

CHAPTER – 2
EXPERIMENTAL

2.1. CATALYST PREPARATION

Co-precipitation (CP) method is the most widely employed catalysts preparation method and used to prepare two or more component catalysts. Advantages of the CP method: homogeneity of component distribution, relatively low reaction temperature, fine and uniform particle size with weakly agglomerated particles and low cost. Disadvantages of the CP method: wide particle size distribution, uncontrolled particle morphology and incomplete precipitation of the metal ions. Nanocasting (NC) method is advantageous for synthesizing rigid meso-structures with high crystallinity. However, it is a costly method involving of the multiple steps such as the preparation of ordered mesoporous silica as the hard template, then impregnation of the metal precursors into the pores, and finally, formation of the metal oxide and removal of the hard template. The deposition co-precipitation (DCP) method is used for preparation of supported metal catalysts. It has similar advantages and disadvantages of CP method.

The unsupported/supported spinel catalysts were prepared using nitrates of Mn and Co by co-precipitation (CP), nanocasting (NC) and deposition co-precipitation (DCP) methods. All the chemicals used in catalysts synthesis were of analytical (AR) grade (99.99%, Merck, India/Sigma Aldrich, USA).

2.1.1. Preparation of unsupported catalyst by co-precipitation method

Catalyst was prepared by CP method, dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2$ (molar ratio = 2:1) in distilled water. Mixed metal salts solution was drop wise added in 1.4 mol/L sodium carbonate solution till pH dropped to 9 and simultaneously co-precipitated homogeneous basic carbonates of Co-Mn. The precipitate was aged in the mother liquor with stirring for 8 h. The precipitate was filtered and washed with distilled water and ethanol to remove traces of nitrates and maintain neutrality. The sample was dried for overnight at 120°C and calcined at 450°C

for 4 h in stagnant air. The calcined catalysts was cooled in a desiccator containing CaCl_2 and stored in an air-tight glass bottles.

2.1.2. Preparation of unsupported catalysts by nano-casting method

Mesoporous KIT-6 silica matrix was used as hard template for the synthesis of MnCo_2O_4 according to the methods described in the literature [40]. First, the standard porous silica template, KIT-6 was prepared following the procedure described by Kalsabi et al., 2012 [41].

The large pore 3D (*Ia3d*) cubic mesostructure KIT-6 was prepared using a structure directing agent (Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) template) and a silica precursor (tetra ethyl ortho silicate, TEOS). In a typical synthesis, 12 g (2.068 mmol) of P123 and 12 g (162 mmol) of n-butanol were dissolved in 540 g (30 mol) of distilled water and 22.8 g (0.230 mol) of concentrated hydrochloric acid (37wt.% HCl). To this mixture, 25.8 g (0.122 mol) of TEOS was added. The mixture was stirred at 45°C for 24 h for the formation of the mesostructured product followed by hydrothermal treatment at 95°C for 24 h. The solid product was then filtered, washed with distilled water and dried at 105°C. Finally, the organic template was removed by calcination in air at 550°C for 6 h. The KIT-6 sample obtained was cooled in a desiccator containing CaCl_2 and stored in an air-tight glass bottles.

Then, KIT-6 (10.0 g) was suspended in dry n-Hexane (700 mL) and stirred for 3 h. Aqueous solution (10.0 mL) containing nitrates of Mn and Co (molar ratio of 1:2) was added dropwise in the suspended solution with mechanical stirring. The mixed solution was kept stirring overnight followed by filtration and drying at 40°C. The dried precursor was divided into three parts to see the effect of following calcination strategies:

First, the precursor was calcined in stagnant air in a muffle furnace at 450°C for 4 h. Second, the precursor was calcined in flowing air (35 mL/min) at 450°C for 4 h. Third, the precursor was calcined in a flowing reactive gas mixture consisting of 4.5% CO in air (35 mL/min), so called reactive calcination (RC). The RC route has been established in our laboratory to produce highly active catalysts for the first time and it has been thoroughly described in paper mentioned as reference [42].

The nano-sized MnCo_2O_4 samples formed in the pores of KIT-6 after calcinations under different strategies were recovered separately by leaching silica template with hot 2M NaOH treatment [43].

Similarly, spinel of NiCo_2O_4 and CuCo_2O_4 were synthesized using their respective nitrate salts. The calcined catalysts were cooled in a desiccator containing CaCl_2 and stored in air-tight glass bottles.

2.1.3. Preparation of Al_2O_3 supported MnCo_2O_4

First, $\gamma\text{-Al}_2\text{O}_3$ was synthesized by calcination of boehmite following the procedure described by Shalini Arora and Ram Prasad [160]. The boehmite was prepared by adding 25% aqueous NH_3 solution in $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution maintaining pH 8.52. The gelatinous precipitate was directly transferred to an autoclave and maintained at 121°C for 6 hours. Then the precipitate (boehmite) was washed 5 times with distilled water and dried overnight at 110°C. The dried precipitate was calcined at 600°C for 24 hours to form $\gamma\text{-Al}_2\text{O}_3$.

The prepared $\gamma\text{-Al}_2\text{O}_3$ was used to synthesize supported MnCo_2O_4 spinel catalyst by deposition co-precipitation method. In a typical synthesis method, the mixed nitrates solution of Mn and Co in 1:2 molar ratio was dropwise added in a slurry of alumina- Na_2CO_3 with stirring. Mixed

metal salts solution was drop wise added in 1.4 mol/L sodium carbonate solution till pH dropped to 9 and simultaneously co-precipitated homogeneous basic carbonates of Co-Mn. The co-precipitate deposited on γ -Al₂O₃ was aged in the mother liquor for 8 h, followed by filtration and washing with distilled water and ethanol to remove traces of nitrates. The sample was dried for overnight at 120°C and cooled in a desiccator containing CaCl₂ and stored in an air-tight glass bottles. The precursor was calcined *in situ* by RC route just prior to SCR reaction. The precipitated basic carbonates were deposited over large surface area γ -Al₂O₃ particles. Then the supported slurry was washed thoroughly free of anions followed by drying at 110°C and calcination by RC route at 450°C. The metal loading was varied from 10-50% MnCo₂O₄/ γ -Al₂O₃ in the catalysts. The calcined catalysts was cooled in a desiccator containing CaCl₂ and stored in an air-tight glass bottles. Alumina was used as support to reduce the cost of the catalyst and to enhance its performance in the SCR of NO_x.

2.1.4. Preparation of Rh-promoted catalysts

The Rh promoted 30% MnCo₂O₄/ γ -Al₂O₃ catalysts were prepared by spraying RhCl₂.6H₂O solution over co-precipitated basic carbonates precursor supported on Al₂O₃ followed by drying and calcination at 450°C by RC route. The amount of promoter in the catalyst were 0.1, 0.2 and 0.3wt% equivalent to Rh. The calcined catalysts was cooled in a desiccator containing CaCl₂ and stored in an air-tight glass bottles. The nomenclature of all the prepared catalysts is given in Table 2.1.

Table 2.1. Nomenclature of catalysts prepared by different modes of calcination at 450°C for 5h

Sr. No.	Catalyst	Composition	Preparation method	Calcination mode
1	Cat-A	MnCo ₂ O ₄	Co-ppt.	Stagnant air
2	Cat-B	MnCo ₂ O ₄	Nano-casting	Stagnant air
3	Cat-C _{SA}	30% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Stagnant air
4	Cat- C _{FA}	30% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Flowing air
5	Cat- C _{RC}	30% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
6	Cat-D	30% NiCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
7	Cat-E	30% CuCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
8	Cat-F	10% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
9	Cat-G	20% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
10	Cat-H	40% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
11	Cat-I	50% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
12	Cat-J	0.1% Rh.30% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
13	Cat-K	0.2% Rh.30% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
14	Cat-L	0.3% Rh.30% MnCo ₂ O ₄ /γ-Al ₂ O ₃	Deposition Co-ppt.	Reactive calcination
15	Commercial catalyst	V-W-Ti (V ₂ O ₅ -WO ₃ /TiO ₂)	(IBEDEN, Japan)	Stagnant air

2.2. EXPERIMENTAL SET-UP

The experimental setup used for the catalytic performance measurement is shown in Figure 2.1. It can be divided into following sections: reactant feeding system, reaction system, product cooling system and product analysis system.

2.2.1. Reactant feeding system

Air, NO, reductant and Ar gases were fed from compressed cylinders to the reactor. The gaseous stream was purified free from moisture and CO₂ by passing through a tower packed with CaO and KOH pellets. Further, the mercaptane content in LPG is ~ 30 ppm which can deactivate the catalyst. So, the feed stream containing LPG was made free of mercaptane by bubbling it through a solution of sodium plumbite. The flow rates of gases were monitored with the help of digital gas flow meters. A safety device in the form of mercury sealing was provided in the feeding line to check any pressure build up.

2.2.2. Reaction system

This section includes split open tubular furnace, reactor and microprocessor temperature controller. A fixed bed compact tubular flow reactor with preheater built within it was chosen for the present study. The reactor was described in details elsewhere [36]. A helical coil of glass tube in between the co-axial tubes served as a pre-heater of the gases mixture as shown in the Fig 2.2.

The reactor was consisting of two co-axial corning glass tubes of 20 mm and 50 mm diameters. There is a hole in the lower part of the outer tube, to take care of breakage due to the expansion or contraction of air in between co-axial tubes as the unit is subjected to the variation of temperature from ambient to the reaction temperature. The reactant gases are pre heated to

catalyst bed temperature. The product stream from the bottom of the reactor is cooled in a water condenser to the ambient condition and then sent for analyses.

The reactor was mounted vertically. The down flow stream of air was used to avoid the distortion of the bed. The catalyst was placed on a thin layer of glass wool which is supported on sintered glass disc inside the inner tube.

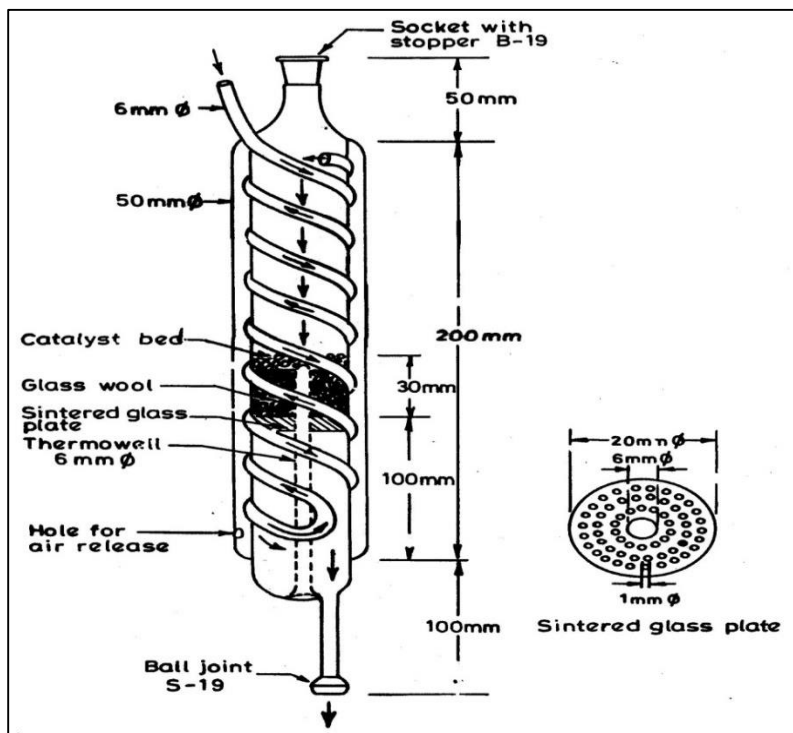


Figure 2.2. Schematic diagram of the Reactor

A thermocouple well made of 4mm diameter glass tube was inserted axially from the bottom all the way to the centre of the disc for temperature measurement and control. The heating system for the reactor consisted of a split open electric furnace. The reactor was heated at a constant rate of 5°C/min, with the help of a microprocessor based temperature controller.

2.2.3. Product cooling system

Products were cooled and condensed the condensable part in the cooler shown in the experimental setup.

2.2.4. Product analysis system

This includes NO_x analyser (Eco Physics CLD 62 chemiluminescence NO/NO₂/NO_x analyzer) and GC (Nucon 5765).

2.2.4.1. Eco Physics CLD-62 NO/NO_x analyser

CLD 62 is modular designed which allows the continuous measurement of concentrations in the range of parts per million shown in Figure 2.3. The inlet and outlet gases of the reactor were analyzed by Eco Physics CLD 62 chemiluminescence NO/NO_x analyzer and online GC. Measuring ranges is from 5 ppm-5000 ppm and minimum detectable concentration 0.5 ppm. The CLD 62 is the ideal instrument for series checks of NO and total NO_x in fixed or mobile stations. This single channel analyser is designed for all applications with an existing gas preconditioning unit to ensure quality control as well as keeping to threshold values.



Figure 2.3. General view of Eco Physics CLD-62 NO/NO_x analyser.

2.2.4.2. Gas Chromatograph

A Gas Chromatograph (Nucon 5765) is used for product gas analysis and it consisted of the following parts:

- i. Sample injection port
- ii. Columns
- iii. Column oven
- iv. Methaniser
- v. Detector

One or more high purity gases are supplied to the GC. One of the gases (called the carrier gas) flows into the injector, through the column and then into the detector. In our case it was nitrogen. A fixed amount of sample is introduced into the injector usually with a micro syringe or an exterior sampling device. In our experiment it was 20 μl . The injector was maintained at 80°C. The vaporized solutes are transported into the column by the carrier gas. The column is maintained in a temperature controlled oven. In our case it was 60°C.

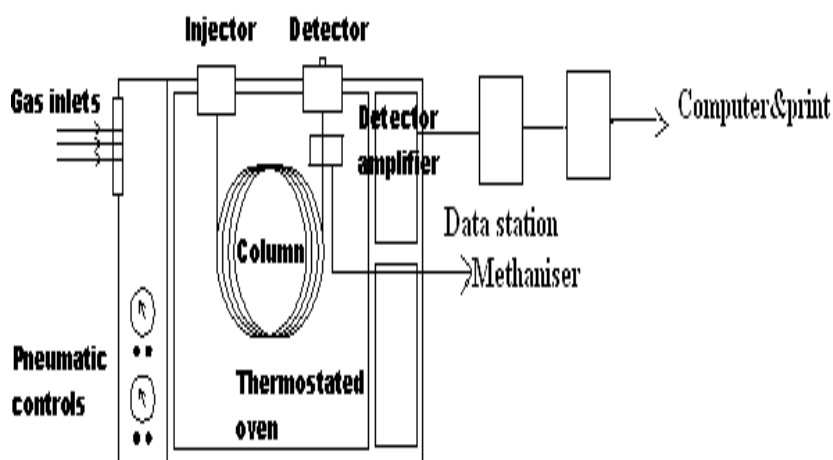


Figure 2.4: Schematic diagram of Gas Chromatograph

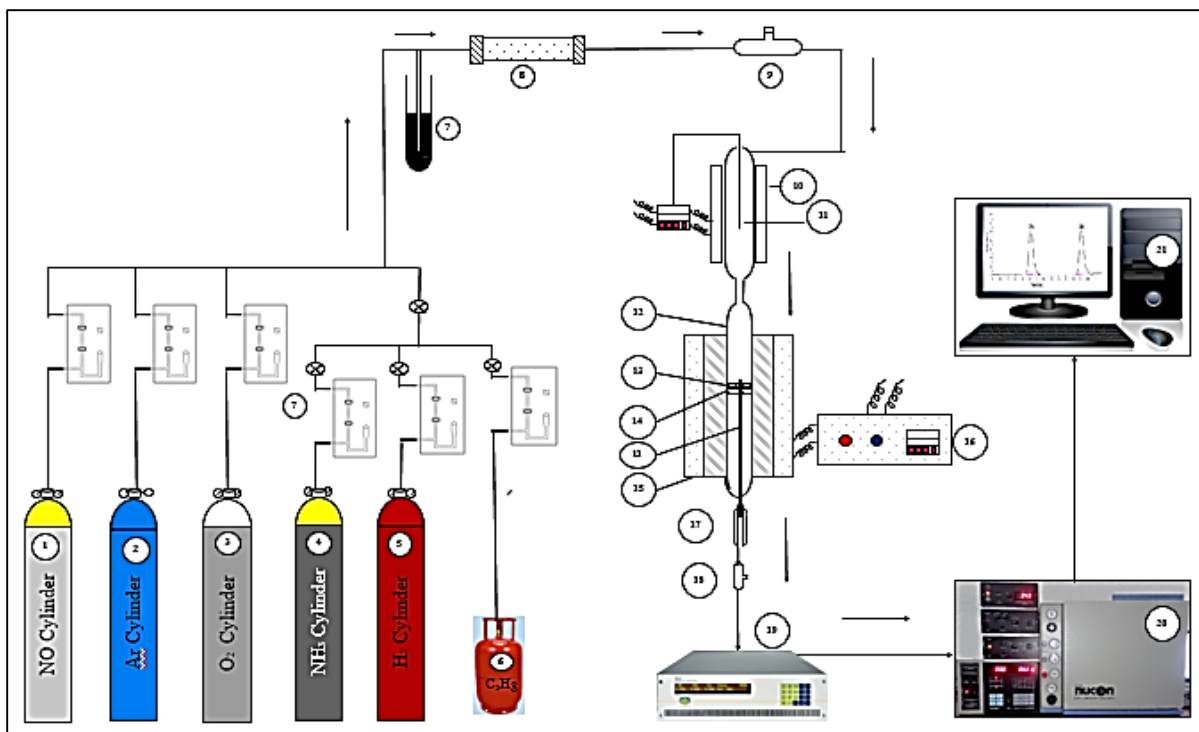


Figure 2.1. Experimental set up for the measurement of catalytic performance

1. NO Cylinder; 2. Ar Cylinder; 3. O₂ Cylinder; 4. NH₃ Cylinder; 5. H₂ Cylinder; 6. C₃H₈ Cylinder; 7. Flow meters; 8. Mercury safety device; 9. Moisture Trap; 10. Gas Sampler; 11. Reactor; 12. Catalyst bed; 13. Glass wool; 14. Thermowell; 15. Split Open Furnace; 16. Microprocessor controller; 17. Cooler; 18. NO_x analyser; 19. GC, data station; 20. Computer.

The solutes travel through the column at a rate primarily determined by their physical properties, and the temperature and composition of the column. The various solutes travel through the column at different rates. The fastest moving solute exits (elutes) the column first then is followed by the remaining solutes in corresponding order. As each solute elutes from the column, it enters the heated methaniser at 300°C which convert CO_x (CO or CO₂) to methane.

The de-NO_x performance (activity, selectivity and stability) of the catalysts using various reductants was measured under the following conditions:

The composition of the gases feed was as follows: 500 ppm NO, 0.1% NH₃ or 1% H₂-1000 ppm C₃H₈, 8% of O₂ in Ar. The total gas flow rate was kept constant at 100 mL·min⁻¹. Ar, NO, O₂ and NH₃ were pre-mixed in required composition in a mixing chamber, followed by pre-heating to a certain temperature (ambient - 450°C) in the pre-heater and then fed into the reactor. The inlet and outlet gases of the reactor were analysed by Eco Physics CLD 62 chemiluminescence NO/NO_x analyzer and online GC. Two separate GCs equipped with porapak Q/ capillary columns and FID/TCD/ECD detectors were used to analyse the CO, CO₂, hydrocarbons/H₂, N₂O respectively. NO and NO₂ measurements were done by Eco Physics CLD 62 chemiluminescence NO/NO₂/NO_x analyzer. The performance (activity, selectivity and stability) of the catalysts were evaluated for SCR of NO in a fixed-bed glass tubular reactor (1.0 in internal diameter) using 200 mg catalyst kept over quartz wool.

The activity of the catalysts was estimated in terms of NO conversion during SCR of NO. The conversion of NO at any instant was calculated on the basis of values of the concentration of NO in the feed and product streams by the following Equation (2.1):

$$X_{NO}(\%) = \left(1 - \frac{[NO_{out}]}{[NO_{in}]}\right) * 100 \quad (2.1)$$

The conversion of C₃H₈ was calculated on the basis of values of the concentration of C₃H₈ in the feed and product using the following Equation (2.2):

$$X_{C_3H_8} = 1 - \left[\frac{A_{C_3H_8_{out}}}{A_{C_3H_8_{in}}}\right] \quad (2.2)$$

Where the concentration of C₃H₈ at any instant is proportional to the area of a chromatogram of C₃H₈ [A_{C₃H₈}]. Selectivity of NO can be written in terms of N₂ calculated by Equation (2.3)

$$N_2 \text{ Selectivity } (\%) = 100 * \left[\frac{[N_2]}{[NO_2] + [N_2]}\right] \quad (2.3)$$

The stability tests of the best selected catalyst for SCR of NO using the best reductant were determined for time on stream run and accelerated ageing of the catalyst under reaction conditions.

2.3. Characterization of catalyst

The full potential of the development of catalyst materials for catalytic applications can be realized only by the comprehensive characterization with respect to crystallinity, phase purity, textural properties (pore size, specific surface area and pore volume) and surface properties. The characterization of catalyst helps to understand the inter-relationship between the activity and selectivity of a catalyst and its different physical and chemical properties. The information based on characterization of the catalyst is useful for catalytic process optimization and for the manufacture of catalyst.

The catalyst characterization, i.e. the investigation of relevant aspects of the catalyst structure may also be required for quality control on the basis of previous empirical observations. The prepared catalysts were used for the characterization of catalyst powder like X-ray diffraction (XRD) analysis, X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectrum (FTIR), Scanning electron spectroscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and Brunauer, Emmett, and Teller (BET) surface area given in table 2.1.

Table 2.1 Techniques used for characterization of catalysts

Technique Applied	Characteristics
X-ray diffraction (XRD)	Mean crystallite size, phase analysis, crystal size, crystal size distribution and lattice parameter
X-ray Photoelectron Spectroscopy (XPS)	Chemical and physical state
Fourier transform infrared spectroscopy (FTIR)	Infrared spectrum of absorption, emission, and photoconductivity
Scanning electron microscopy (SEM)	Surface structure (texture), particle size estimation
Energy-dispersive X-ray spectroscopy (EDX)	Elemental composition
Low temperature N ₂ adsorption or BET surface area	Textural properties: Surface area, pore volume, pore size distribution, average pore diameter

The techniques mentioned above and adopted for the characterization of the catalysts used in this study are appended in Annexure 1.