

CHAPTER 2

OVERVIEW AND BIBLIOGRAPHY SURVEY FOR CATALYTIC PROCESS

This chapter has been divided into four parts: the first part deals with review of various studies on isomerization of hydrocarbons. Second part contains the review of heteropoly acids for isomerization and other reactions. In the third part, a review of literature on the catalytic activity of various types of promoted and modified zirconia, its application, operational parameters, etc. has been reported and fourth part presents mechanism of isomerization reported in literature.

2.1 STUDIES ON ISOMERIZATION OF LIGHT ALKANES

Isomerization is an important and challenging catalytic reaction in the petroleum refineries for the production of clean and high-octane fuel. Isomerization of n-alkanes to branched alkane is an exothermic reaction. Thus, thermodynamically low reaction temperature is favored for branched alkanes [Yasakova et al., 2010; Graeme et al., 2004; Risch et al., 2000]. Therefore, a highly active catalyst is required for this reaction.

2.1.1 Liquid Acid Catalyst (Friedel Craft catalyst)

Friedel crafts catalyst is also known as Lewis acid catalyst (e.g. AlCl_3 , SbCl_3 and FeCl_3 etc.), used as isomerization catalysts since long [Ono, 2003]. These catalysts are highly acidic and active at lower temperature (25-120°C). The advantage of using these liquid acid catalysts is that even the minor amount of H_2O in the feed can lead to the creation of strongly polarized hydroxyl group (-OH), which enhanced the reaction rate. At present,

these catalysts are not preferred due to the corrosion problem of the reactor and inability of their regeneration after used.

2.1.2 Solid Acid/Base Catalysts

Almost all the acid base catalyzed reactions are conventionally carried out using liquid acid and base. But, the implementation of strict environmental guidelines have required the replacement of these environmentally harmful catalysts, with solid acid and base catalyst. Now a day's solid acid/base catalysis is one of the most cost-effective and environmentally important field in the domain of catalysis. More than three hundred solid acid catalysts have been developed in the last four decades [Tanabe and Holderich 1999]. Their structures and surface properties have been explained by the newly advanced sophisticated analytical techniques. The characterized solid acid and base catalysts have been applied in several reactions and the role of their acid-base properties has been studied extensively. The need for material development according to the environmental regulations has led to the explore solid super acid catalysts and liquid super acids with characteristic including (i) high conversion and selectivity towards a reaction, (ii) stability under reaction, (iii) low sensitivity to poisoning, and (iv) easy regeneration.

2.1.2.1 Zeolite Based Catalysts

Zeolites are microporous, alumino-silicate materials frequently used as commercial adsorbents and catalysts support. The utilization of zeolites as microporous materials for refining process has been an industrialized issue, since the development of zeolites in 1994 [Macilli, 2004]. Since 1970-1980, these materials have regularly been used in the petrochemical and chemical industry with or without incorporation of Pt/Pd metal for the production of high-octane gasoline.

Galadima (2009) reported that zeolite based bi-functional catalysts are now gaining industrial attention, mainly in isomerization for enhancing the RON of gasoline. While, the catalysts showed high acidity and catalytic activity, their acidity, its textural properties and isomerization rate could be enhanced by using of some essential modifiers. Pore size of zeolite is also important parameter which for governs the reaction pathway.

Chao et al., (1996) performed isomerization reaction for n-heptane, n-hexane and n-pentane using Pt-hydrogen mordenite catalysts (Pt/HMOR) and Pt-hydrogen beta catalyst (Pt/HBEA) by various silica-alumina ratios in temperature range of 190-310°C. Dispersion of Pt on the zeolite with particle size of 1.3-2.6nm was found to be good approach. Bigger crystallites sizes (i.e. 5nm) were also observed with the 0.5% Pt/HBEA and 0.5% Pt/HMOR. Pt/HBEA catalyst showed higher activity and selectivity. Mg exchange or dealumination of the Pt/HMOR could enhance the activity and selectivity for the isomerization of in n-pentane.

Soualah et al., (2008) performed hydro isomerization of higher alkane (n-hexadecane, n-decane and n-tetradecane) at 220°C with Pt loaded HBEA (80% conversion), HMCM-22 (65% conversion) and HZSM-5 (70% conversion) zeolites. Pt/HBEA found to be more effective among all the catalysts; however, activity decrease with increase in chain length of alkane and also with the formation of cracked product. These results are in good agreement with the results of Claude and Martens (2000) for small pore zeolite-based catalysts.

In 2006, Li et al. introduced Pd in place of Pt and performed hydro isomerization of n-pentane. They performed n-pentane isomerization at 250°C, H₂/n-pentane ratio (12) and 0.5 MPa pressure in fixed bed reactor using various catalyst viz. Pd/BEA, Pd/ZSM-5,

Pd/USY, Pd/SiO₂ and USY. Pd/BEA showed higher activity than Pd/ZSM-5. Pd showed the similar activity and selectivity. It is clear from the literature, that the optimum hydrogenation activity of metals (Pt/Pd) and Bronsted acid sites activity of the catalyst is responsible for the higher isomerization. In essence, the Bronsted acid sites strength and content of metal determine the activity of the catalyst by controlling the lifetime and concentration of the carbanium ion and C-C bond cleavage ration versus isomerization [Caeiro et al., 2006; Ono, 2003; Martens et al., 2001].

Mao and Saberi (2000) found that incorporation of Al³⁺ species over Pt/H-Y-Zeolite improved the concentration of branched isomers and reduced the production of cracked hydrocarbons. The amount of Al and Pt, determined from the TPD and XRD studies were found to be (1-7 wt. %) and 1wt. % respectively. Small amount of Al (< 2 wt. %) caused positive impact on the conversion of (C₅-C₇) branched isomers. When substituted by Al equal concentration of Zn and Cd, similar results were observed. However, the Al content does not affect the acid site density.

2.1.2.2 Zirconia Based Catalysts

In 2014, Rodrigo et al. reported that Pt sulphated mixed oxides (Pt/ZrO₂-SO₄-La₂O₃) could also isomerize n-hexane at 250°C. A series of mixed oxides (ZrO₂-La₂O₃) was examined to found the effect of sulphate ions introduced by different sources. Supports were synthesized by varying the amount of La₂O₃ and the Pt content was (0.37-0.53 wt. %). Sulphation was carried out using concentrated H₂SO₄ and the sulphate contents was 20 wt. %. Tetragonal phase and Lewis Bronsted acid sites was exit in the catalyst. 1.7 % conversion was obtained at 250°C, atmospheric pressure, with 1.9 WHSV for 180 min using Pt zirconia catalyst. Pt sulphated zirconia with La₂O₃ showed 10.7-67.2%

conversion, when sulphuric acid was used as sulphating agent. The conversion decreased to 1.1-41.5%, when ammonium sulphated was used as sulphating agents. Effect of sulphating agent was observed in term of conversion of n-hexane due to the generation of more active catalyst. Shkurenok et al. (2015) studied Pt/WO₃/ZrO₂ for the isomerization of n-heptane. Concentration of Pt and WO₃ was 1% and 10-35wt. % respectively. The reaction was carried out in tabular FBR (2 cm³, 0.2-0.7 mm fraction) under condition i.e. temperature range 140-220°C, pressure 1.5 MPa and WHSV 1h⁻¹. Prior to the reaction, the catalyst was pretreated under the H₂ flow of 300 ml/min for 3hrs. WO₃ amount was increased from 10-25% wt. % leads to enhanced the Bronsted acid sites which is responsible for activity of catalyst. Further increment in the concentration of the WO₃ up to 35 wt. % reduced the total acidity, which is caused reduction in catalytic activity. The maximum conversion and selectivity obtained was 84% and 71.9 % respectively at 170°C with 25 wt. WO₃.

Adzamic et al. (2013) investigated isomerization reactions using commercial sulphated zirconia catalyst in order to determine the influence of hydrogen/feed ratio, space velocity and temperature on the conversion of n-hexane. 70 % conversion was achieved under the optimum condition i.e hydrogen/ feed ratio of 6, space velocity of 2 h⁻¹ and temperature of 170°C. Obtained results showed that methyl pentanes greatly depend on temperature, unlike di-methyl butane, the temperature range was 130-170°C.

Table 2.1 Various Catalysts for Isomerization of Alkanes

Catalyst	Target	Remarks	References
Ni-La/SZA	Hydro-isomerization of n-pentane	<ul style="list-style-type: none"> ■ The zirconia-alumina mixed oxide prepared by co-precipitation method and sulphation with ammonium sulphate by wet incipient method. ■ The impregnation of Ni(1%) and La(1%) by wet incipient method ■ The activity of catalyst was performed in fixed bed reactor (FBR) at 120-320°C. 2Mpa pressure and 1h⁻¹ WHSV. ■ The converted product analyzed by online gas chromatography FL9790 equipped with FID detector. ■ The highest conversion is 60% at 150°C. 	[Song et al., 2015]
Al/Pt-WZ	Isomerization of n-heptane	<ul style="list-style-type: none"> ■ Alumina doped zirconia material prepared by co-precipitation method and WO₃ impregnated over the zirconia by wet incipient impregnation method, Pt also impregnated by wet incipient impregnation method, the Pt and WO₃ content was 1% and 18% respectively. ■ Reaction was performed in FBR at 200°C, atmospheric pressure, WHSV 0.9h⁻¹, and under H₂ flow 30ml/min. ■ Catalyst was activated at 450°C under airflow for 2hrs then 250°C under H₂ flow for 2 hrs. ■ The product analyzed by online gas chromatograph using HP-PONA equipped by FID detector. The conversion was 70%. 	[Shang et al., 2013]
Pt/ST	Isomerization of n-hexane	<ul style="list-style-type: none"> ■ Titanium hydroxide synthesis by sol-gel method and 0.5M sulphuric acid as sulphating agent. ■ Reaction was performed in flow fixed bed reactor at 350°C, WHSV 0.5h⁻¹ and atmospheric pressure for one hr. 	[Manuel et al., 2014]

		<ul style="list-style-type: none"> ■ Product was analyzed by online gas chromatography Varian 3400 equipped with FID detector. ■ 20 wt. % loading of sulphate ion show higher activity for n-hexane isomerization (38%) and propanol dehydration (21%). 	[Soultanidis et al., 2013]
WZ	Isomerization of n-pentane	<ul style="list-style-type: none"> ■ Catalyst prepared by impregnation of WO₃ by wet incipient technique over the amorphous zirconium hydroxide. The amount of WO₃ over the support was 18.5%. ■ Prepared catalyst characterized by XRD, surface area (93 m²/g), pore volume (0.199 cm³/g) and pyridine FTIR. ■ Reaction carried out in down flow packed bed reactor at 250°C and atmospheric pressure. ■ Results 	
HPA/SiO ₂	Isomerization of n-hexane	<ul style="list-style-type: none"> ■ Prepared phosphotungstic acid, silicotungstic acid, borotungstic acid and impregnates over silica by wet incipient method. ■ Prepared Ni-Ce-O and Pd-Ce-O oxides. And used for isomerization with 20wt% HPW/SiO₂. ■ Ni based catalyst prevent the coking deposition and poisoning the catalyst. ■ 50 wt. % Pd-Ce-O oxide and 50 wt.% of (20wt% HPW/SiO₂). ■ 66% conversion reached at WHSV 0.36h⁻¹. ■ Product evaluated by gas chromatography and the activity order are HPW > HSiW > HBW. 	[Hubaut et al., 2006]
HPA/SiO ₂	Isomerization of n-heptane	<ul style="list-style-type: none"> ■ Prepared phosphotungstic acid, silicotungstic acid, borotungstic acid and impregnates over silica by wet incipient methods. ■ Pt-Ce mixed oxide also prepared by co-precipitation methods. Silica used as support with 321 m²/g surface area. ■ Mixture of Pt-Ce (0.1) with HPA/SiO₂ used for the reaction. 	[Abdelaziz et al., 2008]

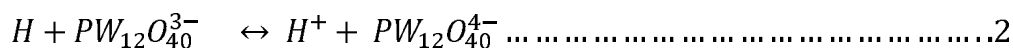
HPA/SiO ₂		<ul style="list-style-type: none"> ■ U type glass fixed bed micro reactor used for the reaction at 498K at atmospheric pressure, the WHSV was 0.40h⁻¹, and hydrogen flow was (21.8ml/h). ■ Product was analyze by gas chromatography SE-30 with an FID detector non-polar capillary column. ■ Conversion was 65.2%, 48.12%, 22.78% with the Pt-Ce/HPW/SiO₂, Pt-Ce/HSiW/SiO₂, Pt-Ce/HBW/SiO₂ respectively. 	
HPA/SiO ₂	Isomerization of n-butane	<ul style="list-style-type: none"> ■ Commercial silica used as support, HPW and HSiW impregnate by wet incipient method. ■ Reaction carried out in flow reactor and batch reactor at 100 to 350°C. ■ More than 97% conversion was observe with silico tungstic acid. ■ Solvent used for impregnation does not so significant effect. ■ At high temperature, the catalysts become less active, probably due to a loss of protons by dehydration. ■ HSiW not only more active but also more selective than HPW. 	[Grinval et al., 2013]
HPA/SiO ₂	Isomerization of n-hexane	<ul style="list-style-type: none"> ■ Prepared all HPAs and impregnated over the silica support. ■ U-type glass FBR used for reaction ■ Catalyst was reduced at 498 K for 4 h under hydrogen with flowing rate of 21.8 mlmin⁻¹ under atmospheric pressure; WHSV was 0.36h⁻¹. The maximum conversion was 27% and the selectivity was 94%. ■ Ce-Ni reduced oxide enhanced the activity and selectivity of catalyst, prevent coke deposition and maintain the structure of silica supported HPA. ■ Conversion order was HPW/SiO₂>HSiW/SiO₂>BW/SiO₂ and the selectivity order was HSiW/SiO₂>HPW/SiO₂>HBW/SiO₂. 	[Kuang et al., 2002]

2.2 VARIOUS STUDIES ON HETEROPOLY ACIDS

Heteropoly acids are complex of protonic acids containing polyoxometalate anions, in which the basic structural units are formed by metal-oxygen octahedral. HPAs are form ionic crystals containing heteropoly anions, ions of H_5O_2^+ , H_3O^+ , H^+ and hydration water. HPAs showed strong Bronsted acidity and the protonation units made up of three types of outer oxygen units [Kozhevnikoe, 1998]. HPAs have discrete and mobile ionic structure; they adsorb a high volume of polar molecules [Misono et al., 1987].

HPAs such as $\text{H}_3\text{PMO}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiMO}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and their metals promoted form are another class of solid acid catalysts having isomerization and other reactions capability. Travers et al. (2001) reported that $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ act as catalyst for n-hexane isomerization using Pt as promoter. Its selectivity for di-branched isomer and the overall catalytic activity was nearly to that of commercial zeolite catalyst. The catalyst was obtained by mixing stoichiometric ratio of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$, Pt was impregnated on it. Fixed bed micro reactor has been used for reaction at temperature range of 180-220°C, pressure of 4bar, and the n-hexane to hydrogen ratio 10. Micro porosity and Bronsted/Lewis acid site ratio was found to be 6.

Isomerization of lower alkanes has been well studied in the presence of 12-tungstophosphoric acid supported on various oxidic matrixes and its cesium, salt at reasonable temperature (around 300°C) [Mishra et al., 2002; Yori et al. 2005]. Ono and coworkers reported that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on Pd/carbon showed 78% conversion and 96% selectivity at 150°C. They explained the formation of hydrogen atoms by the dissociation of Pd into hydrogen, and the formation of proton by the reaction of hydrogen with heteropoly anion, as shown in equations (1) and (2)



Abdelaziz et al., (2007) prepared SiO₂ catalyst using Keggin type heteropolyacids and reduced Pt-Ce oxides for isomerization of n-hexane. These oxides were used alone or in form of mixed type with SiO₂/HPA [Kuang et al., 2002]. These studies indicated that the reduced oxide was responsible for maintaining the structure of SiO₂/HPA and elimination of coke deposition during the reaction.

Guisnet et al. (2000) studied H₃PW₁₂O₄₀ and its acidic cesium salts at 250°C, propane is mainly transformed into butanes through a trimerization, isomerization, cracking process n-butane into Isobutane, propane and pentanes through a dimerization, isomerization, cracking process where as n-hexane into methyl pentanes and 2, 3 dimethyl butane through a monomolecular mechanism. Initially n-butane transformation was much faster than propane transformation in all the samples, rate increases significantly with the changing Cs content i.e. from 25 times with H₃PW₁₂O₄₀ and 350 times with Cs_{2.4}H_{0.6}PW₁₂O₄₀. On the other hand, n-hexane transformation was 2.3 to 7 times faster than n-butane transformation.

Sulphated zirconia was 2-3 times more active than the heteropoly compounds. HMOR-10, showed higher activity for n-hexane transformation and less active for n-butane, especially for propane transformation.

Ivanov et al. (2004) performed the isomerization reaction for n-hexane using Pt-promoted Dawson H₆P₂W₂₁O₇₁ (HP₂W₂₁), H₆P₂W₁₈O₆₂ (HP₂W₁₈) and Keggin type H₃PW₁₂O₄₀ (HPW), H₃PW₁₁Zr (HPW₁₁Zr), HPAs loaded on zirconia. The Pt/HPW/ZrO₂ catalyst shows

high conversion (80%) and selectivity (96-98%) at 190°C. Distorted grafted Keggin ions were active for the catalytic activity confirmed by the DTA and FTIR results. The Pt/HP₂W_n/ZrO₂ or HPW₁₁Zr/ZrO₂ also showed the good activity (80%) at the temperatures 300-400°C than Pt/HPW/ZrO₂.

Pinto et al. (2014) studied mono functional hybrid materials using Keggin type HPAs supported on mesostructured silica for n-hexane isomerization. The heteropolyacids, namely H₃PW₁₂O₄₀ or H₄SiW₁₂O₄₀ were immobilize onto SBA-15 type silica. These hybrid materials showed activity for the gas-phase isomerization of n-hexane. Many reaction parameters and catalyst features were investigated including HPA concentration, contact time, reaction temperature, pressure and nature of the polyanion. Tungstosilicic acid was found to be more selective than tungstophosphoric acid; however the catalyst got deactivated due the coke deposition on acid sites [Morris et al., 2015].

Manuel et al. (2014) studied the effect of HPA on the stability of zirconia (ZrO₂). Tungstophosphoric acid (TPA) was impregnated over the zirconia to evaluate the effect of this acid on the structural and thermal properties of ZrO₂. A stabilizing effect of the crystalline structure was produced by the interaction of HPA anion and zirconia surface and responsible to delay the sintering of the material caused by the thermal treatment, obtaining small crystallite size high specific surface areas. The heteropoly anion coming from tungstophosphoric acid caused a thermal stability effect similar to the obtained with SO₄²⁻, PO₄²⁻ and BO₃³⁻ ions and some metal cations like Y³⁺, La³⁺ and Ce⁴⁺.

2.3 ZIRCONIA MATERIALS

Zirconia is a widely researched material because of its mechanical properties, high thermal stability, and its acidic, basic, reducing and oxidizing surface properties [Nakano et al.,

1979]. Zirconia is a good adsorbent and important transition metal oxide, which is found to be used as a catalyst or as a carrier support material for the catalysts [Tanabe, 1985; Baeza et al., 2008]. Zirconia may exist in three crystalline phases after calcination. At low temperature i.e. less than approximately 1170°C it exists in monoclinic phase. The tetragonal phase becomes the stable phase above about 1170°C and up to 2370°C. Zirconia exists in cubic form up to 2680°C and above that zirconia in liquid form. However, the transition to the monoclinic phase is so rapid that the tetragonal phase cannot be obtained even upon rapidly cooling from a high temperature. The tetragonal phase may be stabilized by the addition of second metal; frequently Y and Ca are used for this purpose. Nevertheless, the tetragonal phase can be generated at much lower temperature than those mentioned above [Blanco et al., 1980].

2.3.1 Sulphated Zirconia (SZ) as Solid Acid Material

SZ is one of the alternatives for the replacement of liquid acid demand for clean technologies [Ahmad et al., 2003; Arata, 1990]. SZ is solid super acid that has been receiving a lot of interest due to its high activity at low temperature for various reactions including isomerization of light alkanes [Song and Sayari, 1996]. Currently the use of SZ is limited in industry for the isomerization of C₅ and C₆ paraffinic cuts to improving the octane number of gasoline. After the pioneering work of Hino et al. (1990), a lot of research has been carried out across the globe to utilize SZ for several acid catalyzed reactions, but its super acidic nature has been a matter of controversy since its discovery [Song and Sayari, 1996].

In 2012, Stojkovic and coworker claimed that the initial activity of sulphated zirconia is high for the isomerization of n-hexane when calcined at low temperature and the activity is low at high calcination temperature due to the partial removal of acid group's content during the thermal treatment. Phosphated zirconia catalysts have low acidity and showed negligible activity despite the positive status of particular property showing the complexity of the active phase/site formation in the catalyst and the conversion was achieved from 1.6-16%. It is obvious that structural benefit is important, but it is not only the major factor, determining catalytic activity. Aboul et al. (2014) used metallic Pt/Re/SZ for the isomerization of n-pentane at lower temperature (20°C). They achieved 100% conversion by impregnation varying amount of Pt/Re over sulphated zirconia.

Table 2.2 Sulphated Zirconia Based Catalyst in Various Conversion Processes

Catalyst	Target	Remarks	References
SZ	Remove of olefins from aromatics	<ul style="list-style-type: none"> ■ The sulphated zirconia catalyst prepared by precipitation method. ■ The optimum temperature was 160°C and 180°C and 30h⁻¹whsv. ■ Reaction was carried out in fixed bed reactor (FBR) and bromine index was used as feed. ■ It is an eco-friendly catalyst as compared to acid treated clay used in industry. ■ A total 80 % aromatics removal was achieved. 	[Yao et al., 2015]
SZ	Transesterification	<ul style="list-style-type: none"> ■ A series of nano-size sulphated zirconia with high surface prepared by one-step liquid- crystal template route. ■ Surface area (36-336m²/g) and the Sulphur content was (1.06-5.33wt %). ■ Soybean oil used for transesterification in a batch reactor and the yield of FAME determined by gas chromatography equipped with FID detector. 	[Sang et al., 2014]
SZ	Synthesis of Benzodiazepines	<ul style="list-style-type: none"> ■ Zirconia catalyst was prepared by precipitation and microwave methods and sulphuric acid (0.1M) used as sulphating agent. ■ Benzodiazepines were synthesized by reacting o-phenylenediamine and few ketones in the presence of catalytic amount of Nanoparticles (52-100nm) 	[Mitesh et al., 2014]

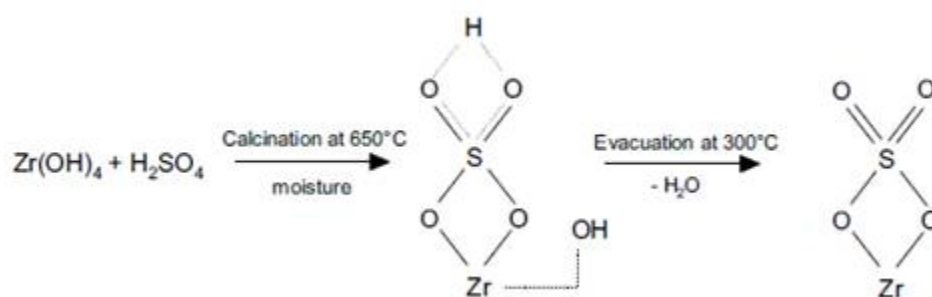
SZ	Dehydration of methanol to dimethyl ether	<ul style="list-style-type: none"> ■ Sulphated zirconia catalyst prepared by wet impregnation of ammonium sulphated over zirconium hydroxide. The sulphate ion content was (1-30%) ■ FBR has been used for reaction and air as carrier gas at 230°C. ■ 10 % of sulphate ion showed highest activity up to 83% and 100% selectivity to dimethyl ether. 	[Abdelaziz et al., 2014]
PdSZ	Isomerization of n-butane	<ul style="list-style-type: none"> ■ Catalyst prepared by impregnation of Pd over the sulphated zirconia. ■ The isomerization activity of the catalyst tested by lab scale flow type fixed bed reactor at temperature 90-290°C and 15-26bar pressure, WHSV was 0.5-5 h⁻¹. ■ Product analyzed by Agilent 6850 GC on DB-1 capillary Column. ■ Molar ratio of H₂/C₄ on the conversion of n-butane studied with a range (0.08-3) at 140°C and 150°C, pressure 25 bar WHSV 1.5h⁻¹, 2h⁻¹ show the highest activity. ■ Reduction of molar ratio from 1-0.1, lead to increases from 32 to 66% and reaches the equilibrium value. ■ At molar ratio > 1, conversion gradually decrease from 33 to 20% 	[Urzhuntsev et al., 2014]
SZ	Complete conversion of hexane-1	<ul style="list-style-type: none"> ■ Sulphated zirconia prepared by precipitation method, PH range (3.98-8.98), calcined at 500-600°C, Sulphur content was (2.8-8.5wt %). Ammonium sulphate used as sulphating agent. ■ Surface area (85m²/g) and total acidity was (.32-.68 mmol/g) ■ 4-100% conversion was found. 	[Vladimir et al., 2013]

SZ	Esterification of myristic	<ul style="list-style-type: none"> ■ Sulphated zirconia prepared by two steps sol-gel method, the final Sulphur content was 3.7 wt. %. ■ A small amount of SZ catalyst (0.125-0.5wt. % to acid) sufficient to conversion (98%) of myristic acid with methanol at 60°C. ■ Conversion decrease as increasing the alkyl chain of alcohol from methanol to butanol and similar conversion achieved with increasing the reaction temperature to 90°C. ■ Catalyst having higher Bronsted acid site successfully reused without loss activity, while catalyst having low Bronsted acid sites decrease the activity (28%) after five cycles. ■ Higher Bronsted acid sites necessary for the better performance and reusable catalyst. 	[Saravanan, et al., 2012]
Pt/SZ	Isomerization-cracking of long chain paraffin's	<ul style="list-style-type: none"> ■ The catalyst characterized by XRD, ICP-AES, FTIR-Py, TPD-Py, TPR and surface area. ■ Commercial sulphated zirconia powder was first converted in cylindrical pellets. ■ Screening the calcination temperature 600-800°C, the calcination temperature was optimized 600°C to produce highest activity and selectivity. ■ The Pt content was 0.5 wt. %. ■ Optimized reaction temperature for n-hexane was 225°C, WHSV 18h⁻¹ and pressure 20 atm for the higher activity and selectivity. ■ Liquid product analyzed by off line Shimadzu GC-8A equipped with FID detector. The highest conversion was 72%. 	[Busto et al., 2011]

Pt/Mo-SZ	Organic synthesis and transformations	<ul style="list-style-type: none"> ■ Impregnation technique was applied for promotion of zirconia. ■ Addition of promoters improved the tetragonal phase of zirconia and the surface acidity. ■ All catalysts showed high catalytic activity for synthesis of coumarines, diphenyl urea, and 1, 5- benzodiazepines, acylation of phenols, alcohols, and amines and protection of carbonyl compounds. 	[Reddy et al., 2005]
SZ	Isomerization of n-butane	<ul style="list-style-type: none"> ■ Sulphated zirconia prepared by zirconium hydroxide with impregnation of ammonium sulphated, Sulphur content was 4%. ■ Surface area of catalyst was 51-169m²/g. ■ The reaction carried out in a FBR, 1g catalyst (30-50mesh) pretreated at 400-700°C for 5 hr. under O₂ flow and the reaction temperature was 115-300°C and pressure 0.1- 6 MPa. ■ Product analyzed by online gas chromatography (Shimadzu, GC-8A IT). ■ Optimum condition of reaction was 215°C and 4.0 Mpa. <p>Lewis acids sites are important for the isomerization of n-butane. Catalyst treated at 500°C shows the higher isomerization activity.</p>	[Funamoto et al., 2005]

Holm and Bailey first described catalytic properties of sulphated zirconia in 1962. SZ was broadly used to catalyze various reactions such as, methanol conversion to hydrocarbon, hydrocarbon isomerization and synthesis of benzodiazepines etc. [Mitesh et al., 2014; Yadav and Nair, 1999]. Incorporation of sulphate ion on the surface makes zirconia highly acidic. Based on Hammett indicator methods, the acid strength of sulphate adsorbed zirconia was found to be 10^4 times more than that 100% sulfuric acid [Arata et al. 1980; Varala et al., 2016]. They claimed that sulphate anion treated with zirconia possesses super acidity with a Hammett acidity $H_0 \leq 16$, which however, varies with the extent and technique of sulphation.

For the preparation of SZ, many preparation techniques have been reported in the literature. Most of them used the classical two steps method [Hini et al., 1979], which consist of the synthesis of an amorphous zirconium hydroxide and its sulphation with sulphuric acid or ammonium sulphate. An alternative is the one-step sol-gel synthesis, to which many of the publications are devoted [Mortera et al., 1997; Li and Gonzalez, 1996]. The structure of SZ as suggested by Kumbhar et al., (1990) is shown in Scheme 2.1.



Scheme 2.1 Structure of Sulphated Zirconia [Kumbhar et al., 1990]

2.3.2 Metal Promoted Sulphated Zirconia (MSZ)

In the year, 1962 Holm and Bailey were first disclosed that Pt containing sulphated-zirconia as an acid catalyst and seems to be able to alkylation of hydrocarbon. A number of transition metals (either as ions and oxides) e.g. (Ti, Mn, Cr, Fe, V, Co, Cu, Ni, Zn, Pd, Ir, Pt, W etc.) have been introduced to SZ and enhanced the activity of catalyst. Incorporation of promoter to the catalyst recipes has significant but ambiguous effect on its activity. For examples addition of promoters, such as Mn and Fe enhance the activity of catalyst at even low temperatures, whereas the addition of Cu and Pt, reduce the deactivation rate. It is not well understood about role of promoters or modifiers and different views exist even for the state of Pt in Pt modified SZ (Pt/SZ) catalyst [Song and Sayari, 1996].

Miao et al. (1996) reported that the doping of SZ with various transition metals, such as Cr or V, could enhance its catalytic activity at moderate temperature in the absence of hydrogen. These catalysts were 2/3 times more active than unpromoted sulphated oxides Fe/Mn/Zr [Jentoft et al., 2004; Moreno et al., 2001; Gao et al., 1998]. The role of the promoters in the presence of hydrogen is still an unsolved issue.

2.3.2.1 Aluminium Promoted Sulphated Zirconia (ASZ)

The addition of p-block metal oxide, such as Al_2O_3 and Ga_2O_3 give an increased steady activity to the catalyst. Many researchers reported that the addition of small amount of Al_2O_3 to SZ system leads to a catalyst with superior activity than the unpromoted SZ [Gao et al., 1998; Miao et al., 1997; Coelho et al., 1995]. The promoting and stabilizing effect of Al on SZ (denoted A and SZ standing for alumina and SZ) was consequently confirmed by other group [Olindo et al., 2000; Moreno et al., 2001]. The remarkable activity and the

stability of Al- promoted catalyst was due to an enhancement in the amount of the weak Bronsted acid sites [Wang et al., 2005].

2.3.2.2 Tin Promoted Sulphated Zirconia (TSZ)

Patel et al. (1997) used tin promoted sulphated zirconia, for the isomerization reaction of n-butane to isobutane, at temperature range of 150-250°C. Addition of Sn to ZrO₂ formed a solid solution, enhanced slightly the weak acid features of ZrO₂, and removed the basic properties of pure SnO₂. SO₄²⁻/SnO₂, was inactive for the isomerization reaction, and 60% less active than for SO₄²⁻/ZrO₂. Sulphation of SnO₂ generated acid sites of moderate strength. The presence of only 10% of SnO₂ in ZrO₂ decreased the reaction rates per SO₄²⁻ by a factor of six for the initial isomerization of n-butane. It is suggested that the presence of Sn decreases the electron acceptor properties of Zr and thus its acid strength. Since the rate per sulphated species of both reactions was decreased in the same ratio. One may consider that on SO₄²⁻/ ZrO₂ and SO₄²⁻/SnO₂-ZrO₂ samples, there was no site of moderate strength which could be able to dehydrate propan-2-ol without isomerizing n-butane.

2.3.2.3 Iron/Cerium Promoted Sulfated Zirconia (FSZ)

The effect of promoter and sulphate concentration on the activity of catalysts has been explained in a limited number of studies. 40 wt. % sulphate content was found to be optimal for catalyst with 1.5 % iron and 0.5% Manganese [Lin and Hsu, 1992]. Whereas as no relationship was observed between activity and sulphate content in iron promoted sulphated zirconia [Hino and Arata, 1996]. Coelho et al. (1995) investigated a series of iron promoted sulphated zirconia catalyst and observed an effect of optimal iron content of 0.2% for sample with 8% nominal sulphate content for similar catalyst. However, under different reaction conditions. Song et al. (1998) reported an optimum activity for 4% iron

without specifically considering the effect of the actual content of the catalysts for the isomerization of n-butane.

2.3.2.4 Platinum Promoted Sulphated Zirconia (Pt/SZ)

It has been reported in several research articles that the presence of a noble metal (Pt) greatly enhances the catalytic performance of SZ and reduced the rate of deactivation [Ebitani et al., 1989; Iglesia et al., 1993]. The role of the addition of Pt on the reactivity of SZ is even less clear. Pt promotion of SZ is suggested to occur by increasing the acidity of SZ [Ebitani et al., 1988; Ebitani et al., 1991; Ebitani et al., 1992], increasing hydride transfer to reaction intermediates [Iglesia et al., 1993], or reducing deactivation of the catalyst by preventing coke formation [Yorin et al., 1995]. It is reported that the Pt to be present on the catalyst surface as metallic Pt, even at calcination temperature as high as 873K and above, these metallic Pt centers play as a role of active sites [Sayari and Dicko, 1994]. On the other hand, Ebitani et al. (1992) explained the role of Pt in enhancing the acidity of Pt/SZ catalysts. They proposed that hydrogen molecules dissociates into hydrogen atoms on Pt sites and then spills over to SZ, where the conversion of an H atoms to H^+ occurs with the formation of H^+ on a Lewis acid site. However, Zhang et al. (1994) reported that the presence of Pt did not affect the distribution of acid sites.

2.3.2.5 Tungsten Promoted Sulphated Zirconia (WSZ)

Kuba et al. (2001) offered a non-catalytic redox process for n-pentane activation using tungsten promoted zirconia. Homolytic C-H bond cleavage reaction involves on WO_x , followed by transferring one-electron resulting surface yield W^{5+} ions, carbenium ions and OH groups. In the catalytic cycle of isomerization, carbenium ion acts as a chain carrier. The C-H bond dissociation could be initiated by the carbenium ion. Thus, the redox

properties of W^{6+} in WO_x are played a key role to initiate the isomerization process. Kourieh et al. (2013) used tungsten-loaded zirconia for catalytic dehydration of fructose and its conversion to 5-hydroxymethylfurfural (5-HMF) by varying loading (1-20 wt. %). Sample showed the amphoteric characteristic when the loading amount was above 10%. The reaction of dehydration of fructose was performed in a batch reactor at 130°C. 66% conversion was achieved with 16.8 wt. % loading.

2.3.3 Double Promoted Sulphated Zirconia

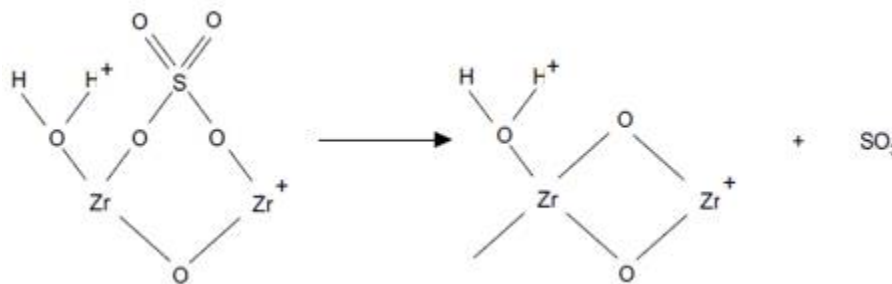
Addition of second promoter such aluminum, iron and gallium on zirconia increase the activity of this doubly promoted zirconia material which shows further upgrading in catalytic activity, selectivity and stability. However, it is unresolved issue until now. Based on the catalytic results and characterization of catalyst following explanations have given on the promotional effect of iron [Lukinskas et al., 2003; Kuba et al., 2003]. (a) Stabilized the platinum particle in a highly dispersed state by ensemble effect, (b) Activated platinum molecules shifted to acid sites by diffusion effect (c) enhanced the reducibility of W^{6+} to W^{5+} in WO_x by redox effect. The combination of these effects may promote the reaction by the promoters. Aluminum promoter and redox effect may explain the action of gallium promoter by an acidity effect [chen et al., 2003, 2004; Wong et al., 2003]. The nature and position of Fe-promoter in the WZ catalyst are of big attention. However, limited studies have been reported on the nature and position of Fe-promoter [Lukinskas et al., 2003; Scheithauer et al., 2000]. Nonetheless, there is a diversity of opinions. Okamoto et al. (2000) explain the metal oxide support interaction in Iron promoted zirconia catalyst by Mossbauer spectroscopy. Recently, carrier et al. (2004) characterized the position of iron promoter in tungsted zirconia (WZ) catalysts and proposed that iron occupied substitutional

position in the first surface layer of zirconia with a distorted octahedral coordination for Fe (III). Unfortunately, no catalytic data was provided to correlate the significance of their characterization results.

2.3.4 Acidity in Sulphated Zirconia

Acidity is an important function of the SZ, which is linked with the presence of SO_4^{2-} because pure zirconia have low acidic properties [Tanabe et al., 1989]. Sulphated zirconia known to act as both Lewis and Bronsted acids (Scheme 2.2) [Corma, 1995]. S=O present in the structure of SO_4^{2-} show, an electron inductive effect, which enhances the electron deficient properties of zirconia atom connected to the sulphate group, thus strengthening the Lewis acidic properties [Kayo et al., 1983].

Addition of anion such as SO_4^{2-} , PO_4^{3-} to modify the structural and catalytic behavior was reported by Yamaguchi et al., 1986. It also believed that these anions enhance the acidity of zirconia and make it a super acid catalyst [Corma, 1995]. Furthermore, the anion disturbs the transition of the crystallographic form of zirconia to another form. This in turn affects the catalytic properties of zirconia.

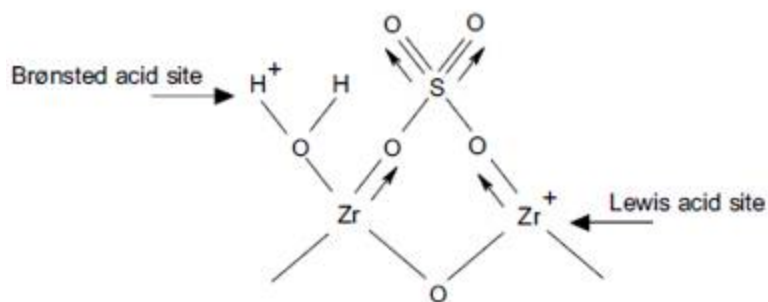


Scheme 2.2 Lewis and Bronsted acid sites in SZ by Davis et al. 1994

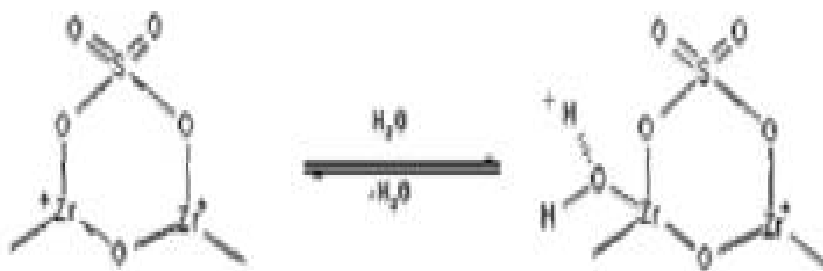
Despite, the presence of both Bronsted and Lewis acid the nature of acid site in the

catalyst is an ambiguous matter of discussion. Various researchers have proposed different model to define the active site of sulphated zirconia.

According to Hino and Arata (1990), surface structure contains sulphate (SO_4) combined with Zr elements in the bridging bidentate state. As a results, Lewis acid site of Zr^{4+} becomes remarkably powerful due to the inductive effect of $\text{S}=\text{O}$ in the complex (Scheme 2.3). Lewis acid site were reported to be converted in Bronsted acid site and vice versa in the presence of water molecules [Hino et al., 1990]. Scheme 2.4.

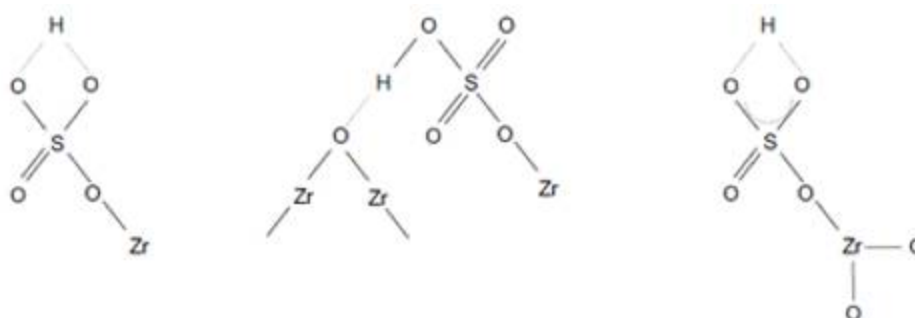


Scheme 2.3 Lewis and Bronsted Acid Site in Sulphated Zirconia [Hino and Arata, 1990]



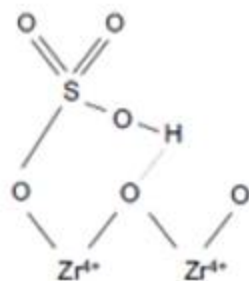
Scheme 2.4 Model for the interconversion of Lewis to Bronsted acid sites [Hino et al., 1990]

Kustov et al. (1994) reported that the terminal ZrOH groups substituted by HSO^4 ions are responsible for the formation of acidic sites in the catalyst. The oxygen atoms of zirconia and sulphate are hydrogen bonded with the protons of the Bronsted acid sites as shown in Scheme 2.5



Scheme 2.5 Three different models for the active site on sulphated zirconia [Kustov et al., 1994]

A surface complex model in which the Bronsted and Lewis acid sites are combined in close proximity is shown in Scheme 2.6. Surface oxygen of zirconia is hydrogen bonded with the OH group of sulphate [Kustov et al. 1994; Adeeva et al. 1995].



Scheme 2.6 Model of the active site in which combine Lewis and Bronsted sites in close proximity by [Adeeva et al., 1995]

2.3.5 Effect of Various Parameters on the Properties of Zirconia (Isomerization Catalyst) Properties

Many parameters have been found to affect the catalytic activity of catalyst. Such as catalyst preparation and pretreatment conditions, sulphur content, total surface area, crystallinity and the concentration of Lewis/Bronsted acid sites [Gonzalez et al., 1997]. Despite extensive research efforts on SZ in the last two decade, our understanding about its preparation, characterization. Active sites and its catalytic mechanism is still not completed.

2.3.5.1 Effect of the Preparation Procedures

Preparation conditions have significant effect on the content of sulphate in zirconia. Tichit et al. (1996) has laid down the stress on the importance of both the pre hydrolysis steps and the conditions in which gelification is obtained in the sol-gel procedure. Morterra et al. (1997) prepared sulphated zirconia catalyst using sol-gel process. The gelification is completed after three weeks using sulphuric acid or with a mixture of acetic acid and sulphuric acid. In such conditions, the content of sulphate around 50% and significantly

exceed the value reported in the literature for sol-gel process. The presence of acetic acid in solution of sulphuric acid is favor to high sulphur content. In all of impregnated samples, the content of sulphur is in the range usually reported by other researcher. Long heating under reflux of the suspension of zirconium hydroxide makes this high reactive and the sulphur content being higher in the heated sample than unheated sample. In addition, the long contact time of the sample with sulphuric acid leads to enhanced the Sulphur content. In conclusion, the use of sulphuric acid for colloidal sol-gel technique leads to a high SO_4^{2-} adsorbent zirconia. The selectivity of zirconia gel has increased when the acetic acid used in the peptization solution comparatively with the peptization carried out only with sulphuric acid.

2.3.5.2 Effect of Sulphating Agent and Precursor

It has been observed that the surface area of the hydrated zirconia significantly affected by presence of precipitating agent such as urea or ammonia [Yamaguchi et al., 1986]. Precipitation with ammonium hydroxide resulting the catalyst with high surface area. The specific surface area of zirconia is lower obtained by sulphating pre-crystallization zirconia than obtained by sulphating amorphous hydrated zirconia and also showed higher activity. The effect of various sulphating agents, such as H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, H_2S , SO_2 and CS_2 have been studied by Sohn and Kim in 1989. It was observed that the sulphur source used for sulphation is responsible for the super acidity in zirconia catalysts. Parera (1992) reported that the higher sulphate concentrations are responsible for higher surface area, obtained by sulphuric acid than ammonium sulphate. The amount of the Bronsted and Lewis acid sites mainly depends on the SO_4^{2-} surface concentration and their nature [Mortera et al., 1993]. The low concentration loading on the zirconia, when only SO_4^{2-} located in the

crystallography, the defective sites are present; there is no Bronsted acid site observed while a good amount of Lewis acid sites formed.

2.3.5.3 Effect of Activation Atmosphere

The atmosphere in which the sample is activated affect the density and the strength of the acid sites. When the activation done in presence of air leads to a slow reduction in the sulphur content. This reduction occurs in same time with a slow reduction in surface area and an enhancement in the acid strength. Therefore, one can suppose that the presence of air catalyzes the nucleation of the superficial sulphate groups.

Calcination of the zirconia under vacuum lower 450°C affects the covalency of the surface sulphates, thus altering the Bronsted: Lewis (B:L) [Morterra et al., 1993]. This effect is depicted in Table 2.3 [Zhang et al., 1994]. Also calcination above 450°C under vacuum, affect the surface sulphate concentration [Bensitel et al., 1988; Morterra et al., 1994]. Some of the sulphates decompose to form SO₂ as suggested through the following pathway [Chen et al., 1993].

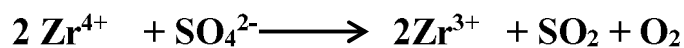


Table 2.3 Percentage of Bronsted type ^a Acid Sites

Treatment		Bronsted sites (% of total)			
Temperature (°C)		0.0wt%	1.17wt%	9.87wt.%	13.6wt.%
Pre	Post	SO ₄ ²⁻	SO ₄ ²⁻	SO ₄ ²⁻	SO ₄ ²⁻
100	100	0	47	98	98 (97) ^c
100	100	0	49	93	95 (89) ^c
400	400	42	-(45) ^b	63	68 (70) ^c
400	400	46	-(45) ^b	80	83 (64) ^c

^a All samples were calcined at 625°C, prior to the pretreatment in situ at 100°C exposed to air or 400°C prior to pyridine adsorption; ^b SO₄²⁻ content of the precursor before 650°C calcination; ^c Numbers in parentheses are for pt. containing material.

2.3.5.4 Effect of Thermal Treatment (Calcination) temperature

The catalytic activity of SZ catalyst are strongly affected by the pre-calcination and calcination temperature. The super acidic SZ can be produced by maintaining pre-calcination temperature between 100-250°C and the calcination temperature upon sulphation is to be kept below 480°C. Pre-calcination temperature beyond 480°C, leads to a reduction in super acidity. In fact, the highly active catalyst for the isomerization can be produced with the optimization of both the concentration of sulphuric acid and calcination temperature [Nascimento et al., 1993; Bikmetova et al. 2016]. For example, 873 K and 0.3 N sulphuric acid or 650°C and 0.5 N sulfuric acid, produce good activities. Table 2.4 shows the effect of calcination temperature on the acidity of SZ [Guo et al., 1994].

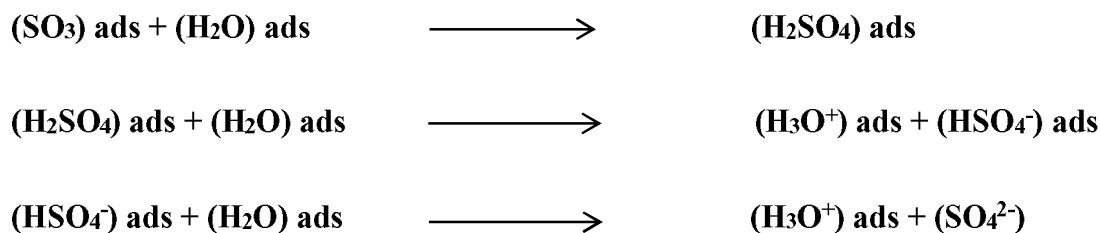
Table 2.4 Effect of calcination temperature on acid strength before and after sulphation

Pre-calcination temperature of Zirconia (°C)	Calcination temperature of SZ (°C)	Acid Strength, H₀
200	650	≥ - 16.12
400	650	≥ - 16.12
500	650	≥ - 13.75
600	650	≥ - 12.70
800	650	> - 12.70
110	200	> - 12.70
110	400	≤ - 12.70
110	650	≤ - 16.12
110	800	≤ - 12.70

2.3.5.5 Effect of Water of Hydration

Some authors have reported that the existence of minor amount of water absorbed on the surface of catalyst enhanced the activity of these catalysts [Tanabe et al., 1990]. On the other hand, some of the researchers reported that even very low concentrations of water is harmful for the activity of catalyst [Wen et al., 1990]. Still there are some other reports, which revealed that the small amount of water has no effect on the activity of catalyst [Parera, 1992].

Some researchers [Morterra et. al., 1993] have explained the nature of adsorbed water. They used a combine TGA/DTA/MS technique and suggested that the adsorbed water on the catalyst transforms some of the strong Lewis acid sites into Bronsted sites but these acid sites are not participate in the reaction. Morterra et al. (1994) reported that SO_4^{2-} on the surface of SZ exhibit a powerful covalent character at moderate to high degree of dehydration. However, partial dehydration initially import a less covalent character on the surface SO_4^{2-} . Higher volume of water transform these SO_4^{2-} to the ionic form. Therefore, amount of water dose result in the conversion of Bronsted sites, which are not catalytically active, at the expense of the strongest Lewis center. Thus, this clarifies the loss of activity on dehydration of these catalysts. The initial activity could be recover by repeating the activation steps. Babou et al. (1995) explained that there is a reversible effect of water on SO_4^{2-} surface, which expected to be in equilibrium with surface water. The mechanism suggested by them is as follows:



The super acidity formation on the surface of sulphated zirconia has been a matter of discussion. Minor volumes of water tend to balance the Lewis and Bronsted acid sites in some specific reactions, leading to much higher activity.

2.3.5.6 Effect of Sulphur Concentration on the Catalytic Activity

Sulphur can also have positive effects on activity of catalyst in metal catalyzed reactions. The Bronsted acid site formation on sulphated alumina identified by pyridine adsorption

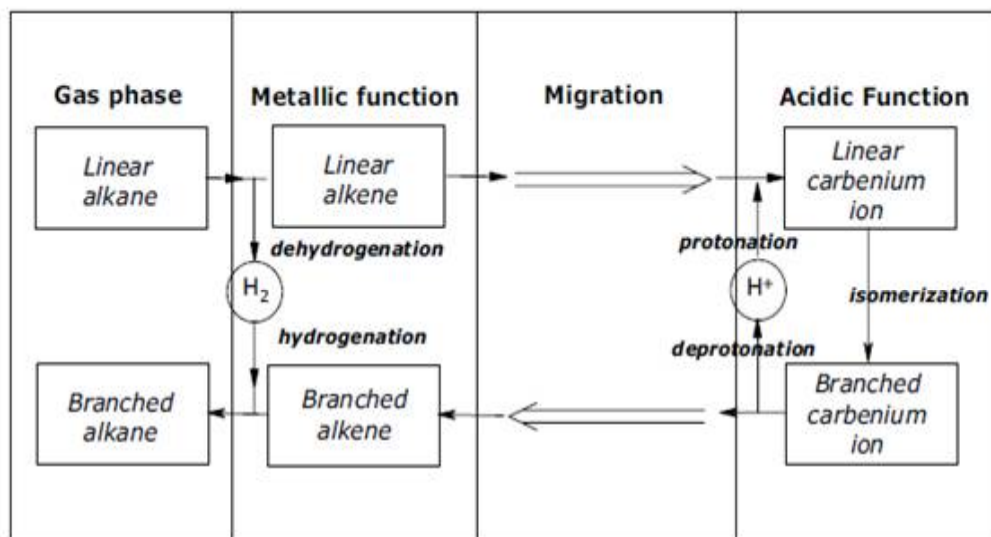
and ascribed due to Al-O-SO₃H species [Auroux et al., 2003; Castillo et al., 2003]. In contrast to sulphated zirconia, the sulphated alumina persisted only weak acid site strength [Gawthrope et al., 2004].

2.4 MECHANISM OF ISOMERIZATION

The reaction pathway for alkane isomerization could be described by two key mechanisms i.e. bi-functional and acid catalysis mechanism. This classification corresponds to the two main types of catalysts as discussed below.

2.4.1 Bi-Functional Mechanism

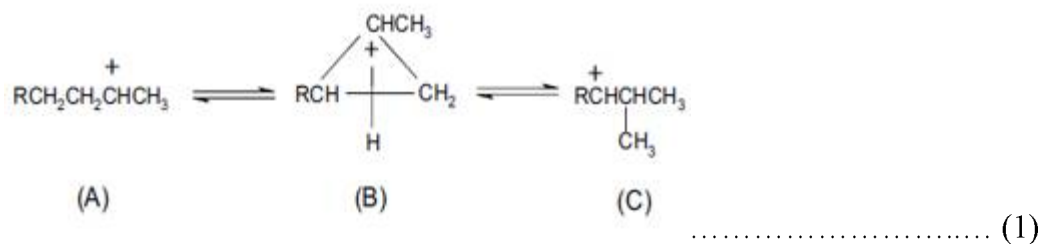
Bi-functional catalysts having acid/base and metal function show high activity, selectivity, and stability for isomerization reactions [Guisnet, 2003]. One of the most noticeable applications for such type's bi-functional catalysts is the isomerization alkanes. It is extensively accepted that it involves of three main individual reaction steps. In the first step, the alkane dehydrogenated to the alkene on the metal [Weisz, 1962]. The alkene adsorbs on Bronsted acid sites and formed an alkoxy group (carbenium ion), which isomerized and finally desorbs (Scheme 2.7). At the last, the iso-olefin hydrogenated to the iso-alkane on the metal. The balance between the acidic and metallic function determines which of the reactions i.e. hydrogenation/dehydrogenation or C-C bond rearrangement, is rate determining and controls activity, selectivity and stability [Guisnet, 2003; Ravi Shankar et al., 1996; Hollo et al., 2002].



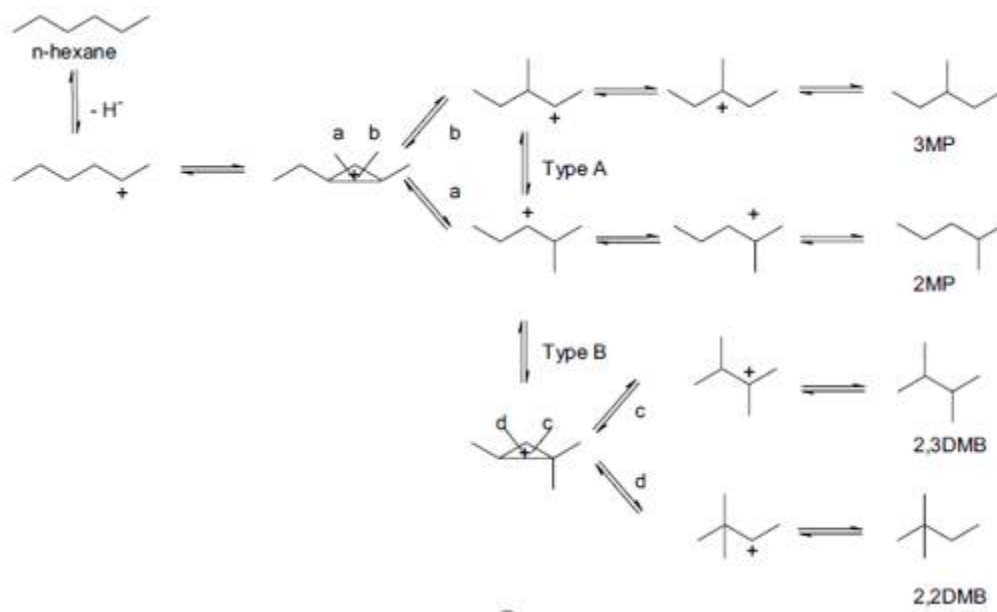
Scheme 2.7 The Classical Bi-Functional Mechanism

2.4.2 Acid Catalyzed Mechanism

The isomerization of alkanes can be observed as a chain reaction, which involves initiation, propagation and termination steps. In acidic mechanism, the formation of carbenium ion in the initiation step over a Brønsted acid site take place. Alkane is protonated by a Brønsted acid site and formed carbonium ions, the penta-coordinated carbonium ion split of dihydrogen and forms the carbenium ion [Duchet et al., 2001]. The propagation step are responsible for the skeletal rearrangement of the carbenium ion and the chain transfer reaction. The skeletal rearrangement includes an intermediate species i.e. the protonated cyclopropane ring. This is a delocalized electron deficient structure with much lower energy than the primary carbenium ion. This pathway is known as monomolecular mechanism.



The isomerization of alkanes with more than five carbon atoms follow the monomolecular mechanism as shown in equation (1) since the species, C then is secondary carbenium ion [Risch et al., 2000]. The acid catalyzed mechanism for isomerization of n-hexane is shown in Scheme 2.8.



Scheme 2.8 Acid catalyzed mechanism for n-hexane isomerization [Bouiti et al., 2003]

2.5 CATALYST DEACTIVATION

Catalyst deactivation is the loss of activity or its selectivity on time on stream. Although, sulphated zirconia is a very strong catalyst for alkane isomerization, but deactivation occurs very fast [Fottinger, 2004]. One of the most common reason is the formation of coke or

oligomers at the active sites [Gonzalez, 1997]. The degree of deactivation has been found to be related with the amount of alkenes, which is coke precursors, in the feed. Many ways of catalyst deactivation such as: formation of coke, phase transformation, sintering, and volatilization of active component, pore blockage, and poisoning. The causes of deactivation are three-fold: chemical, mechanical and thermal.

- I. Poisoning
- II. Fouling
- III. Thermal degradation
- IV. Volatilization of active components
- V. Vapor –solid and solid-solid reaction
- VI. Attrition/ Cursing

As (I), (IV), and (V) are chemical in nature while (II) and (VI) are mechanical. Davis et al. (1994) reported that the sulphate ions stabilize the zirconia surface favoring the formation of the tetragonal crystalline phase at calcination temperature above 540°C, and this is responsible for the enhancing the activity of SZ. Several suggestions have been made in order to explain the deactivation process, among them:

- 1) Formation of hydrocarbon surface deposits (coke) [Vera et al., 1999; Kim et al., 2000].
- 2) Surface reduction ($Zr^{4+} \rightarrow Zr^{3+}$) by the reaction of hydrocarbon [Vera et al., 1999].
- 3) Reduction of the oxidation state of sulphur in the sulphate from S^{6+} to lower oxidation state resulting in acid strength [Li and Gondez, 1997].
- 4) The transformation of the catalytically active surface tetragonal phase into the inactive monoclinic phase [Li and Stair, 1996].
- 5) Surface poisoning by water molecules [Comelli et al., 1995].

- 6) Possible removal of sulfur as H₂S [Flore and Horvat, 1995].
- 7) Changes in the surface acidity [Gonzalez et al., 1997].

2.6 SCOPE OF THE WORK

The importance of the work is upgrading light naphtha fraction (C₄-C₆) by the isomerization process and has increased due to a growing demand for premium gasoline grades and more restricted regulations on gasoline composition. The enhancement of the octane number by isomerization offers the possibility of meeting the required standard demands without the excessive addition of blended octane boosters like MTBE, oxygenates or aromatics. The production of high-octane fuel requires highly active, selective, stable and harmless catalysts. The aim of this thesis is to provide a substantial knowledge about the isomerization catalyst and reaction proceeding on a bi-functional sulphated zirconia and heteropoly acid based catalyst and a way of optimizing isomerization activity and selectivity.

2.7 RESEARCH OBJECTIVES

Isomerization of light petroleum stream is a subject of current research interest. The reaction is favored at low temperature. Therefore, a catalyst that can work effectively at low temperature is being developed for the last more than five decades. The design of such type of a catalyst recipe is very critical in terms of acidity, acid site density and many other parameters, so that side reactions such as cracking can be minimized and favored isomerization. So in this context the development of a suitable catalyst by replacing conventional liquid acid which will be environmental friendly is a subject of current research & the theme objective of this work.

The aim of proposed research work is to develop an effective novel catalyst, which can work at low temperature for the isomerization of light alkanes and the specific objectives of this study are as follow:

- I. Development of zirconia based suitable matrix and characterized these matrixes for their physico-chemical properties.
- II. Impregnation of Tungstophosphoric acid as active component on the developed matrix to understand the critical concentration of TPA on the isomerization activity.
- III. Preparation of various catalyst recipes using different methods such as Hydrothermal synthesis, Precipitation method, Sol-gel method, Microwave synthesis are the main techniques used for preparation.
- IV. Characterization of the catalysts recipe using classical methods and sophisticated state of art tool such as XRD, SEM, FTIR, TGA, N₂ adsorption/desorption, TPD/TPR to know these properties.
- V. Evaluation of prepared catalysts activity and selectivity for isomerization of lower alkanes model hydrocarbons i.e. nC₆.
- VI. Optimization of reaction parameters, reaction temperature, pretreatment temperature, Weight hourly space velocity (WHSV) for optimum isomerization activity using selected best catalyst.
- VII. Evaluation of converted product using Gas Chromatography Technique.