification. If the sample is a mixture, XRD data can be analyzed to determine the proportion of the different minerals present. Other obtained information can include the degree of crystallinity of the minerals present, possible deviations of the minerals from their ideal compositions, the structural state of the minerals and the degree of hydration for minerals that contain water in their structure.

XRD is a reliable technique that can be used to identify mesoporous structure. Typically, the XRD pattern of hexagonal symmetry shows five well-resolved peaks corresponding to lattice planes of Miller indices (100), (110), (200), (210), and (300) [49]. These XRD peaks appear at low angle (2θ angle between 0.7 and 3 degree) because the materials are not crystalline at atomic level, diffractions at higher angles are not observed.

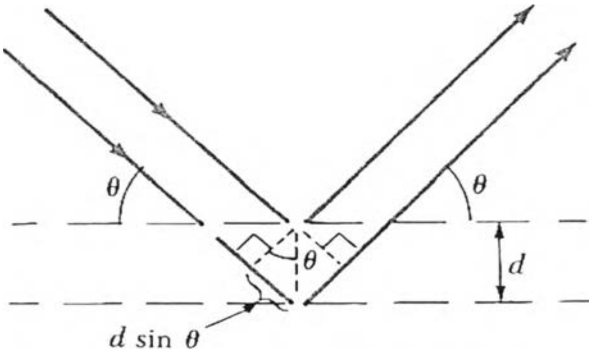

Figure 2.17 Diffraction of X-ray by regular planes of atoms[50].

Figure 2.17 shows a monochromatic beam of X-ray incident on the surface of crystal at an angle Θ. The scattered intensity can be measured as a function of scattering angle 2Θ. The resulting XRD pattern efficiently determines the different phases present in the sample. Using this method, Braggs' law is able to determine the interplanar spacing of the samples, from diffraction peak according to Bragg's angle.

$$n \lambda = 2 \, d \sin\Theta$$

Where the integer *n* is the order of the diffracted beam, Θ is the wavelength; *d* (*d*-spacing) is the distance between adjacent planes of the crystal and Θ is the angle between the incident beam and these planes.

2.8.2 Nitrogen adsorption-desorption technique

The N_2 adsorption-desorption technique is used to classify the porous materials and its physical properties such as surface area, pore volume, pore diameter and pore-size distribution of solid catalysts. Adsorption of gas by a porous material is described by an adsorption isotherm, the amount of adsorbed gas by the material at a fixed temperature as a function of pressure. Porous materials are frequently characterized in terms of pore sizes derived from gas sorption data [51],[52]. The IUPAC classification of adsorption isotherms is illustrated in **Figure 2.18**.

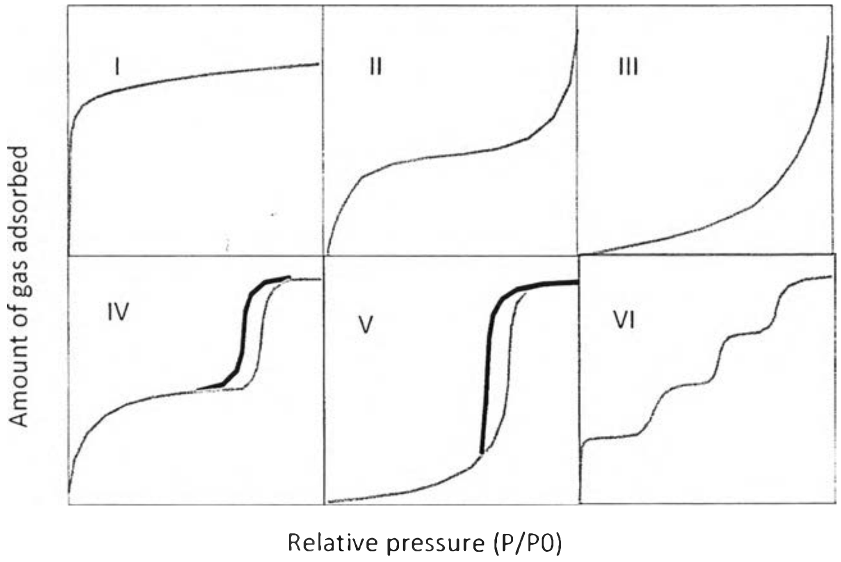

Figure 2.18 The IUPAC classification of adsorption isotherm [15].

As shown in **Table 2.11**, adsorption isotherms base on the strength of the interaction between the sample surface and adsorptive. Pore size distribution is measured by the use of nitrogen adsorption/desorption isotherm at liquid nitrogen temperature and relative pressures (P/P_o) ranging from 0.05-0.1. The large uptake of nitrogen at low P/P_o indicates filling of the micropores (<20 Å) in the adsorbent. The linear portion of the curve represents multilayer adsorption of nitrogen on the surface of the sample, and the concave upward portion of the curve represents filling of mesoporous and macropores. The multipoint Brunauer, Emmett and Teller (BET) method is commonly used to measure total surface area.

$$\frac{1}{W[(P_o/P)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}(P/P_o)$$

Where W is the weight of nitrogen adsorbed at a given P/P_o, W_m is the weight of gas to give monolayer coverage, and C is a constant that is related to the heat of adsorption. A slope and intercept are used to determine the quantity of nitrogen adsorbed in the monolayer and calculate the surface area. For a single point method, the intercept is taken as zero or a small positive value, and the slope from the BET plot is used to calculate the surface area. The surface area depends upon the method used, as well as the partial pressures at which the data are collected.

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The t-plot method uses a mathematical representation of multi-layer adsorption. It is a modified BET plot for micropore volume and external surface area analysis. The thickness, t, of an adsorbate layer increases with increasing pressure and equation id as follows:

$$t = \frac{V_a}{V_m} \times 0.354[nm]$$

0.354 nm is the thickness of monomolecular layer. Standard t-*curve* can be calculated from this equation converting adsorption isotherm of vertical axis to thickness of adsorption layer. For every value of P/Po, the volume adsorbed is plotted against the corresponding value of "t". Here, the increased adsorption amount when adsorption layer increases by one layer (t=0.354nm) is equal to mono-molecular adsorption amount. Thereby, specific surface area a_s [m^2g^{-1}] can be calculated from the following equation with the slope of t-plot, s.

$$a_s = \frac{s \times 0.354}{22414} \times L \times \sigma = 1.541 \times s$$

Where, L is Avogadro constant and σ is cross sectional area of adsorptive.

Table 2.11 Features of adsorption isotherms.

Type	Interaction between sample surface and gas adsorbate	Porosity	Example of sample-adsorbate
I	relatively strong	Micropores	activated carbon-N_2
II	relatively strong	Nonporous	oxide-N_2
III	weak	Nonporous	carbon-water vapor
IV	relatively strong	Mesopore	silica-N_2
V	weak	Micropores	-
		Mesopore	activated carbon-water vapor
VI	relatively strong sample surface has an even distribution of energy	Nonporous	graphite-Kr

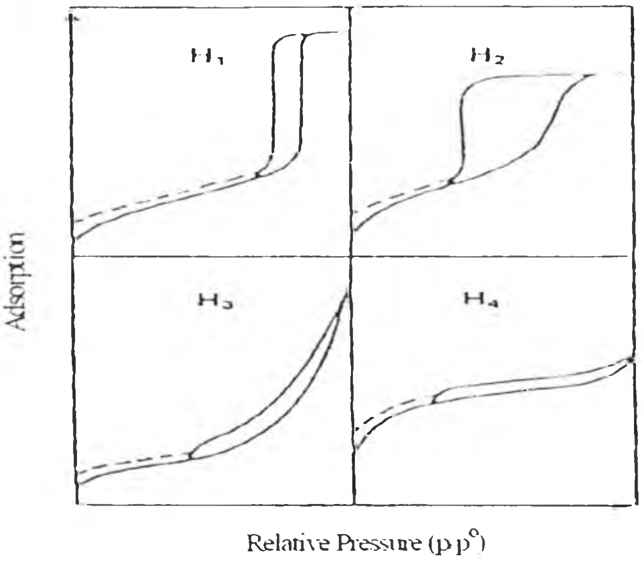

Figure 2.19 IUPAC classification of hysteresis loop.

1. Type H_1: the hysteresis loop associated with pores consisting of agglomerates or compacts of uniform spherical particles with regular array, whose pore size distribution are normally narrow.
2. Type H_2: the hysteresis loop associated with pores with ink-bottle shapes or more complicated network structures.
3. Type H_3: the hysteresis loop associated with slit-shaped pores formed from aggregrates of plate-like particles.
4. Type H_4: the hysteresis loop associated slit-shaped pores with narrower sizes.

2.8.3 Scanning electron microscope (SEM)

The scanning electron microscope (SEM) has unique capabilities for analyzing surfaces and morphology of materials. It is analogous to the reflected light microscope, although different radiation sources serve to produce the required illumination. Whereas the reflected light microscope forms an image from light reflected from a sample surface, the SEM uses electrons for image formation. The different wavelength of these radiation sources result in different resolution levels: electron have much shorter wavelength than light photons, and shorter wavelength are capable of generating the higher resolution information. Enhanced resolution in turn permits higher magnification without loss of detail. The maximum magnification of the light microscope is about 2,000 times; beyond this level is "empty magnification", or the point where increased magnification does not provide additional information. This upper magnification limit is a function of the wavelength of visible light, 2000 Å, which equal the theoretical maximum resolution of conventional light microscope. In comparison, the wavelength of electron is less than 0.5 Å, and theoretically the maximum magnification of electron beam instrument is beyond 800,000 times. Because of instrumental parameters, practical magnification and resolution limits are about 75,000 times and 40 Å in a conventional SEM [37]. The SEM consists basically of four systems:

1. The *illuminating/imaging system* produces the electron beam and directs it onto the sample.
2. The *information system* includes the data released by the sample during electron bombardment and detectors, which discriminate among analyze these information signals.
3. The *display system* consists of one or two cathode-ray tubes for observing and photographing the surface of interest.
4. The *vacuum system* removes gases from the microscope column, which increase the mean free path of electron, hence the better image quality.

2.8.4 Transmission electron microscope (TEM)

TEM is a microscopy technique used for studying the size, size distribution and morphology of particles. TEM involves a beam of accelerated electron, 50-200 keV, emitted by a tungsten filament cathode in vacuum. These electrons are deflected in small angles by atoms in sample and transmitted through a thin sample. Then, these electrons are magnified by magnetic lenses and hitting a fluorescent screen coated with a phosphor to generate the bright field image. A schematic diagram of transmission electron microscope is shown in **Figure 2.20**. The images from electron microscopes indicate the shape of a sample crystallite, which can be used to determine size and morphology of solid nanoparticles [50].

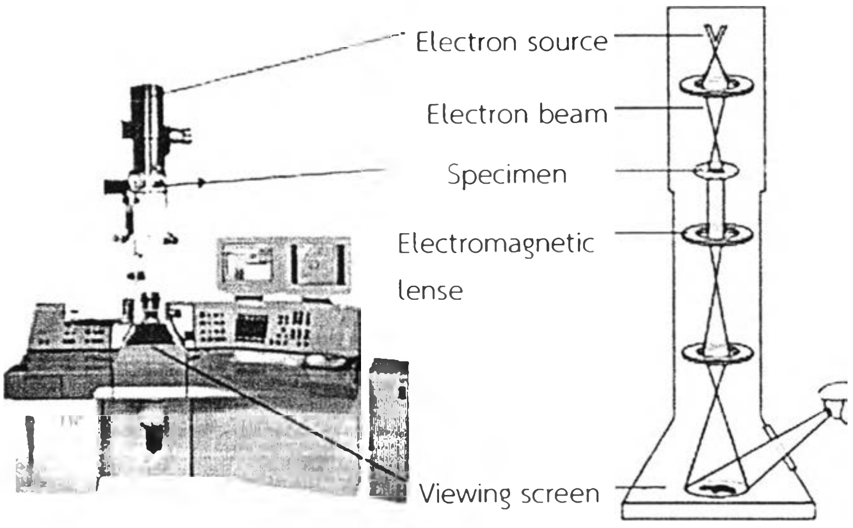

Figure 2.20 Schematic diagram of transmission electron microscope [50].

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2.8.5 Temperature-programmed desorption of ammonia (NH_3-TPD)

Temperature-programmed desorption of ammonia (NH_3-TPD) is the most widely used method to measure the acidic property of solid in mesoporous materials. On widely various solid-acidic catalysts, it was clarified that desorption was controlled by the equilibrium between the adsorbent and the adsorbed ammonia under usually utilized experimental conditions. There are many variations on the method but it typically involves saturation of the surface with ammonia under some set of adsorption conditions, followed by linear ramping of the temperature of the sample in a flowing inert gas stream. The amount of ammonia desorbing above some characteristic temperature is taken as the acid-site concentration, and the peaks desorption temperature have been used to calculate heats of adsorption. It is well-known that desorption temperature of the ammonia molecule can be related to the strength of acidity of the tested materials. The bond formed between the acid site and the ammonia is broken by an energy supply. Thus, the maximum temperature in the NH_3 desorption process is a qualitative indication of the strength of the acidic sites [53].