

CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals

(-)-Sparteine ($C_{15}H_{26}N_2$) was supplied from Aldrich.

Acetone was obtained from Labscan.

Methyl iodide was supplied from Acros Organics.

Diethyl ether was purchased from BDH.

Aluminum isopropoxide was supplied from Acros Organics.

Dowex 1-x8 anion exchange resin was purchased from Fluka Chemical AG.

GeO_2 was obtained from Aldrich.

Tetraethylorthosilicate was purchased from Fluka Chemical AG.

HF (48.1 wt%) was supplied from BDH.

Iron nitrate ($Fe(NO_3)_3$) was obtained from Univar.

Copper nitrate ($Cu(NO_3)_2$) was purchased from Carlo Erba.

Nickel nitrate ($Ni(NO_3)_2$) was supplied from Carlo Erba.

Cobalt nitrate ($Co(NO_3)_2$) was purchased from Fisher.

Zeolite Mordenite ($SiO_2/Al_2O_3 = 19$) was obtained from Tosoh.

3.1.2 Gases

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

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

Ammonia (NH_3) 1.13% in helium was purchased from Thai Industrial Gases (Public) Co., Ltd.

Oxygen (O_2) 21.70% in helium was supplied from Thai Industrial Gases (Public) Co., Ltd.

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

3.1.3 Equipment

Teflon-lined stainless steel autoclave

Mass Flow Controller

Glass Tube Reactor

X-Ray Diffractometer (XRD)

Temperature Programmed Desorption (TPD)

Scanning Electron Microscope (SEM)

Transmission Electron Microscope (TEM)

Gas Chromatograph (GC)

Chemiluminescence NO/NO_x Analyzer (Eco Physics, Model CLD 700 EL)

3.2 **Methodology**

The experiments were divided into 3 parts: (1) catalyst preparation, (2) catalyst characterization, and (3) catalyst activity measurement.

3.2.1 Catalyst Preparation

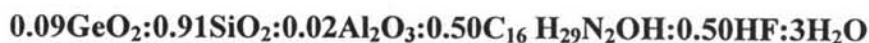
3.2.1.1 *N(16)-methylsparteinium hydroxide Preparation (Cabanas et al., 2005)*

The preparation of N(16)-methylsparteinium hydroxide as the template for ITQ-21 synthesis was performed by the following method: Firstly, 16.23 g of sparteine was mixed with 85.15 ml of acetone. Then, 6.29 ml of methyl iodide was added drop by drop, while the solution was stirred in darkness. After 24 hours, a white creamed-color precipitate appeared. About 160 ml of diethyl ether was added to the solution before filtering. The obtained solid was N(16) methylsparteinium iodide with yield around 99%. To complete the template preparation, 25.53 g of N(16) methylsparteinium iodide was mixed with 74.88 g of deionized water. Then about 69 g of Dowex anion exchange resin was added to the

mixture to convert iodide ions (I⁻) into hydroxide form (OH⁻). After it was stirred for 24 hours, the mixture was filtered and the obtained solution was about 100 g of N(16) methylsparteinium hydroxide (C₁₆H₂₉N₂OH), which was used as template for ITQ-21 synthesis.

3.2.1.2 ITQ-21 Synthesis (Blasco et al., 2004)

The synthesis of ITQ-21 was carried out using N(16)-methylsparteinium hydroxide (C₁₆H₂₉N₂OH) previously prepared, as the organic structure directing agent. Synthesis of ITQ-21 in fluoride media was carried out under hydrothermal conditions from the following gel composition in a Teflon-lined stainless steel autoclave.



In the synthesis of ITQ-21, typically 19.23 g of N(16) methylsparteinium hydroxide was mixed with 0.24 g of GeO₂. Then 4.74 ml of Tetraethylorthosilicate and 0.21 g of aluminum isopropoxide were added to the solution as the silica and alumina sources of zeolites, respectively. The mixture of the two precursors was stirred at room temperature for 3 days until Si and Al were completely hydrolyzed. After that, 0.52 g of hydrofluoric acid (48 wt%) was added as a hydrolyzing agent and was stirred until it was homogeneous. The aging time for the catalyst was 1 day. After that, it was heated for 3 days in a teflon-lined stainless steel autoclave. The final solid was recovered by filtration, washed with distilled water, and dried at 110°C. Then it was calcined at 500°C for 5 hours in airflow to eliminate organic matters and the fluoride ions occluded in its interior.

3.2.1.3 Preparation of Metal/ITQ-21/H-MOR Catalysts

ITQ-21 was physically mixed with H-mordenite as a co-support. The mixing of the two zeolites resulted in 5%ITQ-21/H-MOR support.

The preparation of M/ITQ-21/H-MOR (M= Fe, Cu, Co and Ni) was carried out by wet impregnation method. The appropriate amount of salt solution was dropped onto a weighed quantity of ITQ-21/H-MOR. Then, the mixture was dried in an oven at 110°C overnight. After that, the solid was calcined in the furnace at 500°C for 5 hours.

3.2.1.4 Preparation of Metal/H-MOR Catalysts

To compare the activity on NO_x reduction of M/ITQ-21/H-MOR, a series of metal-loaded mordenites was prepared as the references. The metal/mordenites (M/H-MOR) were prepared from H-MOR (640HOA from Tosoh, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 19$). After calcination at 400°C for 3 hours to clean up the surface, the preparation of M/H-MOR was carried out using the wet impregnation method. The appropriate quantities of copper nitrate, iron nitrate, nickel nitrate, and cobalt nitrate were each added into H-MOR so that the total metal content was around 5% by weight on each single metal-loaded catalysts. The catalysts were dried at 110°C overnight, followed by calcining in a furnace at 500°C for 6 hours.

3.2.1.5 Preparation of 5%Ge/MOR

The Ge/MOR catalyst was prepared in order to investigate the effect of germanium on NO_x reduction. First, GeO_2 was dissolved with 37 wt% HCl, and then the distilled water was added to obtain 50 mL of solution. The solution was used as the stock solution for Ge source in wet impregnation method. An appropriate amount of stock solution was dropped on H-MOR until receiving 5 wt% Ge on the total catalyst. Then, the loaded catalyst was dried at 110°C overnight, followed by calcining in a furnace at 500°C for 6 hours.

3.2.2 Catalyst Characterization

Various techniques were performed to characterize the prepared catalysts, as the followings:

3.2.2.1 Surface Area Measurement (BET)

The specific surface area, total pore volume and average pore diameter of all prepared catalyst samples was determined by Brunauer-Emmet-Teller (BET) method using Sorpmatic System. N_2 gas was used as the adsorbate at liquid N_2 temperature (-196°C). A sample was treated under He atmosphere at 150°C for 2 hours in order to eliminate volatile adsorbates on the surface before measurement.

3.2.2.2 X-ray Diffraction (XRD)

XRD was used to identify the crystal structure, using the $\text{CuK}\alpha$ radiation provided with a graphite secondary monochromator and an

automatic divergence slit fixed at 10 mm of irradiation. The diffraction data were collected at 0.02 (2 θ)/step and 9 s/step between 2.00 to 70.00 (2 θ).

3.2.2.3 Scanning Electron Microscopy (SEM)

The scanning electron micrograph was used to identify the microstructure of the sample, such as the crystalline size of the catalysts.

3.2.2.4 Transmission Electron Microscope (TEM)

The transmission electron micrograph was used to identify the microstructure of the sample at the finer levels.

3.2.2.5 Temperature Programmed Desorption of Ammonia (NH₃-TPD)

NH₃-TPD experiments were carried out in a U-tube reactor made of quartz. Before the experiment, 200 mg of sample was pretreated in He at 500°C for 1 hour to remove adsorbed H₂O and other gases. After the sample was cooled to 100°C, the He flow was replaced by a flow of 1.13% NH₃/He for 10 minutes. The reactor was then purged with He for another 10 minutes. Using He as the carrier gas, the ammonia TPD was performed with the ramping rate of 25°C/min.

3.2.3 Catalytic Activity Measurements

The SCR activity measurements were carried out in a fixed bed reactor. 100 mg of catalyst was packed in the middle of a 1 cm. outside diameter borosilicate glass reactor with glass wool. The typical feed gas composition was as follows: 1000 ppm NO, 1000 ppm NH₃, balanced with He. The total flow rate was 500 ml/min (under ambient conditions). Thus, a very high GHSV (gas hourly space velocity) was applied ($5.7 \times 10^5 \text{ h}^{-1}$). The NO and NO₂ concentrations were continually monitored by a Chemiluminescence NO/NO_x Analyzer (Eco Physics, Model CLD 700 EL). To avoid errors caused by the oxidation of ammonia in the converter of the Chemiluminescence NO/NO_x Analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet of the NO_x analyzer. The products were also analyzed by a gas chromatograph using a 5A molecular sieve column for N₂ and a Porapak Q column for N₂O.