CHAPTER III

EXPERIMENTAL

3.1 Materials

Fumed silica (SiO_2, surface area 473.5 m^2/g, average particle size of 0.007 μm) and aluminum hydroxide hydrate ($Al(OH)_3$, surface area 50.77 m^2/g), were purchased from Sigma Chemical Co. and used as received. They used as raw materials for precursor synthesis.

Tetraethoxysilane (TEOS), tetrabutyl ammonium hydroxide (TBA) and tetra-propyl ammonium bromide (TPA) were purchased from Fluka Chemical AG

Triethanolamine (TEA, $N(CH_2CH_2OH)_3$), and triisopropanolamine (TIS, $N(CH_2CHCH_3OH)_3$) were supplied by Carlo Erba Reagenti and Fluka Chemical AG., respectively, Both were used as received and as raw materials for precursor synthesis.

Ethylene glycol (EG, $HOCH_2CH_2OH$) was obtained from J.T. Baker Inc. It was used as received for precursor synthesis.

Sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from EKA Chemicals and AJAX chemicals, respectively. Both were used as received and as sol-gel agents for zeolite synthesis.

Sodium fluoride (NaF), 99% purity, was supplied by Riedel-de Haen, and used as received.

Acetonitrile (CH_3CN) was obtained from Lab-Scan Co., Ltd., and distilled using standard purification method. It was used as a purifying agent.

Vanadium (III) chloride, 99% purity, was purchased from ACROS Organics and used as received.

3.2 Instruments

FTIR spectroscopic analysis was conducted using Bruker Instrument (EQUINOX55) with a resolution of 2 cm^{-1}. The solid samples were prepared by

mixing 2 mg sample with 60 mg of dried KBr, while the liquid sample were analyzed using Zn-Se window cell.

Mass spectra were obtained using a VG Autospec model 7070E form Fison Instrument with VG data system, using the positive fast atomic bombardment (FAB^+-MS) mode and glycerol as a matrix. CsI was used as a reference, while a cesium gun was used as an initiator. The mass range used was from m/e = 20 to 3,000.

Thermal properties and stability were analyzed using a Perkin Elmer TGA7 analyzer at a scanning rate of 10°C/min under nitrogen atmosphere, and simultaneous thermal analysis (STA) was conducted using Netzsch instrument STA 409 at a scanning rate of 20°C/min under nitrogen and oxygen atmosphere.

SEM micrographs were performed using a JEOL 5200-2AE scanning electron microscope. Electron Probe Microanalysis (EPMA) was used to analyze sample in micro-scale for both qualitative and quantitative analysis of element, using X-ray mode detector (EDX-SEM).

Crystal structure was characterized using a Rigaku X-Ray Diffractometer at a scanning speed of 5 degree/sec, with $CuK\alpha$ as incident radiation and a filter. The working range was 3-50 theta/2 theta, with 1 degree and 0.3 mm setting of divergence for the scattering and receiving slits, respectively.

The elementary ratio was measured by X-ray fluorescence spectroscopy (Bruker model SRS 3400), with 99.8% boric acid as binder.

Hydrothermal treatment by microwave heating technique was conducted using MSP1000, CME cooperation (Spec 1,000 Watt and 2450 MHz). Samples were heated in a Teflon tube, using the inorganic digestion mode, with time-to-temperature programming

3.3 Precursor Synthesis

3.3.1 Alumatrane Synthesis (Al-TIS)

Alumatrane (tris(alumatranyloxy-i-propyl)amine or AlTIS) was synthesized using the method reported by Wongkasemjit et.al[10] by mixing 0.125 mole TIS and 0.1 mole $Al(OH)_3$ in 100 ml of EG and heating the mixture at 200 °C

for 10 hour under nitrogen atmosphere. EG was removed after completion of the reaction by distillation under vacuum (8 mm Hg) at 110 °C until dry crude product was obtained. The pale-yellow solid was washed three times with dried acetonitrile to obtain a fine white powder. The purified product was characterized using XRD, TGA, FTIR and FAB$^+$-MS.

3.3.2 Silatrane Synthesis (Si-TEA)

Silatrane (tris(silatranyloxy-ethyl)amine or SiTEA) was synthesized using methodology identical to that for alumatrane synthesis by heating a mixture of 0.125 mol TEA, 0.1 mol SiO$_2$ and 100 ml of EG at 200 °C for 10 hour under nitrogen atmosphere. The reaction was complete within 10 h and the mixture was cooled to room temperature before distilling off the excess EG under vacuum (8 mmHg) at 110 °C for 3 h. The brownish white solid was washed three times with dried acetonitrile to obtain a fine white powder. The silatrane product was characterized using XRD, TGA, FTIR and FAB$^+$-MS.

3.4 Zeolite MFI Synthesis

3.4.1 Pure Silicate MFI (Silicalite)

SiTEA equivalent to 0.25 g SiO$_2$ was dispersed in 5 ml of water and continuously stirred before adding the template molecule (TBA or TPA). In the case of TBA template, NaOH was added to balance the total hydroxide, and NaCl was added to balance the sodium ion concentration (Na$^+$). In the case of the TPA template, NaOH was added to reach desired hydroxide concentration; NaCl was used for adjusting total sodium ion concentration. Water was then added to all samples, according to the stoichiometric formula. To establish the optimum reaction conditions for pure silicate MFI synthesis with the two templates, TBA and TPA, the effect of aging time, heating times and heating temperature were studied. The effect of formulate composition to the morphology of product was studied as well.

3.4.2 Aluminosilicate MFI (ZSM5)

Since alumatrane is more susceptible to hydrolysis by water, it was added at the end of the above-specified procedure to prepare pure silicate MFI. Again, different ratios of Si/Al, the effect of OH$^-$ and Na$^+$ concentration, and the time

period for addition of alumatrane were varied to elucidate their influence on the morphology of aluminosilicate MFI crystals in both TPA and TBA template systems

3.4.3 Vanadium-MFI (VS-1)

Vanadium (III) chloride was prepared within a glove box under a dry nitrogen atmosphere before adding Si-TEA equivalent to 0.5 g SiO_2 and then adding deionized water. The mixture was stirred continuously before adding the template molecule TPA. Sodium hydroxide was added into the mixture while vigorously stirring the mixture. The sample bottles were sealed using double caps covered with extra wrap of aluminum foil, sandwiched by paraffin wrap. To establish the optimum conditions for incorporation of vanadium into the silicate-1 structure, water content, sodium hydroxide concentration, and temperature were studied. The aging time was fixed at 84 hr at room temperature with continuously stirring and 20 hr of heating under microwave irradiation. The VS-1 as-synthesized products were characterized using XRD and ESR prior to calcination in an electronic furnace set at 550 °C with the heating rate of 1 °C/min. Calcined products were characterized using UV-VIS and XRD. Before analyzing the samples using ESR at 25 °C, calcined samples were washed with 1 N ammonium acetate solution at 75 °C for 12 hr and dried under vacuum at 200 °C for 2 hr. Washed and un-washed samples were reduced using temperature programmed reduction before characterization by ESR.

3.5 Oxidative Dehydrogenation of Propane by VS-1 Catalyst

Oxidative dehydrogenation reaction using the synthesized VS-1 catalyst was performed via a pack bead reactor equipped with online gas chromatography under atmospheric pressure and isothermal conditions. GS-Alumina column was used to separate the obtained hydrocarbon products using an FID detector. Other gas products were separated using Plot-Q and Molsieve connected in series through a by-pass switching valve and equipped with a TCD detector. The reactor diagram was shown in Appendix A. The reaction achieved steady state 30 min after initiation. The reactivity remained constant even when the reaction was continuously run for 20 h. Errors in carbon balance were less than 10%. The catalyst tests were conducted using 0.1 g of VS-1 zeolite in 8mm inner-diameter quartz tube reactor with low dead

volume. The catalyst was pretreated in the reactor prior to the reaction with a mixed gas of nitrogen and oxygen at 550°C for 2 h before cooling down to the reaction temperature of 450°C. Catalytic behavior was then determined as a function of temperature. The catalyst study herein is reported, based on the VS-1 zeolite synthesis parameters, space velocity and the ratio of hydrocarbon to oxygen in the gas steam. Calibration of GS-Alumina column for detection of hydrocarbon compound with FID detector was shown in Appendix B. Calibration of Plot Q and Moleseive column for detection of carrier, reactance and carbon oxide product compound with TCD detector was shown in Appendix C. Calculation of propane and oxygen conversion, products selectivity and carbon balance were shown in Appendix D.