

CHAPTER 2

EXPERIMENTAL METHODOLOGY

2.1 PREPARATION OF THE CATALYST

2.1.1 Preparation of Ni/H-zeolite- β

The Ni supported H-zeolite- β catalyst was prepared by the method of wet impregnation. Nickel nitrate hexahydrate, Ni (NO₃)₂.6H₂O (CDH chemicals Ltd., India) and H-zeolite- β (Sud Chmie Pvt Ltd., India) were used as starting materials for the preparation of the supported metallic catalysts. The H-zeolite- β support used in this preparation has a SiO₂/Al₂O₃ ratio of 40, which is active for the etherification of isopropanol. Approximately 25 wt % Ni metal was loaded into the zeolite support using the wet impregnation method. In a typical preparation procedure, 10.5 g of nickel nitrate was added to a suspension of 7.8 g of Hzeolite- β in double distilled water. The mixture was stirred for 24 h at room temperature and evaporated to dryness. The resulting precursor material was then calcined at 823 K for 12 h in air to form nickel oxide supported on H-zeolite- β , which is subsequently reduced at 623 K for 24 h in hydrogen atmosphere to produce Ni/H-zeolite- β catalyst.

2.1.2. Preparation of 3:1 Ni-Cu/H-zeolite- β

The Ni-Cu (3:1) bimetallic particles supported on H-zeolite- β was prepared using similar procedure described in section 2.1.1. Ni(NO₃)₂.6H₂O, Cu(NO₃)₂.3 H₂O (CDH chemicals Ltd., India) and H-zeolite- β (SiO₂/Al₂O₃= 40) (Sud Chmie Pvt. Ltd., India) were used for the preparation of the supported bimetallic catalysts. The preparation procedure consists of adding a mixture of 10.5 g of nickel nitrate and

2.92 g of copper nitrate to a suspension of 8.3 g H-zeolite- β in water. The mixture was subsequently stirred for a day and evaporated to dryness. The supported oxide phase was obtained after calcining at 823 K for 12 h, which is reduced, further under hydrogen atmosphere at 623 K to obtain the supported bimetallic catalysts.

2.1.3. Preparation of 5:1 Ni-Cu/H-zeolite-b

A series of supported Ni-Cu (5:1 atomic ratio) catalysts were prepared by varying the metal loadings in the range of 5-45 wt %. Typically, for the preparation of 25% Ni-Cu/H-zeolite- β , 42 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 7.3 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were added to an aqueous suspension of 31 g of H-zeolite- β with $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 40 (Ni:Cu atomic ratio 5:1). The mixture was stirred for 24 h at room temperature and heated under stirring to evaporate the water till dryness. This material was then calcined at 823 K for 12 h and reduced under hydrogen atmosphere at 623 K for 24 h prior to the catalytic studies. The 25 % Ni-Cu/H-zeolite- β catalyst was also prepared by using H-zeolite- β with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30 as support.

2.1.4. Preparation of Ni-Cu-Cr/H-zeolite-b (Ni-Cu-Cr/Z-b)

The Ni-Cu-Cr/H-zeolite- β catalyst was prepared using similar procedure described in the previous section. Briefly, 23 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 13.3 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 4.5 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (CDH chemicals Ltd., India) were added to 50 g of H-zeolite β ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30) suspension in water. The solution was stirred for 24 h at room temperature and heated to dryness under constant stirring. The catalyst was calcined at 723 K for 8 h and reduced at 623 K for 24 h prior to the catalytic studies. The Ni-Cu-Cr/H-zeolite- β was also prepared using H-zeolite- β ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$) with 25 wt % loading.

2.1.5. Preparation of Ni-Cu-M/H-zeolite- β (Ni-Cu-M/H-zeolite - β where M=Fe and Mn)

Ni-Cu-Fe/H-zeolite- β ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$) and Ni-Cu-Mn/H-zeolite - β ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$) were also prepared to study the effect of Fe and Mn as a third metal component on the activity of Ni-Cu/H-zeolite- β catalyst. In the preparation procedure, 42 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.3 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 1 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added to an aqueous suspension of 31 g of H-zeolite- β with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 40 (Ni:Cu atomic ratio 5:1). The mixture was stirred for 24 h at room temperature and heated under stirring to evaporate the water till dryness. This material was then calcined at 723 K for 12 h and reduced under hydrogen atmosphere at 623 K for 24 h prior to the catalytic studies. For the preparation of Ni-Cu-Mn/H-zeolite- β , 0.6 g of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was added instead of ferric nitrate to the zeolite with other steps remaining the same.

2.1.6. Preparation of 5 % Ni-Cu-Mg/Zeolite (Zeolite = H-ZSM-5, H-zeolite - β and H-mordenite)

The Ni-Cu doped Mg catalysts loaded on various zeolites such as H-ZSM-5, H-zeolite - β and H-Mordenite were prepared to study their catalytic activity for production of MIBK in a single step from acetone. The catalysts were prepared by adding 8.0 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.8 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 200 mg of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into a 16.6 g aqueous suspension of the protonic form of the Zeolites (H-ZSM-5, H-zeolite - β and H-mordenite). The mixture was stirred for 24 h at room temperature and heated under stirring to evaporate the water till dryness. This material was then calcined at 823 K for 8 h and reduced under hydrogen atmosphere at 623 K for 24 h prior to the catalytic studies.

2.1.7. Preparation of Ni-Cu-Cr/H-zeolite- β from Acetyl acetone precursor

This catalyst was prepared for synthesis of MIBK from acetone and detailed preparation discussed in section 2.1.9.

2.1.8. Preparation of Metal acetyl acetone

Acetylacetonate complexes of Cu, Ni and Cr were prepared and used as precursor materials for the preparation of bi- and tri-metallic catalysts. The metal acetylacetonate complexes were prepared using sodium acetate as proton abstractor. For example, for the preparation of Ni ($C_5H_7O_2$) nickel acetylacetonate complex, 0.75 moles of nickel nitrate solution in 100 ml distilled water was added to 30 ml acetyl acetone in 40 ml methanol and followed by 32 g of sodium acetate. The mixture was stirred for 4 h. The crystalline metal complexes were obtained after cooling and filtering the mother liquor. The solid complexes were dried in hot air oven at 393 K and stored in sealed bottles. The same procedure was followed for the preparation of copper and Cr ($C_5H_7O_2$) chromium acetylacetonate complexes.

2.1.9. Preparation of catalyst Ni-Cu-Cr/H-zeolite- β

The precursor of the catalyst was prepared by adding required amount of Ni ($C_5H_7O_2$) nickel acetyl acetone, Cu ($C_5H_7O_2$) copper acetylacetone and chromium acetyl acetone to the suspension of H-zeolite- β ($SiO_2/Al_2O_3 = 40$) in water and stirred for a day. The mixture was evaporated to dryness followed by calcination at 823 K, which led to the formation of metal oxides on zeolite matrix. The supported oxide materials were further reduced in hydrogen atmosphere for 24 h at 623 K to obtain the supported metallic catalysts.

2.1.10 Preparation of Pt loaded on CDX-975 carbon

The Pt/C catalyst for electrode applications was prepared using formaldehyde reduction method. In this method, appropriate amount of carbon was dispersed in distilled water and required amount of 5 % H_2PtCl_6 was added to it. The pH of the mixture was adjusted to 10-11 using 0.1 M NaOH and required amount of 20 % formaldehyde solution was added. The above mixture was heated at 343 K for one hour under constant stirring. It was then washed thoroughly with distilled water, filtered and dried in hot air oven at 393 K for four hours. The percentage loading of Pt on carbon was varied between 5 to 40 wt %.

2.2 CHARACTERIZATION OF CATALYST MATERIALS

2.2.1 Powder X-ray diffraction (XRD)

The X-ray diffraction patterns of the various samples were recorded using Shimadzu XD-D1 diffractometer employing $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of 2 - 90 degrees at a scan rate of 2 degrees per minute using Bragg-Brantano configuration. For the bimetallic samples prior to the XRD measurement the samples were reduced under hydrogen atmosphere at 723 K for 2 h.

2.2.2 ESR Measurements

The X-band ESR spectra were recorded under ambient conditions and also at liquid nitrogen temperature with a Varian E112 ESR spectrometer. Magnetic field was modulated at 100 kHz and the g values were determined by measuring the magnetic field, H and microwave frequency (ν) in comparison with DPPH (2, 2'-diphenyl-1-picrylhydrazyl) standard ($g = 2.0036$).

2.2.3. Surface Area Measurements

The surface area and pore volume of the catalyst precursors were measured using CE Instruments model Sorptomatic 1990. The samples were out gassed at 423 K and 10^{-3} torr vacuum for 6 - 10 h depending on the sample nature. For adsorption experiments, ultrahigh pure nitrogen is used at liquid nitrogen temperature. BET method was used to evaluate the surface area and pore volume evaluated at the p/p_0 of 0.999.

2.2.4. Thermogravimetric Analysis

Thermogravimetric analysis of catalyst precursor was performed to assign the calcination temperature of the loaded inorganic and organometallic precursors of metals on zeolite support. The analysis were done using Perkin Elmer TGA (Delta series TGA7) instrument with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere

2.2.5. Scanning Electron Microscopic studies (SEM-EDX)

Scanning electron microscopic pictures were taken using JEOL, JSM5610LV microscope (acceleration voltage 15 kV). The sample powders were deposited on a carbon tape before mounting on a sample holder. In order to reduce the charge developed on the sample, gold sputtering was done for 3 min on all the samples.

2.2.6. Cyclic voltammetric measurements

The cyclic voltammograms of Pt/CDX-975 with various loadings were recorded for methanol oxidation activities of the materials. The cyclic voltammograms were measured at the scan rate of 25 mV/sec using BAS Cyclic Voltammetry. The working electrodes for electrochemical measurements were fabricated by dispersing the

platinum loaded catalyst in 0.5 ml deionised water. To the catalyst suspension 5 micro liter of 5 wt % Nafion solution was added and ultrasonicated for 20 minutes. A known amount of suspension was added to the glassy carbon (GC) electrode and solvent was slowly evaporated which results in Platinum/CDX-975 on GC electrode. Pt foil was used as counter electrode and Ag/AgCl/KCl (saturated) was used as reference electrode.

2.3 CATALYTIC ACTIVITY

2.3.1 High-pressure liquid phase reaction

The catalytic activity for transformation of acetone to isopropanol and bimolecular dehydration of IPA to Diisopropyl ether (DIPE) using supported bimetallic and solid acid catalysts was performed using a Parr reactor (Parr Instrument Company, USA, Model No. 4842). For the transformation of acetone to DIPE, hydrogen atmosphere was used with in the temperature range 393 K - 453 K and pressure range of 20-80 bars. All the bimetallic catalysts were reduced at 623 K for 24 h prior to the catalytic experiments and carefully transferred to the reactor vessel. Typically, 2.5 g of the catalyst was added to 40 ml acetone and placed in the reactor. The reactor was then brought to the required pressure and temperature and maintained at constant stirring. Small amount of the reaction mixtures were removed periodically and analyzed by gas chromatography. Pure nitrogen gas was used as a carrier gas at a flow rate of 30 ml/min. The liquid products were collected in an ice trap and analyzed by gas chromatography (AIMIL-Nucon 5765) using flame ionization detector. For the bimolecular dehydration of IPA, nitrogen gas was used to pressurize the parr reactor. The reaction was performed in the temperature and pressure range of 373 K - 423 K and 20 - 60 bars, respectively. The products were periodically removed and analyzed by gas chromatography (Carbowax 20 M column) using flame ionization detector.

The GC analysis was carried out under isothermal mode at 50 °C. The detector and injector temperatures were maintained as 100 °C.

2.3.2 High-pressure vapor phase reactions

Isopropanol dehydration was carried out in the vapor phase at elevated pressures using a vapor phase high pressure reactor (SOTELEM Fig. 2.1). 5 g of the solid acid catalysts such as H-ZSM-5 and H-zeolite- β were used in the temperature and pressure range of 413 K - 433 K and 10 to 30 bar respectively. The reactor was packed with quartz wool and alpha alumina along with the catalysts, which was placed at the middle of the reactor bed with proper exposure to the heating zone of the furnace. The reactor was pressurized using ultra high pure nitrogen. Isopropanol was passed through the reactor using high-pressure pump at the required reaction temperature. The products were collected through the chiller and analyzed by GC with carbowax column and Flame ionization detector.

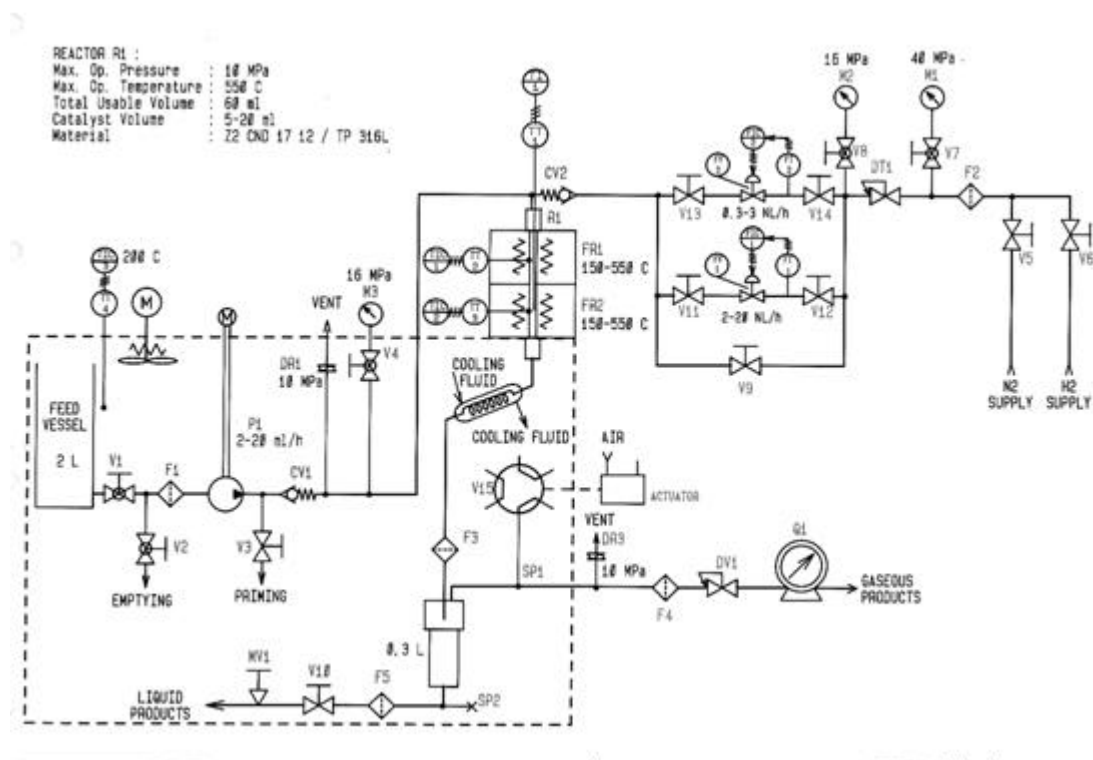


Fig. 2.1 High pressure vapour phase two zone reactor