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Ni-Co Bimetallic Catalyst Synthesis by Co-impregnation Method for Hydrogen Rich Gas Production from Olive Pomace

Vildan Aker and Nezihe Ayas

***Abstract*—Hydrogen is defined as an ideal energy carrier among sustainable, clean and renewable energy sources, so it is important to produce hydrogen and to develop the sustainable hydrogen economy. Catalyst plays a vital role in the production of hydrogen at low cost and high efficiency. Selection of support and active material, catalyst preparation methods considerably affect the activity of the catalysts. In this work, Ni-Co bimetallic based catalysts were synthesized by the co-impregnation method using different support materials (Al_2O_3, ZrO_2, ZnO, Al_2O_3-ZrO_2) in order to obtain the highest hydrogen-rich gas from biomass. Ni-Co bimetallic catalysts were synthesized and characterized by XRD, XRF, TGA, SEM and FT-IR techniques. The activities of Ni-Co/Al_2O_3, Ni-Co/Al_2O_3-ZrO_2 catalyst were studied in gasification of olive pomace. It was found that the H_2 yield of the Ni-Co/Al_2O_3 (10.76 mole H_2/kg Olive pomace) was higher than Ni-Co/Al_2O_3-ZrO_2 (5.37 mole H_2/kg Olive pomace).**

***Index Terms*—Catalyst, co-impregnation, hydrogen, olive pomace gasification.**

I. INTRODUCTION

Research on alternative energy has increased considerably since fossil fuel reserves will soon be exhausted, and cause environmental pollution and health problems [1], [2]. Renewable energy is the most important alternative energy source since it is clean, sustainable and more stable than fossil fuels in terms of price [3]. Hydrogen is regarded as a clean energy carrier [3], [4]. Biomass, one of the hydrogen production sources, draws attention as a supply of CO_2 as neutral energy because CO_2 generated in the conversion process is consumed by biomass growth [3]. Catalysts play a crucial role in hydrogen production [5]. Active catalysts should maximize hydrogen selectivity, minimize coke formation, and prevent CO production [6]. Non-noble metal catalysts such as Ni- and Co- metallic based are often preferred in catalyst production studies. Although nickel is highly preferred by the reason of low cost, good activity, selectivity, ability in cleavage C-C, C-O and C-H bonds, some problems such as coke formation and metal sintering are encountered [3], [7]. Bimetallic catalysts have been developed in order to achieve higher catalyst performance and improve the electronic properties of the metal surface [8]. Ni-Co bimetallic catalyst increases the water-gas shift reaction which plays an important role in hydrogen yield [7]. Ni-Co with high dispersion of the active phase, strong metal-support fundamental interaction and high coke resistance is developed [9]. Several oxides have been investigated as a support material to provide optimum metallic distribution, the thermal stability of the metal phase and to participate in the catalytic process [5].

Mediterranean countries such as Turkey have mainly olive oil industry. Olive oil mill waste produced in large quantities in a short time in the Mediterranean regions represents an important environmental problem. Turkey annually produces approximately 700 kt and 120 kt olive pomace. A large portion of olive oil wastes contains valuable resources such as organic matter and recyclable nutrients. The estimated amounts of wastes derived from the olive oil industry in Europe are 6.8 million tons/year, which is about 18 MJ / kg promising energy content [10].

Although there are studies about olive pomace in the literature, few studies are on the olive pomace gasification.

Puig-Gamero et al. compared the gasification of olive pomace, coal, petcoke and binary or triple mixtures. The maximum H_2/CO ratio of pomace-petcoke mixture, coal and olive pomace was determined as 0.0250, 0.0145, 0.00611, respectively [11].

Borello et al. have investigated thermo-economical analysis of heat and energy of synthetic gas produced from olive pomace by gasification. The low heating value (LHV) (on dry material basis) of the synthesis gas was found to be 5.4 MJ/kg [12].

Sert et al. gasified olive pomace by hydrothermal gasification in the presence of trona, K_2CO_3, and KOH using batch autoclave reactor. The maximum H_2 yield was obtained as 16.80 mol/kg biomass at 600°C in the presence of KOH catalyst [10].

Within this work, the influence of different support materials (Al_2O_3, ZrO_2, ZnO, Al_2O_3-ZrO_2) of the catalyst on the formation of crystal morphology and on the distribution of catalytic active species was investigated. Ni-Co based catalysts were synthesized using co-impregnation method. Catalysts were characterized by XRD (X-ray diffraction measurements), XRF (X-ray fluorescence spectroscopy), SEM (Scanning Electron Microscope) and TGA (Thermo Gravimetric Analyses) techniques. The activity of the catalyst was determined by performing gasification of olive pomace.

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II. EXPERIMENTAL

A. Materials

Nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] and Cobalt (II) nitrate hexahydrate [$Co(NO_3)_2.6H_2O$] were purchased from Sigma-Aldrich which were used as nickel and cobalt active metal phase precursors, respectively.

Aluminum oxide [Al_2O_3], zirconium (IV) oxynitrate hydrate [$ZrO(NO_3)_2 \cdot xH_2O$], zinc oxide [ZnO], zirconium (IV) oxide [ZrO_2] were purchased from Sigma-Aldrich. All the chemicals were used without any pre-treatment. Olive pomace was supplied from olive oil factory in Turkey and dried before gasification.

B. Catalyst Preparation

Ni-Co bimetallic catalyst was synthesized by the co-impregnation method using Al_2O_3, ZrO_2, ZnO, Al_2O_3-ZrO_2 (10% ZrO_2 (wt/wt) as support materials. The amount of active metal loaded was kept constant as Ni 10% (wt/wt) and Co 5% (wt/wt).

Synthesizing Al_2O_3-ZrO_2 (10% ZrO_2 (wt/wt) support material: The required amounts of precursors were dissolved in distillated water with 1:5 catalysts:water ratio (wt/wt), the solution was stirred in a magnetic stirrer water bath at 70°C for 3 hours. After aging the mixture at room temperature for a day, it was dried at 105°C overnight and then calcined at 550°C (2°C/min) for 3 hours under an air flow.

Loading active metals over the support: The appropriate amount of nickel and cobalt nitrates were dissolved in distilled water with a 1:5 catalyst: water ratio (wt/wt). The nitrate aqueous solutions were added over the support material and placed in a water bath at 70°C and stirred for 3 hours and then the mixture was aged at room temperature for a day then dried at 105°C overnight and calcined at 550°C (2°C/min) for 3 hours under an air flow.

C. Catalyst Characterization

TGA (Thermo Gravimetric Analyses) was carried out using Netzsch STA 409 PG model thermal analysis system at 900°C in N_2 atmosphere at a heating rate of 10°C/min.

XRD (X-Ray Diffraction) patterns were performed with a Rigaku Rint 2200 X-ray diffractometer employing the graphite filtered Cu-Kα radiation over $2\theta=15$-$85°$ and scanning rate 4°/s.

XRF (X-ray fluorescence spectroscopy) was determined by Rigaku ZSX model XRF instrument to determine the mass composition of the catalysts.

SEM (Scanning Electron Microscope) was conducted on Zeiss EVO 50 VP model scanning electron microscope at 20 kV.

FT-IR analyses were performed at room temperature on a Thermo Scientific Nicolet IS10. Spectra are recorded in the range 400-4000 cm^{-1} with an accumulation of 64 scans and a resolution of 4 cm^{-1}.

D. Catalytic Activity Test

The catalytic tests were performed using an updraft tubular reactor (Φ1×90 cm). The reactor was heated with an electrical power supply which was capable of increasing the temperature from ambient temperature to maximum 850°C in 60 s. The schematic diagram is shown in Figure 1.

The biomass and catalyst mixture were loaded into the reactor then, the reactor was placed in a ceramic insulator. The power supply was turned on and the air was introduced from the bottom of the reactor.

During the gasification process, the gaseous product was continuously collected in a gas collecting bag.

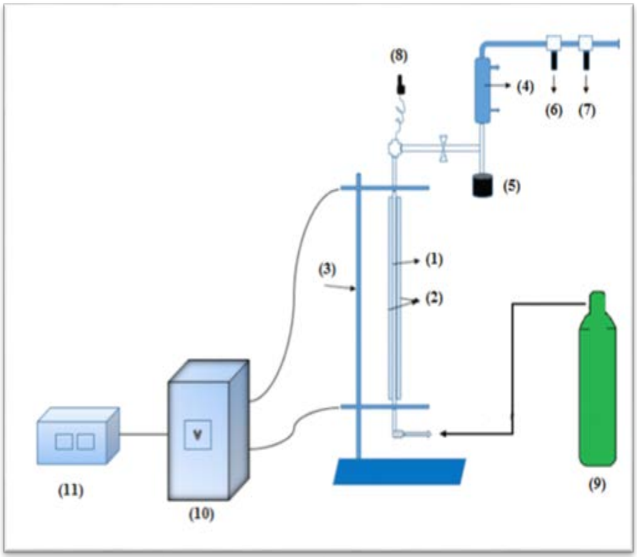

Fig. 1. The schematic diagram of experimental apparatus; 1-tubular reactor, 2-isolation cylinder, 3-stand, 4-liquid-gas separator, 5-liquid product chamber, 6-filter for particles, 7-filter for moisture, 8-thermocouple, 9-air supplier, 10-power supplier, 11-controller.

Gasification reactions were carried out at 650°C for 20 minutes using 20% wt catalyst/wt biomass. Prior to the activity tests, the catalysts were reduced at 800°C using 20% H_2 and N_2 mixture with the flow rate of 300 mL/min for 30 min.

The gas product was analyzed SRA Technologies Micro Gas Chromatograph (μ-GC) (T-3000 series) equipped with MS5A (Molar sieves 5Å) and PPQ (Polar Plot Q) columns coupled to thermal conductivity detector (TCD). While the standard gas mixture was used for μ-GC calibration, helium and argon were used as a carrier.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

TGA analyses of catalysts are given in Figure 2.

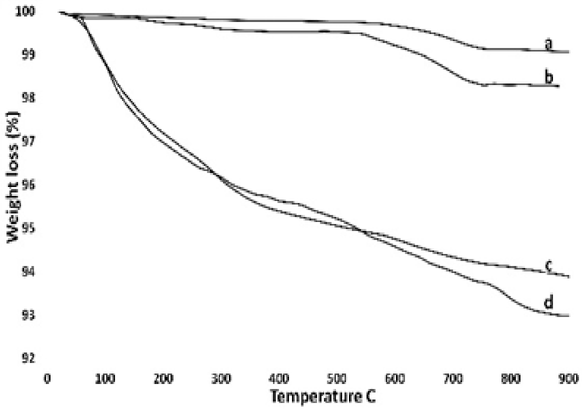

Fig. 2. TGA profiles of Ni-CO based catalyst. a) Ni-Co/Al_2O_3 b) Ni-Co/ZrO_2 c) Ni-Co/ZnO d) Ni-Co/Al_2O_3-ZrO_2.

As it is displayed in Figure 2, overall weight loss for the catalyst is about 2-7 wt. %. The mass changes up to 200°C are associated with the removal of adsorbed water and volatile material present in the catalyst. This water is caused by surface water and hydrates in metal nitrates. At about 300-400°C, the weight loss was attributed to the conversion of metal hydroxides to metal oxides.

The mass loss of the catalyst seems to continue to about 550°C, and it is negligible after 550°C. It is seen that the calcination temperature of the catalysts of 550°C overlaps with the TGA graph.

B. *XRD Analysis*

XRD patterns of bimetallic catalysts calcined at 550°C are shown in Figure 3.

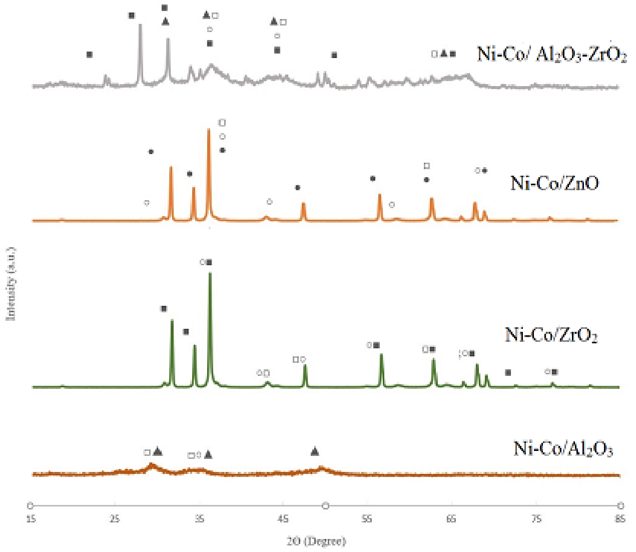

Fig. 3. The XRD diffraction patterns (□: NiO, ○:Co_3O_4, ▲: Al_2O_3, ■: ZrO_2, ●: ZnO).

The XRD diffraction patterns (Figure 3) show that the catalysts have NiO characteristic peaks at 2θ=37.3°, 43.2°, 62.9° and 79.4°, Co_3O_4 characteristic peaks at 2θ=44.2°, 51.4°, 75.7°, the characteristic peaks of γ-Al_2O_3 at 2θ=37.3°, 45.7° and 60.8°, ZrO_2 at 2θ=30.2° and 50.3°.

The molecular structure of Ni-Co/ZnO and Ni-Co/ZrO_2 catalysts are highly crystalline. In contrast, Ni-Co/Al_2O_3 and Ni-Co/ Al_2O_3-ZrO_2 catalysts are amorphous. The decrease of the intensities of the NiO, CoO and Al_2O_3 peaks is observed by adding ZrO_2.

Partial overlap is observed in the diffraction peaks of Ni and Co due to similar morphology. For this reason, it is difficult to discriminate between Co and Ni species.

C. *XRF Analysis*

The XRF results of Ni-Co based catalysts are given according to different support materials in Table 1. Ni and Co (wt./wt.) loading rates were calculated over Ni and Co, and XRF results are given in NiO and Co_2O_3.

Table 1 clearly lists that Ni and Co contents are close to the desired values. As calculations are based on metallic Ni and Co, XRF results are higher than the desired value since they are in oxide form. Due to the impurities of the precursors used in the catalysts, there have been negligible deviations in the amount of support material loading.

The results display clearly that crystallite size of metal depends on support material of catalyst. The smallest average crystallite size calculated from XRD patterns was determined to be 0.45 nm with Ni-Co/Al_2O_3 catalyst.

TABLE I: XRF RESULTS OF N-CO CATALYSTS

Catalysts	**Components (wt./wt.)**					**Crystallite size (nm)**[a]
	NiO	Co_2O_3	Al_2O_3	ZnO	ZrO_2	
Ni-Co/Al_2O_3 (10/5/85)	13.15	6.52	78.79	-	-	0.45
Ni-Co/ ZnO (10/5/85)	13.13	7.00	-	79.18	-	8.06
Ni-Co /ZrO_2 (10/5/85)	13.80	7.51	-	-	76.29	7.18
Ni-Co/ Al_2O_3-ZrO_2 (10/5/85)	10.48	5.91	73.04	-	6.17	7.25

a Determined by XRD- calculated by the Scherrer formula.

D. *SEM Images*

The result of the SEM analysis (Fig. 4) clearly indicates the surface of all catalysts appears to be porous. Some aggregates formed by very small particles are also present.

It can be seen that Ni-Co/Al_2O_3 is coarse, porous, and spherical compared to other catalysts, hence it should have a large BET surface area. Irregular shaped large particles with variable sizes and forms are observed in Ni-Co/ZnO. The Ni-Co/Al_2O_3-ZrO_2 catalyst exhibits surface morphology similar to Ni-Co/ZrO_2 catalyst by addition of ZrO_2.

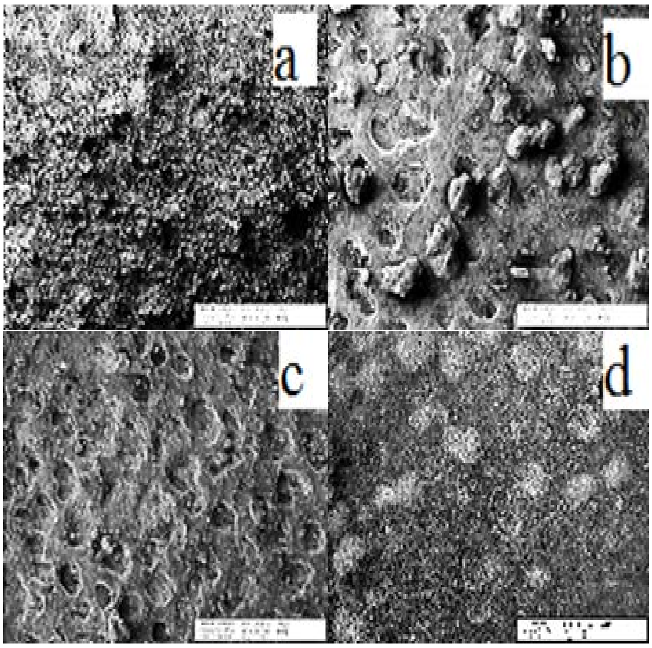

Fig.4. SEM images of the synthesized catalysts with different support materials. a) Ni-Co/Al_2O_3 b) Ni-Co/ZnO c) Ni-Co/ZrO_2 d) Ni-Co/Al_2O_3-ZrO_2.

E. *FT-IR Analysis*

FT-IR results of fresh calcined catalyst are demonstrated in Figure 5.

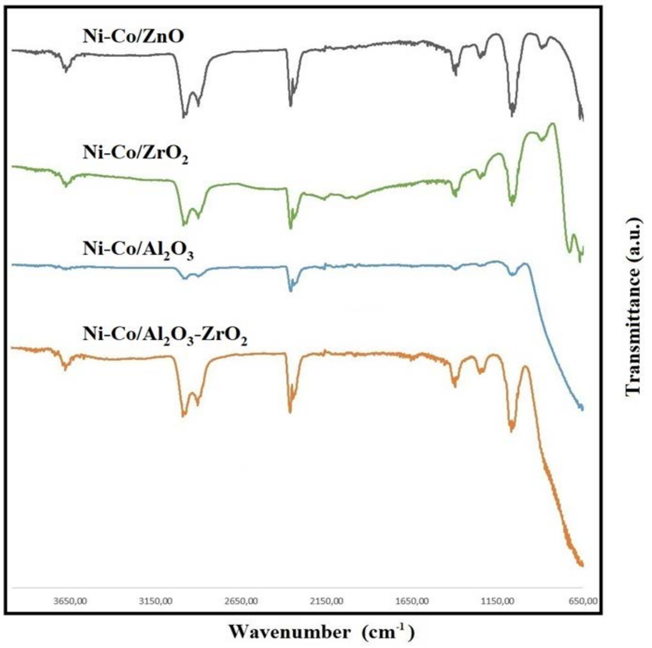

Fig.5. FT-IR spectra of catalyst.

Figure 5 presents, the FT-IR peaks observed in the lower than 1000 cm^{-1} are present due to metal oxides (NiO, Co_3O_4) arising from interatomic vibrations. The low-level definition of this band is due to the amorphous state. This confirms the results obtained from the XRD characterization (Fig.3) of the high metal distribution. Vibrational modes in the range 1100 cm^{-1} correspond to the adsorbed water and M-OH (M= Ni, Co, Al, Zr).

The peaks around 1000-1500 and 3000-4000 cm^{-1} are present due to Al-OH (hydroxyl groups) and Zr-OH. Surface OH species have positive effects such as removal of carbon from the surface.

The peak which indicated about 2300 cm^{-1} is caused by the asymmetric stretching frequency of CO_2 which is resulted in the aerial CO_2.

The peaks around 2857–2920 cm^{-1} are assigned to stretching vibration for structural C–H bands.

F. Activity Tests

The activity of catalyst was determined in the gasification of olive pomace (Figure 6).

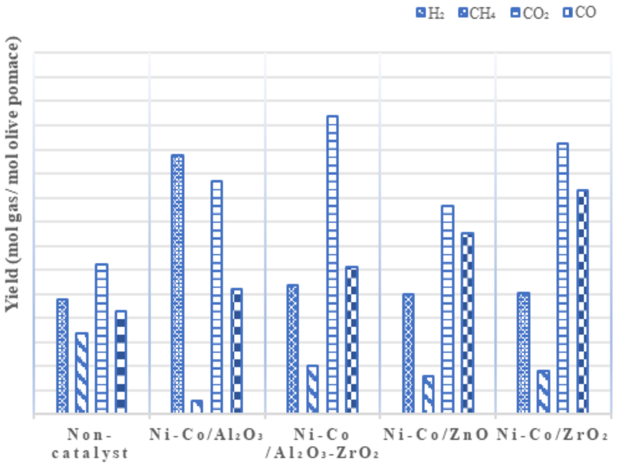

Fig. 6. Effect of support on gaseous product composition (650°C, 20 min reaction time and 20 wt.% catalyst ratio).

Figure 6 shows the yield of the main component of the gas product which are H_2, CH_4, CO and CO_2. The H_2 yield followed the order Ni-Co/Al_2O_3> Ni-Co/Al_2O_3-ZrO_2> Ni-Co/ZrO_2> Ni-Co/ZnO.

While H_2 yield was 4.78 mol/kg olive pomace without the catalyst, it reached maximum value with 10.76 mol H_2/kg olive pomace in the presence of Ni-Co/Al_2O_3, which could be attributed its high metal dispersion (Fig. 3, Fig.4). Further, minimum H_2 yield was obtained as 5.02 mol H_2/kg olive pomace with Ni-Co/ZnO.

As the maximum of methane yield was obtained as 3.37 mol CH_4/kg olive pomace in the absence of the catalyst and minimum methane yield was obtained as 0.54 mol CH_4/kg olive pomace using Ni-Co/Al_2O_3.

Besides, Ni-Co / ZnO catalyst produced at least CO_2 (8,63 mol CO_2/kg olive pomace) as a by-product compared to other catalysts, while maximum CO_2 yield was obtained as 12.39 mol CO_2/kg olive pomace in the presence of Ni-Co/Al_2O_3-ZrO_2.

CO yield ranges between 8.63 and 12.39 mol CO/kg olive pomace at catalytic activity studies. The minimum CO yield in the product gas composition was obtained as 6.23 mol CO/kg olive pomace without the catalyst.

The higher production of H_2 and CO_2, and the much lower production of CH_4 and CO showed that the contribution of the methane steam reforming and the water gas shift reaction were much favored.

As a result, Ni-Co/Al_2O_3 catalysts were found to be favorable catalysts for gasification of olive pomace.

IV. CONCLUSION

As a conclusion; Ni-Co/Al_2O_3, Ni-Co/ZrO_2, Ni-Co/ZnO, Ni-Co/Al_2O_3-ZrO_2 catalysts were synthesized and characterized by XRD, XRF, TGA, SEM and FT-IR analyzes. Activity studies were carried out by performing gasification of olive pomace.

The highest hydrogen yield was found as 10.76 mol/kg olive pomace at the gasification conditions of 650°C, 20 min reaction time and 20 wt.% catalyst ratio in presence of Ni-Co/Al_2O_3. When the yield was compared with literature, Sert et al. obtained higher hydrogen yield (16.80 mol/kg biomass at 600°C). The reason for the difference is due to the use of hydro-thermal gasification method.

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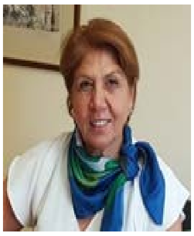

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