

CHAPTER 5

PERFORMANCE AND EVALUATION OF CATALYST FOR N- HEXANE ISOMERIZATION

The performance of all the synthesized catalysts was tested in fixed bed micro reactor (FBR) using n-hexane as model hydrocarbon. Catalyst evaluation was done in three steps: (i) pretreatment of catalyst (reduction) in the presence of hydrogen; (ii) isomerization in the presence of n-hexane (iii) evaluation of the product using gas chromatography.

5.1 CATALYTIC ACTIVITIES FOR N-HEXANE ISOMERIZATION

The prepared catalysts were tested in the fixed bed micro reactor for evaluating their performance for the isomerization of lower hydrocarbons. n-hexane was used as feed i.e. model hydrocarbon for the reaction. Pretreatment temperature, pretreatment time, carrier gas flow, reaction temperature and weight hourly space velocities (WHSV) were chosen as the prime variables to control the reaction. All the variables were studied on the same catalyst sample. The product was analyzed using gas chromatography and detailed hydrocarbon analysis (DHA).

5.1.1 Effect of Pretreatment Temperature

Prior to any reaction, pretreatment (reduction) of the catalyst is important for its high activity. The optimized pretreatment temperature is desirable for maximum conversion of the feed into the product, after which increasing temperature causes further reduction of metal and matrix then the desired form [Larsen et al., 1996; Oliveira et al., 2015; Guemini et al., 2008]. The prepared samples were pretreated (reduced) at three different

temperatures, i.e. 200, 250 and 350°C in the flow of hydrogen to bring the catalyst in its reduced state. The pretreatment temperature for the isomerization of n-hexane could be optimized at 250°C [Khalid et al., 2011].

5.1.2 Effect of Pretreatment Time

Pretreatment time was studied as a variable from 2-12 hrs at 250°C under hydrogen flow. Results indicated maximum conversion, when the catalyst was pretreated for 5hrs.

5.1.3 Effect of Hydrogen Flow

Pretreatment of catalyst was done at 250°C under variable flow of hydrogen, i.e. 50ml/hr, 100 ml/hr, 200 ml/hr and 250 ml/hr. Results indicated maximum conversion at 200ml/hr. flow of hydrogen gas.

5.1.4 Effect of Reaction Temperature

After pretreating the catalyst under hydrogen flow (200 ml/hr) at 250°C for 5hrs the feed was brought in contact with the catalyst at various temperatures ranging from 150-250°C. The maximum conversion was shown at 225°C. Ivanov et al., (2004) performed the experiment on HPA based catalyst for the isomerization of n-hexane at temperature ranging from 160-300°C, maximum conversion was observed at 240°C. Song and other researcher also studied the effect of temperature on the activity of catalyst [Song et al., 2015; Wang et al., 2009; Dhar et al., 2017]. Bayati and coworker conduct experiment at reaction temperature from 150-350°C and the maximum conversion was obtained at 180-220°C, below 180°C no conversion was observed. Further increment in reaction temperature results in a slow rise in the conversion [Bayati et al., 2016]. At high

temperature, the catalysts become less active, probably due to loss of protons through dehydration [Grinerval et al., 2013].

5.1.5 Effect of Weight Hourly Space Velocity (WHSV)

Weight hourly space velocity (WHSV) is an important parameter for the activity of catalysts. It is defined as the weight of feed running per unit weight of the catalyst per hour. Since weight of the catalyst, feed in to the reactor is always same, so any difference in flow of liquid per hour will disturb the WHSV. Space velocity is inverse to the contact time; i.e. for how much time the liquid is in contact with the catalyst under the conditions of operation. Quantity of the catalyst feed in to the reactor is a known parameter. For simplification of calculation, take 1 kg= 1000 g of catalyst. If 1000 gm of water is flowing through the reactor per hour, then $\text{WHSV} = \frac{1000 \text{ gm of feed}}{1000 \text{ gm of catalyst in the reactor}} = 1.0$ i.e. WHSV is 1.0

Mostly, the density of hydrocarbons is less than 1.0

For Naphtha, density is 0.76 gm/cm^3

For Calculating WHSV 1.0, using naphtha as feedstock instead of water, then 760 gm of naphtha flows over 1000 gm of catalyst ($\frac{760 \text{ gm}}{0.76 \text{ densities}} = 1 \text{ cm}^3$ per hour Naphtha). So, $\text{WHSV} = 1$

WHSV is an important parameter, which affects the catalytic activity. After pretreating the catalyst at 250°C under hydrogen flow (200ml/min) for 5hrs, the feed was brought in contact with the catalyst at various WHSV ranging from 1-1.5 h^{-1} . Maximum conversion was achieved at 1.25/hr. Bayati and coworker study the effect of WHSV in the range of 0.1-0.8 h^{-1} using Pt/ zeolite catalyst and the maximum conversion was

achieved at 0.27h^{-1} [Bayati et al., 2016]. Other researchers also studied the effect of WHSV ranging from $1.64\text{-}3.28\text{ h}^{-1}$ with increase in WHSV, the conversion decreased while the selectivity of isomer increased [Talebi et al., 2008].

5.1.6 Effect of Loading of Tungstophosphoric acid (TPA)

The effect of loading concentration of TPA over the sulphated zirconia was studied by varying the amount of TPA from 10-60 wt. % over the sulphated zirconia. 55% loading of TPA showed the maximum conversion. With increase in amount of TPA, conversion also increased due to enhancement in acidic sites. However, conversion decreases after a certain limit due to the physical adsorption of TPA on the surface when chemically adsorbed monolayer was fully formed (Fig 5.13) [Jin et al 2006; Sawant et al., 2007]. The other reason for lower performance can be due to reduction of active surface blocked by three-dimensional TPA clusters.

5.2 CATALYST ACTIVITY

The catalytic activity of all the catalyst prepared by different routes were tested in a fixed bed micro reactor (FBR). Fixed bed reactor are frequently used for study of solid catalyst. It is a cylindrical tube filled with catalyst particles, where reactants flow through the bed and being converted into products. The thermowell is placed in the center of the reactor to support the catalyst particles. Another layer of inert ceramic beads is placed on the catalyst bed for the uniform distribution of the feed. The catalyst may have multiple configurations including: one large bed, several horizontal beds, several parallel packed tubes, and multiple beds in their own shells. These different configurations may be adapted depending on the need to maintain temperature control

within the system. Ideal plug flow behavior is the main advantages of using fixed bed reactor, low cost maintenance and decrease the loss due to wear and attrition. Heat managing is an important feature in designing the FBR. Improper heat transfer may also result in thermal degradation of catalyst. However, these conditions occurs in large fixed bed reactor and in highly endothermic or exothermic reactions, when difficulty to temperature control. It is very difficult to regenerate or replace of catalyst in the fixed bed reactor without shutdown the process, high-pressure drop due to the coke deposition occurred by plugging of bed is another major disadvantage of reactor. Use of small beads or pellet of catalysts is also responsible for high-pressure drop. However, the limitation of pore diffusion increased by increasing pellets size. The main advantages of fixed bed system are the simplicity of equipment and relatively inexpensive. The pellets may be spherical, cylindrical, or randomly shaped pellets ranging from 0.25 cm to 1.0 cm in diameter. The flow of a fixed bed reactor is kept typically downward. This type of reactor has been used for isomerization of alkanes by many researcher since long [Song et al., 2015; Chem et al., 2006; Chem et al., 2004; Barrera et al., 2012; Talebi et al., 2008]. The flow scheme of reactor is shows in Fig 5.1.

Simplicity in handling and easily available FBR have been choosed for isomerization reaction. Usually, FBR are operated either with gas phase reactions or in a trickle-bed mode, whereby a liquid reactant trickles through the bed from top to bottom. Here, fixed bed reactors with reactants in the liquid phase is used.

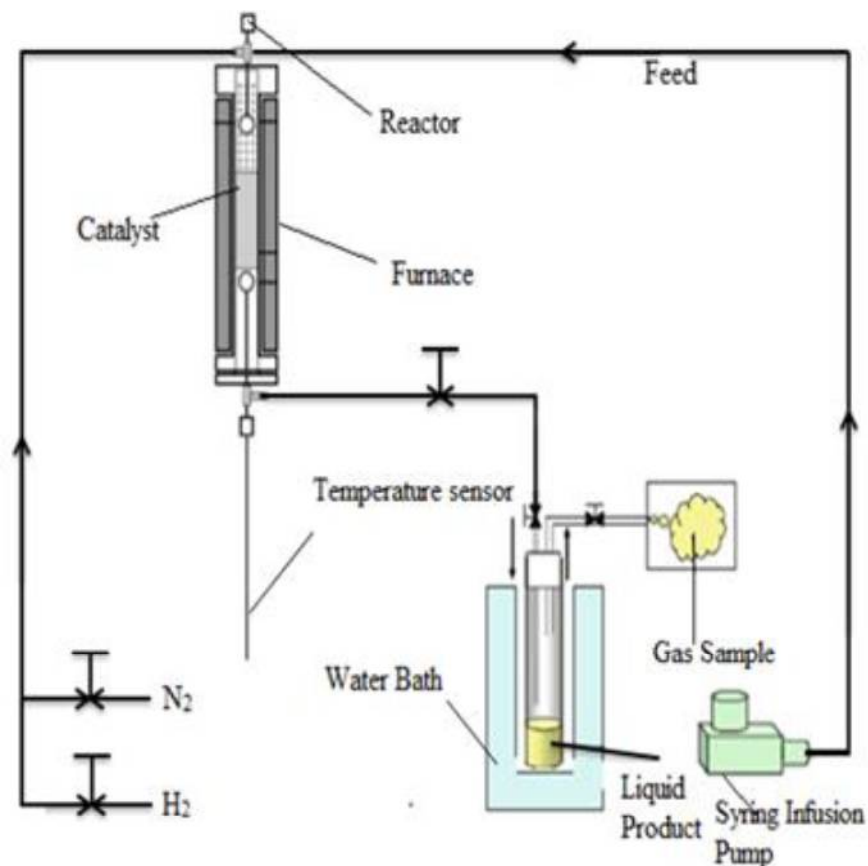


Figure 5. 1 Flow scheme of fixed bed reactor

FBR for industrial synthesis are generally operated in a stationary mode (i.e., under constant operating conditions) over prolonged production runs. However, un-stationary operation is unavoidable during startup and shutdown as well as during load change or in the case of automatic control actions. In particular, FBR with a strongly exothermic reaction sometime exhibits surprising dynamic behavior, which can affect operational safety. Catalytic activity of the synthesized catalysts were tested for the isomerization of n-hexane in FBR as shown in Fig 5.3. The reactor made by stainless steel tube with the following specifications:

The reactor has been design by myself and fabricated by J.S Enterprises, Dehradun

Specification of reactor: Stainless steel tube

Length: 400 mm

Outer diameter: 8 mm

Inner diameter: 6 mm

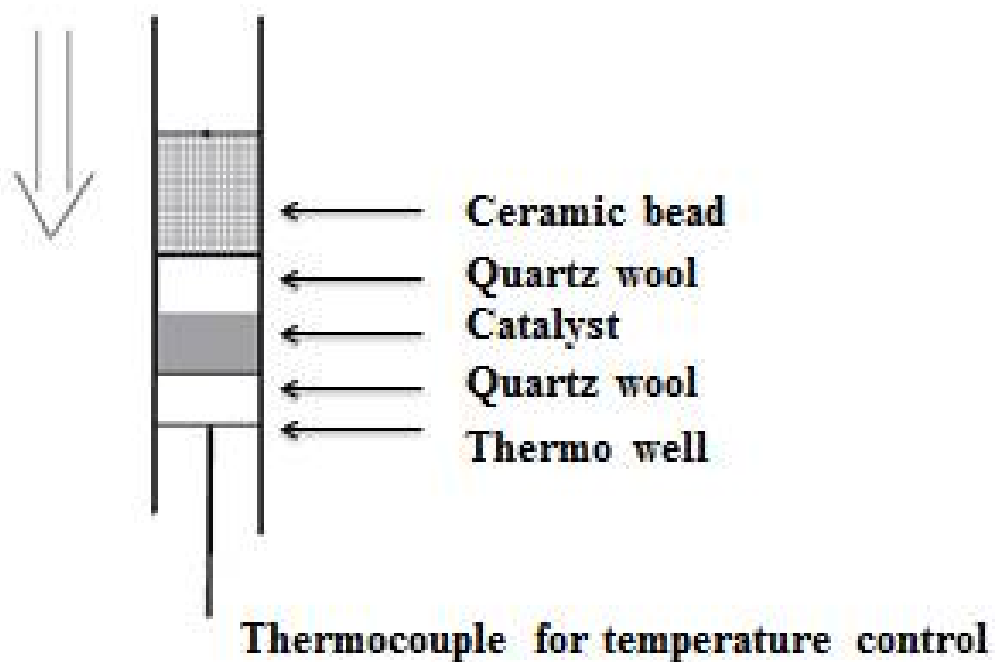


Figure 5. 2 Cross section for the catalyst bed



Figure 5. 3 Fixed bed reactor used for isomerization

5.2.1 Gas chromatography analysis:

The isomerized product was analyzed by off line Gas Chromatography (Nucon 5700 series) using capillary column. Carrier gas (nitrogen) flow rate was at 5ml/min and capillary column dimensions [Serial no. 5061] are 30 m length, 0.25 mm ID and 0.27 mm outer diameter). Injector temperature, column temperature and flame ionized detector (FID) temperature was 240°C, 40°C and 240°C respectively.

Boiling point of n-hexane is 68.7°C. Various isomers of n-hexane, i.e. 3-methyl pentane, 2-methyl pentane (isohexane), 2,3-dimethyl butane and 2,2-dimethyl butane (neohexane) possess lower boiling points than n-hexane, i.e. 63.3, 60.3, 58.0 and 49.7°C respectively. Based upon the concept of separation of compounds by gas chromatography using non-polar column, low boiling components appear first with less retention time. It is important to note that based on retention time in (Fig 5.13), it can be validated that the product obtained contains a mixture of isomers of n-hexane, as all the important peaks in the gas chromatograms appears before the base peak of n-hexane.

5.2.2 Detailed Hydrocarbon Analyzer (DHA)

Detailed Hydrocarbon Analysis (DHA) is a preferred gas chromatography based technique to determine the hydrocarbon steams composition of individual hydrocarbons. The technique is based on the separation of individual hydrocarbon components by utilizing ultra-high resolution capillary gas chromatography and reference component databases based on retention time. DHA supports petroleum refining and production clients helping them optimize production, meet regulatory requirements and enhance profitability (ASTM D7169). The converted product analyzed by DHA (GC Agilent 7890A). Carrier gas (helium) flow rate was at 3ml/min and column dimensions (102m X 250um X 0.5um).

Injector temperature, column temperature and flame ionized detector (FID) temperature was 250°C, 35°C and 250°C respectively carrier gas helium 3ml/min (Fig 5.14).

The performance and evaluation of the catalyst prepared by different methods and the reaction conditions are discussed in following heading

5.2.3 Catalytic Activity of Catalyst

The catalytic activity of catalyst prepared by hydrothermal synthesis are as follow:

5.2.3.1 Catalyst name: SZTW10

Pretreatment condition:

Catalyst particle Size: 1-2 mm

Catalyst weight: 300 mg

Bed height: 40 mm

H₂ Flow: 200ml/min

Total Pressure: 1Bar

Temperature; 250°C for 5hrs

Reaction condition:

Reaction temperature: 150-250°C

WHSV: 1-1.5hr⁻¹

Pressure: Atmospheric pressure

The isomerization reaction was performed in a FBR using n- hexane as model hydrocarbon. 300 mg of catalyst was placed in the middle supported on quartz wool of the steel tube micro reactor (stainless steel, Length= 400mm, ID= 6mm, OD= 8mm) as shown

in Fig 5.2, operating isothermally at atmospheric pressure with a bed height 40mm and cover with the quartz wool. Another layer of ceramics beads was put on the top of quartz wool to fill the dead volume and uniform distribution of feed in the reactor. The thermocouple was placed at the bottom of the catalyst bed. The reactor pathway was tested for leakage by flushing it with hydrogen gas at 5-bar pressure for 5hrs. Prior to the reaction, the catalyst was reduced under the hydrogen flow (50-200 mlmin⁻¹) at 250°C with the rate 10°C min⁻¹ for 5hrs. H₂ was metered by mass flow meter. The pressure in the reactor was controlled by a back pressure regulator. The reactor was cooled down to temperature below the reaction temperature (150-250°C). Then, pure n-hexane (99.99%) was feed in to the reactor via a syringe infusion pump. The feed was fed to maintain WHSV of 1-1.5hr⁻¹. The first aliquot of product was collected after 30 minutes from the start of reaction and then after collected at every 15 min of interval in a liquid collecting vessel. The reaction time (time on stream) was 120 min and the product was evaluated by gas chromatography, where few selected samples were also tested for DHA.

The activity of the catalyst SZTW10 for the isomerization of n-hexane is summarized in Table 5.1, 5.2, 5.3 under variable WHSVs (Fig 5.4, 5.5, 5.6). Data indicates although is very low but maximum conversion was obtained at WHSV 1.25h⁻¹ in 30 minutes (Fig 5.7). The maximum time on stream was 120 min, after this deactivation of catalyst occurred due to coking deposition. The deactivation of catalysts may occurred due to change in sulphur oxidation state, loss of sulphur, deposition of hydrocarbon fragments or transformation of the crystalline structure [Zalewski et al., 1999; Vazquez et al., 2010].

Table 5.1 Reaction conditions Vs conversion for SZTW10 Catalyst

Reaction time (min)	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120
WHSV (h⁻¹)	1							1							1							1							1						
TPA(10%)	1							1							1							1							1						
Temperature (°C)	150							175							200							225							250						
Pressure	Atmospheric							Atmospheric							Atmospheric							Atmospheric							Atmospheric						
Conversion (%)	1	1	0	0	0	0	0	2	0.5	0	0	0	0	0	2	1	0	0	0	0	0	3	3	1	0	0	0	0	2	2	0	0	0	0	0

Table 5.2 Reaction conditions Vs conversion for SZTW10 Catalyst

Reaction time (min)	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120
WHSV (h⁻¹)	1.25							1.25							1.25							1.25							1.25						
TPA(10%)	1.25							1.25							1.25							1.25							1.25						
Temperature (°C)	150							175							200							225							250						
Pressure	Atmospheric							Atmospheric							Atmospheric							Atmospheric							Atmospheric						
Conversion (%)	2	1	0	0	0	0	0	3	2	0	0	0	0	0	4	2	0	0	0	0	0	6	4	2	0	0	0	0	4	2	1	0	0	0	0

Table 5.3 Reaction conditions Vs conversion for SZTW10 Catalyst

Reaction time (min)	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120
WHSV (h⁻¹)	1.5							1.5							1.5							1.5							1.5						
TPA(10%)	1.5							1.5							1.5							1.5							1.5						
Temperature (°C)	150							175							200							225							250						
Pressure	Atmospheric							Atmospheric							Atmospheric							Atmospheric							Atmospheric						
Conversion (%)	2	1	0	0	0	0	0	3	2	0	0	0	0	0	3	2	0	0	0	0	0	4	3	2	0	0	0	0	3	3	1	0	0	0	0

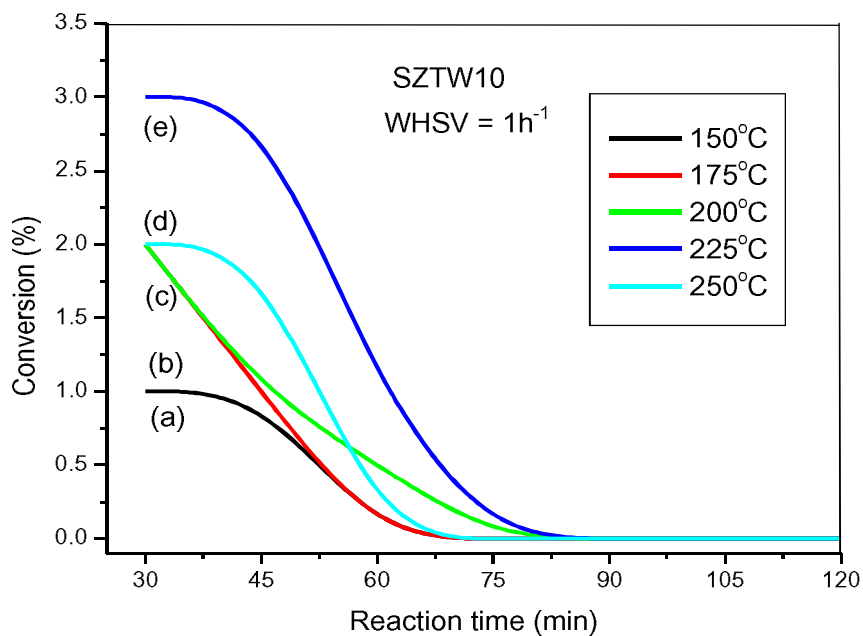


Figure 5. 4 Reaction time Vs Conversion; (a) 150°C (b) 175°C (c) 200°C (d) 225°C (e) 250°C

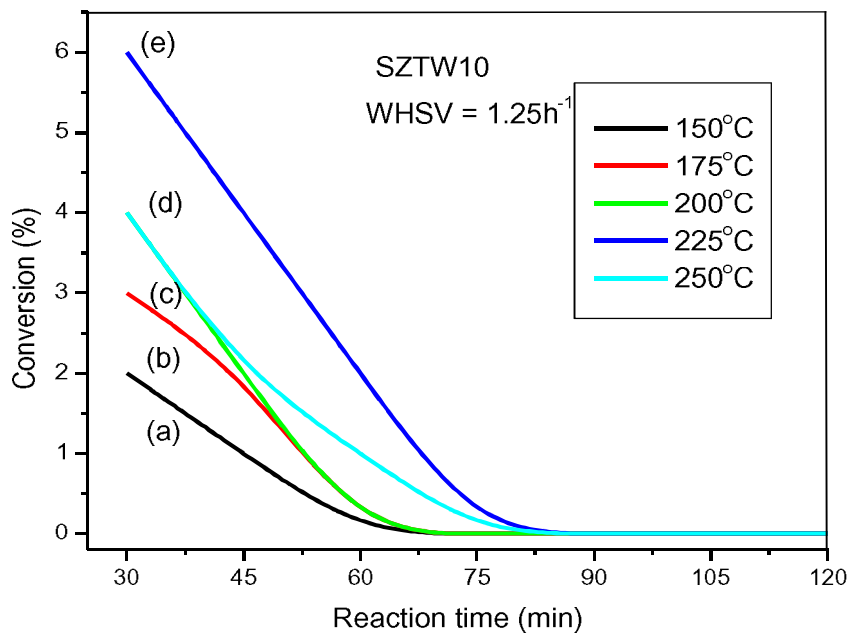


Figure 5. 5 Reaction time Vs Conversion; (a) 150°C (b) 175°C (c) 200°C (d) 225°C (e) 250°C

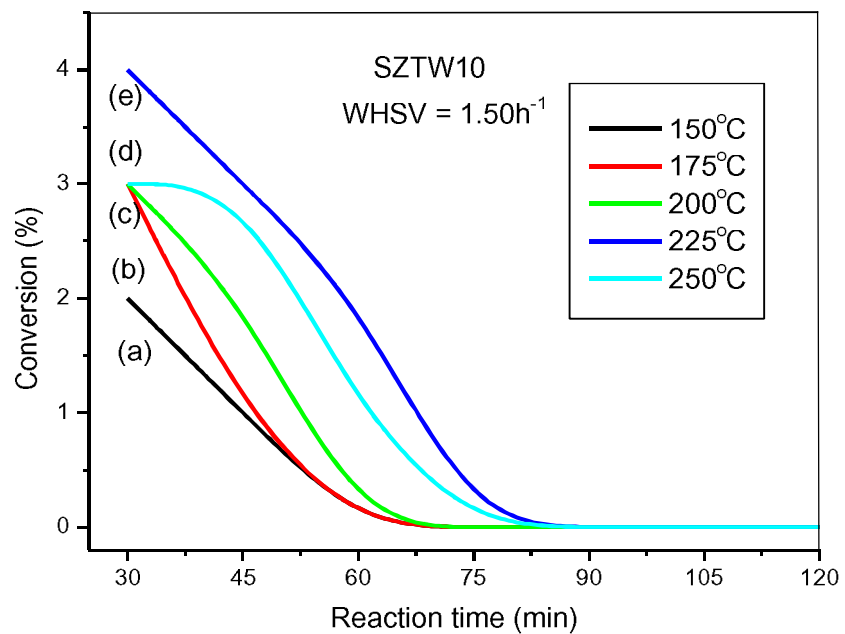


Figure 5. 6 Reaction time Vs Conversion; (a) 150°C (b) 175°C (c) 200°C (d) 225°C (e) 250°C

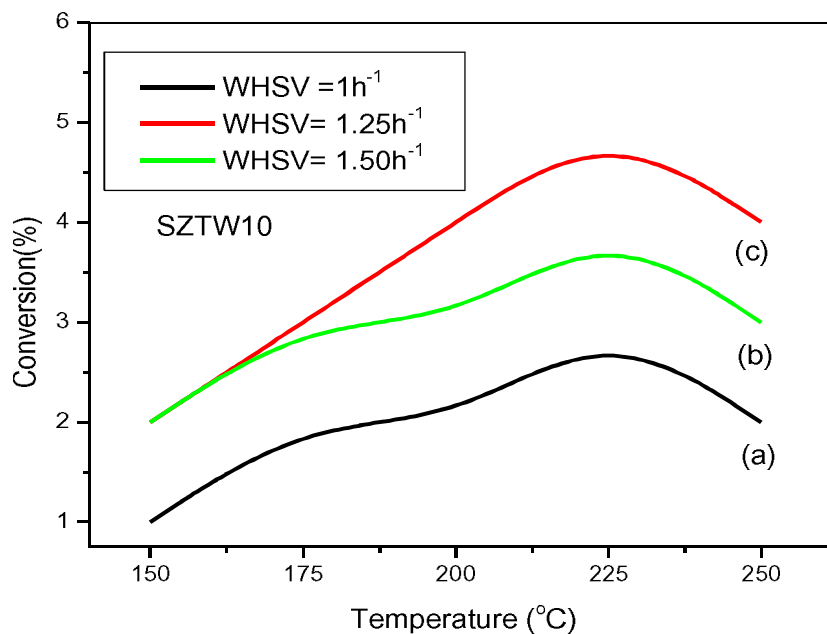


Figure 5. 7 Effect of temperature on the activity of SZTW10 (a) WHSV= 1 (b) WHSV= 1.50 (c) WHSV=1.25

5.2.3.2 Catalyst name: SZTW20

The catalytic activity of SZTW20 catalyst was tested for isomerization reaction at the same conditions as for SZTW10 catalyst. Similar pattern of conversion was obtained for this catalyst also. The conversion increases with increasing in loading amount of TPA and conversion also increases as temperature increased up to 225°C. Further, increment in temperature leads to reduce the conversion as shown in Table 5.4-5.6 (Fig 5.8-5.10). The maximum conversion of 13 % was achieved at 225°C with WHSV 1.25h⁻¹ (Fig 5.11).

Using these two catalysts the reaction conditions were optimized for testing the activity of other catalysts. Therefore the activity of other catalysts, 225°C temperature and 1.25 h⁻¹ WHSV was fixed for performing the experiments.

Table 5.4 Reaction conditions Vs conversion for SZTW20 Catalyst

Reaction time (min)	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120
WHSV (h ⁻¹)	1							1							1							1							1						
TPA(20%)	1							1							1							1							1						
Temperature (°C)	150							175							200							225							250						
Pressure	Atmospheric							Atmospheric							Atmospheric							Atmospheric							Atmospheric						
Conversion (%)	3	1	1	0	0	0	0	3	2	1	0	0	0	0	5	3	1	0	0	0	0	7	5	2	2	1	0	0	6	4	2	1	0	0	0

Table 5.5 Reaction conditions Vs conversion for SZTW20 Catalyst

Reaction time (min)	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120
WHSV (h ⁻¹)	1.25							1.25							1.25							1.25							1.25						
TPA(20%)	1.25							1.25							1.25							1.25							1.25						
Temperature (°C)	150							175							200							225							250						
Pressure	Atmospheric							Atmospheric							Atmospheric							Atmospheric							Atmospheric						
Conversion (%)	4	2	2	1	0.5	0	0	4	2	2	1	0	0	0	10	5	5	3	1	1	0	13	11	9	6	2	2	0	11	7	3	2	0	0	0

Table 5.6 Reaction conditions Vs conversion for SZTW20 Catalyst

Reaction time (min)	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120	30	45	60	75	90	105	120
WHSV (h ⁻¹)	1.5							1.5							1.5							1.5							1.5						
TPA(20%)	1.5							1.5							1.5							1.5							1.5						
Temperature (°C)	150							175							200							225							250						
Pressure	Atmospheric							Atmospheric							Atmospheric							Atmospheric							Atmospheric						
Conversion (%)	4	2	1	1	0.5	0	0	5	1	2	1	0	0	0	8	4	4	3	1	0	0	11	9	7	5	1	0	0	9	5	2	2	1	0	0

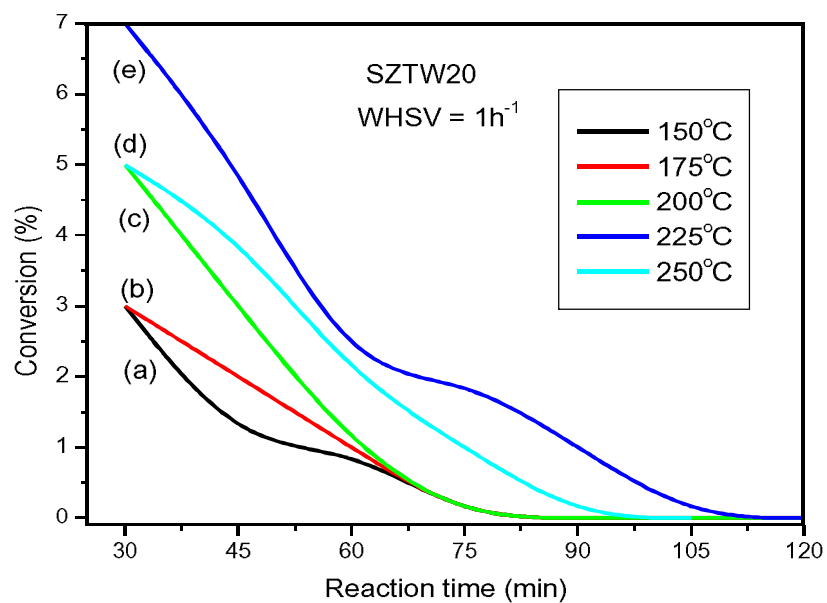


Figure 5. 8 Reaction time vs Conversion; (a) 150°C (b) 175°C (c) 200°C (d) 225°C (e) 250°C

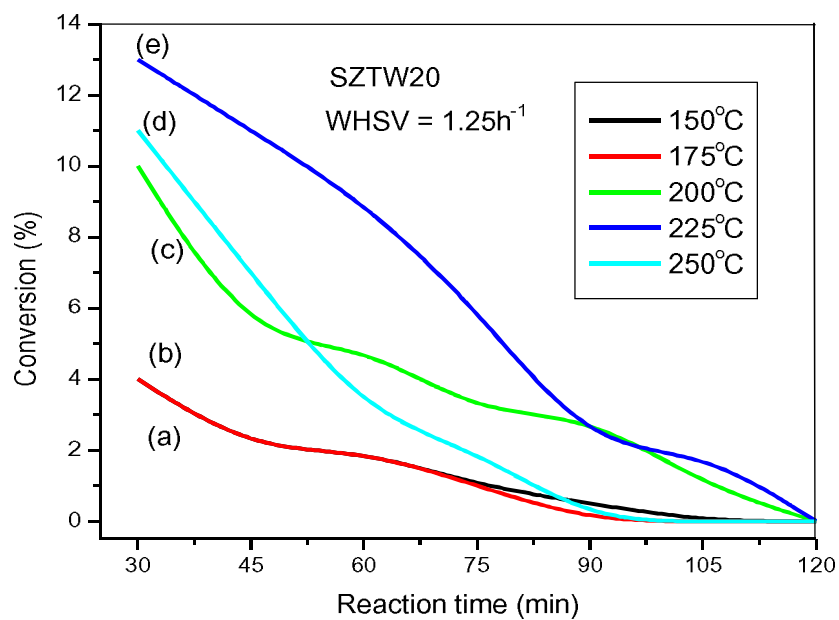


Figure 5. 9 Reaction time Vs Conversion; (a) 150°C (b) 175°C (c) 200°C (d) 225°C (e) 250°C

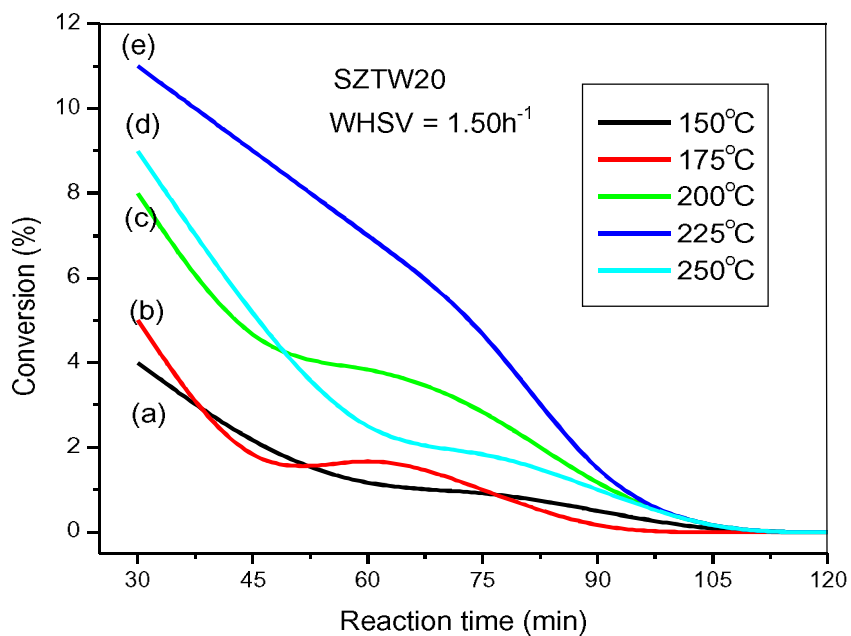


Figure 5.10 Reaction time Vs Conversion; (a) 150°C (b) 175°C (c) 200°C (d) 225°C (e) 250°C

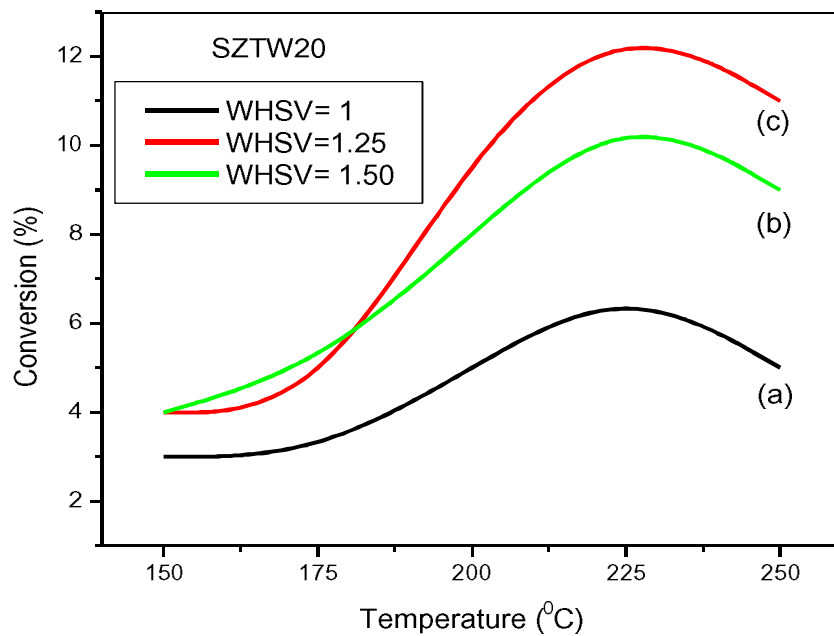


Figure 5.11 Effect of temperature on activity of SZTW20, (a) WHSV= 1 (b) WHSV= 1.50 (c) WHSV=1.25

5.2.3.3 Catalyst name: SZTW30

Table 5.7 Reaction conditions Vs conversion for SZTW30

SZTW30	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	20	10	6	2	2	0.5	0

5.2.3.4 Catalyst name: SZTW40

Table 5.8 Reaction conditions Vs conversion for SZTW40

SZTW40	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	45	25	10	6	2	0.5	0

5.2.3.5 Catalyst name: SZTW50

Table 5.9 Reaction conditions Vs conversion for SZTW50

SZTW50	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	58	35	10	6	2	1	0

5.2.3.6 Catalyst name: SZTW55

Table 5.10 Reaction conditions Vs conversion for SZTW55

SZTW55	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	69	55	30	10	2	0.5	0.5

5.2.3.7 Catalyst name: SZTW60

Table 5.11 Reaction conditions Vs conversion for SZTW60

SZTW60	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	55	40	25	6	2	0.5	0

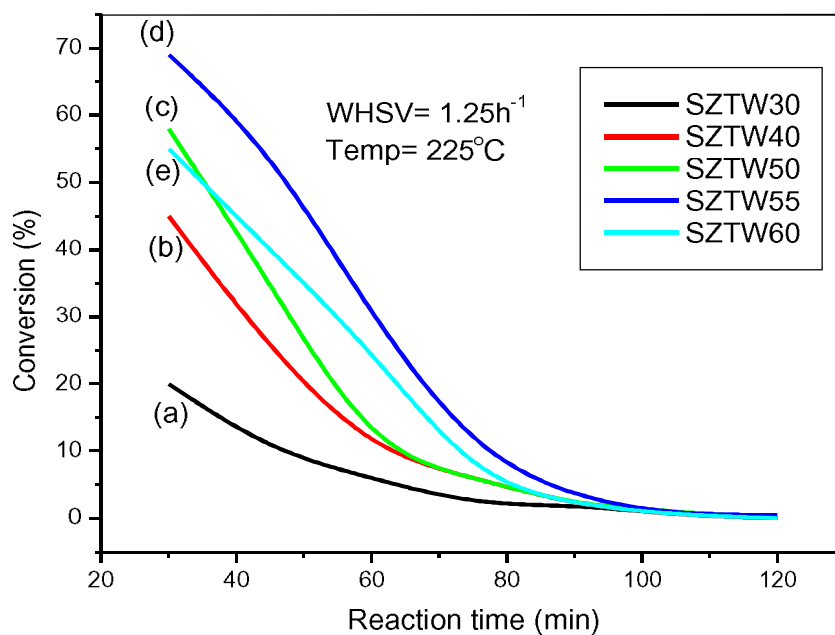
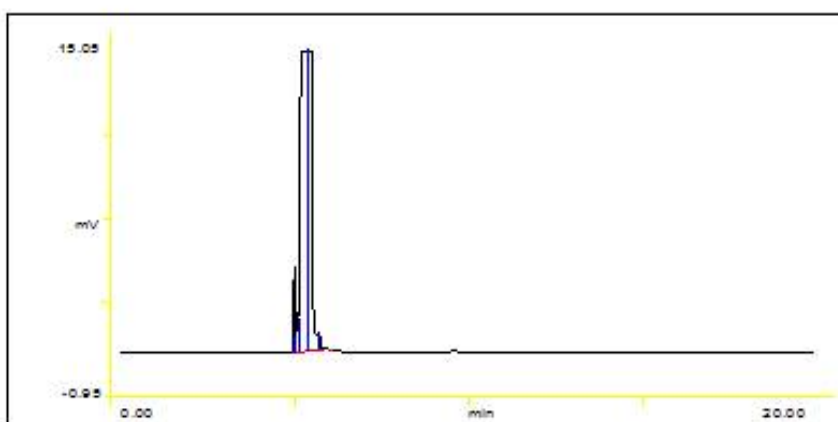


Figure 5.12 Reaction time Vs Conversion, comparison for all prepared (SZTW30-60) catalysts

REPORT

Sample Name:
 Data File: D:\NuChrom\Amit\SZ TE 2.DAT
 Method File: referenciod.MET
 Detector: FID. System: GC
 Date: 4 Feb 2016 Time: 17:15:40
 Run: ch1: 0
 Type of Analysis: Percent On Area
 Report printed on : 9/2/2016 at : 17:40:24

Pl. Width	Peak Thrsh.	Area Rej.	Hr.Rej.	Time Scale
4	30	5	4	20.0



No.	R.T.	Area	Area %	Pl Ty	Comp Name
1	5.01	138709	0.1672	BV	
2	5.10	69011	0.0832	VV	
3	5.37	57488009	69.3156	VV	
4	5.48	25205739	30.3916	VV	
5	5.73	33657	0.0406	VB	
6	5.99	1440	0.0017	BB	
		82936564	100.0000		

Figure 5. 13 Gas chromatogram of SZTW55

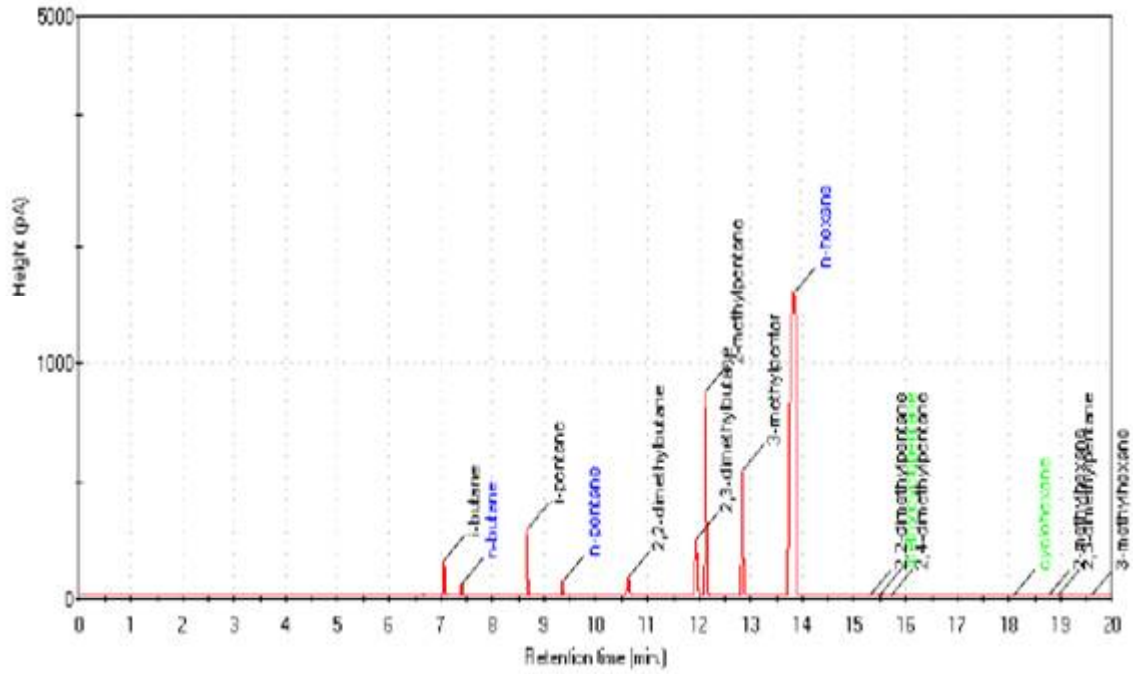


Figure 5. 14 DHA profile SZTW55

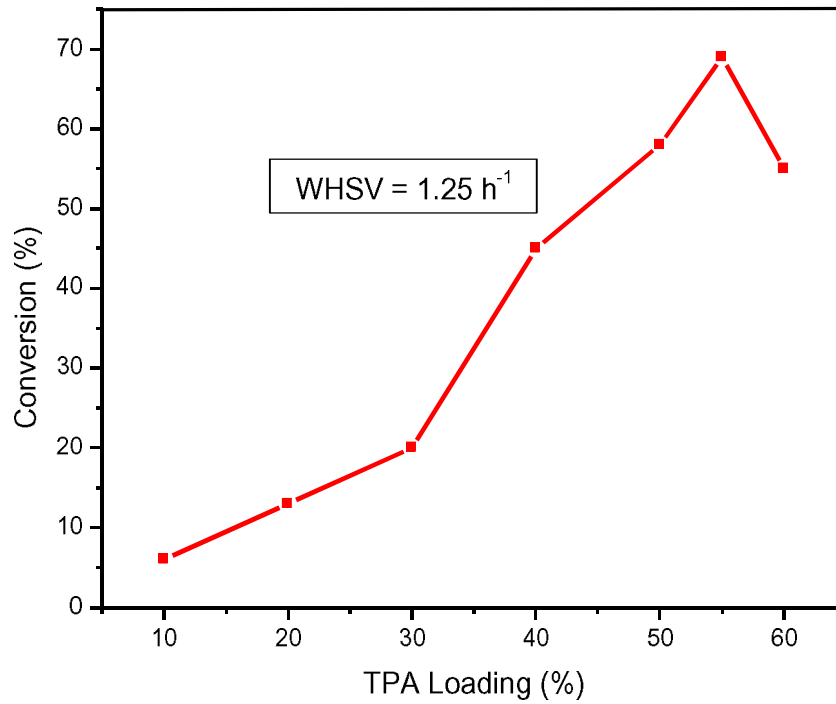


Figure 5. 15 TPA loading Vs Conversion for SZTW10-60

5.2.4 Catalytic Activity of SZMW55

After optimizing all reaction parameters and TPA loading over the sulphated zirconia support it was found that, the 55% loading showed the higher conversion (69%). Then 55% loading of TPA was chosen as optimum loading.

Activity of the catalyst prepared by microwave synthesis was tested for the isomerization of n-hexane with the same fixed bed micro reactor by maintaining the same reaction conditions. The maximum conversion achieved was 40% as shown in Table 5.12 (Fig 5.16) and the DHA profile for isomers is show in Fig 5.17.

Table 5.12 Reaction conditions Vs conversion for SZMW55

SZMW55	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹) TPA (55%)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	40	25	10	6	2	0.5	0

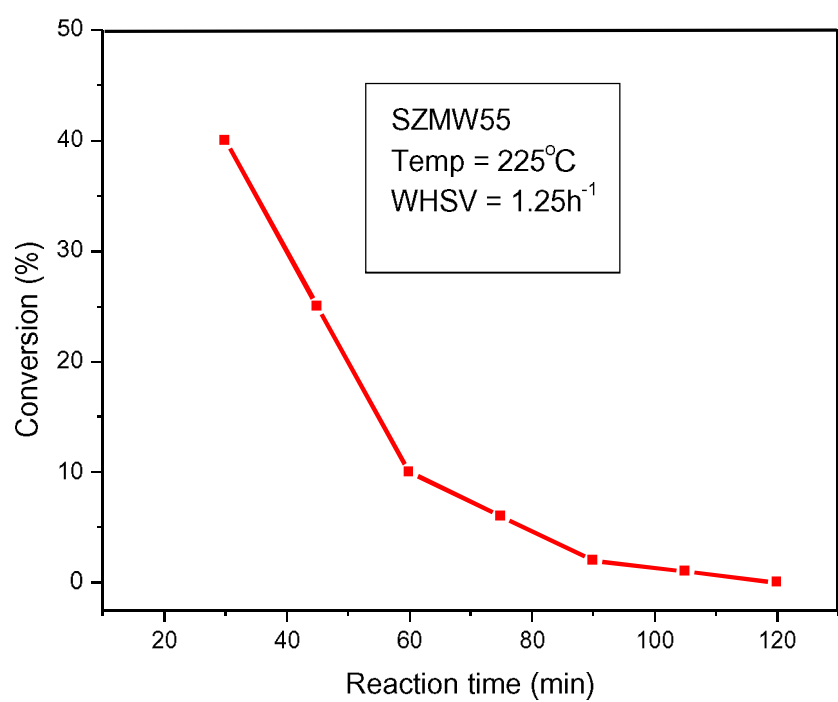


Figure 5. 16 Reaction time Vs Conversion SZMW55

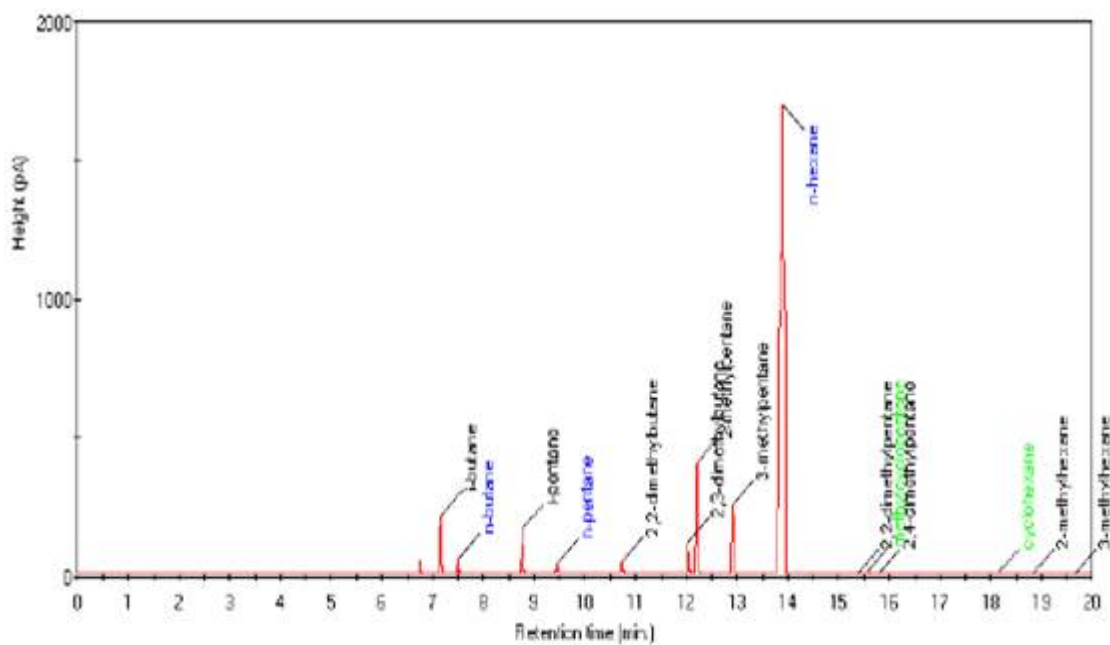


Figure 5. 17 DHA profile of SZMW55

5.2.5 Catalytic Activity of SZPW55

SZPW55 showed maximum conversion of 45%, shown in Table 5.13 Fig (5.18) and the DHA profile is shown in Fig 5.19.

Table 5.13 Reaction conditions Vs conversion for SZPW55

SZPW55	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹) TPA (55%)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	45	30	18	8	5	1	0

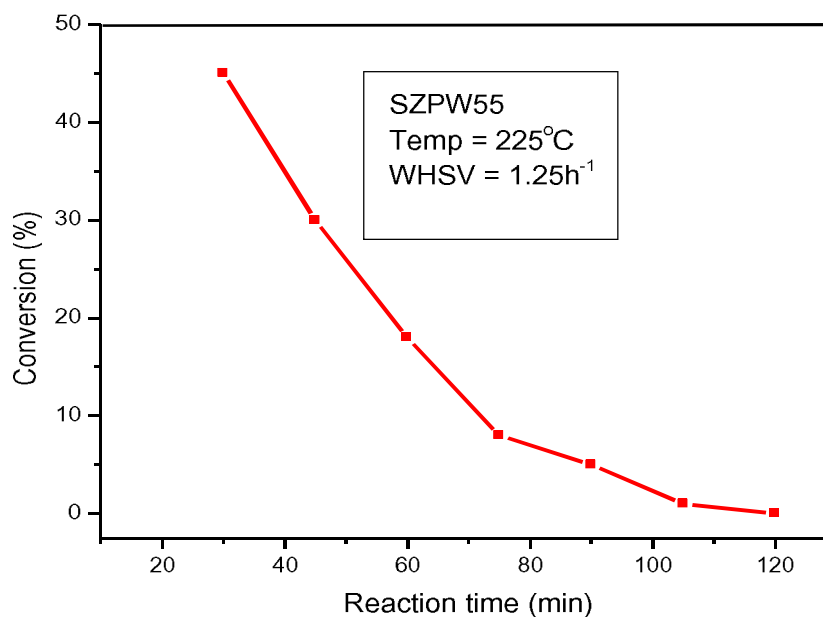


Figure 5. 18 Reaction time Vs conversion for SZPW55

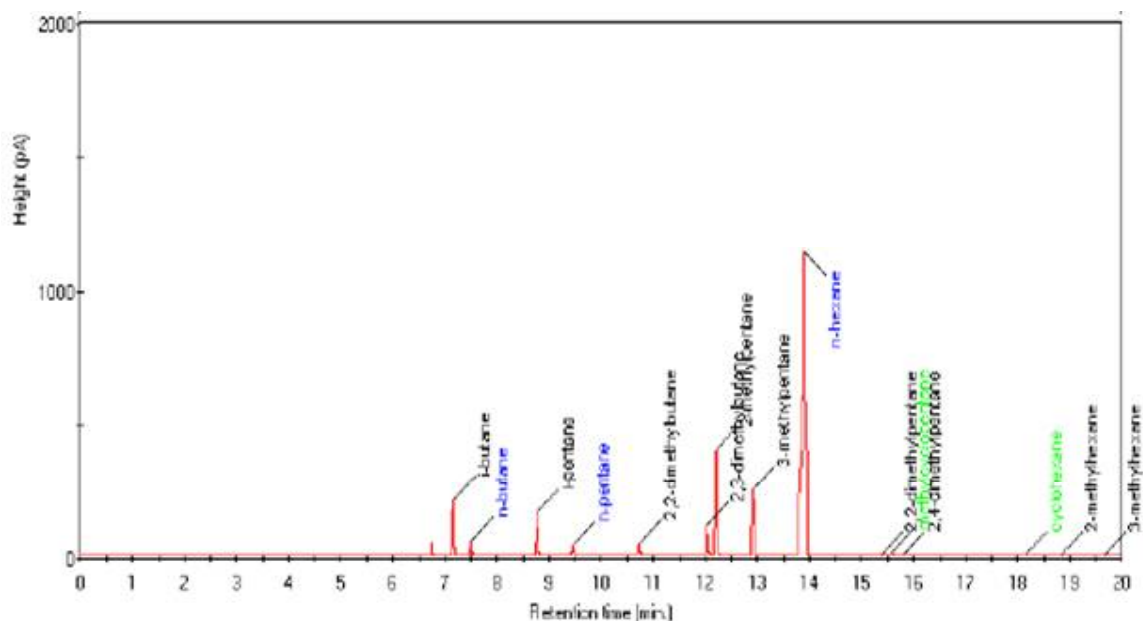


Figure 5. 19 DHA profile of SZPW55

5.2.6 Catalytic Activity of SZGW55

SZGW55 showed maximum conversion of 30% as shown in Table 5.14 Fig (5.20) and the DHA profile is shown in Fig 5.22.

Table 5.14 Reaction conditions Vs conversion for SZGW55

SZGW55	Reaction time (min)	30	45	60	75	90	105	120
	WHSV (h⁻¹) TPA (55%)	1.25						
	Temperature (°C)	225						
	Pressure	Atmospheric						
	Conversion (%)	30	15	10	5	2	1	0.5

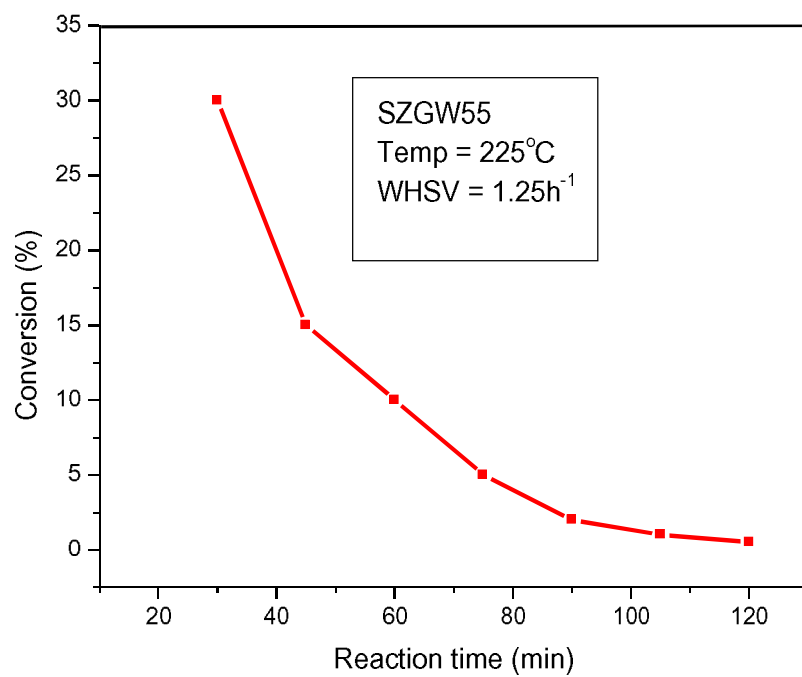


Figure 5. 20 Reaction time Vs Conversion for SZGW55

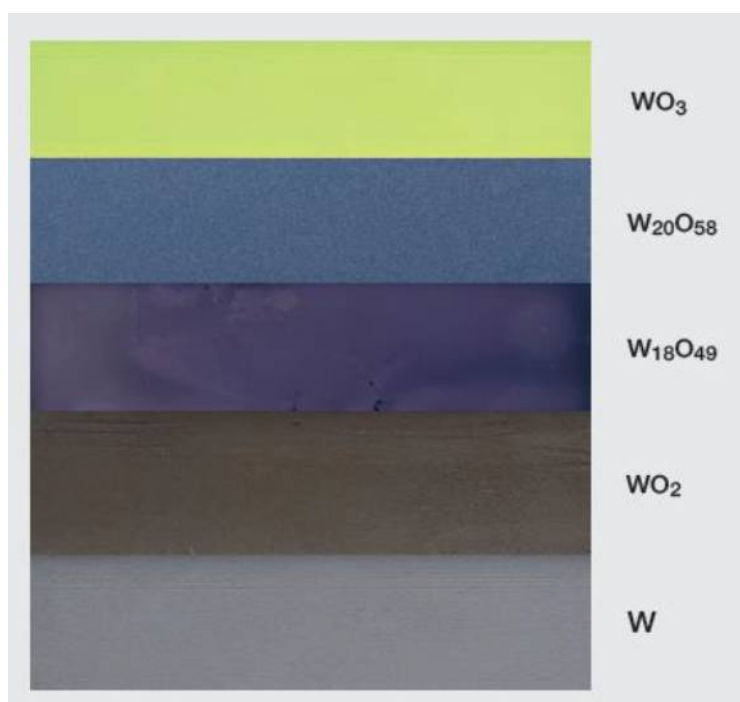


Figure 5. 21 Various Color of TPA

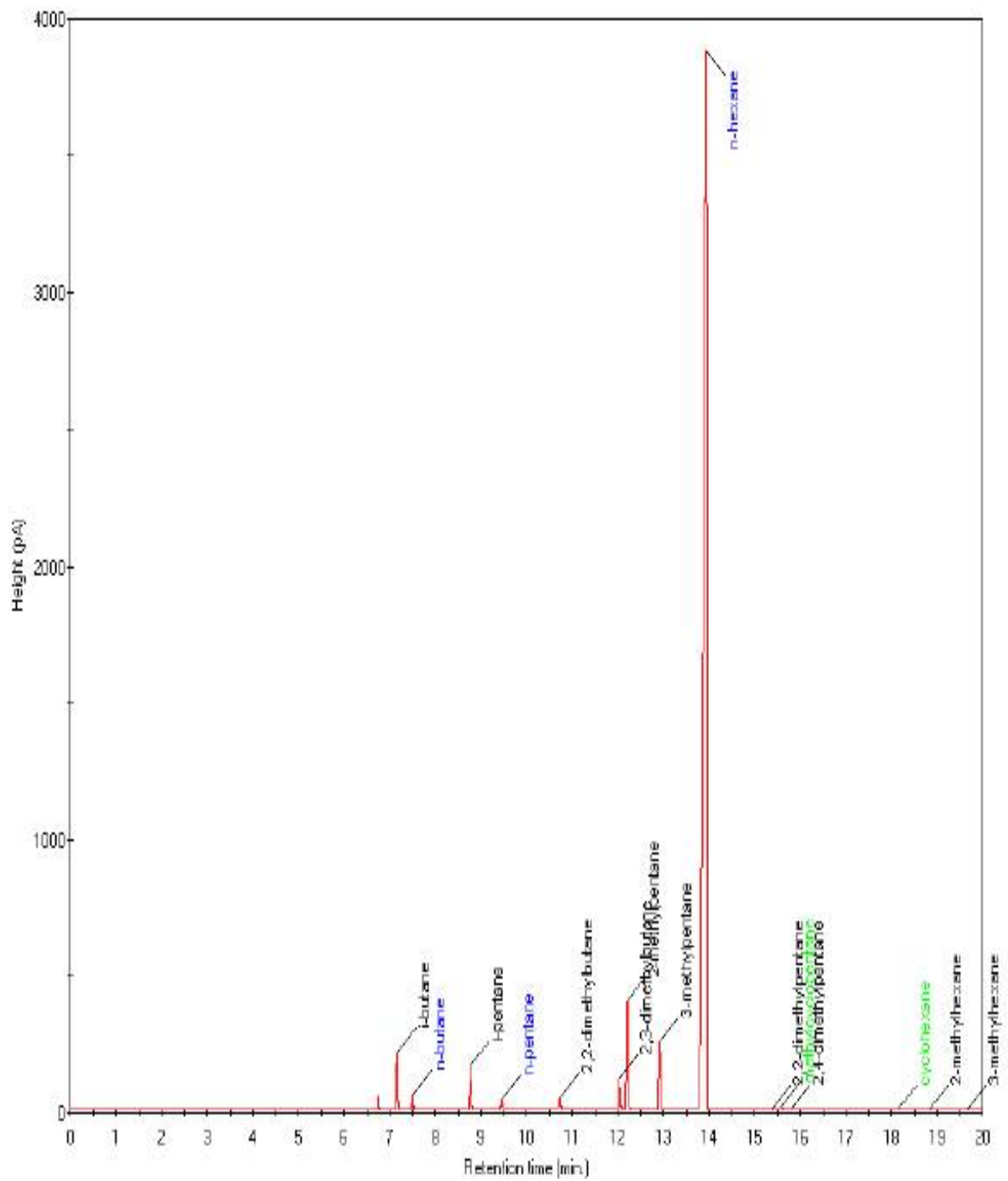


Figure 5. 22 DHA profile SZGW55

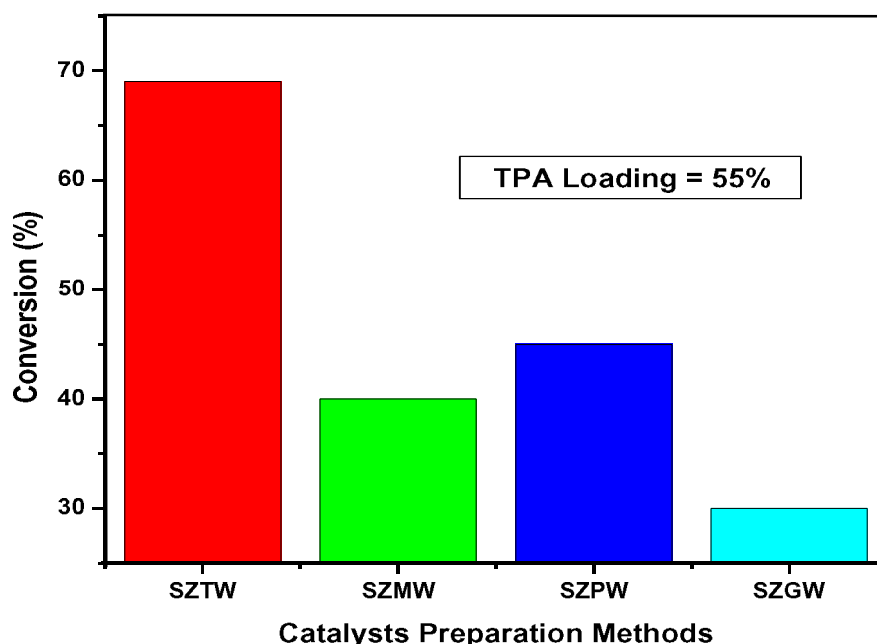
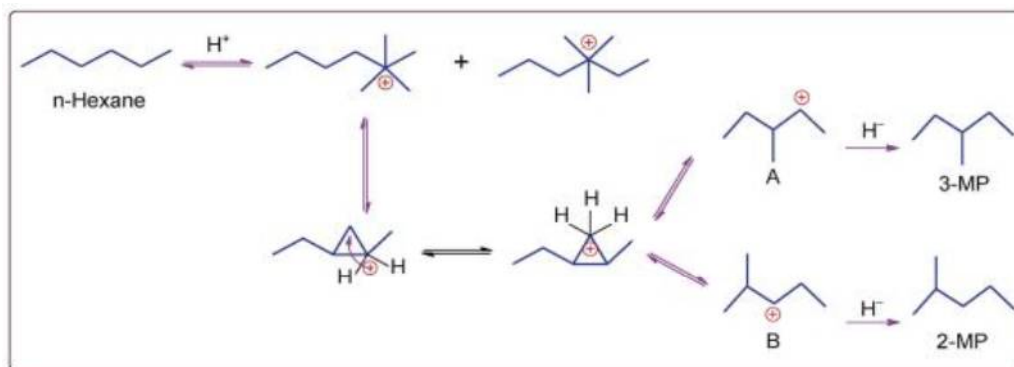
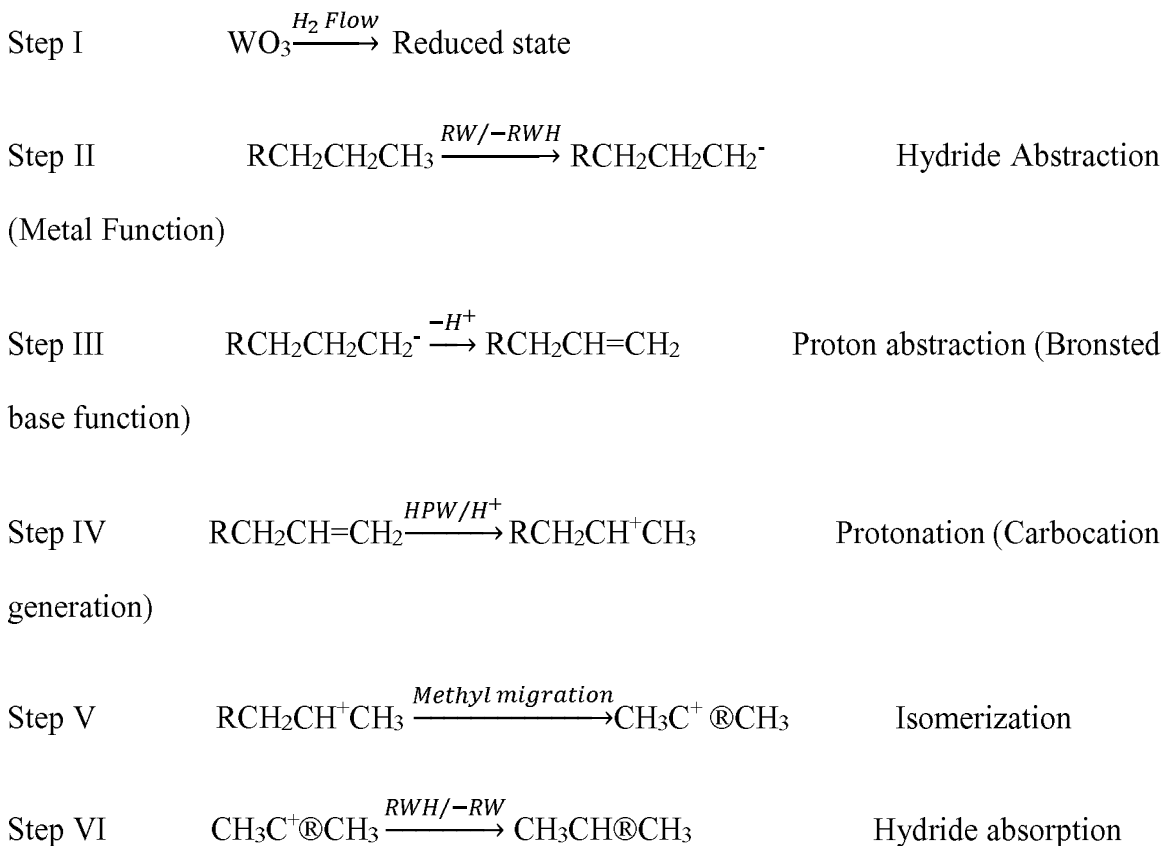


Figure 5.23 Conversion vs Catalyst Type

5.3 DISCUSSION

Based upon the mechanism and kinetics involved, isomerization is an exothermic reaction, favorable at relatively lower temperature. TPA acid is highly acidic material and exists in keggin type structure, responsible for the catalytic activity of the catalyst [Ivanov et al., 2004] (as is clear from FTIR spectrum). During pre-treatment step, tungsten oxide in TPA is reduced to tungsten as shown in Fig (5.23) [Tungsten Newsletter June 2013]. It causes hydride extraction (metal function) from normal alkane generating carbocation, which upon proton abstraction over oxide support gets converted to olefins. It then accepts a proton from TPA (acidic function) to generate branched alkane, pass through methyl shift and absorption of hydride by the carbocation as intermediate during the reaction. The metal function and acid function of the catalyst is enhanced with rise in temperature due to kinetic

reason. But at optimum temperature, the active sites of the catalyst do not remain available any more to promote the reaction. The isomerization reaction mechanism is shown below.



Scheme 5.1 Mechanism of isomerization in presence of TPA

In the first stage of the reaction (pretreatment), tungsten oxide (WO_3) in phosphotungstic acid reduced to tungsten (W) [step I] which was proved by its color available in literature (Fig. 5.23) (Tungsten Newsletter, 2013). This caused hydride abstraction (metal function) from the normal alkane generating carbocation [step II], which upon proton abstraction (Bronsted base function) by the structured oxide support was converted to alkene [step III]. The formation of alkene due to dehydrogenation of alkane in this step was confirmed by bromine water test. Alkene thus formed accepted a proton from phosphotungstic acid (acidic function) to generate carbocation as intermediate [step IV], in which methyl shift took place which cause isomerization [step V]. Thus, the newly generated carbocation (more stable) accepted the hydride back from the reduced form of metal generated in step II, to produce branched alkane [step VI].

The catalytic activity of the catalyst mostly depends on density and strength of acid sites. Higher the acid sites strength, resulting in higher activity of the catalyst. The TPA concentration effect on catalytic activity of catalyst is shown in Fig.5.15. The activity of catalyst grows simultaneously with an increase in the concentration of TPA. It reaches to maximum as the concentration of TPA is close to 1.2-1.5 monolayer [Trolliet et al., 2001]). The high concentration of TPA over the support reduced the isomerization activity of catalyst. High concentration of TPA responsible for high density, which is promising to the interaction of molecules, adsorbed on adjacent centers [Rezgui et al., 1996]. This process increased the performance of catalysts, particularly, in the bimolecular reaction for n-butane isomerization. A bimolecular oligomerization cracking reaction occurred as side reaction, which is responsible for the reduction in selectivity in the monomolecular conversion of higher alkanes, and the other reason in the reduction of activity may be due

to the reduction of active surface blocked by three-dimensional TPA clusters. Hence, the moderate and low density of highly acidic sites is suitable for avoiding the side reaction and high activity of the catalyst.

In this research works the effect of various parameters on the activity of catalyst for the isomerization of n-hexane was studied. The maximum conversion was achieved at 250°C, pretreated for 5hr in the presence of hydrogen 200ml/min flow. The reaction temperature range was studied from 150-250°C and the maximum conversion was obtained at 225°C for all the samples. It was also observed that increase in TPA concentration results in increase in conversion due to the improvement in the active site of the catalyst. The maximum conversion was observed with 55% TPA loading while conversion decrease this due to the reduction in surface area and pore volume of the catalyst (Fig 5.15).

On the basis of the experimental results discussed in this chapter, the isomerization activity of catalysts prepared by various synthesis methods found to following order: ZT> ZP> ZM>ZG and the selectivity of isomer of n-hexane was in following order: 2-methylpentane > 3-methylpentane > 2,3-dimethylbutane> 2,2-dimethylbutane which have high octane number and are the main component of gasoline.