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Potential of empty fruit bunch clinker as a support for nickel and cobalt catalysts in methane dry reforming: waste to wealth approach

Chin Kui Cheng*, Han Jie Chan

Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

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ABSTRACT

The current work reports on the synthesis of 20 wt% Co/80 wt% EFB clinker and 20 wt% Ni/80 wt% EFB clinker catalysts via wet-impregnation technique, followed by various characterization techniques such as BET, XRD, XRF, TGA and FESEM. The BET specific surface area of 20 wt% Co/80 wt% EFB clinker and 20 wt% Ni /80 wt% EFB clinker catalyst were 3.85 m²/g and 3.88 m²/g, respectively. In addition, XRD diffractogram of EFB clinker showed two highest peaks at around $2\theta = 27.2^\circ$ and 31.5° , which can be attributed to CaO and K₂O species, respectively. This finding was also consistent with XRF analysis where potassium (K) and calcium (Ca) were positively identified. Subsequently, methane dry reforming studies revealed that the average conversion of CH₄ for both sets of catalysts was nearly similar at 80.0%. When reaction temperatures were varied, the activation energy over the Co-based catalyst was 124.4 kJ/mol while that for the reaction over the Ni-based catalyst was 113.0 kJ/mol. In addition, during 12 days of dry reforming reaction, the conversion of CH₄ was relatively stable over both sets of catalysts indicative of stability of their properties.

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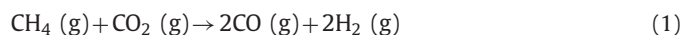
1. Introduction

Tropical countries such as Malaysia and Indonesia with abundant arable lands are home to large acreages of oil palm plantations [1,2]. Collectively, the processing of crude palm oil requires the utilization of steam for bunch sterilization and extraction of oil from the fresh fruit palm [3]. This steam is generated from the burning of empty fruit bunch (EFB) in a high temperature furnace, which is often accompanied by the formation of clinkers as waste [4]. Several works on the sustainable use of EFB clinker has been reported. Empty fruit bunch clinker has been reportedly used to reinforce concrete as well as used as catalyst in biodiesel production [5–7].

One of the ways to sustainably use EFB clinker is by utilizing it as catalyst support. Characterization studies by Yaakob et al. [6] showed that the EFB clinker is made up of about 62% of CaO, and 10% of K₂O, which can enhance the dispersion of the active metal on the support. The use of synthesized metal catalyst on alkaline support such as MgO and CaO for dry reforming of methane has been reported [8]. The findings from this study show that MgO and CaO support reduce carbon deposition and enhanced the stability of the catalyst due to their basicity [8]. Amongst the different

methane reforming processes that have been investigated using alkaline supported catalyst, dry reforming has gain wide interest. This is due to the utilization of CO₂ and CH₄, two main components of greenhouse gases as feedstock [9].

Dry (CO₂) reforming of methane is a well-studied reaction that is of both scientific and industrial importance. This reaction produces syngas (cf. Eq. (1)) which serves as feedstock for production of wide range of products using Fischer Tropsch synthesis (FTS) [10].



Conventional production of syngas is via natural gas steam reforming [11]. Steam reforming is presently employed in commercial production of hydrogen and syngas over alkaline promoted nickel catalyst [12]. However, challenges such as catalysts deactivation from sintering, carbon deposition and poisoning has aroused the interest of researchers finding a more suitable and stable catalysts for syngas production [13]. Furthermore, steam reforming process does not have the capacity to mitigate greenhouse gases.

Several metal-based catalysts has been investigated for dry reforming of methane using convectional supports such as Al₂O₃, SiO₂, MgO and TiO₂ [14–16]. These supports have been reported to provide a good thermal stability for the catalysts thereby reducing the degree of catalysts deactivation [17]. However, due to acidic nature of supports such as SiO₂ and γ -Al₂O₃, lower activities were reported for these supports. Hence, these supports

* Corresponding Author. Tel.: +60 9 549 2896; fax: +60 9 549 2889/+60 9 549 2896.

E-mail address: chinkui@ump.edu.my (C.K. Cheng).

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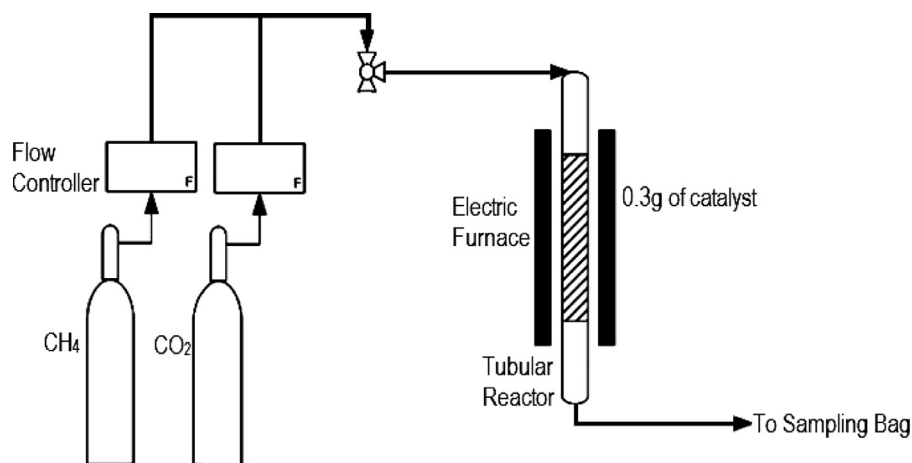


Fig. 1. Experimental rig layout for conducting methane dry reforming reaction.

with acidic properties would not be suitable for reaction involving acidic gas such as CO_2 . Significantly, the use of unconventional catalysts such as EFB clinker has not been investigated for dry reforming of methane. Besides constituting about 62% of CaO which makes it a potential basic support, its utilization would help reduce health risk in the environment. In this study, the use of EFB clinker as catalyst support for the impregnation of Ni and Co metals for methane dry reforming application was assessed. Furthermore, the physicochemical properties of the support as well as its role in enhancing the thermal stability and catalytic activity were also being investigated.

2. Materials and methods

2.1. Catalysts synthesis

The empty fruit bunch (EFB) clinker, which was sourced locally, was crushed using a mortar grinder. It was then sieved to particle diameters that ranged from 100 to 250 μm . Subsequently, 16.0 g of EFB clinker was stirred rigorously with solution containing cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (equivalent to 4.0 g of Co) for 3 h to produce 20 wt% Co/80 wt% EFB clinker. Another set of catalyst, which employed nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (equivalent to 4.0 g of Ni) as catalyst for 20 wt% Ni/80 wt% EFB clinker catalyst, was also prepared using the same procedure, in the presence of 16.0 g of EFB clinker. This formulation was typical of metal loading required for catalyst synthesized via wet-impregnation procedure and also reported before by Cheng et al. [18,19]. Post impregnation, the slurry was oven-dried at 403 K for overnight, followed by calcination at 1073 K for 6 h employing a ramping of 10 K/min.

2.2. Fresh catalyst characterization

The metal-EFB clinker support interaction was studied from the thermal-programmed calcination (TPC) of the fresh dried catalyst using a TGA Q-500 instrument. Non-isothermal temperature-programmed calcination was carried out from room temperature to 1173 K with heating rates at 10 K/min and a continuous flow of 50 ml/min of high purity air. The BET specific surface area and pore-size distribution of the freshly-calcined catalysts were obtained from the multipoint Brunauer-Emmett-Teller (BET) method. The raw isotherm data were sourced from N_2 physisorption at 77 K conducted in a Thermo Scientific Surfer Gas Adsorption Porosimeter unit. Prior to the analysis, the fresh catalysts were pre-treated overnight under vacuum at 573 K. The surface structure and elemental composition of the solid samples were obtained from the

FESEM-EDX model JOEL/JSM-7800F. The powder X-ray diffraction (XRD) pattern of the calcined catalyst was acquired with a Rigaku Miniflex II unit using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) operated at 15 mA and 30 kV. From the pattern, the crystallite size was calculated using the Scherer equation, $d_{\text{crystallite}} = 0.94\lambda / (\phi \cos \theta)$, where $d_{\text{crystallite}}$ is crystallite size, λ is the wavelength of the radiation, ϕ is the full-width at half maximum (FWHM) of the diffraction peak and θ is the half of the diffraction angle.

2.3. Catalyst evaluation

Fig. 1 shows the experimental set up for the catalytic evaluation tests. The catalytic evaluation was carried out in a stainless steel fixed-bed reactor with 9.42 mm ID, 12.7 mm OD and a length of 400 mm that was positioned inside a split tube furnace. The catalyst bed, which comprised of 0.3 g of catalyst powder, was supported by quartz wool. The performance of each catalysts was evaluated from 1023 to 1173 K with various CO_2 -to- CH_4 ratios ($0.5 < \text{CMR} < 2.0$) under atmospheric pressure. CH_4 and CO_2 of purity $>98\%$ were supplied by Air Products and used as-received. All the inlet gas flow rates were regulated with an Alicat Scientific electronic mass flow controller (Model: MC-500SCCM-D). The exit gas was collected using 1-L Tedlar gas sampling bag, and the composition was determined by an online Agilent 19095P Gas Chromatography (GC) equipped with HP Plot Q column and HP Molecular Sieve column. The He gas was used as a carrier with flow rate of 20 ml/min, operating column temperature of 393 K and detector temperature of 423 K.

2.4. Reaction metrics

The catalyst performance was evaluated in terms of the methane conversion, X_{CH_4} , and the reaction rate, r .

The methane conversion to gaseous products is defined as:

$$X_{\text{CH}_4} = \frac{[F_{\text{CH}_4}]_{\text{in}} - [F_{\text{CH}_4}]_{\text{out}}}{[F_{\text{CH}_4}]_{\text{in}}} \times 100 \quad (2)$$

The rate of formation of gaseous compounds is given by:

$$r_i \left(\frac{\text{mol}}{\text{g}_{\text{cat}}\text{S}} \right) = \frac{y_i \times F_{T\text{out}}}{W}; \quad i = \text{H}_2 \text{ and CO} \quad (3)$$

The rate of consumption of CH_4 is:

$$r \left(\frac{\text{mol}}{\text{g}_{\text{cat}}\text{S}} \right) = \frac{F_{\text{in}} - (y_i \times F_{T\text{out}})}{W} \quad (4)$$

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