Influence of CO$_2$ Partial Pressure on Ethanol Dry Reforming Using 5%Ce-10%Co/Al$_2$O$_3$ Catalyst for Hydrogen Production

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Abstract— The influence of CO$_2$ partial pressure on ethanol dry reforming has been studied over Ce-promoted Co catalyst supported on Al$_2$O$_3$ from 20 to 50 kPa, C$_2$H$_5$OH was kept at 20 kPa and under atmospheric pressure. The catalyst was synthesized using wet impregnation method and tested in a quartz fixed-bed reactor. X-ray diffraction analysis indicated the formation of CeO$_2$, Co$_3$O$_4$ and spinel CoAl$_2$O$_4$ phases on catalyst surface. CoO and Co$_3$O$_4$ and CeO$_2$ phases were formed during temperature–programmed calcination and 5%Ce-10%Co/Al$_2$O$_3$ catalyst has a total high surface area of 137.35 m^2 g^{-1}. Both C$_2$H$_5$OH and CO$_2$ conversions was improved with increasing CO$_2$ partial pressure from 20 at 50 kPa and an optimal selectivity of H$_2$ and CO was obtained at 50 kPa.

Keywords—Ethanol dry reforming; Hydrogen; Ce promoter; Co-based catalyst

1. INTRODUCTION

With rise in world's population and energy demand have stimulated an initiative to find the alternative energy source with clean and eco-friendly source. The fossil fuels are accounted more than 80% to meet energy demand of the world. It has created serious environmental problems, such as greenhouse gases and climate changes [1], [2]. In addition, the problems generated by the environmental pollution are considered as a critical challenge for the next generations. Developed countries are investing in the development of fuel processing technology and gaseous fuel for power generation by fuel cells [3]. The production of syngas (a mixture of H$_2$ and CO) by steam reforming and dry reforming has been emerged as a promising method to produce synthetic fuel or a clean energy carrier. In past few decades, numerous research articles have been published on dry reforming of methane. In this process, greenhouse gases (CO$_2$ and CH$_4$) were used as feed-stock to produce eco- friendly syngas [4], [5]. A non-renewable methane, an important component of natural gas is utilized [6]. From the environmental perspective, ethanol is preferred to methane because of easy availability, abundance and cost effectiveness. It is also known as less toxic and renewable fuel [7]. Moreover, ethanol can be produced from biomass, which is one of the most abundantly available renewable resource, can be obtained from forestry waste and residues [8].The steam reforming of ethanol is also widely acknowledged for syngas production. However, this technique can effectively utilize greenhouse gases (CO$_2$) and also curtail the rise in level of CO$_2$ emission [7]. Therefore, ethanol dry reforming using 5%Ce-10%Co/Al$_2$O$_3$ catalyst for production of syngas has been thoroughly investigated for syngas production because it can minimize the impact of CO$_2$ on the environment, by effectively utilizing the ethanol and CO$_2$ in the reaction [9]. The aim of this research to investigate the physical properties of catalyst and influence of CO$_2$ partial pressure on ethanol dry reforming for H$_2$ production over 5% Ce-promoted 10%Co/Al$_2$O$_3$ catalyst.

2. EXPERIMENTAL

A. Catalyst preparation

The Gamma-Al_2O_3 support was purchased from Sasol (PURALOX SCCa150/200) and calcined in air at 1023 K for 5 h with heating rate of 5 K min^{-1} to ensure thermal stability. The 5%Ce-10%Co/Al_2O_3 catalyst was prepared by using the wet impregnation method. Then, accurately weighted amount of $Ce(NO_3)_3.6H_2O$ and $Co(NO_3)_2.6H_2O$ aqueous solutions (supplied by Sigma-Aldrich) were mixed with calcined alumina support and magnetically stirred for 3 h at room temperature and followed by drying at 383 K overnight and dried sample was calcined at 773 K for 3 h in air.

B. Catalyst characterization

The catalyst surface area, pore volume and pore diameter were determined in a Thermo Scientific Surfer unit using N_2 physisorption at 77 K. The crystal structures of γ-Al_2O_3 support and 5%Ce-10%Co/ Al_2O_3 catalyst were investigated using the X-ray diffraction (XRD), in a Rigaku Miniflex II system with wavelength, $\lambda = 1.5418$ Å at 30 kV and 15 mA. The diffraction patterns were recorded from $2\theta = 3°$ to 80° with 1° min^{-1} scan speed and a step size of 0.02°.
Temperature-programmed calcination (TPC) runs was performed for uncalcined 5%Ce-10%Co/ Al_2O_3 catalyst using TGA Q500 unit (TA Instrument). For complete removing of moisture and volatile compounds, sample was initially preheated at 373 K with 10 K min^{-1} heating rate for the 30 min in the flow of N_2 as flow of 100 ml min^{-1}. The sample was heated at 1023 K with different heating rates of 10-20 K min^{-1} in the gas mixture of $4N_2:1O_2$ (100 ml min^{-1}) for 30 min kept isothermally and subsequently sample was cooled down at room temperature in the same gas mixture.

C. Catalytic tests

The catalytic activity test have been performed in a quartz fixed-bed reactor (L = 17 inches and O.D. = 3/8 inches) placed vertically in a split tubular furnace with varying CO_2 partial pressure from 20-50 kPa and C_2H_5OH was kept at 20 kPa during reaction and reaction temperature of 973 K under atmospheric pressure. Approximately, 0.1 g_{cat} of catalyst with average particle size of 125-160 μm was mounted by quartz wool in the center of quartz reactor. The inlet flow of gas hourly space velocity, GHSV = 42 L g_{cat}^{-1} h^{-1} was used for all runs to minimize both internal and external transport resistances. The C_2H_5OH was fed into the reactor by using the syringe pump (KellyMed KL-602). Both CO_2 and N_2 flow rates were controlled through the Alicat mass flow controllers. The total flow rate of CO_2, C_2H_5OH, and N_2 gas employed to the reactor was 70 ml min^{-1}. The collected gas from the reactor was analysed using an Agilent GC 6890 series gas chromatograph provided with thermal conductivity detector (TCD) and flame ionization (FID) detectors.

3. RESULTS AND DISCUSSION

A. BET Surface area

The physical properties of γ-Al_2O_3 support and 5%Ce-10%Co/Al_2O_3 catalyst were obtained from N_2 physisorption measurements summarized in Table 1. The BET surface area of 5%Ce-10%Co/Al_2O_3 catalyst was 137.35 m^2 g^{-1} and lower than the BET surface area of γ-Al_2O_3 support 175.29 m^2 g^{-1}. After impregnation and calcination, the reduction in surface area and average pore volume from 0.46 cm^3 g^{-1} to 0.37 cm^3 g^{-1} was observed with presence of active metal on the surface of catalyst. This result was due to pore blockage with the presence of Ce and Co metal oxide phases.

Table 1: Textual properties of γ-Al_2O_3 support and 5%Ce-10%Co/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	175.29	0.46	92.96
5%Ce-10%Co/Al_2O_3	137.35	0.37	82.8

B. X-ray diffraction measurments

The XRD patterns of calcined gamma-Al_2O_3 and 5%Ce-promoted 10%Co/Al_2O_3 catalyst are shown in Fig. 1. The formation of gamma-Al_2O_3 phase was detected at 2θ = 32.73º, 36.79º, 44.20º, 45.62º, 55.40º and 67.06º whilst almost same peaks were observed on the surface of 5%Ce-promoted 10%Co/Al_2O_3 catalyst. Additionally, the peaks were identified on the surface of 5%Ce-promoted catalyst at 2θ = 31.15º and 36.97º belonged to Co_3O_4 phase whilst 2θ of 59.38º and 65.33º formation of spinel $CoAl_2O_4$. The peak was detected 2θ = 28.50º corresponded to the formation of CeO_2 phase for 5%Ce-promoted catalyst. These results were in agreement with other finding [10].

C. Thermogravimetric studies

The derivative weight profiles of 5%Ce-10%Co/Al_2O_3 catalyst during the temperature-programmed calcination are shown in Fig. 2. The peak P1 positioned at low temperature of 420-495 K with high intensity was due to the metal nitrates decomposition to the metal oxides equations (1) and (2), respectively.

$$Co(NO_3)_2 \rightarrow CoO + 2NO_2 + 0.5O_2 \tag{1}$$

$$2Ce(NO_3)_3 \rightarrow Ce_2O_3 + 3N_2O_5 \tag{2}$$

During the air calcination, the second peak (P2) at high temperature of 500-550 K was ascribed to the oxidation of CoO to Co_3O_4 and Ce^{3+} to Ce^{4+} equations (3) and (4), respectively. Furthermore, beyond 550 K, there were no peak observed for all three heating ramps due to the completed decomposition of metal precursors to metal oxides (CoO and Co_3O_4) on catalyst surface during the temperature-programmed calcination analysis. This result in good agreement with Mahadi *et al.* [11].

$$3CoO + 0.5O_2 \rightarrow Co_3O_4 \tag{3}$$

$$Ce_2O_3 + 0.5O_2 \rightarrow 2CeO_2 \tag{4}$$

D. Influence of CO_2 partial pressure

The influence of CO_2 partial pressure on ethanol dry reforming was performed at temperature of 973 K with varied CO_2 partial pressure from 20 to 50 kPa and kept C_2H_5OH at 20 kPa. The C_2H_5OH and CO_2 conversions of 5%Ce-10%Co/Al_2O_3 catalyst was shown in Fig. 3. Both C_2H_5OH and CO_2 conversions with increasing of P_{CO2} increased to about 43.96%, and 35.13%, respectively. This result was due to the existence of extra CO_2 Partial pressure in feed which improved the secondary reaction i.e. CH_4 dry reforming for converting CH_4 intermediate product to syngas [12]. Jankhah *et al.* have studied that the ethanol dry reforming conversions obtained at high ratio of CO_2 and C_2H_5OH [13]. Furthermore, the properties of high oxygen storage capacity of Ce loading in the catalyst to enhanced the catalytic activity and stability in the reaction [14]. The influence of CO_2 partial pressure on selectivity of H_2, CO and CH_4 exhibited in Fig. 4. The selectivity of H_2 and CO increased linearly with growing CO_2 partial pressure from 18.03-26.64% and13.93-20.24%, respectively whilst the selectivity of CH_4 was decreased from 25 to 18% with growing CO_2 partial pressure. This result indicated that the CH_4 and CO_2 reacted through the secondary reaction, i.e. dry reforming of CH_4. Additionally, CH_4 and CO can produced a synthetic gas and improve the H_2 and CO selectivity [15].

4. CONCLUSIONS

5%Ce-10%Co/Al_2O_3 catalyst was prepared using a wet impregnation method and examined for ethanol dry reforming reaction in a quartz fixed-bed reactor at P_{CO2} (20-50 kPa), P_{C2H5OH} = 20 kPa and 973 K. Both γ-Al_2O_3 support and 5%Ce-10%Co/Al_2O_3 catalyst possessed that high surface area of 175.29 and 137.35 m^2 g^{-1}, respectively. The formation of Co_3O_4, CeO_2 and $CoAl_2O_4$ phases on surface of catalyst indicted by XRD measurements. The complete decomposition of metal precursors to metal oxides (CoO and Co_3O_4) observed at temperature beyond 550 K during the TGA analysis. The optimal C_2H_5OH and CO_2 conversions were obtained at P_{CO2} = 50 kPa. Significantly, with rising CO_2 partial pressure from 20-50 kPa, H_2 and CO selectivity was increased whilst CH_4 selectivity decreased at the same condition.
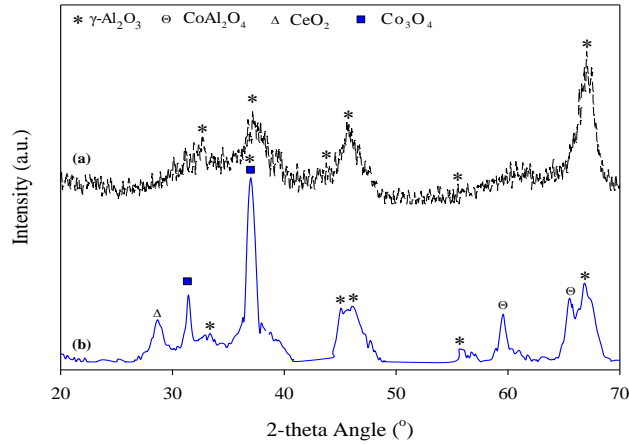
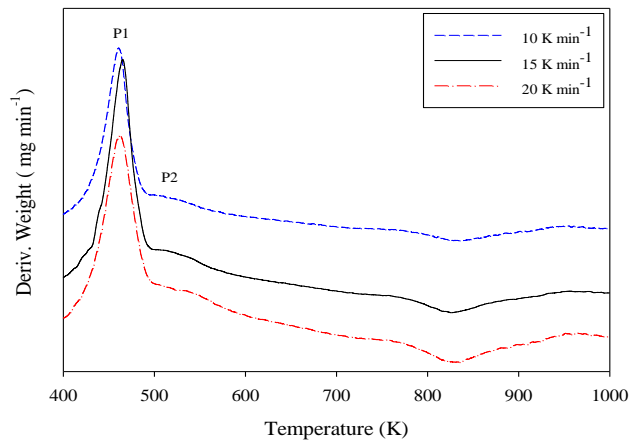Figure 1: X-ray diffractograms of (a) γ-Al$_2$O$_3$ support and (b) 5%Ce-10%Co/Al$_2$O$_3$ catalyst.

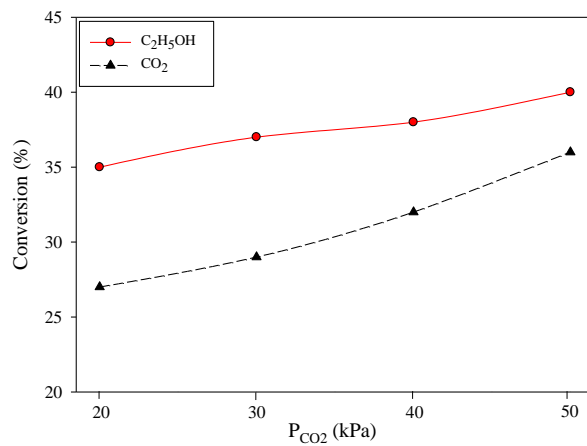Figure 2: Derivative weight profiles for temperature-programmed calcination runs of 5%Ce-10%Co/Al$_2$O$_3$ catalyst.

Figure 3: Influence of P$_{CO2}$ on C$_2$H$_5$OH and CO$_2$ conversions of 5%Ce-10%Co/Al$_2$O$_3$ catalyst at P$_{C2H5OH}$ = 20 kPa and 973 K.
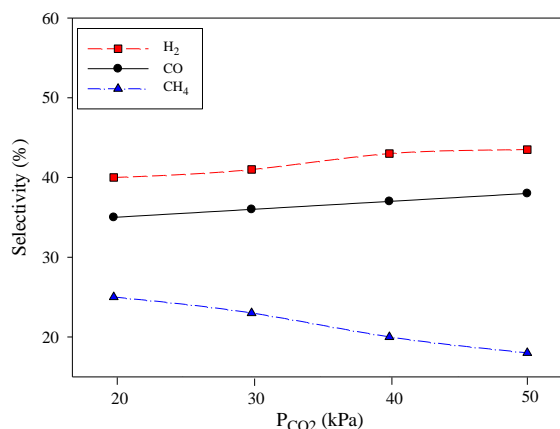
Figure 4: Influence of P_{CO2} on selectivity of H_2, CO and CH_4 at P_{C2H5OH} = 20 kPa and 973 K.

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