

## Bio-syngas Production from Glycerol Dry Reforming Over Cement Clinker-Supported Nickel Catalyst

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### Abstract

This paper describes glycerol dry (CO<sub>2</sub>) reforming system for producing H<sub>2</sub>:CO mixture with ratios 1.0 to 2.0 suitable for downstream Fischer-Tropsch (FT) synthesis. Conventional glycerol steam reforming suffers from carbon deposition on catalysts, CO<sub>2</sub> greenhouse gas production and high H<sub>2</sub>:CO product ratios. Glycerol dry reforming (GDR) is a new area with no prior publications. Significantly, thermodynamic predictions in previous work showed that GDR is able to produce 6.4 moles of syngas per mole of glycerol [Wang *et al.*, 2009]. Ni-based catalysts have been widely used in industry due to its low cost compared to the noble metals but prone to coking. Coking can be alleviated or reduced by the introduction of strong Lewis base oxide such as CaO [Ruckenstein and Hu, 1995]. Cement clinker (CC) contains 63.28% CaO [Kurdowski, 2002], hence a natural choice as catalyst support. Most importantly, CC is abundantly available from cement industry in Malaysia and possesses high level of thermal stability. In this work, the reactivity of glycerol dry reforming over the CC-supported Ni catalyst, kinetic behaviour and type of carbon species deposited were reported.

New breed of nickel catalyst (with Ni loadings of 5, 10, 15 and 20 wt%) supported on cement clinker was synthesized using wetness impregnation method. Characterization of the catalysts was performed by thermogravimetric analysis (TGA), x-ray fluorescence (XRF), x-ray diffraction (XRD) and BET (Brunauer-Emmett-Teller) surface area measurement. Glycerol was pumped into a 7-mm diameter fixed-bed quartz reactor catalyzed by 0.1 g of catalyst at 1023 K. CO<sub>2</sub> to glycerol ratio (CGR) were adjusted to determine the ratio of product produced. Composition of syngas produced was determined by online Agilent 3000 micro-gas chromatography (GC) with Backflush Molecular Sieve 5A and Plot U column. Kinetic behaviour of catalysts was analyzed by using gas solid reaction kinetic models.

BET surface area of the catalysts increased with Ni metal loading. 100% CC surface area was relatively low with surface area of 0.55 m<sup>2</sup>/g and increased up to 17.83 m<sup>2</sup>/g upon loading with 20% Ni. This indicates the formation of new compound that altered the surface structure of the catalysts. Table 1 shows that 100% CC was a mixture of oxide metals with CaO as the major ingredient (61.98%). Bunsenite (NiO) compound recorded a jump from 62 ppm to 34.38% whilst the percentage of CaO and SiO<sub>2</sub> in catalysts decreased. This observation is consistent with the XRD results (cf. Fig. 1). XRD showed that the addition of Ni has promoted the formation of β-belite species from alite crystal. NiO (crystalline size in the range of 152 Å-186 Å) and β-belite (Ca<sub>2</sub>SiO<sub>4</sub>) were found to be the main crystals with Ni loading of more than 15%. In 100% CC, the main crystal compound presents was monoclinic alite (Ca<sub>3</sub>SiO<sub>5</sub>) at peaks 29.45°, 34.41° and 41.31° with crystalline size of 318 Å, 472 Å and 412 Å respectively.

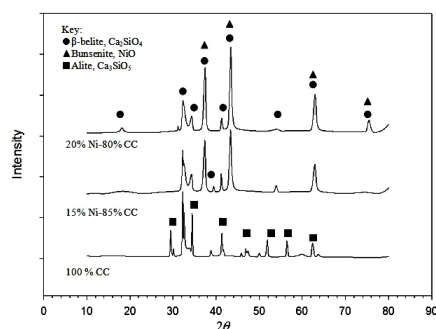
TGA analysis (profiles not shown) of 100% CC showed a thermal stability with no decomposition. Calcination profiles for 15% Ni-85% CC and 20% Ni-80% CC catalysts showed approximately similar trend of decomposition. For both Ni catalysts, there were formations of peaks around 504 K to 620 K and 620 K to 794 K respectively. The first peak was due to the transformation of Ni<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>(OH)<sub>4</sub> to NiO in consensus with Estellé *et al.* [2003]. The second peak at 620 K-720 K is

indicative of NiO formation due to the decomposition of nickel nitrate hexahydrate precursor. The modeling of the TGA calcination results (cf. Table 2) indicated that 1<sup>st</sup>-Order Reaction Model gave the best description to the gas-solid mechanistic interaction with  $E_A$  from 233 to 387 kJ mol<sup>-1</sup> for 20% Ni-80% CC (as representative).

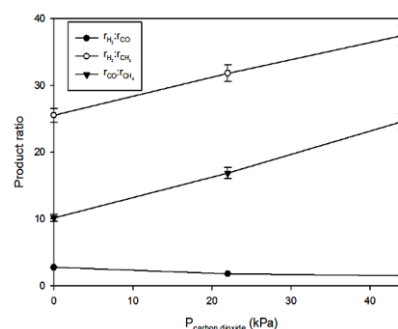
Fig. 2 shows the product ratio profiles for glycerol dry reforming carried out at 1023 K over 20%Ni-80%CC catalyst. Overall, H<sub>2</sub>, CO and CH<sub>4</sub> were produced. The slight decrease of H<sub>2</sub>:CO ratio with  $P_{\text{carbon dioxide}}$  was an attribute of reverse-water-gas-shift reaction. Nonetheless, the H<sub>2</sub>:CO ratio remained > 1.0. More importantly, the H<sub>2</sub>:CO ratio of 1.2 to 1.9 registered is even suitable for Fischer-Tropsch (FT) synthesis. The H<sub>2</sub>:CH<sub>4</sub> and CO:CH<sub>4</sub> ratios increased with  $P_{\text{carbon dioxide}}$  due to the decrease in CH<sub>4</sub> formation rate as CO<sub>2</sub> may have reacted with CH<sub>4</sub> to produce CO.

**Table 1: XRF, BET and Density of the Catalyst (\* in ppm)**

| Compound     | CaO   | NiO    | SiO <sub>2</sub> | BET surface area (m <sup>2</sup> /g) | Density (g/cm <sup>3</sup> ) |
|--------------|-------|--------|------------------|--------------------------------------|------------------------------|
| Catalysts    | (wt%) | (wt %) | (wt%)            |                                      |                              |
| 100% CC      | 61.98 | 62*    | 17.21            | 0.55                                 | 2.99                         |
| 15% Ni/85%CC | 44.11 | 27.63  | 9.28             | 17.30                                | 3.12                         |
| 20% Ni/80%CC | 38.66 | 34.83  | 6.77             | 17.83                                | 3.22                         |



**Figure 1: XRD Analysis of the Catalysts**



**Figure 2: Product Ratio for GDR**

**Table 2: Activation Energy of 20% Ni-80% CC at Different Ramping Rates (with N<sub>2</sub>)**

| Gas Solid Reaction Model | N <sub>2</sub>             |                |                            |                |                            |                |
|--------------------------|----------------------------|----------------|----------------------------|----------------|----------------------------|----------------|
|                          | 10 K min <sup>-1</sup>     |                | 15 K min <sup>-1</sup>     |                | 20 K min <sup>-1</sup>     |                |
|                          | Ea (kJ mol <sup>-1</sup> ) | R <sup>2</sup> | Ea (kJ mol <sup>-1</sup> ) | R <sup>2</sup> | Ea (kJ mol <sup>-1</sup> ) | R <sup>2</sup> |
| <b>First order</b>       | 233.28                     | 0.96           | 387.00                     | 0.95           | 277.25                     | 0.92           |

In conclusion, cement clinker-supported Ni catalyst could be a cheaper catalyst to produce syngas by glycerol dry reforming. CC with addition of Ni has improved the BET surface area. XRD examination showed formation of complex oxide phases depending on the Ni loading. Interestingly, glycerol dry reforming reaction yield H<sub>2</sub>:CO < 2.0, suitable for FT synthesis.

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