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# EVALUATION OF Co-PROMOTED Ni/Al$_2$O$_3$ CATALYST FOR CO$_2$ REFORMING OF ETHANOL

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## ABSTRACT

The performance of Co-promoted Ni/Al$_2$O$_3$ catalyst prepared by co-impregnation method has been investigated for syngas generation through ethanol dry reforming in a tubular fixed-bed reactor at 973 K and various partial pressures of reactants. Both γ-Al$_2$O$_3$ support and 3%Co-10%Ni/Al$_2$O$_3$ catalyst exhibited high surface area of 174.13 and 89.15 m$^2$ g$^{-1}$, respectively. Temperature-programmed calcination and XRD measurements detected the formation of NiO, Co$_3$O$_4$, NiAl$_2$O$_4$ and CoAl$_2$O$_4$ phases on catalyst surface. In addition, the activation energy for the formation of these phases varied from 148.5 to 296.5 kJ mol$^{-1}$. The conversion of both C$_2$H$_5$OH and CO$_2$ was stable with time-on-stream at beyond 6 h. An increase in CO$_2$ partial pressure enhanced the selectivity of H$_2$ and CO but decreased CH$_4$ selectivity due to the dry reforming reaction of CH$_4$ intermediate product. The optimal C$_2$H$_5$OH partial pressure was obtained at 30 kPa in terms of H$_2$ and CO yield.

**Keywords:** co-promoter, ethanol dry reforming, syngas, ni-based catalysts, and hydrogen.

## 1. INTRODUCTION

The shortage of energy, noticeably high price of crude oil and environmental problems associated with the combustion of fossil fuels have gained a significant attention. Additionally, the utilization of fossil fuels resulted in substantial greenhouse gas emissions leading to undesirable global warming effects. Hence, there is urgent requirement of an alternative and renewable energy for substituting petroleum-based energy. Syngas referring to a mixture of H$_2$ and CO has been employed as feedstock for Fischer-Tropsch synthesis to generate synthetic fuel for fossil fuel replacement [1]. Dry reforming of CH$_4$ has been regarded as a promising synthesis route for producing syngas since it consumes two greenhouse gases (i.e. CH$_4$ and CO$_2$) and produces value-added products [2]. However, CH$_4$ is also one of unrenewable energies possibly depleting in near future. Hence, the production of H$_2$ and CO through ethanol dry reforming (EDR) has become an alluring and potential approach since both bio-derived ethanol and undesirable CO$_2$ emission are used as feedstock's in this method [3, 4]. In fact, ethanol has been considered as an attractive and sustainable feedstock because of its high availability, relatively high hydrogen content, and non-toxicity [5]. In addition, ethanol can be derived from the large amount of biomass sources such as wood wastes and agricultural crops [6, 7].

Ethanol steam reforming has been widely researched over both noble metal (such as Pt [8], Pd and Rh [9]) and non-noble metal catalysts including Ni- and Co-based catalysts [9-11]. Nevertheless, the knowledge regarding EDR reaction is still little-known and requires further exploration in terms of catalytic optimization. Hu and Lu reported that EDR over Ni/Al$_2$O$_3$ catalyst exhibited high catalytic activity, selectivity and produced syngas with a desirable H$_2$/CO ratio for downstream Fischer-

Tropsch synthesis [12]. However, Ni-based catalyst can be deteriorated due to deposited carbon and sintering. Thus, modifying Ni-based catalysts for enhancing the catalytic activity and stability of EDR by the utilization of suitable promoters is essential. In the study of methane dry reforming, a secondary reaction of EDR, de Sousa *et al.* found that Co catalyst possessed great carbon resistance [13]. Therefore, the aim of this research was to investigate the effect of Co-promoter on the physicochemical properties of 10%Ni/Al$_2$O$_3$ catalyst and determine the influence of reactant partial pressure on catalytic performance of ethanol dry reforming.

## 2. EXPERIMENTAL

### 2.1. Catalyst preparation

Co-promoted 10%Ni/Al$_2$O$_3$ catalyst was prepared by co-impregnation method using Co(NO$_3$)$_2$.6H$_2$O and Ni(NO$_3$)$_2$.6H$_2$O as metal precursors. Prior to catalyst synthesis, γ-Al$_2$O$_3$ support was calcined in air for 6 h at temperature of 973 K to guarantee thermal stability. Metal precursors were mixed with pretreated γ-Al$_2$O$_3$ support and the slurry mixture was stirred constantly for 3 h at ambient temperature followed by drying in an oven at 383 K overnight. The resulting solid was further calcined in a Carbolite furnace at temperature of 873 K for 5 h with a heating rate of 5 K min$^{-1}$ to obtain a 3%Co-10%Ni/Al$_2$O$_3$ catalyst.

### 2.2. Catalyst characterization

BET surface area, pore volume and pore diameter of 3%Co-10%Ni/Al$_2$O$_3$ catalyst were obtained from N$_2$ physisorption at 77 K using a Thermo Scientific Surfer unit. Temperature-programmed calcination (TPC) was performed for uncalcined catalyst on a TGA Q500 unit

from TA Instruments. Prior to TPC run, sample was heated from ambient temperature to 373 K with a ramping rate of 10 K min$^{-1}$ in 100 ml min$^{-1}$ of N$_2$ flow and held isothermally at this temperature for 30 min to ensure the complete removal of volatile compounds and moisture. The specimen was subsequently heated up to 1023 K in flowing gas mixture of 4N$_2$:1O$_2$ (100 ml min$^{-1}$) with different heating rates of 10-20 K min$^{-1}$ followed by an isothermal treatment for 30 min before being cool down to room temperature in the same gas mixture. X-ray diffraction measurement of 3%Co-10%Ni/Al$_2$O$_3$catalyst was conducted on a Rigaku Miniflex II system using Cu target as radiation source with wavelength, λ of 1.5418 Å operating at 30 kV and 15 mA. The low scan speed of 1° min$^{-1}$ and small step size of 0.02° were employed to obtain high resolution during the scanning from 3° to 80°.

### 2.3. Ethanol dry reforming reaction

EDR runs were carried out in a quartz fixed-bed reactor at temperature of 973 K and 1 atm. Approximately 0.1 g of catalyst placed in the middle of tubular reactor by quartz wool was reduced in situ at 973 K with a heating rate of 5 K min$^{-1}$ and kept isothermally at this temperature for 2 h in 70 ml min$^{-1}$ of 50%H$_2$/N$_2$ mixture before EDR reaction. Gas hourly space velocity, GHSV = 42 L g$_{cat}$$^{-1}$ h$^{-1}$ and catalyst particle size limited to 100-140 µm were used for each run to ensure the negligible transport resistances. The influence of CO$_2$ and C$_2$H$_5$OH partial pressures on EDR performance was studied by varying CO$_2$:C$_2$H$_5$OH ratios of 1:2.5 to 2.5:1. Ethanol was injected into the reactor by a KellyMed KL-602 syringe pump while CO$_2$ and N$_2$ flow rates were accurately controlled by Alicat mass flow controllers. The composition of effluent gas from the bottom of reactor was analyzed with time-on-stream (TOS) using an Agilent GC 6890 Series gas chromatograph equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors.
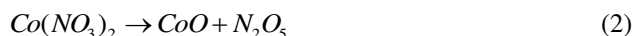
### 3. RESULTS AND DISCUSSION

### 3.1. Physicochemical properties

Table-1 summarizes the textural properties of γ-Al$_2$O$_3$ support and 3%Co-10%Ni/Al$_2$O$_3$ catalyst. Both γ-Al$_2$O$_3$ support and 3%Co-10%Ni/Al$_2$O$_3$ catalyst possessed high BET surface area of 174.13 and 89.15 m$^2$ g$^{-1}$, respectively. However, an obvious reduction in surface area and average pore volume of catalyst (about 2 times) compared with γ-Al$_2$O$_3$ support was expected due to pore blockage with the presence of Co and Ni metal oxide phases.

**Table-1.** N$_2$ physisorption results of γ-Al$_2$O$_3$ support and 3%Co-10%Ni/Al$_2$O$_3$ catalyst.

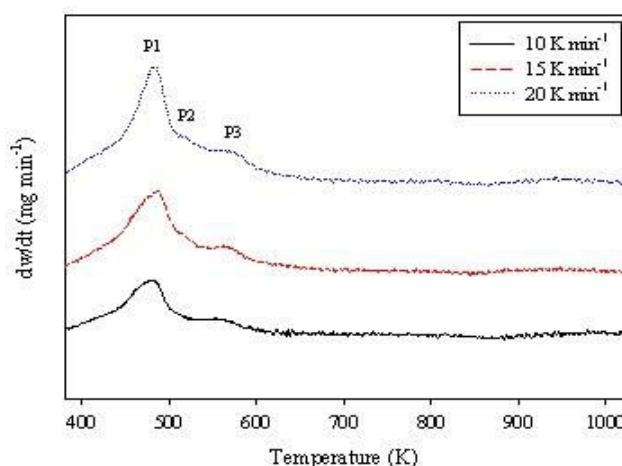| Catalyst | BET surface area (m$^2$ g$^{-1}$) | Average pore volume (cm$^3$ g$^{-1}$) | Average pore diameter (Å) |
|---|---|---|---|
| γ-Al$_2$O$_3$ | 174.13 | 0.38 | 54.56 |
| 3%Co-10%Ni/Al$_2$O$_3$ | 89.15 | 0.16 | 55.95 |

The derivative weight profile of the uncalcined 3%Co-10%Ni/Al$_2$O$_3$ catalyst during temperature-programmed calcination is shown in Figure-1. The high intensity peak, P1 located at low temperature of 478-486 K corresponded to the decomposition of metal nitrates to metal oxides (cf. Eqns. (1) and (2)).

$$Ni(NO_3)_2 \rightarrow NiO + N_2O_5 \qquad (1)$$

$$Co(NO_3)_2 \rightarrow CoO + N_2O_5 \qquad (2)$$

The small shoulder, P2 detected at temperature range of 504-514 K was assigned to the oxidation of CoO to Co$_3$O$_4$ phase during air calcination as given in Equation (3)

$$3CoO + 0.5O_2 \rightarrow Co_3O_4 \qquad (3)$$

whilst the high temperature peak, P3 at 563-570 K indicated the formation of metal aluminates (cf. Equation. (4) and (5)) on catalyst surface in agreement with results from Foo *et al.* [14].
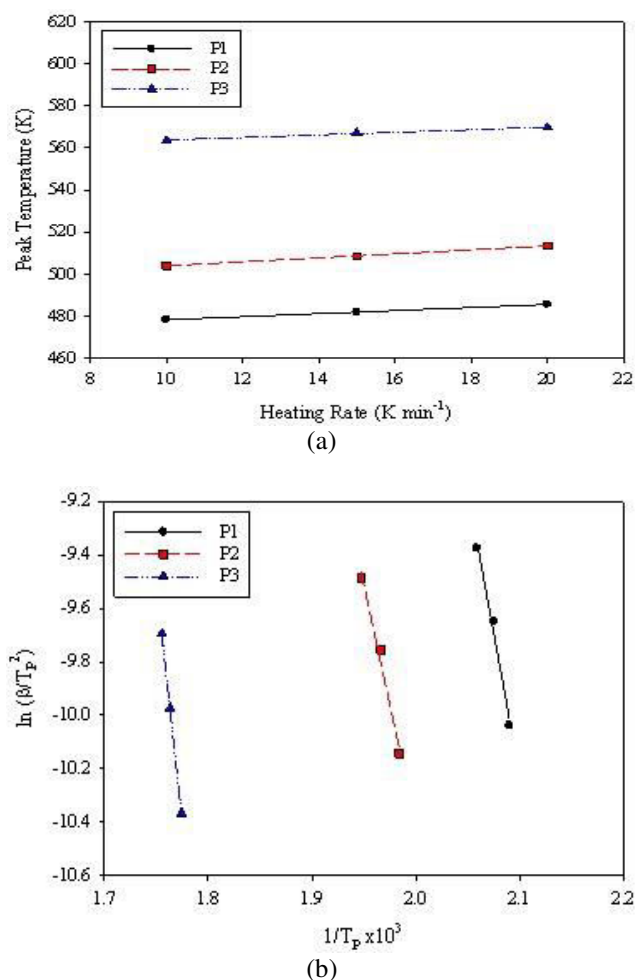
$$CoO + Al_2O_3 \rightarrow CoAl_2O_4 \qquad (4)$$

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4 \qquad (5)$$



**Figure-1.** Derivative weight profile for temperature-programmed calcination of 3%Co-10%Ni/Al$_2$O$_3$ catalyst.

As illustrated in Figure-1, there were no visible peaks detected beyond 600 K for all three heating ramps suggesting that metal precursors were completely decomposed to metal oxides during calcination. Besides, peak temperature for all peaks (P1, P2 and P3) was shifted linearly to higher temperature with the increment of heating rate during TPC as seen in Figure-2(a). Therefore, the activation energy ($E_a$) and pre-exponential factor ($A$) for the formation of metal oxide, spinel CoAl$_2$O$_4$ and NiAl$_2$O$_4$ can be estimated using Kissinger equation [15];

$$\ln\left(\frac{\beta}{T_P^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_P} \qquad (6)$$

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where $\beta$ represents heating rate whilst $T_P$ is peak temperature and R is the universal gas constant. The linear regression of TPC profile to Kissinger equation (cf. Eqn. (6)) exhibited a reasonable fit with $R^2 > 0.98$ (cf. Figure-2 (b)). Hence, the associated Arrhenius parameters can be calculated from the slope and intercept of the plots for ln $(\beta/T_P^2)$ against $1/T_P$ and are summarized in Table-2.
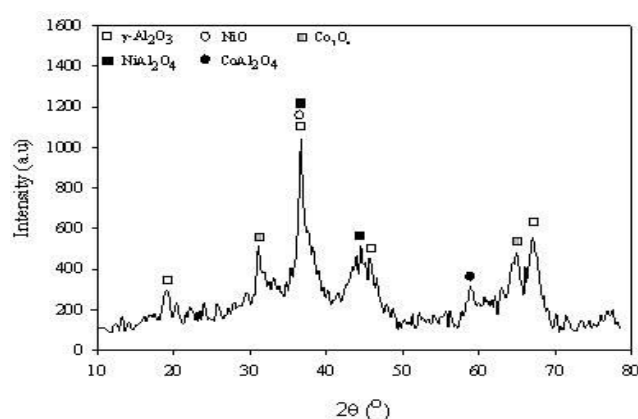


(a)



(b)

**Figure-2.** (a) Peak temperature versus heating rate and (b) estimates of activation energy for the formation of metal oxides and metal aluminates during TPC on 3%Co-10%Ni/Al$_2$O$_3$ catalyst.

**Table-2.** Summary of activation energy and pre-exponential factor values during TPC run over 3%Co-10%Ni/Al$_2$O$_3$ catalyst.

| Peak No. | Activation energy, $E_a$ (kJ mol$^{-1}$) | Pre-exponential factor, $A$ (s$^{-1}$) |
|---|---|---|
| P1 | 176.07 | $1.59 \times 10^{19}$ |
| P2 | 148.50 | $1.77 \times 10^{15}$ |
| P3 | 296.54 | $3.42 \times 10^{27}$ |

The XRD pattern of 3%Co-10%Ni/Al$_2$O$_3$ catalyst shown in Figure-3 was analyzed based on the Joint Committee on Powder Diffraction Standard (JCPDS) database [16]. The diffraction peaks detected at $2\theta$ angle of 19.45°, 36.99°, 45.69° and 67.20° corresponded to $\gamma$-Al$_2$O$_3$ phase. Additionally, the characteristic peaks for Co$_3$O$_4$ phase formation was observed at $2\theta = 31.13°$ and 65.00° whilst NiO phase was detected at $2\theta$ of 36.99°. Besides, the typical peaks corresponding to the presence of spinel NiAl$_2$O$_4$ ($2\theta = 36.99°$ and 44.5°) and CoAl$_2$O$_4$ ($2\theta$ of 59.0°) phases were also identified on the catalyst surface. Interestingly, the XRD results were corroborated with observation from TPC run (cf. Figure-1) and consistent with findings from Foo $et\ al.$ [17] and Batista $et\ al.$ [18].



**Figure-3.** XRD pattern of 3%Co-10%Ni/Al$_2$O$_3$ catalyst.

### 3.2. Catalytic evaluation

As seen in Figure-4(a), CO$_2$ (red curve) and C$_2$H$_5$OH (black curve) conversions initially decreased with time-on-stream. However, both conversions seemed to be stable at beyond 6 h. Ethanol conversion was higher than CO$_2$ conversion reasonably due to the involvement of side reactions, $viz.$ ethanol decomposition and dehydrogenation reactions. The effect of CO$_2$ partial pressure on catalytic performance was carried out by varying CO$_2$ partial pressure from 20 to 50 kPa with constant P$_{C2H5OH}$ of 20 kPa at 973 K. Both H$_2$ and CO selectivity increased linearly with growing P$_{CO2}$ from 20-50 kPa (cf. Figure-4(b)). However, the selectivity of CH$_4$ experienced a significant drop from about 20% to 10% with rising P$_{CO2}$. These observations would suggest that CH$_4$ intermediate product was further reacted with CO$_2$ via the secondary reaction, i.e. CH$_4$ dry reforming (cf. Equation (7)) to generate syngas and hence increasing selectivity of H$_2$ and CO [12].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (7)$$

In another set of runs, the influence of C$_2$H$_5$OH partial pressure on EDR performance was also investigated at 973 K with P$_{CO2}$ = 20 kPa. As seen in Figure-4(c), H$_2$ and CO yields were improved with an increase in P$_{C2H5OH}$ and achieved the optimal values of 32.22% and 23.13%, respectively at P$_{C2H5OH}$ = 30 kPa. However, both product yields showed a considerable

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reduction at $P_{C2H5OH} > 30$ kPa possibly due to the suppression of $CO_2$ adsorption on catalyst surface under the excessive presence of ethanol. This observation was in agreement with results reported by de Oliveira-Vigier *et al.* [19]. Nevertheless, $CH_4$ yield exhibited a slight enhancement with rising $P_{C2H5OH}$ from 20-50 kPa.
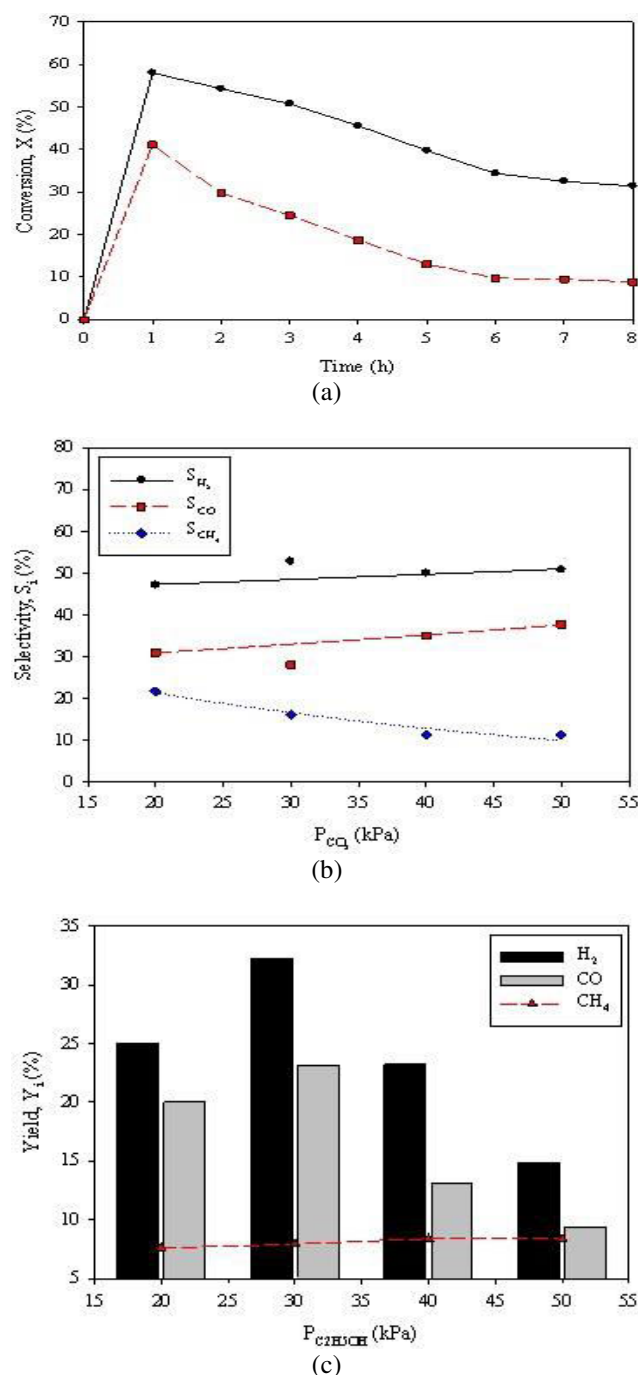


**Figure-4.** (a) Ethanol and $CO_2$ conversions versus time-on-stream, (b) effect of $P_{CO2}$ on gaseous product selectivity and (c) influence of $P_{C2H5OH}$ on product yield at temperature of 973 K.

## 4. CONCLUSIONS

This research has investigated the catalytic performance of 3%Co-10%Ni/Al$_2$O$_3$ catalyst on EDR reaction for syngas production. Multi-point BET surface area measurements showed that γ-Al$_2$O$_3$ support and 3%Co-10%Ni/Al$_2$O$_3$ catalyst possessed high surface area of 174.13 and 89.15 m$^2$ g$^{-1}$, correspondingly. Temperature-programmed calcination measurement observed the complete decomposition of metal precursors to metal oxides (NiO and Co$_3$O$_4$) at temperature below 520 K and the formation of spinel NiAl$_2$O$_4$ and CoAl$_2$O$_4$ phases ( at T > 560 K) on catalyst surface. EDR evaluation showed that conversion trend for both reactants appeared to be unchanged with time-on-stream after 6 h on-stream. Interestingly, H$_2$ and CO selectivity was improved with increasing CO$_2$ partial pressure from 20-50 kPa but CH$_4$ selectivity experienced a linear decline with the growth of $P_{CO2}$. Both H$_2$ and CO yields increased with an improvement in $P_{C2H5OH}$ and achieved an optimal yield at $P_{C2H5OH}$ of 30 kPa.

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