CHAPTER-II

EXPERIMENTAL METHODOLOGY

II.1 PURITY AND PURIFICATION OF REAGENTS

Hydrogen, helium and nitrogen were of IOLAR-2 grade (99.993%) and were further purified by removing traces of oxygen and moisture by passing through traps of freshly reduced copper gauze at 573 K and dry ice respectively. Commercial ammonia gas was made free of moisture by passing through calcium chloride before use. Oxygen (IOLAR-2, 99.998%) and commercial nitrogen (IOL) with around 22 ppm oxygen were used as such. Argon gas supplied by GSFC, Baroda (GUJARGON-1) was of 99.999 % purity and was used as such.

Deionised water used for the preparation of catalysts had a conductivity of 5×10^{-7} mho/cm. The other common reagents were of BDH ANALAR grade or equivalent. Chloroplatinic acid supplied by Johnson Matthey & Co. Ltd., London, Tin metal (99.8% pure) from S.Merck, India, Indium metal (99.6% pure) from S.A.S Chemicals, Bombay, Silver nitrate AR from Indian Drugs and Pharmaceuticals Ltd. Hyderabad, Antimony trioxide (GR) from Sarabhai M. Chemicals, Baroda, Lithium hydroxide (AR) from BDH, England were used for the catalyst preparations. Aluminium metal powder (INDAL Grade-10) was supplied by Indian Aluminium Company, Kalwa, India. n-Dodecane and 1-dodecene used for activity and selectivity studies were obtained from Merck- Schuchardt and were 99.6% pure. All carboxylic acids used for alumina preparation were BDH ANALAR grade and were used as recieved.

II.2 PREPARATION OF SPHEROIDAL ALUMINA: SOL-GEL/OIL DROP METHOD

This process involves various stages as detailed below and shown in Figure II.1.

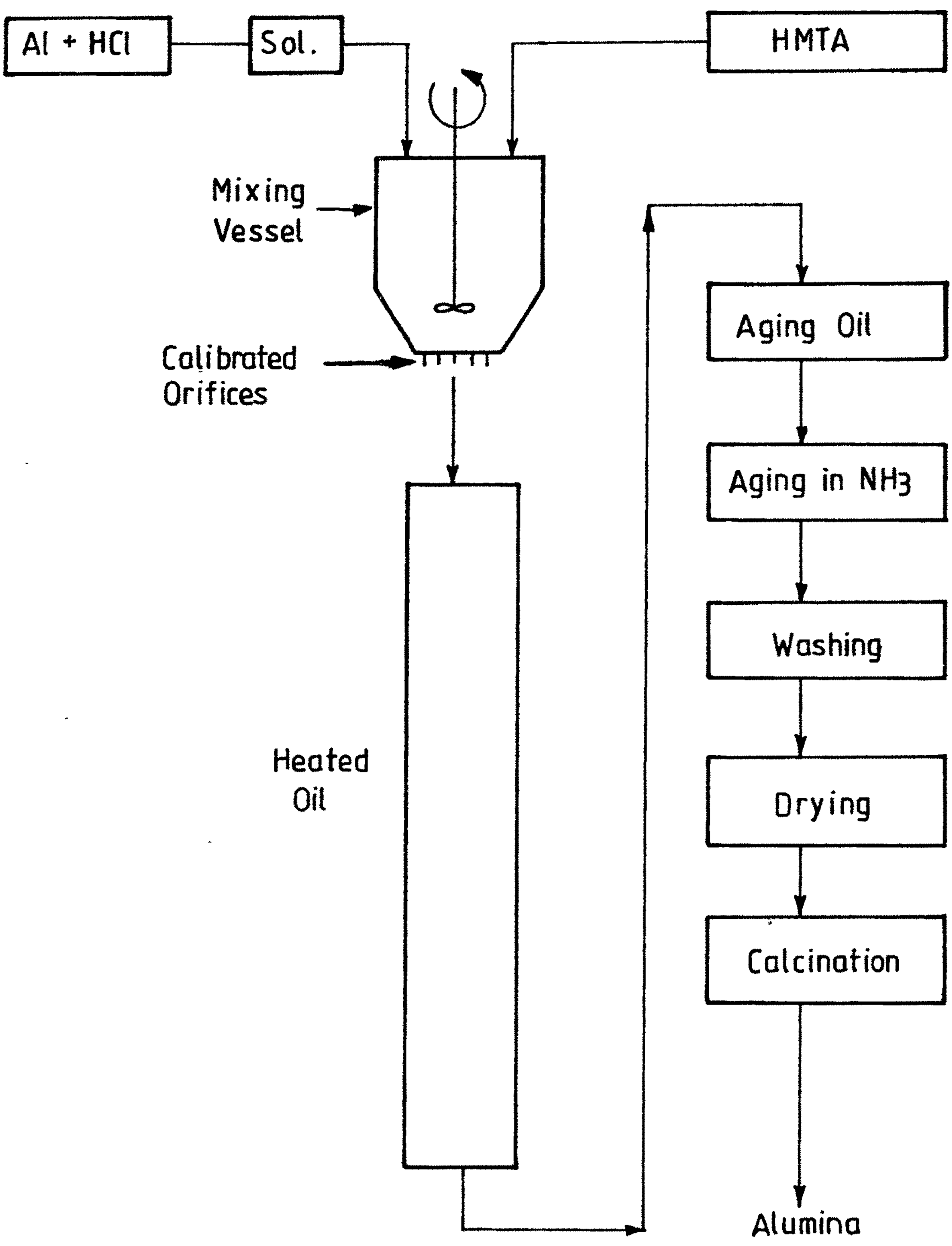

Fig. II.1. Simplified oil drop process

a. Preparation of alumina sol.

100 g of pure aluminium metal powder was digested slowly in a mixture of 492 ml 4.23 N hydrochloric acid and 150 ml of water at 388 K, in a two necked flask fitted with a water condensor. Since reaction between Al powder and HCl is extremely fast with vigorous evolution of hydrogen, very small amounts of powder was added in steps with utmost care to control the violent reaction **(CAUTION)**. After 12 h digestion the sol was filtered and made up to 550 ml with deionised water. The sol was cooled below 283 K and stored for further use.

Modification of the procedure was done by adding various carboxylic acids to dil. HCl before the digestion with Al metal. The amount of additives added were equivalent to 10% of the total number of equivalents of chloride ions. The additives used were (1) Acetic acid (2) Propionic acid (3) Oxalic acid (4) Malonic acid (5) Succinic acid (6) Maleic acid (7) Citric acid (8) Tartaric acid and (9) Adipic acid.

The sols thus prepared were tested for viscosity, pH and density at 313 K.

b. Preparation of hexa methylene tetramine (HMTA) solution.

125 g of pure HMTA was weighed out in a beaker, dissolved in deionised water and made up to 500 ml. This solution was also cooled below 283 K and stored.

c. Mixing of sol and HMTA solution.

Equal volumes of the sol and HMTA solution were mixed and aged for not less than 15 min. at room temperature.

d. Gellification and aging.

The sol + HMTA mixture was allowed to flow through specially fabricated system of calibrated nozzles into a heated paraffin oil column kept at 360-370 K. The droplets got solidified and were collected at the bottom. They were aged in the same paraffin oil for 16 h at the same temperature.

e. Aging in ammonia.

The oil aged spheres were separated from the oil by decantation and aged in 5% (w/v) ammonia solution at 360-370 K in a closed vessel for 6 h.

f. Filteration and washing.

The ammonia aged spheres were filtered and washed with hot 0.05 % (w/v) ammonia solution amounting to about 4 liters per 100 g alumina on a dry basis.

g. Drying and calcination.

The washed spheres were dried at 423 K for 1 h. and calcined at 823 K for 2 h. in a tubular furnace in a humid atmosphere. The final calcined samples were preserved in sealed tubes for further characterisation.

II.2.1 Designation of Alumina Samples.

Alumina samples were represented by a general code X-000 were X denotes the name of the additive acid and "000", the pretreatment temperature. For example, Acetic-423 indicates the alumina sample prepared with acetic acid dried at 423 K and Citric-823, alumina prepared with citric acid calcined at 823 K.

II.3 PREPARATION OF CATALYSTS

200 g of bare alumina support was modified by the incorporation of Li according to the procedure detailed below. Water pore volume of the sample was found to be 1.35 ml/g. 7.25 g $LiOH.H_2O$ was dissolved in deionised water and made up to 270 ml. The bare alumina was impregnated with this solution by pore filling method. The sample was rotated in open vessel and the solution was sprayed uniformly onto it with a sprayer under controlled gas pressure to avoid liquid loss. The impregnated alumina was then dried at 373 K followed by calcination at 823 K for 3 h. in a flow of oxygen at the rate of 100 ml/min. This 0.6% (w/w) Li loaded alumina was used as the support for the catalyst preparations.

Five catalysts containing 0.45% (w/w) Pt and promoters like Ag, In, Sn, and Sb in the atomic ratio 1:2 were prepared by the same impregnation method detailed above. Weighed amounts of the Li/alumina sample were impregnated with the mixture of respective salt solutions, dried at 343 K and calcined at 673 K for 3 h. The calcined samples were then moisture treated at 773 K for 20 h. to reduce the chloride content. Water was admitted at the rate of 0.3 ml/h with the help of a syringe pump (Orion Sage Instruments, model 352)and oxygen flow was maintained at the rate of 30 ml/min. A Stanton Redcroft Temperature Programmer, (model 3029) equipped with a Pt-10%Rh/Pt thermocouple was used for accurate temperature control.

The compositions of the solutions used for the preparation of 10 g batches of catalysts are listed below. Chloride content of the solutions was always maintained at a total of 1000 mg by adding HCl. This was necessary to get uniform Pt distribution. Coimpregnation was used in all other systems except for Pt-Ag, where $AgNO_3$ solution was first impregnated, dried, calcined and then chloroplatinic acid was impregnated.

a. Pt-Li/alumina.

4.73 ml chloroplatinic acid solution (9.5 mg Pt and 89 mg chloride/ml), 2.3 ml 7.099 N HCl and 6.5 ml H_2O.

b. Pt-Ag-Li/alumina.

(a) 13.5 ml solution containing 0.078 g of $AgNO_3$ in water.

(b) 4.73 ml chloroplatinic acid solution and 2.3 ml 7.099 N HCl and 6.7 ml water.

c. Pt-In-Li/alumina.

4.73 ml chloroplatinic acid solution, 2.3 ml 7.099 N HCl and 5.3 ml indium nitrate solution (10 mg In/ml) and 1.2 ml water.

d. Pt-Sn-Li/alumina.

4.73 ml chloroplatinic acid solution, 2.8 ml tin chloride solution (20 mg Sn and 30.6 mg chloride/ml), 2.1 ml 7.099 N HCl and 3.9 ml water.

e. Pt-Sb-Li/alumina.

4.73 ml chloroplatinic acid solution, 0.067 g antimony trioxide, 2.3 ml 7.099 N HCl and 6.5 ml water.

II.3.1 Designation of Catalyst Samples.

Catalyst samples are denoted by the general code Pt-X-Li/alumina where X denotes the promoter element.

II.4 CHARACTERISATION OF CATALYSTS AND SUPPORTS.

II.4.1 Chemical Analysis.

All the above described catalysts were analysed for the platinum, promoter and chloride contents, by wet chemical methods.

a. Platinum.

1 g of the catalyst was digested in 25 ml 1:1 H_2SO_4. Then 1-2 ml of H_2O_2 solution (100 vol) was added followed by 5 ml conc. HCl. Addition of HCl and heating were continued till the solution was free of H_2O_2, cooled and made up to 100 ml with water. 25 g of $SnCl_2.2H_2O$ was dissolved in 25 ml conc. HCl by warming gently and made up to 100 ml with water separately.

10 ml of catalyst solution, 4 ml $SnCl_2$ solution and 6 ml conc. HCl were mixed in a 25 ml volumetric flask and made up to the mark with water. The UV absorbance of this solution was measured at 403 nm with a Shimadzu UV-Vis spectrophotometer (model 260) after allowing to stand for 1 h. Absorbance per microgram (ppm) is 0.04 (228).

b. Promoters.

The promoter elements were brought into solution by digestion with suitable acids and then analysed by atomic absorption spectroscopy under standardised conditions.

c. Chloride.

0.5 g of the catalyst was digested in 25 ml 1:1 H_2SO_4 followed by the addition of 3-4 drops of formic acid. Heating was continued for 30 min., filtered and made up to 100 ml with chloride free water. Estimation of chloride was then performed with an Orion Research Microprocessor Ionalyser, model 901 equipped with a precalibrated chloride sensitive electrode system.

II.4.2 Determination of Physical Properties.

a. Apparent bulk density (ABD)

ABD of the samples were determined by weighing known volumes of uniformly packed spheroids in a measuring cylinder of internal diameter 3 cm.

b. Crushing strength(C.S.)

C.S. of the spheroids were determined with a specially fabricated instrument in which the individual particles are kept in between two parrellel plates and force applied continuously on it. The force applied at the point of crumbling of the particle can be directly read from the dial in kilogram units.

c. Attrition loss.

The loss on attrition was determined by rotating known weight of the samples in closed tubes at a rate of 25 rpm for 15 min. and then determining the percentage powder formation.

d. Average sphere size(ASS).

ASS were calculated by measuring the diameter of a number of individual particles and then taking averages.

II.4.3 Textural Properties.

a. Adsorption-desorption isotherms of nitrogen.

Adsorption-desorption isotherms of nitrogen were recorded on a Carlo-Erba, Sorptomatic Series 1800, model 1810 (ITALY) at 77 K after degassing the sample at 423 K for 8 h. From the isotherms, specific surface area values were calculated according to BET method. Analysis of the type and shape of pores were carried out on the basis of the shapes of adsorption isotherms, volume of nitrogen adsorbed Vs. thickness of multilayer plots and the hysterisis loops according to de Boer's method.(95,118-120)

b. X-ray diffraction (XRD).

XRD patterns in the range of 10-90 degrees (2θ) at a scanning rate of 2 degree/min were recorded on a Philips (The Netherlands) PW-1130/90 X-ray diffractometer with Ni filtered CuK_{α} radiation and a proportional counter. Phase identification of all the alumina samples were carried out by comparing the d-values calculated from the diffractograms with the standard values reported in the powder diffraction files.

Average crystallite sizes were calculated using the Scherrer formula with respect to the signal corresponding to the reflection from the (4 4 0) plane. Correction for instrumental aberration was applied using crystallised quartz as standard.

XRD patterns of the promoted catalysts were recorded at a rate of 0.5 degree/min. inorder to identify the alloy phases.

II.4.4 Infrared Spectroscopic Studies(IR).

IR spectra of all the samples were recorded using KBr pellets with a Shimadzu IR spectrophotometer (model IR-408)

II.4.5 Thermal Analysis.

Differential thermal analysis (DTA) of the dried alumina samples were performed with a Shimadzu DT-30 (JAPAN) thermal analyser in the range of 300-1273 K (heating rate 20 K/min).

II.4.6 Electron Microscopy.

Scanning electron micrographs (SEM) of the calcined alumina samples were obtained on a Jeol JSM-35C (JAPAN) scanning electron microscope. Spheres were coated with gold (200 A°) with a JFC-1100 ion sputter before taking micrographs.

II.4.7 Dispersion Measurements.

Pt dispersion in the catalysts were measured by H_2-O_2 titration technique. The experimental set up and the reactor are schematically shown in Figures II.2 and 3. A Shimadzu gas chromatograph (model GC-7AG) with a thermal conductivity detector was used for detecting the residual adsorbate gases in the carrier gas stream and the signals were monitored with a Shimadzu data processor (model C-R1B). The reactor and oxygen trap were heated by means of tubular furnaces controlled by Stanton Redcroft temperature programmers and the actual temperatures were indicated by digital indicators (JIVAN, Baroda) equipped with chromel-alumel thermocouples. For accurate temperature control, the controlling thermocouple was placed outside the reactor and the indicating one was positioned inside the catalyst bed. The adsorbate gases were pulsed upstream of reactor by a six port two way valve. The linearity of the G.C. signals with respect to different volumes of adsorbate gases under chemisorption conditions were tested and accordingly a suitable pulse size was chosen. Moreover, using loops of different volume, the dead volume of the gas sampling valve was also determined.

1 g of the sample was loaded in the reactor and reduced at 748 K for 2 h in hydrogen flowing at the rate of 100 ml/min.

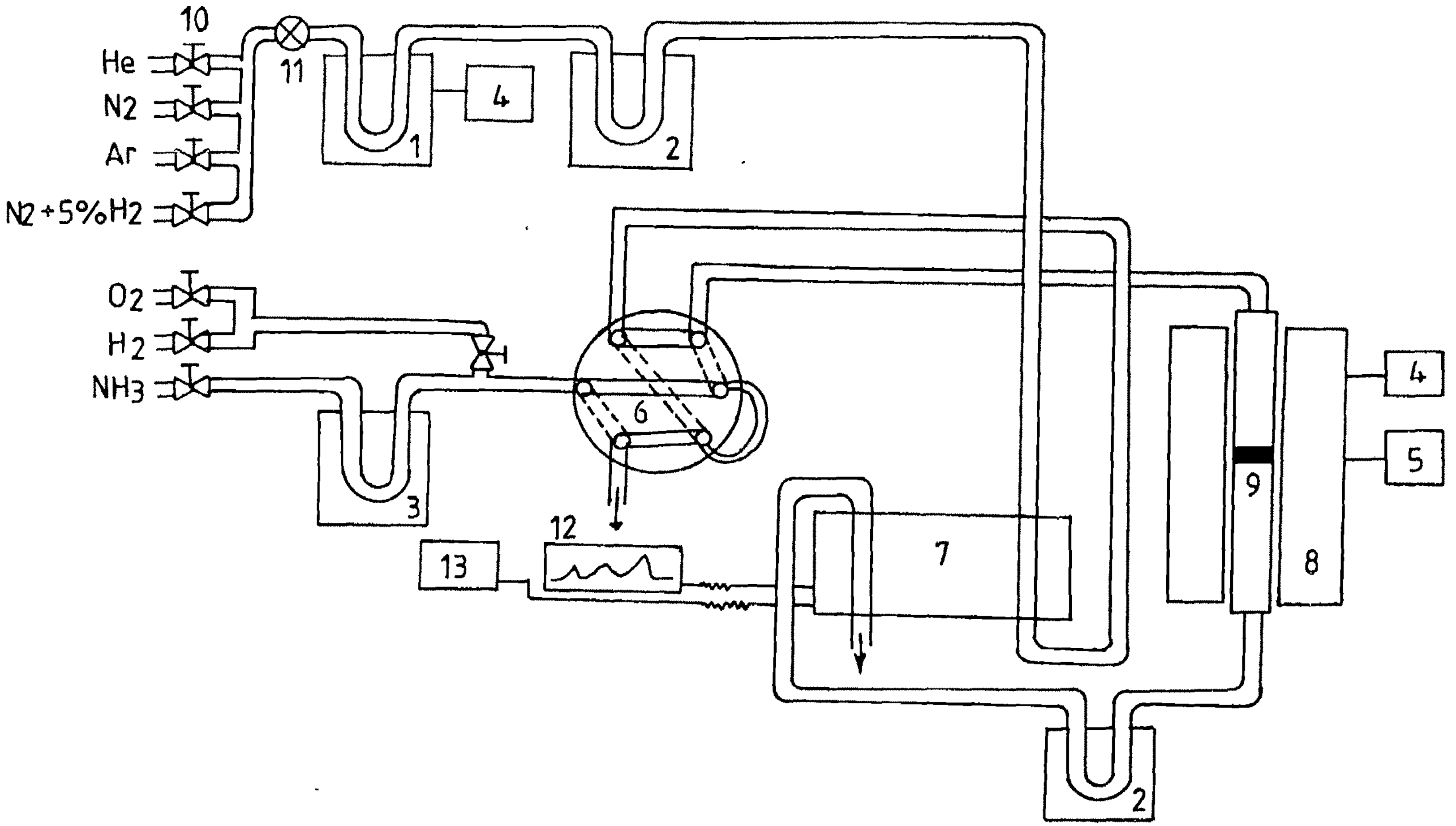

Fig. II.2. TPR-TPD-Chemisorption assembly.

1. Copper trap, 2. Dry ice trap, 3. Calcium chloride trap, 4. Temperature controller, 5. Temperature indicator, 6. 6-Port 2-way gas sampling valve, 7. Thermal conductivity detector, 8. Furnace, 9. Catalyst charge, 10. Control valves, 11. Mass flow controller, 12. Recorder, 13 Integrator.

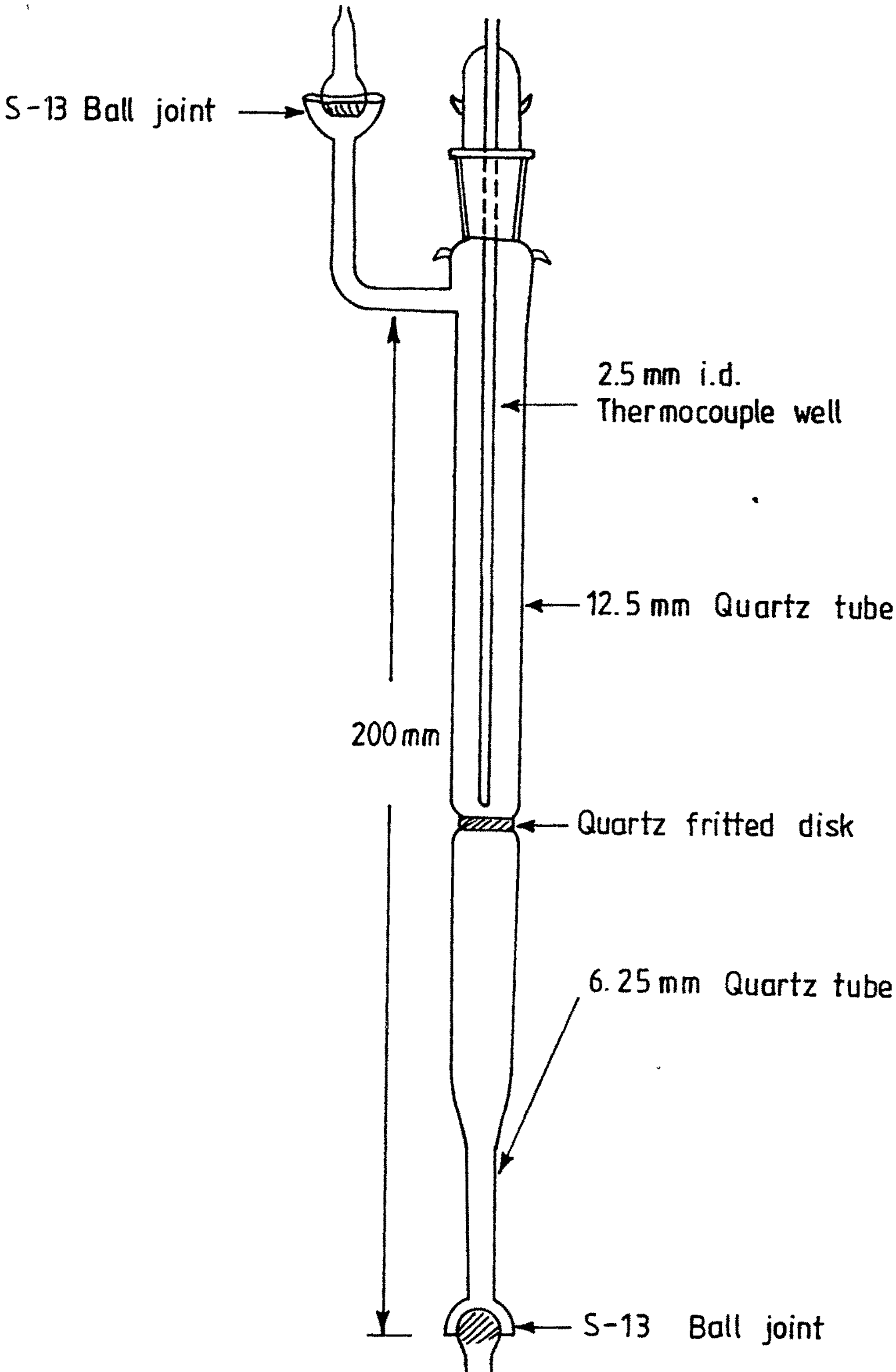

Fig. II.3. Quartz reactor used for TPR, TPD and chemisorption studies.

After reduction, hydrogen was substituted with argon gas at the same temperature and allowed to stand for 30 min. Then the reactor was cooled to room temperature and pulses of hydrogen were admitted till the sample gets saturated. Then adsorbed hydrogen was titrated with oxygen by pulsing oxygen gas. Cycles of H_2-O_2 titration were repeated a number of times and dispersion values were calculated based on 1:1:3 ($H_{ad}:O_{ad}:H_t$) stoichiometry. The reproducibility of the measurements was tested with a selected number of samples. The conditions used for the chemisorption experiments are listed in Table II.1.

II.4.8 Ammonia Chemisorption and Temperature Programmed Desorption (TPD)

Surface acidity and acid site distribution of the alumina samples were determined by ammonia chemisorption and TPD.

TABLE II.1

Experimental conditions for temperature programmed methods.

Experiment	Carrier gas and flow rate(ml/min)	Pretreatments	Temperature (K)	Sample size (mg)	Pulse size (ml)
NH_3 Chemisorption	Helium, 60	Heated in He at 773 K for 2 h	373	300	0.73
NH_3 TPD	Helium, 60	Saturated with NH_3 at 373 K	373-773	300	----
TPR	N_2+10%H_2, 50 mixture	Heated in N_2 at 673 K for 2 h	RT-773	300	----
H_2-O_2 titration	Argon, 50	Reduced in H_2 at 748 K for 2 h	RT	1000	0.15
TPO	N_2+5%O_2, 100 mixture	Coked, flushed with He at 723 K	RT-773	300	----

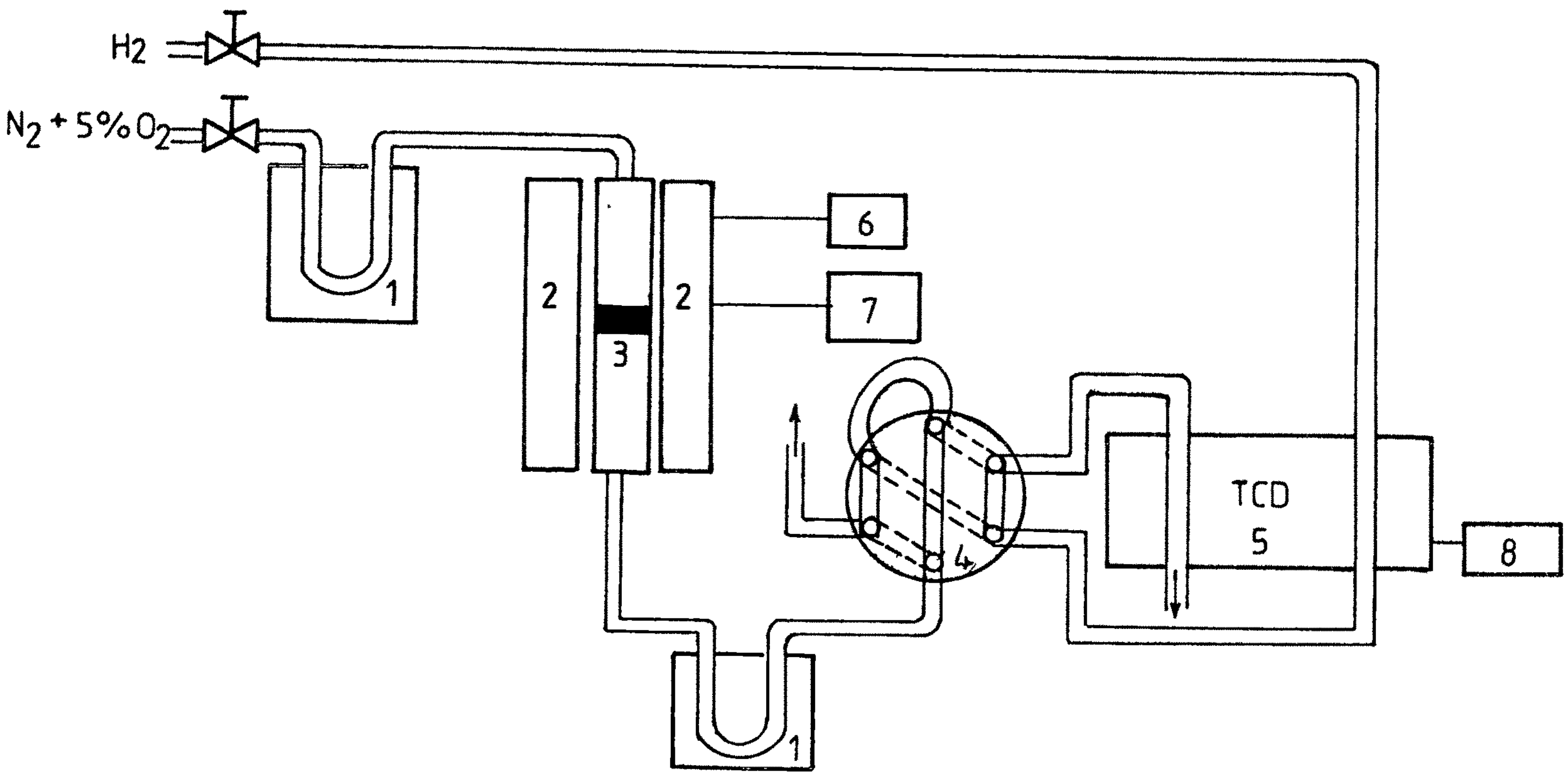

Fig. II.4 Temperature programmed oxidation setup

1. Moisture trap , 2. Furnace , 3. Catalyst charge 4.,6. Port 2-way gas sampling valve ,5. Thermal conductivity detector , 6. Temperature indicator , 7. Temperature controller or programmer , 8. Integrator

The experimental set up was the same as shown in Figure II.2 and the conditions are presented in Table II.1. After the pretreatment the temperature of the furnace was lowered to 373 K and ammonia was pulsed into the reactor till the recorder responses of two successive pulses were within 1 %.

For TPD the system was purged thoroughly free of ammonia by continuing the helium flow and maintaining the temperature at 373 K. The reactor temperature was then programmed linearly at the rate of 10 K/min. and the ammonia concentration in the carrier gas was continuously monitored by thermal conductivity detector.

II.4.9 Temperature Programmed Reduction (TPR).

Schematic representation of the experimental set up and reactor are given in Figure II.2 and 3. After the pretreatment in nitrogen the reactor was cooled to 300 K and changed over to N_2+H_2 mixture (90:10v/v). Then the reactor was heated at the rate of 10 K/min and the hydrogen consumption as a function of temperature was continuously monitored with a thermal conductivity detector. The conditions of the experiment are presented in Table II.1.

II.4.10 Temperature Programmed Oxidation (TPO)

TPO of coked catalyst samples were carried out with a dynamic system as shown in Figure II.4. The catalysts were coked at 723 K for equal duration of 3 h under reaction conditions with n-dodecane feed. The coked samples were purged free of adsorbed hydrocarbons with helium at the same temperature.

Oxidation of the coke on the catalyst was performed with a 5% O_2+ 95 % N_2 mixture. The temperature of the reactor was increased at the rate of 1.8 K/min. and the progress of the reaction was monitored with the help of online gas chromatograph which measures the amount of carbon dioxide formed at definite intervals. Hydrogen was used as the carrier gas in the G.C. and a Porapak-Q column having a length of 2 m was used to separate the products. Pulsing of the effluent gas was performed with the help of a six port two way gas sampling valve located between the reactor and gas chromatograph.

II.4.11 Diffuse Reflectance Spectroscopy (DRS).

DRS of the catalysts were recorded in the oxidised and reduced states on a Shimadzu UV-Vis spectrophotometer (model 240) having facility for mounting solid samples. The spheroidal catalyst samples were powdered and compressed before recording the spectra. Li/alumina was used as the reference and the spectra were recorded in the range of 200 to 600 nm in absorbance mode.

II.4.12 Electron Spectroscopy for Chemical Analysis (ESCA).

ESCA of reduced monometallic and bimetallic catalysts were recorded on a VG SCIENTIFIC ESCALAB MK-II spectrometer using Mg Kα radiation source for excitation. Powdered catalysts were subjected to reduction at 748 K for 2 h in a stream of pure hydrogen. After reduction catalysts were sealed in hydrogen. Powdered samples were then mounted on sample holder with the help of double-sided adhesive tape and were transfered to the fast entry lock of XP Spectrometer with minimum exposure to air. Each sample was kept overnight in preparation chamber and then transfered to the analyser chamber, where a vacuum better than 5×10^{-8} mbar was ensured. Binding energy measurements were made using C(1s) photoelectron line at 285.0 eV as reference.

II.5 ACTIVITY EVALUATION.

Activity of the catalysts (promoted and unpromoted) towards dehydrogenation of n-dodecane was evaluated in a continuous flow fixed bed reactor at 723 K. The reaction was conducted in region free of internal and external mass transfer limitations. The particle size used was 0.5 to 0.8 mm and the flow of n-dodecane and hydrogen were 0.088 moles/h and 0.5268 moles/h respectively. The H_2:HC ratio was maintained at 6 for all the experiments. The experimental set up used for this purpose is presented schematically in Figure II.5.

II.5.1 Dehydrogenation of n-Dodecane.

0.05 g. of the catalyst with particle size 0.5 to 0.8 mm was loaded in a tubular glass reactor having an i.d. of 0.4 cm. The position of the catalyst bed was so adjusted that it is located in the isothermal region along the axis of the tubular furnace. A constant temperature was maintained along the length of the catalyst bed with the help of a S.S. tube (wall thickness 1 cm) inserted in the tubular furnace. The controlling thermocouple was placed between the outer surface of the S.S. tube and inner surface of the furnace. The indicating thermocouple was placed at the centre of the catalyst bed just outside the reactor.

Initially, the catalyst bed temperature was raised to 748 K at the rate of 10 K/min. and the catalyst was reduced for

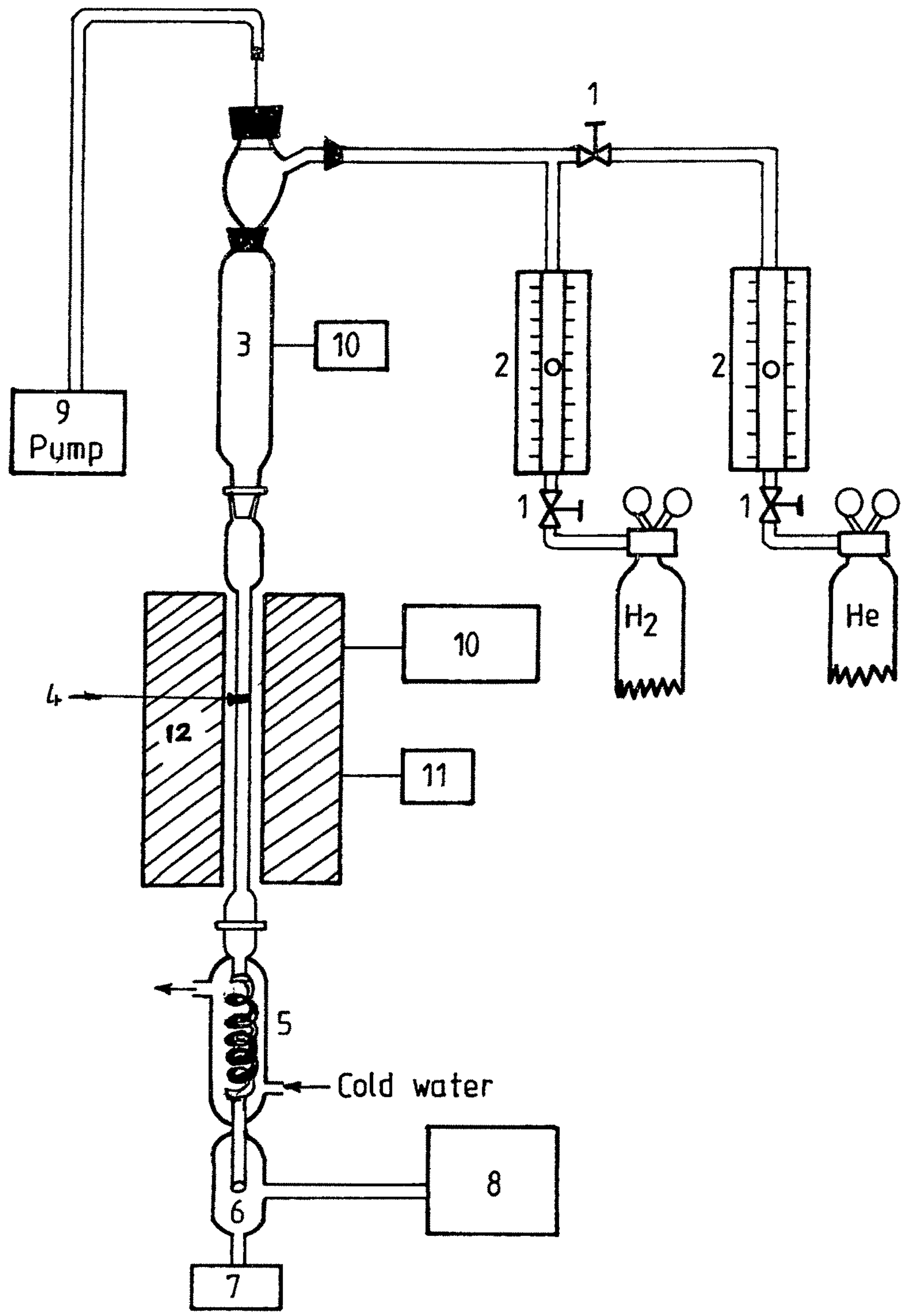

Fig. II.5 Atmospheric pressure reactor system

1. Control valves, 2. Flow meters, 3. Preheater 4. Catalyst charge, 5. Condensor, 6. Gas liquid separator, 7. Receiver, 8. Wet gas flow-meter, 9. Liquid pump, 10. Temperature controller, 11. Temperature indicator, 12. Furnace.

2h in flowing hydrogen (300 ml/min.). Then the temperature of the catalyst bed was lowered to the reaction temperature (723 K).

The paraffin was fed into a preheater kept at a temperature of 623 K using an ISCO LC-500 syringe pump at the prescribed rate with an accuracy of ± 0.1 ml/h. The preheater is packed with inert alpha alumina balls of 1 cm diameter. The reaction products pass through a coil condenser kept at 278 K with the help of a Julabo F-30 thermostated water circulator. The condensed products of the reaction were collected at definite intervals of time and analysed in a Varian 6000 Gas Chromatograph attached with a Varian DS 600 Data System and a Hewlet Packard Think Jet Printer Plotter. The separation of the products was achieved by a 9 m long S.S. column (3 mm o.d.) packed with 25% w/w polyphenyl ether (6 ring) on Chromosorb-P (60-80 mesh) and the products were detected by a thermal conductivity detector. The identification of the products were performed with mass spectroscopy. The total conversion was obtained from the disappearance of n-dodecane and the selectivity towards each of the products namely cracked products ($< C_{12}$), mono olefins, aromatics and diolefins were obtained from their appearance in the product.

II.6 KINETICS OF n-DODECANE DEHYDROGENATION ON Pt-Sn-Li/ALUMINA.

II.6.1 Type of Reactor and Reactor Aspect Ratios.

The dehydrogenation of n-dodecane to monoolefins was studied in the vapour phase as a gas-solid heterogeneous reaction in a tubular fixed bed reactor. Since the reaction is reversible and endothermic, back mixing was expected to be detrimental to conversion and hence plug flow of the reactant was preferred. To approximate plug flow residence time distribution behaviour, suitable axial and radial aspect ratios were adhered to, according to the guidelines of Denbigh and Tarhan (238,239).

Axial aspect ratio, $\frac{L}{d_p} > 50$

where L = catalyst bed length and d_p = particle diameter

Radial aspect ratio, $\frac{D_t}{d_p} = 8$

where D_t = Reactor tube internal diameter

The reactor used was a glass tube with projections at the center for supporting the catalyst bed and fitted with ground glass joints. A pictorial representation of the reactor is given in Figure II.6.

II.6.2 Mass Transfer Studies.

(a) Internal mass transfer.

Reactions were carried out at constant temperature (733 K) and constant space time (1.24 g cat h/g mole) by varying the particle size in the range of 0.18 to 2.0 mm to study the internal mass transfer limitations.

(b) External Mass transfer.

At constant space time (1.24 g cat h/g mole) and temperature (733 K), the effect of varying flow velocities on conversion in the range of 0.3 to 2.3 cm/s were determined.

II.6.3 Data Collection For The Determination of Kinetics.

Based on the studies carried out on the mass transfer behaviour of the system, a region of space time and particle size

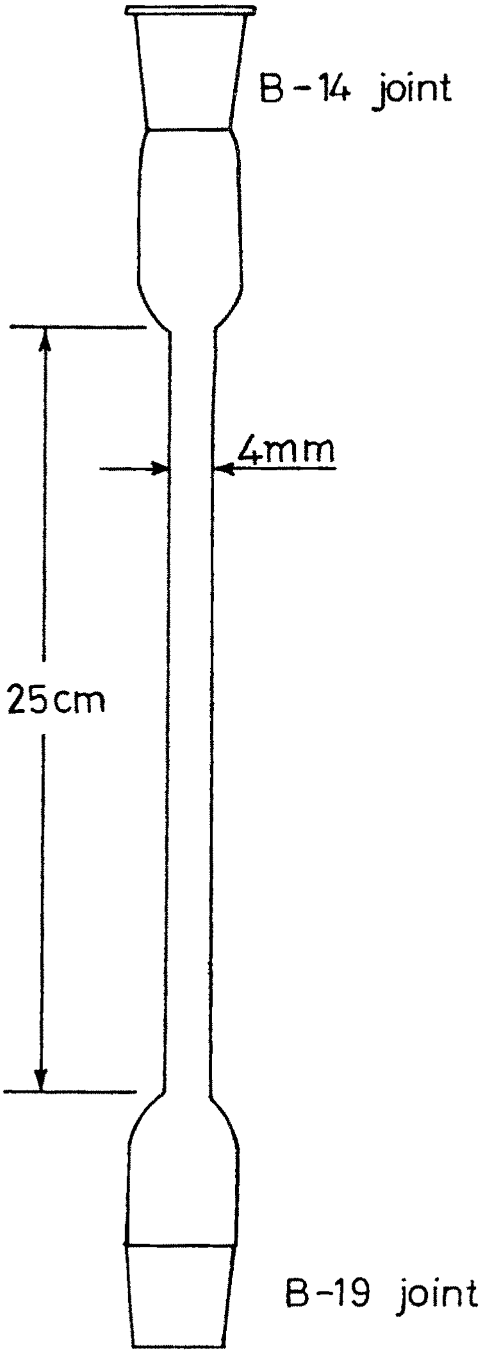

Fig. II.6 Reactor used for evaluation and kinetic studies free of mass transfer limitations was selected for the kinetic experiments. Data were collected at various temperatures namely 658, 673, 688 and 703 K with different space velocities. Similarly the effect of varying partial pressures of hydrocarbons and hydrogen were evaluated at three different temperatures.

1. Effect of space velocity on conversion.

Conversion data for the dehydrogenation of n-dodecane to monoolefins were collected at constant temperature for varying space velocities ranging from 1.0 to 6 moles/g cat h. For each space velocity, data were collected at three different temperatures 658, 673 and 703 K.

2. Effect of partial pressures.

(a) Effect of change in partial pressure of paraffin.

Effect of change in partial pressure of n-dodecane was studied at 673 K and the partial pressure of paraffin was varied from 0.03 to 0.15. The change in partial pressure of paraffin was acheived by substituting equal number of moles of n-dodecane with an inert gas, helium.

(b) Effect of change in partial pressure of hydrogen.

The effect of change in partial pressure of hydrogen was studied at 673 K, by progressively replacing hydrogen with helium. The hydrocarbon flow (0.439 mole g/h) and hence, the space time were kept constant. Partial pressure of hydrogen was varied from 0.96 to 0.19.

II.6.4 Data Analysis.

The data collected as per the previous sections have been used for the following purposes.

(i) Determination of the minimum reactant linear flow velocity required to exclude interphase mass transfer effects for facilitating collection of data for determination of intrinsic kinetics.

(ii) Determination of optimum catalyst particle size to avoid intraphase mass transfer limitations.

(iii) Initial rate studies for determining order of reaction as well as for elucidation of the rate controlling mechanism and also for obtaining estimates of kinetic constants for use in differential analysis of data.

(iv) Differential analysis of data on conversion as a function of reactant space time. The data was suitably smoothened and differentiated to obtain reaction rate at given space time. It was then tested with different models for a fit and for estimation of values of the kinetic constants. A suitable technique of optimisation based on minimisation of a least squares objective function was used.

(v) Integral analysis of data on conversion as a function of space time was also attempted in view of the opinion of Froment (240), that taking differentials along the conversion-space time curve, as is done in differential analysis, is prone to error.

Both adsorption and power law models have been tested. The latter which consists of the form;

$$-r = \text{kinetic term} \times \text{driving force term}$$

is simple and is advantageous in incorporating mass transfer effects and catalyst deactivation. These models are easy to use in design. The adsorption models present a sound basis in terms of inclusion of terms for adsorption and in interpreting adsorption related phenomena like rate-temperature maxima, but they are complex in form, require many assumptions to be made for simplification in the use of design, do not yield results superior in any way in terms of design and can lead to multiple solutions. Therefore, it can be seen that both classes of models have their own advantages and disadvantages, hence both have been used in the present study. The adsorption models have the general form,

$$-r = \frac{\text{kinetic term} \times \text{driving force term}}{\text{resistance term}}$$

Finally the Arrhenius relationship of the constants have been determined.