



CHAPTER III EXPERIMENTAL

3.1 Materials

- Methylcyclohexane reaction (MCH, Aldrich)
- FAU, MFI, BEA zeolites
- Zirconyl Chloride ($ZrOCl_2 \cdot 8H_2O$, Aldrich)
- Ammonium hydroxide (NH_4OH)
- Ammonium chloride
- Silver nitrate ($AgNO_3$)
- Ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$, Aldrich)
- Hexachloroplatinic acid (Acros)
- Ammonia
- Alumina (inert for reactions)
- Deionized water
- Gas: hydrogen, helium, oxygen, and air

3.2 Catalyst Preparation

Both zeolitic and non-zeolitic materials were studied in this work. Commercially available Na-FAU (Si/Al = 5.3), H-MFI (Si/Al = 90), and H-BEA (Si/Al = 2.5) were obtained from UOP, where as the CBV faujasite zeolites (CBV400, Si/Al = 2.5; CBV720, Si/Al = 30) were obtained from Zeolyst International. In addition to the zeolites, tungstated zirconia (WO_x/ZrO_2 , WZ), amorphous non-zeolitic material, was used as the catalyst and the support.

3.2.1 Ion-exchange of Na-form Zeolite

The Na-FAU zeolite was transformed to proton form zeolite (FAU) by an ion-exchange with an ammonium chloride solution. Four successive exchanges

were conducted with an aqueous solution containing 120.5 g ammonium chloride dissolved in a liter of deionized water with 100 g of Na-FAU. Each suspension was refluxed and stirred with a magnetic plate for 2 h. The solid was then filtered and washed with deionized water. After each ion exchange step, the sample was filtered and washed. In the final step, the sample was thoroughly washed with deionized water until it was chloride-free. The solid was finally dried in air at 383 K and kept in a desiccator. Before using, the samples were calcined in flow of air at 773 K for 2 h at the heating rate of 0.5 K/min.

3.2.2 Tungstated Zirconia (WZ) Synthesis

In addition to Na-FAU, WZ samples were prepared by incipient wetness impregnation (IWI) of zirconium oxyhydroxide ($\text{ZrO}_x(\text{OH})_{4-2x, x < 2}$) solids with ammonium metatungstate solutions. High-surface-area $\text{ZrO}_x(\text{OH})_{4-2x}$ was prepared by hydrolysis of a 0.5 M zirconyl chloride solution ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Aldrich, >98 wt.%, Hf <0.5 wt.%, 500 cm^3/h feed) using the controlled addition of NH_4OH (14.8 N) to obtain a constant pH of 10. This pH was chosen based on previous studies (Gimblett *et al.*, 1981), in which the mesoporosity, surface area, and total pore volume of $\text{ZrO}_x(\text{OH})_{4-2x}$ were shown to increase with increasing precipitation pH. The precipitate was immediately filtered and washed repeatedly by deionized water in order to remove residual chloride. After each wash, a couple of drops of a 3 M AgNO_3 solution were added to the filtrate liquid until it showed no visible signs of AgCl formation (<10 ppm residual Cl^-).

The $\text{ZrO}_x(\text{OH})_{4-2x}$ gel was dried at 383 K overnight, crushed, and sieved to retain particles with 0.12 – 0.38 mm diameter. The dried particles were impregnated to the point of incipient wetness with ammonium metatungstate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$, Aldrich, 99.9%) solutions to give the 21 wt% W after oxidation treatments. The impregnated samples were dried at 383 K overnight and oxidized in flowing dry air at 960 K, suggested by (Barton *et al.*, 1999). All samples were oxidized in shallow quartz boats inside a 25-mm-diameter quartz tube with flowing air (Zero Grade, 3.3 cm^3/s). The samples were heated at a rate of 10 K/min to the final temperature (measured in a quartz thermowell just above the sample bed), held for 3 h, and cooled to room temperature in flowing air.

3.2.3 Pt-containing Catalysts Preparation

The Pt-containing catalysts were prepared by incipient wetness impregnation of both the proton form zeolites (H-FAU, H-BEA, H-MFI, CBV400, and CBV720 zeolites) and WZ with 1 wt% Pt. An appropriate concentration was prepared from hexachloroplatinic acid (Acros) solution. Before the impregnation, the supports were pretreated in air at 773 K for 3 h; and after the impregnation, the catalysts were dried at 383 K overnight and then calcined in air at 573 K for 3 h. Prior to each activity measurement, the sample was reduced in situ.

3.3 Catalyst Characterization

3.3.1 Temperature Programmed Desorption of Adsorbed Ammonia

The acidity densities of the catalysts were determined by temperature programmed desorption (TPD) of adsorbed ammonia. The tests were conducted in a 1/4" quartz tube reactor containing 50 mg of catalyst that was pretreated at 773 K for 1 h in He flow. Then, the sample was cooled down to room temperature under He flow; at which point, 2% NH₃/He was passed over the sample in an amount that greatly exceeds the total number of acid sites to assure saturation of all sites. To remove the excess and weakly adsorbed ammonia, the sample was purged in He flow at room temperature for 2 h. Subsequently, the sample was linearly heated to 973 K in flow of He at a heating rate of 10 K/min while the evolution of ammonia was monitored in a thermal conductivity detector. After each TPD, the amount of ammonia desorbed was determined by a calibration curve obtained by varying volumes of 2% NH₃/He.

3.3.2 Raman Spectroscopy of Zirconia

The Raman spectra of calcined catalysts were obtained by a Jovin Yvon-Horiba LabRam 800 equipped with an air-cooled CCD detector equipped with a He-Ne laser (632.8 nm). Typical laser powers ranged from 1.0 to 2.0 mW; integration times were around 100 s for each spectrum; 3 Raman spectra were averaged for each sample.

3.4 Catalytic Activity Testing

The methylcyclohexane reaction (MCH, Aldrich, >99%) was conducted in a 3/8" stainless steel reactor equipped with a thermowell and the thermocouple inside, which was placed in the center of the bed. Prior to each run, the designed amount of catalysts was diluted with inert alumina to make a volume of a catalyst bed of 2 ml and placed in the center of the reactor. The top part of the catalyst bed was filled with glass beads of 1 mm in a diameter, to ensure effective preheating and minimize heat loss. Before the activity measurement, the zeolitic catalysts were reduced in situ at 673 K for 2 h in hydrogen flow. The catalytic activity was measured at the temperature of 533 K, at the total pressure of 2 MPa and at a H₂/MCH molar ratio of 40. Unlike zeolitic catalysts, the WZ sample was first treated in dry oxygen at 673 K for 1 h, purged with helium at 673 K for 30 min to remove all the oxygen, and then reduced at 673 K for 2 h in flowing hydrogen. The space velocities were systematically varied by changing either the catalyst amount (50 to 200 mg) or the feed rate (0.1 to 1 ml/h). In all experiments, the product gas mixtures were analyzed periodically on-line with a HP5890 gas chromatograph equipped with a HP-5 column and a FID detector. The temperature program was started at 308 K. It was held for 15 minutes before ramping to 423 K with a heating rate of 40 K/min.