CHAPTER III

EXPERIMENTS

3.1. Reagents

Tetraethoxysilane (TEOS, ≥98%) and cetyltrimethylammonium bromide (CTAB, 98%) were purchased from Fluka. Methanol (CH_3OH), ethanol (C_2H_5OH), heptane (C_7H_{14}) and nitric acid (HNO_3) were received from Merck. $Cu(NO_3)_2{\cdot}3H_2O$ (99%), $Co(NO_3)_2{\cdot}6H_2O$ (99%) and $Ni(NO_3)_2{\cdot}6H_2O$ (≥99%) from Fluka were used to prepare metal ion solutions. Metal solutions of sodium, potassium, and calcium were prepared from analytical grade nitrates receiving from Carlo Elba, Merck, and Fluka, respectively. Deionized water (Milli Q, model millipore ZMQS5V00Y) was used throughout the sample preparation. 1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP) was synthesized according to Jensen [37].

3.2. Apparatus

UV spectra were obtained on an HP8453 UV-Visible spectrophotometer. The nitrogen adsorption isotherm was measured on micrometric ASAP2000 instrument following calcination of sample at 540 °C for 10 hours and out gassing at 350 °C under vacuum for 8 hours. X-ray diffraction was performed on RINI2000 wide angle goniometer (Cu-$K_{\alpha 1}$ radiation, $\lambda = 1.5406$ Å) and measured by the Petrochemical College, Chulalongkorn University. The thermogravimetric analysis was performed on NETZSCH STA 409 and measured by Scientific and Technology Research Equipment Centre. The particle size of materials was performed on Mastersizer S long bed Ver. 2.11 and measured by Scientific and Technology Research Equipment Centre. Metal ion contents of extraction solutions were measured on a Perkin Elmer AAnalyst100 atomic absorption spectrometer.

3.3. Experimental

The experiment is divided into two parts. The first part is the study of the synthesis of HPMSP doped mesoporous silica. The influences of the NaOH concentration as catalyst and quantity of HPMSP on the synthesis of HPMSP doped mesoporous silica were investigated. The physical properties and copper extraction

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properties of the resulting HPMSP doped mesoporous silica were also studied in this part. The physical properties of prepared HPMSP doped mesoporous silica were determined through BET surface area measurement, thermogravimetric analysis (TGA), and X-ray powder diffraction technique. Organic matter contents and accessible HPMSP in doped mesoporous silica were also measured. In the second part, the extraction behaviors of HPMSP doped mesoporous silica with respect to copper, cobalt, and nickel were examined. The parameters influencing the sorption process, such as types of medium, concentration and pH of metal solution, extraction time, mass of HPMSP doped mesoporous silica, and interference by other cations were studied. In addition, the metal ion desorption properties were also investigated.

3.3.1. Synthesis of materials

HPMSP doped mesoporous silica was prepared as stated by Boos and co-workers [6]. The amount of TEOS using in each synthesis was equaled to 0.025 mole. All syntheses of silica were carried out according to the following general procedure unless specified otherwise.

CTAB was dissolved in an aqueous solution of NaOH under stirring and the mixture was maintained at 60 °C for 4 hours. Methanol was then added. The doping molecule (HPMSP) was next introduced into the mixture, still under stirring at 60 °C. After HPMSP was added into the mixture for 4 hours, TEOS was added. The final molar composition of the solution was 1 TEOS : 140 H_2O : 13 CH_3OH : 0.18 CTAB : x HPMSP, where x is specified in section 4.1 of the next chapter: synthesis of HPMSP doped mesoporous silica. A few minutes after the addition of TEOS, silica precipitation was observed. The stirring was maintained at 60 °C for 1 hour, and the mixture was stirred at ambient temperature for 24 hours. The yellowish precipitate was filtered, washed copiously with water and 0.001 M HNO_3 until neutral pH of washing solution was obtained. All of the filtrates (supernatant and washing solutions) were collected and extracted with heptane to determine the quantity of doping molecule that might be leaching out through the synthesis and washing process. Finally, the HPMSP doped mesoporous silica was dried in an oven at 110 °C overnight. The synthesis procedure for HPMSP doped mesoporous silica is summarized in Figure 3.1.

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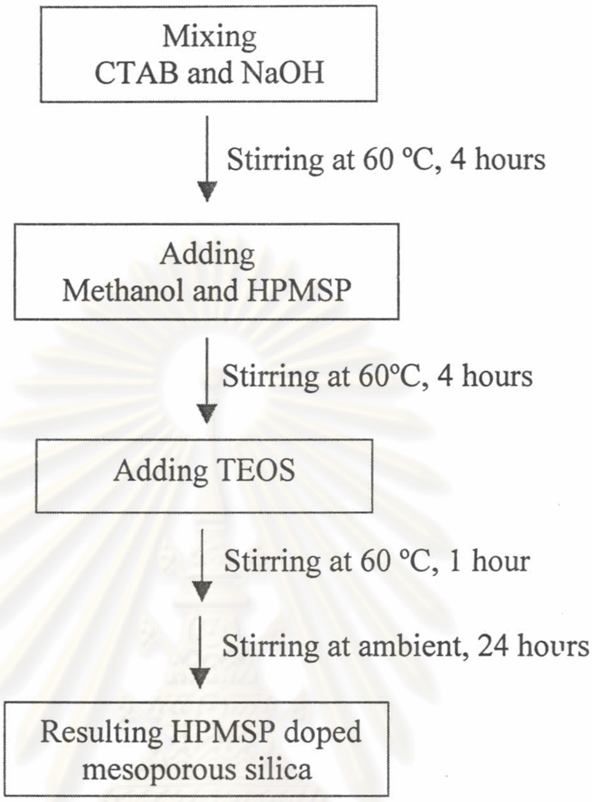

Figure 3.1 The synthesis procedure for HPMSP doped mesoporous silica.

Similarly, controlled silica that did not contain the HPMSP ligand was prepared to be used as a blank.

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3.3.2. Characterization

The characterization of the materials comprised content of organic matters, content of accessible HPMSP, mesoporosity, surface area, pore size, and crystallinity.

3.3.2.1. Organic matters

Organic matter contents in HPMSP doped mesoporous silica were determined using calcination and thermogravimetric methods. The procedure for calcination method is as follows. Mesoporous silica with a constant weight after dried at 110 °C was placed in a muffle furnace. The sample was heated from room temperature to 100 °C at a rate of 1 °C/min, held the temperature at 100 °C for 60 min, and finally heated to 540 °C at a rate of 1 °C/min, at which point the temperature was held constant for 10 hours. After calcination process, the weight loss for sample was calculated. Thermal profile for calcinaton is shown in Figure 3.2.

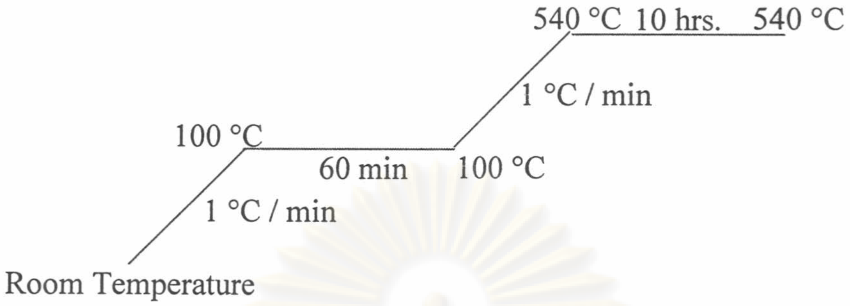

Figure 3.2 Thermal profile for calcination of material.

For thermogravimetric method, mesoporous silica with a constant weight was placed on platinum dish suspended on the reference hook of the TGA equipment. The starting weight of sample was recorded. The weight of the sample in a controlled atmosphere was continuously recorded as a function of temperature. The thermograms were obtained under the nitrogen flow, which was heated from room temperature to 100 °C at the rate of 20 °C/min.

3.3.2.2. Accessible HPMSP

Accessible HPMSP content shows the reactive HPMSP molecule in HPMSP doped mesoporous silica. The determination of an accessible HPMSP content is as follows. 25 mL of solvent mixture of heptane/ethanol (1:1) and 50 mg of HPMSP doped mesoporous silica were added to extraction vessel. The vessel containing the mixture was stirred for 24 hours at ambient temperature. The solution was separated immediately by centrifugation. The concentration of the HPMSP in solution was measured by UV- visible spectrophotometry.

3.3.2.3. Mesoporosity, surface area, pore size, crystallinity, and particle size

The mesoporosity of materials was determined by nitrogen adsorption-desorption measurement. Prior to the experiments, both non-doped and doped mesoporous silica were calcined according to the thermal profile stated previously.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

The calcined samples were outgassed at 350 °C for 8 hours before measurements were performed. Specific surface area values were obtained using BET (Brunauer-Emmet-Teller) equation. The calculation of the pore-size distribution (PSD) was performed using the desorption branches of the nitrogen adsorption isotherm and the Barrett-Joyner-Halenda (BJH) formula.

The crystallinity of materials was investigated by X-ray diffraction technique. The samples were scanned from 1.5 to 10° (2θ) in steps of 0.02° with speed 200° per minute.

The particle size of materials was measured by the Malvern laser diffraction technique. The sample was dispersed in water, passed through the laser beam. The diffraction angle of the laser beam inverted proportional to particle size was measured.

3.3.2.4. Extraction properties

All experiments were performed at 25 °C in thermoregulated baths and carried out according to the general procedure.

Batch experiment

200 mg of HPMSP doped mesoporous silica was added to 25 mL of metal solution. The mixture was stirred for 24 hours. The liquid was separated from the solid by centrifugation and the final pH value was measured. The metal concentration in the aqueous solution was measured by flame atomic absorption spectrometry. The number of mole adsorbed per gram of sorbent was calculated.

ศูนย์วิทยทรัพยากร
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Kinetic experiment

200 mg of HPMSP doped mesoporous silica was added to 25 mL of metal solution, and the mixture was stirred. The solutions for the kinetic extraction study were withdrawn in the amount of 0.3 mL in each selected time. The concentrations of the metal remained in the solutions were measured by flame atomic absorption spectrometry.