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Catalytic Reaction of Ethanol into Light Olefins Over 2wt%CuO/HZSM-5

Abstract- There was increasing in the international needing for fossil fuel, which is formed from nonrenewable materials such as crude oil. Bio-ethanol considered one of the materials that can be produced from renewable sources like the fermentation of sugar cane. 2wt% CuO doped HZSM-5 has been modified by the impregnation method. All experimental runs have conducted at 500 °C, 1 atmosphere pressure and WHSV 3.5 h^{-1} in a fixed bed reactor. Catalyst, which modified in this work, was analyzed by SEM and XRD as well as TGA experiment. The analysis hydrocarbons products have done by gas chromatographs provided with flame ionization detector (FID) and thermal conductivity detector (TCD). It has been studied CuO doped HZSM-5 catalyst gives higher ethanol conversion and yield especially light olefins as compared to HZSM-5 parent catalyst. In addition, reduces the coke formation over HZSM-5, therefore, enhanced the life of HZSM-5 catalyst.

Keywords- HZSM-5, ethanol to hydrocarbons, Catalyst, coke, deactivation

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1. Introduction

Catalytic reaction conversion of ethanol into light olefins has raised considerable interest in the scientific community in the last years, particularly since the price of fossil fuels increased and environmental policies became stricter. ETH has been studied due to raising the need of hydrocarbons in the markets[5-14] Objective of this work is to study the effect of CuO doping catalyst on the performance of this HZSM-5 catalyst. Ethanol conversion to hydrocarbons is used as fuel. Ethylene and propylene (Light olefins) are remarkable intermediates in petrochemicals factory especially ethylene. Zeolite was created as HZSM-5 from 1970 at that time of crude oil demand, using HZSM-5 in the conversion of ethanol into chemicals as propylene is promising. Ethanol is particularly attractive because it can be obtained from the fermentation of biomass such as sugar cane. Preparation HZSM-5 using 2wt%copper oxide increasing the conversion and yield of chemical products especially light olefins. Loading different metals over HZSM-5 catalyst using the impregnation method has been studied [1-6]. Ethanol conversion to ethylene and ethanol to aromatics over zeolite
HZSM-5 have been studied [1-4]. The objective of this work is to hold out the influence of copper oxide loading on the catalytic performance of HZSM-5.

2. Catalyst Preparation

Impregnation technique was used in present work for preparing the catalyst 2wt% of copper oxide. HZSM-5 (Si/Al=80) is used for the catalytic reaction of ethanol to hydrocarbons. Parent HZSM-5 has been taken as a support for copper oxide. Catalyst has been modified by doping 2wt% of CuO onto HZSM-5 catalyst, the final solution was stirred for 12 h at 303 K. after that the catalyst slurry was put under vacuum to a rotary evaporator to remove excess water at 353K 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 to remove all impurities and decompose copper oxide over HZSM-5.

3. Catalyst Characterization

XRD is a technique was used to measure the phases present in a substance. The important property of zeolite is well defined crystalline structure. X-Ray diffraction patterns of all the HZSM-5 catalyst used to characterize the crystallinity of the catalyst. X-Ray diffraction was studied by using ADX-2500 X-ray Diffraction Instrument. A scanning electron microscopy SEM that produce an image of a sample by scanning its focused beam of electrons. The electron interacts with an atom in the sample produce various signals that can be detected and can give information about the sample surface topography and composition. The morphology of the catalysts is studied using Netherlands SEM type inspect50.

4. Experimental Work

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Catalytic conversion of ethanol to hydrocarbon has been conducted in fixed bed reactor at 500 °C using 2.5gm parent and modified HZSM-5 catalyst with 2wt% CuO and to compare the performance of these catalysts for the catalytic conversion of ethanol to hydrocarbons especially light olefins. Experimental runs have been done for parent and modified HZSM-5 catalyst under similar conditions. The reaction temperature was measured by a thermocouple in the reactor. Liquid ethanol has been fed and evaporated at 200 °C by pre-heater and finally ethanol-fed to the reactor by a peristaltic pump at WHSV 3.5 h-1. The reactor effluent was analyzed by two gas chromatograph equipped with a Flame Ionization Detector and Thermal Conductivity Detector.

5. Results and Discussions

TGA analysis was performed to investigate how the coke deposits on HZSM-5 (0) and HZSM-5 modified catalyst after a 12 hrs duration. The parent catalyst was HZ(0) and HZ(2) was the modified HZSM-5 catalyst.

HZSM-5 fresh and modified catalyst after 12 hrs reaction has been moved to an oven at a temperature of 120 ˚C to get rid of moisture. It was taken 0.15gm from each catalyst and transferred to muffle furnace to burn the coke that formed over HZSM-5 catalyst. From this experiment, it was focused that the weight loss was more in case of HZ (0) that means HZSM-5 catalyst modified with 2wt% CuO had less formation of coke that has shown in Table 1.

Table 1. Burning catalyst samples after 12hr runs. HZ (0), HZ(2)

HZSM-5 Samples	Weight before muffle furnace	Weight after muffle furnace
HZ (2)	0.15 gm	0.143 gm
HZ (0)	0.15 gm	0.138 gm

HZSM-5 Samples Weight before muffle furnace Weight after muffle furnace
HZ (2) 0.15 gm 0.143 gm
HZ (0) 0.15 gm 0.138 gm

The major products of this conversion were ethylene, propylene, methane, ethyl methyl ether, xylene, toluene, ethyl benzene, isopropyl benzene, and ethyl toluene. Propylene and ethylene (light olefins) were more than others. One of the main problems related to the operation of catalytic conversion is the loss of the activity with time on stream due to coke formation. Effect of CuO addition to HZSM-5 parent catalyst on the conversion and yield which was studied in Fig .1.a and b. Figure 1 shows the effect of time on the conversion with parent and modified catalysts. Conversion of bio-ethanol has been decreased with time. The conversion of HZM(2) and HZM(0) were 92.5% and 77% at first respectively, and after 15 h run the conversion of ethanol has been decreased to 68% and 59% respectively for these two catalysts. Fig. 1.b. studied the hydrocarbons yield with run time. The increase in time of stream led to a decrease in hydrocarbons yield. It was shown in Figure 1.b hydrocarbon yield was decreasing with an increase in time on stream. Initial hydrocarbon yield of HZM(2) and HZM(0) were 45% and 38% respectively and after 15 hrs from the reaction, hydrocarbon yield goes to 33% and 29% respectively. Addition of copper oxide to parent catalyst helped to increase the active sites on parent catalyst and the selectivity to light olefins.

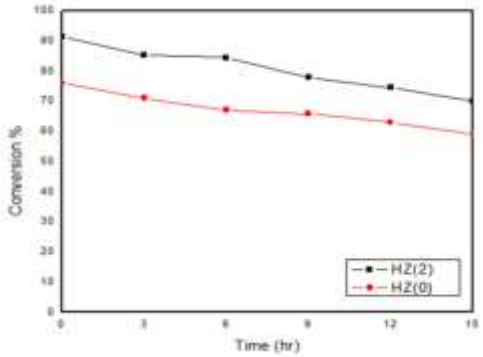

Figure 1: a Conversion of ethanol versus Time in a Fixed Bed Reactor [T=500°C, P=1 atm and WHSV=3.5h-1]

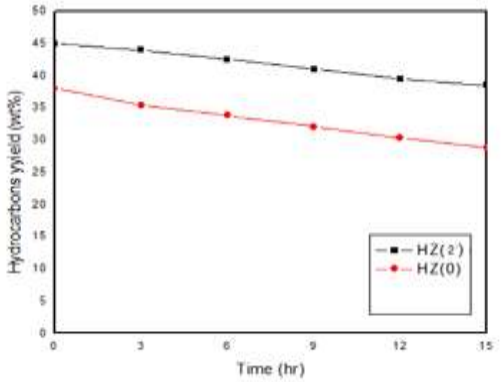

Figure 1: b Yield of Hydrocarbon versus Time in a Fixed Bed Reactor [T=500°C, P=1 atm and WHSV=3.5h-1]

To study the morphology of HZSM-5 parent and modified catalyst, SEM has been analyzed using Netherlands SEM type inspect 50. SEM samples were noticed to be spherical polycrystalline clumps and undefined shapes of particles were also present and shown in Figure 2.a and Figure 2.b.

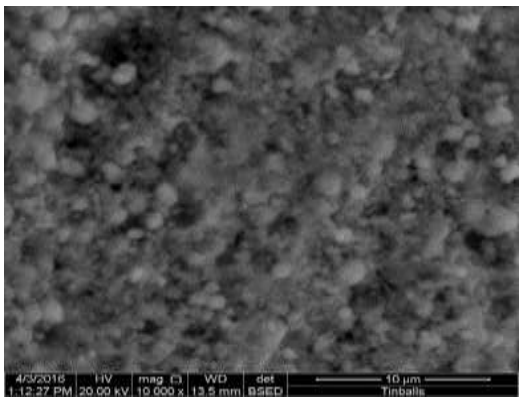

Figure 2: a SEM Image 2 wt% HZ(CuO) [T=500°C, P=1 atm and WHSV=3.5h1]

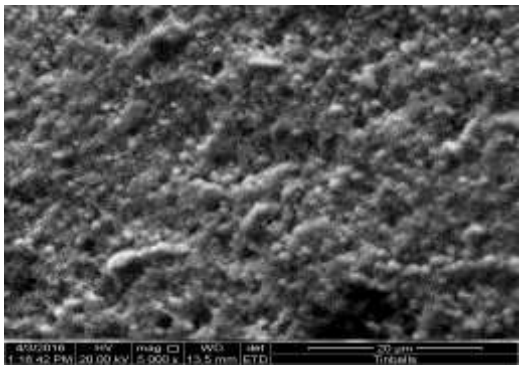

Figure 2: b SEM Image HZ(0)

XRD patterns are shown in Figure 3. 2wt% CuO doped HZSM-5 and parent HZSM-5 catalyst. There is a similarity of XRD patterns between unmodified HZSM-5 and modified HZSM-5 catalyst. It was found the original structure of HZSM-5 has not been destroyed during the impregnation process. It was observed from Fig.3 that no CuO species could be identified and significant changes were not observed in XRD patterns as compared with parent HZSM-5 catalyst. Figure 3 shows that the crystalline phase present in HZ(1) and HZ(0) catalyst. XRD revealed crystalline shape in the ZSM-5 (CuO) catalyst after modification. It was shown that the overall structure of catalysts remained the same.

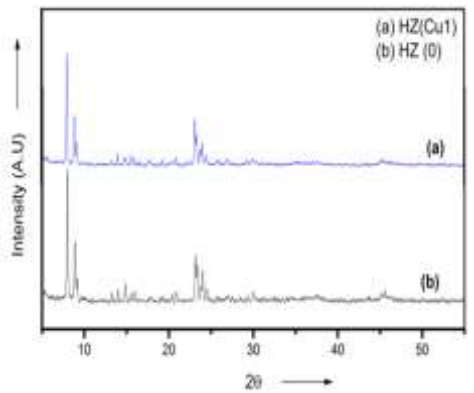

Figure 3: XRD patterns of HZ (0): HZSM-5, HZ (1): 2wt%copper oxide [T=500°C, P=1 atm and WHSV=3.5h-1]

5. Conclusions

The deactivation of the catalyst in the catalytic reaction of ethanol to hydrocarbons is mainly due to coke deposition, which increases with time on stream. Incorporation of CuO onto HZSM-5 (Si/Al=80) enhances the ethanol conversion and hydrocarbons yield due to the generation of additional active sites, facilitating the dehydrating activity of the catalysts and formation of hydrocarbons. The deactivation of the catalyst in the transformation of ethanol to hydrocarbons is mainly due to coke deposition, which increases with the time on stream. Incorporation of ZnO over HZSM-5 (Si/Al=80) enhances the ethanol conversion and hydrocarbons yield due to the generation of additional active sites which facilitate the dehydrating activity of the catalysts.

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