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Hydrogen Production From catalytic reforming of greenhouse gases (CO_2 and CH_4) Over Neodymiun (III) oxide supported Cobalt catalyst

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ABSTRACT: Hydrogen production from CO_2 reforming of methane over 20wt%.Co/Nd_2O_3 has been investigated in a fixed bed stainless steel reactor. The 20wt%.Co/Nd_2O_3 catalyst was synthesized using wet impregnation method and characterized for thermal stability, textural property, crystallinity, morphology and nature of chemical bonds using techniques such as TGA, XRD, N_2 adsorption-desorption, FESEM, EDX and FTIR. The CO_2 reforming of methane was performed at feed ratio (CH_4:CO_2) between 0.1-1 and reaction temperature ranged 973-1023 K. The catalyst displayed good activity towards selectivity and yield of hydrogen as well as CO, a by product. The selectivity and yield of Hydrogen increases with feed ratio and reaction temperature. The 20wt%.Co/Nd_2O_3 catalyst displayed promising catalytic activity for hydrogen production with the highest yield and selectivity of 32.5% and 17.6% respectively.

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***Keywords*:** Cobalt**;** Greenhouse gases; Hydrogen; Reforming;; Neodymium (III)Oxide

Since the first synthentic production of Hydrogen in the early 16th century, there has been a lot of technological advancement in the production process through reseach and development (National Hydrogen Association, 2010). Nowadays, hydrogen can be produced using varieties of feedstocks mostly from fossil and renewable resources (Balat & Kirtay, 2010; Kirtay, 2011). Hydrogen production from fossil resources include coal or biomass gasification and natural gas reforming using steam, O_2 or CO_2 (Salkuyeh & Adams, 2013).

The production of hydrogren from coal gasification became popular during the oil crisis in the late 1970s (Self, Reddy, & Rosen, 2012). During gasification, coal is broken down into H_2, syngas and CO_2 (Li, Zhang, & Bi, 2010). Coal gasification presently account for 15% commercial global hydrogen production (Man et al., 2014). However, the process is major contributory to the emissions of greenhouse gases (Man et al., 2014). Hydrogen production using steam reforming is a well developed and mature technology. Presently, about 48% of the world commercial production of hydrogen is produced from steam reforming (IEA, 2006). The production of hydrogen by steam methane reforming involve two primary reactions namely reforming and water gas shieft reaction represented in Equations (1) and (2) respectively (Koo et al., 2014).

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad (1)$$

$$CO + H_2O \leftrightarrow 3CO_2 + H_2 \quad (2)$$

Although, steam methane reforming is a well established process for hydrogen production, challenges of catalyst deactivation has been a major concerns of researches over the years (Sehested, 2006). Nickel catalysts which is commonly used for the steam methane reforming process is easily susceptible to catalyst deactivation from poisoning, sintering and carbon depositions (Legras, et al., 2014). Besides catalyst deactivation, CO_2 produced from steam methane reforming process is one of the key components of greenhouse gases responsible for global warming.

A more environemental friendly process for hydrogen production is by utilizing both CO_2 and CH_4, key principal components of greenhouse gases as feedstock for hydrogen or syngas production (Equation (3) (Braga et al., 2014). Besides, the advantage of mitigating greenhouse gases emissions, CO_2 reforming of methane is also suitable for production of H_2/CO ratio < 2 suitable as chemical intermediate for the production of synthetic fuel via Fitscher-Tropsch synthesis (Yao et al., 2011). The CO_2 reforming of methane is however not fully developed into commercial process due to constraint from catalyst deactivation mainly from carbon deposition (Ruckenstein & Wang, 2002).

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad (3)$$

Literature review by Budiman et al. (2012) shows that several metal-based catalysts such as as Pt, Ir, Co, Pd, Ru, Rh and Ni have been investigated for CO_2 reforming of methane as reported. Amongst these metal catalysts, Rh and Ru have been shown to have the highest activites and good thermal stability. However, these catalysts are not economical for large scale production. Ni-based catalysts which are

inexpensive have been widely studied and reported to have good catalytic activity (Gonçalves, et al., 2006; Ryi et al., 2013). Nevertheless, these catalysts are easily prone to catalytic deactivation from sintering and carbon deposition (Sehested, 2006)
.
Supported Co catalysts have been reported to have comparable catalytic activity and stability to Ni-catalysts (Budiman et al., 2013). Studies have also shown that supported Co catalysts are stable at high temperature during CO_2 reforming of methane (Luisetto et al., 2012). Co-based catalysts has been synthesis by impregnating aqueous solution of the Co precursors into supportes such as CeO_2, ZrO_2, MgO, Al_2O_3, SiO_2, TiO_2 (Budiman et al., 2012; Budiman et al., 2013). These supports have been reported to have effects on the catalytical behavior and the extent of carbon depositions on the catalysts.

Significantly, rare earth metal oxides such as CeO_2, ZrO_2 and La_2O_3 have been shown to have good features as catalyst supports due to their high oxygen retention capacity (Abasaeed et al., 2015; Fonseca et al., 2014). High catalytic activity and stability was reported for CeO_2 and ZrO_2 supported Co catalysts for hydrogen production from CO_2 reforming of methane (Abasaeed et al. 2015). Sokolov et al. (2012) reported that the addition of La_2O_3 to ZrO_2 supported Ni catalysts significantly increased the catalytic activity and stability. The catalyst was shown to have no distortion in activity over 180 h time-on-stream. Literature on the use of Nd_2O_3 supported Co catalyst for Hydrogen production from CO_2 reforming of methane is very scarce.

In the present study, catalytic performance of Nd_2O_3 supported Co catalyst for hydrogen production via CO_2 dry reforming is investigated. The Nd_2O_3 support was prepared by thermal decomposition of Neodymuim (III) nitrate hexahydrate at 773 K for 2 h and subsequently used for synthesis of the Co catalyst by wet impregnation method.

MATERIALS AND METHOD

*Catalysts preparation***:** The schematic diagram of the catalyst preparation is depicted in Figure 1. First, the catalyst support (Nd_2O_3) was synthesized by thermal decomposition of $Nd(NO_3)_3.6H_2O$ (99.99% purity, Sigma-Aldrich) at 773 K for 2 h (Mohammadinasab et al., 2014). The 20wt.% Co/Nd_2O_3 catalyst was prepared by wet impregnation method. Aqeous solution of $Co(NO_3)_2.6H_2O$ (99.99% purity, Sigma-Aldrich) equivalent to 20wt.% Co loading was impregnated into the Nd_2O_3 support. The mixture was continuously stirred for 3 h, followed by drying at 393 K for 24 h and calcination at 873 K for 5 h.

Catalyst characterization: The as-sythensized 20wt.%Co/Nd_2O_3 catalyst was characterized for physicochemical properties by temperature programmed calcination, N_2 adsorption-desorption isotherm, X-ray diffraction, Fourier transform infrered spectroscopy (FTIR), field emission scanning electroscopy (FESEM), energy dispersion X-ray spectroscopy (EDX) and particle size distribution analysis. Information about the thermal stability of the fresh 20wt.%Co/Nd_2O_3 catalyst was obtained from temperature programmed calcination using thermal gravimetric analyzer (TA instruments, Q500). The catalyst sample was calcined under the flow of compressed air (99.99% purity) from room temperature to 1173 K. The thermal stability of the catalysts was analyzed as a function of weight loss (%) and the derivative weight loss (%/K) using Platinum software. The analysis for the BET specific surface area and pore volume was done by liquid N_2 adsorption-desorption at 77 K using Thermo scientific surfer analyzer. The BET surfer intrument consist of two components namely the analyzer and the sample preparation degasser. The catalyst sample was degassed at 573 K in a vacuum for 3 h. The pore volume and pore diameters were estimated from the desorption section of the N_2 adsorption-desorption isotherm using modeled derived by Barrett, Joyner and Halenda (BJH) (Huang et al., 2014). The crystallinity of the catalyst was obtained from XRD difractograms which were collected on a RIGAKU miniflex 600 diffractograms using Cu Kα (λ=0.154 nm) radiation. The nature of chemical bonds of the catalyst was determined by Thermo Scientific FT-IR (Nicolet iS 50) spectrometer. The sample spectra was collected within wave number 4000-500 cm^{-1} using attenuated total reflectance. Morphology and elemental composition of the catalyst were determined by FESEM equipped with EDX. The particle size distribution was done by mastersizer particle size analyzer (Mastersizer 2000). *Catalytic activity:* The catalytic activity of the 20wt.% Co/Nd_2O_3 catalyst for H_2 production via CO_2 reforming of methane was performed in a fixed bed stainless steel reator. The catalyst weighing 200 mg was supported with quartz wool in the fixed bed reactor which was vertically positioned in a furnace with four heating zones. The temperature of the catalytic bed was monited by a Type-K thermocouple. Prior to the commencement of the reforming reaction, the catalyst was reduced *in situ* under flow of 60 ml/min of H_2/N_2 (1:5). The CO_2 reforming of methane over the 20wt.% Co/Nd_2O_3 was performed at reaction temperature ranging from 973 to 1123 K at 1 bar and gas hourly speed velocity of 30000 mmol/gcatalyst/min. The feed ratio of the reactant (CH_4:CO_2) was varied between 0.1 and 1 to determine its effect on yield and selectivity. The composition of the products (H_2 and CO) as well as the reactants were analyzed by a gas chromatography (GC) equipped with thermal conductivity conductor (TCD) (Agilent, Q 6400). The product yield and selectivity were calculated using Equation (4) –(7) respectively.

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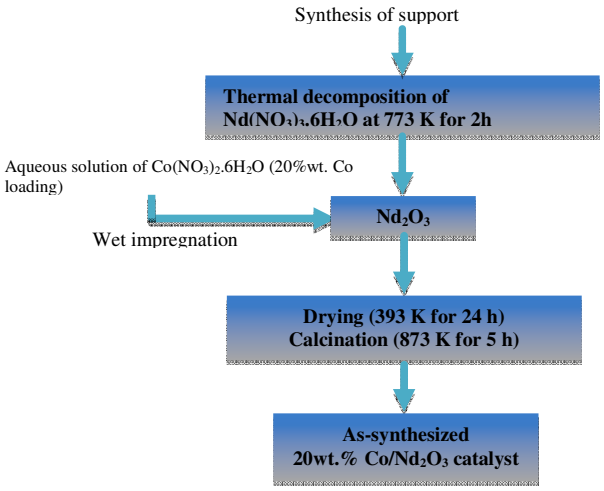

Fig 1: Schematic diagram for 20wt.% Co/Nd_2O_3 catalyst preparation

$$H_2 \text{ yield } (\%) = \frac{F_{H_2,out}}{2F_{CH_4,in}} \quad (4)$$

$$CO \text{ yield } (\%) = \frac{F_{CO,out}}{2(F_{CH_4,in} + F_{CO_2,in})} \quad (5)$$

$$H_2 \text{ selectivity } (\%) = \frac{F_{H_2,out}}{F_{H_2,out} + F_{CH_4,in} + F_{CO_2,in} + F_{CO}} \quad (6)$$

$$CO \text{ selectivity } (\%) = \frac{F_{CO}}{F_{CH_4,in} + F_{CO_2,in} + F_{CO}} \quad (7)$$

RESULT AND DISCUSSIONS

Catalyst characterization: The thermal stability analysis by temperature programmed calcination of the fresh catalyst is depicted in Figure 2. Significantly, four stages (I-IV) of weight losses can be identified from the temperature programmed calcination (Equation (8) –(11)).

$$Co(NO_3)_2 . 6H_2O \rightarrow Co(NO_3)_3 . 4H_2O \quad (8)$$

$$Co(NO_3)_2 . 4H_2O \rightarrow Co(NO_3)_3 . 2H_2 \quad (9)$$

$$Co(NO_3)_2 . 2H_2O \rightarrow Co(NO_3)_3 \quad (10)$$

$$Co(NO_3)_2 \rightarrow Co_3O_4 + N_2O_5 \quad (11)$$

Stage I-III (Equation (1) – (3)) could be attributed to sequential loss in both physical and hydrared water (Foo et al., 2011). Decomposition of $Co(NO_3)_2$ to obtained Co_3O_4 could be assigned to stage four.

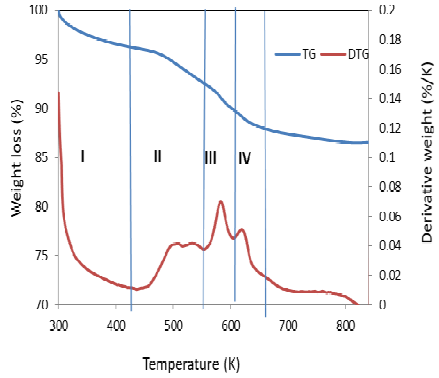

Fig 2: Temperature programmed calcination of the fresh 20wt.%Co/Nd_2O_3 catalyst.

Figure 3 shows type IV N_2 adsorption-desorption isotherm of the 20wt.%Co/Nd_2O_3 catalyst. This signifies that the catalyst is mesoporous with pore volume of 0.0061 cm^{-1} and average pore diameter of 2.19 nm. The catalyst exhibited BET surface areas of 18.67 m_2/g.

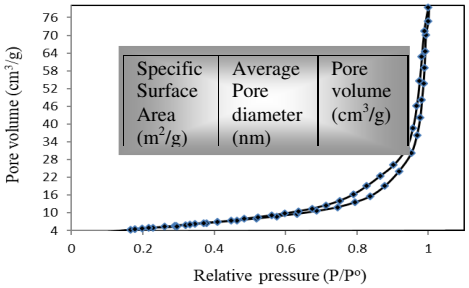

Fig 3: N_2 physisorption isotherm of the of the fresh 20wt.%Co/Nd_2O_3 catalyst.

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The XRD pattern of the fresh 20wt.%Co/Nd_2O_3 catalyst is depicted in Figure 4. The XRD diffraction peaks 2θ = 16.17, 23.80, 38.71, 40.64, 41.59, 44.80, 50.02 and 70.59[2] correspond to spinel Co_3O_4 while those 2θ = 27.08, 31.05, 33.74, 48.40 and 60.21 can be attributed to Nd_2O_3.

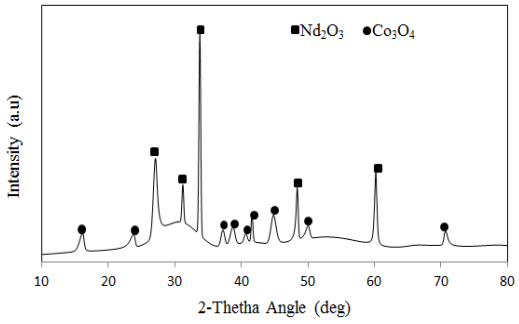

Fig 4: XRD pattern of the fresh 20wt.%Co/Nd_2O_3 catalyst.

Information on the nature of metallic bond that exists in the as-synthensized 20wt.%Co/Nd_2O_3 is depicted in Figure 4. The FTIR spectra display band at 3417, 1489, 790 and 634 cm^{-1} respectively. The band at 3417 and 1489 cm^{-1} can be attributed to atmospheric mosture and dissolved CO_2 respectively. Band 790 and 634 cm^{-1} can be attributed to medium vibration metal-oxide (M-O) bonds due to the presence of Co-O and Nd-O respectively (Kępiński et al., 2004).

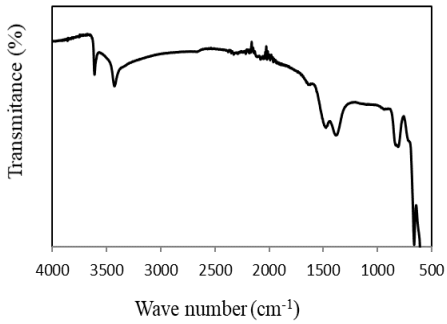

Fig 5: FTIR spectra of the fesh 20wt%.Co/Nd_2O_3 catalyst

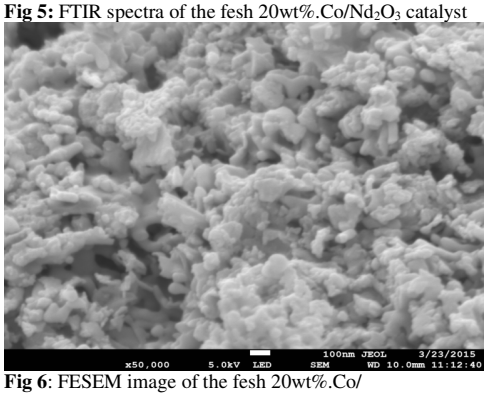

Fig 6: FESEM image of the fesh 20wt%.Co/

The morpholy and elemental composition of the as-synthesized 20wt%.Co/Nd_2O_3 catalyst represented the FESEM image and EDX mitograph are depicted in Figure 5 and 6 respectively. The agglomeration of catalyst particles can be seen from the FESEM image while the elemental compositions of the as-synthesized 20wt%.Co/Nd_2O_3 catalyst is consistent with that obtained fron the EDX mitograph (Figure 5). This further confirm the efficiency of employing wet impregnation method for catalyst preparation.

The catalytic performance of the 20wt%.Co/Nd_2O_3 in terms of yield of H_2 and CO as well as syngas (H_2+CO) at feed ratio and temperature ranged 0.1-1 and 923 – 1023 K respective;y are depicted in Figures 10–12. It is noteworthy that H_2, CO and the syngas yield increases with feed ratios for all the reaction temperatues. However, the catalyst shows better activity towards H_2 production as it is evident from the highest yield of H_2 produced compared to CO (Naeem et al., 2014). Similar trend by Ibrahim et al. (2014) was also observed in their study on hydrogen production via CO_2 reforming of methane over strontium promoted Alumina supported Ni and Co catalysts. This implies that CO_2 reforming of methane over 20wt%.Co/Nd_2O_3 is a potential technological route for the production of H_2

The particle size distribution of the 20wt%.Co/Nd_2O_3 catalyst on volume-based is depicted in Figure 7. The d_{10}, d_{50} and d_{90} of the catalyst particles are 3.991 µm, 22.44 µm and 70.96 µm respectively. The particle distributions of the catalyst is within the stipulated range that will not influence to the effect of mass transfer on the rate of reaction (Gribb & Banfield, 1997).

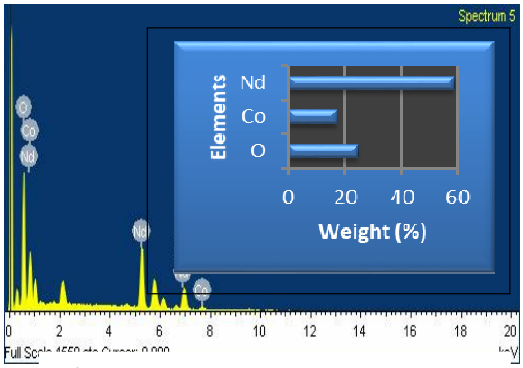

Fig 7: EDX Monograph showing the elemental compostion of the fesh 20wt%.Co/Nd_2O_3 catalyst

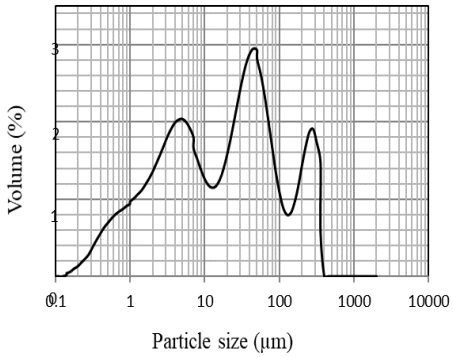

Fig 8: Particle size distribution of the fesh 20wt%.Co/Nd_2O_3 catalyst

*Effect of feed ratio and temperature on product selectivity and yield***:** The CO_2 reforming of methane was performed over 20wt%.Co/Nd_2O_3 catalyst. The catalytic performance of the 20wt%.Co/Nd_2O_3 catalyst as function of H_2 and CO yields in the CO_2 reforming of methane are depicted in Figures 8 and 9 respectively. Significantly, the selectivity of both H_2 and CO increases with feed ratio and temperature with the highest values obtained at feed ratio and temperature of 1 and 1023 K respectively. However, the catalyst shows a higher selectivity towards H_2 production than CO. This trend is consistent with the findings of Tu & Whitehead (2014) and Naeem et al. (2014). The findings from both studies shows that H_2 selectivity increases as the temperature increase from 773 to 1073 K..

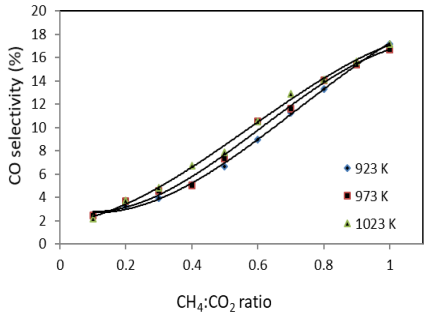

Fig 9: Effect of feed ratio and temperature the on 20wt%.Co/Nd_2O_3 catalyst selectivity toward H_2

Conclusion: In this study, the production of H_2 and CO via CO_2 reforming of methane over 20wt%.Co/Nd_2O_3 catalyst has been investigated. The CO_2 reforming of methane reaction was performed at temperature ranged 923-1023K and feed ratios between 0.1 and 1.. The best catalytic activities of the 20wt%.Co/Nd_2O_3 catalyst in terms of yield and selectivity were recorded at 1023 K and feed ratio of 1. The catalyst characterization corroborate the catalytic performance of the 20wt%.Co/Nd_2O_3 catalyst in terms of yield and selectivity of the products of the methane dry reforming

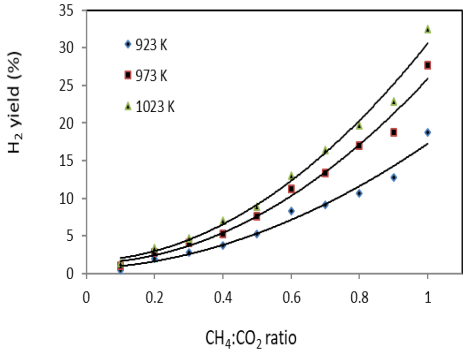

Fig 10: Effect of feed ratio and temperature the on 20wt% Co/Nd_2O_3 catalyst selectivity toward CO

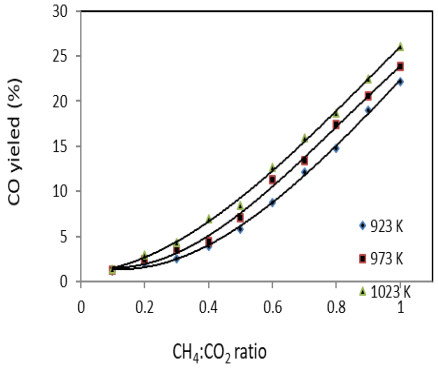

Fig 11: Effect of feed ratio and temperature the on 20wt%.Co/Nd_2O_3 catalyst activity toward H_2 yield

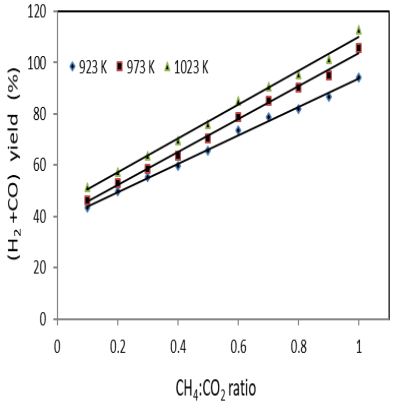

Fig 12: Effect of feed ratio and temperature the on 20wt% .Co/Nd_2O_3 catalyst activity toward syngas (H_2 + CO) yield

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