SYNTHESIS, CHARACTERIZATION AND CATALYTIC PERFORMANCE OF CERIA-SUPPORTED COBALT CATALYST FOR METHANE DRY REFORMING TO SYNGAS

(Sintesis, Pencirian dan Prestasi Mangkin Kobalt Sokongan Ceria untuk Penghasilan Semula Metana Kontang Kepada Gas Sintesis)

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Abstract

In this study the synthesis, characterization and catalytic performance of CeO_2 (Ceria) supported Co catalyst was investigated. First, the ceria was synthesized by direct thermal decomposition of $Ce(NO_3)_3.6H_2O$ and subsequently impregnated with 20 wt.% Co using aqueous solution of $Co(NO_3)_2.6H_2O$ as a precursor. The synthesized catalyst was characterized using TGA, N_2-adsorption-desorption, X-ray Diffractometry (XRD), Field Emission Scanning Electron Microscope (FESEM-EDX), and Fourier Transformation Infrared (FTIR). The catalytic property of the ceria-supported cobalt catalyst was tested in methane dry reforming using a stainless steel fixed bed reactor. The dry reforming reaction was performed at the temperature range of 923-1023 K under a controlled atmospheric pressure and constant gas hourly space velocity (GHSV) of 30000 h^{-1}. The effects of reactant (CH_4 and CO_2) feed ratio was investigated on reactants conversion, product yields, and selectivity. The ceria-supported cobalt catalyst recorded highest catalytic activity at a CH_4: CO_2 ratio of 0.9 and temperature of 1023 K. The highest values of 79.5% and 87.6% were recorded for the CH_4 and CO_2 conversions respectively. Furthermore, highest yields of 41.98% and 39.76%, as well as selectivity of 19.56% and 20.72%, were obtained for H_2 and CO respectively. Syngas ratio of 0.90 was obtained from the dry reforming of methane, making it suitable as feedstock for Fischer-Tropsch synthesis (FTS).

Keywords: ceria, cobalt, Fischer-Trosch synthesis, methane dry reforming, syngas

Abstrak

Dalam kajian ini, sintesis, pencirian berserta prestasi tindakbalas pemangkin Co/CeO_2 telah dijalankan. Terdahulu, ceria disintesis daripada penguraian terma secara langsung ke atas $Ce(NO_3)_3.6H_2O$, diikuti oleh formulasi dengan 20% logam Co menggunakan larutan akueus $Co(NO_3)_2.6H_2O$ sebagai pelopor. Mangkin yang diperolehi dicirikan dengan menggunakan kaedah TGA, N_2-penjerapan penyaherapan, pembelauan sinar X (XRD), Mikroskop Pengimbas Elektron Pancaran Medan – Sinar-X Serakan Tenaga (FESEM-EDX) dan Inframerah Tranformasi Fourier (FTIR). Prestasi pemangkin Co/CeO_2 telah diuji untuk tindakbalas penghasilan metana kontang di dalam reaktor keluli tahan karat. Tindakbalas kimia tersebut telah dijalankan pada suhu berjulat daripada 923-1023 K, tekanan 1 atm serta GHSV bersamaan 30000 h^{-1}. Kesan nisbah reaktan (CH_4 and CO_2) terhadap penukaran reaktan serta hasil dan pemilihan produk telah disiasat. Mangkin Co/CeO_2 mencatatkan aktiviti pemangkin paling tinggi pada nisbah CH_4/CO_2 bersamaan 0.9 dan suhu 1023 K. Penukaran CH_4 and CO_2 mencatatkan nilai tertinggi bersamaan 79.5% dan 87.6%. Tambahan pula, hasil tertinggi bersamaan 37.6% dan 40% berserta sifat pemilihan bersamaan 19.56% dan 20.72% untuk H_2 dan CO telah direkodkan. Nisbah gas sintesis bersamaan 0.9 telah diperolehi daripada penghasilan semula metana kontang bersesuaian untuk tindakbalas sintesis Fischer-Trosch.

Introduction

The utilization of energy derived from fossil sources as transportation fuel has been one of the major concerns of researchers in the past five decades [1,2]. This is due to the emissions of greenhouse gases such as CO_2 into the biosphere during the combustion of these fuels [3,4]. Several reports have shown that these greenhouse gases are the main causes of global warming through "greenhouse effect" [5–7]. Efforts of researchers have been concentrated on how to mitigate the emissions of these greenhouse gases [3,8,9]. Methane (CH_4) is one of the key components of greenhouse gases as well as a major source of fossil fuel [10]. It is inexpensive and abundance in nature, hence a good building block for C_1 chemistry [11]. One way to mitigate the emissions of the greenhouse gases, as well as increasing energy output via dry reforming process [9].

Dry reforming of methane depicted in Equation (1) has received wide research attention due to its advantage to utilize both CO_2 and CH_4, the two principal components of greenhouse gases for production of synthesis gas (a mixture of H_2 and CO) [12–14]. This syngas can be used as chemical intermediates for the production of synthetic fuel via Fischer-Tropsch synthesis (FTS) [15,16].

$$CO_2 + CH_4 \rightarrow H_2 + CO \qquad \Delta H_{1023K} = 261 \text{kJ} mol^{-1} \qquad (1)$$
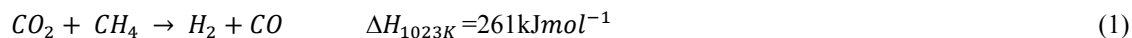
Dry reforming of methane as a highly endothermic process is majorly constraint with catalyst deactivation from sintering and carbon deposition [17,18]. There have been concerted efforts by researchers in the field of catalysis in designing and developing catalysts with high activity and stability to overcome challenges of sintering and carbon depositions [19,20].

Up to date, the activity and stability of supported metal-based catalysts such as Pt, Pd, Ru, Rh, Ir, Ni and Co, have been investigated for dry reforming of methane [21]. Reports have shown that supported noble metals catalysts such as Pt, Pd, Ru, Rh, and Ir are very active and highly stable during dry reforming of methane [22–24]. However, these noble-metal catalysts are not readily available and very expensive [25]. Hence, the application of these noble metals to catalyze dry reforming of methane will not be economical in the event of scale up. Supported Ni-based catalysts have high activity and are inexpensive [26]. Nevertheless, the usage of Ni-based catalysts in dry reforming of methane has been constraint by their susceptibility to catalyst deactivation via sintering and carbon depositions [27]. Supported Co-catalyst which is less expensive compared to noble-metal catalysts has been reported as a good alternative to Ni-based catalysts in terms of stability [28].

In addition to using good metal-based catalysts, its play a significant role in enhancing the thermal stability of catalysts during dry reforming of methane [29]. Reports have shown that efficient dispersion of active metals on supports such as SiO_2, α-Al_2O_3 CeO_2, La_2O_3 and ZrO_2 to a large extent affect the pore morphology, confinement and chemical effect of the catalysts [30]; [14]. This will invariably retard coke formation as well as reduce the tendency of the active metal to sinter. The use of ceria (CeO_2)-supported Co catalyst has been extensively studied for ethanol steam reforming [31–33]. However, there are limited studies on the dry reforming of methane over ceria supported Co catalyst [34, 35].

This present study focuses on the synthesis, characterization and catalytic performance of ceria supported Co catalyst for dry reforming of methane. The ceria support was prepared by thermal decomposition of cerium (III) nitrate hexahydrate and subsequently used for the synthesis of the Co/CeO_2 catalyst via wet impregnation method [36].

Materials and Methods

Catalyst synthesis

The schematic diagram depicting the steps involved in the catalyst synthesis is shown in Figure 1. First, the ceria support used for the catalyst synthesis was prepared by thermal decomposition of $Ce(NO_3)_3.6H_2O$ (99.99% trace metal basis, Sigma-Aldrich) at 773 K for 2 hours to obtained CeO_2 powder [36,37]. The CeO_2 powder was

subsequently impregnated with aqueous solution of $Co(NO_3)_2.6H_2O$ (20 wt% Co loading) by wet impregnation method and then stirred continuously for 3 hours at room temperature. Thereafter, the mixture containing the catalyst precursor and the support was dried at 393 K for 24 hours and then calcinate at 873 K for 5 hours.

Catalyst characterization

The physicochemical properties of the fresh 20 wt% Co/CeO_2 catalyst were determined by temperature programmed calcination using thermogravimetric analyzer (TA instrument, Q 500). The catalyst sample was heated from 298 to 1173 K at heating rates of 10, 15 and 20 K/min. The specific surface area, pore volume and average pore diameter of the catalyst were measured by N_2 adsorption-desorption isotherm at 77 K using Thermo Scientific Surfer Analyzer. Prior to the N_2 adsorption-desorption experiment, the catalyst was degassed at 573 K for 3 hours. Phase identification, as well as the crystallinity of the 20 wt% Co/CeO_2 catalyst, was determined by Rigaku X-ray powder diffraction analysis (XRD) (Miniflex II) with Cu Kα (45kV, 0.154 nm) radiation.

The morphology and elemental composition of the catalyst sample were carried out using JEOL FESEM (JSM-7800F) equipped with EDX. Temperature-programmed reduction (TPR) of the fresh catalyst was performed in a fixed bed reactor. The catalyst weighing 200 mg was heated from 373 – 1073 K in a flow of 60 ml/min of H_2/N_2 (1:5). The amount of hydrogen consumed was measured using gas chromatography (GC) equipped with thermal conductivity detector (TCD). The GC consists of two packed columns namely Supelco Molecular Sieve 13x (10 ft × 1/8 in OD × 2 mm ID, 60/80 mesh, Stainless Steel) and Agilent Hayesep DB (30 ft × 1/8 in OD × 2 mm ID, 100/120 mesh, Stainless Steel). Helium gas with flow rate of 20 ml min^{-1} was used as the carrier at operating column temperature of 393 K.

The nature of chemical bond of the catalyst was measured using Perkin Elmer Fourier transform infrared (FTIR) (Nicolet iS-50) spectrometer. The sample was analysed using an attenuated total reflectance (ATR) method within 4000-400 cm^{-1}.
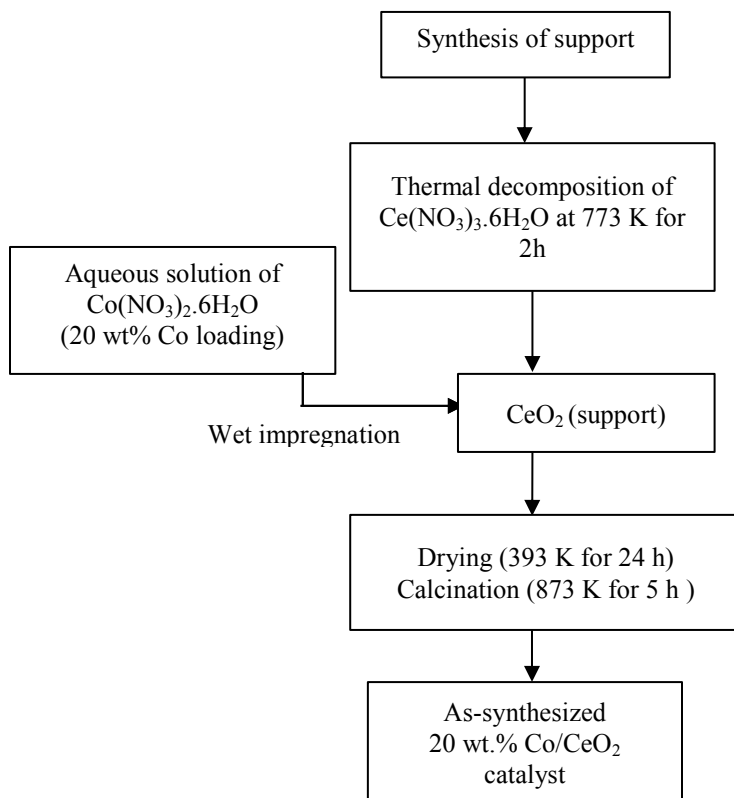

Figure 1. Schematic diagram of steps involved in the synthesis of the 20 wt% Co/CeO_2 catalyst

Catalyst activity test
The catalyst activity test was performed in a stainless steel fixed bed reactor under controlled atmospheric pressure. The stainless steel tubular reactor was loaded with 200 mg catalyst sample supported with quartz wool. The fixed bed reactor was positioned in a furnace equipped with a Type-K thermocouple to monitor the temperature of the catalytic bed. Prior to the commencement of the activity test, the catalyst was reduced *in situ* in a flow of 60 ml/min of H_2/N_2 (1:5) at 873 K for 1 h. The flow of the reactant gases (CH_4 and CO_2) into the reactor was monitored using Alicat digital mass flow controller. The dry reforming of methane was performed at varying feed ratios ranged 0.1-1.0 and reaction temperature ranged 923 – 1023 K. The compositions of the reactant gases as well as the products (H_2 and CO) were monitored using GC-TCD. The activity of the catalyst was measured based on the conversions of the reactants, the yield, and selectivity of the products formed as shown in equations (2) – (7).

$$CH_4 \text{ conversion (\%)} = \frac{F_{CH_4in} - F_{CH_4out}}{F_{CH_4in}} \times 100 \tag{2}$$

$$CO_2 \text{ conversion (\%)} = \frac{F_{CO_2in} - F_{CO_2out}}{F_{CO_2in}} \times 100 \tag{3}$$

$$H_2 \text{ yield} = \frac{F_{H_2out}}{2 \times F_{CH_4in}} \times 100 \tag{4}$$

$$CO \text{ yield} = \frac{F_{COout}}{F_{CH_4in} + F_{CO_2in}} \times 100 \tag{5}$$

$$H_2 \text{ Selectivity} = \frac{F_{H_2out}}{F_{H_2out} + F_{CH_4out} + F_{CO_2out} + F_{CO}} \times 100 \tag{6}$$

$$CO \text{ Selectivity} = \frac{F_{H_2out}}{F_{CH_4out} + F_{CO_2out} + F_{COout}} \times 100 \tag{7}$$

$F_{CO_2in,}$ = inlet molar flow of CO_2; F_{CO_2out} = outlet molar flow of CO_2; $F_{CH_4in,}$ = inlet molar flow of CH_4; F_{CH_4out} = outlet molar flow of CH_4; $F_{H_2out,}$ = outlet molar flow of H_2; F_{COout} = outlet molar flow of CO.

Results and Discussion

Catalyst characterization
The temperature programmed calcination of the fresh catalyst is shown in Figure 2. Four distinct peaks (I to IV) can be identified from the TGA curve. Peaks I-III can be attributed to sequential loss of physical and hydrated water while peak IV depicts decomposition of the cobalt nitrate to obtain Co_3O_4. This trend is consistent with the findings of [38] in their study on dry reforming of methane over alumina supported cobalt catalyst.
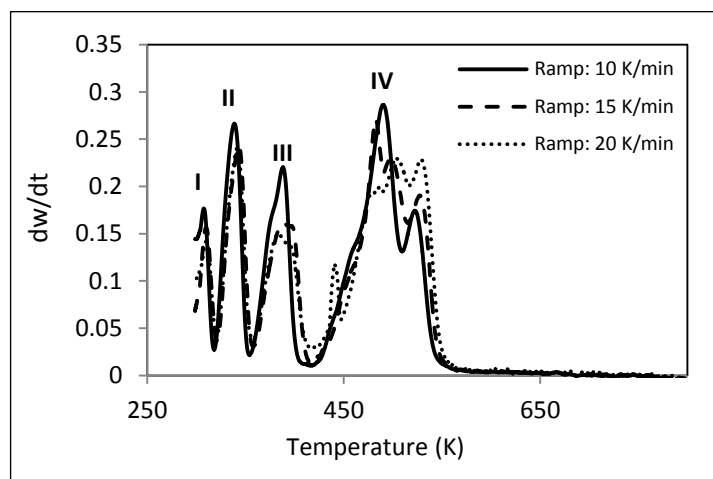

Figure 2. Temperature Programmed Calcination of the 20 wt% Co/CeO_2 catalyst

The determination of the mesoporous structure and specific surface of the 20 wt% Co/CeO_2 catalyst from N_2 adsorption-desorption isotherm is depicted in Figure 3. The Co/CeO_2 catalyst isotherm has a characteristic of Type IV isotherm curve with H3 hysteresis loop. Since the relative pressure $(P/P°)$ is > 0.55, the catalyst exhibited uniform mesoporous structure with capillary condensation. The BET specific area of the catalyst was estimated from the sorptomatic data processing software as 39.89 m^2g^{-1} while the pore volume and average pore diameter obtained from Barrett, Joyner, and Hallenda (BJH) method were estimated to be 0.0141 cm^3g^{-1}, and 1.16 nm respectively.
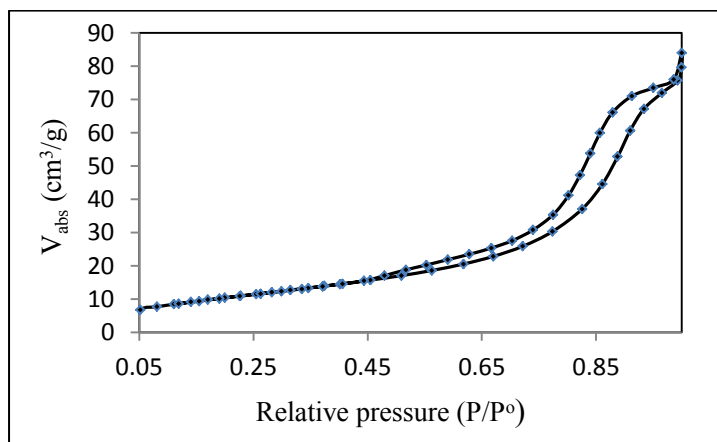

Figure 3. N_2 adsorption-desorption isotherm of the 20 wt% Co/CeO_2 catalyst

The XRD pattern of the catalyst sample is depicted in Figure 4. Distinct peaks of CeO_2 and Co_3O_4 crystals can be seen at $2\theta = 29.4°, 38.4°, 48.7°, 57.9°$ and $2\theta = 31.3°, 44.5°, 59.7°, 65.1°, 67.7°, 77.1°$ respectively. The diffraction peaks obtained for CeO_2 can be assigned to the crystalline phase of (111), (220), (311), (220) and (422) which represent faced-centre cubic structure [39].
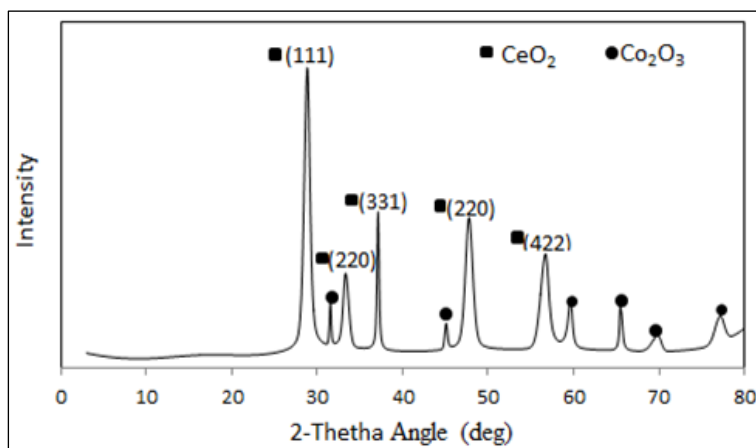

Figure 4. XRD pattern of the 20 wt% Co/CeO_2 catalyst

The FESEM micrograph and EDX dot mapping showing the morphology and the elemental composition of the 20 wt% Co/CeO_2 catalyst are depicted in Figures 5-7 respectively. The FESEM micrograph (Figure 5) shows the

irregularity and the agglomeration of the catalyst particle sizes. While the EDX dot mapping (Figure 6) confirms the presence of Co, Ce and O as stimulated during the synthesis of the catalyst. The elemental compositions of the catalysts obtained from the EDX dot mapping (Figure 7) corresponds to the stimulated amount used for the catalysts synthesis.
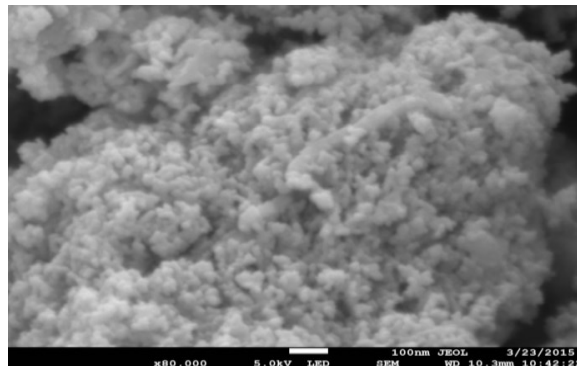

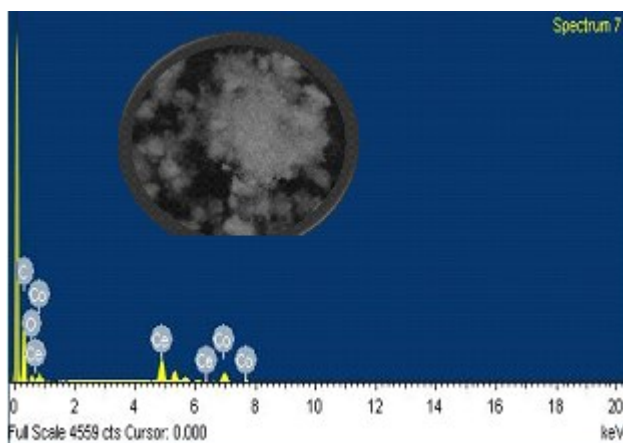Figure 5. The FESEM micrograph of the 20 wt% Co/CeO$_2$ catalyst

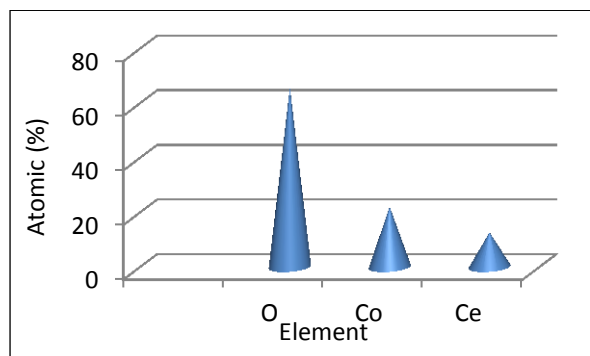Figure 6. The EDX dot mapping of the 20 wt% Co/CeO$_2$ catalyst

Figure 7. The elemental composition of the 20 wt% Co/CeO$_2$ catalyst obtained from EDX-mapping

In order to check the reducibility of the catalyst in a flow of H_2, the catalyst was subjected to H_2-TPR. Significantly, two peaks centralized at a temperature of 423, and 673 K can be identified from the H_2-TPR profile. The peaks could be attributed to the sequential reduction of Co_3O_4 to Co crystallite represented in equation 8. The peak at 423 K could be attributed to the reduction of Co_3O_4 which has a weak interaction with the support to CoO. The peak at 577K with a stronger interaction can be attributed to the reduction of CoO to Co [40].
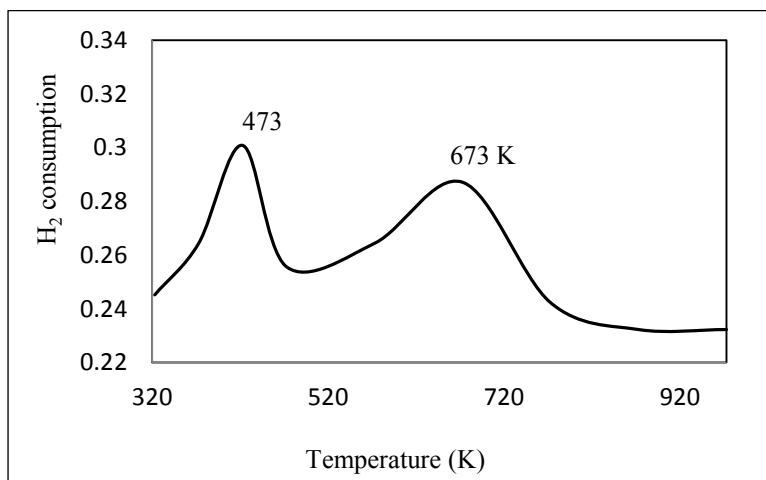
$$Co_3O_4 \rightarrow CoO \rightarrow Co \tag{8}$$

Figure 8. H_2-TRP profile of the 20 wt% Co/CeO$_2$ catalyst

The FTIR spectra of the catalyst are shown in Figure 9. The spectra band can be identified at 3400, 1670, 667 and 567 cm^{-1} respectively. The bands at 3400 and 1670 cm^{-1} can be attributed to OH^{-} which is due to water moisture and COO from dissolved atmospheric CO_2. The band obtained at 1670 and 667 cm^{-1} can be attributed to stretching metal oxides (M-O) bond from Co-O and Ce-O respectively.
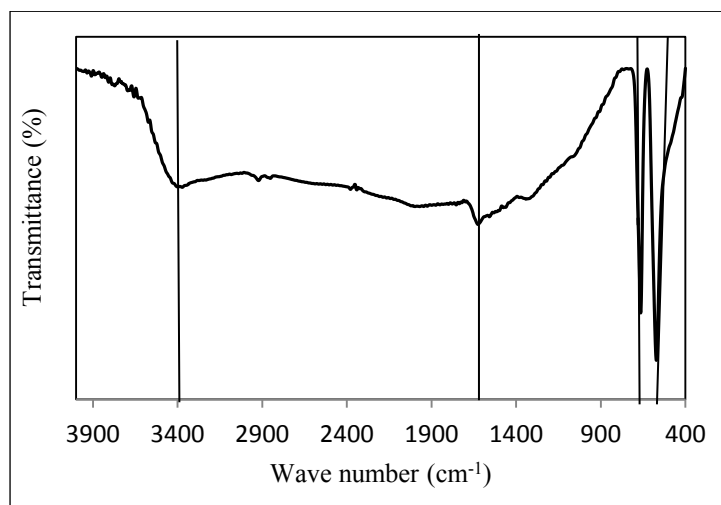

Figure 9. FTIR spectra of the 20 wt% Co/CeO$_2$ catalyst

Catalyst activity

The performance of the ceria supported Co catalyst was measured from the conversions of the reactant gas to syngas, the yields of the syngas produced as well as the products selectivity. The effects of feed ratios (0.1-1.0) and temperature (923 – 1023K) were investigated on the catalyst activity in terms of conversions, yields, and selectivity in methane dry reforming process. The conversions of CH_4 and CO_2 depicted in Figures 10 and 11 increases with feed ratio and temperature signifying the temperature dependent nature of the dry reforming reaction. The conversion of CH_4 increases from 43.2% to a maximum value of 79.5%. Similarly, conversion of CO_2 increases from 17.8% to 87.6%. The catalyst shows higher activity towards CO_2 conversion compared to CH_4. This could be as a result of reversed water gas shift reaction shown in equation 9 [41].

$$CO_2 + H_2 \rightarrow H_2O + CO \quad \Delta H_{298} = 41\text{kJmol}^{-1} \tag{9}$$
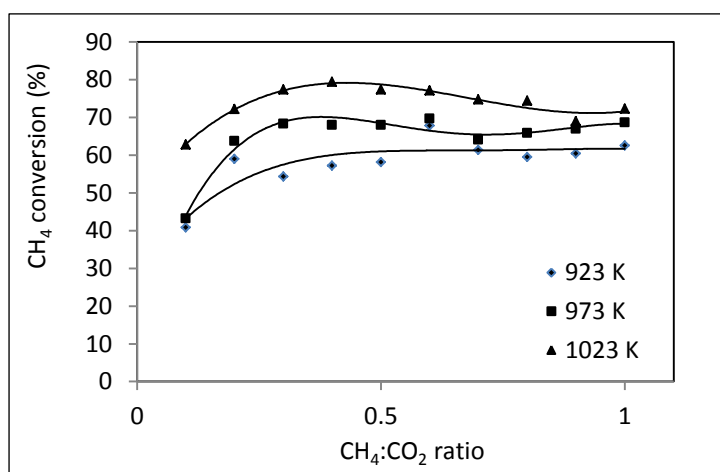

Figure 10. Effect of feed ratio and temperature on conversion of CH_4 over 20 wt% Co/CeO_2 catalyst
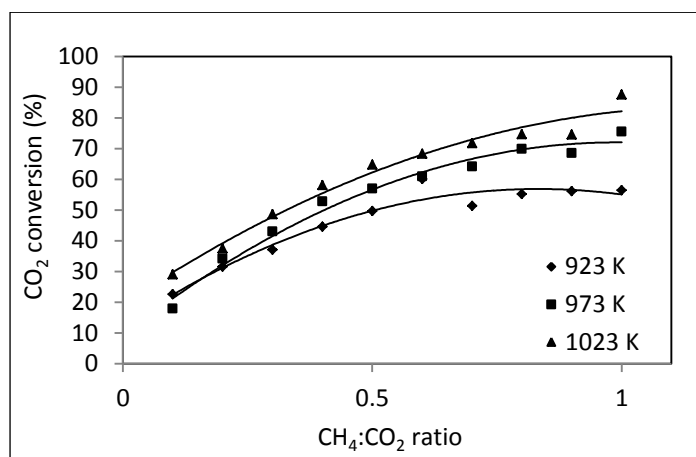

Figure 11.   Effect of feed ratio and temperature on conversion of CO_2 over 20 wt% Co/CeO_2 catalyst.

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The catalytic performances of the 20 wt% Co/CeO_2 catalyst in term of products (CO and H_2) yields are depicted in Figures 12 and 13, respectively. It is noteworthy that both H_2 and CO yields increase with feed ratios and temperature. The yield of H_2 increases from 1.69% to reach a maximum value of 41.98%. While the yield of CO increases from 6.56% to the maximum value of 39.76%. A similar observation has been reported by Sajjidi et al. [42] for dry reforming of methane over Ni–Co/Al_2O_3–ZrO_2 nanocatalyst. The highest yield of 42% and 58% were obtained for H_2 and CO respectively. In the present study, at the highest yield of H_2 and CO, syngas ratio of 1.05 was obtained. This makes the syngas produced from the dry reforming of methane over the 20 wt% Co/CeO_2 catalyst suitable as a chemical intermediate to produce oxygenated fuel via FTS. Apparently, the catalyst shows a higher activity towards H_2 yield compared to CO yield. The observation could be attributed to temperature dependent nature of CH_4 decomposition. The decomposition of CH_4 increases with temperature leading to an increase in the formation of H_2 [43].
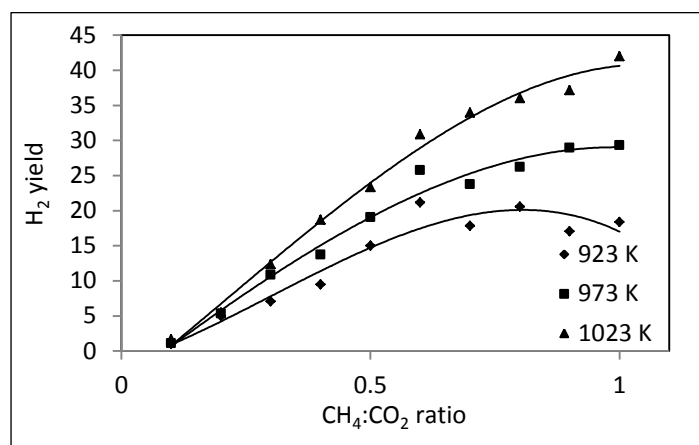

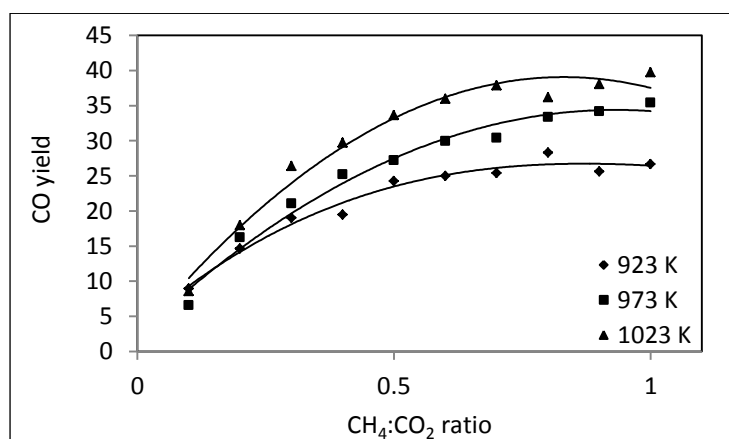Figure 12. Effect of feed ratio and temperature on the yield of H_2 over 20 wt% Co/CeO_2 catalyst

Figure 13. Effect of feed ratio and temperature on the yield of CO over 20 wt% Co/CeO_2 catalyst

The selectivity of the 20 wt% Co/CeO_2 catalyst towards H_2 and CO production is shown Figures 14 and 15, respectively. The H_2 and CO selectivity significantly increase with feed ratio and temperature from 1.16% and 8.56% to reach a maximum value of 19.56% and 20.72% respectively. This observation is consistent with the findings of Zheng et al. [44] who employed Co/γ-Al_2O_3 for dry reforming of methane to syngas. The authors,

however, obtain a higher selectivity of 95% and 85% for H_2 and CO. The difference in result could be linked to high surface area γ-Al_2O_3 used as support compared to Ceria as well as the difference in experimental conditions.
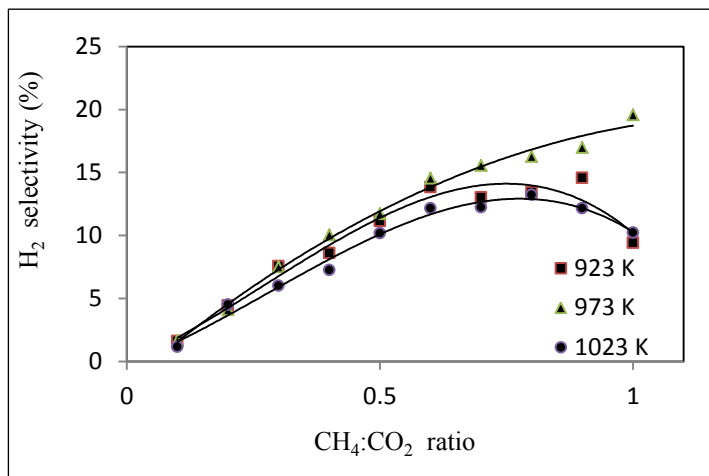

Figure 14. Effect of feed ratio and temperature on the selectivity of H_2 over 20 wt% Co/CeO_2 catalyst
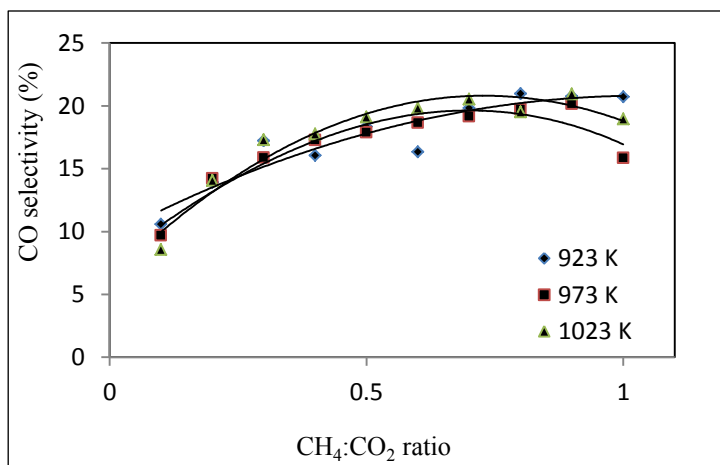

Figure 15. Effect of feed ratio and temperature on the selectivity of CO over 20 wt% Co/CeO_2 catalyst

Conclusion

In this study, we have reported the synthesis, characterization and catalytic performance of ceria supported Co catalyst. The catalyst was synthesized by wet impregnation method and characterized by different physicochemical properties using techniques such as TGA, N_2-adsorption-desorption, XRD, FESEM-EDX, and FTIR. The catalytic performance of the as-synthesized catalyst was tested in dry reforming of methane for the production of syngas. The catalyst shows good performance towards reactant conversion, products yield, and selectivity. Syngas ratio of 0.9 was produced from the dry reforming of methane over the ceria supported catalyst, making the process suitable for the production of feedstock for FTS process.

Acknowledgement

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