



## Promoted Ni–Co bimetallic catalysts for glycerol dry reforming: Understanding the physiochemical properties and carbon formation

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### ARTICLE INFO

Handling Editor: Prof I Tolj

#### Keywords:

Bimetallic catalysts  
Promoter  
Syngas  
Alumina  
Glycerol dry reforming  
Hydrogen

### ABSTRACT

Glycerol dry reforming (GDR) is one of the alternatives for syngas production by utilizing glycerol, a by-product of biodiesel. This current work focusing on the effect of Ce, Ru and Pd as promoters on Ni–Co/Al<sub>2</sub>O<sub>3</sub> catalysts. Ultrasonic-assisted impregnation was utilized to synthesize the catalysts and GDR was carried out by varying the reactant partial pressure CO<sub>2</sub> to glycerol ranging from 10 to 40 kPa at 1073 K. Characterization studies showed that incorporation of promoter reduced Ni–Co agglomeration and increased metal dispersion on Al<sub>2</sub>O<sub>3</sub> support. This resulted in smaller crystallite size and more consumption of H<sub>2</sub> and CO<sub>2</sub> based on H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD analyses. Irrespective of reactant partial pressure, the catalytic performance was increased with following trend; Ni–Co/Al<sub>2</sub>O<sub>3</sub> < Ce–Ni–Co/Al<sub>2</sub>O<sub>3</sub> < Ru–Ni–Co/Al<sub>2</sub>O<sub>3</sub> < Pd–Ni–Co/Al<sub>2</sub>O<sub>3</sub>. The best reactant partial pressure (CO<sub>2</sub> and glycerol) was achieved at 20 kPa and the effect of competing reactant caused a significant decline in catalytic performance beyond 20 kPa. Oxygen storage capacity, basic nature and redox cycle of promoters assisting in the carbon reduction on catalysts surface. Overall, Pd–Ni–Co/Al<sub>2</sub>O<sub>3</sub> recorded the highest catalytic activity and lowest carbon formation (7.25%) compared to other promoted catalysts credited to their smallest crystallite size (7.12 nm), great metal dispersion (77.4%, 2.95), highest H<sub>2</sub> production, CO<sub>2</sub> consumption and oxygen storage capacity.

### 1. Introduction

Global energy consumption has continued to grow, contributing to climate change and global warming by hastening the depletion of non-renewable fossil fuels and the emission of energy-related CO<sub>2</sub> gas into the atmosphere [1]. In order to lessen the reliance on non-renewable sources in the existing energy system, it is essential to explore renewable, diverse with sustainable energy sources to replace hydrocarbon-based energy with cleaner solutions. Syngas or hydrogen-based energy is a form of renewable energy that is universally recognized as a clean energy source, and it can help reduce greenhouse gas emissions, smoke, and acid rain when used as fuel [2,3]. On a commercial basis, methane reforming is employed to produce syngas. Nevertheless, this approach has certain drawbacks, including generation

of by-products and the unsustainable consumption of natural gas [4]. Therefore, the use of biomass-derived feedstocks, particularly glycerol, has lately piqued the interest of numerous reforming methods. Studies show that the biodiesel transesterification process produces over 1.4 million tonnes of glycerol, which is up to 63% of total global production of glycerol. Besides, the manufacturing of glycerol progressively increased from 2015 to 2021 and is anticipated to reach 4046.9 million liters in 2026 [5]. The presence of several impurities, such as alcohol, unreacted glycerides and fatty acids, render crude glycerol unfit for direct application. Furthermore, there are persisting difficulties associated with disposal and environmental considerations in industrial-scale production of glycerol. This situation makes glycerol reforming to be a desirable option as feedstock for reforming reaction [6,7].

Using glycerol, a by-product of biodiesel manufacturing, in

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<https://doi.org/10.1016/j.ijhydene.2023.12.146>

Received 3 August 2023; Received in revised form 28 November 2023; Accepted 14 December 2023

Available online 30 December 2023

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