Effective combination of metal-support for bimetallic catalysts system in ethanol and glycerol reforming: A review

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Extended Abstract

The reliance on fossil fuels to meet the world energy demands throughout these years has led to future insecurity of non-renewable energy sources. Thus, the necessity to provide the energy requirement as we are moving forward falls into renewable and environmentally friendly options. Syngas or hydrogen-based energy rise as potential alternatives credited to high efficiency and clean emissions [1]. In addition, production of hydrogen from biomass keep gaining attention from industrial and academic expertise especially for the reforming technologies. Ethanol and glycerol are emerged as alternatives feedstock for hydrogen production in the last several years due to ethanol is a high hydrogen-containing compound and can be easily derived from renewable biomass resources wheat, sugarcane and organic fractions from forestry residue or municipal [2,3] whereas, glycerol is by product of biodiesel that expected to surplus in amount in near future [4]. Additionally, there are many routes that led to production of syngas or hydrogen namely, steam reforming, partial oxidation, pyrolysis, bi-reforming, CO_2 reforming, autothermal reforming, aqueous phase reforming. Ni-based catalysts widely employed in the aforementioned reforming process attributed to its affordable cost compared to noble metals, strong capability of rupturing C-C and C-O bonds and high availability [5]. Nevertheless, Ni-based catalysts tend to deactivate due to carbon formation and thermal Ni sintering [6]. The introduction of bimetallic or polymetallic is one of the significant solutions to reduce carbon formation and catalysts deactivation in reforming process since it can produce more stable catalysts from interaction between two metals [7]. Thus, the aim of this review is to emphasize the application of bimetallic catalysts in glycerol and ethanol reforming based on metal combination. The combination of transition metal will be included the effect of actives site and carbon formation, noble metal pairing will be focused on metal dispersions and transition-noble metal combination will be explained the effect of reduction rate and redox properties as well as the role of support. In addition, the brief explanation of reforming technologies and the summarized findings of structure, classification along with catalysts preparation method will be described in this review.

Bimetallic catalysts, composed of two metal elements in either alloy or intermetallic form, often emerge as materials of a new category with catalytic properties [8]. A number of methods have been introduced to form bimetallic catalysts and each types of methods lead to different structures based on its metal properties, metal-support interaction, atmosphere and temperature [7]. Dal Santo et al. stated that commonly, the bimetallic nano particles structure can be classified to core-shell structures, alloys and intermetallic shown in Figure 1. In addition, Wang and Li (2011) suggested the bimetallic classification are divided into core–shell, heterostructure, or intermetallic and alloyed structures [9]. The study from Guczi et al. (2010) proposed structure of bimetallic catalysts based on changes in magnitude and sign of enthalpy (ΔS) in which can be identified as alloys, intermetallic, mono or bi-phase alloys and surface alloying or clusters [10].

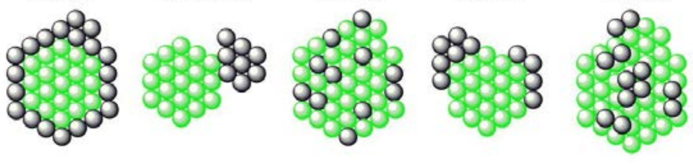

Fig. 1: Types of bimetallic structures proposed from literature [7].

The combination of meta in bimetallic catalysts plays an important role in reforming reaction to reduce carbon and sulphur formation, high tolerance towards high temperatures and active for high hydrocarbons for various properties [11]. Moreover, the development of bimetallic catalysts generally related to preparation method, metal combination, selection of support to incorporate the ideal composition of catalyst. Due to the deactivation mechanisms, the properties of catalysts in reforming regularly changed over time. Therefore, there are numerous adjustments to overcome catalyst deactivation and improve catalyst evaluations. Metal combination in bimetallic catalysts can be divided into noble-noble metals, noble-transition metals and transition-transition metals.

Wang et al. (2018) study the effect of bimetallic for glycerol steam reforming on several combination of transition metal supported by attapulgite (ATP) including Ni/ATP, Ni-Co/ATP, Ni-Cu/ATP and Ni-Zn/ATP. The authors concluded that bimetallic catalysts show high stability for 30 h reaction compare to Ni/ATP. In addition, the high performance of bimetallic catalysts due to high metal dispersions and reducibility with small crystallite size [12]. The combination between noble-transition metal, Pt-Sn from Pastor-Perez et al. (2017) in steam reforming shows the metals are less agglomerate compare to monometallic Pt/C catalysts based on TEM images. The Sn addition can enhance oxidations process and prevent methanation. Additionally, Pt sintering can be reduced from the introduction of Sn-metal along with decline in carbonaceous species [13]. The study of bimetallic by Cifuentes et al. (2015) for steam reforming of ethanol involving Rh-Pt/CeO_2 shows a stable performance in stability test or 27 h with highest H_2 yield of 3.1 mol H_2/mol ethanol inlet. Furthermore, the stable performances most likely from the small catalyst particles with less than 5 nm in which consisted on the Rh-Pt alloys with a Pt surface enrichment. The situation makes both metals completely oxidized and hence, contributes to strong bimetallic interaction [14].

The idea to expand the implementation of bimetallic catalysts in reforming process is highly appropriate from the several studies from glycerol and ethanol reforming that has been discussed earlier. Bimetallic catalysts can enhance the catalytic performance and reduce the carbon formation compared to its monometallic counterpart. The interaction between two metals in bimetallic system is playing a huge role to reduce metal sintering and avoid catalysts deactivation. However, there are a few progress and recommendations that can be explore for future study namely, to discover more combination between transition metals apart from Ni-metal, to develop more advanced catalysts preparation methods to produce more stable bimetallic systems and to expand the study involving the effect of support to improve the bimetallic-support interaction.

Keywords: *Bimetallic catalysts, reforming process, glycerol, ethanol, Syngas, Hydrogen*

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