

Syngas production from CO₂ reforming of methane over ceria supported cobalt catalyst: Effects of reactants partial pressure



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ABSTRACT

The production of syngas from CO₂ (dry) reforming of methane is an environmental friendly process since it contributed to the mitigation of CH₄ and CO₂, the two principal components of greenhouse gases. In this study, ceria-supported cobalt catalyst was synthesized using wet-impregnation method and tested for the production of syngas from methane dry reforming. The main objective of this study is to investigate the effects of partial pressures of the reactants (CH₄ and CO₂) on the performance of the ceria-supported cobalt catalyst for syngas production via methane dry reforming. The CH₄ and CO₂ partial pressures were investigated within the range of 5–50 kPa at reaction temperatures of 923–1023 K in a fixed bed reactor at atmospheric pressure and gas hourly velocity of 30,000 h⁻¹. The highest conversion of CH₄ and CO₂ were obtained to be 78 and 80% at CH₄ partial pressure of 45 and 25 kPa respectively. Syngas ratio of 1.0 was produced at CH₄ partial pressure of 40 kPa (reaction temperature of 1023 K). The maximum yield of 40% and 38% were obtained for H₂ and CO, respectively. The used catalyst was characterized by temperature programmed oxidation (TPO) for possible carbon deposition. The TPO analysis revealed the formation of graphitic carbon. The findings from this study show that syngas production from methane dry reforming over ceria-supported cobalt catalyst is significantly influenced by the variation in the partial pressure of the reactants.

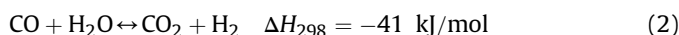
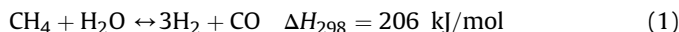
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1. Introduction

Synthesis gas (syngas), a mixture of H₂ and CO is an important intermediate for the downstream production of synthetic fuels and value-added chemicals through Fischer–Tropsch Synthesis (FTS) (Yao et al., 2011). Various carbonaceous compounds can be employed as the starting materials to produce syngas, i.e. biomass (wood), coal, and natural gas as feedstock via gasification, pyrolysis and reforming processes (Boerrigter, 2006; Ry et al., 2013; Salkuyeh and Adams, 2013). The commercial production of syngas has been mostly based on coal gasification which has been in used for over seven decades, and presently used by Sasol in South Africa (Xiong et al., 2014). However, one of the major constraint of this process is the emission of CO₂ and other poisonous gas into the environment (Minchener, 2014).

Besides coal gasification, syngas can also be produced from the

reforming of methane (CH₄) using steam, oxygen or carbon dioxide (Song and Pan, 2004). Methane steam reforming involves the catalytic oxidation of natural gas (CH₄ as principal constituent) with steam (Bianchini et al., 2013) as represented in Equation (1). Additional H₂ is produced through the reaction of the CO in Equation (2) with steam (water gas shift reaction).



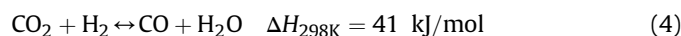
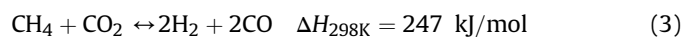
Although methane steam reforming process has achieved commercial scale, the process nonetheless produce CO₂, a major component of greenhouse gases as evinced in Equation (2). Consequently, the scientific community over the years has focused on developing an alternative process which can utilize CH₄ and CO₂, the two principal components of greenhouse gases.

Dry reforming of methane which employs CO₂ and CH₄ (naturally available in oil reservoir) as feedstock (cf. Equation (3)) has been touted as a better alternative for syngas production, since the two main components of greenhouse gases are utilized for the

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reaction (Braga et al., 2014). The main reaction also occurs concurrently with the reverse-water gas shift reaction (refer to Equation (4)).



Significantly, syngas ratio close to unity is produced in the dry reforming reaction; hence more suitable as feedstock for downstream production of synthetic fuels and other valuable chemicals via FTS (Tsakoumis et al., 2010). Nevertheless, since both steam reforming and dry reforming of methane are highly endothermic, a lot of energy is required for the process (Souza and Schmal, 2005). Most catalysts can easily deactivate at high temperature through sintering and cooking (Ruckenstein and Wang, 2002). Consequently, over the years much effort has been dedicated to developing highly stable and active catalysts for this process (Budiman et al., 2012).

One way to suppress carbon deposition and sintering is by using promoters or basic supports. Significantly, ceria has been used extensively as a promoter in catalyst formulations for reactions to syngas viz. steam reforming, partial oxidation and dry reforming of methane (Laosiripojana et al., 2005; Zhang et al., 2007; Aw et al., 2014; Fonseca et al., 2014; Yu et al., 2014). Addition of ceria as promoters has been reported to significantly enhance the stability of the catalysts in terms of its resistance to carbon deposition (Laosiripojana et al., 2005). Moreover, ceria-supported Ni, Ag, Ir, Pd, Rh as well as Co catalysts has been investigated for syngas production but mostly for ethanol and glycerol reforming which are nonetheless not hydrocarbon species (Zhang et al., 2007, 2008; Martono and Vohs, 2012; da Silva et al., 2011). Significantly, our search in the open literature in particular, found that effect of reactant partial pressures on ceria supported Co catalyst for catalytic syngas production from methane dry reforming has not been reported. Therefore, novelty of the present work lies in the investigation of the effect of reactant partial pressures on syngas production via dry reforming of methane over ceria-supported cobalt (Co/CeO₂) catalyst. The 20wt%Co/80wt%CeO₂ catalyst was synthesized via wetness impregnation. Specifically, effects of partial pressures of CO₂ and CH₄ on the conversion, H₂ and CO yields, and syngas ratio were investigated.

2. Experimental

2.1. Catalyst synthesis

Wet-impregnation technique was employed for the catalyst preparation. Cerium (III) nitrate hexahydrate (Ce(NO₃)₃·H₂O, (99.999% trace metal bases, Sigma–Aldrich) was thermally decomposed at 773 K for 2 h to obtain cerium oxide (ceria) which was subsequently used as a support. Synthesis of the 20wt%Co/80wt%CeO₂ was achieved by impregnating the required amount of Cobalt (II) nitrate hexahydrate (Co(NO₃)₂·H₂O (99.999% trace metal bases, Sigma–Aldrich) aqueous solution as a cobalt precursor into the ceria solid powder and continuously stirred for 3 h, followed by drying for 24 h at 393 K. The dried precursor was then calcined at 873 K for 6 h.

2.2. Catalyst characterization

X-Ray powder diffraction (XRD) analysis was employed for examining the crystalline phase of the catalyst. The XRD pattern of the catalyst was acquired on RIGAKU miniflex II X-ray diffractometer from 3° to 145° in 2θ scanning range employing Cu-Kα

radiation with wavelength (λ) of 0.154 nm. The textural property of the catalyst was investigated by N₂-physisorption technique. The BET surface area and porosity measurement were done by N₂ multilayer adsorption–desorption analysis using Thermo Scientific Surfer analyser. The instrument is equipped with degasser and surfer acquisition (version 1.2.1) software for processing the N₂ isotherm data. The techniques incorporate determination of external and pore area to estimate the total specific surface area (m²/g). The catalyst sample was degassed at 523 K for 4 h and the N₂ adsorption–desorption isotherm measured at 77 K. The total pore volume was estimated from the amount of N₂ desorbed at a relative pressure. The Barret–Joyner–Halenda (BJH) method was employed to determine the pore size distributions and the average pore diameter from the desorption section of the isotherm. The morphology, particle size as well as the elemental composition of the as-synthesized catalyst were evaluated using JEOL FESEM-EDX analyser. In FESEM, high resolution imaging of catalyst features down to nanoscale was enabled with a high brightness schottky-type field emission cathode with small beam diameter. Moreover, the elemental composition of the catalyst was obtained from EDX dot mapping by excitation of inner shell electrons resulting to characteristic X-rays with appropriate intensity for analytical information. The used catalyst was characterized for the amount of carbon deposition on the surface by temperature programmed oxidation using thermogravimetric analyzer (TA instruments, Q 500 series). The sample was introduced into alumina pan and heated from 298 to 1173 K at heating of 10 K min⁻¹ in a flow of pure oxygen.

2.3. Experimental set up for catalytic production of syngas

The as-synthesized catalyst was sieved to 90–140 μm using stacked-trays sieve for the catalytic reaction studies. The desired particle range was necessary to avoid pressure drop across the catalyst bed as well as ensuring the minimization of physical transport limitation. The catalytic methane dry reforming over 20wt%Co/80wt%CeO₂ catalyst was carried out in a stainless steel fixed-bed reactor (with an external diameter of 10 mm and a length of 35 cm). The fixed-bed reactor was packed with 200 mg of the catalyst supported by quartz wool. The temperature of the catalyst bed was measured with Type-K thermocouple. The inlet gases to the reactor were made of CH₄, CO₂ and N₂ with total flowrate of 100 ml/min which was individually controlled by Alicat scientific digital mass flow controllers. Gas hourly space velocity of 30,000 h⁻¹ was maintained throughout the reaction. Before the commencement of the reaction runs, the catalyst which has been calcined at 873 K was reduced *in-situ* in 60 ml/min of 20% H₂ and 80% N₂ mixture at 1073 K for 1 h. The reduction temperature was higher than the maximum reactions temperature in order to prevent any structural change in the catalysts that might occur as a result of temperature difference during the catalytic reaction. The dry reforming reaction was performed between 923 and 1023 K at atmospheric pressure with the variation in the partial pressure of CH₄ and CO₂ from 0 to 50 kPa. The composition of the outlet syngas was measured using Agilent gas chromatography (GC) couple with thermal conductivity detector (TCD). Two packed columns were used viz. Supelco Molecular Sieve 13 × (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). He gas was used as a carrier with flowrate of 20 ml min⁻¹ with operating column temperature of 393 K and detector temperature of 423 K (column pressure < 90 psi). Separation and quantification of gas analytes viz. hydrogen (H₂), methane (CH₄) and carbon dioxide (CO₂) were performed using Hayesep DB column; whilst CO were analyzed using the Molecular Sieve 13 × column. The conversion of CH₄ and

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