



## Syngas production from CO<sub>2</sub> reforming of methane over neodymium sesquioxide supported cobalt catalyst



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### ABSTRACT

This paper reports for the first time the catalytic dry (CO<sub>2</sub>) reforming of methane over 20 wt%Co/80 wt% Nd<sub>2</sub>O<sub>3</sub> catalyst. The catalyst was synthesized by wet-impregnation procedure and its physicochemical properties were characterized by TGA, XRD, FESEM, EDX, FTIR, H<sub>2</sub>-TPR and TPD followed by activity testing in a fixed-bed reactor. The effects of feed ratios (CH<sub>4</sub>: CO<sub>2</sub>) ranged 0.1–1.0, reactant (CH<sub>4</sub> and CO<sub>2</sub>) partial pressure (0–50 kPa) and temperature ranged 923–1023 K on the activity of the catalyst were investigated. The conversion of both reactants increased with the feed ratio and reaction temperature reaching maximum values of 62.7% and 82% for CH<sub>4</sub> and CO<sub>2</sub>, respectively. The CO<sub>2</sub> reforming of methane resulted into the formation of syngas with maximum yields of 59.91% and 62.02% for H<sub>2</sub> and CO, respectively, leading to formation of syngas ratio of 0.97. The mechanistic proposition includes the CH<sub>4</sub> and CO<sub>2</sub> adsorption, activation of CH<sub>4</sub> by methane cracking and gasification of carbon deposited on the catalyst surface. The experimental data were fitted by Langmuir Hinshelwood kinetic models. Activation energy values of 21.89 and 62.04 kJ mol<sup>-1</sup> were obtained for the consumption of CO<sub>2</sub> and CH<sub>4</sub> respectively from Langmuir-Hinshelwood models. The lower values of activation energy obtained for CO<sub>2</sub> compared to that of CH<sub>4</sub> shows that the rate of consumption of CO<sub>2</sub> was faster than that of CH<sub>4</sub> leading to higher conversion of CO<sub>2</sub>.

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### 1. Introduction

The sustainability of the energy derived from fossil sources has been a major subject of discussion by researchers in the last five decades (Ediger et al., 2007; Shafiee and Topal, 2009). The major concerns that have attracted wide attentions are the fast depletion in the world's fossil fuels reserve and the emission of greenhouse gases such as CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O into the environment from the utilization of energy derived from fossil fuels (Clarke et al., 2009; Shafiee and Topal, 2009). These have led to concerted efforts in searching for renewable and sustainable energy sources (Hashim

and Ho, 2011). Renewable energy sources from biomass for the production of biofuels such as bioethanol, biodiesel and bio-jet fuels have been widely investigated (Rabelo et al., 2011; Ramírez-Verduzco, 2012; Timko et al., 2011). It is still however, debatable if biofuel can substitute the conventional fossil fuel in meeting the ever increasing global energy demand (Giampietro et al., 2006).

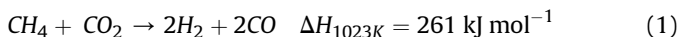
One way to simultaneously meet the global energy demand, as well as reduction in emission of these greenhouse gases is, via catalytic reforming process (Braga et al., 2014; Ross, 2005). The catalytic methane dry reforming can effectively mitigate the amount of greenhouse gases in the atmosphere which will invariably lead to the reduction in global warming (Djinović et al., 2012). Besides the advantage of reducing the emission of greenhouse gases, CH<sub>4</sub> which is one of the feedstock of the reforming process, constitutes about 95 mol % of natural gas (Union gas, 2015). Natural gas, although non-renewable, is inexpensive and abundant in

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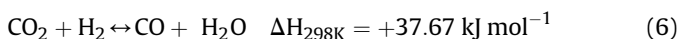
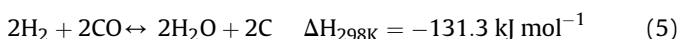
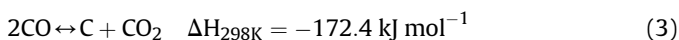
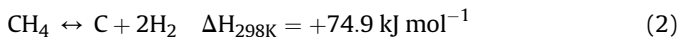
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nature with a proven world reserve of 187.1 trillion cubic metres (tcm) at the end of 2014 (British Petroleum, 2013). Natural gas as an essential commodity has been used as a major source of electricity generation, transportation fuel to power natural gas vehicles, as well as for domestic cooking and heating (Moore et al., 2014). However, the utilization of natural gas in all these processes contributes to emission of CO<sub>2</sub> (Shearer et al., 2014).

The methane dry reforming as in Equation (1) produces syngas, a mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) which is suitable for the production of oxygenated fuels such as gasoline, biodiesels, and jet fuel via Fischer-Tropsch synthesis (Khodakov et al., 2007; Laosiripojana et al., 2005).



Besides the main reaction (cf. Equation (1)), the methane cracking, Boudouard reaction, reverse water gas shift reaction, reduction of CO<sub>2</sub> and reduction of CO as in Equations (2)–(6), respectively, are the other side reactions commonly occur during the methane dry reforming (Lavoie, 2014) that unfortunately yielded carbon deposit (Han et al., 2013; Serrano-Lotina and Daza, 2014).



Studies showed that carbon deposition is one of the major causes of catalyst deactivation in methane dry reforming in addition to the sintering and poisoning effects (Lakhapatri and Abraham, 2009; Nair et al., 2014). There have been a lot of attentions on synthesizing catalysts that are thermally stable and less prone to deactivation by carbon deposition (Sato and Fujimoto, 2007; Tungkamani and Phongaksorn, 2013; Zhang et al., 2007). To date, noble metals/transition metals such as Pd, Pt, Ru, Rh, Ni and Co dispersed on supports, i.e. Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SBA-15 and SiO<sub>2</sub> have been investigated for methane dry reforming (El Hassan et al., 2016; Abasaheed et al., 2015; Ba et al., 2014; Bouarab et al., 2004; Itkulova et al., 2005; Mattos et al., 2003; Sokolov et al., 2013; Ocsachoque et al., 2011). Previous studies have shown that the use of rare earth metals oxides such as CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> as supports for metal-based catalysts enhance the catalytic activities and stability (Ayodele et al., 2015a; Verykios, 2003). The enhanced performance of these rare earth metal oxides supported metal-based catalysts is due to their basic surface characteristic as well as high oxygen storage-release capacity (Sato et al., 2009; Zhang et al., 2006). Although extensive studies have been done on the use of rare earth metal oxides such as CeO<sub>2</sub> for synthesis of Co-based catalyst in methane dry reforming, to the best of our knowledge, literature on the catalytic performance of Nd<sub>2</sub>O<sub>3</sub> supported Co catalyst for the methane dry reforming has not been reported. Therefore, the present study focuses on the synthesis, characterization and catalytic performance of 20 wt%Co/80 wt% Nd<sub>2</sub>O<sub>3</sub> catalyst for application in methane dry reforming. The application of Nd<sub>2</sub>O<sub>3</sub> as support for the dispersion of Co, is based on its advantages as reported by (Sato et al., 2009). According to Sato et al. (2009), the surface characteristic of Nd<sub>2</sub>O<sub>3</sub> is basic rather than acidic. This implies that the synthesis of Co on the Nd<sub>2</sub>O<sub>3</sub> will

enhance the activation of CO<sub>2</sub> during the methane dry reforming reaction since CO<sub>2</sub> is an acidic gas. Moreover, Nd<sub>2</sub>O<sub>3</sub> as a rare earth metal oxide has a high oxygen storage-release capacity. During methane dry reforming valence oxygen can be released from the Nd<sub>2</sub>O<sub>3</sub> for gasification of deposited coke on the catalysts surface. The choice of 20 wt% Co-loading used in this study was based on the findings of Budiman et al. (2016), Jacobs et al. (2002) and Ma et al. (2004) who investigated the effect of Co loading (2 wt%–35 wt%) on the catalytic performance of supported Co catalysts. The authors concluded that the catalyst with 20 wt% Co-loading had better performance compare to those with lower Co-loadings (<20 wt%).

## 2. Experimental

### 2.1. Synthesis of 20 wt%Co/80 wt%Nd<sub>2</sub>O<sub>3</sub> catalyst

Prior to the catalyst synthesis, the Nd<sub>2</sub>O<sub>3</sub> powder was obtained from thermal decomposition procedure, in accordance with reported literature (Ayodele et al., 2016a; Hussein, 1996; Kępiński et al., 2004). The Nd<sub>2</sub>O<sub>3</sub> precursor, Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9% trace metal basis, Sigma-Aldrich) was heated under the air flow at 773 K for 2 h, to obtain Nd<sub>2</sub>O<sub>3</sub> powder. The Nd<sub>2</sub>O<sub>3</sub> powder was subsequently crushed to obtain required particle size suitable for the synthesis of the Co-catalyst. For the preparation of the 20 wt%Co/80 wt%Nd<sub>2</sub>O<sub>3</sub> catalyst, 15.52 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.99% trace metal basis, Sigma-Aldrich) equivalent to 20 wt% Co loading were dissolved in 20 ml distilled water. The aqueous solution was subsequently impregnated into 20 g of the Nd<sub>2</sub>O<sub>3</sub> powder to obtain the catalyst slurry. The slurry was continuously stirred for 3 h, followed by drying at 393 K for 24 h and calcination under air flow at 873 K for 5 h.

### 2.2. Characterization of catalyst

Several techniques such as thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), N<sub>2</sub> adsorption-desorption analysis, temperature programmed reduction (H<sub>2</sub>-TPR) temperature programmed desorption (TPD), and Fourier transform infra-red spectroscopy (FTIR) were employed for characterization of the as-synthesized 20 wt%Co/80 wt%Nd<sub>2</sub>O<sub>3</sub>. The weight changes of uncalcined, fresh catalyst as a function of temperature was performed by a TGA instrument (TA instruments, Q500). The thermogravimetric (TG) and the differential thermogravimetric (DTG) profiles representing the non-isothermal catalyst weight loss and derivative weight loss, respectively, were measured over temperatures that ranged from 298 to 1273 K employing heating rates of 10, 15 and 20 K min<sup>-1</sup>, respectively, in a flow of compressed air. The activation energy of the decomposition of dried fresh catalyst (Co(NO<sub>3</sub>)<sub>2</sub>/Nd<sub>2</sub>O<sub>3</sub>) was evaluated using Kissinger equation as in (7) (Blaine and Kissinger, 2012).

$$\ln \left[ \frac{\beta}{T_m^2} \right] = \ln \left[ \frac{ZR}{E} \right] - \frac{E}{RT_m} \quad (7)$$

where β, T<sub>m</sub>, R, Z and E are the heating rate, peak temperature, universal gas constant, Arrhenius pre-exponential factor and activation energy, respectively. Carbon deposited on the spent catalyst was analysed by temperature programmed oxidation (TPO) under compressed air atmosphere (20% O<sub>2</sub> and 80% N<sub>2</sub>, total flow = 50 ml/min) using the same TA Q500 series instrument.

The crystalline phase of the calcined catalyst was determined by

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