PRODUCTION OF HYDROGEN-RICH GAS BY BIOETHANOL STEAM REFORMING OVER Co/ZnO CATALYST

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Abstract - In this study, Co/ZnO catalysts were synthesized by the impregnation method with various active metal loading ratio. Characterization of the catalysts was performed by XRD, SEM, XRF, FT-IR and TGA techniques. Catalytic activities were investigatedthroughsteam reformingof ethanol with a 3: 1 vapor: carbon molar ratio, 600°C reaction temperature, and 0.05 L/g_{cat}.h LHSV. With all catalysts, ethanol was completely converted to gas product. The highest hydrogen yield and the highest heating value were found as 2.62 mol H_2/mol ethanol 65.26 MJ/kg, respectively in presence of Co/ZnO (20wt% Co loading)

Keywords - Bioethanol, Steam Reforming, Catalyst, Hydrogen

I. INTRODUCTION

Hydrogen, which hasa number of uninterrupted and highlyefficientuses, is ideal for supporting sustainable energy development, and is defined as a clean energy carrier because water is the only product. In addition, hydrogen energy is 143 MJ/kg, three times more energy potential than liquid hydrocarbon fuels [1].

Steam reforming is the industry's most preferred method for producing hydrogen from hydrocarbons [2]. The advantages of the steam reforming process compared to the partial oxidation reforming and auto-thermal reforming processes is that the steam reforming process does not require oxygen, has a high H_2/CO ratio and a lower operating temperature[3][4].

Even if hydrogen production by methane steam reforming is the most widely used technology, among the various raw material alternatives, alcohols come into prominence in hydrogen production from biomass [5]. Though methanol reforming is the most commonhydrogen production method, it is not environmentally friendly due to high CO_2 emissions during the process and its fossil-based structure. Ethanol exhibits lower toxicity than methanol [2]. Easy storage, transportation, easy accessibility, low production cost, and safety make ethanol attractive as a raw material [6]. Ethanol has many advantages such as high hydrogen content (H:C=3:1), biodegradability, and is obtained from the fermentation of renewable sources such as lignocellulosic biomass and energy plants [7]. The ethanol thus produced contains ethanol: water at a molar ratio of 1:13 (about 12% ethanol) and is called bioethanol[1].

Catalyst is one of the important parameters, as well as the reaction conditions. Studies on catalyst synthesis with high activity and stability, low cost are still ongoing. The catalysts are generally divided into two groups depending on the active metal loading, which are noble metal and non-noble metal catalysts. Among ethanol steam reforming studies, Ru, Rh, Pt, and Pd noble metals display high activity and selectivity, but because of their high cost, their use is limited and the research focuses on non-noble metals [1]. Ni, Co, Cu are transition metals commonly used in steam reforming between non-noble metals [8]. It has been observed that cobalt plays an important role in CO activation, an increase of H_2 yield, acetaldehyde, and CO_2 partial oxidation. Another important factor in catalyst synthesis is the support material. MgO, ZnO, CeO_2, La_2O_3, Al_2O_3, ZrO_2 support materials are seen as suitable support materials with their basic properties such as H_2 production, stability, and support of ethanol dehydrogenation but prevention of dehydration [9].

Whereasthere are various studies in the production of hydrogen with bioethanolsteam reforming in the literature, hydrogen reforming with bioethanol in the presence of Co/ZnO catalyst is generally carried out on different supports and precursor but there is not much work with active metal loading ratio.
Llorca et al. [10], performed catalytic tests of the Co/ZnO catalyst (10wt% Co loading)using different cobalt precursors in the steam reforming reaction of ethanol. 5.28 mol H_2/mol ethanol was produced at 1:4 by volume of ethanol:water, 5000 h^{-1} GHSV and 450°C.

Chiou et al. [11],investigated the activity studies of monometallic Co_x/ZnO and bimetallic Pt_yCo_{10}/ZnO catalysts synthesized by impregnation method with different Co and Pt loading in hydrogen production using ethanol steam reforming. The catalytic activity tests were evaluatedwith a fixed bed reactor using a molar ratio of H_2O/EtOH 13:1 and gas hourly space velocity (GHSV) 22,000 h^{-1}. As the best result, the

product dispersion was determined at 325°C and the H_2, CO_2, CH_4, and CO composition being 73.2, 23.8, 2.4,0.6% respectively. Llorca et al. [12], Co-based catalysts (1 wt% Co loading) synthesized with different support materials were tested in ethanol vapor reforming. The highest selectivity was achieved with a Co/ZnO catalyst of 71.3% H_2, 20.2% CO_2 and 0.8% CH_4 at a ratio of 13 1 ethanol:water, at 5000 h^{-1} GHSV and a temperature of 450°C. CO was not observed. In this study, the Co/ZnO catalyst was synthesized by the impregnation method. Unlike literature, catalysts have been studied at different active loading rates. Characterization of catalysts X-ray diffractometry (XRD), scanning electron microscopy (SEM), X-ray fluorescence spectroscopy (XRF), thermogravimetric analysis (TGA) and Fourier transform infrared spectrometer (FT-IR) analyzes were achieved. The activities of thecatalysts were illustratedto obtain hydrogen-rich gas product by ethanolsteam reforming. Catalytic selectivity, gas yield, and heating value were studied at 600°C, 0.05 L/g_{cat}.h LHSV (liquid hourly space velocity) and 3: 1 steam:carbon molar ratio.

II. MATERIAL AND METHODS

A.Material

Bioethanol (96.1%)used in experimental studies is by product Sugar Factory in Turkey.

Cobalt (II) nitrate hexahydrate wassupplied from Sigma-Aldrich which was used as cobalt active metal phase precursors. Zinc oxide was purchased from Sigma-Aldrich. All the chemicals were used without any pre-treatment.

B.Catalyst preparation

The catalyst was synthesized using cobalt (II) nitrate hexahydrate and zinc oxide precursor by impregnation method with 5, 10, 20, 30 and 40 (wt/wt%) cobalt loading amount.

The calculated amount of cobalt (II) nitrate hexahydratesalt was dissolved in distilled water at a ratio of 1:5 catalyst:water (wt/wt) and added tozinc oxide which was used as support material. The prepared solution was impregnated in a water bath with a magnetic stirrer at 70°C for 3 hours. After impregnation, the mixture was allowed to age at room temperature for one day and dried overnight in an oven at 105°C for 24 h. The material whose particle size was reducedwas calcined under dry air at 650°C for 3 h in a tubular furnace.

C.Catalyst characterization

The mass composition of the catalysts wasinvestigated by an XRF device of the Rigaku ZSX model.

XRDpatterns were collectedusing the RigakuRint 2200 X-Rays diffractometer. Cu-Kα radiation was used as the X-ray source over 15-85° (2θ) and 4°/min scanning rate. Average crystalline size was derived by the Scherrer equation.

The weight loss as a function of temperature was recorded by a TGA device of model Netzsch STA 409 PG. TGA measurements were analyzed by heating to 900 ° C with a heating rate of 10 °C/min under nitrogen flow.

Surface images of the catalysts were taken by SEM model Regulus 8230. Measurements were examined at different magnification rates under 10-6 torr vacuum at 15 WD at 20 kV.

The vibration properties of chemical bonds and the determination of chemical functional groups were studied by Thermo Science Nicolet IS10 FT-IR. Analyzes were recorded in the range of 400-4000 cm^{-1} with 64 scans and 4 cm^{-1} resolution.

D.Catalytic test

The activities of the catalysts were tested by steam reforming ethanol under atmospheric pressure in a fixed bed continuous flow quartz reactor (PID Eng&Tech Micro Efficiency). Diagram of the processwas schematized in Fig. 1

In the experiments, 0.1 g catalyst was fed to the reactor by mixing with 1: 25 (wt%) SiC and the reactor was placed in the isolated furnace. The synthesized catalysts were reduced prior to activity tests at a heating rate of 10°C/min to 800°C and under a flow of hydrogen at 30 mL/min for 30 min.

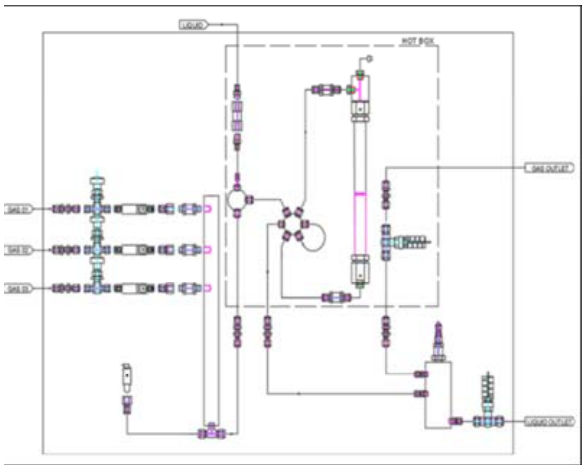


Fig 1. Schematic diagram of the process

After reduction, water and ethanol were fed to the system by HPLC pump at flow rates calculated based on steam: carbon ratio. Activity tests were carried out at a 3:1 molar ratio of S:C, LHSV of 0.05 L/g_{cat}.h. The reactions were continued for an average of 12 analyzes. The products formed as a result of the reaction were sent to the gas-liquid separator, condensed at 10°C and

separated gas and liquid products. The gas product was periodically analyzed (10 minutes) by the online micro gas chromatography apparatus.

The ethanol conversion (X_{ETOH}), hydrogen yield (Y_{H2}), H_2 selectivity are calculated with Equation 1, 2 and 3 respectively.

$$X_{EtOH} = \frac{ni_{EtOH} - nf_{EtOH}}{ni_{EtOH}} \quad (1)$$

ni_{EtOH}: ethanol feed amount (mol)

nf_{EtOH}: the amount of unreacted ethanol in the product (mol)

$$Y_{H_2} = \frac{n_{H_2}}{n_{FEED\ ETOH}} \quad (2)$$

Y_{H2}: Hydrogen yield (%)

n_{H2}: Amount of hydrogen in the gas product (mol)

$n_{FEED\ ETOH}$: Ethanol (moles) fed to the system

$$S_{H_2} = \frac{n_{H_2}}{\sum n_{H_2}} * 100 \quad (3)$$

S_{H2}: Hydrogen selectivity

n_{H2}: The amount of hydrogen in the gas product (mol)

$\sum n_{H2}$: Total gas amount of hydrogen in the product (mol)

The selectivity of CO, CH_4, and CO_2(Equation 4) was registeredas the fraction of the carbon content of the produced carbon monoxide, methane, and carbon dioxide in the product.

$$S_i = \frac{n_i}{\sum n_C} * 100 \quad (4)$$

S_i: Product selectivity

n_i: Desired quantity of a product in the gas product (mol)

$\sum n_C$: Total amount of carbon in the gas product (mol)

E. Gaseous Product Analysis

The composition (mol/mol%) of the gas product mixture was analyzed online for ten minutes with the Agilent 490 Micro GC.Detection of gaseous products was provided by a thermal conductivity detector, equipped withthe two different modules. Argon was used as a carrier gas in both modules. In the first module CH_4, CO and H_2 gases are separated, in the second module CO_2, ethylene, ethane, propylene, and propane are attained. The composition of the gas product is determineddepending on the calibration gas mixture. Thermal values of gas products were calculated automatically.

III. RESULTS AND DISCUSSION

A. Catalyst characterization

XRF analyses were performed to evaluate the chemical composition of the synthesized catalysts.The XRF results of Co/ZnOcatalysts with different cobalt loading are depicted inTab. 1.

Catalyst	Amounts to be loaded	CoO (wt/wt%)	ZnO (wt/wt%)
Co/ZnO	5/95	7.35	90.31
	10/90	13.82	83.14
	20/80	26.03	70.49
	30/70	37.71	58.83

Table 1. XRF results of Co/ZnO catalyst

As can be seenfrom Tab. 1, XRF results are very close to the desired values. While loading calculations are based on metallic Ni and Co, it is possible that the XRF results are higher than the calculated values since the results are given in oxide form. It is thought that some deviations in the support material ratios are caused by impurities in the precursor used and experimentalerror. XRD analyses wereexecutedto determine the crystal structure of the catalysts. Fig. 2 shows the XRD analyzes after calcination of Co/ZnO catalysts.

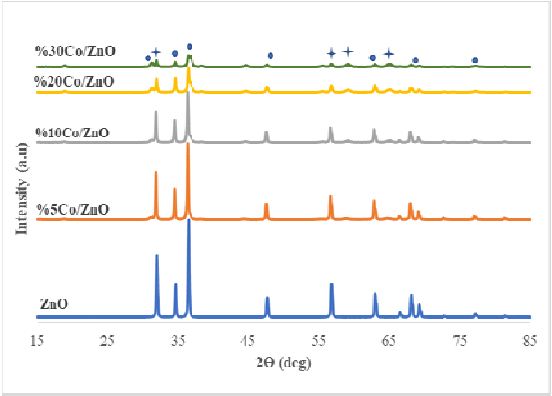


Fig 2. XRD diffraction patterns of Co/ZnO (+: CoO, ●: ZnO)

The XRD diffraction pattern of Co/ZnO catalysts (Fig. 2) illustrated sharp and severe peaks, which is explained by the fact that the Co/ZnO catalysts have a crystalline structure. ZnO characteristic peaks in the crystal structure are 2θ= 30.8, 33.5, 36.3, 46.6, 62.9, 67.9, 69.1, 76.9°, Co_3O_4 characteristic peaks are 2 = 31.1, 55.4, 59.1 and 64.9°. As the cobalt content of catalysts increased, lower peaks were acquired. This can be explained by the fact that the amount of zinc oxide in the crystal structure decreases due to the increase in the cobalt loading amount and the structure becomes less crystalline with decreasing zinc oxide.Tab.2 provides average particle size.

	Loading amount (wt%)	Average Crystal Size (nm)
ZnO	-	7.52
Co/ZnO	5/95	8.84
	10/90	8.10
	20/80	4.86
	30/70	3.67

Table 2. Avaragecrystalline size of Co/ZnO catalyst

Tab. 2presents that Co/ZnO catalysts play an important role in the cobalt loading ratio in the crystal size. The average crystal size of the Co/ZnO catalysts ranges

from 8.84 to 3.67 nm. While the average crystal size of the ZnO support material was 7.52 nm, this value increased to 8.84 nm with 5% cobalt loading by weight.In general, this may be due to the strong bonding of the support to the metal phases, as the weakly bound metal phases tend to collide and form larger crystals while stabilizing the phases [8]. As the cobalt loading rate increased, a decrease in crystal size was observed. The crystal size, which was 8.10 nm with 10% cobalt loading by weight, reached 4.86 nm with 20% cobalt loading and the smallest value of 3.67 nm with 30% cobalt loading. As a result, up to sixty percent reduction in the crystal size of the catalysts was achieved with an increase of twenty percent active metal.

TGA/DTG analyzes were recordedto investigate the thermal stability and behavior of the catalysts.The TGA and DTG data of Co/ZnOis given in Fig. 3

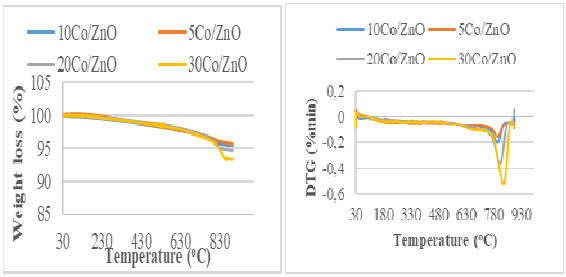


Fig 3. a) TGA b) DTA of Co/ZnO catalysts

The approximate mass loss of Co/ZnO(Fig. 3) to 700°C is only 3%, indicating that the catalysts have high thermal stability. The small mass loss in the 135-200°C range is usually associated with the removal of water at the interface [13]. Depending on the heating rate used, it is difficult to distinguish between mass losses due to decomposition and dehydration but extends to approximately 700°C on a slightly inclined level almost horizontally [14]. The endothermic peak seen after 800°C is associated with the conversion of the catalyst to the active metal form by reduction. The change in peak intensities is associated with metal loading.

FT-IR spectrum wascollected to investigate the chemical bond structures in the catalyst. Fig. 4 shows the FT-IR analysis results of Co/ZnO catalysts with different cobalt loading ratios.

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The peaks in the wavelength range 500-700 cm-1 (Fig. 4) the presence of ZnO[15]. Vibrations around 800 cm^{-1} are associated with the Co-O tape. Peaks corresponding to the Zn-OH mode are observed in the range of 1100-1600 cm^{-1}[16]. The 1400cm^{-1} bands are assigned C=O stretching modes. The peak that occurs around 2300 cm^{-1} is due to the CO_2 frequency adopted from the air [17]. The wide band at 2900-3700 $cm^{-1}$is described by overlapping bands of C-H and O-H [15][16]. The surface area morphology of the catalysts, SEM analyzes for particle size distribution and EDS analyses were conductedfor the elemental composition. Fig. 5 displays SEM images of the Co/ZnO catalyst with 20% by weight active metal loading. As seen from Fig. 5, Co/ZnO SEM images are consistent with XRD analysis and appear to be crystalline. Particle sizes vary between 3.48-2.28 µm at X5000 magnification. The crystal size calculated by XRD (Table 3) is 3.67 nm. EDS analyzes confirm the presence of Co, Zn and O. In addition, when the peak intensities are examined, it is seen that the cobalt concentration is approximately the same and homogeneously distributed in all three regions. It is seen that zinc is more in the first spectrum than the others. Looking at the SEM image of the region where the spectrum is taken, it is thought that a large crystal structure is formed in this region and the high zinc content is caused by this large crystal structure which is the result of agglomeration.

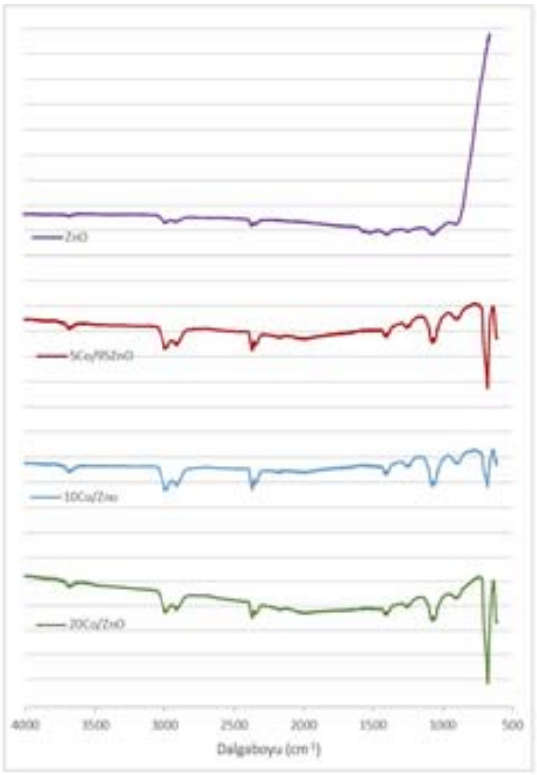
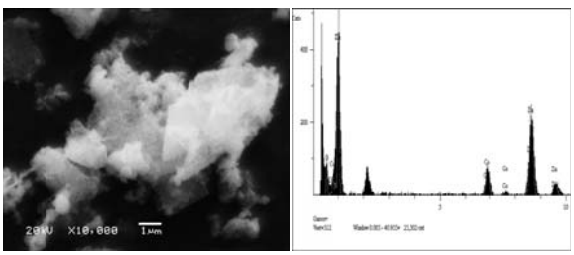


Fig 4. The FT-IR spectrum of Co/ZnO catalysts



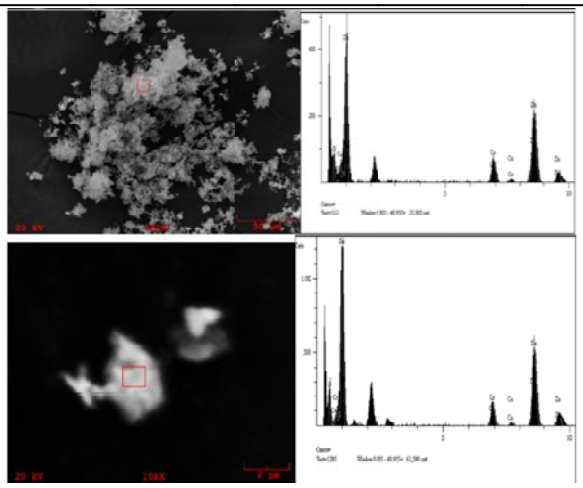


Fig 5. SEM/EDS analysis results of Co/ZnO

B. Catalytic test

The effect of catalysts on hydrogen yield, product selectivity,and the high heating value wasinvestigated by activity tests.Fig. 6representsthe effect of Co/ZnO catalysts on hydrogen yield.

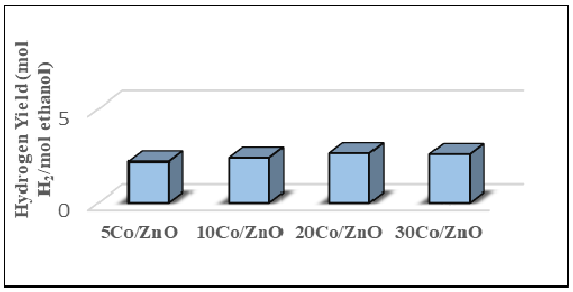


Fig 6. Effect of active metal loading ratio of Co/ZnO catalyst on hydrogen yield (600°C, 0.05 L/g_{cat}.h LHSV and 3:1 S:C molar ratio)

As demonstrated in Fig. 6, as the cobalt ratio (wt/wt) is increased from 5% to 20%, an increase in hydrogen yield is observed. In all studies with catalysts, ethanol is completely transformed into a gas product. Hydrogen efficiency, which was 2.18 mol H_2/mol ethanol in 5% Co loading, increased to 2.38 mol H_2/mol ethanol when Co loading was increased to 10%. The maximum value reached as 2.63 mol H_2/mol ethanolwith 20% Co loading.As the Co loading was increased to 30%, thehydrogen yield decreased slightly andwas2.58 mol H_2/mol ethanol. The effect of Co/ZnO catalysts on product selectivityis summarized Fig. 7.

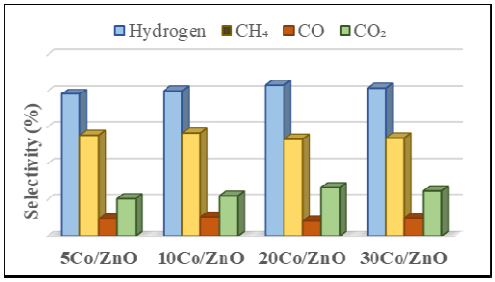


Fig 7.Effect of active metal loading ratio of Co/ZnO catalyst on product selectivity (600°C, 0.05 L/g_{cat}.h LHSV and 3:1 S:C molar ratio)

When the effect of active metal loading rate on product selectivity (Fig. 7)is considered, it is observed that hydrogen selectivity increases as the active metal loading rate increases in 5-20% loading range.

Coloading increased from 5% to 10% and hydrogen selectivity increased from 78.29% to 80.2%.At 20% Co loading, the increase of hydrogen selectivity continued and the maximum value reached 83.25%. As the Co loading was subtracted by 30%, a small decrease was observed in the hydrogen selectivity and the hydrogen selectivity reduced 81.69 %. This decrease in hydrogen selectivity is thought to be due to highly active metal loading blocking pores and low surface area.

CO_2 selectivity exhibited similar behavior with hydrogen selectivity and CO_2 selectivity increased with Co loading. CO_2 selectivity, which was 20.51% in 5% Co loading, was 22.01% when 10% of Co loading was subtracted. At 20% Co loading, it was 26.82% and reached its maximum value. The increase in CO_2 selectivity as Co loading increases is explained by the effectiveness of cobalt in reforming and water gas shift reactions[18].

CH_4 selectivity is almost the same in all catalysts and varies between 53-57%. The maximum CH_4 selectivity was found to be 56.8% using 10% Co loading. The low CH_4 selectivity seen in 20% and 30% Co loads compared to other loading rates is described as high cobalt concentrations reduce methane formation[19].

CO selectivity is very low compared to other product selectivity and varies between 8-11%. CO selectivity decreased to the minimum value of 8.24% at 20%Co loading but increased again to 9.87% at 30% Co loading.

Fig. 8 shows the effect of Co/ZnO catalysts on the high heating value.

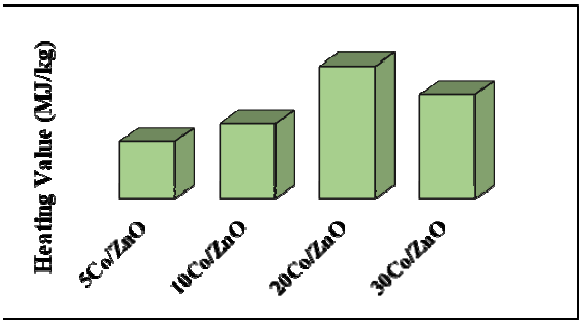


Fig 8. Effect of the active metal loading ratio of the Co/ZnO catalyst on the high heating value (600°C, 0.05 L/g_{cat}.h LHSV and 3:1 S:C molar ratio)

Ascan be seen from Fig. 8, the maximumhigh heating value was reachedat 20% cobalt loading (65.26

MJ/kg). The heating value of 61.11 MJ/kg attained at 5% cobalt loading. When the loading rate was increased to 10%, no significant increase in heating value (62.09 MJ/kg) was observed due to similar gas product composition. When the Co loading rate was increased to 20%, the heating value increased to 65.26 MJ/kg with a higher hydrogen selectivity than other catalysts, although there was a slight increase in CO_2content.

IV. CONCLUSION

Co/ZnO catalysts were synthesized by impregnation method at 5, 10, 20, 30wt% Co loading. Catalysts were characterized by SEM, XRD, FT-IR,XRF, and TGA analyzes. Catalytic activity studies were carried out by keeping the 3:1steam:carbon molar ratio, 0.05 L/g_{cat}.h LHSV and 600°C reaction temperature constant. The effects of catalyst on ethanol conversion, gas yield, and composition were investigated.

The highest hydrogen yield (2.63 mol H_2/mol ethanol), hydrogen selectivity (83.25%) and the high heating value (65.26 MJ/kg) were obtainedwith the Co/ZnO catalystat 20% cobalt loading.

Studies on hydrogen production with bioethanol steam reforming in the presence of cobalt-based catalysts have generally focused on different support materials, but there has not been much work on loading rates. When the values attained at Co/ZnO catalysts were compared with the literature, it was observed that there was no difference in ethanol conversions, the hydrogen yield was lower but the hydrogen selectivity was higher in this work.

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