CHAPTER III

EXPERIMENTS

3.1. Reagents

Tetraethoxysilane (TEOS, 98%) and cetyltrimethylammonium bromide (CTAB, 98%) were purchased from Fluka. Ethanol (C_2H_5OH) and nitric acid (HNO_3) were obtained from Merck. $Co(NO_3)_2 \cdot 6H_2O$ (99%), $Cu(NO_3)_2 \cdot 3H_2O$ (99%), $Mn(CH_3COO)_2 \cdot 4H_2O$ (99%), $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (99%) from Merck and $MnCl_2 \cdot 4H_2O$ (99%) from J. T. Baker were used to prepare metal ion solutions. The reagent for synthesizing Schiff's base ligands, salicylaldehyde, *o*-phenylenediamine, ethylenediamine, 2-hydroxyacetophenone and 2-propylenediamine, were purchased from Fluka and were used without further purification. Deionized water (Milli Q, model Millipore ZMQS5V00Y) was used throughout.

3.2. Apparatus

UV spectra were obtained on a HP8453 UV-Visible spectrophotometer. The FT-IR spectra were recorded on a Nicolet fourier transform infrared spectrophotometer model Impact 410. X-ray diffraction was determined using a Riguku DMAX 2200/Ultima$^+$ X-ray diffractometer. The nitrogen adsorption-desorption isotherms and BET surface area were carried out using a Quantachrome Autosorb-1 nitrogen adsorptometer. Thermogravimetric analysis was performed on NETZSCH STA 409. Elemental analyses were carried out on a CHN ANALYZER (Perkin Elmer PE2400 SeriesII). The particle size of materials was performed on a Malvern (Model Mastersizer S) instrument. The morphology of materials was observed using a JEOL JSM 5410LV scanning electron microscope. All four latter techniques were investigated at the Scientific and Technology Research Equipment Center, Chulalongkorn University. Atomic absorption measurement of metal ions was performed with a Perkin Elmer AAnalyst 100 atomic absorption spectrometer.

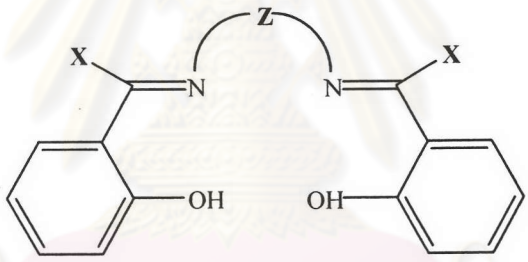
3.3. Experiments

The experiment studied in this thesis could be divided into three parts. The first part concerns the synthesis of Schiff's base doped mesoporous silica. The amount of incorporated Schiff's base molecules into the silica was measured. In the second

part, physical properties of materials such as their morphology, mesoporosity, surface area and pore size distribution were characterized using X-ray diffraction method (XRD), nitrogen sorption measurement and thermogravimetric analysis (TGA). Also, the amount of accessible Schiff's base was determined. Finally, the extraction properties and the optimum extraction conditions were explored in details. The selectivity and the metal desorption preperties of these modified silica were also investigated.

3.3.1. Synthesis of Schiff's base

Four Schiff's base ligands illustrated in Figure 3.1 were prepared by slowly adding an interested aldehyde or ketone (2 mol-equiv.) to a solution of primary diamines (1 mol-equiv.) in methanol. The resulting mixture was stirred at room temperature until precipitate occurred. The solid was then filtered off, washed and recrystallized by an appropriate solvent.



salen X = H, Z = $-CH_2CH_2-$ **saltn** X = H, Z = $-CH_2CH_2CH_2-$

salophen X = H, Z = $-(o-C_6H_4)-$ **haen** X = $-CH_3$, Z = $-CH_2CH_2-$

Figure 3.1 Structure of Schiff's base ligands.

3.3.2. Synthesis of materials

The synthesis procedure of Schiff's base doped mesoporous silica in this work was inspired by Boos and co-workers [48]. All silica were prepared by keeping the constant mole ratio of TEOS : water (0.1 M NaOH as a catalyst) : CTAB : EtOH : Schiff's base at 1 : 140 : 0.18 : 13.0 : x respectively, where x denoted in the next chapter. The synthesis of modified silica was performed in two different ways dependent on the addition time of doping molecules during the synthesis. For the first method, Schiff's base molecules in ethanol solution were added simultaneously with

the addition of TEOS whereas in the second method the introduction of functionalized molecules was occurred prior to the addition of silica source. The synthesis process of both methods was described as follows.

Method I: CTAB was dissolved in 0.1 M sodium hydroxide solution. After stirring the mixture for 1 h, TEOS and Schiff's base solution in ethanol were then added to the above mixture, which was further stirred at 60°C for 1 h. After a few minutes, the resulting yellowish silica was formed. Subsequently, the mixture was kept stirring for 23 h at room temperature. Thereafter, such formed yellowish precipitate was then filtered and washed with 10^{-3} M HNO_3 and water until pH 7.0. All filtrates were then collected to determine the quantity of doping molecules that might be leaching out during the process of synthesis and washing. Next, this modified silica was dried at 110 °C overnight.

Method II: The Schiff's base ligand was dissolved in ethanol at 60 °C for 1 h. A solution of sodium hydroxide (0.1 M) and CTAB were then added to the Schiff's base solution. Consequently, TEOS was added into the above mixture. The solution was stirred for 1 h at 60 °C and subsequently aged for 23 h at room temperature. The observed silica was filtered, washed with 10^{-3} M HNO_3 and water until neutral pH. Doping molecules that might be leaching were also determined using UV-visible spectroscopy. Finally, the modified silica was dried in an oven at 110 °C overnight.

The synthetic routes of method I and method II were summarized in Figure 3.2.

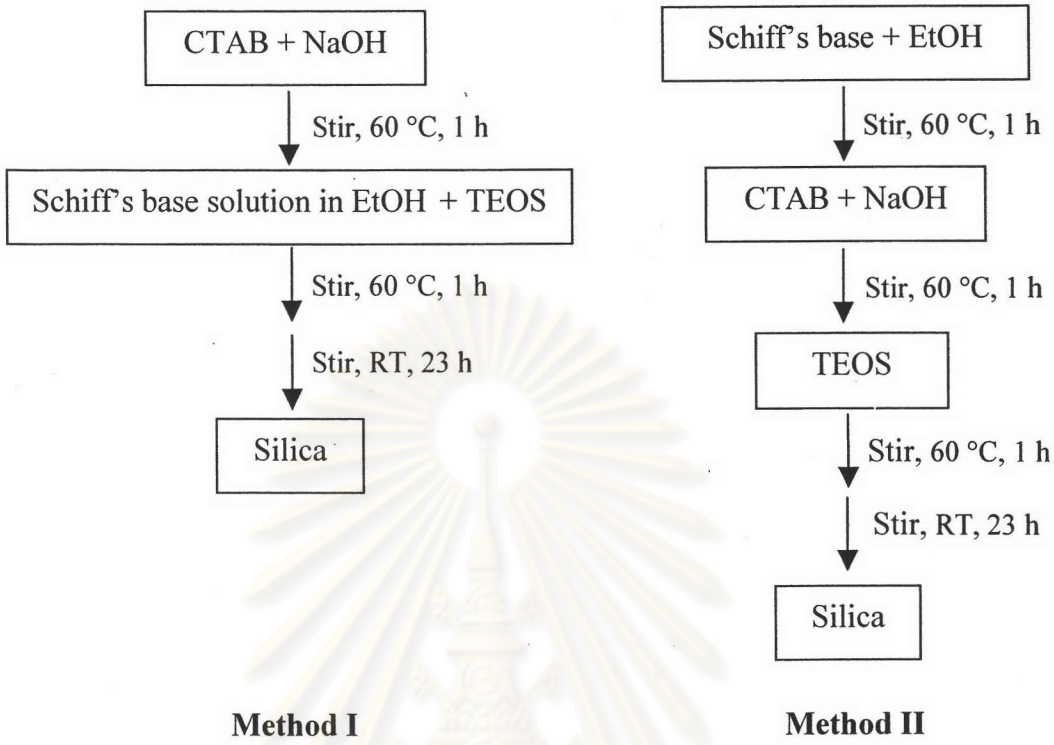


Figure 3.2 The two synthetic methods of Schiff's base doped mesoporous silica.

3.3.3. Characterization of materials

The characterization of the synthesized silica comprised the determination of organic matters in silica and the amount of accessible Schiff's bases. Other physical properties of materials such as crystallinity and morphology were also investigated.

3.3.3.1. Determination of organic matter contents in mesoporous silica

In order to determine the amount of organic matters containing in the modified mesoporous silica, the calcination of the as-synthesized mesoporous silica and thermogravimetric method were used. The procedure for calcination is as follow.

100 Milligrams of the as-synthesized silica after dried at 110 °C was placed in a muffle furnace. It was first heated to 100 °C at a rate of 1 °C/min and kept for 60 min at that temperature prior to further heating to 540 °C at a rate 1 °C/min. It was finally held at that temperature for another 10 h. After calcination process, the weight of sample loss was calculated. The heating program is demonstrated in Figure 3.3.

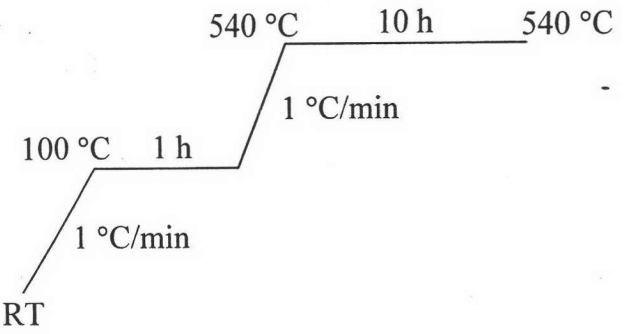


Figure 3.3 The heating program for the calcination of as-synthesized mesoporous silica.

3.3.3.2. Determination of accessible Schiff's bases

The amount of accessible Schiff's base ligands showed the active Schiff's base molecules in the synthesized Schiff's base doped mesoporous silica. In order to measure the amount of accessible Schiff's base, the experimental process was conducted as follows.

100 Milligrams of the dried silica was added to 10 ml of solvent mixture of ethanol : water (1 : 1, v/v). The mixture was stirred at room temperature for 8 h. After the specific time, the solid was separated by centrifugation. The concentration of accessible Schiff's base molecules in the solution was analyzed by using UV-visible spectroscopy.

3.3.3.3. Crystallinity and Morphology

The crystallinity phase identification of the materials was carried out by X-ray diffraction (XRD) using a nickel filtered CuK_α radiation (λ = 1.5406 Å) at 40 kV, 30 mA. Diffraction data was recorded from 1.0° to10.0° (2θ). A scanning speed of 2°/min was adopted.

The morphology of the materials was measured using N_2 sorption analysis at 77 K. Specific surface area values were obtained using the BET equation. Pore volume and pore size distributions were estimated by analysis of the adsorption and desorption curve using the BJH method. Scanning electron microscopy (SEM) was used to visualize the structure of synthesized mesoporous silica.

3.3.4. Extraction properties of materials

The extraction properties of Schiff's base doped mesoporous silica toward Co(II), Cu(II), Fe(II), Fe(III) and Mn(II) were determined in triplicate using batch equilibrium technique. Various parameters including pH, effect of salts in metal solution, temperature and amount of silica were investigated for optimum condition. All extraction experiments were carried out as follows.

200 Milligrams of the dried silica was added to 25 ml of 200 ppm metal solution. The mixture was stirred for 24 hours at 25 °C in the thermoregulated bath. The solution was then recovered by centrifugation. The unextracted metal ion in the solution was analyzed by using flame atomic absorption spectroscopy.