# Effect of Added Zinc Oxide on the Conversion of Ethanol to Hydrocarbons over HZSM-5 Catalyst

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## ABSTRACT

***At present due to a huge demand for energy, there is continued depletion of fossil fuel. Recently lot of work has been conducted for the development of renewable energy source. Biomass (e.g lignocelluloses, hemicelluloses and cellulose) in present work is used as a raw material for the production of bioethanol which is converted to hydrocarbons using ZnO doped HZSM-5 catalyst. All experimental runs were conducted under identical conditions such as operating temperature is kept at 410 °C, pressure= 1 atm and WHSV 3.5 $hr^{-1}$. It was observed that 2wt% ZnO over HZSM-5 catalyst has high activity and selectivity towards the conversion of ethanol to hydrocarbons. It was also investigated that HZSM-5 catalyst looses activity faster as compared to HZSM-5 doped catalyst. Addition of ZnO reduces the rate of deactivation of the catalyst due to reduction in acidic site.***

***Keywords: HZSM-5 catalyst; Bioethanol Transformation, ZnO modification; Hydrocarbons***

## 1. INTRODUCTION

The biomass can be used for the production of fuel and chemicals in near future due to the limited availability of fossil fuel and also because fossil fuel causes pollution and increases the global warming due to release of $CO_2$ [1- 10]. At present there is high demand of hydrocarbons and it was observed that ethanol can be use as a raw material for the production of hydrocarbons. Ethanol is particularly in abundance in India because it can be obtain from renewable biomass such as sugarcane. The conversion of bioethanol into hydrocarbons is due to shape, selectivity and acidity on HZSM-5 catalyst. Modification of ZSM-5 has been done with different metals for the conversion of bioethanol into hydrocarbons such as Fe [1], Ni [2], P [3], Zn and Ga [4], La [5], Ce [6], Ga [7], Co [8], La and Zn [9]. Catalytic conversion of ethanol into hydrocarbons over HZSM-5 has been reported [1, 2, 4, 8]. In this study it was investigated the influence of ZnO loading on the catalytic performance of modified HZSM-5 catalyst for the conversion of ethanol into hydrocarbons. Catalysts were prepared, characterized and experimental runs were conducted.

## 2. EXPERIMENTAL WORK

HZSM-5 was used as support for Zinc oxide, catalyst was prepared by impregnation method technique with 2 wt%, Zinc Oxide doped HZSM-5 catalyst and the final solution was stirred for 12 hours at 323 K, and the final slurry was transferred to rotary evaporator to remove excess water under vacuum at 353 K, followed by drying in an oven at 393 K for 6 hr, the dried pellet was calcined in the furnace at 823 K for 5 hours.

HZSM-5 is the catalyst used for ethanol to hydrocarbon conversion. The starting HZSM-5 was used as a support for calcium oxide, copper oxide and zinc oxide respectively. Other starting material such as copper nitrate salt, zinc nitrate salt and calcium nitrate salt was procured from Merck. Catalyst was prepared by doping 2wt% ZnO onto HZSM-5 prepared by impregnation techniques. The final solution was stirred for 12 h at 303 K. The final catalyst slurry was transferred to a rotary evaporator to remove excess water under vacuum at 353 K followed by drying in an oven at 393 K for 12 h. The dried pellets were calcined in a furnace at 823 K for 5 h.

The surface areas and pore volumes of the catalysts were determined by using ASAP 2010 (Micromeritics, USA) by adsorption with nitrogen (99.99 % purity) at 77 K, employing the static volumetric technique. Prior to the analysis the catalysts samples were degassed for 6 h at 383 K under vacuum. The samples were placed in the evacuated sample tube, cooled to cryogenic temperature and then exposed to the analysis gas at precisely controlled pressures. With each incremental pressure, the number of gas molecules adsorbed on the surface increases. The pressure at which adsorption equilibrium occurs was measured and quantity of gas adsorbed was determined. Adsorption/desorption sets of data were used to describe the isotherms. Analysis of the isotherm gave information about the surface characteristics of the material and was done by microcomputer processing software (ASAP 2010).

ETH reaction was conducted at 410 °C in fixed bed reactor using. All the catalysts were compared for their performance for ethanol conversion by conducting experiments under identical conditions. Liquid ethanol was evaporated by preheater at 200°C. Ethanol was fed to reactor by a dosing pump and vaporized ethanol was made to enter in reactor at WHSV=3.5$h^{-1}$.The reactor effluent was analyzed by two gas chromatographs equipped with flame ionization detector and thermal conductivity detector.

## 3. RESULTS AND DISCUSSION

The surface area and pore volume of the catalyst were determined by BET surface area technique. The BET surface area analysis results are shown in Table 1. The surface area of catalyst decreases on increasing zinc oxide loading. Volume of $N_2$ adsorbed decreased with 2wt% of zinc oxide. Due

to partial coverage of the surface with zinc oxide, there is decrease in pore radius of the ZnO doped HZSM-5 as compared to parent HZSM-5 (as shown in Table 1). Effect of ZnO addition on conversion and products yield as function of time on stream has been shown in Fig. 1 and Fig. 2. Compared to HZSM-5 catalysts there was an increase in conversion and hydrocarbon yield was observed with 2wt%ZnO/HZSM-5 [HZ(Zn)] however these values were significantly less when compared with ZnO doped catalysts. The major products of the reaction were methane, ethylene, propylene, dimethyl ether, toluene, ethyl benzene, xylene, isopropyl benzene, ethyl toluene, and trimethyl benzene and tetra methylbenzene. Fig. 1 shows a comparison of effect of run time on conversion with HZ (0) and HZ (Zn) catalysts. As can be seen from Fig. 1, conversion of ethanol decreases with increase in time on stream. Initial conversion of HZ (Zn) and HZ (0) were 91.4% and 76.3% respectively and after 15 h run methanol conversion decreased to 68.2% and 59% respectively for these two catalysts. Fig. 2 shows the yield of hydrocarbons with respect to time. The increase in time of stream also results in decrease in the yield of hydrocarbons. Fig. 2 also shows a comparison of effect of run time on hydrocarbon yield with HZ (0) and HZ (Zn) catalysts. As can be seen from this Fig. 1, hydrocarbon yield of ethanol decreases with increase in time on stream. Initial hydrocarbon yield of HZ (Zn) and HZ (0) were 45.15% and 38% respectively and after 15 h run, hydrocarbon yield decreased to 33.1% and 29.1% respectively. Addition of ZnO increases the active sites on HZSM-5, which are highly selective to hydrocarbons.

## 4. CONCLUSIONS

2wt% ZnO modified HZSM-5 catalyst showed very high reactivity and stability as compared with HZ (0) catalyst in ethanol conversion to hydrocarbons. It was also observed that HZ (ZnO) catalyst convert higher amount of ethanol to hydrocarbons before catalyst was completely deactivated.

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**Table 1 BET Surface Area and Pore Volume of Fresh catalyst.**

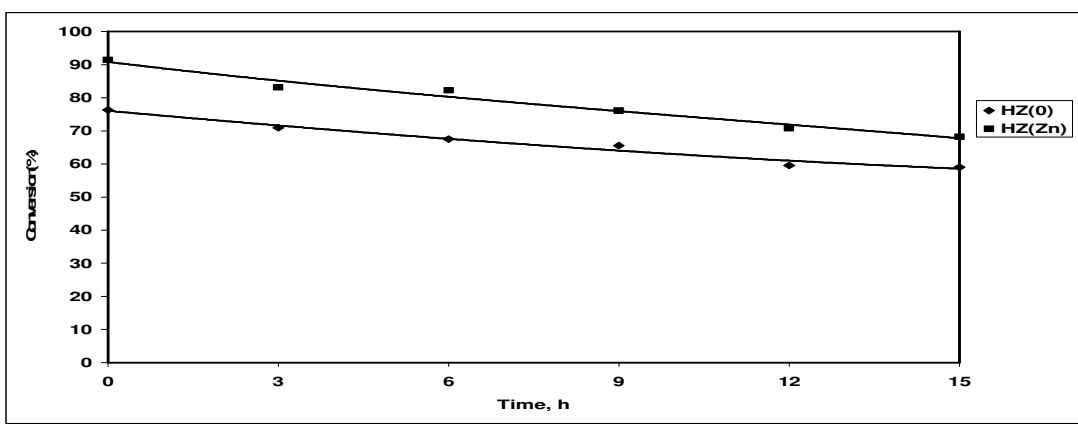


**Fig. 1 Conversion of ethanol versus Time in a Fixed Bed Reactor [T=410 °C, P=1 atm and WHSV=3.5h$^{-1}$]**

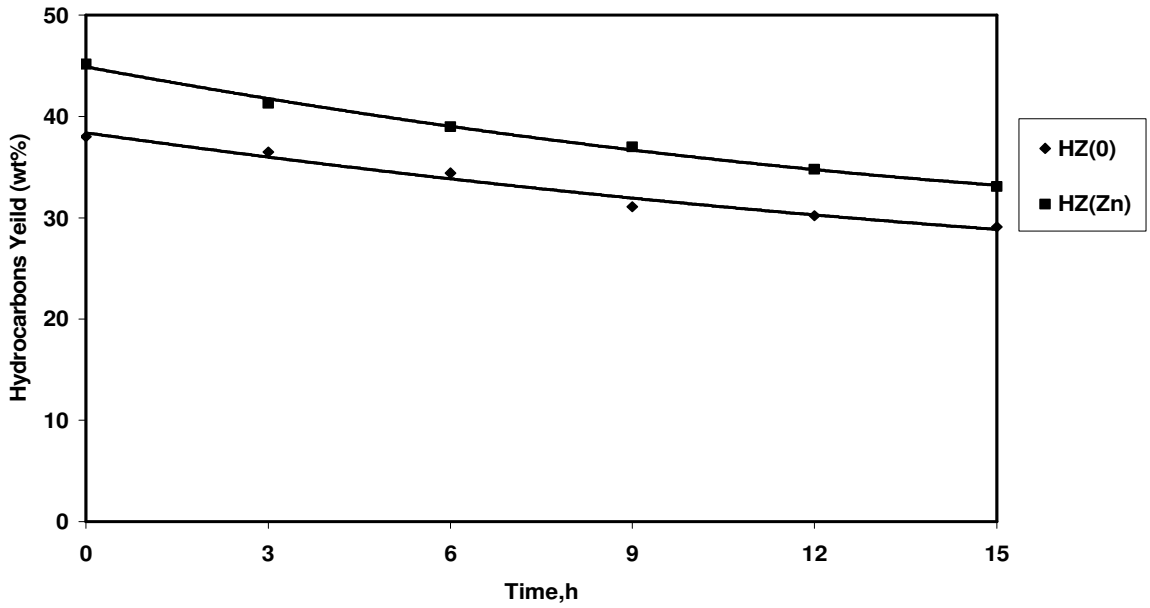


**Fig 2 Yield of Hydrocarbon versus Time in a Fixed Bed Reactor [T=410°C, P=1 atm and WHSV=3.5h$^{-1}$]**

**Table 1 BET Surface Area and Pore Volume of Fresh catalyst**

| Catalyst | Metal content (wt%) ZnO | $S_{BET}$ ($m^2/g$) | Pore volume ($cm^3/g$) |
|---|---|---|---|
| HZ(Zn) | 2 | 205 | 0.27 |
| HZ(0) | 0 | 227 | 0.278 |