

Cu/Ni loaded CeO₂-ZrO₂ catalyst for a water gas shift reaction: effects of loaded metals and CeO₂ addition

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Abstract

In this work, two different types of metals (Cu and Ni), and the effect of CeO₂ addition to produce a CeO₂-ZrO₂ co-supporter were investigated through a water gas shift reaction (WGS). It was found that the WGS activity could be enhanced with CeO₂ addition. At relatively high temperature, Ni-loaded catalysts exhibited higher CO conversion while Cu-loaded catalysts demonstrated better performance at low temperature. Moreover, the stability and yield of CO₂ and H₂ products of Cu-catalysts were higher than those of Ni-catalysts. These results may be caused from an irreversible adsorbed CO on Ni and reverse water gas shift reaction being formed on the Ni-catalysts. In addition, DRIFTS data suggests that the WGS mechanism likely proceeded via formate species.

Keywords: Ceria, Copper, DRIFTS, Nickel, Water gas shift, Zirconia

1 Introduction

Water gas shift reaction (WGS), $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, is well known to be an alternative way to produce of H₂ and convert poisonous CO into CO₂. This reaction is a moderately exothermic reaction; therefore, it is very important to attain a very active catalyst that can yield a high conversion of CO at a low temperature range. Many works have been reported that some novel metals such as Pt and Au present excellent WGS activity [1–6]. However, high cost of Pt and its deactivation when it is used in a real WGS streams are serious drawback, which must be taken into account. On the other hand, it has been found that Cu and Ni are strong candidates for being used as catalysts for a WGS reaction [6, 7–13] due to their low cost and high activity at low temperature (150 – 400 °C) [7, 14–15]. Principally, a WGS is carried out in two stages, at high temperature shift (HTS) followed by low temperature shift (LTS) [16]; therefore, the performance of catalysts at a wide range of temperature must be concerned. In order to achieve this performance a mixed metal has been applied. Lin *et al.* [14] reported that Ni/CeLaO_x was very active at high temperature for a WGS while at temperature below 250 °C CH₄, which was a side product, was preferably formed than CO₂. On the other hand, a mixed oxide of CuO-ZnO-Al₂O₃ was active at lower temperatures (180 – 200 °C) [17]. These differences in responses to temperature when comparing the catalytic performance of doped metals can be fascinating.

Since CeO₂ has an ability of rapid oxidation and reduction, it can be acted as an oxygen buffer under exhaust conditions by releasing/acquiring oxygen through redox-

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processes involving the Ce^{4+}/Ce^{3+} couple. Also, CeO_2 can be a stabilizer for other metal oxide supports especially for ZrO_2 which was reported to enhance the structure stability of CeO_2 toward sintering. For that reason, many researchers attempted to apply mixed CeO_2 - ZrO_2 support for many reaction such as ethanol steam reforming [18], CO_2 steam reforming of CH_4 [19–20], three way catalysts [21] and also water gas shift (WGS) reaction [2,5].

In this work, two types of metals, Cu and Ni, were loaded on ZrO_2 support and tested for a WGS reaction under the temperature range of 200–400 °C. Moreover, the effect of CeO_2 addition forming CeO_2 - ZrO_2 mixed support on the physical properties and catalytic performance was also investigated. The associative mechanism, adsorbed species and intermediates occurred during the reaction were proposed by a mean of an in situ Diffuse Reflection Infrared Fourier Transform Spectroscopy (DRIFTS).

2 Materials and Methods

2.1 Catalyst preparation

Cu or Ni based CeO_2/ZrO_2 catalysts were prepared via an incipient wetness impregnation method. Briefly, $Zr(OH)_4$ (MEL chemicals XZO 880/01) was calcined with a heating rate of 2 °C /min to 700 °C and kept at this temperature for 2 h to prepare a ZrO_2 support. Based on 1 g of prepared catalyst, 0.126 g of $Ce(NO_3)_3 \cdot 6 H_2O$ was dissolved in water in order to obtain 20 wt.% of CeO_2 , then it was mixed with 0.75 g of ZrO_2 -support. After that the suspension was dried and calcined at 450 °C for 2 h. The obtained yellow powder was mixed with a solution of $Cu(NO_3)_2 \cdot 3H_2O$ or $Ni(NO_3)_2 \cdot 3H_2O$ to achieve 5 wt% metal. Finally, the suspension was dried and calcined again at 450 °C for 2 h. The synthesized products of Cu/CeO_2 - ZrO_2 and Ni/CeO_2 - ZrO_2 were named as CCZ and NCZ, respectively. In order to study the effect of CeO_2 addition, the whole processes were repeated without an addition of CeO_2 and the obtained products of Cu/ZrO_2 and Ni/ZrO_2 were defined as CZ and NZ, respectively.

2.2 Catalyst characterization

2.2.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of all samples were obtained using a XPERT - PRO diffractometer with $Cu K\alpha$ radiation operating at 40 kV and 40 mA scanning from 10 to 80° with a step of 0.02°.

2.2.2 Physisorption

A BET surface area and porosity of the supports and catalysts were determined by a nitrogen adsorption at -196 °C applying a Quantachrome Autosorb-1C instrument. Subsequently, specific BET (S_{BET}) was estimated for P/P_0 values between 0.05–0.30. Additionally, an average pore diameter and total pore volume were obtained from adsorption data of P/P_0 at 0.99.

2.2.3 In situ IR adsorption

An in situ Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS) (Bruker VERTEX 70) of adsorbed carbon monoxide as a probe molecule was used to

determine oxidation states of Cu and Ni metals, interaction between metal and support, and also all the chemical compounds produced during the reaction occurred. The spectra were obtained in the range of 3,500 to 1,000 cm^{-1} by averaging 128 scans with an aperture of 1.5 mm. The catalysts were reduced at 350°C and then the reaction was carried out at temperature between 50–300°C.

2.3 Catalytic activity test

The catalytic activities for water gas shift reaction were tested in a fixed bed reactor at atmospheric pressure and were carried out in the temperature region of 200–400°C after the samples were reduced at 400°C. Typically, 0.5 g of catalyst was placed between two quartz glass wool plugs inside a quartz tube, in which the temperature was controlled by a thermocouple connected with a Eurotherm temperature controller. The sample was reduced with 5% H_2 in He for 1 h., after reduction process the reactant gases consisting of 3% CO, 7.5% H_2O balanced with He were fed into the reactor at total flow rate of 60 ml/min. Gaseous products (CH_4 , CO and CO_2) were detected and analyzed by a HP 6890 Series GC system using HP-PLOT Q column and a flame ionization detector (FID). The produced H_2 as well as other effluent gases were also analyzed by a Pfeiffer Prisma Plus (QMG 220 F1) mass spectrometer. The conversion of CO and yield of CO_2 were then calculated by following equations:

$$\text{CO conversion (\%)} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (1)$$

$$\text{CO}_2 \text{ yield (\%)} = \frac{[\text{CO}_2]_{\text{formed}}}{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}} \times 100 \quad (2)$$

3 Results and Discussion

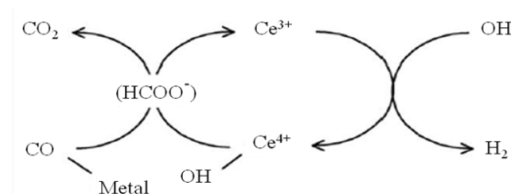
3.1 Physical properties of catalysts

It is clearly seen in Fig. 1 that all peaks exhibit the same pattern of ZrO_2 , which was the major component while both CCZ and NCZ catalysts synthesized with CeO_2 addition show the obvious peaks at about 33.4 and 47.1° indicating the existence of CeO_2 phase [22–23]. NZ and NCZ catalysts show two diffraction peaks at 37.3 and 44.3°, which correspond to NiO [14]. Besides, it was found that after an addition of CeO_2 in NCZ sample the intensity of NiO peaks was decreased significantly. This was caused from a better dispersion of NiO over the ZrO_2 support with CeO_2 enhancement, resulting in a decrease of crystallite size of NiO as shown in Table 1. However, corresponding peaks of CuO at 35.7, 39.0 and 49.2° cannot be observed solely for the CZ and CCZ catalysts [14] because they are overlapped with the diffraction peaks of ZrO_2 .

The physical properties of synthesized materials including BET surface area and average pore size are shown in Tab. 1. After the impregnation of Cu and Ni on the ZrO_2 support the specific surface areas of both CZ and NZ were slightly increased, resulting from extra surface formed from deposition of small metallic particles on the ZrO_2 surface. However, the deposition of metal inside the pores caused a decrease in average pore size. Moreover, it is clearly shown that the addition of 20 % CeO_2 in the CCZ and NCZ catalysts increased the surface area of both catalysts. This increase is due to a much larger surface area of pure CeO_2 than that of pure ZrO_2 .

3.2 Catalytic activity

CO conversion and CO₂ yield obtained from the WGS reaction are presented in Fig. 2 (a) and (b), respectively. Clearly, when the temperature was increased, the CO conversion obtained from all catalysts increased. In addition, at 400°C Ni-doped catalysts (i.e., NZ and NCZ) show the highest CO conversion at about 80 % that is about 20 % higher than that obtained from using Cu-doped catalysts (i.e., CZ and CCZ). The difference can be attributed to the higher adsorption of CO species on Ni than that of Cu, which may be influenced by a sintering effect leading to the lower activity [11, 24]. On the other hand, at relatively low temperature CZ catalyst exhibited better performance than NZ catalyst. These results are in good agreement with the work reported by Lin *et al.* [14]. It can be described that the decrease of activity of NZ catalyst was resulted from an irreversible adsorption of CO on Ni (the data was discussed in details later). Furthermore, it is evident that both NCZ and CCZ catalysts containing CeO₂ can maintain high CO conversion over wider range of temperature than NZ and CZ catalysts. This can be attributed to the presence of CeO₂, which has an oxygen storage capacity and also can act as a stabilizer as well as a promoters [2, 13,25], promoting the formation of CO₂ as shown in the following diagram [26]:



From the CO conversion and by assuming second order reaction, the activation energies of the conducted WGS using different catalysts were calculated and the result is presented in Table 1. It is clearly seen that the reactions by NZ and CZ catalysts have the activation energies about 10 times higher than that of NCZ and CCZ catalysts.

As further shown in Fig. 2 (b), the maximum yield of CO₂ (89 %) was achieved when NCZ catalyst was applied at 400 °C. However, the CO₂ yield drastically dropped to below 10 % when temperature was decreased to 200 °C. It was found that CH₄ was formed following the methanation reaction: $\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$. Additionally, not only the formation of CH₄ but also the arising of reverse water-gas shift reaction (RWGS), $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$, has been reported to occur as a side reaction in preferential oxidation reactor [27]. These side reactions caused the sharp drop of CO₂ yield from the main reaction (i.e., WGS). The same trend is also observed from using NZ catalyst but with lower values. Conversely, Cu-doped catalysts, especially CCZ, could maintain the CO₂ yield over a wider range of temperature. However, the CZ catalyst seemed to promote side reactions at above 250 °C. It implies that Ni-doped catalysts were active in promoting the methanation and RWGS over a low temperature range. The results obtained from a mass spectroscopy shown in Fig. 3 also confirm these conclusions. It is clear that based on detected H₂ amount (Fig. 3 (a)), which is a main product from the WGS, the CCZ catalyst exhibited the same pattern of performance over the testing temperature, whereas the NCZ catalyst did change its catalysis pattern from WGS favor at high temperature to side reactions favor at low temperature, as seen in Fig. 3 (b) as three step drops of H₂ and continuing increases of CH₄ and CO.

3.3 In situ DRIFTS

Fig. 4 shows the spectra collected from a DRIFTS analysis of the CCZ and NCZ catalysts after CO adsorption and subsequently evacuation. It is clearly seen that the spectra of CCZ catalyst (Fig. 4 (a)) shows adsorption peaks in a range of 2,080–2,110 cm^{-1} corresponding to CO adsorption on Cu [28–30] and CO adsorption on Lewis acid sites of ZrO_2 -base at 2186 cm^{-1} [31]. After evacuation, the whole peak is totally disappeared. It means that all adsorbed CO was desorbed. It implies that the interaction between CO and active sites of catalyst was quite weak. On the other hand, in case of NCZ catalyst (Fig. 4 (b)), several low intensity peaks are observed suggesting the adsorbed CO forming di-, tri-carbonyls as well as bridged carbonyls with Ni. The bands in a region of 2,155–2,110 cm^{-1} correspond to weak adsorption forming $\text{Ni}^{(I)}\text{-CO}_3$ complex [32] while two bands detected at 2067 and 1963 cm^{-1} correspond to a CO adsorbed on $\text{Ni}^{(0)}$. The former points out an adsorbed CO in linear form and the later reveals a bridge-bonded CO [31, 33]. After evacuation, two broad peaks at 2,067 and 1,963 cm^{-1} still remain. Accordingly, it can be concluded that some parts of adsorbed CO had strong interaction with NCZ catalyst and were irreversible.

During the WGS reaction occurred, peaks in the region of 1,300–1,650 cm^{-1} were detected indicating a formation of bicarbonate and mono-bidentate formate species while the peaks at 2,840 and 2,945 cm^{-1} were associated to C-H stretching vibration of formate species [34]. It was found that as the temperature was decreased, the intensity of all peaks increased. This may be due to the fact that formate species with COO vibration increased their stabilities with the ZrO_2 support. The strongly and irreversibly adsorbed carbonate species remained on the metal surface at relative low temperature leading to a decrease of catalytic activity. These results are consistent with previously published works stating that WGS reaction occurs via a formate associative mechanism having surface formate decomposition as a rate limiting step [2, 11]. On the other hand, carbonate species were more easily to be decomposed toward CO_2 when the temperature was increased. As a result, at relatively high temperature there are two bands clearly presented at about 2,322 and 2,369 cm^{-1} indicating the existence of asymmetric stretching of CO_2 and the intensity of these bands decreased with the decreased temperature.

Consequently, it could be described that the formate species acted as intermediates of the WGS reaction and the decomposition of formate is considered to be a rate limiting step. Briefly, active surface OH groups were generated on the ceria sites and formate species (HCOO^-) were formed after reduction process. Next, the bicarbonate formate species were decomposed into bidentate formate species which finally were broken down to produce H_2 and CO_2 . Therefore, the bands of formate species decreased in intensity as the bands related to CO_2 increased remarkably. This result is also in agreement with Jacobs's work [34], in which the formate mechanism in metal/ceria systems for WGS reaction was proposed. In addition, the rate of formate formation, an initial step of WGS, would increase with the concentration of surface OH groups, which were enhanced to be formed on ceria sites. Therefore, the catalytic activity was increased when 20 wt% of CeO_2 was added as mentioned earlier.

4 Conclusions

In this work, it was clearly observed that the addition of CeO_2 in the ZrO_2 support enhanced both WGS reaction activity and the formation of gaseous products including H_2 and CO_2 , resulting from a high oxygen storage capacity of CeO_2 . Regard to metals doped, it was found that the Ni-catalysts showed better CO conversion than Cu-catalysts at high temperature while Cu-catalysts showed better performance at relatively low temperature. In addition, there were methanation and RWGS reaction occurred during the WGS was carried

out, affecting the yield of CO₂. Moreover, Ni doped catalysts exhibited high impact from the RWGS reaction, leading to drastically decrease in CO₂ yield. From the DRIFTS analysis, it is evident that the associated mechanism of WGS would occur via the formation of formate species and their decomposition is considered to be a rate limiting step.

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Table 1. Physical property of synthesized materials

Sample	S _{BET} (m ² /g)	Avg pore diameter (nm)	Metal crystallite size (nm)	Activation Energy ^a (kcal/mol)
ZrO ₂	227	379	-	-
CZ	371	175	-	1,177
NZ	372	173	46	1,845
CCZ	512	97	-	162
NCZ	577	94	34	250
CeO ₂	1,044	122	-	-

^a for the WGS reaction

Figure Captions:

Figure 1. X-ray diffraction of Ni/Cu-catalysts synthesized with and without CeO₂ addition (all unmarked peaks correspond to ZrO₂)

Figure 2. (a) CO conversion and (b) yield of CO₂ from the WGS reaction

Figure 3. Mass spectroscopy of output gases from the WGS reaction using (a) CCZ and (b) NCZ catalysts

Figure 4. CO adsorption on (a) CCZ and (b) NCZ catalysts

Figure 5. In situ DRIFTS of (a) CCZ and (b) NCZ under reaction carried out at 50–300°C

Figure 1

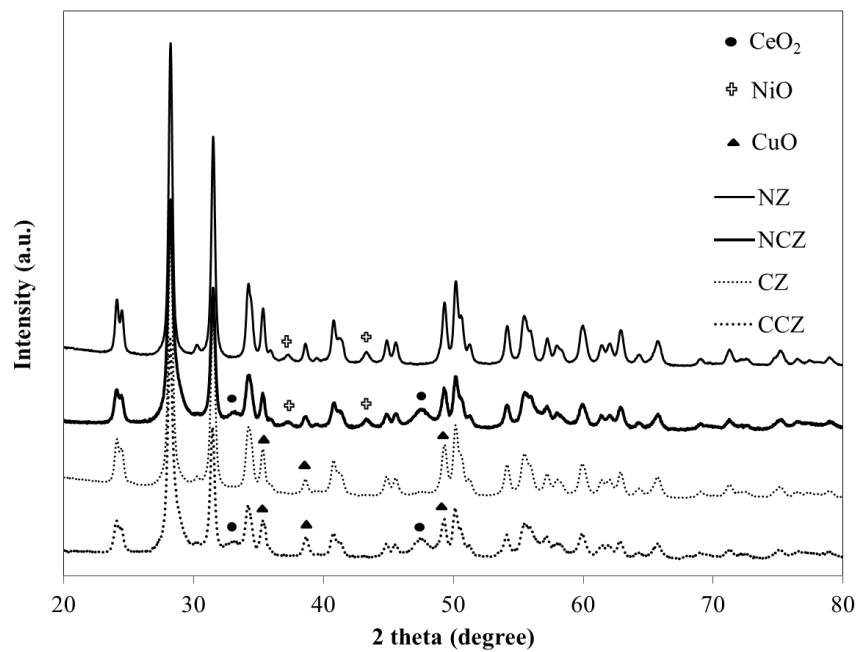


Figure 2

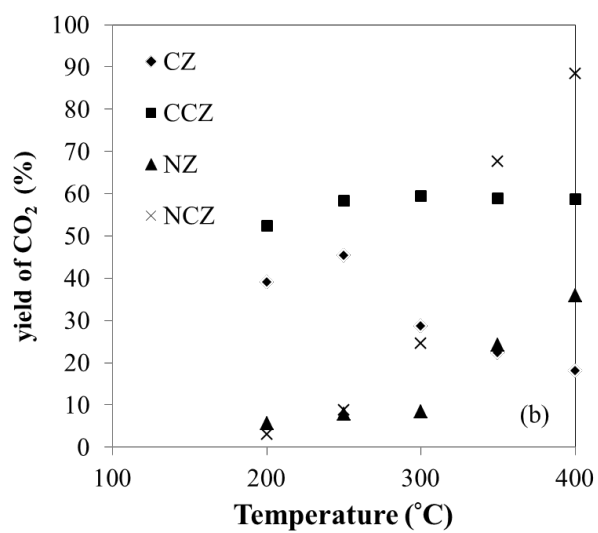
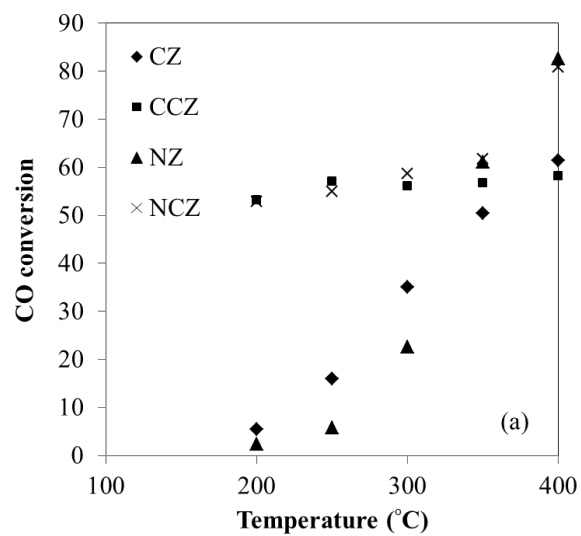


Figure 3

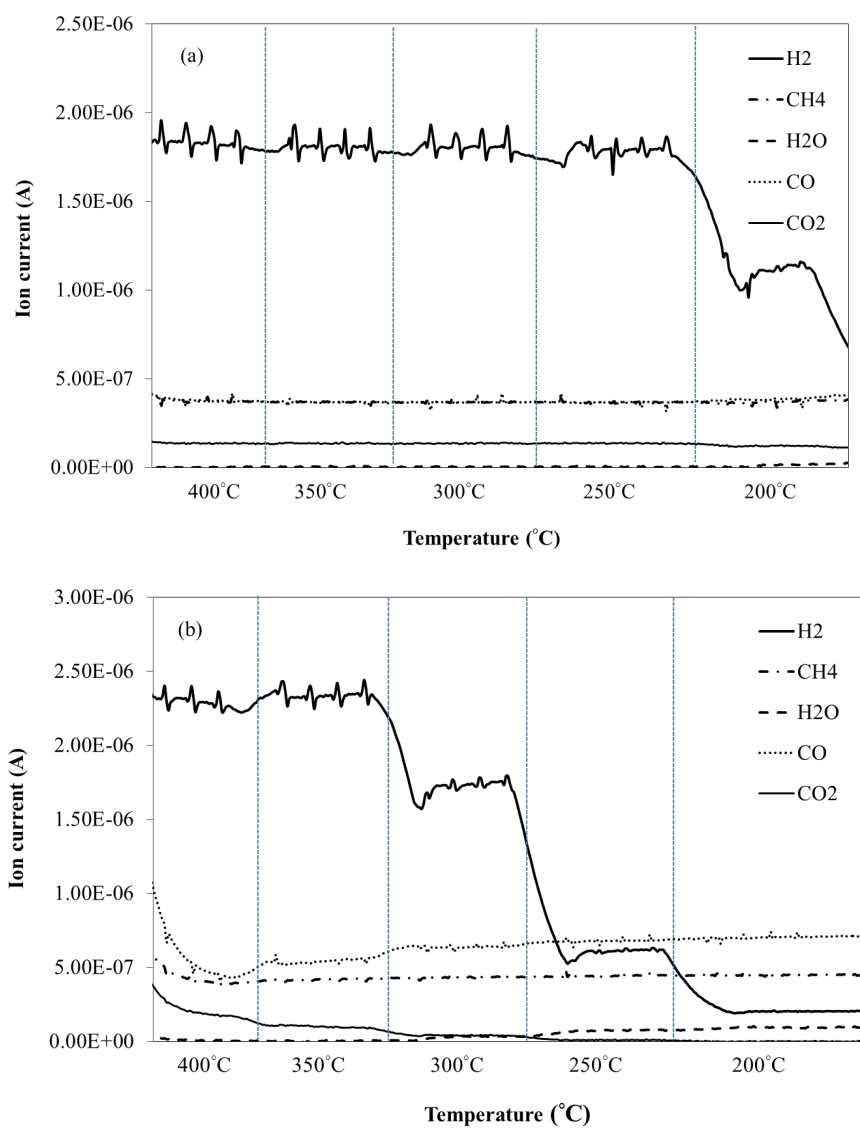


Figure 4

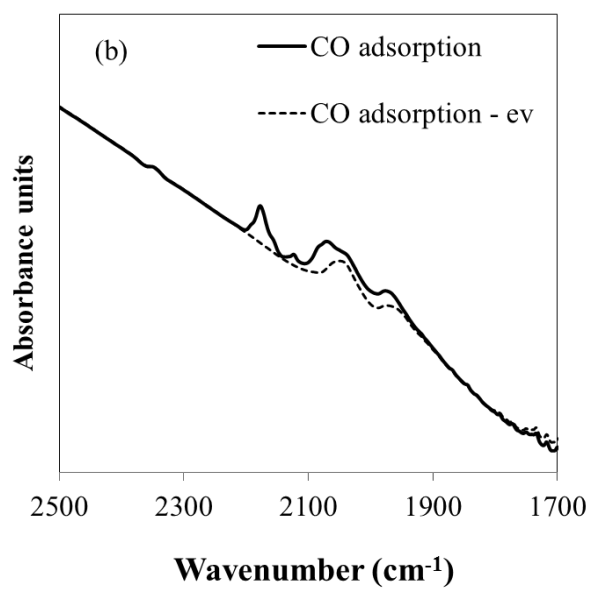
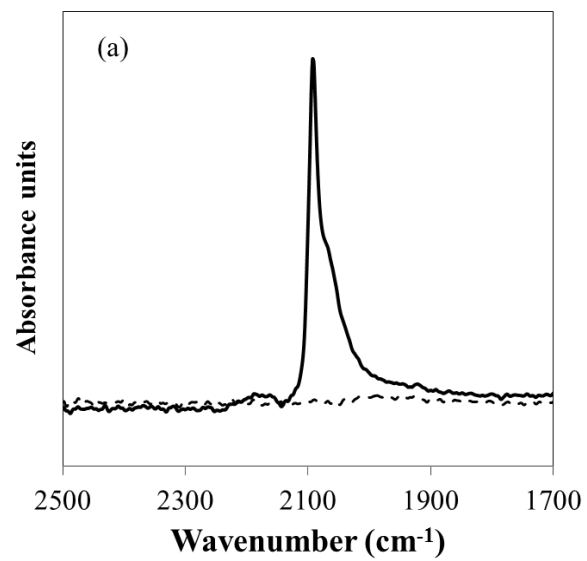
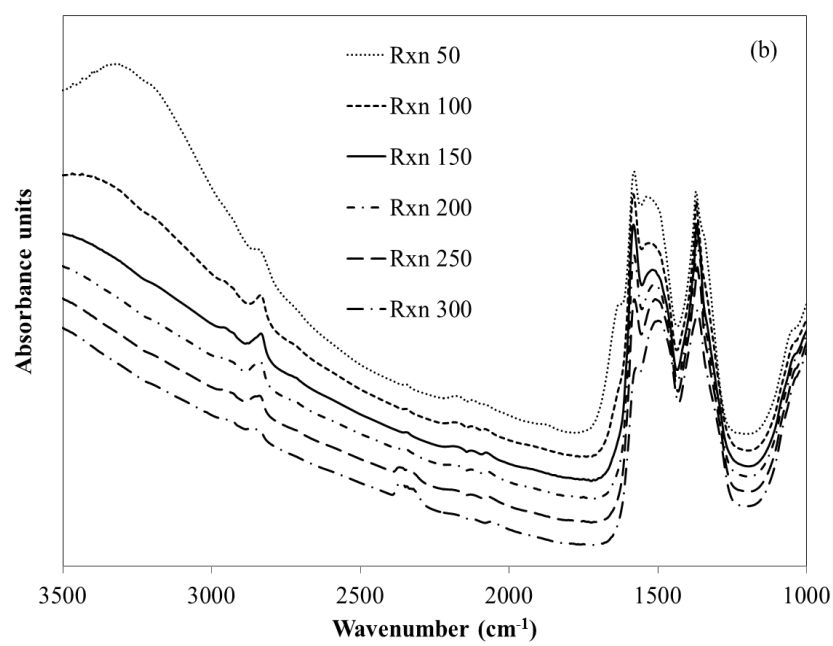
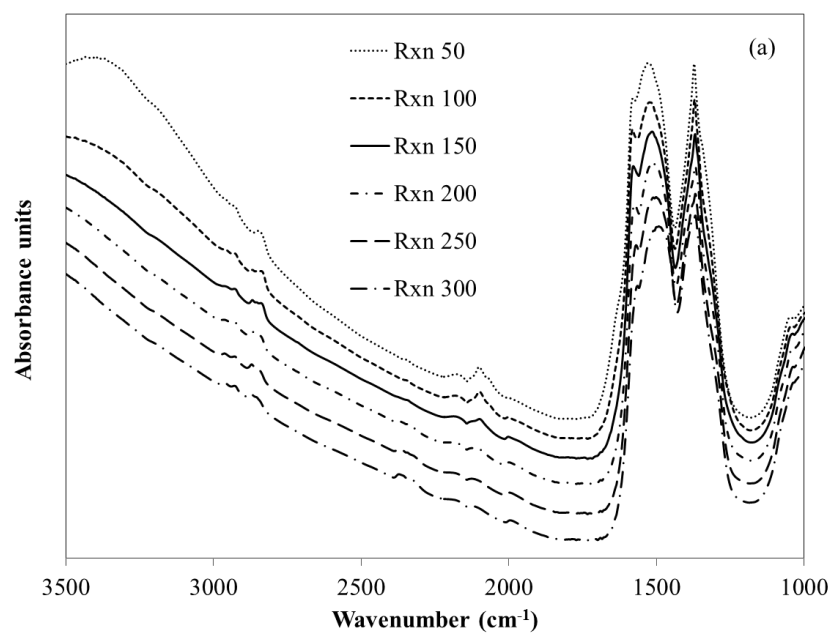


Figure 5



Highlights

- Use of Cu and Ni on $\text{CeO}_2\text{-ZrO}_2$ were studied through a WGS reaction.
- CeO_2 addition enhances the WGS activity.
- Ni-loaded catalysts exhibited higher CO conversion at relatively high temperature
- Cu-loaded catalysts have a better performance at relatively low temperature.
- The associated mechanism of WGS occurs via the formation of formate species.

GRAPHICAL ABSTRACT

