CHAPTER II

THEORY AND LITERATURE REVIEW

The details presented in this chapter are the explanation of solid-phase extraction principle. The synthesis of silica and its physical properties were then described. Also, the general procedure for the functionalization of silica was reviewed. In addition, several characterization techniques for such silica were written. Finally, the related research of materials modified with Schiff's base molecules was delineated.

2.1. Solid-phase extraction

2.1.1. Principle

Solid-phase extraction (SPE) is the most popular sample preparation method. This technique has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples [17]. Moreover, it is an attractive technique that reduces solvent usage and exposure, disposal costs and extraction times [17, 18]. The principle of solid-phase extraction involves partitioning between a liquid (analyte sample) and a solid (sorbent) phase [19]. The analyte is distributed between the liquid sample and the solid surface, either by simple adsorption to the surface or through penetration of the outer layer of molecules on the surface. When an equilibrium phase is set up, which can define this distribution by coefficient, K_D (2.1).

$$K_D = [\text{analyte}]_{\text{sorbent}} / [\text{analyte}]_{\text{sample}} \qquad (2.1)$$

For metal extraction, there are three-step processes relevant to a solid-phase extraction method, namely mass transfer, adsorption and desorption. The amount of metal ions on the sorbents and the distribution ratio of the metal are calculated according to the following equation [20].

$$q = (C_i - C_e) \times L / W \qquad (2.2)$$

$$D = q / C_e \qquad (2.3)$$

Where
D = distribution ratio of metal (L/kg)

q = amount of metal on the sorbent (mol/kg)

C_i = initial metal concentration (mol/L)

$$C_e \quad = \quad \text{metal concentration in the liquid phase}$$
$$\text{at equilibrium (mol/L)}$$
$$L \quad = \quad \text{volume of the ligand phase (L)}$$
$$W \quad = \quad \text{weight of the sorbent (kg)}$$

The most importance topic in this technique performance is the sorbent characterization. Under this topic are included adsorption isotherms and particle properties (size, shape and pore properties).

2.1.2. Type of solid supports

The nature and properties of the sorbent are of prime importance for effective retention of sample. Careful choice of the sorbent is thus crucial to the development of SPE methodology. Sorbent can be mainly categorized as organic based ones and inorganic based ones. Organic based sorbents may be divided into polymeric and non-polymeric sorbents. The most widely used polymeric sorbents are the PS-DVB copolymers, which have a hydrophobic surface. Inorganic based sorbents are mainly made of silica even through other inorganic oxides may be used. Silica gel based sorbents present the advantage of mechanical, thermal and chemical stability under various conditions. Apart from silica, other inorganic oxides have been tested for the adsorption of trace elements. Whereas SiO_2, due to its acidic properties, is expected to adsorb only cations, basic oxides (such as magnesia MgO, alumina Al_2O_3) should adsorb only anions.

2.1.3. Adsorption mechanism [17]

There are four principle mechanisms of separation in solid-phase extraction (SPE). Reverse phase mechanism involves the partitioning of organic solutes from a polar mobile phase into a non-polar phase. Common reverse-phase sorbents are C-8 and C-18 hydrocarbons. The mechanism of isolation is a non-polar interaction, called van der Waals, dispersion forces, or partitioning. The partitioning mechanism is a low-energy process and is analogous to a molecule being removed from water in a liquid-liquid extraction. Normal-phase SPE refers to the sorption of an analyte by a polar surface. The mechanism of isolation is a polar interaction, such as hydrogen bonding, dipole-dipole interaction, π-π interaction, and induce dipole-dipole interactions. The sorption by normal-phase is a low to moderately strong interaction.

The types of non-bonded phase used for normal-phase SPE are silica, alumina, and magnesium silicate. Ion exchange mechanism involves the ion exchange of a charged organic solute from either a polar or non-polar solvent onto the oppositely charged ion-exchange sorbent. The mechanism is a high energy, ionic interaction. Sorbents are termed strong cation or anion exchangers if they have a permanent fixed charged, either negative or positive, respectively. Factors that affect sorption in ion exchange include the charge on the analyte that is being exchanged, as well as the charged on the competing ions. Adsorption mechcanism involves the interaction of an organic solute with a surface of the sorbent. This mechanism can be characterized in terms of the fundamental physical and chemical properties of the solute, the sorbent and the solvent (water). The organic solute is usually adsorbed on solid phases through van der Waals forces or hydrophobic interaction.

2.2. Silica

2.2.1. Generality [6, 21, 22]

Silica is an inorganic polymer with the general structure formula of $(SiO_2)_x$. Silica gel is the most popular substrate for surface studies because it is the first commercially available high specific surface area material with constant composition, enabling easy analysis and interpretation of results. The primary advantage of silica is its availability in a wide range of well-defined surface area and pore sizes. Also, it can be successfully used as adsorbing agents, as it does not swell or strain, has good mechanical strength and can undergo heat treatment. At the surface of silica consists of the structure terminates in either siloxane group ($\equiv$Si-O-Si$\equiv$) with oxygen atom, or one of the several forms of silanol group ($\equiv$Si-OH). The silanol group can be classified in three types: isolated, geminal and vicinal silanol group. The structure in each type of silanol groups is demonstrated in Figure 2.1.
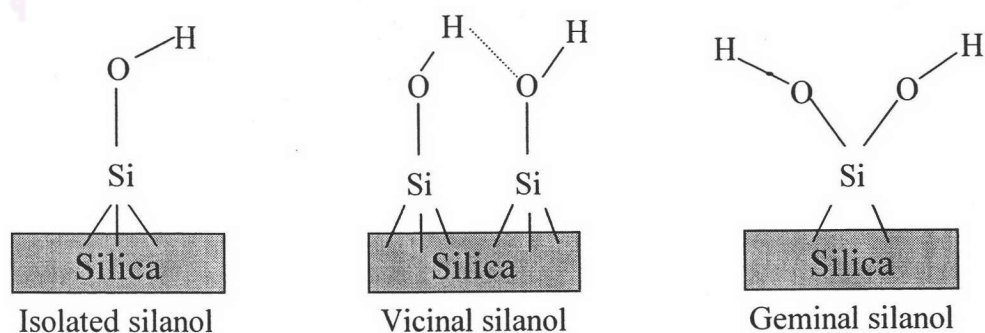

Figure 2.1 Types of silanol groups.

In addition, the pores of silica are divided in different classes depending on their size as follow:

1. Microporous silica (pore size < 2 nm)
2. Mesoporous silica (2 nm < pore size < 50 nm)
3. Macroporous silica (pore size > 50 nm)

Pore can have a regular or, more commonly, an irregular shape. Furthermore, the active silica surface with large area is of great importance in adsorption and ion exchange.

Several different functional groups can be present at the surface, depending on the preparation of materials. Silica has a surface charge character that is defied by the relative concentrations of H^+ and OH^- (the potential determining ions) in solution, as shown by the following equations.

$$Si\text{-}OH + H^+ \rightleftharpoons Si\text{-}OH_2^+ \qquad (2.4)$$

$$Si\text{-}OH + OH^- \rightleftharpoons Si\text{-}O^- + H_2O \qquad (2.5)$$
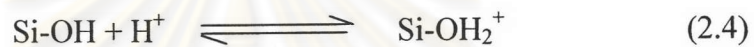
It is the reactive magnitude of the equilibrium constant in Eq. (2.4) and Eq. (2.5) that determined the charge on the silica surface. The isoelectric point (iep) for silica occurs at approximately pH 2.0. The point of zero charge for silica, which is pH-value at the net surface charge of zero, occurs at approximately pH 2.0 [22]. Also, the hydroxyl groups on the porous silica have also an acidic character, which the reaction is displayed as follow.

$$\equiv Si\text{-}O\text{-}H \rightleftharpoons Si\text{-}O^- + H^+ \qquad (2.6)$$
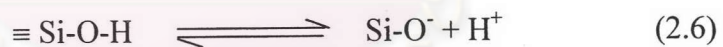
The pKa value of the reaction is about 6.8 ($\pm$ 0.5).

2.2.2. Synthesis of silica [6, 23, 24]

One of the current methods in the synthetic silica is the preparation via sol-gel process, which occur through the hydrolysis and condensation reaction of the metal alkoxides. Most sol-gel techniques use low molecular mass tetraalkoxysilanes precursors, mainly tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). The overall chemical sol-gel reaction can be described as follows.

Hydrolysis:

$$\equiv Si\text{-}OR + H_2O \rightleftharpoons \equiv Si\text{-}OH + ROH \qquad (2.7)$$

Alcohol condensation:

$$\equiv Si\text{-}OR + HO\text{-}Si\equiv \rightleftharpoons \equiv Si\text{-}O\text{-}Si\equiv + ROH \qquad (2.8)$$

Water condensation:

$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightleftharpoons \equiv Si\text{-}O\text{-}Si\equiv + H_2O \qquad (2.9)$$

In a typical procedure, tetraalkoxysilane is mixed with water typically in a mutural solvent such as methanol followed by addition of a catalyst (e.g. hydrochloric acid). During the sol-gel formation, the viscosity of the solution gradually increases as the sol (colloidal suspension of small particles, 1-100 nm) becomes interconnected through polycondensation reactions to form a rigid, porous network-the gel.

The technological importance of the sol-gel process is due to simplicity in its preparation. This method has shown attractiveness due to the possibility of controlling the physicochemical properties of the resulting materials, they are not extensively used as metal ion sorbents. There is some report of using hybrid sol-gel material containing sulfur or nitrogen atoms to remove metal ions selectivity from aqueous solutions. Also, the sol-gel technique provides flexibility in the geometric configuration of the materials and a simple way to immobilize organic reagents in porous solid supports.

2.2.3. Functionalization of silica [23]

Impregnation, chemical derivatization or grafting and the newly introduced sol-gel doping are technologies currently used to immobilize chemical reagents in porous supports. Chemical immobilization was direct chemical bonding of organic reagents to silica. This method has found many applications due to the high stability of the chemical bond. However, this type of encapsulation is very specific and reaction conditions have to be specially tailored for each case. Considerations of cost limit the usefulness of such techniques to expensive devices or to general purpose materials amenable to mass production such as the octadecylsilane media used in chromatography and solid-phase extraction. Impregnation techniques are physically adsorbed, chemisorbed or physically encased in porous supports. Typical impregnation procedures are carried out by exposing the porous support to a concentrated solution of the reagent in organic solvent, which after drying gives a support coated in reagent. The technology is highly versatile and the same solvents, manufacturing apparatus and impregnation protocol can be use to immobilize different reagents in a variety of organic and inorganic materials. However, the adhesion of the reagent to the support is rather weak, excluding in vivo application

and limiting the practical operation and shelf life of the materials. Doping technology is the same immobilization procedure. It can be applied with slight modifications to encapsulate a plethora of organic reagents in various metal oxides. This method is gaining popularity for immobilization of organic compounds in the inorganic support due to its high versatility. The application of this technology was restricted to organic polymer supports. The advent of low temperature sol-gel syntheses of metal oxides opened the way for the development of similar inorganic/organic combinations.

2.2.4. Mesoporous silica

Mesoporous silica, which can have surface area as high as 1000 m^2/g, is expected to provide superior extraction ability of metal ions from aqueous solution [25]. The preparation of mesostructured silica particles is usually done by a micelle-templated sol-gel polymerization method. The syntheses rely on surfactant micelles or liquid-crystal arrays of micelles as structure directing agents (templates) for the assembly and subsequent polymerization of inorganic precursors at the surfactant-solution interface. Electrostatic charge-matching between long-chain quaternary ammonium cation surfactants (S^+) and inorganic precursors (I^-) is especially effective in generating mesostructures with hexagonal, cubic, or lamellar symmetry. This family of materials generically called MS41 have large channels from 1.5 to 10 nm ordered in a hexagonal (MCM-41), cubic (MCM-48), and lamellar (MCM-50) array. The system with a hexagonol array of pores, known as MCM-41, is the most important member of the family, possesses hexagonally arranged uniform pore structures [26]. The importance characteristics of this novel material are its large BET surface area, high porosity, controllable and narrowly distributed pore sizes that manifest itself as a very promising candidate as solid support, adsorbent and host for host-guest encapsulation to develop advanced composite materials [27].

2.3. Characterization of materials

2.3.1. Characterization of porous structures [28-30]

2.3.1.1. Generality

Porous materials are defined in term of their adsorption properties. The term adsorption originally denoted the condensation of gas on a free surface as opposed to its entry into the bulk as in absorption. Pores of materials can have a regular or, more commonly, an irregular shape. The most similar geometric form is used to represent

pore shape: cylinders, slits and voids between connected solid spheres, as shown in Figure 2.2. These models assume that each pore has a uniform size along the length, but very often they are ink-bottle shaped or funnel shaped.
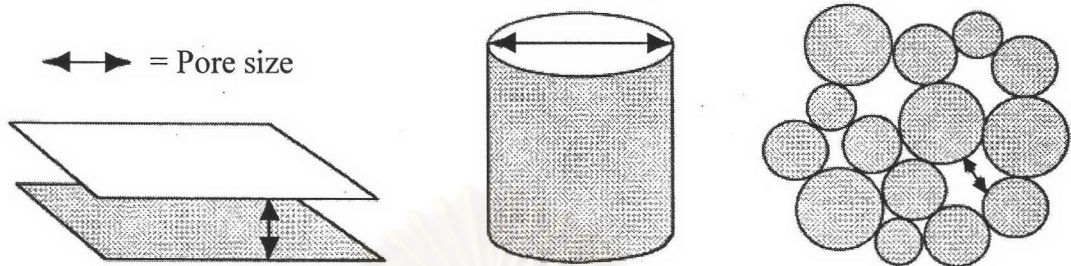

Figure 2.2 Common models of pores [29].

Pores can be closed (not accessible from the external), blind (open at only one end), or through (open at both ends). Each pore can be isolated or, more frequently, connected to other pores to form a porous network (Figure 2.3).
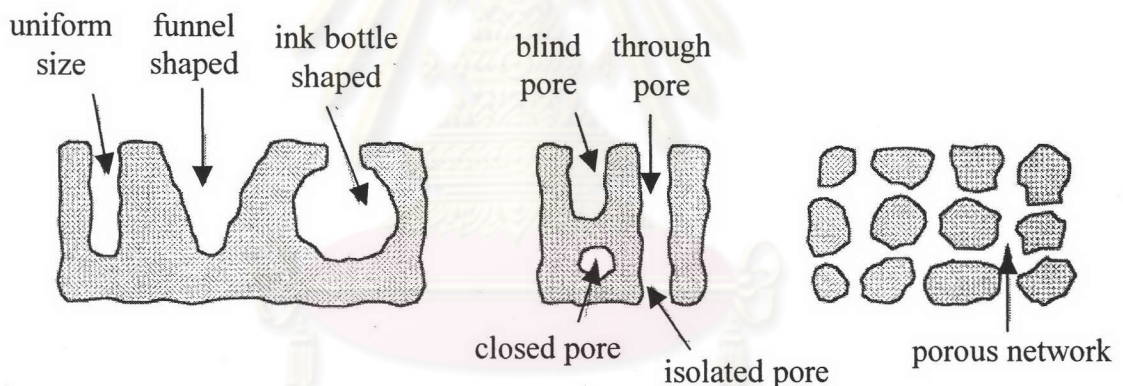

Figure 2.3 Types of pores [29].

The irregular shape of pores and their connectivity cause a molecule to cover a distance greater than the granule size when pass through the particle granule. The ratio between distance covered and granule size is sometimes called tortuosity factor.

2.3.1.2. Adsorption

Adsorption is often described in term of isotherms, which showed the relationship between the bulk activity (concentration) of adsorbate and the amount adsorbed at constant temperature. One isotherm that was both easy to understand theoretically and widely applicable to experimental data was due to Langmuir and

know as the Langmuir isotherm. The Langmuir equation is derived from application of the mass law, in a similar way as the surface complex formation equilibrium. In principle at a constant pH there is no difference between a Langmuir constant and a surface complex formation constant. The most simple assumption in adsorption is that the adsorption sites, S, on the surface of a solid (adsorbent) become occupied by an adsorbate from the solution, A. Implying a 1:1 stoichiometry.

$$S + A \rightleftharpoons SA \tag{2.10}$$

Where
$$S = \text{surface site of adsorbents}$$
$$A = \text{adsorbate in solution}$$
$$SA = \text{adsorbate on surface sites}$$

The maximum concentration of surface sites, S_T, is given by

$$[S_T] = [S] + [SA] \tag{2.11}$$

S and SA can be expressed in mol/L or in mol/m^2. For simplicity, it is used first mol/L. Appling the mass law to Eq. (2.11). Usually the Langmuir equation is known in the form of Eq. (2.12) as follow.

$$\theta = [SA]/[S_T] \tag{2.12}$$

The conditions for the validity of a Langmuir type adsorption equilibrium are

i) Thermal equilibrium up to the formation of a monolayer, $\theta = 1$.

ii) The energy of adsorption is independent of θ (i.e., equal activity of all surface sites).

The concept of adsorption is a dynamic equilibrium between a gas and a solid surface resulting in a surface layer that is only one molecule thick, a concept that quite naturally led to the Brunauer, Emmett, and Teller (BET) treatment of multilayer adsorption. The BET equation is still commonly used for the determination of surface areas of porous solids.

2.3.1.3. Classification of adsorption isotherms

Porous materials are most frequently characterized in term of pore sizes derived from gas sorption data, and IUPAC conventions have been proposed for classifying pore and gas sorption isotherms that reflect the relationship between porosity and sorption [28]. Adsorption by mesopores is dominated by capillary condensation, whereas filling of micropores is controlled by stronger interactions

between the adsorbate molecules and pore walls. The IUPAC classification of adsorption isotherms is illustrated in Figure 2.4.
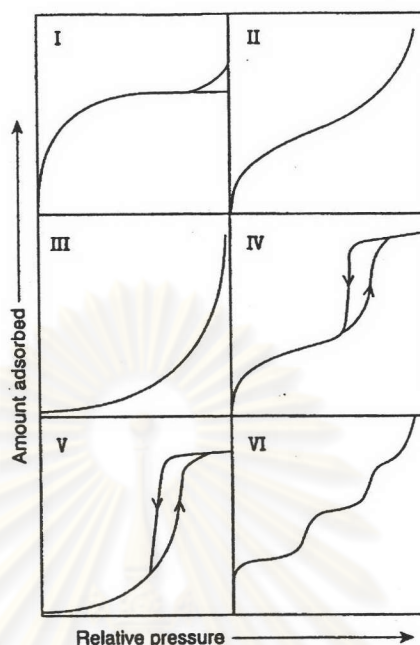

Figure 2.4 IUPAC classification of adsorption isotherms [28].

The six types of isotherm are characteristic of adsorbents that are microporous (type I), nonporous and macroporous (type II, III, and VI) or mesoporous (type VI and V). The difference between types II and III isotherms and between types IV and V isotherms arise from the relative strengths of the fluid-solid and fluid-fluid attractive interactions: type II and IV are associated with stronger fluid-solid interaction and types III and V are associated with weaker fluid-solid interaction. The hysteresis loops usually exhibited by type IV and V isotherms are associated with capaillary condensation in the mesopores. The type VI isotherm represents adsorption on nonporous or macroporous solids where stepwise multilayer adsorption occurs.

2.3.1.4. Adsorption hysteresis

The adsorbate desorption, after saturation is reached, is the opposite of the adsorption, but evaporation from mesopores usually takes place at a pressure lower than that of capillary condensation giving an hysteresis. This is due to pore shape and four types of hysteresis have been recognized, according to IUPAC classification. [28].
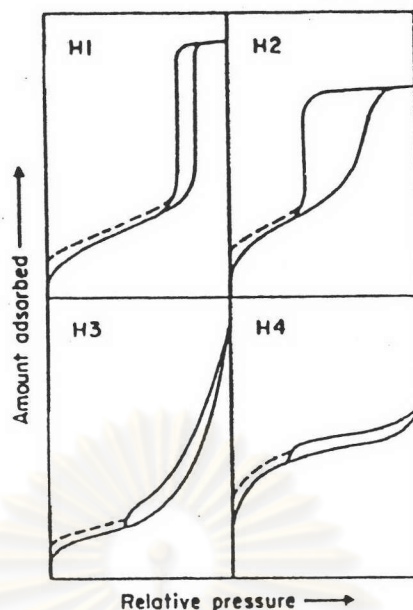
Figure 2.5 IUPAC classification of adsorption hysteresises [28].

Two extreme types are shown as H1 and H4. In the former the two branches are almost vertical and nearly parallel over an appreciable range of gas uptake, whereas in the latter they remain nearly horizontal and parallel over a wide range of p/p_o. In certain respects types H2 and H3 may be regarded as intermediate between these two extreme. Type H1 is often associated with porous materials having narrow distribution of pore size. Many porous materials (e. g. inorganic oxide gel and porous glasses) tend to give Type H2 loops. The type H3 loop, which does not exhibit any limiting adsorption at high p/p_o, is observed with aggregates of plate-like particles giving rise to slit-shaped pores. Similarly, the Type H4 loop are usully found on solid consisting of aggregates or agglomerates of particles forming slit shaped pores, with uniform size shape.

2.3.1.5. Application of the BET (Brunauer-Emmett-Teller) method

In spite of alternative equation to describe the isotherm, the BET equation has retained its utility for many years. Subsequent proposed schemes are useful for certain situations but the BET equation is still widely used. The BET equation is

$$\frac{P}{n(P_o-P)} \quad = \quad \frac{1}{nC} \quad \frac{(C-1)}{n_mC} \quad \frac{P}{P_o} \qquad (2.13)$$

Where n is the amount adsorbed at the relative pressure P/P_0 and n_m is the monolayer capacity. From n_m, calculated from the experimental data using the above equation, the area is determined from equation.

$$A\,(BET) = n_m \cdot L \cdot a_m \qquad (2.14)$$

Where A is the apparent surface area (m^2g^{-1}), n_m is the experimental monolayer volume ($molg^{-1}_{solid}$) for an adsorbent of cross section area, a_m (m^2), and L is Avogadro' s number. Normally A is determined from nitrogen adsorption on the basis of the BET equation. Nitrogen is generally considered to be the most suitable adsorptive for surface area determination and it is usually assumed that the BET monolayer is close-packed giving $a_m\,(N_2) = 0.162$ nm^2 at 77 K.

2.3.1.6. Mesoporosity

Many methods, based on Kelvin equation, have been developed to describe the adsorption capillary condensation process that take place in mesopores. The BJH method, which is proposed by Barrer, Joyner and Halenda, is the most widely used to performed calculation on mesopores. The model is simple. In the capillary condensation region ($P/P_0 > 0.4$), each pressure increase causes an increase of the thickness of layer adsorbed on pore wall and capillary condensation in pores having a core size, r_C, defined by Kelvin equation:

$$r_C = \frac{-(2\gamma W_m Cos\theta)}{RT\,ln(p/p_0)} \qquad (2.15)$$

Where r_C represent the radius for cylindrical pores, the distance between walls for slit share pores, γ the surface tension, W_m the molar volume and θ the contact angle.

In such a way, by examining step by step the isotherm in the range $0.42 < P/P_0 > 0.98$, the mesopore volume and the mesopore size distribution can be obtained.

2.3.2. X-Ray Diffraction (XRD) [31-33]

X-ray diffraction is currently of prime importance in elucidating the structure of materials. It provides direct information of the pore architecture of materials. For mesoporous materials, diffraction patterns are in the low angle range, 2θ less than 10 degree. No reflections are observed at higher angles; thereby, it has been concluded

that the pore walls are mainly amorphous. The order of lines can be indexed according to lattice planes.

When X-ray radiation passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the atoms are organized in planes (i.e. the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur (Figure 2.6). This results in diffraction where X-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures called planes. Most crystals can have many sets of planes passed through their atoms. Each set of planes has a specific interplanar distance and will give rise to a characteristic angle of diffracted X-rays. The relationship between wavelength, atomic spacing (d) and angle was solved as the Bragg Eq. (2.16).

$$n\lambda = 2d \sin\theta \qquad (2.16)$$

This equation is a fundamental relationship in X-ray diffraction analysis, as it permits the interplanar distance, d, to be calculated from the measured diffraction angle, θ, for a known wavelength of the primary radiation. Quantity, n, corresponds to the diffraction order.
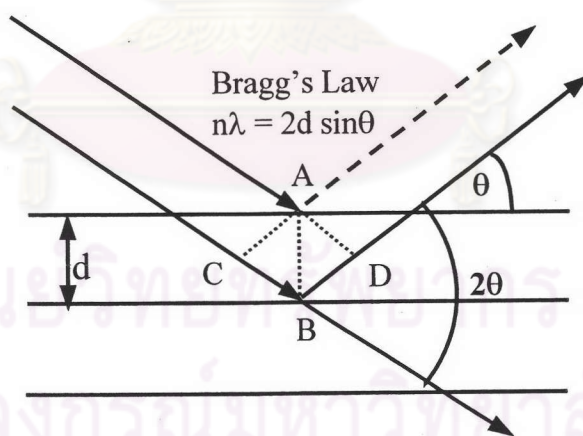

Figure 2.6 Diffraction of X-ray by a crystal.

2.3.3. Fourier-transform infrared spectroscopy (FT-IR) [34, 35]

Infrared spectroscopy is a powerful technique for analyzing samples; both qualitatively and quantitatively, inorganic as well as organic, and can be applied to samples in all three states of matter; gases, liquids and solids.

To better understand the effect of parameter selections, a basic understanding of terms used to describe the data collection from a Fourier-transform infrared (FT-

IR) spectrometer is needed. The FT-IR method is based on the combination of an interferometer, usually of the Michelson type, with a sensitive infrared detector and computer.

Source $\longrightarrow$ interferometer $\longrightarrow$ Sample $\longrightarrow$ Detector $\longrightarrow$ Computer $\longrightarrow$ Data Output

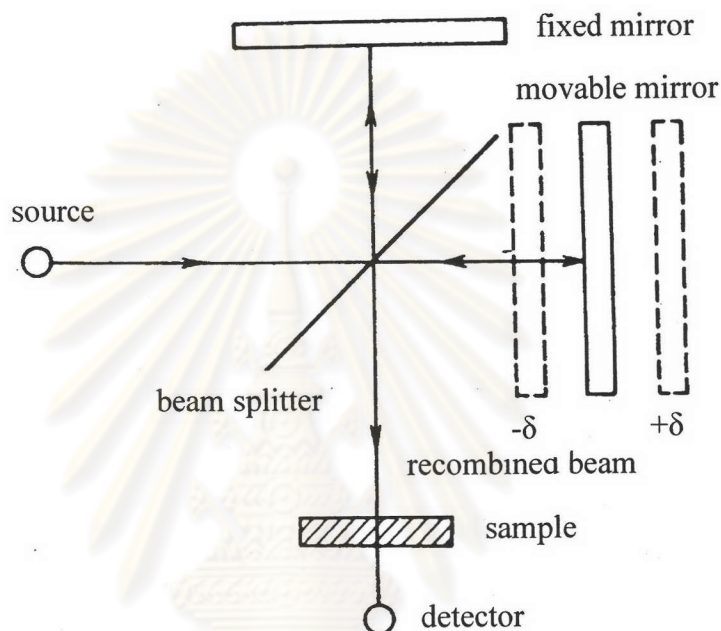The principle of the Michelson interferometer is depicted in Figure 2.7.

Figure 2.7 A diagram of the Michelson interferometer [34].

In an FT-IR spectrometer, the signal "seen" by the detector is termed an interferogram. The region of maximum signal in the interferogram is called the centerburst and corresponds to the point when the moving and fixed mirrors in the interferometer are equidistant from beamsplitter. The interferogram is transfered mathematically by the fourier transform to produce a single beam spectrum. The fourier transform takes the data recorded as a function of mirror movement in distance and produces data as a function of frequency in cm^{-1} (wave number).

2.3.4. Thermogravimetric analysis (TGA) [26, 36]

Thermogravimetric analysis (TGA) is used to measure the fraction of sample weight lost as a function of temperature or time. The loss of sample weight implies that some portions of the sample are evolved into the surrounding purge gas stream.

In order to enhance the steps in the thermogravimetric curve, the derivative thermogravimetric (DTG) trace is frequently drawn. Remember that this is the plot of the rate of mass change, with time, dm/dt.

As with most thermal analysis systems, measurements of mass changes during heating are made with a thermobalance. The thermobalance has four major parts:

1. The electrobalance and its controller
2. The furnace and temperature sensors
3. The programmer or computer
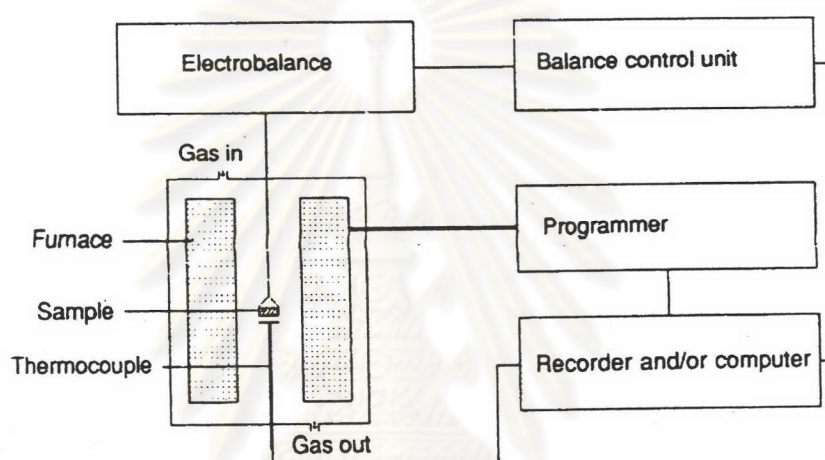4. The recorder, plotter or data acquisition device

Figure 2.8 Schematic diagram of thermobalance system [36].

The sample is put into a container or crucible, which is then placed in contact with the sensor which is to measure the particular property. A temperature sensor must also be present at the sample to follow its temperature as the experiment progresses. The sensor assembly then fits into a special furnace and the atmosphere around the sample is established. The furnace is controlled by a temperature programmer and is set by the operator to raise (or lower) the temperature of the furnace at whatever rate has been chosen as most suitable. The data are collected by the sensor system and, after processing are displayed on a screen or recorder as a thermal analysis (TG) curve. The output TG curve is a plot of either the actual mass or the percentage of the origin mass against temperature and provides information about drying process, loss of solvent of crystallization, thermal decomposition reactions. The output from the balance can be also be differentiated electronically to

give a derivative thermogravimetric (DTG curve), making it easier to interpret complex TG curves.

2.4. Schiff's base molecules

Schiff's base can be thought of as the imine product of the condensation reaction of a primary amine with an aldehyde or ketone [37]. They are well known as ligand that are easy to be synthesized and have structural rigidity, and they are used also as selective extraction reagents for several kinds of metal cations. The favourable tetradentate ligand, which is an 2O-2N donating Schiff's base has ensured continued interest in their complexes for many year. They have been attracting increasing attention because of their importance in the metal extraction which are used in the determination of Cu(II), Co(II), Be(II), Mg(II), Ca(II) Al(II), Ga(II), Ni(II), Mn(II), Mn(III), Fe(III), *etc*. [13, 38, 39]. In this research, four Schiff's base ligands such as 2,2'-{ethane-1,2-diylbis[nitrilo(*E*)methylylidene]}diphenol (salen), 2,2'-{propane-1,3-diylbis[nitrilo(*E*)methylylidene]}diphenol (saltn), 2,2'-{1,2-phenylenebis[nitrilo(*E*) methylylidene]}diphenol (salophen) and 2,2'-{ethane-1,2-diylbis[nitrilo(1*E*)eth-1-yl-1-ylidene]}diphenol (haen) were selected as an extractant molecules in modified mesoporous silica for metal extraction. The structures of four Schiff's base ligands were shown as below:
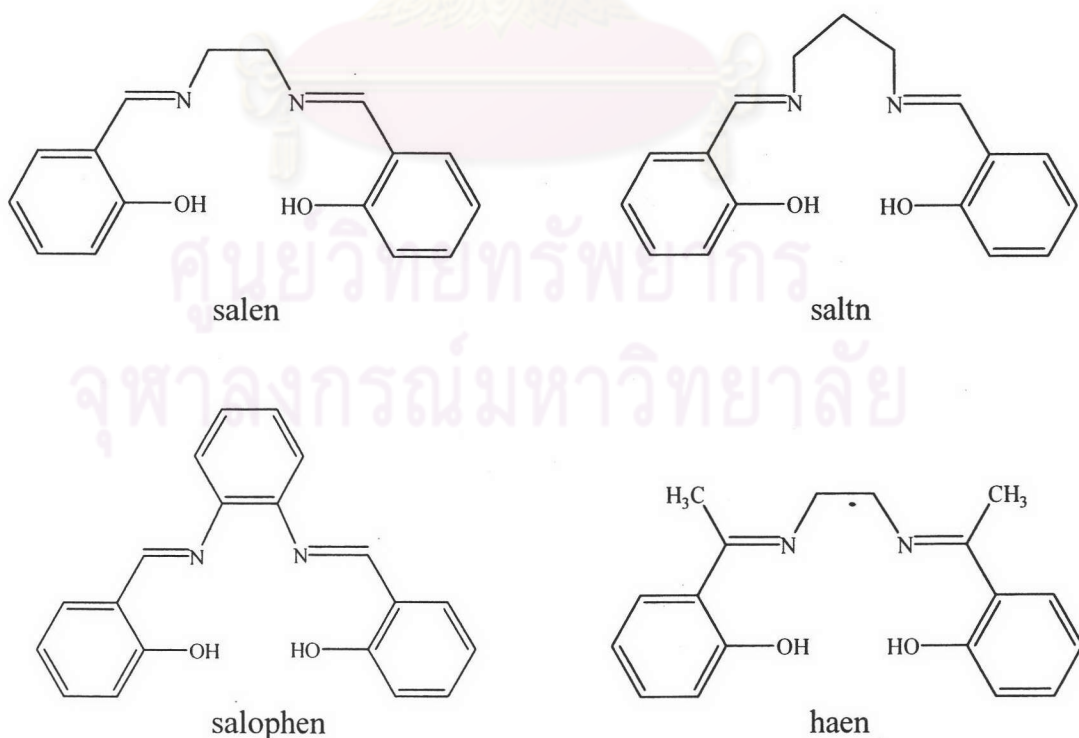

Figure 2.9 Structures of Schiff's base ligands used in modified mesoporous silica.

2.5. Literature Review

Research in the preparation of the novel modified materials in order to used as a solid phase adsorbent is stimulated a renewed interest since these materials have greater applicability than traditional solvent extraction. A variety of functionalization methods such as grafting, impregnation, and doping techniques has been studied extensively for the modification of sorbent [40-42]. Shiraishi *et al.* [20] reported the synthesis of several modified inorganic sorbents (i.e. silica gel, MCM-41, and aluminium oxide) functionalized with ethylenediaminetetraacetic acid (EDTA) and diethylenetriamine-pentaacetic acid (DTPA) using grafting method and the application of these materials as a sorbent for metal extraction. The results displayed that silica gel modified with EDTA (silicaED) was the most effective sorbent for the extraction of transition metal even at very low pH. Mercier and Pinnavaia [43] described the synthesis of mesoporous materials modified by 3-mercaptopropyltrimethoxysilane using impregnation technique. The prepared sorbent showed the good extraction capacity for Hg^{2+} from aqueous solution. Khan and co-worker [44] presented a successful route to prepare the new sol-gel silica sorbent using 1-(2-thiazolylazo)-2-naphthol (TAN) as a doping molecule and applied the prepared material for the removal of Zn(II) ions from aqueous solution. The study results found that the maximum adsorption of Zn(II) ions onto the TAN doped sol-gel were 2.33 mg/g (0.035 mmol/g). Also, this silica showed the maximum regeneration value at as high as 99.0 %.

Several researches had recently reported on the synthesis of such organically modified mesoporous materials under basic conditions. For example, Dai *et al.* [45] reported a new and more efficient methodology for functionalizing surfaces of ordered mesoporous silica. This material was prepared by a surfactant assembly pathway that involving in mixing cetyltrimethylammonium bromide (CTAB), water, NaOH and ethanol (used as solvent). This method showed a simplified experimental procedure and also increased the loading of the functional ligand. The molar composition ratio of TEOS : CTAB : H_2O : NaOH was 1 : 0.12 : 130 : 0.7. In addition, Cai and co-workers [46] demonstrated that mesoporous silica could be produced throught reaction of CTAB with TEOS in the NaOH solution. The size and other morphology of this synthesized silica were controlled by varying the content of the solvent used.

As previously reported [47-49], the functionalized mesoporous silica using organic molecules gave the good physical materials. Also, the different characteristic properties of each material were observed when various organic molecules were used as an organic modifier. Schiff's base was another ligand, which is known to be an attractive analytical reagent used for metal complexation. Several reports concern the application of Schiff's base complexes as a catalyst. For example, Sabater *et al*. [50] synthesized a chiral Mn(III)-salen complex encapsulated within zeolite Y to use as a heterogeneous enantioselective catalyst for the epoxidation of alkenes. Also, Ortiz and Park [51] described the preparation of Co(II)-salen and Co(II)-salophen. Both synthesized compounds could be acted as oxygen reduction catalysts. Furthermore, Mirkhani and co-workers [52] prepared Mn(III)-salophen complex and used it as a new catalyst for oxidative decarboxylation of carboxylic acid to the corresponding carbonyl derivatives. In addition, Lau *et al*. [53] presented a novel MCM-41 supported Mn(III) complex with the nitrogen donor Schiff's base ligand, namely 1,11-bis(2-pyridyl)-2,6,10-triazaundec-1,10-diene and 3-[N,N′-bis-3-(salicylideneamino) propylamine] for used as a catalyst for cyclohexene oxidation. Another research for the preparation of a novel Schiff's base[1,2-bis(salicylideneamino)-phenylene] cobalt complex catalyst bonded on carbamate modified silica gel was synthesized by Kumar and co-workers [54]. The oxidation reaction of linear alkenes, such as n-hexene and n-heptane with molecular oxygen occurred in presence of silica gel supported with this complex.

In addition, over the past decade, the synthesis of materials modified with Schiff's base ligands and used them as a solid phase sorbent for metal extraction was found a few papers. Shamsipur *et al*. [11] explained the preparation of octadecyl silica membrance disks modified by a naphthol-derivative Schiff's base in order to use in the SPE for the determination of copper(II) ions. This proposed SPE was successful to apply for the separation and determination of copper in real samples. Also, the preparation of octadecyl silica membrance disks modified by a new S-containing Schiff's base for SPE procedure was studied later by Hashemi *et al*. [16]. The maximum capacity of these membrane disks, which had 5 mg of newly ligands was found to be 700 μg Pb^{2+} retained. In addition, silica gel modified by diethylenetriamine mono- and bis-salicylaldehyde and naphthaldehyde Schiff's base

to use for metal ions extraction was synthesized. The prepared sorbent had capacities to selective extraction of Cu(II) and Fe(III) ions.

According to review, the previously literature research showed that Schiff's base ligands had ability to act as a very successful extracting agent. However, only after a few papers had been reported for metal extraction using Schiff's base ligands as an extractant molecule immobilized in mesoporous silica. Therefore, the attempt to prepare the mesoporous silica modified with Schiff's base ligands by doping technique was becoming interest.

2.6. Objective

1. To synthesize Schiff's base doped mesoporous silica.

2. To study the physical properties of Schiff's base doped mesoporous silica.

3. To study the effect of parameters on the metal extraction efficiency of Schiff's base doped mesoporous silica.