



# Catalytic evaluation of Pd-promoted Ni-Co/Al<sub>2</sub>O<sub>3</sub> catalyst for glycerol dry reforming: Assessing hydrogen-rich syngas production, kinetics and mechanisms

Mohd-Nasir Nor Shafiqah<sup>a</sup>, Hassan Mohamed<sup>b</sup>, Joongjai Panpranot<sup>c</sup>,  
Sumaiya Zainal Abidin<sup>d,e,\*</sup>

<sup>a</sup> Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Lebuhr Persiaran Tun Khalil Yaakob, 26300 Kuantan, Pahang, Malaysia

<sup>b</sup> Institute of Sustainable Energy, Universiti Tenaga Nasional (UNITEN), Putrajaya Campus, Jalan Ikram-Uniten, Kajang, Selangor 43000, Malaysia

<sup>c</sup> Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330 Thailand

<sup>d</sup> Centre for Research in Advanced Fluid & Processes (FLUID CENTRE), Universiti Malaysia Pahang Al-Sultan Abdullah, Lebuhr Persiaran Tun Khalil Yaakob, 26300 Kuantan, Pahang, Malaysia

<sup>e</sup> Faculty of Chemical Engineering, Industrial University of Ho Chi Minh City, 12 Nguyen Van Bao St, Go Vap, Ho Chi Minh City, Viet Nam

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## ABSTRACT

The Pd-promoted Ni-Co bimetallic catalysts were prepared using ultrasonic-assisted impregnation, and their performance was subsequently assessed in a fixed-bed reactor. The catalyst's performance was evaluated in glycerol dry reforming (GDR) over a range of temperatures, from 873 K to 1173 K and reactant partial pressures ranging from 10 kPa to 40 kPa. The results indicated that as the temperature was raised from 873 K to 1073 K, there was a noticeable rise in both reactant conversion and product yield. However, beyond 1173 K, catalytic performance declined due to glycerol thermal cracking and sintering of the support at high temperatures, resulting in increased carbon formation. The presence of excessive CO<sub>2</sub> was found to suppress glycerol adsorption on the catalyst surface, causing a decline in catalytic activity with a CO<sub>2</sub> partial pressure of more than 20 kPa, regardless of reaction temperature. Additionally, excess CO<sub>2</sub> were found to enhance the side reaction, particularly reverse water-gas shift (RWGS) that related to produce intermediate H<sub>2</sub>O. Similarly, the glycerol partial pressure was found to impact catalytic performance, with a decrease in performance beyond 20 kPa due to competing reactants between glycerol and CO<sub>2</sub>. According to the Langmuir-Hinshelwood kinetic mechanism, a dual molecular adsorption site for glycerol and CO<sub>2</sub> was appropriate for this GDR reaction, with an associated activation energy of 47.3 kJ mol<sup>-1</sup>. The GDR reaction was identified as a kinetically controlled process due to its high activation energy, more than 25 kJ mol<sup>-1</sup>. The plausible mechanism of GDR over Pd-Ni-Co/Al<sub>2</sub>O<sub>3</sub> occurred through the dissociative-type of adsorption of on active metallic sites of the catalysts for both reactant (glycerol and CO<sub>2</sub>). This was further facilitated by the bifunctional mechanisms based on H<sub>2</sub> generated from dissociative adsorption involving both catalyst's basic sites and metallic active sites. This was ascribed to the highly dispersed and strong interaction between metal-support in Pd-promoted Ni-Co bimetallic catalysts.

## 1. Introduction

In the current global environmental crisis, there is a growing imperative to reduce our reliance on fossil fuels and actively explore environmentally-friendly and sustainable alternatives. Renewable energy (syngas or hydrogen) are expected to play a crucial role in the

worldwide transition to cleaner and less polluting energy sources, thanks to its remarkable properties as an energy carrier (Kong et al., 2023). However, the current global hydrogen production relies heavily on the reforming of fossil methane (Desgagnés and Iliuta, 2022). Hence, it is possible to effectively harness renewable and sustainable hydrogen-rich syngas from eco-friendly sources, such as glycerol. In this regard,

\* Corresponding author at: Centre for Research in Advanced Fluid & Processes (FLUID CENTRE), Universiti Malaysia Pahang Al-Sultan Abdullah, Lebuhr Persiaran Tun Khalil Yaakob, 26300 Kuantan, Pahang, Malaysia.

E-mail address: [sumaiya@ump.edu.my](mailto:sumaiya@ump.edu.my) (S. Zainal Abidin).

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