

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Materials

All reactions are moisture sensitive, therefore, all operations were carried out with careful exclusion of moisture and air. Reactions were run under inert atmosphere, such as N<sub>2</sub> [UHP grade; 99.9% N<sub>2</sub> purity, supplied from Thai Industrial Gases Public Company Limited (TIG)]. Glassware and chemicals were oven dried prior to use.

Ethylene glycol (EG, HOCH<sub>2</sub>CH<sub>2</sub>OH) was purchased from Farmitalia Carlo Erba (Barcelona), and distilled before use. Used EG was recycled by double fractionation distillation under N<sub>2</sub> atmosphere. Pure EG was collected at 198°C/760 torr, and stored in an oven-dried (at 110°C) bottle.

Aluminum hydroxide hydrate [Al(OH)<sub>3</sub>.XH<sub>2</sub>O], magnesium (Mg, 99% purity) powder, and magnesium oxide (MgO) were purchased from Aldrich Chemical Co. Inc (USA), Fluka Chemical (Switzerland), and Carlo Erba, respectively. They were used as received.

Triethanolamine [TEA, N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>, 99.5% purity] was purchased from Merck Chemical Co. (Germany) and used as received.

## 2.2 Instrumentation

### 2.2.1 Positive Fast Atom Bombardment Mass Spectroscopy (FAB<sup>+</sup>-MS)

Spectra were recorded on a FISIONS Instrument (707 VG Autospec-ultima mass spectrometer, Manchester, England) with a VG data system, employing a direct probe inlet and using the Cs gun to ionize sample molecule. The peaks were calibrated using CsI as the reference. The sample was mixed with glycerol, used as a matrix. The mass range of samples was set from  $m/z = 40$  to 3000. The 3 min scanning time for each sample was used.

### 2.2.2 X-ray Diffraction (XRD)

X-ray diffraction patterns were obtained on a Phillips PW 1830/00 No. DY 1241 diffractometer. Sample (0.1-0.2 g) was ground with alumina mortar, spread on a glass slide specimen holder, and examined between  $5-80^\circ 2\theta$  at a scan speed of  $1.5^\circ 2\theta/\text{min}$  in  $0.02^\circ 2\theta$  increments.  $\text{CuK}\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) radiation was used as an X-ray source and operated at 40 kV, 30 mA. Peak positions were compared with standard JCPDS files, to identify crystalline phases.

The XRD patterns were used for average particle diameter estimation (West, 1989) by line broadening measurements in the Debye-Scherrer equation,

$$t = K\lambda / B_d \cos\theta$$

where  $\lambda$  is the wavelength (nm)

$K$  is the Debye-Scherrer constant which is equal to 0.9

$B_d$  is the angular width of the peak in the terms of  $\Delta(2\theta)$ (radian)

$\theta$  is the Bragg angle of the reflection (degree)

$t$  is the mean crystallite diameter (nm)

### 2.2.3 Instrument for Humidity Measurement

Solartron 1255 Frequency Response Analyzer (FRA) was used for impedance measurements in the range of  $10^{-2}$ - $10^5$  Hz coupled with a home-made impedance adaptor to read values up to  $10^{11}$   $\Omega$ . The resistance values were calculated on the complex impedance plane plots from the intercepts of the semicircle, extrapolated if necessary, with the real axis. The relative humidities between 2-90 % were obtained by mixing water saturated air and dry air. Monitoring of relative humidity (RH) was performed using a Multisens Inc. hygrometric probe, which gave accuracy to within  $\pm 2$  %. Temperature was also controlled in the test chamber.

### 2.2.4 Mercury Porosimeter

The pellet microstructures were examined using a mercury porosimeter from Carlo Erba Strumentazione mod. 2000. The volume of mercury penetrating the pores of the sample was measured as a function of the pressure exerted. The pore radii and volumes were calculated and pore size distribution in the sample was determined.

### 2.2.5 Thermogravimetric Analyses (TGA)

NETZSCH TG 209 Thermogravimetric analyzer was used for TGA studies. Samples (approximately 5 -20 mg) were loaded in an alumina crucible and heated in flowing  $N_2$  and  $O_2$  (10 ml/min). The normal heating rate program and heating range were  $10^\circ\text{C}/\text{min}$  and from room temperature to  $1000^\circ\text{C}$ , respectively.

### 2.2.6 BET Surface Area Measurement

The surface areas of all powder samples were determined by the four point BET method using a Micromeritics Flowsorb II model 2300. The P/P° ratios were 0.0490, 0.1177, 0.1765, and 0.2354. A gaseous mixture of nitrogen and helium using a gas mixer was allowed to flow through the system at a constant rate of 30 cc/min. The nitrogen gas having an effective cross-sectional area of  $16.2 \times 10^{-20} \text{ m}^2/\text{molecule}$  was used as the adsorbate (5, 12, 18, 24% by volume). It was injected using an one milliliter syringe to calibrate the analyzer for each gas composition. Each powder sample was dried at 473 K and degassed in the sample holder for 1 h.

The relationship between the average particle diameter and the specific surface area (assuming that all particles are spherical and of uniform diameter D) was shown in the form of

$$D = 6 / (\rho_s \cdot A)$$

where D is the diameter of particles (m)

$\rho_s$  is the density of spinel ( $3.58 \text{ g/cm}^3$ )

A is the specific surface area ( $\text{m}^2/\text{g}$ )

### 2.2.7 Scanning Electron Microscopy (SEM)

The scanning electron micrographs were carried out to identify the microstructure of the powder sample. The sample was characterized by the Jeol Scanning Electron Microscope, model JSM-35CF with 6 nm resolution and Phillips mod. 505. The powder sample was mounted on aluminum stubs using a liquid carbon paste. Samples were sputter coated with Au/Pd to avoid particle charging.

### 2.2.8 $^1\text{H}$ - and $^{13}\text{C}$ - Nuclear Magnetic Resonance Spectrometer

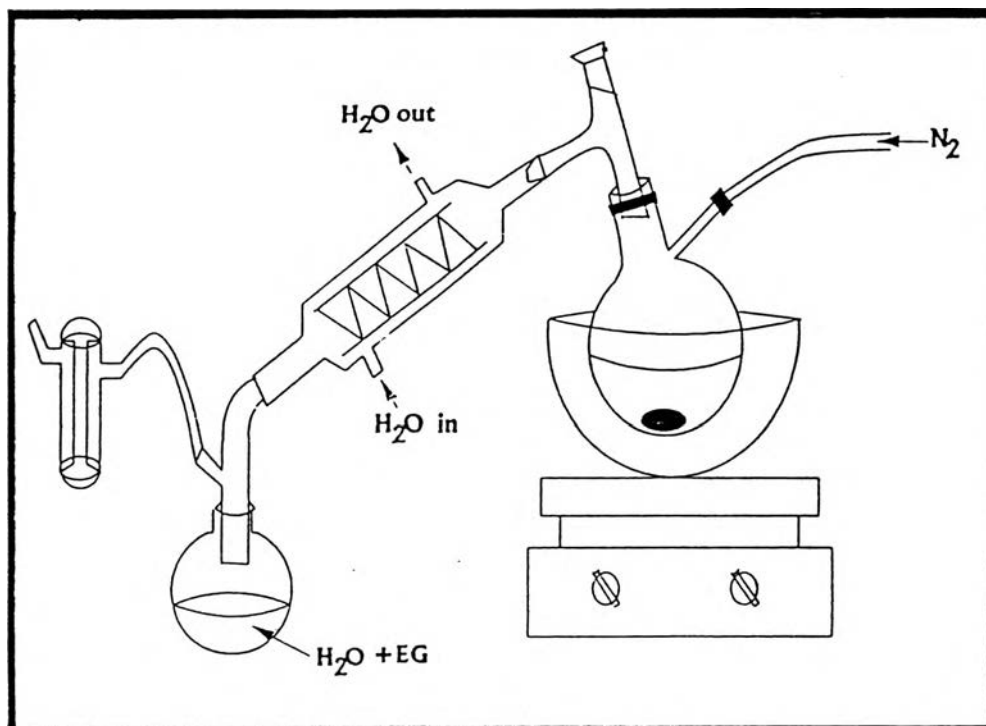
A Bruker AM 400 NMR Spectrometer at the University of Rome “Tor Vergata”, Italy, and at the Chulabhorn Research Institute, Thailand, operating in the quadrature mode was used to obtain  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra. All chemical shifts are given in ppm and tetramethylsilane  $[(\text{CH}_3)_4\text{Si}$ , TMS] was used as the reference. Typical spectra consisted of 64-128 transients of 8192 data points over a 8 KHz bandwidth using a  $5.8\ \mu\text{s}$  at  $90^\circ$  pulse. Typical  $^{13}\text{C}$ -NMR spectra consisted of 12000 transients on a 35 KHz bandwidth using a  $10\ \mu\text{s}$  at  $90^\circ$  pulse. Deuterated chloroform ( $\text{CDCl}_3$ ) was used as a standard solvent.

## 2.3 Procedure

### 2.3.1 Preparation and Characterization of Magnesium Aluminate

#### Spinel by the OOPS Process

As shown in Figure 2.1, the reaction was performed in a 250 mL, two-necked, round bottom flask equipped with a nitrogen gas inlet, a magnetic stirrer, 3-way adaptor, condenser, vacuum adaptor and a 250 mL receiving flask. The reaction mixture was heated with a heating mantle under a dry and inert (nitrogen) atmosphere condition.



**Figure 2.1** The reaction apparatus.

Firstly, aluminum hydroxide hydrate (16.26 g, 100 mmol, 62.7% as  $\text{Al}_2\text{O}_3$  by TGA), magnesium oxide (4.24 g, 100 mmol, 95% as  $\text{MgO}$  by TGA), three moles of triethanolamine (40 mL, 300 mmol), and 150 mL of EG as solvent, were put into a 250 mL two-necked round bottom flask. The mixture gave a milky solution. It was then heated under nitrogen at  $200^\circ\text{C}$  to distill off EG and by-product water that was produced during the reaction. The reaction was continuously distilled for approximately 7 h to obtain the spinel precursor, and the precursor was then distilled further under vacuum (approximately 0.01 torr, according to the attached manometer) at  $100^\circ\text{C}$  to remove excess EG for 6 h. The products obtained were characterized by  $\text{FAB}^+\text{-MS}$ ,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR.

Pyrolysis studies were carried out using a Carbolite horizontal tube furnace (Type 15/75/450, Aston Lane, Hope Sheffield, England), equipped with a Eurotherm temperature controller. The precursor was pyrolyzed in an alumina boat at 400°C for 2 h, using a ramp rate of 10°C/min and further pyrolyzed subsequently at 500°, 600°, 700°, 800°, 900°, 1000°, and 1100° for 2 h at each temperature. The powder samples were then characterized by XRD, BET, and SEM.

### 2.3.2 Preliminary Studies of Magnesium Aluminate Pellets as Humidity Sensors

The spinel powders prepared as mentioned in the section 2.3.1 were uniaxially pressed by hydraulic pressing at 20 MPa into discs 12 mm in diameter and 1 mm in thickness. Pellets were sintered in air at 1300°C for 8 h and at 1100°C for 2 h. The microstructure of the pellets was investigated by mercury porosimeter measurements and SEM.



**Figure 2.2** The pellet sample holder for impedance measurements.

On both sides of pellet samples, gold electrodes, 10 mm in diameter, were applied by vacuum evaporation. The pellets, heat-cleaned at 400°C for 1 h before each measurement, were placed in the sample holder, as shown in Figure 2.2, and measured using a.c. impedance spectroscopy. The pellet samples were tested at different levels of relative humidity (RH) at 40°C, ranging from 2 to 90 %.

### 2.3.3 Preparation of Spinel Directly from Aluminium Hydroxide and Magnesium Hydroxide

Aluminum hydroxide hydrate (16.26 g, 100 mmol, 62.7% as  $\text{Al}_2\text{O}_3$  by TGA), magnesium oxide (4.24 g, 100 mmol, 95% as MgO by TGA) were weighed and mixed by ball-milling for 1 h. The mixture was transferred to the alumina crucible for sintering at 1100°C for 15 and 20 h (West, 1989). The powder samples obtained were characterized by XRD, BET, and SEM .

### 2.3.4 Preparation of Spinel from Alumatrane and $\text{Mg}(\text{OMe})_2$

Firstly, aluminum hydroxide hydrate (16.26 g, 100 mmol, 62.7% as  $\text{Al}_2\text{O}_3$  by TGA), triethanolamine (26.7 mL, 200 mmol), and 100 mL of EG, as solvent, were put into a 250 mL two-necked round bottom flask. The mixture was stirred and heated under nitrogen at 200°C to distill off EG and by product water produced during the reaction. The reaction was continuously distilled for approximately 6 h. Clear and yellow color product obtained was characterized by  $\text{FAB}^+$ -MS.

Magnesium powder (2.45 g, 100 mmol) was weighed and dissolved in 75 ml dried methanol. Turbid solution,  $\text{Mg}(\text{OMe})_2$ , was obtained after the mixture was stirred for 3 h. Then, triethanolamine (13.4 mL, 100 mmol), prepared alumatrane, and 100 mL of ethylene glycol were added into the mixture of  $\text{Mg}(\text{OMe})_2$ . The mixture was heated and distilled continuously



for 2 h. Clear and yellow solution resulted was then distilled further under vacuum (approximately  $10^{-2}$  torr, according to the attached manometer) at 100 °C to remove excess EG for 6 h. Viscous, clear, and brown color product obtained was characterized by FAB<sup>+</sup>-MS, <sup>1</sup>H-NMR and TGA.

Pyrolysis studies were carried out using a Carbolite horizontal tube furnace (Type 15/75/450, Aston Lane, Hope Sheffield, England), equipped with a Eurotherm temperature controller. The precursor was pyrolyzed in an alumina boat at 400°C for 2 h, using a ramp rate of 10°C/min and further pyrolyzed subsequently at 500°, 600°, 700°, 800°, 900°, 1000°, and 1100° C for 2 h at each temperature. The powder samples were then characterized by XRD, BET, and SEM.