

## CHAPTER II EXPERIMENTAL



### 2.1 Materials

Fumed silica ( $\text{SiO}_2$ ) was purchased from Aldrich Chemical Co. Ethylene glycol ( $\text{OHCH}_2\text{CH}_2\text{OH}$ ) and triethanolamine (TEA,  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ ) were supplied by Labscan and used as received. Acetonitrile ( $\text{CH}_3\text{CN}$ ) was obtained from Labscan and distilled before use. Hexadecyltrimethyl ammonium bromide (CTAB) and sodium hydroxide were purchased from Sigma Chemical Co. Vanadium chloride was purchased from Acros.

### 2.2 Instrumental

Mass spectra of silatrane precursor were obtained using a FISON Instruments 707 VG Autospec-ultima mass spectrometer (Manchester, England) with VG data system, using the positive fast atom bombardment ( $\text{FAB}^+\text{-MS}$ ) mode. FTIR spectroscopic analysis was conducted on a Bruker Instrument (EQUINOX55) with a scanning resolution of  $4\text{ cm}^{-1}$ . Thermal properties were analyzed by thermogravimetric analysis (TGA) using Du Pont Instrument TGA 2950 with the  $\text{N}_2$  flow rate of 50 ml per min.

The mesoporous product was characterized using a Rigaku X-ray diffractometer at a scanning speed of 2 degree/sec, and  $\text{CuK}\alpha$  as source. The working range was  $2\theta = 1.5\text{-}10$ . Electron microscope study (TEM micrographs and electron diffraction patterns) was carried out using Joel 2010F. Surface area and average pore size were measured by BET method using a Quantasorb JR. (Autosorb-1). The product was degassed at  $250^\circ\text{C}$  for 12 hr. prior to analysis. The calcination was achieved using Carbolite Furnace (CFS 1200) with the heating rate of  $5^\circ\text{C}/\text{min}$ .

The diffuse reflectance UV-vis spectra were recorded on a SHIMADZU UV-2550 UV-VISIBLE spectrophotometer. The powdery sample was loaded in a teflon cell, and the spectra were collected in 190-600 nm range with a reference of BaSO<sub>4</sub>.

H<sub>2</sub>-temperature programmed reduction (TPR) measurements were carried out on AUTOCHEM 2003. In a typical experiment, 200 mg of sample was first pretreated in a U-type quartz reactor with a gas flow containing He (20 ml/min) at 200°C for 2 hr. After cooling to 30°C, H<sub>2</sub>-Ar (5% H<sub>2</sub>) gas mixture was introduced into the reactor and the temperature was increased to 800°C at a rate of 10°C/min.

### 2.3 Silatrane Synthesis [Si(TEA)<sub>2</sub>]

Wongkasemjit's synthetic method is followed by mixing 0.10 mol silicon dioxide and 0.125 mol triethanolamine in a simple distillation set using 100 mL ethylene glycol solvent. The reaction was taken place at the boiling point of ethylene glycol under nitrogen atmosphere to remove water as a by-product along with ethylene glycol from the system. The reaction was complete after 10 hrs and excess ethylene glycol was removed under vacuum (10<sup>-2</sup> torr) at 110°C. The brownish white solid was washed with dried acetonitrile for three times. The white powder product was characterized using FTIR, TGA, DSC and FAB<sup>+</sup>-MS.

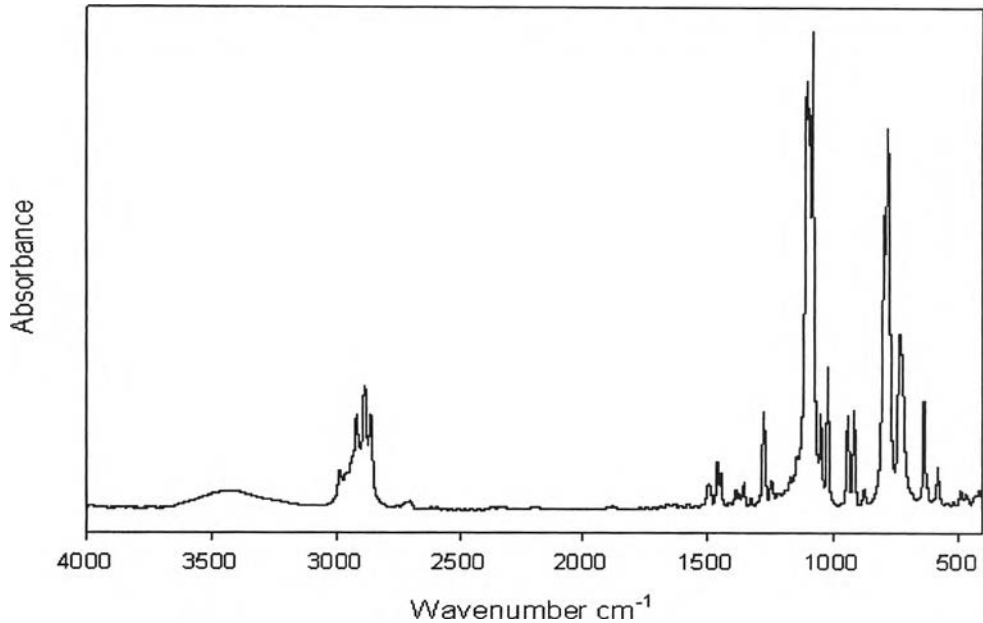


Figure. 2.1 FTIR result of silatrane precursor.

FTIR result as you see in figure 2.1, FTIR: 3000-3700  $\text{cm}^{-1}$  (w, intermolecular hydrogen bonding), 2860-2986  $\text{cm}^{-1}$  (s,  $\nu\text{C-H}$ ), 1244-1275  $\text{cm}^{-1}$  (m,  $\nu\text{C-N}$ ), 1170-1117 (b-s,  $\nu\text{Si-O}$ ), 1093 (s,  $\nu\text{Si-O-C}$ ), 1073 (s,  $\nu\text{C-O}$ ), 1049 (s,  $\nu\text{Si-O}$ ), 1021 (s,  $\nu\text{C-O}$ ), 785 and 729 (s,  $\nu\text{Si-O-C}$ ) and 579  $\text{cm}^{-1}$  (w,  $\text{Si} \leftarrow \text{N}$ ). TGA: one sharp mass loss transition at 390°C and 18.47 %ceramic yield corresponding to  $\text{Si}((\text{OCH}_2\text{CH}_2)_3\text{N})_2\text{H}_2$ .  $\text{FAB}^+$ -MS: the highest m/e at 669 of  $\text{Si}_3((\text{OCH}_2\text{CH}_2)_3\text{N})_4\text{H}^+$  and 100% intensity at 323 of  $\text{Si}((\text{OCH}_2\text{CH}_2)_3\text{N})_2\text{H}_3^+$ . From FTIR,  $\text{FAB}^+$ -MS and TGA showed main product of silatrane in figure 2.4.

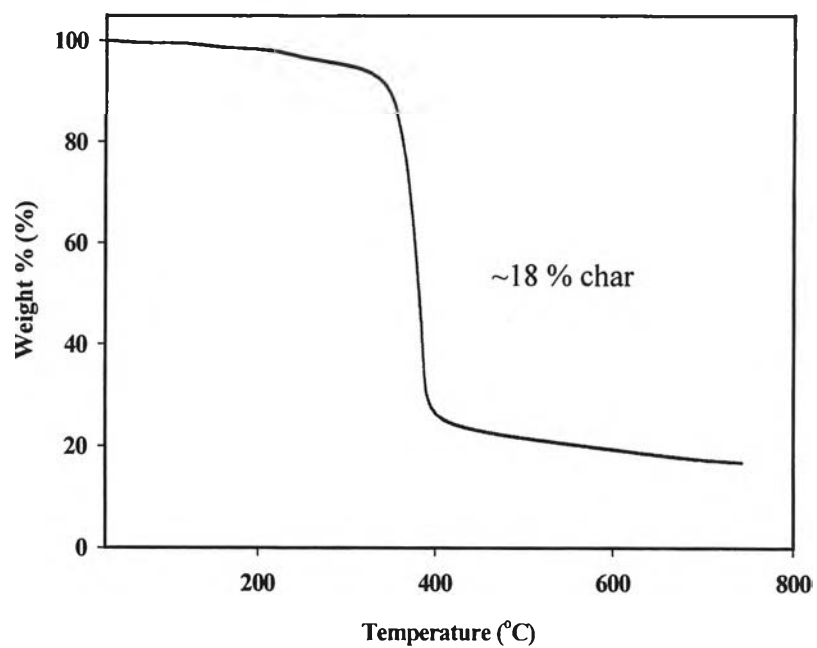


Figure 2.2 TGA result of silatrane precursor.

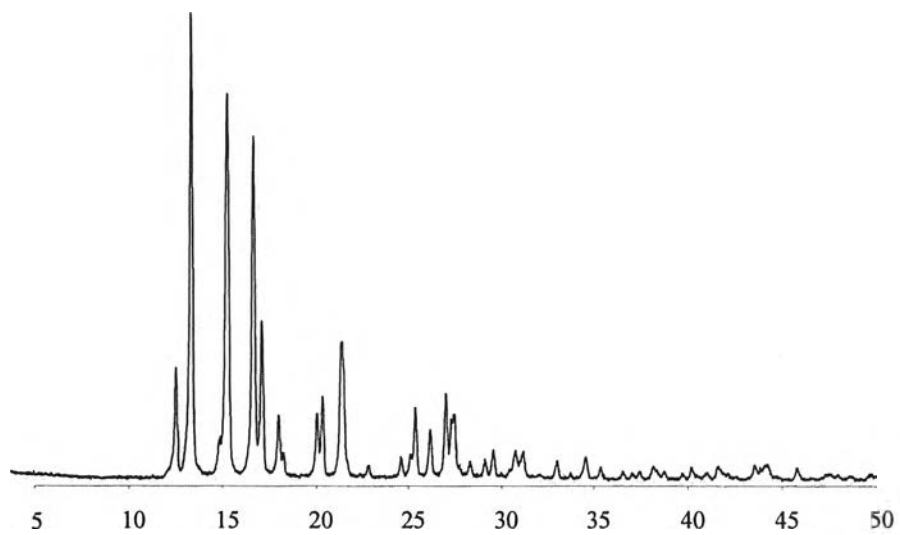


Figure 2.3 FAB<sup>+</sup>-MS of silatrane precursor.

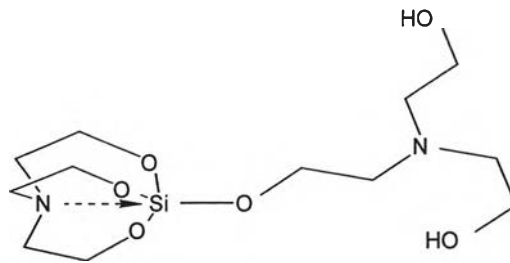


Figure 2.4 Structure of silatrane precursor.

## 2.4 Synthesis of MCM-41

0.004 Mol silatrane precursor was added into a solution containing  $x$  mol of CTAB,  $y$  mol of NaOH and 0.014 mol of TEA. 0.36 Mol of water was then added with a vigorous stirring. The mixture was stirred for various times to follow the reaction using XRD, BET and TEM. The obtained crude product was filtered and washed with water to obtain white solid. The white solid was dried at room temperature and calcined at  $550^{\circ}\text{C}$  for 7 hr to obtain mesoporous MCM-41. In this study, surfactant concentration, ion concentration, mixing temperature and aging time were varied to find an optimum condition.

## 2.5 Synthesis of V-MCM-41

V-substituted mesoporous material (V-MCM-41) has been synthesized following the one-pot synthesis using vanadium chloride as the vanadium source with the molar composition of 0.004 silatrane precursor:0.014TEA:0.5CTAB:NaOH: $x\text{VCl}_3$

The silatrane precursor was added into a solution containing CTAB, NaOH and TEA. Then,  $x$  mol of vanadium solution was added with a vigorous stirring. The mixtures were stirred for a fixed time, followed by filtering and washing with water to obtain white solid. The white solid was dried at room temperature and calcined at  $550^{\circ}\text{C}$  for 7 hr to obtain mesoporous V-MCM-41. In this study, vanadium concentration was

varied to find an optimum condition. The obtained products were characterized using XRD, DR-UV spectrometer and TPR.