CHAPTER 3

EXPERIMENTAL TECHNIQUES

3. Experimental Techniques

In this chapter, various experimental techniques employed to prepare the catalysts under examination have been described. They were subjected to extensive characterization techniques such as the determination of textural properties, reduction behaviour, acidic properties, active metal dispersion etc. These catalysts were evaluated for dehydrogenation of n – decane to its corresponding monoolefin, n – decene. The coked catalysts were subjected to oxidation studies which are also discussed in this chapter. All the experimental setup hitherto used is pictorially described.

3.1. Preparation of alumina using oil drop technique

3.2. The method

In 1962, Hoekstra et al **(1)** invented a process to prepare spheroid alumina, which later came to be known as the oil drop method. This method is conventionally used to synthesize γ - alumina spheres, and consists of several steps, the details of which are covered in following pages (Figure 3.1).

3.3. Aluminium chloride sol

100g 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 115°C, in a two necked flask fitted with a water condenser. The reaction between aluminium powder and HCl is extremely exothermic, fast and liberates hydrogen vigorously and can become uncontrollable and violent. So the Al powder was added in very small amounts, in stages, at equal time intervals. The resulting sol was digested for 12 h and filtered and made up to 550ml with deionised water. The sol was cooled below 10°C and stored for further use. The table 3.1 gives the composition of the sol.

Table 3.1 Composition of the Alumina sol

Alumina content (%)	11.7
Chloride content (%)	8.49
Specific gravity at 36.5 °C	1.29

3.4. Preparation of Hexa Methylene Tetra Amine (HMTA) solution

250 g of pure HMTA was weighed out in a beaker, dissolved in de-ionized water and made up to 1 liter. This solution was also cooled below 10°C and stored.

Mixing of sol and HMTA solution

Equal volume of the sol and HMTA solution were mixed at 10°C and aged for not more than 15 minutes at room temperature.

Gellification and ageing

The sol + HMTA mixture was allowed to flow through specially fabricated system of calibrated nozzles into a heated paraffin oil column kept at 90 – 98°C. 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.

Ageing in ammonia

The oil-aged spheres were separated from the oil by decantation and aged in 5% (w/v) ammonia solution at ~95°C for 4 h.

Filtration and washing

The ammonia-aged spheres were filtered and washed with hot water to remove ammonia.

Drying and calcination

The washed spheres were dried at 150°C for 1 h. and calcined at 550°C for 4 h. in a tubular furnace in a in a downward flow of air. The final calcined samples

were crushed and sieved to obtain a particle size distribution of 150 – 300μ. These particles were preserved in sealed tubes for further characterization and catalyst preparation.

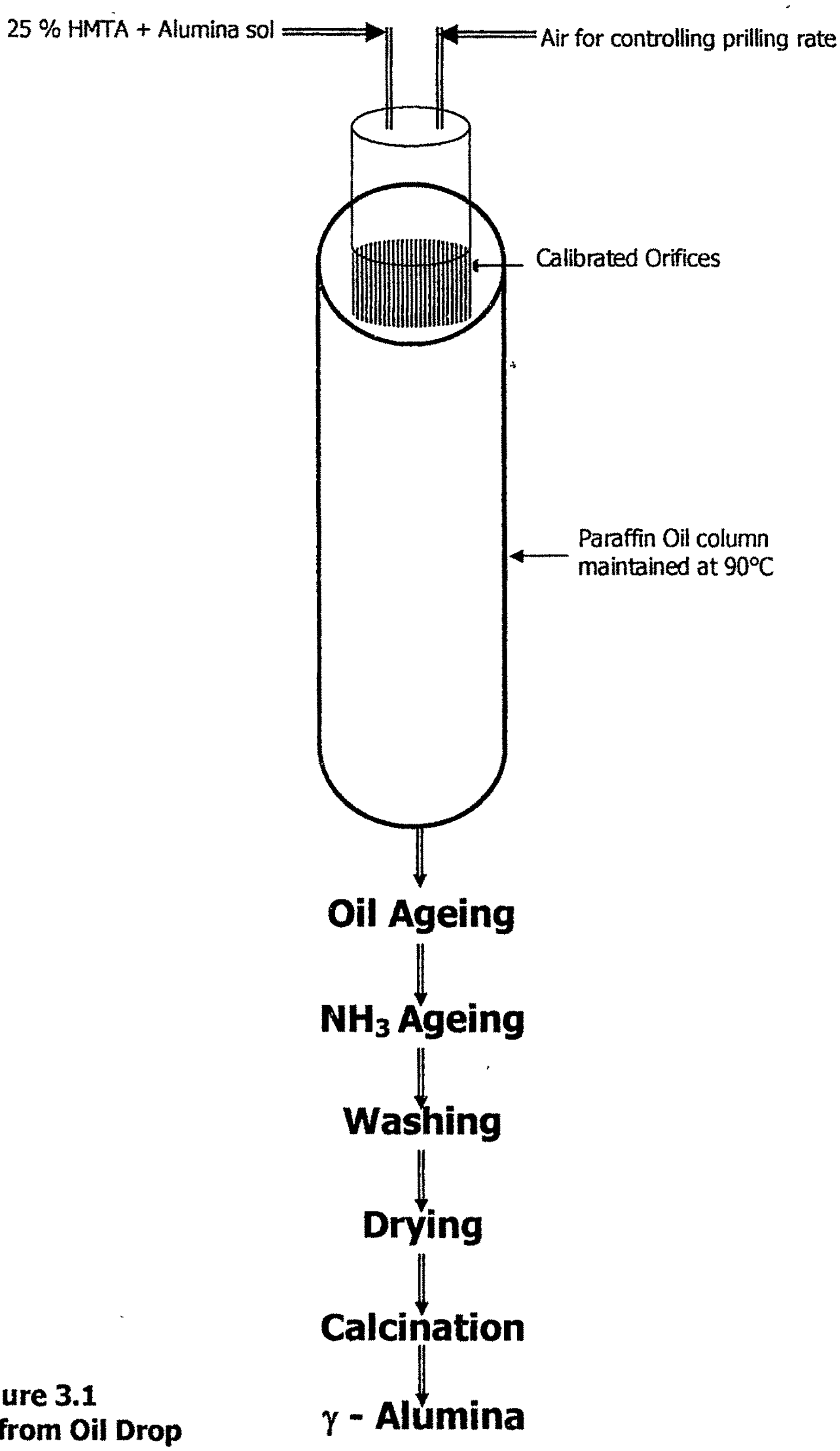
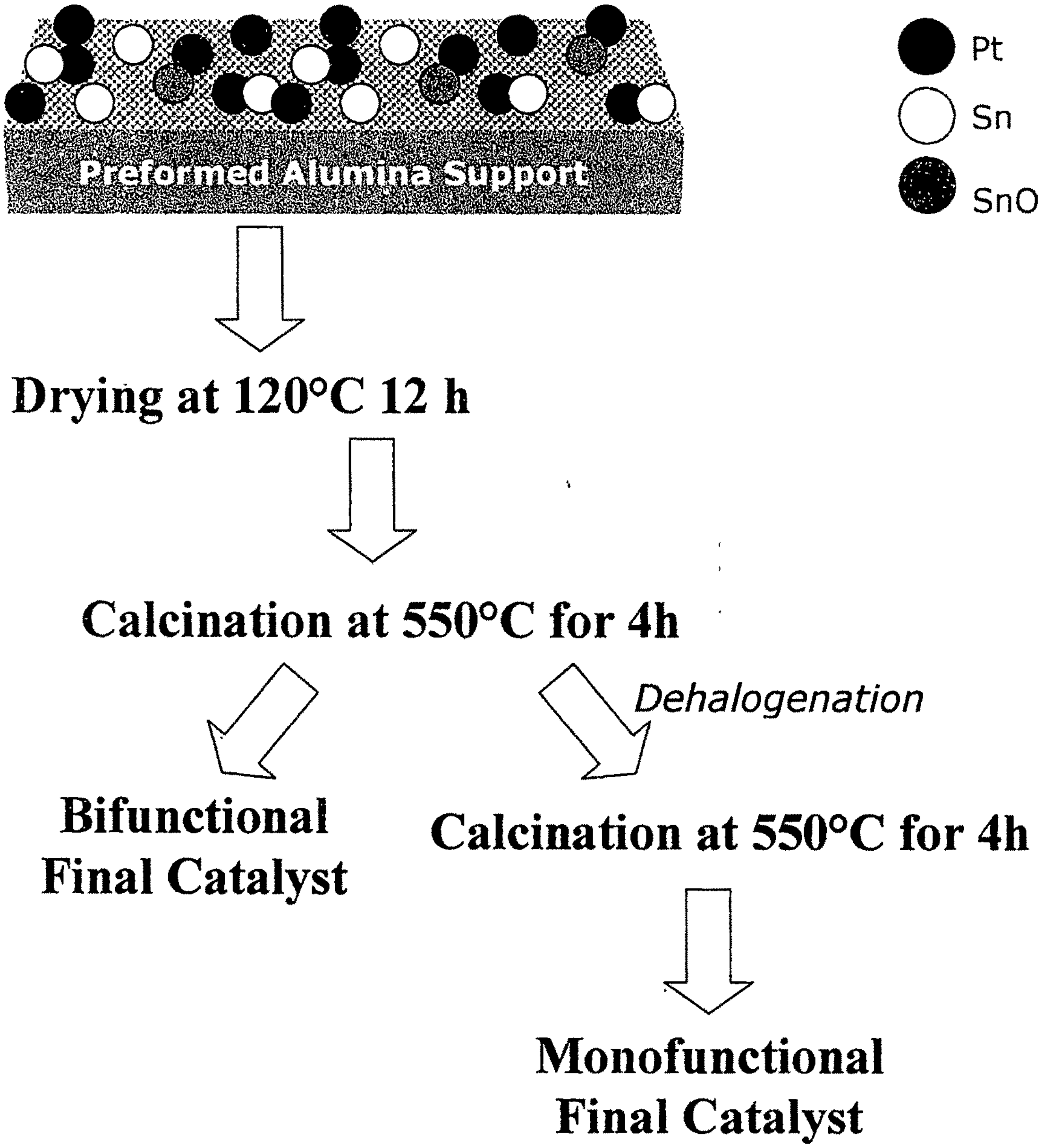


Figure 3.1
Alumina from Oil Drop method



Scheme 3.2: Preparation of IMP catalyst series

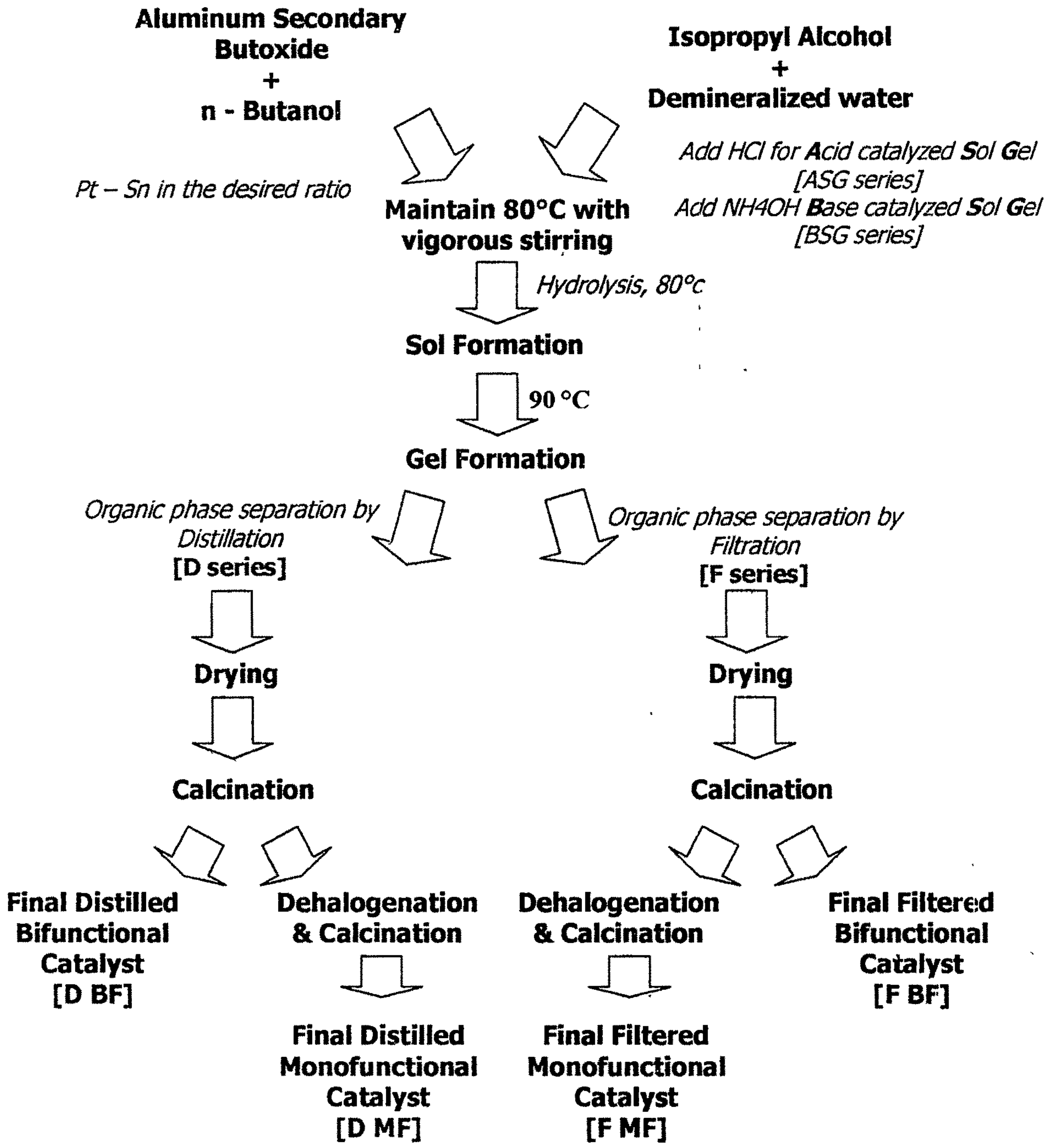


Figure 3.3: Methodology of catalyst preparation by sol gel route and their codes

3.5. Chemistry of Oil Drop technique

When the aluminum chloride sol at 10°C is added to a gelling agent (HMTA), at 10°C, there is absolutely no reaction between them. At 90° C, the basic HMTA decomposes, liberating ammonia. This ammonia then neutralizes the acidic sol and bulky amorphous precipitates containing large amounts of water and anions are formed. These are termed as hydrogels. These precipitates are then aged in same ammoniacal solutions, which results into the pseudo boehimite form. Care should be taken to maintain the pH between 7 and 10 because at a pH value higher than 10, bayerite is formed.

This pseudo boehimite is then dried slowly and calcined at 540°C for 4 h in a continuous downward flow of air. The calcined material is γ-alumina.

3.6. Preparation of catalysts: The IMP series

10 g of bare γ-alumina support was taken for the preparation of each of the catalysts. Water pore volume of the support was measured to be 1.7 ml/g. Four catalysts containing 0.4 wt % platinum as an active component and tin as promoter in the tin to platinum atomic ratio 0 (mono metallic), 2, 4 and 8 were prepared by incipient wetness technique. For each preparation, 10 g of the support was sprayed with 17 ml liquid consisting of platinum–tin complex in hydrochloric acid equal to 10 %chloride content on γ-alumina and deionised water.

The orange – red spheres were dried in an oven at 120°C for 12 h and calcined in a flow of dry air, initially at 150°C for an hour to remove moisture and then at 550°C for 4 h.

The resulting catalyst contained ~1.0% residual chloride. 5g of this lot was retained as such to obtain bifunctional catalysts. Remaining 5 g of the catalyst was refluxed with 5 % w/v ammonia solution to minimize residual chloride, dried and calcined again at 550°C. These four catalysts were termed as mono functional with residual chloride levels less than 0.1% (Figure 3.3).

3.7. Preparation of alumina support and catalysts by sol-gel technique

As described in Chapter 1, alumina could be synthesized by sol-gel method with several variations in the preparation conditions. In the present work, alumina and alumina-supported catalysts were prepared by sol-gel technique, but broadly by two different routes as described in Figure 3.2.

3.8. Acid catalyzed synthesis of alumina and Pt-Sn/Al_2O_3 catalysts by sol gel technique

In a two- necked round bottom flask, normal butanol (180 ml) was heated to 80° C with vigorous stirring. After about two h, 0.1 M (24.5 g) of Aluminum Secondary Butoxide (ASB) was added quickly and the mixture was heated at 80°C for another hour until the solution was crystal clear. At this stage pH of the solution was maintained at 3.0 by addition of dilute HCl.

3.8.1. Hydrolysis

Almost immediately, a mixture of water (180 ml) and isopropanol (180 ml) was added slowly at the rate of 1 ml /min. using a peristaltic pump with continuous and vigorous stirring. The hydrolysis was allowed to continue at the same temperature (the temperature will decrease due to addition of water) over a period of 18 h. At the end of the hydrolysis, the sol that was formed was aged at the same temperature with stirring for about 6 h.

3.8.2. Condensation

The temperature was raised to 90°C and maintained for two hours . This initiates condensation resulting into gellification and with time, the solid-liquid separation occurs (ramification of gel). The contents of the flask now consisted of a heterogeneous mix of the gel and the alcohols.

Excess alcohol was distilled off and the gel was dried at 110°C for 12 h to obtain a xerogel, which was subsequently calcined at 550°C to obtain sol-gel alumina.

In the preparation of Pt-Sn/Al_2O_3 catalysts by the same route, appropriate quantities of Pt and Sn (only Pt in the case of mono metallic catalysts and mixture of H_2PtCl_6 and $SnCl_2$ in appropriate proportions to obtain 0.4 w/w% Pt loading and Sn/Pt atomic ratios of 2, 4 and 8) were added to the solution containing ASB in n-butanol and pH was maintained at 3.0 by addition of dilute hydrochloric acid, and hydrolysis was then initiated. All subsequent steps up to the formation of gel were similar to those adopted for the preparation of alumina. Further treatments of the gel and alcohol mixture were different with respect to the preparation of alumina.

The gel and alcohol were separated from each other in two ways:

- In the first method, the temperature of the reaction mixture was raised to 110°C, wherein the liquid phase, (mostly a mixture of n – butanol, isopropanol and water) was evaporated off. The gel was transferred to a petridish and kept for drying in an oven between 110° - 120°C for 12 hrs. This was a time consuming process.
- In the second method, the separation was carried out by direct filtration under vacuum. This was relatively a fast process, and in about an hour, the gel could be obtained in the form of a cake, which was dried in the oven at between 110° - 120°C for 12 h.

The resulting xerogels were calcined at 540 °C for 4 h in a downward flow of air to obtain the catalyst. Normally 10 g lots of the catalysts were prepared in this manner, which contained ~1.0% residual chloride. 5 g of this lot was retained as such to obtain bifunctional catalysts. Remaining 5 g of the catalyst was refluxed with 5 % w/v ammonia solution to minimize residual chloride, dried and calcined again at 550°C. These four catalysts were termed as mono functional catalysts with residual chloride levels less than 0.1%

3.9. Base catalyzed synthesis of alumina and Pt-Sn/Al_2O_3 catalysts by sol gel technique

In this method, all the steps starting from the preparation of a solution of ASB in n-butanol, hydrolysis, condensation and formation of sol and gel were similar to those described in the section 2.1 for the preparation of alumina and catalysts by acid catalyzed sol-gel route. The only variation was with respect to the pH of the solution of ASB in n-butanol prior to initiation of hydrolysis, which was maintained at 10 by addition of dilute ammonia. Similar to the steps described in section 2.1, gel and alcohol in each case were separated by two methods, distillation and filtration. The catalysts were then divided into two types mono and bi functional, depending on the levels of residual chloride in the final calcined catalysts.

3.10. Characterization of Alumina and catalysts

3.10.1. Surface area and porosity

Adsorption-desorption isotherm of nitrogen was recorded on a Carlo-Erba, Sorptomatic Series 1900, and model VC 140 at – 196°C after degassing the sample at 200°C for 4 h. From the isotherms, specific surface area values were calculated according to BET equation (3.1)

$$\boxed{S_v = \frac{V_M cp}{[p_0 - p][1 + (c+1)p/p_0]}} \quad \text{................ 3.1}$$

Where

V -volume of adsorbed N_2, cm^3
V_M - Volume of the monolayer adsorption, cm^3
c - Constant for a given material
p - Pressure of adsorption, Torr
p_0 -Saturation pressure at measurement temperature, Torr

Rearranging equation 3.1, and plotting $1/[V(p_0/p-1)]$ against p/p_0, a straight line is obtained, of which the value of V_M can be calculated from the slope and the intersect; the BET surface area (m^2/g) of the sample S_{BET}, is therefore determined taking 16.2 $\times 10^{-20}$ as the cross-sectional area (m^2) of one nitrogen molecule adsorbed on the surface and W is the weight (g) of the sample.

$$\boxed{S_{BET} = \frac{(V_M)(6.023 * 10^{23})(16.2 * 10^{-20})}{22400W}} \quad \text{................ 3.2}$$

Analysis of the type and the 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 hysteresis loops according to de Boer's method **(2)**.

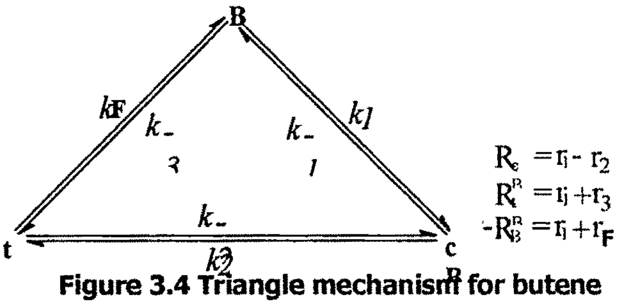


Figure 3.4 Triangle mechanism for butene isomerization

3.10.2. Butene Isomerisation

Various experimental methods are known for comparing the acidic character of catalysts/supports viz. ammonia adsorption / desorption, butene isomerisation, pyridine adsorption etc. The double bond isomerisation of 1-butene to cis and trans -2-butenes is a useful tool to investigate the acidity of supports/catalysts. The extent of isomerization of butene-1 gives a measure of total acidity and the cis/trans ratio of 2-butenes produced is an indication of the strength of acidity. There are a number of studies reported by different researchers. As far as the kinetic features of butene isomerisation is concerned Kallo et al **(3)** has done an excellent work containing summarized

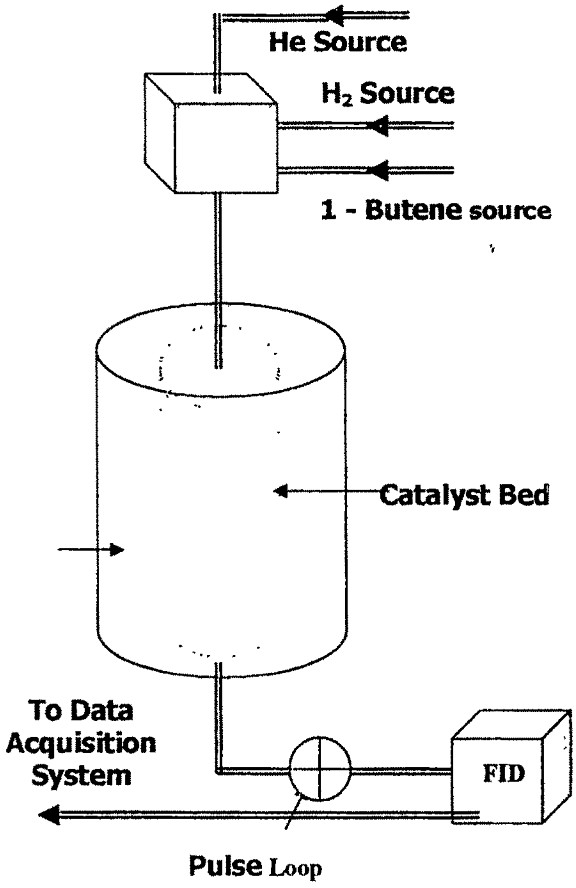


Figure 3.5 Schematic diagram of experimental setup for butene isomerization

thermodynamic data and describing the reaction with a completely reversible triangle mechanism (Fig. 3.4). Recently, Gaceia-Ochoa and Santo **(4)** also proposed kinetic modeling for the reaction. Beres et al **(5)** used 1-butene isomerisation as a test reaction to find acid-base character of catalysts. Also a number of other articles on 1-butene isomerisation over supports and catalysts are available (**6 - 18**).

In house fabricated set up with a tubular reactor (quartz, 10mm diameter) as shown in Fig. 3.5, was used. The reaction temperature employed was 350 ^{0}C and 100 mg of sample of particle size 500 microns was used. The 1-butene used was 99.9% pure with traces of isobutene, cis and trans-2-butenes. The sample was preheated to 350 ^{0}C in inert atmosphere (helium, 60ml/min) and 1-butene was admitted at a rate of 6ml/min along with helium. The product was analyzed at equal intervals of time using a flame ionization detector in GC Shimadzu Model GC-7AG. A 80/100 CARBOPACK™ coated with 0.19% w/w picric acid column having the length 3.5m effected the separation of products. The signals were processed by ORACLE™ GC data acquisition software.

3.10.3. Temperature programmed reduction

Temperature-programmed reduction (TPR) is a method that has been used to a large extent to study supported metal and metal oxide systems. Hurst et al and others have written detailed reviews about the method **(19 – 21)**.
TPR has been used on the Pt-Sn system to determine whether the metals have a good contact, whether an alloy has been formed, and to calculate the oxidation state of Sn **(22 – 26).**

TPR is particularly useful for supported metal monometallic and bimetallic catalysts wherein the metal loadings are very less and their dispersions high. The reaction between metal oxide and hydrogen to form metal and water vapor can be represented by:

$$MO + H_2 \rightarrow M + H_2O$$

When the metal oxide is subjected to thermal treatment in the presence of a reducing gas mixture, it undergoes reduction to metal / low valance state in single or multiple steps. The identification of these stages and quantification of hydrogen consumption can provide valuable information about the species present and their valance states. The reduction of an oxide, when supported, may be hindered or favored depending on their mutual interaction.

The shapes of the TPR profiles provide valuable information on the bimetallic system. When the profiles of the two monometallic catalysts, Pt and Sn, are added, the sum will not match the profile from the bimetallic Pt-Sn catalyst. The peak at the low temperature is larger, and some of the tin in the Pt-Sn catalyst must have been reduced at a lower temperature than in the Sn catalyst. This is most probably caused by platinum catalyzing the reduction of the tin. This indicates that the two metals are in close contact. Hobson et al **(27)** observed that this was not the case for a commercial Pt-Sn/Al_2O_3 catalyst prepared by a co-gelation method. They found no Pt-Sn interaction. Their explanation was that the support, and not the metal, was modified by the tin addition during the catalyst preparation.

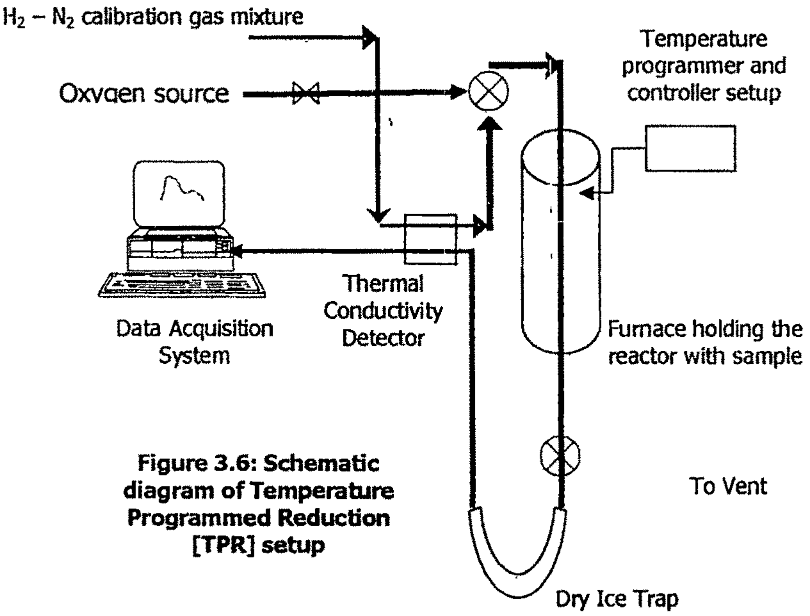


Figure 3.6: Schematic diagram of Temperature Programmed Reduction [TPR] setup

The nature of reduction of the metals can be found in table 3.3 below. The oxides of Pt and Sn progressively reduce towards their respective metallic forms, in steps. The reduction reactions were assumed to be $SnO_2 + H_2 \rightarrow SnO + H_2O$ and $PtO_2 + 2H_2 \rightarrow Pt + 2H_2O$. The signal from the alumina carrier was subtracted from the other samples to compensate for support effects.

The reason for evaluating the results at the highter temperature is that many authors have stopped their experiments at about 500 – 600°C.

Table 3.3: Reduction temperatures for various phases in Pt-Sn systems

Free/ bound oxides of Platinum	100 to 200°C
Platinum oxychloro species, Pt O_xCl_y	230 to 250°C
Simultaneous reduction of Pt and Sn/ Pt-Sn ensembles	270 to 350°C
Reduction of free/bound tin oxide	Above 400°C

When carrying out the chatacerisaton of a catalyst by this technique, conditions like sample size, rate of carrier gas flow, rate of heating were chosen to maintain σ value very close to unity. The carrier gas flow is very vital here since readsorbtion of desorbed gas can lead to erroneous results.

0.1 gm of the sample with particle size 300 μ to 500μ is charged into the reactor and is pretreated, in flowing oxygen (60 ml/min) from room temperature to150°C @ 10°C/min and maintained for an hour to remove any traces of moisture on the catalyst. Then the temperature was raised to 550°C @ 10°C/min and maintained there for 4 h, to ensure the complete oxidation of the active metal species on the catalyst. The sample was then cooled to room temperature. At this point, the gas flow was changed over to UHP nitrogen.

The catalyst was heated in the reducing gas mixture of 5.0% hydrogen in argon at a heating rate of 10°C /min from room temperature to 800°C. The hydrogen consumption as a function of temperature was constantly monitored with a thermal conductivity detector (TCD).

Schematic representation of the experimental set – up is given in the fig 3.6

3.10.4. Temperature programmed Coke Oxidation [TPCO]

Temperature-programmed oxidation (TPO) has become a common method for studying coke formed on a catalyst. It is possible to determine the amount of coke to get information about where on the catalyst the coke is deposited – on the metal or support.

The coke reacts with oxygen and forms carbon dioxide and water. By following the carbon dioxide evolution, the amount of coke can be obtained. The hydrogen-to-carbon ratio (H/C ratio) in the coke can be determined either by measuring the water production or by detecting the oxygen consumption.

In the present work, Temperature-programmed coke oxidation was performed in a microbalance and the weight was continuously monitored, in an apparatus for thermal analysis i.e. SDT 2960 Simultaneous DTA TGA **(28 – 31)**. Loss of coke as CO_2 was recorded as weight loss with respect to temperature.

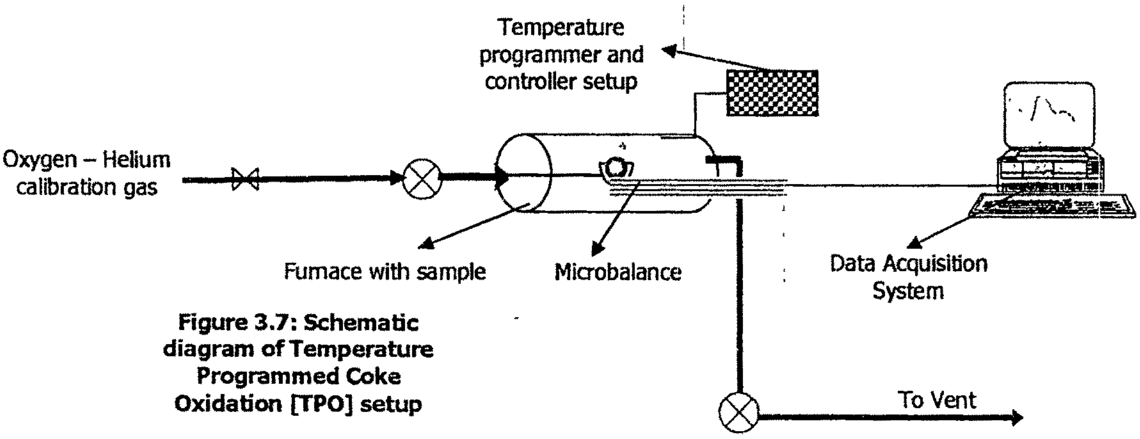


Figure 3.7: Schematic diagram of Temperature Programmed Coke Oxidation [TPO] setup

The Coke bearing deactivated samples were finely powdered and charged into the TGA unit and the temperature of the furnace was raised to 200°C @ 10°C/min and maintained there for 30 minutes in an atmosphere of flowing air. At this point, adsorbed hydrocarbons like n – decane, decenes etc., are removed, thereby offering purely a carbonaceous surface.

Then the temperature is further raised from 200°C to 800°C @ 5°C / min. The loss of weight due to the conversion of coke to CO_2 and water is recorded as a function of temperature. Weight losses occurring in the range 200-400°C are attributed to coke from the metal sites while those above 500°C due to coke from support sites **(33).** Coke is formed initially on metal sites due to condensation reactions and is subsequently transferred to support. This undergoes further condensation resulting to a decrease in the caron / hydrogen ratio. For coke present on metallic sites, the oxidation temperature would be low. Since, the metallic site itself catalyses the coke oxidation, coke on support is then oxidesed on high temperature..

Schematic representation of the experimental set – up are given in the fig 3.7.

3.10.5. Temperature programmed Desorption of Ammonia [TPD]:

Surface acidity and acid site distribution of all the samples were determined by ammonia chemisorption and TPD. The experimental setup was the same as shown in fig 3.8. Accurately weighed 50 mg catalyst is pretreated in helium at 500°C to remove surface impurities and adsorbed moisture. The temperature was lowered to 100°C and ammonia was pulsed into the reactor, till the integrator responses of two successive

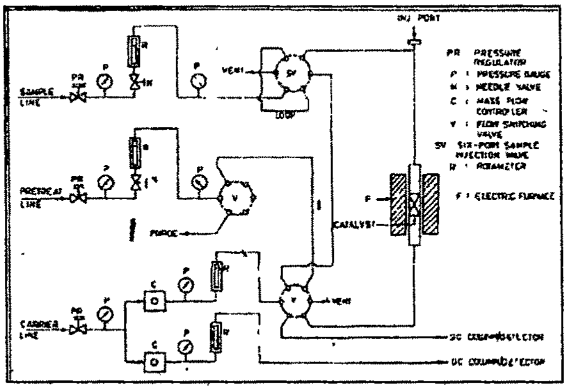


Figure 3.8: Schematic diagram of Temperature Programmed Ammonia Desorption [ATPD] setup

pulses were within 1 %, indicating complete saturation of the catalyst with ammonia. This temperature was chosen to avoid physical adsorption of ammonia on its surface. The system was purged thoroughly with helium at 100°C to ensure ammonia–free atmosphere within the reactor. The reactor temperature was then programmed linearly @ 10°C/min and the ammonia concentration in the carrier gas was continuously monitored by a TCD. Based on the amount of ammonia adsorbed, total acidity of the sample has been calculated. The information about strength of acid centers is derived from ammonia TPD patterns.

3.10.6. Platinum Dispersion Measurement

Platinum dispersion of the catalysts was measured by $H_2 - O_2$ titration technique. The experiment was carried out in an automatic catalyst characterization unit, ZETON ALTAMIRA, USA, Model AMI 100. A Thermal Conductivity Detector was used to detect the residual adsorbate gases in the carrier gas stream and the signals were monitored using the AMI 100 software. All the gases used in this study, were 99.99% pure

1 g of sample was charged into the quartz reactor, fixed by a wad of quartz wool just above and below it. The catalyst was reduced in a stream of flowing hydrogen at 470°C for 2 h. The hydrogen flow rate was maintained at 100 ml/min. 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 saturation. Two consecutive peaks with almost constant counts, assure this. Then the adsorbed hydrogen was titrated with oxygen by pulsing oxygen gas. Cycles of $H_2 - O_2$ was repeated a number of times. The same exercise of $H_2 - O_2$ titration was carried out after heating the catalyst sample to 150°C. This temperature was chosen since, at 150°C, activated chemisorption of H_2/O_2 on alloyed Pt sites according to the method developed by Rajeshwer et al **(34)**.

3.10.7. Infra Red (IR) Spectroscopy

IR spectra of the representative dried and calcined samples were recorded using KBr pellets with a Nicolet Magna 550 IR Spectrophotometer.

This was mainly done to determine the optimal calcination temperature and time, wherein there is complete transformation of dried boehmite samples to γ - alumina with of free hydroxyl group. This technique was also employed to see if there is a complete disappearance of the precursor organic moiety after calcination at that temperature.

3.10.8. Thermogravimetric Analysis (TGA)

Differential Thermal analysis of the representative dried samples were recorded on a Simultaneous DTA TGA of TA Instruments, model: SDT 2960 in the range 25°C - 1000°C at a heating rate of 10°C/min in a stream of flowing air. The aim of this study is to identify phases and phase transformations taking place during various pre-treatments.

3.10.9. Powder X – Ray Diffraction (XRD)

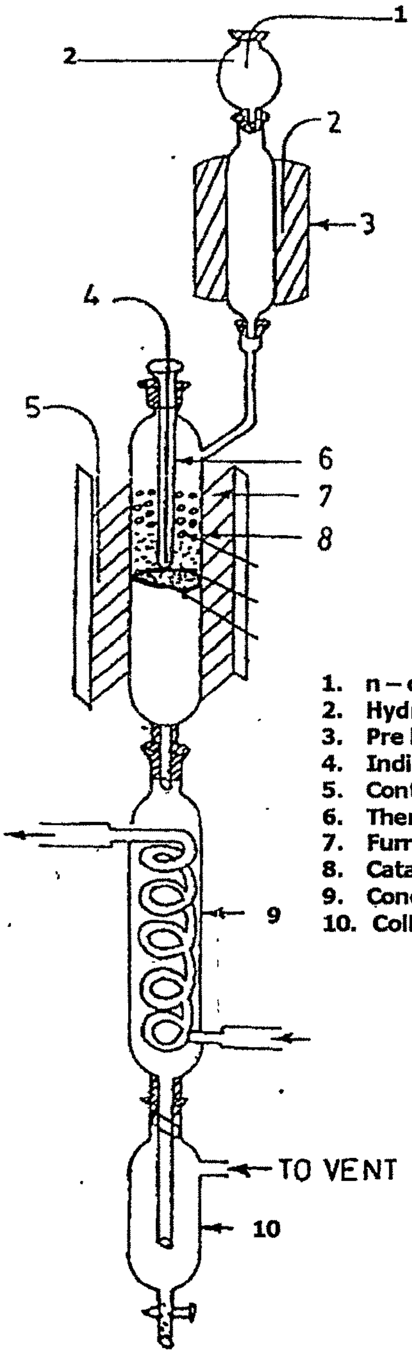
XRD patterns in the 2θ range of 10 – 90 degrees at a scanning rate of 2 degrees / min were recorded on a DRUCKER AXS X –ray spectrophotometer. Phase identification of all the alumina and catalyst samples were carried out by comparing the d – values calculated from the Diffractograms with the standard values reported in the powder diffraction files.

3.10.10. Scanning Electron Microscopy (SEM)

The morphology of all the alumina samples prepared by the sol gel route as well as the oil drop technique was characterised by SEM (JOEL JSM T300). The textural variations arising by varying the preparation conditions were studied.

3.10.11. Catalytic Activity Evaluation

Activity of the all the catalysts (prepared by conventional as well as sol gel route – both monofunctional and bifunctional) towards dehydrogenation of n – decane was evaluated in a continuous flow fixed bed reactor at 450°C. The reaction was carried out in a region free of internal and external mass transfer limitations. The particle size used was 300 - 500μ so as to avoid internal mass transfer **(35)**. The flow of n – decane and hydrogen were maintained at 0.15 moles/h and 0.90 moles/h respectively. The hydrogen to n – decane mole ratio was fixed at 6, value normally recommended in commercial processes, wherein deactivation due to coke formation would be minimum. Schematic diagram of the experimental setup is shown in figure 3.9.



1. **n – decane inlet**
2. **Hydrogen inlet**
3. **Pre heater**
4. **Indicating thermocouple**
5. **Controlling thermocouple**
6. **Thermowell**
7. **Furnace**
8. **Catalyst bed**
9. **Condenser**
10. **Collector**

Figure 3.9: Schematic diagram of n – decane dehydrogenation reaction at atmospheric conditions setup

3.10.12. Dehydrogenation of n- decane

1 ml of the catalyst with particle size 300-500μ was loaded in a two – necked, tubular glass reactor fitted with a sintered disc (G–0) and having an internal diameter of 8 mm. The position of the catalyst bed was so adjusted that it is located in the isothermal region along the axis of the tubular furnace. Constant temperature was maintained along the length of the catalyst bed by controlling the power input to the furnace with the help of temperature programmer and Chromel Alumel thermocouple. The controlling thermocouple was placed between the outer surface of the reactor and the inner surface of the furnace. The indicating thermocouple was placed in a thermowell at the centre of the catalyst bed inside the reactor.

Initially the catalyst was heated in hydrogen flow (372 ml/min) to 150°C @ 5°C/min. and was maintained at 150°C for an hour to remove any traces of adsorbed moisture. Then temperature was raised to 470^0 C at the rate of 5^0C/min. and the catalyst was reduced for 12 h at 470°C. Then the temperature of the catalyst bed was lowered to the reaction temperature (450°C).

The paraffin was fed into a preheater kept at a temperature of 300°C using ISCO LC 5000 Syringe pump at the rate of 25 ml/min. The preheater was packed with inert alpha alumina balls of 1cm diameter. The reaction products pass through a coil condenser kept at 10^0C with the help of a Julabo F-30 thermostat water circulator. The condensed products of the reaction were collected at 15 minute intervals for an hour and at half hourly intervals of time for the next five h. Liquid yield of these samples were noted. The samples were analyzed in a Shimadzu gas chromatograph GC-17A attached to a Shimadzu CBM-101 and a Shimadzu auto injector AOC-17. The separation of the products was achieved by a carbowax™ capillary column and the products were detected by using a flame ionisation detector (FID).

Total conversion was determined from the disappearance of n-decane and the selectivity towards each of the products namely cracked products (less than C_{10}), mono-olefins, aromatics and diolefins were obtained from their appearance in the chromatogram, which were earlier confirmed by mass spectrometry.

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