

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst Preparation Materials

Fumed silica (SiO_2) and Iron (III) chloride were supplied from Aldrich Chemical.

Ethylene glycol ($\text{OHCH}_2\text{CH}_2\text{OH}$) used as the reaction solvent, was obtained from J.T. Baker.

Triethanolamine (TEA, $\text{N}[\text{CH}_2\text{CH}_2\text{OH}]_3$) were purchased by Labscan.

Sodium hydroxide (NaOH) was purchased from EKA Chemicals.

Tetra-propyl ammonium bromide (TPA) was obtained from Fluka Chemical AG.

Acetonitrile (CH_3CN) was obtained from Lab-scan Co., Ltd. and distilled prior to use.

3.1.2 Reactant Gases

Nitric Oxide (NO) 1.52% in helium was supplied from Air Products and Chemicals Co., Ltd.

Carbon monoxide (CO) 24.85% in helium was supplied from Thai Industrial Gases (Public) Co., Ltd.

Oxygen (O_2) 21.30% in helium was supplied from Praxair (Thailand) Co., Ltd.

High purity helium was supplied from Thai Industrial Gases (Public) Co., Ltd.

3.2 Catalyst Preparation Procedure

3.2.1 Silatrane Synthesis (Si-TEA)

Silatrane (tris(silatranyloxy-ethyl) amine or SiTEA) was synthesized by heating a mixture of 0.125 mol TEA, 0.1 mol SiO_2 and 100 ml of EG at 200°C 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. 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 and FTIR.

3.2.2 Fe-MFI Synthesis

Silatrane and TPA were dispersed in water using the $\text{SiO}_2:0.1\text{TPA}:0.4\text{NaOH}:144\text{H}_2\text{O}:0.01\text{FeCl}_3$ formula, and continuously stirred before adding iron (III) chloride. Stoichiometric amount of sodium chloride was further added into the mixture. To establish the optimum reaction conditions for the ratio of Si/Fe equal to 100 in the gel, the effects of aging time, heating time and heating temperature were studied. Additionally, the effect of the Si/Fe ratio was also studied by varying the ratio from 100 to 19. The as-synthesized Fe-MFI products were calcined in an electronic furnace set at 550°C with the heating rate of 0.5°C/min. The calcined products were characterized using XRD, SEM, DR-UV and XRF.

3.3 Catalyst Characterization

The characteristics of the prepared catalysts were investigated by techniques described below.

3.3.1 Fourier Transforms Infrared Spectroscopy (FTIR)

FTIR was used to determine the chemical characteristics of the precursor. It 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 and pressed to form pellets.

3.3.2 Thermogravimetric Analysis (TGA)

Thermal properties and stability was analyzed on a Perkin Elmer TGA7 analyzer at the scanning rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

3.3.3 Scanning Electron Microscopy (SEM)

The scanning electron micrographs was performed using a JEOL 5200-2AE scanning electron microscope. Electron probe microanalysis (EPMA) was performed to identify the microstructure of the sample.

3.3.4 X-Ray Diffractometer (XRD)

Rigaku XRD was used to characterize the crystal structure at a scanning speed of 5 degree/sec, with $\text{CuK}\alpha$ as incident radiation and a filter. The working range was 3-50 2theta, with 1 degree and 0.3 mm setting of divergence for the scattering and receiving slits, respectively.

3.3.5 Diffuse Reflectance UV Spectroscopy (DR-UV)

DR-UV spectra were registered using Perkin-Elmer Lambda 15 type spectrometer, working under computer guidance in the 200-900 nm wavelength range and using MgO as reference. The spectra were taken at ambient conditions without special precautions.

3.3.6 X-ray Fluorescence Spectroscopy (XRF)

The Si/Fe ratio was determined by X-ray fluorescence (XRF) spectroscopy (Bruker model SRS 3400).

3.4 Apparatus

Figure 3.1 shows the schematic flow diagram of experimental equipments. In this work, the experimental apparatus was divided into 3 sections: (i) gas blending system (ii) catalytic reactor, and (iii) analytical instrument.

3.4.1 Gas Blending System

The reactant mixture consisted of 0.1% nitric oxide, 1% carbon monoxide, and 0.45% oxygen balanced in helium. To obtain the desired component of the typical reactant mixture, a mass flow controller (Sierra Instrument, Inc. model &40) was applied to control the flow rate of each reactant gas. After that, the reactant mixture was passed through a check valve to protect reverse flow. Finally, the reactant mixture was passed to the reactor.

3.4.2 Catalytic Reactor

The activity of synthesized catalyst was carried out by using the selective catalytic reduction of NO reaction. 100 mg. of catalyst was packed in the middle of a 1 cm. outside diameter borosilicate glass reactor with glass wool. The experiment was performed at atmospheric pressure with the space velocity of 42,000 h^{-1} . Moreover, the reaction temperature ranged from 323 to 723 K which was

controlled by PID controller equipped with K-type thermocouple (Yokohama, Model UP27). Finally, the product gas was passed to the analytical instruments.

3.4.3 Analytical Instruments

The effluent gas was analyzed both quantitatively and qualitatively. A product gas from the reactor was separated into two parts. First, O₂ and N₂ concentration was determined by using Hewlett Packard 3365 series II chemstation and a molecular seive 13X column. Another part, the product gases were passed to the high level Chemiluminescence NO-NO₂-NO_x analyzer from ECO physics Model CLD 700 EL in order to determine the nitric oxide (NO) and nitrogen oxide (NO₂) concentration. In addition, the concentration of N₂O was calculated from mass balance.

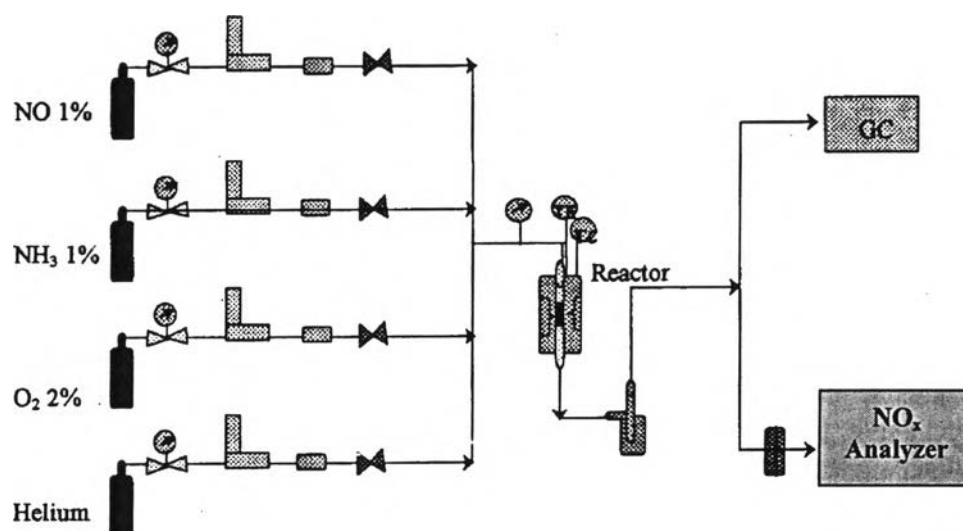


Figure 3.1 Schematic flow diagram of experimental equipments (Rochanutama *et al*, 2003).