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# A study on the kinetics of syngas production from glycerol over alumina-supported samarium–nickel catalyst

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## ABSTRACT

The current paper reports on the kinetics of syngas production from glycerol pyrolysis over the alumina-supported nickel catalyst that was promoted with samarium, a rare earth element. The catalysts were synthesized via wet-impregnation method and its physico-chemical properties were subsequently characterized. Reaction studies were performed in a 10 mm-ID stainless steel fixed bed reactor with reaction temperatures maintained at 973, 1023 and 1073 K, respectively, employing weight-hourly-space-velocity of  $4.5 \times 10^4 \text{ ml g}^{-1} \text{ h}^{-1}$ . The textural property examination showed that BET specific surface area was  $2.09 \text{ m}^2 \text{ g}^{-1}$  for the unpromoted catalyst while the samarium promoted catalyst has  $2.68 \text{ m}^2 \text{ g}^{-1}$ . Interestingly, the results were supported by the FESEM images which showed that the promoted catalyst has smaller particle size compared to the unpromoted catalyst. Furthermore, the  $\text{NH}_3$ - and  $\text{CO}_2$ -TPD analyses proved that the strong and weak acid-basic sites were present. During glycerol pyrolysis, the syngas was produced directly from the glycerol decomposition. This has created  $\text{H}_2$ :CO ratios that were always lower than 2.0, which is suitable for Fischer-Tropsch synthesis. The activation energy based on power law modeling for the unpromoted catalyst was  $35.8 \text{ kJ mol}^{-1}$  and  $23.4 \text{ kJ mol}^{-1}$  for Sm-promoted catalyst with reaction order 1.20 and 1.10, respectively. Experimental data were also fitted to the Langmuir–Hinshelwood model. Upon subjected to both statistical and thermodynamics consistency criteria, it can be conclusively proved that single-site mechanisms with associative adsorption of glycerol best describe the glycerol pyrolysis over both unpromoted and Sm promoted catalyst in the current work, with regression coefficient values of more than 0.9.

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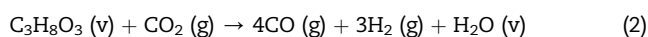
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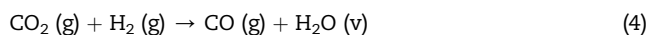
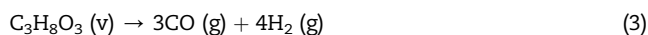
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## Introduction

Glycerol is co-produced as a byproduct of biodiesel synthesis from the transesterification of vegetable oils. Traditionally, glycerol is primarily employed as an additive in sectors such as food, cosmetics, pharmaceutical, etc.; nonetheless it requires purification step [1]. Purification of crude glycerol however, needs high refining cost. From commercialization perspective, in consideration of glycerol production and utilization plays important roles with regards to the economics and also sustainability of biodiesel industry, the expansion of novel processes for glycerol valorization is absolutely required. Hence, one of the most attractive ways to increase the value of the glycerol economy is by converting glycerol into syngas (mixture of H<sub>2</sub> and CO) [1,2]. To date, most of the works in this area has utilized catalytic methods such as steam reforming [3] and also dry reforming [4]. The reactions involved are as shown in Eqs. (1) and (2):



Although the theoretical chemical reaction equations indicate that there is a direct interaction between H<sub>2</sub>O(steam)/CO<sub>2</sub> with glycerol during the reforming reaction, it is still a subject of ambiguity whether these two agents (refers to H<sub>2</sub>O and CO<sub>2</sub>) really partake in the aforementioned reactions. Interestingly, previous works by Siew et al. [5] showed that during glycerol dry reforming, the glycerol substrate did not react with CO<sub>2</sub>. From their work, it is proposed that during glycerol dry reforming, glycerol molecule would decompose as in Eq. (3) to yield CO and H<sub>2</sub>. The roles of CO<sub>2</sub> are restricted to reverse-water-gas-shift reaction as in Eq. (4) and also to gasify deposited carbon (cf. Eq. (5)).



Therefore, direct catalytic glycerol decomposition/pyrolysis into syngas is the subject of current investigation in order to build a clear understanding of the kinetics of catalytic glycerol decomposition/pyrolysis.

The kinetics of glycerol pyrolysis was normally investigated via power law and mechanistic model fittings. The power law model was widely used because of its simplicity in application and determination. However, this model only adequate for small range of partial pressure data [6]. Based on adsorption kinetics model at constant temperature, Langmuir–Hinshelwood (LH) is a developed model to relate the pressure with amount of adsorbed gas [7]. Indeed, there have been various mechanistic routes proposed for reforming

reaction in order to express reaction rate and kinetics parameter, referenced herein [8–12]. In particular, Cheng et al. [10] reported that LH model based on molecular adsorption of glycerol with surface reaction as the rate-controlling step, best described syngas production from glycerol over bimetallic Co–Ni supported on alumina catalyst. It was determined that reaction rate was 0.25 with respect to partial pressure of glycerol with activation energy of 63.3 kJ mol<sup>-1</sup>.

Significantly, gas phase decomposition of glycerol, or also known as glycerol pyrolysis has been studied before. Pyrolysis which is also known as selective thermal processing [13] can be divided into three modes viz. fast, moderate and slow pyrolysis [14,15]. In order to obtain the maximum yield of liquid products, the fast pyrolysis necessitates either rapid heating rates or short residence times [16–18]. On the other hand, slow pyrolysis or also known as conventional pyrolysis is for solid product (char) preparation. On the other hand, the glycerol pyrolysis to syngas is carried out primarily in the moderate pyrolysis mode, accompanied by residence time of 1–5 s and temperature exceeding 873 K [19,20]. The catalytic glycerol decomposition in the current work differs from the pyrolysis as it involves heterogeneous catalysts. Most importantly, this work serves as a continuation of our previous work in this area, for the further understanding of direct syngas production from glycerol.

Syngas production typically requires high reaction temperature (1123–1173 K). Therefore, support needs to be stabilized to minimize on-stream sintering. In view of stabilizing alumina support, the dopants based on alkaline-earth elements and/or rare earth metals can be employed to avoid conversion to any unwanted phases influenced by high working temperatures. According to the literature, K, Mg, Sr, Ba, Ca, Zr, Pr, Ce, La and Sm as promoters, act as the thermal stabilizers of alumina with capability to improve the textural properties [21–27]. Moreover, promoters are also normally introduced to the support to improve both the metal dispersion and to inhibit coke formation. In lieu of this, the present work reports for the first time, the catalytic glycerol decomposition over the Sm-promoted Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, aiming at understanding the kinetics of direct syngas production from glycerol.

## Materials and method

### Catalyst synthesis

The alumina support was pretreated in a muffle Carbolite furnace at 1073 K for 6 h employing a heating rate of 10 K/min. Then, it was sieved to 140–425 μm particle range. For the catalyst preparation, the sieved alumina was accurately weighed and transferred into a beaker that contained calculated amount of aqueous solution of Ni/(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O for the preparation of 3wt%Sm-20wt%Ni/77wt%Al<sub>2</sub>O<sub>3</sub> catalyst. For comparison, the unpromoted 20wt%Ni/80wt%Al<sub>2</sub>O<sub>3</sub> catalyst was prepared via the same procedure. During the metals impregnation, the slurry was magnetic-stirred for 3 h at ambient condition. Subsequently, it was oven-dried at 393 K for overnight. The dried catalyst was then air-calcined at 1073 K for 5 h with a heating rate of 10 K min<sup>-1</sup>.

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