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Evaluation of Co-promoted Ni/Al_2O_3 Catalyst for CO_2 Reforming of Ethanol

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Abstract

The performance of Co-promoted Ni/Al_2O_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_2O_3 support and 3%Co-10%Ni/Al_2O_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_3O_4, $NiAl_2O_4$ and $CoAl_2O_4$ 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_2H_5OH 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_2H_5OH 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; 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 feedstocks 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_2O_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_2O_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_2O_3 catalyst was prepared by co-impregnation method using $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ as metal precursors. Prior to catalyst synthesis, γ-Al_2O_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_2O_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_2O_3 catalyst.

2.2 Catalyst Characterization

BET surface area, pore volume and pore diameter of 3%Co-10%Ni/Al_2O_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_2O_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^o min^{-1} and small step size of 0.02^o were employed to obtain high resolution during the scanning from 3^o to 80^o.

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_2H_5OH partial pressures on EDR performance was studied by varying CO_2:C_2H_5OH 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_2O_3 support and 3%Co-10%Ni/Al_2O_3 catalyst. Both γ-Al_2O_3 support and 3%Co-10%Ni/Al_2O_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_2O_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_2O_3 support and 3%Co-10%Ni/Al_2O_3 catalyst

Catalysts	BET surface area (m^2 g^{-1})	Average pore volume (cm^3 g^{-1})	Average pore diameter (Å)
γ-Al_2O_3	174.13	0.38	54.56
3%Co-10%Ni/Al_2O_3	89.15	0.16	55.95

The derivative weight profile of the uncalcined 3%Co-10%Ni/Al_2O_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. Eqs. (1) and (2)).

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

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

The small shoulder, P2 detected at temperature range of 504-514 K was assigned to the oxidation of CoO to Co_3O_4 phase during air calcination as given in Eq. (3).

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

whilst the high temperature peak, P3 at 563-570 K indicated the formation of metal aluminates (cf. Eqs. (4) and (5)) on catalyst surface in agreement with results from Foo *et al.* [14].

$$CoO + Al_2O_3 \rightarrow CoAl_2O_4 \quad (4)$$
$$NiO + Al_2O_3 \rightarrow NiAl_2O_4 \quad (5)$$

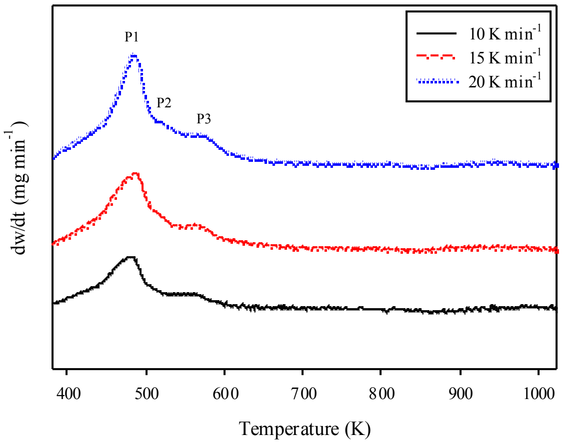

Figure 1: Derivative weight profile for temperature-programmed calcination of 3%Co-10%Ni/Al_2O_3 catalyst

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 $CoAl_2O_4$ and $NiAl_2O_4$ can be estimated using Kissinger equation [15];

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

where β 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. Eq. (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.

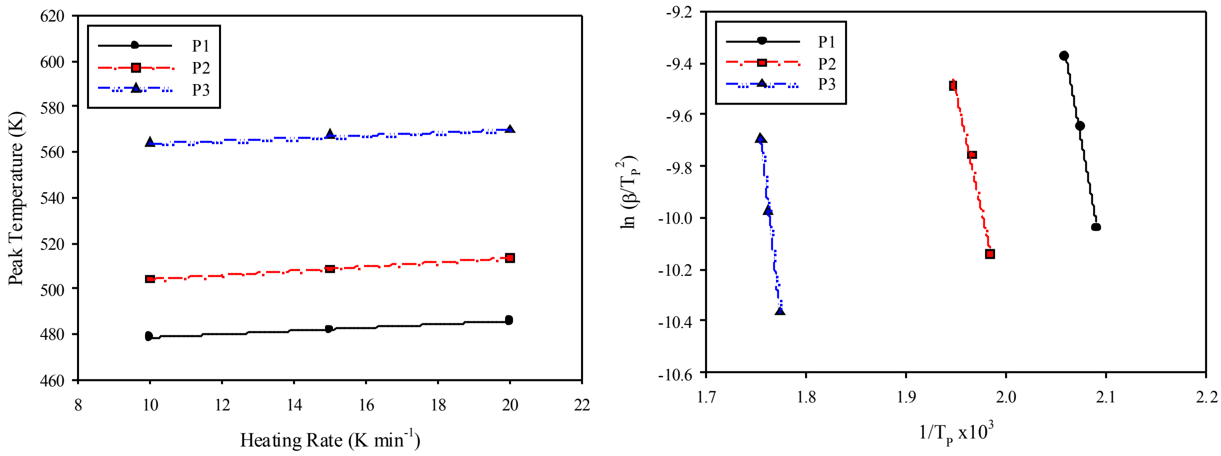

Figure 2: (a) Peak temperature versus heating rate and (b) estimates of activation energy for the formation of metal oxides and metal aluminates during TPC on 3%Co-10%Ni/Al_2O_3 catalyst

Table 2: Summary of activation energy and pre-exponential factor values during TPC run over 3%Co-10%Ni/Al_2O_3 catalyst

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

The XRD pattern of 3%Co-10%Ni/Al_2O_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 2θ angle of 19.45°, 36.99°, 45.69° and 67.20° corresponded to γ-Al_2O_3 phase. Additionally, the characteristic peaks for Co_3O_4 phase formation was observed at 2θ = 31.13° and 65.00° whilst NiO phase was detected at 2θ of 36.99°. Besides, the typical peaks corresponding to the presence of spinel $NiAl_2O_4$ (2θ = 36.99° and 44.5°) and $CoAl_2O_4$ (2θ 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].

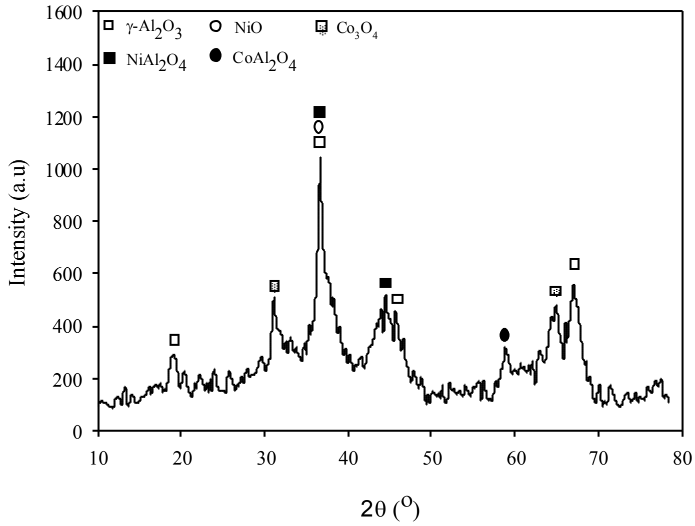

Figure 3: XRD pattern of 3%Co-10%Ni/Al_2O_3 catalyst

3.2 Catalytic Evaluation

As seen in Figure 4(a), CO_2 (red curve) and C_2H_5OH (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].

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

In another set of runs, the influence of C_2H_5OH 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 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.

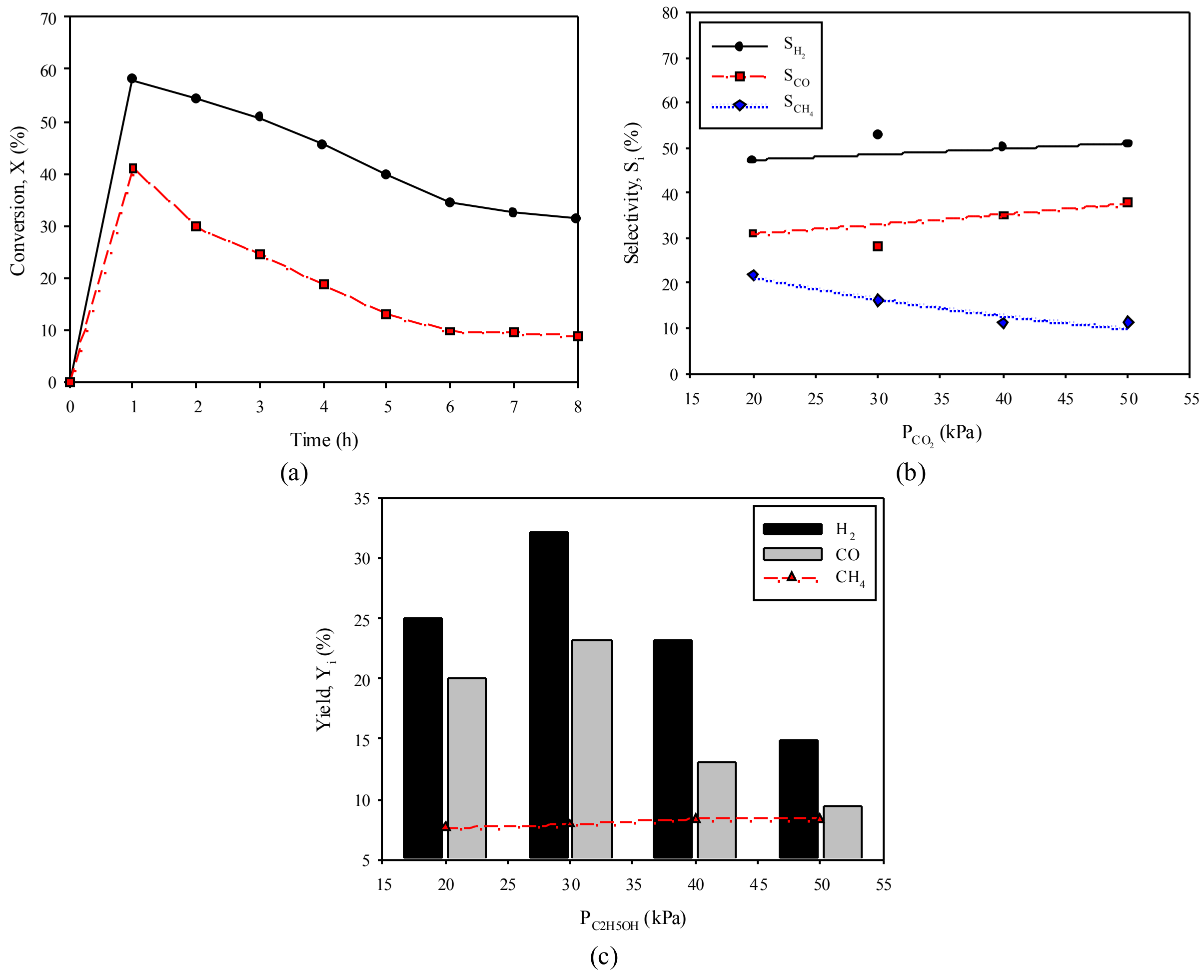

Figure 4: (a) Ethanol and CO_2 conversions versus time-on-stream, (b) effect of P_{CO2} on gaseous product selectivity and (c) influence of P_{C2H5OH} on product yield at temperature of 973 K

4. Conclusions

This research has investigated the catalytic performance of 3%Co-10%Ni/Al_2O_3 catalyst on EDR reaction for syngas production. Multi-point BET surface area measurements showed that γ-Al_2O_3 support and 3%Co-10%Ni/Al_2O_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_3O_4) at temperature below 520 K and the formation of spinel $NiAl_2O_4$ and $CoAl_2O_4$ 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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References

[1] Vo, D.-V.N., Nguyen, T.-H., Kennedy, E.M., Dlugogorski, B.Z., and Adesina, A.A, 2011, "Fischer-Tropsch Synthesis: Effect of Promoter Type on Alumina-supported Mo Carbide Catalysts," Catalysis Today, 175, 450-459.

[2] Bradford, M.C.J., and Vannice, M.A., 1999, "CO_2 Reforming of CH_4," Catalysis Reviews Science and Engineering, 41, 1-42.

[3] Haryanto, A., Fernando, S., Murali, N., and Adhikari, S., 2005, "Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review," Energy & Fuels, 19, 2098-2106.

[4] López, E., Divins, N.J., Anzola, A., Schbib, S., Borio, D., and Llorca, J., 2013, "Ethanol Steam Reforming for Hydrogen Generation Over Structured Catalysts," International Journal of Hydrogen Energy, 38, 4418-4428.
[5] Batista, M.S., Santos, R.K.S., Assaf, E.M., Assaf, J.M., and Ticianelli, E.A., 2004, "High Efficiency Steam Reforming of Ethanol by Cobalt-based Catalysts," Journal of Power Sources, 134, 27-32.
[6] Kirtay, E., and Balat, H., 2010, "Hydrogen from Biomass -Present Scenario and Future Prospects," International Journal of Hydrogen Energy, 35, 7416-7426.
[7] Comas, J., Mariño, F., Laborde, M., and Amadeo, N., 2004, "Bio-ethanol Steam Reforming on Ni/Al_2O_3 Catalyst," Chemical Engineering Journal, 98, 61-68.
[8] He, Z., Yang, M., Wang, X., Zhao, Z., and Duan, A., "Effect of The Transition Metal Oxide Supports on Hydrogen Production from Bio-ethanol Reforming," Catalysis Today, 194, 2-8.
[9] Frusteri, F., Freni, S., Spadaro, L., Chiodo, V., Bonura, G., Donato, S., and Cavallaro, S., 2004, "H_2 Production for MC Fuel Cell by Steam Reforming of Ethanol Over MgO Supported Pd, Rh, Ni and Co Catalysts," Catalysis Communications, 5, 611-615.
[10] Fierro, V., Akdim, O., Provendier, H., and Mirodatos, C., 2005, "Ethanol Oxidative Steam Reforming Over Ni-Based Catalysts," Journal of Power Sources, 145, 659-666.
[11] Li, M., Wang, X., Li, S., Wang, S., and Ma, X., 2010, "Hydrogen Production from Ethanol Steam Reforming over Nickel Based Catalyst Derived from Ni/Mg/Al Hydrotalcite-like Compounds," International Journal of Hydrogen Energy, 35, 6699-6708.
[12] Hu, X., and Lu, G., 2009, "Syngas Production by CO_2 Reforming of Ethanol Over Ni/Al_2O_3 Catalyst," Catalysis Communications, 10, 1633-1637.
[13] de Sousa, F.F., de Sousa, H.S.A., Oliveira, A.C., Junior, M.C.C., Ayala, A.P., Barros, E.B., Viana, B.C., Filho, J.M., and Oliveira, A.C., 2012, "Nanostructured Ni-containing Spinel Oxides for The Dry Reforming of Methane: Effect of The Presence of Cobalt and Nickel on The Deactivation Behavior of Catalysts," International Journal of Hydrogen Energy, 37, 3201-3212.
[14] Foo, S.Y., Cheng, C.K., Nguyen, T.-H., and Adesina, A.A., 2010, "Oxidative CO_2 Reforming of Methane on Alumina-supported Co-Ni Catalyst," Industrial & Engineering Chemistry Research, 49, 10450-10458.
[15] Brown, M.E., Introduction to Thermal Analysis: Techniques and Application, Kluwer Academic Publishers, The Netherlands, 2001.
[16] JCPDS Powder Diffraction File, International Centre for Diffraction Data, Swarthmore, PA, 2000.
[17] Foo, S.Y., Cheng, C.K., Nguyen, T.-H., and Adesina, A.A, 2011, "Evaluation of Lanthanide-Group Promoters on $Co-Ni/Al_2O_3$ Catalysts for CH_4 Dry Reforming," Journal of Molecular Catalysis A: Chemical, 344, 28-36.
[18] Batista, M.S., Santos, R.K.S., Assaf, E.M., Assaf, J.M., and Ticianelli, E.A., 2003, "Characterization of The Activity and Stability of Supported Cobalt Catalyst for The Steam Reforming of Ethanol," Journal of Power Sources, 124, 99-103.
[19] De Oliveira-Vigier, K., Abatzoglou, N., Gitzhofer, F., 2005, "Dry Reforming of Ethanol in The Presence of a 316 Stainless Steel Catalyst," The Canadian Journal of Chemical Engineering, 83, 978-984.