Journal of http://www.satursonpublishing.com/
Research in Multidisciplinary Methods and Applications
ISSN: 2957-3920

Volume 1, Issue 7, November 2022

Methanol To Hydrocarbons Over Ga/Zsm-5 Catalyst and Simulated By MATLAB

Jaikishor Mavai

Aligarh Muslim University, India

Corresponding To: Jaikishor Mavai

Abstract: The rise in the crude oil price, catalytic conversion of methanol to hydrocarbon (MTH) has attracted the attention of numerous experts. The MTH process is an alternative method for producing gasoline and another valuable hydrocarbon from natural gas and coal. MTH process, MTO, and MTG process were used to convert useful products. Most researchers have used HZSM-5 catalyst to get gasoline hydrocarbons. The acid strength, catalyst topology, temperature, pressure, space velocity, process variables all influence the nature and extent of the reaction. The influences of metal oxide such as Ga oxide over HZSM-5 during methanol to hydrocarbons have been investigated. GaO to the HZSM-5 catalyst were used to increase the desired hydrocarbons' conversion, yield, and selectivity. Methylene, ethylene, propylene, dimethyl ether, toluene, ethylbenzene, xylene, tri methylbenzene, and tetra methylbenzene were the main products of the process. The liquid and gas products were analyzed using a flame ionization detector (FID) and a thermal conductivity detector (TCD). The catalysts' morphology was analyzed using scanning electron microscopy (SEM). A Lumped kinetic model was proposed in the literature were validated with the experimental data. The influence of metal doping over the HZSM-5 catalyst enhances the catalyst stability during the time on stream. Although Ga-modified HZSM-5 has the highest methanol conversion, the 1.5wt% Ga/HZSM-5 treated with oxalic acid catalyst was more resistant to deactivation than the GaO- HZSM-5 catalyst.

Keywords- Methanol, Hydrocarbon, ZSM-5

1 INTRODUCTION-

Limited non-renewable resources such as crude oil, coal, natural gas, etc. availability and also due to enormous demand for petroleum products result in higher crude oil prices. Fossil fuel has been depleted due to massive use in transportation and industrialization oil us. Presently there is insufficient petroleum products, and these products will be depleted after 40 years as predicted. Presently coal is the most abundant fossil fuel in India, mainly utilized for cooking and heating purposes in the industries.

Earlier coal was used in the locomotive engines used to transport goods and passengers. Coal is emitted air pollution as it contains lot of impurities presently strict rules are followed due to the increase in air pollution, due to this coal has been discarded.

Methanol can be made from synthesis gas (CO + H2), coal gasification, or natural gas steam reforming, and a zeolite-based acid catalyst with the correct shape has been utilized to convert MTH. Because of its shape and particular crystalline structure, homogeneous pores, thermal stability, and selectivity, ZSM-5 has a high efficiency as a catalyst. Methanol is converted to aromatics, and other hydrocarbons are finally converted to gasoline range hydrocarbon.

Gasoline is obtained from crude oil is one of the essential fuels used in transportation. Due to the high demand hike in the price of gasoline and is very important to investigate new methods for producing gasoline through other resources (Zaidi et al., 2014, Shao et al., 2017). Methanol can be obtained by various resources such as natural gas, coal, and biomass due to which it can be considered an acceptable choice for this purpose. 673K is the optimum temperature for the conversion of ZSM-5 catalyst to convert methanol to olefins and aromatics. Various multistep processes were used to obtain dimethyl either due to dehydration of methanol which is subsequently into lighter olefins, and these olefins converted into aromatics (Wang et al., 2015).

The stages involved in converting methanol to hydrocarbons are as follows: (Chang et al., 1977). DME is used to convert light olefins to is paraffins and alkyl aromatics by hydrogen transfer, alkylation, isomerization, and other secondary reactions, as well as oligomerization (Ronaghi et al.,2011).

The primary goal of this research is to determine the influence of GaO loading on HZSM-5 support for MTG range hydrocarbon conversion. For their performance on methanol conversion and hydrocarbon yield, a series of GaO/HZSM-5, HZSM-5 was produced, described, and tested. With various GaO modified HZSM-5 catalysts, the effect of run-time methanol conversion and hydrocarbon yield has been investigated.

The experimental results obtained across a wide variety of hydrocarbon operating circumstances were used to assess the validity of the kinetic model proposed in the literature for the MTH process. For lumped kinetics models, the kinetic parameter is determined by solving the mass conservation equation in the reactor. The proposed kinetic models matched the experimental data in the literature quite well.

Objectives of the present research work-

To prepare the catalyst for catalytic conversion of hydrocarbons from methanol.

To characterize the catalyst for the hydrocarbon transformation from methanol.

To examine the effect of the catalyst activity due to catalyst deactivation and coke deposition over catalyst.

To investigate the impact of run time on conversion and yield due to coke deposition over catalyst.

Establish a kinetic model for MTG and estimate the parameter mod

2 Material And Methods

2.1 *Catalyst Preparation*

The impregnation method was used to prepare different wt% of metal oxide doped on catalysts such as GaO/CuO/HZSM-5 (Si/Al = 50). Which is employed as a catalyst transformation of hydrocarbon from methanol merc supplied gallium nitrate using impregnation method technique. The catalyst was prepared by doping 1.5%wt Gao over the HZSM-5 catalyst at 303K. The solution was agitated at 12h. A rotary evaporator transported the entire solution to remove most of the water. The total solution was then transported to a rotary evaporator under vacuum at 353K before being dried for 12h at 393K. Finally, the dried sample was calcined in a muffle furnace to decompose the Ga complex into GaO.

2.2 *Experimental Setup*

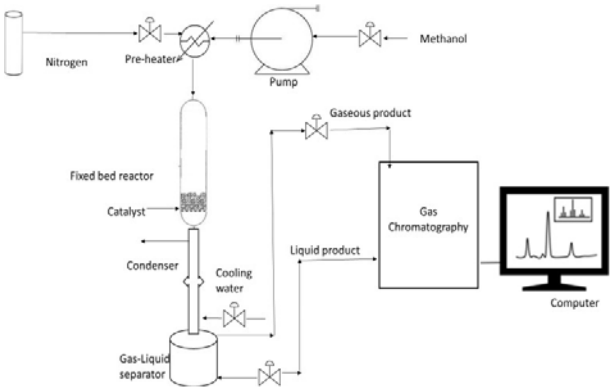

Figure 1. Experimental Setup For Methanol Conversion To Hydrocarbon

The experimental setup for converting methanol to a hydrocarbon. A microtube pump was used to pump methanol from a graded burette at a flow rate of 0.1 ml/min. A preheater with a temperature of 150°C was used to transfer methanol through. Methanol was combined with nitrogen before being injected into the reactor. The electric furnace was used to heat the reactor in three zones at 400°C. To measure the axial temperature profile, one thermocouple was attached to the reactor. The catalyst holding support was formed by welding a circular plate with holes to the upper thermo-well. Isothermal conditions were maintained by placing the weighted catalyst in the reactor's middle part.

3 Result And Discussion

3.1 *Catalyst Characterization*

The various catalyst for use in methanol to gasoline range hydrocarbon to determine various characterization were used during the methanol transformation, product yield analysis surface area characterization, and catalyst deactivation due to coke deposition. The best catalyst was selected for detailed kinetic as well as deactivation study of methanol conversion. SEM was used to investigate the size distribution of the catalyst particles and representative micrographs of various samples are shown in given Figures

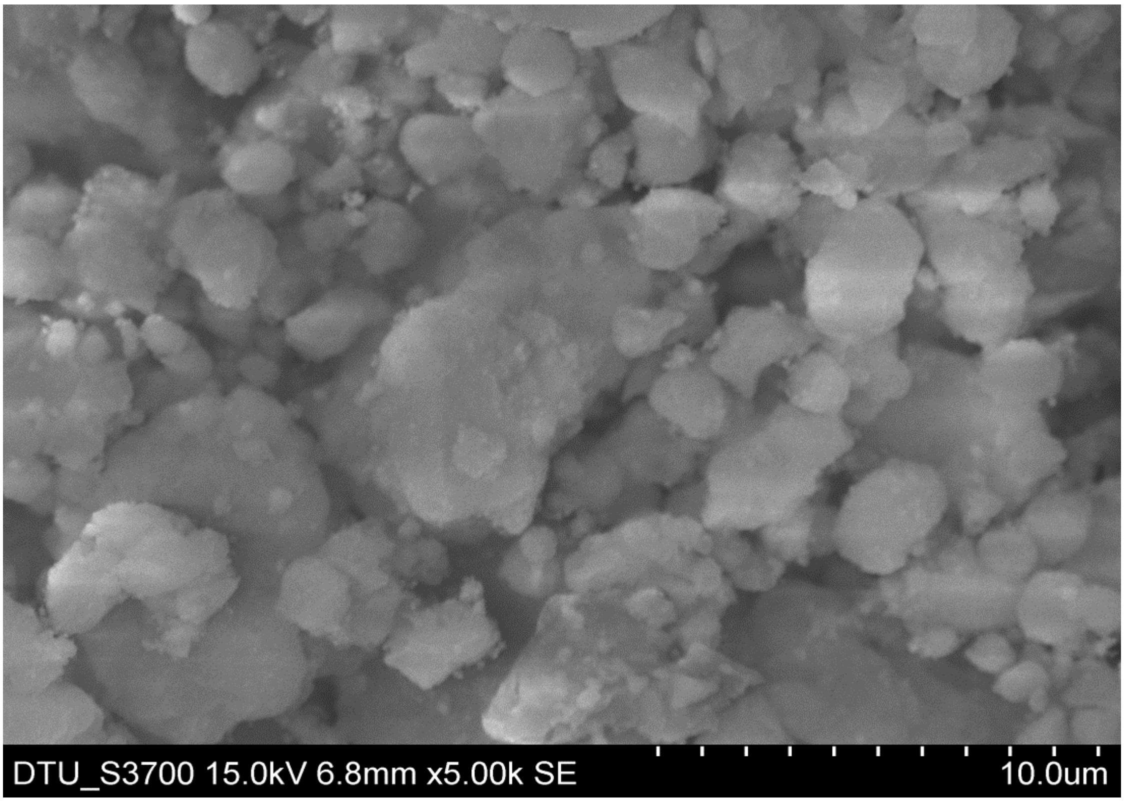

FIGURE 2.SEM PHOTOGRAPH OF HZ(0) CATALYST [P = 1 ATM, T = 673 K].

The morphological changes in the parent and doped catalyst and doped catalyst were observed using scanning electron microscopy. The topography and morphological study were carried out with the help of Joel SEM equipment. The SEM was used to examine the morphology of sample crystal the formation of micropores, and the sample surface properties. As shown in show that the HZSM-5 catalyst was spherical.

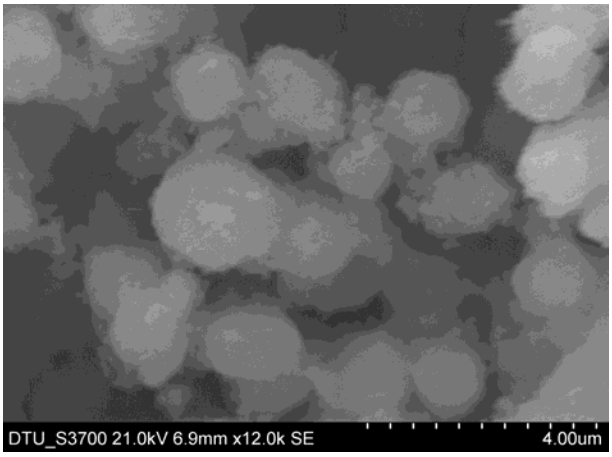

FIGURE3. SEM PHOTOGRAPH OF HZ(GAOX) CATALYST [P = 1ATM, T = 673K].

3.2 DEACTIVATION STUDIES

The catalyst coking ability causes a larger problem in the heterogeneous process by decreasing its activity with time on stream. HZ (0), HZ(GA), and HZ(GAOX) were HZSM-5, 1.5 wt% GaO/HZSM-5, and oxalic acid treated 1.5 wt% GaO/HZSM-5, respectively. The oxalic acid treatment was done to lengthen the deactivation period of HZ(GA) catalyst. Many researchers have investigated the acidic properties which affect the activity of catalysts during methanol conversion to hydrocarbons (Wei et al., 2015), (Doluda et al., 2019), (Liu et al., 2018), (Zaidi et al., 2010), (Zaidi et al., 2005), (Zaidi et al., 2014)). shows the effect of GaO loading over the parent HZ (0) catalyst with time on stream. Hydrocarbon yield transformation during the MTH process when compared to HZ(GA) and HZ(0) catalyst conversion of methanol, as well as yield of hydrocarbon, were improved during HZ(GAOX) catalyst during increase time on stream. 1.5 wt% GaO/HZSM-5 [HZ(GA)] has a higher yield of hydrocarbon as well as methanol conversion as compared to HZ (0) catalyst methane, ethylene, propylene, dimethyl ether, toluene, ethylbenzene, xylene, iso- propyl benzene, ethyl toluene, and tetra methylbenzene and C5+ hydrocarbons were the major product. depicts the product's hydrocarbon conversion variation vs. time on stream.

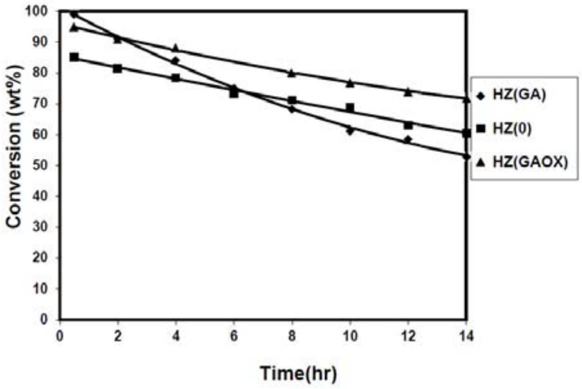

Figure 4: Methanol Conversion Versus Time In A Fixed Bed Reactor [T = 673K, P = 1 Atm, Whsv = 0.48 Hr].

The amount of hydrocarbon decreased as the reaction progressed; the incorporation of GaO for the hydrocarbon production increased the active site HZ (0) catalyst depicts the effect of GaO doped HZSM-5 catalyst, specifically how hydrocarbon yield decreased as increases in reaction time. The starting hydrocarbon yields of HZ(GA), HZ(GAOX), and HZ (0) were 46wt%, 41 wt%, and 36 wt%, respectively and after a 14-hour experimental run was conducted and yields were 20wt%, 29wt%, and 24 wt%. The 1.5 wt% GaO modified HZSM-5 catalyst demonstrated the highest hydrocarbon transformation and yield HZ(GA) as well as HZ(GAOX). The higher aromatic production in the aromatics produces higher coke over the surfaces, in contrast, the HZ(GAOX) catalyst produced lower aromatics due to which brought lower coke formation over the catalyst surface shows the Product Distributions for the Conversion of Methanol over Different Catalysts [T = 673K, WHSV=0.48 hr, P = 1 atm].50

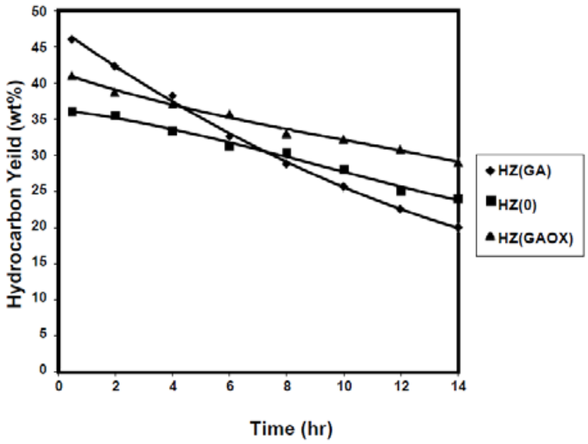

Figure 5: Hydrocarbon Yield Versus Time In A Fixed Bed Reactor [T = 673K, P = 1 Atm, WHSV =0.48 Hr-1].

Experiments were conducted using (GAOX) catalyst at various residence times (WHSV) and at constant temperatures at 673K. indicate the effects of residence time during methanol conversion and hydrocarbon yields as shown in . It was observed that methanol conversion and hydrocarbon yield increase with the increases in WHSV ranges from0.076 to 0.48 hr-1.

represents Hydrocarbons such as alkanes, olefins, aromatics, and C5+ showed the highest yields at various residence durations. As the WHSV increased, the aromatic yield increased while the dimethyl ether and olefins yield decreased. shows the gaseous and liquid hydrocarbons products with different temperatures ranging from 638K to 723K. It was observed that 723K is the optimum temperature to give the better hydrocarbons yield as compared to other temperatures.

Table 1: Product Distributions For The Conversion Of Methanol Over Different Catalysts [T = 673K, WHSV=0.48 Hr P = 1 Atm].

Catalyst	HZ(Ga)	HZ(GaOX)		HZ (0)
Conversion (%)	99	95		85
CH4	0.9	0.33		1.2
C2	3.03	2.46		4.2
C3	3.93	2.85		1.9
C4	3.28	3.8		4.3
C5	2.11	2.8		0.7
C5+	10.12	7.2		8.1
C6H6	0.08	0.04		0
C7H8	1.2	1		0.8
C8H10	9.09	8.5		2.5
C9H12	8	7.02		4.8
C10H14	1.41	0.8		0
CH3OCH3	2.85	4.2		7.5

Volume 1, Issue 7, November 2022

Hydrocarbons yield (wt %)	46	41		36
Water (wt %)	38	35		32
Others*(wt %)	15	19		17

*Others include CO and CO2

It could be because olefins and DME are intermediary products in the synthesis of aromatics and hydrocarbons in the higher molecular weight gasoline range.120

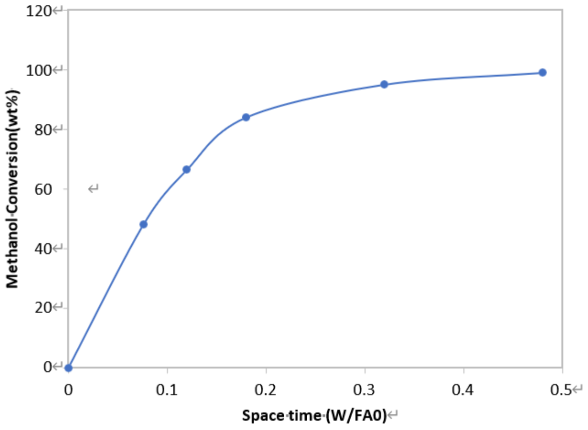

Figure 6: Variation Of Methanol Conversion With Contact Time Over The HZ(GaOx) Catalyst [T= 673K]

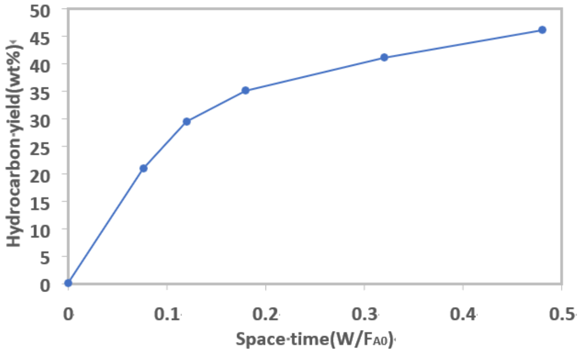

Figure 7: Variation Of Hydrocarbons Yield With Contact Time Over The HZ(GaOx) Catalyst.

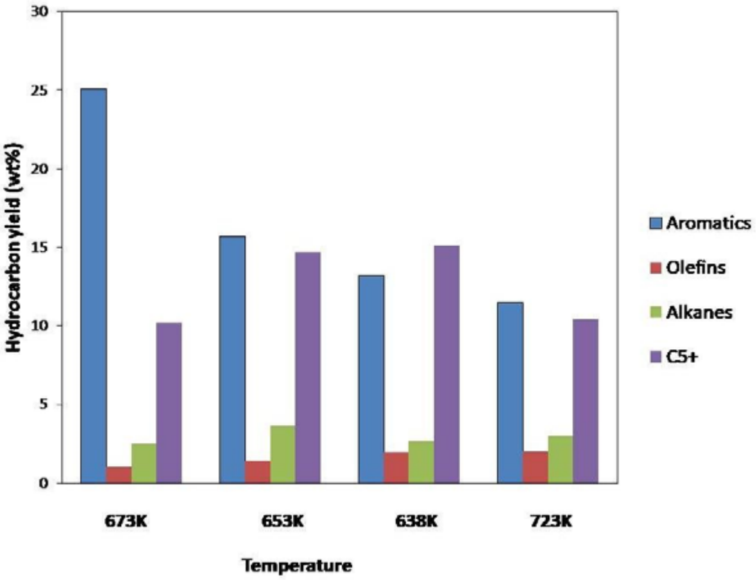

Figure 8: Effect Of Temperature On The Yield Of Total Hydrocarbons [T = 673K, P = 1atm, WHSV= 0.48 Hr]

4 SIMULATION AND VERIFY WITH MATLAB

The kinetic expression is crucial for determining which reactor is best for a given reaction and operation. There are two sorts of reaction kinetics models: detailed parameter models that address particular reaction phases and lumped parameter models that are simple to grasp and look like the actual thing. The kinetic formulae of type (a) require a long time or are practically impossible to solve in general.

For most issues, type (b) kinetics can be employed for design purposes (Keilet al.1999; Zaidi et al., 2010). Various characteristics, such as reactor temperatures, pressures, and inlet configurations, must be taken into account when using kinetic equations (Keil et al., 1999). The kinetic model constants were calculated in this study by fitting the experimental values of varied lump mass fractions to similar mass conservation equations. The kinetic constant numbers we obtain describe analogous reactions in complex systems with many different types of lumps with variable concentrations. Many kinetic models of processes involving catalysts employ the technique that was used in this study. The initial conditions for the reactor were isothermal, ignoring the radial concentration gradient, and ignoring the water in the product stream as well as the catalyst inside the reactor, the mass conservation equation was

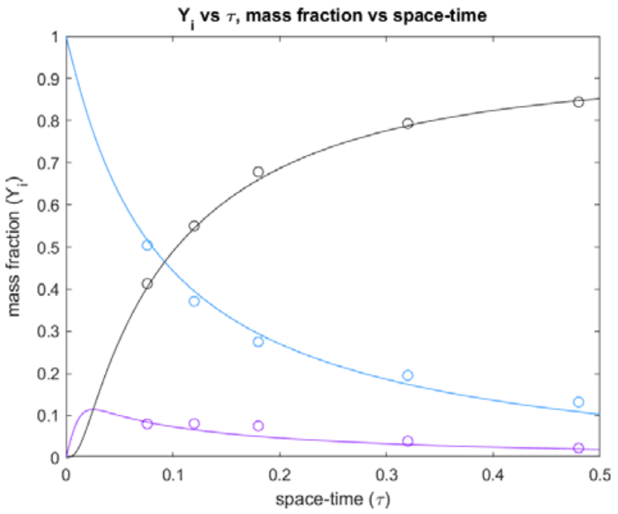

FIGURE 9. COMPARISON BETWEEN EXPERIMENTAL RESULTS AND SIMULATED VALUES OF MASS FRACTION (WATER-FREE BASIS) AT 673K, WHSV= 0.48 HR AND P=1 ATM

The equations were solved by Runga-Kutta method. The kinetic constant after fitting the equations with the experimental data as represented in equations.

The weight fractions of oxygenates, light olefins, and the rest of the hydrocarbons are compared using experimental data. The model parameters' (W/ FAO) space-time was calculated by minimizing the difference between experimental and simulated conversion values. The (W/ FAO) space-time of model parameters was evaluated by minimizing the deviation between the experimental and simulated conversion values. Yi represented wt fraction of component on the water free basis, and (W/ FAO) space- time of model parameters was evaluated by minimizing the deviation between the experimental and simulated conversion values. The kinetic model's fit to the experimental data is shown

5 CONCLUSION-

The oxalic acid treated HZSM-5 catalyst [HZ(GAOX)] has higher reactivity and selectivity as compared to HZ(GA) and HZ (0) catalyst. During methanol conversion to hydrocarbon such as methane, ethylene, propylene, dimethyl ether, toluene, ethylbenzene, xylene, iso-propyl benzene, ethyl toluene, and tetra methyl benzene was the major product. During methanol conversion to hydrocarbon, the oxalic-acid treated HZ(GA) catalyst initially shows extra resistance to deactivation and a lower yield of hydrocarbons than the HZ(GA) catalyst. It was observed that catalyst deactivation with time on stream due to the deposition of coke over its surface. Before the HZ(GAOX) catalyst is deactivated, a massive quantity of methanol is transformed into a hydrocarbon. The validation of the kinetic model was evaluated by minimizing the difference between experimental and theoretical values of hydrocarbon yields. The validity of the proposed kinetic model was evaluated based on reducing the difference between theoretical and experimental values of hydrocarbon yields.

ACKNOWLEDGE

I am thankful to Aligarh Muslim university was provide me good research environment.

REFERENCES

[1] Chang, C. D., Silvestri, A. J. (1977). The conversion of methanol and other O- compounds to hydrocarbons over zeolite catalysts. Journal of Catalysis, 47(2), 249–259

[2] Doluda, V. Y., Matveeva, V. G., Lakina, N. v., Sulman, E. M., Sulman, M. G.,&Brovko, R. v. (2019). Modified zeolites in methanol to hydrocarbons transformation. Chemical Engineering Transactions, 74, 499–504.

[3] Ehsan Kianfar, Mahmoud Salimi, &BehnamKoohestani. (2020). Methanol to Gasoline Conversion over CuO / ZSM-5 Catalyst Synthesized and Influence of Water on Conversion. Fine Chemical Engineering, 74–81.

[4] Juybar, M., Khorrami, K., &BagheriGarmarudi, A. (2039). Conversion of methanol to aromatics over ZSM-5/11 intergrowth Zeolites and bimetallic Zn-Cu-ZSM- 5/11 and Ga-Ag-ZSM-5/11 catalysts prepared with direct synthesis method. Journal of Chemical Sciences.

[5] Keil, F. J. (1999). Methanol-to-hydrocarbons: Process technology. Microporous and Mesoporou Materials, 29(1–2), 49–66.

[6] Kianfar, E., Salimi, M., Pirouzfar, V., &Koohestani, B. (2018). Synthesis of modified catalyst and stabilization of CuO/NH4-ZSM-5 for conversion of methanol to gasoline. International Journal of Applied Ceramic Technology, 15(3), 734– 741.

[7] Li, M., Zhou, Y., Oduro, I. N., & Fang, Y. (2016). Comparative study on the catalytic conversion of methanol and propanal over Ga/ZSM-5. Fuel, 168,68-75

[8] Meng, X., Chen, C., Liu, J., Zhang, Q., Li, C., & Cui, Q. (2016). Effects of zinc incorporation on hierarchical ZSM-11 catalyst for methanol conversion. Applied Petrochemical Research, 6(1), 41–47.

[9] Obsbye, U., Svelle, S., Bjrgen, M., Beato, P., Janssens, T. V. W., Joensen, F., Bordiga, S., &Lillerud, K. P. (2012). Conversion of methanol to hydrocarbons: How zeolite cavity and pore size controls product selectivity. International Edition (Vol. 51, Issue 24, pp. 5810–5831). John Wiley & Sons,

[10] Rownaghi, A. A., & Hedlund, J. (2011). Methanol to gasoline-range hydrocarbons: Influence of nanocrystal size and mesoporosity on catalytic performance and product distribution of ZSM-5. Industrial and Engineering Chemistry Research, 50(21), 11872–11878.

[11] Shao, J., Fu, T. J., Chang, J. W., Wan, W. L., Qi, R. Y., & Li, Z. (2017). Effect of ZSM-5 crystal size on its catalytic properties for conversion of methanol to gasoline. RanliaoHuaxueXuebao/Journal of Fuel Chemistry and Technology, 45(1), 75–83.

[12] Wang, X., Gao, X., Dong, M., Zhao, H., & Huang, W. (2015). Production of gasoline range hydrocarbons from methanol on hierarchical ZSM-5 and Zn/ZSM-5 catalyst prepared with soft second template. Journal of Energy Chemistry, 24(4), 490–496.

[13] Wei, Z., Xia, T., Liu, M., Cao, Q., Xu, Y., Zhu, K., & Zhu, X. (2015a). Alkaline modification of ZSM-5 catalysts for methanol aromatization: The effect of the alkaline concentration. Frontiers of Chemical Science and Engineering, 9(4), 450–460.

[14] Yang, M., Fan, D., Wei, Y., Tian, P., & Liu, Z. (2019). Recent Progress in Methanol- to-Olefins (MTO) Catalysts. Advanced Materials (Deerfield Beach, Fla.), 31(50).

[15] Zaidi, H. A., & Kishore Pant, K. (2010). Combined experimental and kinetic modeling studies for the conversion of gasoline range hydrocarbons from methanol over modified HZSM-5 catalyst. Korean J. Chem. Eng, 27(5), 1404– 1411.

[16] Zaidi, H. A., & Pant, K. K. (2005). Transformation of methanol to gasoline range hydrocarbons using HZSM-5 catalysts impregnated with copper oxide. Korean Journal of Chemical Engineering, 22(3), 353–376

[17] Zaidi, H. A., & Pant, K. K. (2008). Activity of oxalic acid treated ZnO/CuO/HZSM-5 catalyst for the transformation of methanol to gasoline range hydrocarbons. Industrial and Engineering Chemistry Research, 47(9), 2970–2975.

[18] Zaidi, H. A., & Pant, K. K. (2014). An oxalic-acid-treated ZnO/CuO/ HZSM-5 catalyst with high resistance to coke formation for the conversion of methanol to hydrocarbons. International Journal of Green Energy, 11(4), 376–388.