

CHAPTER 3

PREPARATION OF ISOMERIZATION CATALYSTS FOR LIGHTER ALKANES CONVERSION

3.1 GENERAL

This chapter deals with the preparation of catalyst used for isomerization reaction. Preparation technique, preparation conditions and physico-chemical properties of the precursors are strongly affect the catalytic properties of isomerization catalysts. The strategy for catalysts preparation included synthesis of support matrix, its sulphation and conversion to final catalyst by impregnation of tungstophosphoric acid (TPA).

3.2 METHODS OF PREPARATION

High thermal stability, mechanical properties, and reducing, acidic, basic, and oxidizing surface properties have made zirconia a very useful materials [Nakano et al., 1997]. It can be prepared by various methods such as: (i) Precipitation [Rezaei et al., 2006; Wang et al., 2006], (ii) Co- Precipitation [Chau et al., 1989; Mishra et al., 2002], (iii) Sol-Gel [Fiona et al., 2004; Akkari et al., 2007], (iv) Hydrothermal [Kaya et al., 2002; Feng et al., 2008], (v) Microwave synthesis [Alvaro et al.,2014]. These methods are advantageous as they help in forming bonds between Zr and doped metal at atomic levels. Preparation conditions and parameters have a significant effect on the crystal phase and structure of zirconia [Srinivasan et al., 1992, Davis, 1994].

3.2.1 Materials Used For Synthesis

Muffle furnace, hot plate magnetic stirrer, whatmann filter paper No 42, Silica disc, distillation unit, vacuum filtration assembly, pH paper, pH meter, sintered glass crucible, silica crucible, platinum crucible, heating mantle, autoclave, microwave, extruder machine etc. were used for the preparation of isomerization catalyst. Glassware included round bottom flask (100ml, 150ml, 500ml), Beakers (1000ml 500ml 250ml 100ml 50ml), pipette (1ml, 5ml, 10ml, 25ml) glass rod, magnetic bead, funnel etc.

Following chemicals were used for the preparation of catalyst:

- I. Zirconium oxychloride octahydrate [$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$], 96% AR, Loba Chemie, India
- II. Ammonia solution [NH_4OH], 30%, sp grade LR, S d fine India.
- III. Silver nitrate [AgNO_3 N/50, LR], S d fine India.
- IV. Di-ammonium hydrogen phosphate, [LR], Merck, Mumbai India
- V. Sulphuric acid [35% LR], Fischer scientific India.
- VI. Oxalic acid [$\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ LR 95 %] S d fine, India.
- VII. Sodium hydroxide [NaOH] (97% LR), Merck, Mumbai, India
- VIII. Tungstophosphoric acid [$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 9\text{H}_2\text{O}$, AR] Sigma Aldrich
- IX. Double distilled water self-Prepared by distillation assembly.

3.2.2 Preparation and Standardization of Zirconium Oxychloride [$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$]

Solution

0.5M (1N) solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was prepared in 500ml volume by using doubled distilled water to prepare its 0.5 M (1N) solution. The concentration and strength of the solution was determined by using the following standard procedure [Vogel, 1966]. 5 ml of the above prepared zirconium oxychloride solution was diluted up to 250 ml in a

volumetric flask. 10 ml of this diluted solution was taken in a 500 ml glass beaker using pipette. 100 ml of 10% di-ammonium hydrogen phosphate was added to this solution followed by 30 ml of concentrated sulphuric acid in a drop wise manner with constant stirring. The final volume of the solution was make up to 300 ml using distilled water. Similarly, two more replicate sets were prepared as describe above and all the three sets were heated in a water bath for 1hr. Then the solution were cooled to 50°C and the precipitate was filtered using Whatmann filter paper No. 42. The precipitate was washed first using distilled water and then with 1M acid solution. Finally, to make the precipitate sulphate free, they were washed using 10% aqueous ammonium nitrate solution. The precipitate, along with the filter paper were transferred to platinum crucible and dried at 50°C for 3hrs. Then calcined at 1000°C for 5hrs, in a muffle furnace and weighed the dried materials (zirconium pyrophosphate (ZrP_2O_7)). Finally, the strength of the prepared solution was estimated to be 0.5M.

3.2.4 Preparation and Standardization of (0.5M) Sulphuric Acid Solution

0.5M sulphuric acid solution was prepared by addition of 49 ml of H_2SO_4 in 500 ml of slightly hot double distilled water with continuous stirring. Furthermore, it is transferred in 1L volumetric flask and the volume was make up to the mark using double distilled water. The exact strength of the solution was determined by using the standard procedure describe by (Scott, 1959). Sulphuric acid solution was standardized using NaOH solution by back titration method which was formerly standardized by standard method [Lambert and Muir 1965; Scott, 1959].

3.2.5 Preparation and Standardization of Tungstophosphoric acid (TPA)

Pre-weighed amount of Tungstophosphoric acid was dissolved in 50 ml beaker using double distilled water. It was then transferred to a 100 ml volumetric flask and the volume was made up to the mark by adding double distilled water. The TPA solutions of varying strength i.e. 10-60 % were prepared similarly.

3.3 STRATEGY OF ISOMERIZATION CATALYST DEVELOPMENT

Unsupported catalysts represent an enormous class and are useful in numerous industrial applications. For commercial production of unsupported catalysts, several techniques were adopted in last decades, such as precipitation, fusion of catalyst components, flame hydrolysis, co-precipitation, sol gel method, thermal decomposition and hydrothermal synthesis. It is revealed that from literature, that isomerization catalyst required two functions, one hydrogenation /dehydrogenation and second acidic function. In order to achieve the first requirement, oxides were chosen as a support material, where metal present in it could behave as Lewis acid and can carry out dehydrogenation function. Along with dehydrogenation function, oxide support also provide large surface area, which is a pre-requisite of any catalyst. The acidic requirement of the catalyst was achieved using heteropoly acids as an active ingredient. The other issue related with catalyst is its strength. Literature indicates the use of few metal oxides as support material and noble metal as active component and promoter for reaction. But in the present study, sulphated zirconia with TPA is used instead of noble metals. The metal oxide was used to provide the large surface area, some acidity and strength to the catalyst. In order to increase the strength, binder was also used along with the catalyst recipe (heteropoly acid dispersed over oxide support).

The developed catalyst consist of following component:

- 1) Support (sulphated zirconia).
- 2) Strengthening material (Binder).
- 3) Active ingredient (Heteropoly acid).

3.3.1 Synthesis of Support

In this research work zirconia support was prepared through four different routes and the effect of the synthetic routes was analyzed on the catalyst activity. The detailed systematic procedure for synthesis of support is describe in following sections.

3.3.1.1 Hydrothermal Synthesis

Hydrothermal synthesis is a good technique and includes the technique of crystallizing substances at high temperature and high vapor pressures. Hydrothermal technique can be used for the synthesis of single crystal that depends on the solubility of minerals under high pressure in hot water. The crystal growth is carried out in a vessel called an autoclave. But, the autoclave material must be inert with respect to the solvent. In most of the experiments, steel corroding solutions are used in hydrothermal synthesis. To prevent the internal cavity corrosion of the autoclave, protecting insets are commonly used. Insets may be made up of carbon free iron, silver, copper, platinum, gold, glass (quartz), titanium, or Teflon, depending on the temperature and solution require (Fig 3.2). Advantages of the hydrothermal method includes the ability to form crystalline phases, which are not stable at the melting point. Materials which have a high vapor pressure, close to their melting points can also be synthesized by this method. The main disadvantages of this method is that the need of expensive autoclave and the crystal growth observation is not possible.

It is an important technique for zeolites, metal oxides and for other molecular sieves preparation [Hayashi et al., 2010; Thomas et al., 1997; Bian et al., 2017]. Presently, the importance of zeolites and oxides in industry as catalyst is increasing day by day. The use of zeolites and oxides as catalysts or catalyst supports in petrochemical processes and production of fine chemicals.

3.3.1.1.1 Preparation of Support by Hydrothermal Synthesis

250 ml of 0.5M zirconium oxychloride solution was taken in 500 ml beaker. It was then precipitated by the dropwise addition of NH_4OH (30% solution) until the pH reached to 10 with continuous stirring at 600 rpm. The precipitate was then transferred to the Teflon lined autoclave and kept in an oven at 150°C for 5hrs. (Fig 3.2). Autoclave was kept for cooled down to room temperature and then the precipitate was filtered, washed until the pH did not reduce from 10 to 7 and the filtrate was not free from chloride ions. The presence of chloride ions were tested using silver nitrate solution. Zirconium hydroxide cake was then dried in an oven at 120°C overnight, slightly crushed and sieved to $75\mu\text{m}$. The dried sample was calcined in a muffle furnace at 600°C for 4hrs at the rate of $1^\circ\text{C}/\text{min}$ and coded to as ZT. The flow scheme is shown in Fig 3.1.

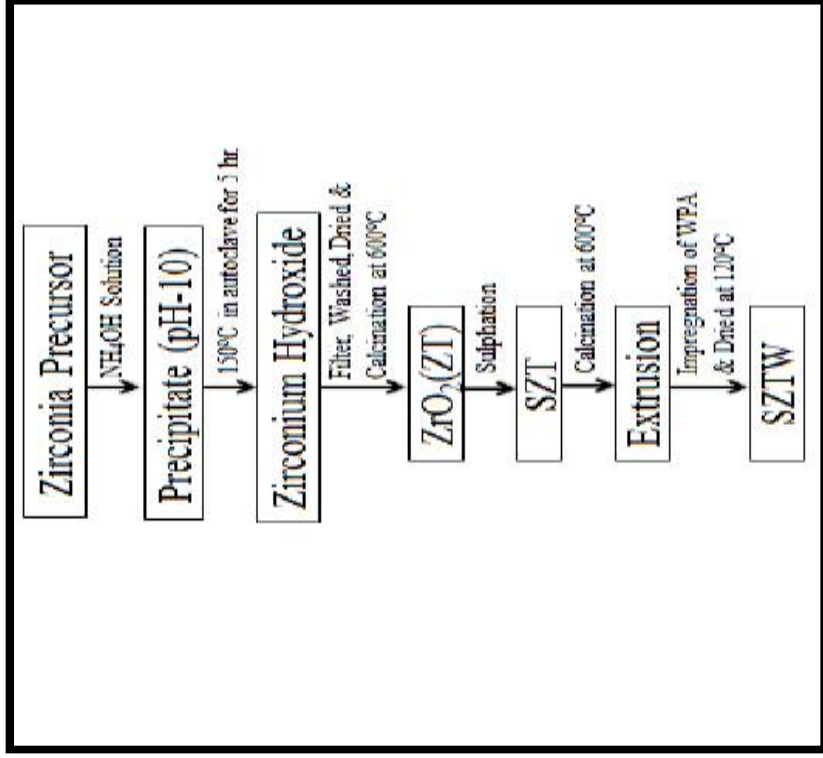


Figure 3. 1 Flow scheme of hydrothermal synthesis

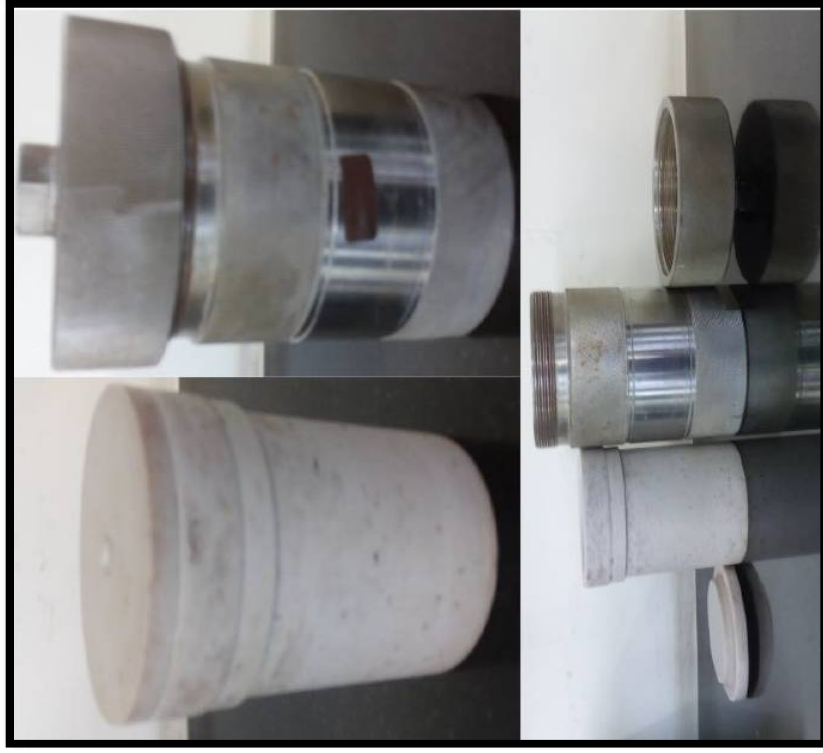


Figure 3. 2 Autoclave Teflon and steel part



Figure 3.3 Hydrothermal synthesis processes



Figure 3.4 Zirconia in precipitate form



Figure 3.5 Zirconia after filtration



Figure 3.6 Zirconia powder after calcination



Figure 3.7 Zirconia in extrude form



Figure 3.8 Sulphated Zirconia after impregnation of TPA

3.3.1.2. Microwave Synthesis

Microwave technique is a technique in which, the microwave irradiation are used for carrying out the chemical reactions. [Mitesh et al., 2014; Baghbanzadeh et al., 2011; Tsuji et al., 2005 Nuuchter et al., 2004] explained the microwave technology, its engineering and microwave dielectric heating. Dipolar polarization and ionic conduction a mechanism are used in this technique. Generally, microwave heat any materials containing mobile electric charges such as conducting ions or polar molecules in a solvent or in a solid. During microwave heating, polar molecules such as water molecules try to orientate along with the fast changing alternating electric field; thus heat is produced by the friction, rotation and collision of molecules (dipolar polarization mechanism). In case of ions, ions in solution travel through the solution based on the orientation of the electric field [Collins et al., 2010]. Microwave heating technology is emerging as an alternative heat source for rapid volumetric heating having shorter reaction time, higher reaction rate and selectivity. Homogeneous nucleation in microwave technique helps in obtaining with high surface areas, rapid crystallization rates and phase controlled synthesis [Jin et al., 2013; Shalmani et al., 2012; Jun et al., 2011; Utchariyajit et al., 2010].

Microwave heating has been demonstrated to influence the reaction kinetics and selectivity in a chemical processes. It is a progressively significant tool in the synthesis of nanoporous materials. It is simpler, cleaner, low cost, and more energy efficient technique than the conventional methods [Schanche et al., 2003]. Therefore, it is consider as promising method for the production of catalyst. So far the microwave irradiation has been used for the synthesis of several materials. [Cundy et al., 2003; Kim et al., 2004; Serrano et al., 2004; Jhung et al., 2004].

3.3.1.2.1 Preparation of Support by Microwave Synthesis

250 ml of 0.5M zirconium oxychloride solution was taken in 500 ml beaker. It was then precipitated by the dropwise addition of ammonium hydroxide (30% solution) until the pH reached 10 with continuous stirring at 600 rpm. The precipitate was kept in microwave oven [RAGA'S microwave system] (Fig 3.10) for 20 min with 420 W power at 80°C. The resulting precipitate was carefully filtered using vacuum pump, washed with double distilled water, until the pH of the solution decreased from 10 to 7 and free from chlorine ions. The content was dried at 120°C in hot air oven [Spectra Lab] overnight. The material was grinded to get sieve size 75µm using a pestle-mortar and then calcined in muffle furnace [Ambassador] at 600°C for 4 hours at ramp rate of 1°C/min. The sample synthesized by this method was coded to as ZM. The flow scheme is shown in Fig 3.9.

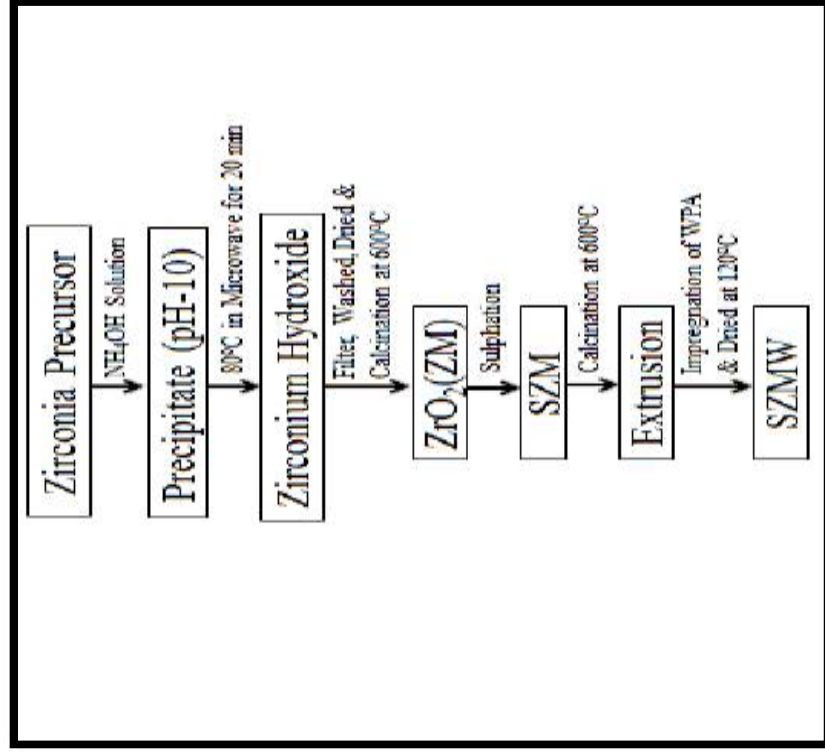


Figure 3.9 Flow scheme of microwave synthesis

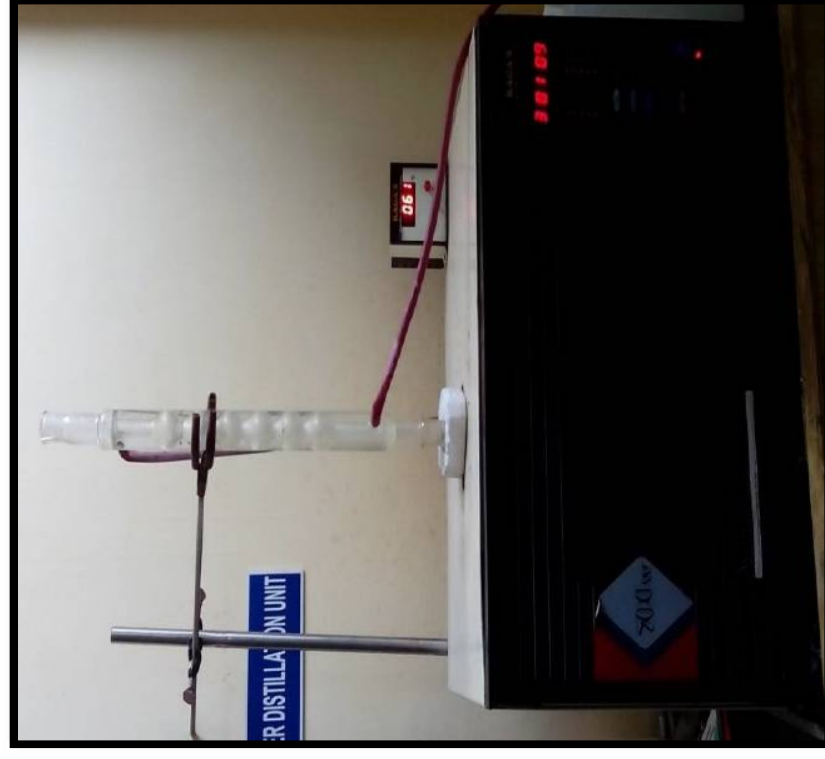


Figure 3.10 Microwave Oven used for Zirconia Synthesis

3.3.1.3 Precipitation Synthesis

Precipitation methods are the frequently used technique for preparation of catalyst support materials [Yao et al., 2015; Sang et al., 2014]. The precipitation method is used for preparation of material such as SiO₂, Al₂O₃, ZrO₂, TiO₂, etc. The precursors such as metal salts, such as sulphates, nitrates, chlorides precipitated by potassium, carbonates and ammonium hydroxide. Byproducts such as alkali metal sulphates or nitrates formed during the reaction must be washed out from the precipitate. Liquid mixing/super saturation, nucleation, crystal growth to form primary products and aggregation of the primary particles takes place. The main advantages of the precipitation method is the possibility of forming high purity and homogenous oxides. However, the main drawback of this process is to forming large volume containing salt solutions during the precipitation step and during washing of the precipitate.

3.3.1.3.1 Preparation of Support by Precipitation Synthesis

250 ml of 0.5M zirconium oxychloride solution was taken in 500 ml flat bottom flask and it was then precipitated by the dropwise addition of ammonium hydroxide until the pH reached to 10. The precipitate was agitate for 5hrs at 100°C in an oil bath with continuous stirring at 600rpm (Fig 3.12). Resulting precipitate was carefully filtered using vacuum pump, washed with double distilled water, until the pH of the solution decreased from 10 to 7 and free from chlorine (tested by silver nitrate test). The solid content was dried at 120°C in hot air oven [Spectra Lab] for overnight. After drying, the oxide was grinded to get sieve size of 75µm in a pestle-mortar, and then calcined in a muffle furnace [Ambassador] at 600°C for 4hrs at ramp rate of 1°C/min. The sample synthesized by this method was coded as ZP. The flow scheme is shown in Fig 3.11.

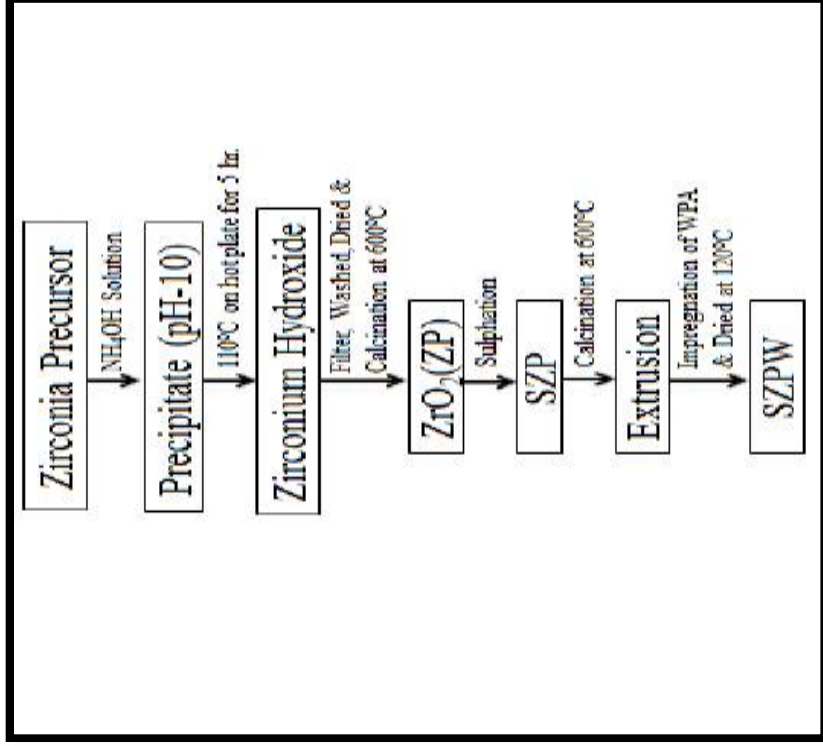


Figure 3.11 Flow scheme of Precipitation Method

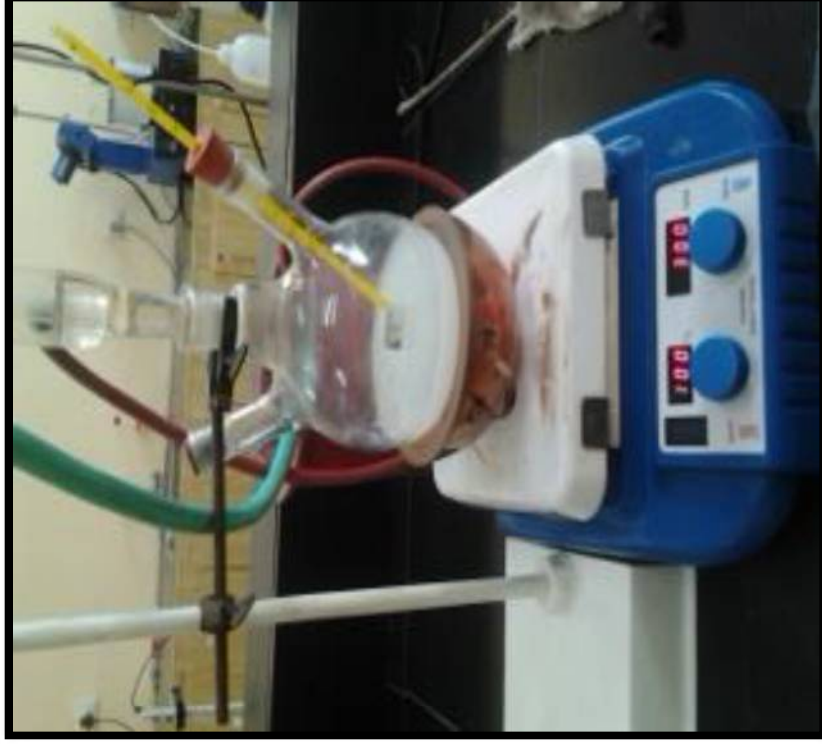


Figure 3.12 Precipitation method with hot plate magnetic stirrer



Figure 3.13 Zirconia cake after filtration



Figure 3.14 Zirconia Powder after calcination

3.3.1.4 Sol-Gel Synthesis

Sol-gel process [Ko et al., 1997] includes the creation of a sol, followed by the formation of a gel. A sol is obtained by the hydrolysis and condensation of a metal alkoxide or inorganic materials. The formation of gel followed by the condensation of sol into a three dimensional network. Silicon oxide and aluminium oxide can be prepared from sodium silicate and sodium aluminate by adding nitric acid, sulphuric acid or hydrochloric acid by using this technique [Ko et al., 1997; Saravanan et al., 2012]. Removed the salt contents (NaNO_3 , Na_2SO_4 , NaCl) by washing for avoiding the bursting of beads. Finally, the resulting materials must be dried and calcined at relevant temperature [Thomas et al., 1997]. By using this process, good quality materials such as Al_2O_3 , ZrO_2 , TiO_2 , can prepare for bulk production. Sol-gel process has the advantages of produce that it form the ultra-fine zirconia.

3.3.1.4.1 Preparation of Support by Sol-Gel Synthesis

The starting material used for the preparation of zirconia sol was zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$). 250 ml of 0.5M Zirconium oxychloride solution was taken in a conical flask. 3M Oxalic acid ($(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$) was added by dropwise manner with stirred continuously of 1:0.7 vol ratios to get white gel [Mary et al., 2012]. Gel was heated at 80°C , until white powder was obtained. The content was dried for overnight at 120°C in a hot air oven. After drying, the oxide was grinded to get sieve size of $75\mu\text{m}$ in a pestle mortar and then calcined in a muffle furnace [Ambassador] at 600°C for 4hrs at ramp rate of $1^\circ\text{C}/\text{min}$. The flow scheme is shown in Fig 3.15. The sample synthesized by this method was coded to as ZG.

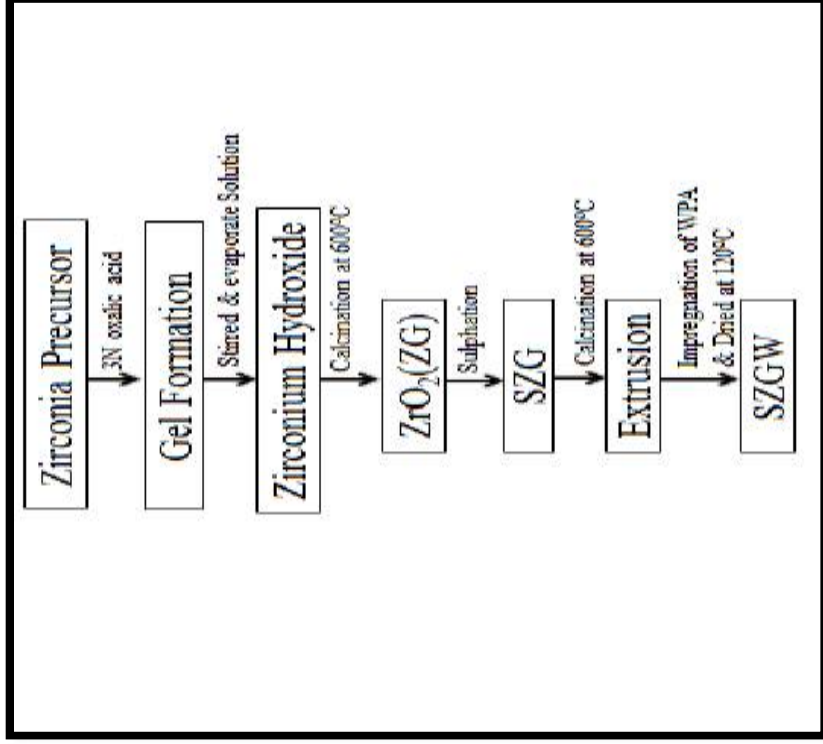


Figure 3. 15 Flow scheme of Sol-gel Synthesis



Figure 3.16 Gel formation



Figure 3.17 Zirconia powder after calcination

3.3.2 Preparation of Sulphated Zirconia

Addition of sulphate ions to zirconia create very strong acidic site in it. [Yamaguchi et al., 1990; Hino and Arata, 1980; Dar et al., 2014; Haridas et al., 2003]

15ml of aqueous sulphuric acid solution (0.5M) was added drop wise manner to per g of zirconia support (prepared in each method) [Parera et al., 1992; Saravanama et al., 2014]. The solution was stirred at 600 rpm for 1hr at room temperature. It was then filtered, dried at 120°C for overnight. The fine powder obtained was converted to extrudates using binder and dilute nitric acid as peptizing agent. The sample were coded as SZT, SZM, SZP and SZG.

3.3.3 Extrusion

The shape and size of the catalysts particles, depend on the type reactions and on the type of reactors in which reaction was performed. Reactions in the liquid phase need small catalyst particles (50-200 nm). Extrusion of catalyst powder or paste, lubricants and binders is a commonly used in industries [Richardson et al., 1989; Busto et al., 2011]. The pressure screw extruders and press extruders are frequently used extruder machine for pastes materials. In both cases, pastes are pressed through a die and the extrudates is cutted to preferred size. [Richardson et al., 1989]. Powdered stearine, poly vinyl alcohol, and aluminium stearate are commonly used as lubricants. Nitric acid used as peptizing agents for improving the mechanical strength of materials if alumina containing materials being extruded [Richardson et al., 1989]. Calcium aluminate cement also used as binder, and steam treatment used to set the materials [Richardson et al., 1989; Stiles et al., 1995]. The extruded samples can have various shapes, such as hollow cylinders (macaroni), cylinders (noodles) or ribbed cylinders. Pore forming agents and organic solvents can be removed by calcination. Pelletizing is expensive then extrusion, but pellets have high resistance to abrasion than extrudates. Extrudates are commonly used and suitable for various types of FBRs.

Zirconia extrudates of 1mm diameter and 3mm length were prepared with hand extruder machine using kaolin (15%), alumina (10%) as binder and nitric acid as peptize agent. The extrudates were dried for overnight at room temperature followed by drying in hot air oven at 120°C for overnight. The sample was then calcined in a muffle furnace at 600°C for 4hrs.

3.3.4 Calcination (Thermal treatment)

The main objective of calcination is to stabilize chemical, physical and catalytic properties of the materials. In this process, thermally unstable compounds (organic compounds, carbonates, hydroxides), decompose and transformed to oxides. The mechanical strength and pore structure of catalysts can also change and the possibility to the formation of new compounds, specially, if the high temperature is maintained for calcination [Delmon et al., 1997] and amorphous material get converted into crystalline. Several crystalline changes can observed i.e. reversible or irreversible changes. The calcinations temperature is generally somewhat higher than the catalyst reaction temperature. Here all the samples were calcined at 600°C for 4hrs.

3.3.5 Impregnation of Tungstophosphoric acid (TPA)

Impregnation by pores filling (wet incipient method) is a frequently used technique for production of catalysts [Fulton et al., 1986; Che et al., 1997]. The main objective of this technique is to fill pores of the support materials by the addition of metal precursor solution, e.g., a metal salt precursor solution of necessary concentration to obtain the desired loading. If higher loading is required, the impregnation is to be repeat after drying or calcination of the catalyst. Catalysts obtained by the pores filling method are Ga and Zn impregnate over zeolites, Ag or Ni doped on Al₂O₃, noble metals doped on carbon, etc. [Richardson et al., 1989; Fulton et al., 1986].

One of the desirable parameter of the catalyst is high surface area is required to carry out isomerization of paraffins. Although heteropoly acids are highly acidic in nature, but possess very low surface area (1-15m²/g). Thus, they are impregnated on oxide supports to get a catalyst with high surface area. Acidity in the catalyst was provided by the

impregnation of the support with calculated amount of heteropoly acid. Impregnation of heteropoly acid on the support was done by wet incipient method. In this technique, based upon the pore volume of the materials, an aqueous solution of known concentration of heteropoly acid is prepared and a calculated volume is added to the sulfated zirconia support (SZT, SZM, SZP, and SZG). Sulphated zirconia extrudates were kept in a beaker and TPA solution was added dropwise manner. The solution was agitated for 1hr at room temperature, dried at 110°C in a hot air oven until the constant weight was obtained. About (10 to 60wt %) TPA has been impregnated over sulphated zirconia support.

Zirconia support were synthesis by four different routes followed by the impregnation of TPA by wet incipient method. The structure and physico-chemical properties of catalyst is discussed in chapter IV in detail.