DEVELOPMENT OF CATALYST FOR PRODUCTION OF AROMATICS FROM BIO-NAPHTHA

Submitted as a part of the requirement for the partial fulfillment of the course work of CSIR-Harnessing Appropriate Rural Interventions and Technologies (CSIR-HARIT) for the award of Degree of PhD.

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Declaration: I Vijendra Singh, hereby certify that the work presented in this Report entitled "Development of Catalyst for Production of Aromatics from Bio-Naphtha" in partial fulfillment of the course requirement for award of the Degree of PhD, being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of Project Research work carried out by me at Catalytic Reforming Area during the period Jan 2020 - March 2020 and under the supervision of Dr. N. Viswanadham.

Date 24|09|2020

Signature of the Student

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1. Introduction

Global consumption of crude oil and the impacts of climate change induced by greenhouse gas emissions have led to intensive research efforts to develop renewable and sustainable transportation fuels and industrial chemicals. Increased environmental consciousness and global energy crisis have aroused a growing interest focus by industry and academia on utilizing renewable carbon-based fuels as alternative energy resources to replace the traditional fossil fuels. Renewable resources are the key to meet the growing energy needs of the world in a sustainable as well as environment friendly way. One of alternatives is biodiesel which can reduce dependence on fossil fuels. Nowadays, harnessing of natural resource wealth has been considered as a great transformative opportunity. CSIR laboratories are also (mainly CSIR-IIP) involved in the utilization of various natural resources (bio-mass) for the production of useful chemicals and fuels.

Vegetable oils manufactured from crops such as palm, jatropha, soybean, rapeseed, and residues can be used for producing bio-diesel along with naphtha (approximately 15wt%) and kerosene. The formation of low value bio-naphtha (boiling point 30-200 ^{0}C) as byproduct makes these processes less economic. Production of aromatics (BTX) through catalytic process will improve the process economics. Worldwide, approximately 185 million tonnes of BTX are produced per year. However, there is a vast demand for BTX due to their gasoline and petrochemical importance. It is estimated that the demand of aromatics shall reach to more than 200 thousand tons per in the next 2020 year, that increase the rate of their prices roughly about USD 5395 per ton. The rising demand for aromatics is discovering a green route to convert bio-derived naphtha into aromatics will pave a new route towards increase the aromatics production. Solid acid based catalysts such as ZSM-5 [1, 2] and Al_2O_3 [3, 4] have been tremendously employed for the conversion of bio-naphtha into aromatics. The broad objective of the present work is to develop a solid acid based catalyst with suitable properties to produce aromatics with high selectivity.

2. Objective

Main objective of the present work is to develop a catalytic process for the production of aromatics from low value bio-naphtha obtained out of bio-jet fuel process using high pressure micro reactor unit at 5-7 g level.

3. Catalyst Preparation

The solid acid supports ZSM-5 (extrudates) and Al_2O_3 (spherical) have been commercially purchased. The Ga, Pt and Sn loaded ZSM-5/Al_2O_3 samples were prepared by wet impregnation method using Galium nitrate monohydrate (Merck), hexachloroplatinic acid (Merck) and tin chloride (Sigma-Aldrich) salts. To prepare Ga/ZSM-5, Pt/ZSM-5 and Pt-Sn/Al_2O_3 catalysts, suitable amount of respective metal precursor solution was slowly added to the solid acid support (ZSM-5/Al_2O_3), and then it was dried at ambient temperature for overnight followed by drying at 110 °C for 8-12 hrs and calcination at 550 °C for 4 hr. The obtained samples were named as Ga/ZSM-5, Pt/ZSM-5 and Pt-Sn/Al_2O_3.

4. Physico-chemical characterization

NH_3-TPD was carried out to study the acidic properties of prepared Ga/ZSM-5, Pt/ZSM-5 and Pt-Sn/Al_2O_3 samples (Fig.1), which is one of the key factors in the catalytic transformation of bio-naphtha to BTX. The both sample exhibited two distinct desorption peaks in the region of 120 ^{0}C-150 ^{0}C and 430 ^{0}C -450 ^{0}C are the characteristics of weak acid sites and strong acid sites, respectively [5,6]. It was also observed that Ga/ZSM-5, Pt/ZSM-5 sample show higher acid sites as compared to Pt-Sn/Al_2O_3 sample.

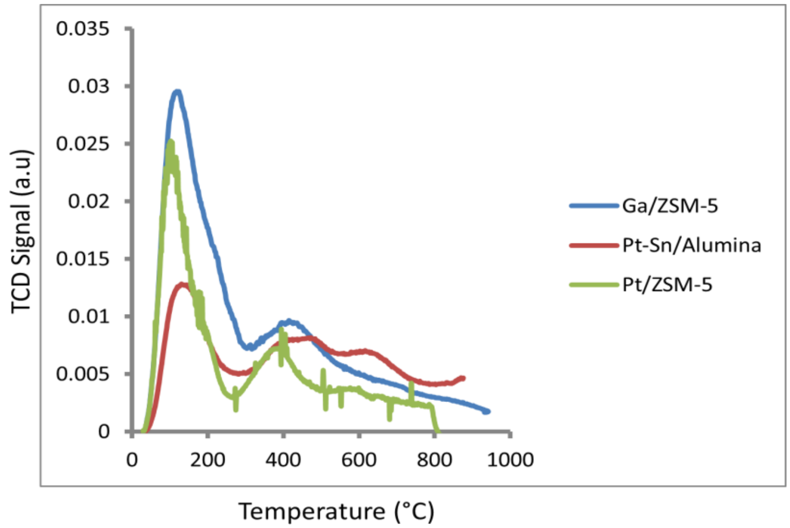

Fig. 1 NH_3-TPD results

FT-IR spectra of Ga/ZSM-5, Pt/ZSM-5 and Pt-Sn/Al_2O_3 samples exhibited a broad band around 3500 cm^{-1} ascribed due to –OH stretching vibrations related to lattice water molecules. Also the presence of weak band at 1330 cm^{-1} is due to the stretching vibration of Si-OH/Al-OH groups. In addition to these, two intense broad bands were observed around 750 and 550 cm^{-1} respond to the vibration of Al-O-Al/Si-O-Al and metal oxide, respectively [7, 8].

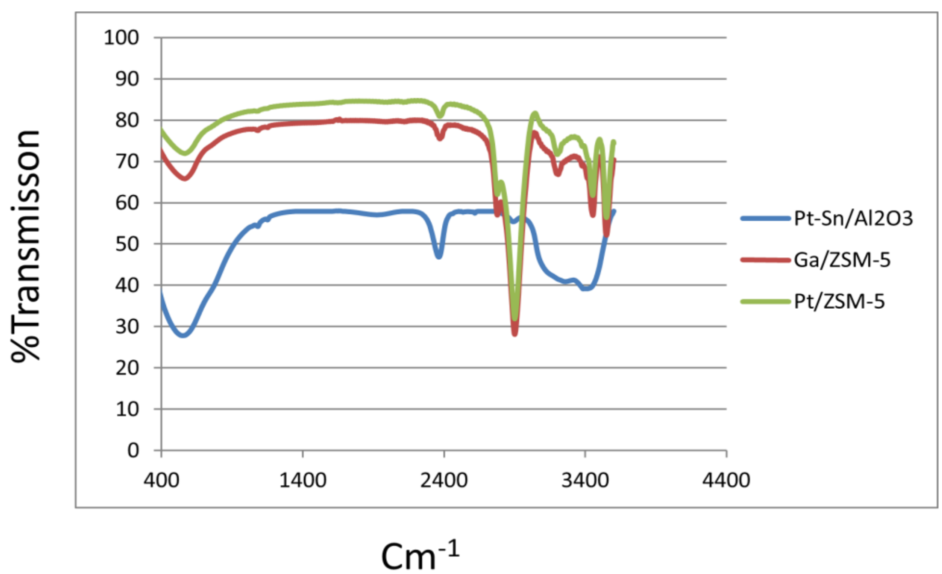

Fig. 2 FT-IR results

5. Catalyst performance study

(i) Feed analysis

Initially bio-naphtha feed about has been collected from the on-going FTT project at IIP (bio-jet fuel process). In order to understand the conversion and selectivity of reaction, the composition of obtained feed was investigated. Feed analysis report reveal that the bio-naphtha is mainly contains compounds such as paraffins and naphthenes with low RON value as shown in the Table 1. The main aim of the present work is to produce aromatics (BTX) from low value bio-naphtha through catalytic process.

Table 1 Feed Quality Analysis

Component	**Wt%** (RON-58)
Parraffins	78.52
Olefins	2.94
Naphthenes	16.1
Aromatics	2.32
Unknown	0.09

(ii) Catalyst performance

About 5-10 gm of prepared catalyst was loaded in middle zone of the reactor with pre and post heating zone were filled with α-Al_2O_3. The overall the micro reactor unit is illustrated in Fig. 3. Prior to the run, catalyst is reduced at suitable temperature under hydrogen gas flow of 10-30 lit/hr for 5-10 hr. Later it is cooled down to desired reaction temperature in hydrogen flow. After attaining the desired process conditions, the system was stabilized for 1hr. Then feed was passed to the fixed bed down flow reactor under suitable conditions. The reaction product from the reactor was cooled by cold circulating bath and separated in high-pressure separator. Liquid product from high-pressure separator is collected in atmospheric tank and gaseous product separated from high-pressure separator and product tank is vented out through wet gas meter. The obtained product has been analyzed by DHA and discussed bellow.

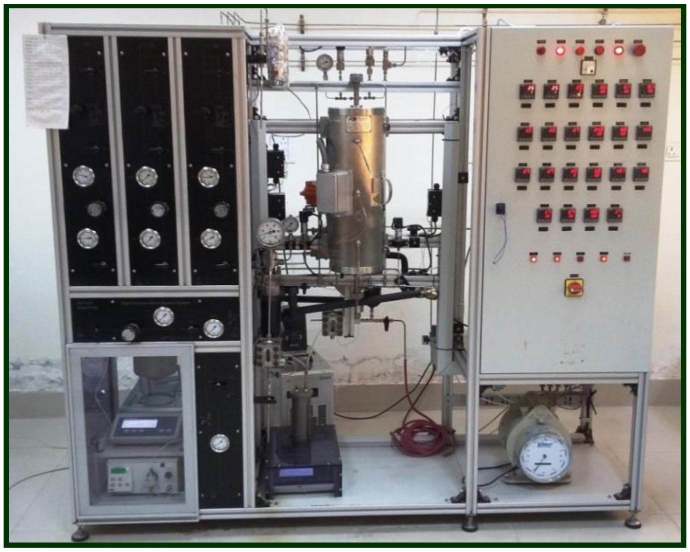

Fig. 3 High Pressure Micro Reactor Unit

(iii) Product analysis

Catalytic performance of Ga/ZSM-5, Pt/ZSM-5 and Pt-Sn/ZSM-5 catalyst in the conversion of bio-naphtha to aromatics has been carried out, obtained results are (Table 2) clearly indicating the Pt-Sn/Al_2O_3 catalyst shows higher liquid yield and aromatics as compared to Pt/ZSM-5, which may be ascribed due to low acidity of Pt-Sn/Al_2O_3 which leads to prevention of over cracking of hydrocarbons. It also observed that RON value of Pt-Sn/Al_2O_3 was found to be higher than the Ga/ZSM-5 and Pt/ZSM-5.

Table 2 Catalytic activity results

Catalyst	Feed	Liquid yield (wt%)	Aromatics (wt%)	RON
Ga/ZSM-5	Bio-Naphtha	54.75	71.82	89.2
Pt/ZSM-5	Bio-Naphtha	64	34	80
Pt-Sn/Al_2O_3	Bio-Naphtha	84	44	92

Conditions: T=450-600 ^{0}C, P=5-15 bar, N_2 gas flow 15-30 l/h, WHSV=1-3h^{-1}

6. Conclusion

The present study demonstrates the preparation of solid acid based catalysts (Ga/ZSM-5, Pt/ZSM-5 & Pt-Sn/Al_2O_3) for the production of aromatics from bio-naphtha obtained out of FTT project at IIP (bio-jet fuel process). Overall results suggest that Pt-Sn/Al_2O_3 shows higher liquid yield (54.75wt%) and Ga/ZSM-5 shows higher aromatics (71.82 wt%) ascribed due to the presence of suitable properties such as metal function as well as sufficient acidity. Further aromatics yield (>71.82 wt%) will be increased by tuning the catalytic properties and reaction conditions, which is under progress.

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