A Single Step Catalytic Process for the Production of Higher Range Hydrocarbon Fuel Stocks from Naphtha

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Abstract: A novel concept of cracking-based oligomerization of naphtha (C_5-C_8) to produce higher range hydrocarbons (C_9-C_{15}) suitable for the jet fuel applications has been explored by using various zeolite type catalysts. Among the bi-metallic BEA, MOR, Y, ZSM-5 and Nano ZSM-5 based catalysts, the bi-functional Pt-Sn/Nano ZSM-5 catalyst exhibited promising catalytic activity to give higher range hydrocarbons in a single step vapor phase reaction. The catalyst produced 47 wt.% higher range hydrocarbons (C_9-C_{15}) from naphtha (C_5-C_8) at 400 ºC and 15 bar pressure, which is first of its kind to observe on any solid acid catalyst to the best of our knowledge. Further, the studies are also conducted on various other zeolites metal functionalized by similar manner so as to understand the effect of zeolite type and the metals.

Keywords: Oligomerization, ZSM-5, Cracking, Naphtha, Catalyst preparation, Characterization.

1. INTRODUCTION

Recent advent of environment legislations and decreasing quality of fossil fuel based feedstock's demand the development of efficient catalysts and processes for the production of high quality fuels from available fossil sources and alternate sources. The recent report indicates about 80% of world's energy demand will be still depend on fossil fuels by the year 2035 [1]. This situation emphasizes the urgent need for establishing value up gradation processes for low value fossil fuel based feedstocks in an innovative and demand-oriented direction.

Naphtha is one of the fossil based feedstock's rich in lighter hydrocarbons and is available for value up gradation through chemical conversion routes. The feedstock mainly contains mixture of light paraffins along with small amount of naphthenes and aromatics. Traditionally, the feed is used for the production of gasoline through catalytic reforming. However, the recent demand for middle distillate range fuels encourages the new processes for conversion of naphtha directly into high boiling range fuels. For example, in Europe the strong surplus of gasoline production compared to middle distillates is observed due to the continuous increase of diesel-powered passenger vehicles when compared gasoline-powered passenger vehicles. This has resulted in a strong increase of middle distillate/gasoline ratio along with a slight increase of the total demand between 2010 and 2020 [2-4]. Recently, alkylation of aromatics with olefins is used for the production of middle distillate range heavy hydrocarbons [5-7], where solid acid materials gained much importance for catalyzing such conversions. In this connection, recently, a new zeolite type ITQ-39 was reported to exhibit improved catalytic properties for the production of alkyl aromatics boiling in the range of middle distillates due to its improved resistance towards coke formation [8]. Joining the short chain olefins to produce heavy hydrocarbons (such as poly diesel) is another important route for middle distillate production. So far, the C_5-C_8 range light olefins are used as reactants for the production of middle distillate range hydrocarbons on various solid acid catalysts through oligomerization reaction [9-12]. Here, oligomerization reaction facilitates the increase of carbon chain length of the hydrocarbon required for middle distillate formation. Going one step ahead, conversion of paraffins directly into higher hydrocarbons is more interesting, profitable and provides the solution for the direct conversion of naphtha into middle distillate range hydrocarbons that saves the energy with process efficiency. But, the attempts are scarce in the literature except a recent study of Cosyns *et al.* who used a four-stage four-

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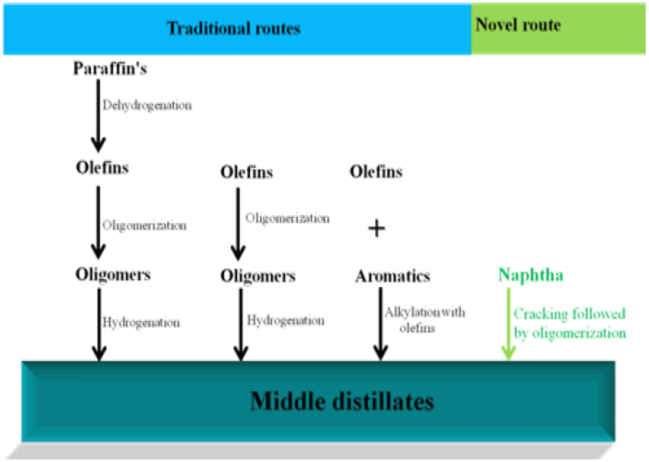
reactor system working on three sequential catalytic steps, namely, dehydrogenation of paraffin's, oligomerization of olefins and saturation of oligomers in three different reactors [13]. Thus, looking for a single step conversion process for the direct carbon number increase of short chain paraffinic feedstock to the higher boiling range fuels is still interesting yet challenging due to the fact of mismatch in thermodynamically different reaction conditions required for dehydrogenation, oligomerization and hydrogenation reactions (the dehydrogenation reaction is favored at high temperature and low pressure conditions, while the oligomerization needs low temperature and high pressure conditions).

Herein we report a simple single-step vapor phase catalytic process for the production of middle distillates range hydrocarbons (C_9-C_{15}) from naphtha (C_5-C_8) using a bi-metallic Pt-Sn/Nano ZSM-5 with zeolite framework Si/Al ratio of 100, where a novel concept of cracking based light olefin production is adopted to join the olefin fragments through oligomerization that eventually produce the high boiling range hydrocarbons Scheme **1**. The bi-metallic bi-functional Pt-Sn/Nano ZSM-5 catalyst provides the low density acid sites as well as metal sites required for the production of olefins and oligomers intermediate which up on hydrogenation/ hydrogen transfer yield the middle distillate range hydrocarbons. The highest yield of 47 wt.% higher range hydrocarbons (C_9-C_{15}) obtained in a single-catalyst single-step process is first of its kind to report from light hydrocarbon feedstock naphtha to the best of our knowledge.



Scheme 1: Novelty of the cracking based oligomerization reaction with existing traditional routes for the middle distillate production.

2. EXPERIMENTAL

2.1. Zeolite Synthesis and Preparation Procedures of Bi-Metallic Catalysts

Nano ZSM-5 with framework silica-to-alumina ratio (SAR) of 100 has been synthesized by the following procedure. In this synthesis Tetra ethyl ortho silicate (TEOS, Merck) was used as silica source. TEOS being an organic silica source is supposed to come in the aqueous phase slowly. Al source was added slowly to pre cooled TPAOH solution and after that TEOS was added drop wise. The components were mixed with constant stirring. After adding all the ingredients the solution was left to hydrolyze at room temperature for 41 h. The gel thus obtained was heated at 80 ^{o}C to evaporate water and ethanol formed during the hydrolysis of TEOS and to obtain a concentrated gel. The concentrated gel was charged in a Teflon lined autoclave for hydrothermal synthesis at 170 ^{o}C for duration of 48 h. The crystalline white solid obtained at the end of the procedure was transferred on to a filtering funnel, washed with plenty of warm distilled water, followed by allowing it for drying at room temperature over night. The white crystalline powder obtained after drying was heated to 100 °C for 6 h followed by its calcinations in presence of air at 550 °C for 6 h to remove the organic template.

The micro scale ZSM-5 of similar Si/Al ratio, Y, MOR and BEA were obtained from Sud-chemie India Ltd., in powder form. The powder form of each sample was converted into extrudates form by mixing with pseudo boehmite binder in zeolite : binder weight ratio of 3 : 2, followed by its peptization with 3 vol.% glacial acetic acid solution for 3 h and extruding the resultant wet paste to 1 mm dia extrudates. The extrudates after drying at 100 °C for 24 h and calcinations at 500 °C for 6 h were taken as support for metal loading. Two metals namely, Pt (0.6 wt.%) and Sn (1.2 wt.%) have been loaded on the support adopting incipient wet impregnation method and the extrudates were dried at 100 °C for 24 h and calcined at 500 °C for 6 h. The resultant catalysts are designated as Pt-Sn/Zeolites (Nano ZSM-5/ZSM-5/Y/MOR/BEA)

2.2. Catalyst Characterization

The Powder X-ray diffraction patterns of the catalyst were characterized by D8 advance instrument, Bruker, Germany. The morphology of the sample was examined with a SEM images recorded on Quanta 200f instrument, Netherland. The acidity of the catalyst was measured by temperature programmed desorption of

NH_3 (NH_3-TPD) using a Micromeritics chemisorbs 2750 pulse chemisorption system. The textural characteristics of the catalyst were determined by N_2 phisisorption at 196 °C using a Thermo Quest Sorptomatic 1990 porosimeter. Prior to the analysis, the sample was out-gassed at 250 °C for 4 h under high vacuum.

2.3. Feed Characterization

The analysis of the pre-treated haldia naphtha (90–140 ^{o}C) received from M/s IOC, Haldia Refinery; West Bengal, India has been given in Table **2**. Though the boiling range of the naphtha is 339 K (IBP) to 427 K (FBP), the feed contains major amount of (> 90%) C_5-C_8 hydrocarbons (Table **1**). The feed contains about 30 major hydrocarbon components, and the entire range of these hydrocarbons has been classified into four groups namely, n-paraffins, iso-paraffins, naphthenes and aromatics. The feedstock contains major amount of n-paraffins (35.7 wt.%) followed by i-paraffins (33.0 wt.%), naphthenes (19.5 wt.%) and aromatics (10.7 wt.%). The RON and MON of the pre treated Haldia Naphtha is 43.8 and 42.0 respectively.

Table 1: Composition of Naphtha Feed

Carbon No (wt.%)	n-Paraffins	i-Paraffins	Naphthenes	Aromatics
C_5	0.0	0.0	0.1	-
C_6	3.5	1.6	2.3	0.3
C_7	16.1	17.5	7.2	3.6
C_8	13.2	12.8	8.7	6.0
C_9+	2.9	1.1	1.2	0.8
Total	35.7	33.0	19.5	10.7

2.4. Reaction Procedure

A fixed bed down flow reactor (0.705 liter volume and 1320 mm length) was used for the catalyst evaluation where 15 g of catalyst is loaded in the centre of the reactor and α-alumina (inert material) was loaded above and below the catalyst bed. Prior to the reaction, the oxide form of metal on the catalyst was reduced at 773 K under hydrogen gas flow of 12 l/h for 8 h (*in situ*) and the reaction is conducted at the following reaction conditions; reaction temperature = 673-723 K, pressure = 15 bar, WHSV = 3.0 h^{-1} and N_2 = 30 l/hr. The product obtained in gas and liquid phases was analyzed by Varian capillary column (CP Al_2O_3/KCl, 50 m * 0.53 mm * 10 μm) and Petrocal DH (100% dimethyl polysiloxane as stationary phase, 100 m * 0.25 * 0.5μm) respectively. The detailed hydrocarbon analysis was obtained following ASTM 6730 method and using standard software Hydrocarbon Expert.

3. RESULTS AND DISCUSSION

The bi-metallic zeolite sample is characterized for its properties where, the XRD (Figure **1a**) indicates the structure of ZSM-5 framework along with a sharp peak below 1° 2θ (Figure **1b**) revealing the presence of larger meso-porosity in the synthesized material [14].

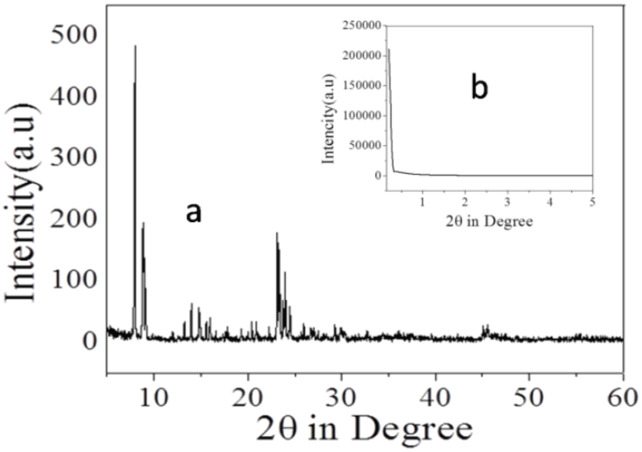


Figure 1: a and **b** are the wide and low angle XRD patterns of Pt-Sn/Nano ZSM-5.

The N_2 sorption measurements of the sample indicated area (392.1 m^2/g) and pore volume (0.425 cm^3/g) suitable for catalytic applications. The porosity of the sample measured by N_2 relative pressure of 0.01 indicates (Figure **2a**) the filling of the micropores that is commonly observed for larger mesopores and provides

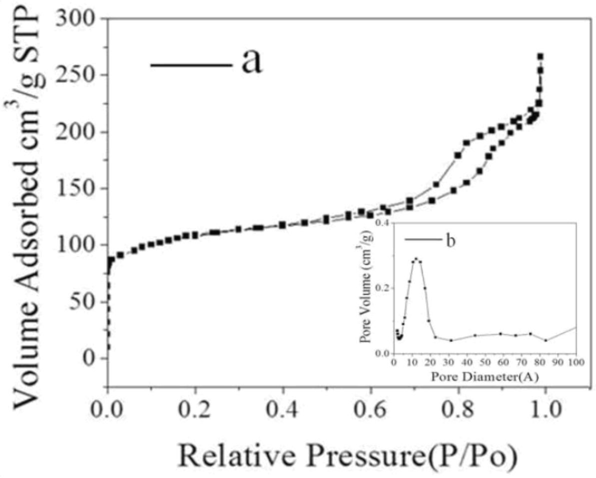


Figure 2: a and **b** is the N_2 adsorption-desorption isotherm and BJH pore size distribution of Pt-Sn/Nano ZSM-5.

a direct evidence for the presence of worm like mesopores in these samples.

The isotherm indicates the occurrence of well-defined capillary condensation at relative pressure (P/Po) of 0.01–1.0. The BJH pore size distribution curve (Figure **2b**) reveals the presence of micro as well as mesopores with various pore diameters. The data given in Table **2** indicates that majority of the pore volume (~61%) is due to the mesopores with the corresponding mesopore surface area and meso pore volume of 182.4 m^2/g and 0.26 cm^3/g respectively. The meso pores are distributed from 2-100 nm pore diameter (Figure **2b**). However, the detailed distribution of the pores given in Table **1** indicates the presence of pores with wide range of pore diameters from <2nm, 2-10nm, 10-20nm, 20-50nm and >50nm that revealing the hierarchical nature of the mesopores.

The sample exhibited uniform crystal size with spherical morphology in SEM (Figure **3a**), while the presence of defined particle size of ~40 nm along with inter particle voids are seen in TEM (Figure **3b**). The Pt-Sn/Nano ZSM-5 sample exhibited the uniformly distributed metal particles of ~5-10 nm on the ZSM-5 crystal surface (Figure **3c, d**).

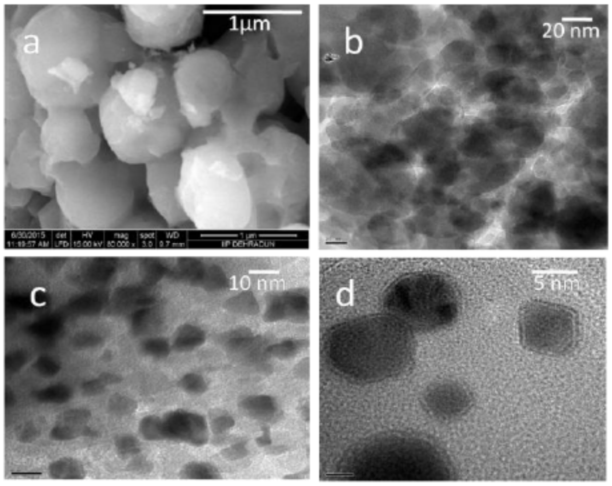


Figure 3: a and **b** are SEM and TEM of Nano ZSM-5, while c and d are TEM and HR-TEM of Pt-Sn/Nano ZSM-5.

The sample exhibited acidity measured by TPD (Figure **4**), where, the presence of two NH_3 desorption peaks; one broad peak centred at 423 K and the other around 673 K representing the weak and strong acid sites respectively, were observed. In general, the evidences obtained from the physico-chemical investigations indicate that the sample possesses both acidity and metal functionality required for facilitating hydrocarbon transformation in naphtha feed.

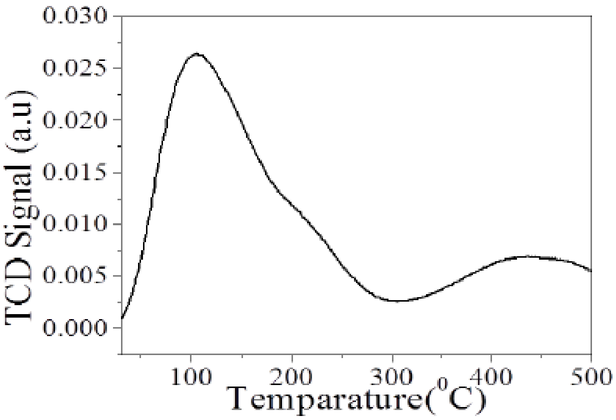


Figure 4: TPD Spectra of Pt-Sn/Nano ZSM-5.

The objective of present study is to produce olefins from naphtha by means of acid functionality for cracking and metal functionality for dehydrogenation which are source for the oligomerization reactions to form high range hydrocarbons. The performance of Pt-Sn/Nano ZSM-5 towards the production of higher hydrocarbons from naphtha is shown in Figure **5**. The naphtha conversion is very low at below 350 ºC and above this temperature the naphtha got converted to give higher range hydrocarbons (C_9-C_{15}). The highest yield (47 wt.%) of higher range hydrocarbons was observed at 400 ºC and above this reaction temperature the yields are again decreased for this product (Figure **5a**). The yield of BTX (C_5-C_8) hydrocarbon product is negligible up to 375 ºC and increased gradually with increase of reaction temperature. The decrease in the yields of higher range hydrocarbons along with simultaneous increase in BTX above 400 ºC clearly

Table 2: Surface Area and Pore Size Distribution of Pt-Sn/Nano ZSM-5

BET Sa (m^2/g)^a	Micro SA (m^2/g)^b	Meso SA (m^2/g)^c	Total PV (cm^3/g)^d	Micro PV (cm^3/g)^e	Meso PV (cm^3/g)^f
392.1	209.7	182.4	0.425	0.165	0.26
Pore size distribution (% Volume in pore Diameter)					
<2nm	**2-10nm**	**10-20nm**	**20-50nm**	**>50**	
39	13	19	7	22	
^{a}BET Surface area, ^{b}Micro pore Surface area,^{c}Mesopore Surface area, ^{d}Total pore Volume, ^{e}Micropore Volume and ^{f}Mesopore Volume					

indicates the effective conversion of olefins and oligomers towards thermodynamically favoured endothermic aromatization reactions at higher temperatures. Similarly, the studies on reaction pressure also indicated the need of optimization of the pressure, where the highest yield of higher hydrocarbons was obtained at 15 bar pressure (Figure **5b**). Lower pressures (below 15 bar) encouraged the aromatic (BTX) formation while higher pressures (above 15 bar) resulted in the formation of lower olefins, perhaps due to decrease in oligomerization reaction at higher pressures. Overall, the catalyst produced 47 wt.% higher range hydrocarbons (C_9-C_{15}) from naphtha (C_5-C_8) at 400 ºC and 15 bar pressure, which is first of its kind to observe on any solid acid catalyst to the best of our knowledge. Further, the studies are also conducted on various other zeolites metal functionalized by similar manner so as to understand the effect of zeolite type and the metals.

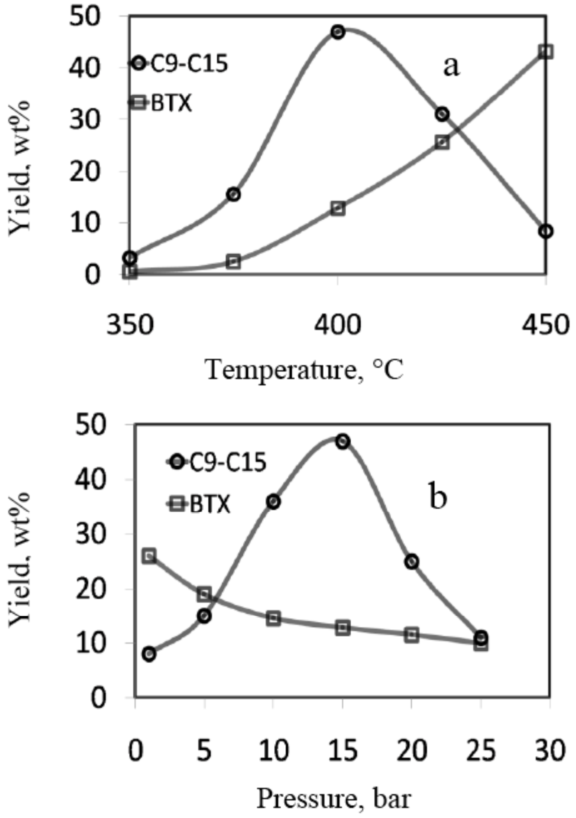


Figure 5: Product patterns with **a**) reaction temperature and **b**) reaction pressure in naphtha conversion on Pt-Sn/Nano ZSM-5.

The reaction data given in Table **3** indicates very low yields of higher range hydrocarbons on other zeolite based catalysts (other than ZSM-5) at the similar reaction conditions. The ZSM-5 zeolite is known to produce light olefins due to its acidity and narrow size pores which restrict hydrogen transfer reactions. This property of ZSM-5 is widely explored in the refinery processes like FCC (Fluid Catalytic Cracking) [15]. Since, the present reaction also depends on the formation of olefins, which are essential source for higher hydrocarbon formation; the better performance of ZSM-5 in the present reaction can be ascribed to its olefin formation tendency. At the similar metal loadings and reaction conditions, the Pt-Sn functionalized normal ZSM-5 (Pt-Sn/Z) also produced some amount of higher hydrocarbons (15 wt.%) but its performance is much lower to the Nano ZSM-5 based catalyst (Pt-Sn/NZ). This observation again emphasizes the role of the nature of ZSM-5 support. Since, the Nano ZSM-5 exhibits higher surface area and presence of mesopores in addition to the microporous zeolite channels, the improved diffusion of the bulky intermediates and larger hydrocarbon molecules in the Nano ZSM-5 catalyst may be responsible for its enhanced performance over normal ZSM-5 based catalysts. But, without the loading of Pt-Sn metals, the pure Nano ZSM-5 could not produce considerable amount of higher hydrocarbons (only 8.5 wt.%). This observation clearly suggests the important role of metal sites in the formation of higher hydrocarbons, perhaps through facilitating effective oligomerization reaction. Pt-Sn/ZSM-5 is also reported to produce light olefins from shorter n-paraffins but at relatively higher reaction temperatures (> 550 ^{o}C) [16]. Since, higher reaction temperatures are favourable for aromatic (BTX) formation; one has to optimize the olefin formation on one hand and the oligomerization on the other to produce heavy hydrocarbons. The reaction conditions of 400 ºC and 15 bar pressure adopted in the present study could give the effective production of higher hydrocarbons on the metal functionalized nano ZSM-5 catalyst.

The formation of higher range hydrocarbons thus can be explained by the reaction pathways shown in Scheme **2**. The paraffins, iso-paraffins and naphthenic groups in the feed produce light olefins through cracking and dehydrogenation reactions on the acid-metal bi-functional catalyst (routes 2-4). The light olefins thus formed can undergo oligomerization (route 6) to produce higher olefins which evntually form alkyl aromatics (route 8) through dehydro cyclization reaction or higher range isoparaffins through saturation (route 9). The lower olefins from reaction routes 2-4 also react with the aromatics present in the feed to produce alkyl aromatics through alkylation reaction (route 5). Further, the light olefins formed in reaction routes 2-4 can also react with isoparaffins present in

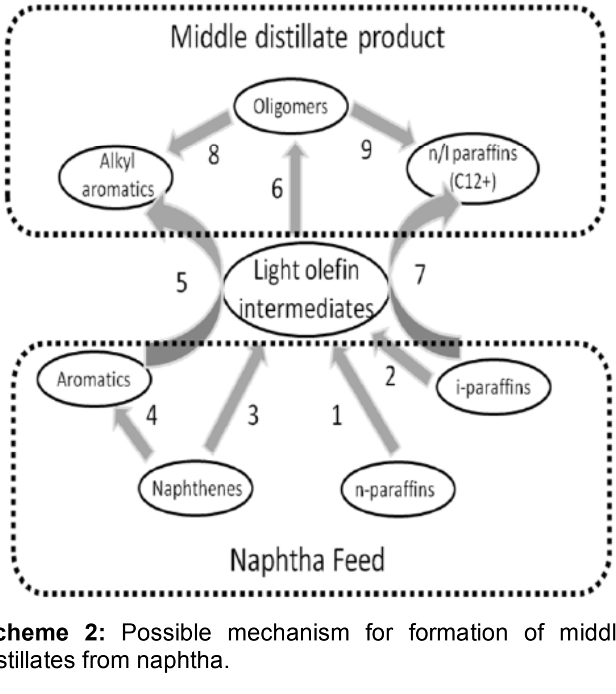
Table 3: Performances of Various Zeolite Based Catalysts

Product Yield (wt.%)	NZ	Pt-Sn/NZ	Pt-Sn/Z	Pt-Sn/MOR	Pt-Sn/BEA	Pt-Sn/Y
Gas	8.2	13.6	26.0	3.5	1.8	1.5
H_2	0.4	1.0	1.7	0.0	0.0	0.0
C_1+C_2	2.8	1.5	1.7	0.5	0.6	0.5
C_3+C_4	4.2	7.5	18.8	2.1	1.2	1.0
C_2-$C_4^=$	0.8	3.6	3.8	0.4	0.0	0.0
Liquid	91.8	86.4	74.0	96.5	98.2	98.5
C_5-C_8	87.3	39.4	59.0	95.0	97.0	98.0
C_9-C_{15}	8.5	47.0	15.0	1.5	1.2	0.5

Reaction conditions: Temperature = 400 °C, Pressure = 15 bar, WHSV = 3 h^{-1}, reaction time = 6 h, carrier gas flow = 30 lit N_2. h^{-1}.

the naphta feed to produce higher range hydrocarbons (route 7). Thus, the cracking based reaction adopted in the present study provides a route for the formation of light olefins from various hydrocarbn types (n-paraffins/iso-paraffins/naphthenes) that play centre role for the production of higher hydrocarbons (C_9-C_{15}) through oligomerization and alkylation reactions (routes 5-9).

Since, light olefins are the common intermediates for the entire reaction network, diverting the reaction path towards a slective product is influenced by several catalytic and reaction parameters. The considerably high yields of C_9-C_{15} hydrocarbons obtained in the present study provides promising activity of metal functionalized ZSM-5 zeolite and further scope in the development of catalytic processes for the effective conversion of naphtha to higher range hydrocarbons such as diesel and jet fuel which are in great demand.



Scheme 2: Possible mechanism for formation of middle distillates from naphtha.

4. CONCLUSION

In summary, The bi-metallic medium pore acid catalyst Pt-Sn/Nano ZSM-5 material developed in the present study exhibited promising catalytic application in the production of higher range hydrocarbons from naphtha through a cracking based oligomerization reaction. The high density of the product (0.8430 g/ml) with its higher C_9-C_{15} content is a suitable product for jet fuel applications. ZSM-5 based catalysts are so far know for the production of gasoline, but the considerable amount of middle distillate range hydrocarbons produced in the present study reports the new property of this zeolite to produce high boiling range fuels directly from naphtha.

The cracking-based chain increase of paraffins adopted in the present study provides a new concept for effective conversion of paraffins to desired products. The subject opens up a new property of the bi-metallic ZSM-5 materials as suitable catalysts, where the nature of product can be controlled by loading the appropriate metal functionality on the ZSM-5 catalyst. Here the combination of Pt and Sn seems to facilitate the production of middle distillates and the study indicates further scope in improvement of the catalytic activity through the optimization of the metal amount and reaction condition for expansion of its applications to other selective hydrocarbon production reactions.

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