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Research Paper

Bimetallic Ni-M (M = Co, Cu and Zn) supported on attapulgite as catalysts for hydrogen production from glycerol steam reforming

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ABSTRACT

Monometallic Ni and bimetallic Ni-Co, Ni-Cu, and Ni-Zn catalysts supported on attapulgite (ATP) were prepared by chemical precipitation method and evaluated in the glycerol steam reforming (GSR) reaction under the following conditions W/G = 9, N_2 flow ratio = 0.16 L/min and GHSV = 9619 h^{-1}. The prepared calcined and/or reduced samples were characterized by ICP-OES, N_2 adsorption-desorption, XRD, TEM, FT-IR, XPS and H_2-TPR. The analysis results showed the addition of second metals obviously decreased the crystal size and suppressed the reducibility of active metal, by improving the metal-support interaction. These were optimized characters could promote the steam reforming reaction and water-gas shift reaction (WGSR) to improve the catalytic performance. The experimental results of catalytic activity revealed the glycerol conversions and H_2 yields over bimetallic catalysts were significantly higher than those over Ni/ATP catalyst. Among them, the Ni-Cu/ATP exhibited the highest the highest glycerol conversions and H_2 yield in GSR reaction, while it had larger particle size (12.2 nm) than Ni-Co/ATP (8.6 nm) and Ni-Zn/ATP (10.3 nm), and the higher reducibility than other two bimetallic catalysts. It may be deduced that the crystal size and reducibility of catalyst all showed pivotal to impart suitable catalytic activity, while these characteristics should have an optimal proportion for obtaining the outstanding catalytic performance. The effect of temperature on catalytic performance over all catalysts was also investigated. It was found that increasing temperature was favorable for glycerol conversions and H_2 yield, while the increase rate of H_2/CO ratio was suppressed and CO/CO_2 ratio were increased for all catalysts at high temperature range of 600–700 °C. It was attributed to that increasing temperature although improved the breakage of C—C, C—H, and C—O bonds in glycerol, the WGSR mainly side-reaction for producing H_2 was suppressed. The long-term experiments (30 h) were also conducted over all catalysts at W/G = 9, T = 600 °C, N_2 flow ratio = 0.16 L/min and GHSV = 9619 h^{-1}. The results demonstrated the outstanding stability was obtained over Ni-Zn/ATP catalyst. In order to account for the causes resulted in catalyst deactivation, all spent catalysts were characterized by XRD, TEM, TPO and TG-DTG. The results shown catalyst deactivation was mainly affected by the sintering of active species and coke formation on catalyst surface. The Ni-Zn/ATP bimetallic catalyst showed the outstanding stability attributed to the excellent anti-sintering and carbon deposition, which resulted from the formation of unique metal-support interaction.

1. Introduction

The problems originating from the heavy use of non-renewable sources (such as coal, petroleum, and natural gas) have been widely concerned in the last few decades. They mainly relate to the finite storage of these fossil fuels, which conversely raises the issues in terms of accessibility, affordability, security of supply and competition among state supportive actors, and the influence of greenhouse gases emission on the global climate [1–3]. In addition, the fuels currently used in the transport sector are almost totally based on these resources. For the sake of attenuating the dependence on fossil fuels, a feasible scheme may be provided by biofuels, which are ultimately derived from biomass materials and can thus be regarded as carbon neutral [4,5]. Biodiesel, as one of promising biofules, is produced widely in many states and increased by 3000% especially in European Union during 2000–2012 [6,7]. Inevitably, about 10% of by-product glycerol would be formed during biodiesel production through the transesterification reaction of vegetable oils and animal facts [8]. Unlike applications of

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pure glycerol in chemicals, pharmaceuticals and cosmetics, the re-utilization of by-product glycerol is limited, due to it comprises several other impurities (such as inorganic salts, methanol, free fatty acids, methyl esters, un-reacted reactants and a plenty of water) [9,10]. Therefore, it has high toxicity and low commercial value, and further refining is expensive, tasteless but wasteful to discard [11].

In order to take full advantage of by-product glycerol, which is also prepared from the hydrogenolysis of sorbitol [12] or the fermentation of glucose [13] and obtained as a co-product in lignocellulose-to-ethanol conversion [14] or soap manufacture [15], it can be employed for producing hydrogen. Hydrogen is always considered as a clean energy source and favorable raw materials for chemical synthesis, and then its demand would be expected to significantly increase in the future, since the technological advancements during the fuel cell and ammonia synthesis industries [16–18]. Glycerol is a good substitution for producing hydrogen in comparison with methanol and ethanol, mainly due to it does not make the Nafion membrane swell in PEMFC [19]. In present, the technologies of hydrogen production from glycerol mainly though the catalytic reactions, such as steam reforming [20–24], aqueous phase reforming [25], auto-thermal reforming [26,27], and supercritical water reforming [28,29]. Among them, hydrogen production from glycerol steam reforming (GSR) is attractive because every mole of glycerol participated in reaction can theoretically generate seven moles of hydrogen according to Eq. (1). As is known to all, the GSR reaction is always carried out at high temperature (> 400 °C), thus the decomposition of glycerol (Eq. (2)) is ineluctably happened and the produced carbon monoxide will react with steam to form water-gas shift reaction (WGSR) (Eq. (3)), which is considered as effective for hydrogen production in steam reforming reaction (SRR) [8,30]. In addition, there are also some other side reactions, such as methane steam and dry reforming (Eq. (4)–(6)), and a series of coke formation reactions (Eq. (7)–(9)) based on employing different catalysts and operating conditions [21,31–33].

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2\ \Delta H^0 = 123\ kJ/mol \quad (1)$$

$$C_3H_8O_3 \rightarrow CO, CO_2, CH_4, H_2 \ldots \quad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2\ \Delta H^0 = -41\ kJ/mol \quad (3)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2\ \Delta H^0 = 206\ kJ/mol \quad (4)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2\ \Delta H^0 = 165\ kJ/mol \quad (5)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2\ \Delta H^0 = 274 kJ/mol \quad (6)$$

$$2CO \leftrightarrow CO_2 + C\ \Delta H^0 = 172\ kJ/mol \quad (7)$$

$$CH_4 \leftrightarrow 2H_2 + C\ \Delta H^0 = 75.6\ kJ/mol \quad (8)$$

$$CO + H_2 \leftrightarrow H_2O + C\ \Delta H^0 = 131\ kJ/mol \quad (9)$$

For the catalysts applied into GSR, the research hotspots principally focus on the catalysts that have superior ability of breaking the C—C, C—H and O—H bonds and maintaining the C—O ones, resulting in obtain higher H_2 selectivity and lower CH_4 selectivity [30,32,34]. Herein, a large number of scholars have bent themselves to develop catalysts based on monometallic and bimetallic systems supported on various unmodified and/or modified metal oxides carriers. Obviously, the noble metals, such as Pt [35–37], Pd [38], Rh [39,40], Ru [41,42] and Ir [38], and bimetallic systems that combined with transition metals [43–45], have obtained considerable attentions, due to their predominant feedstock conversion, high selectivity for target product and exceptional stability. Pompeo et al. [37] reported the GSR reaction over Pt supported different carriers (such as SiO_2, γ-Al_2O_3, ZrO_2, and α-Al_2O_3 modified with Ce and Zr, respectively) for obtaining hydrogen/synthesis gas at low temperatures (< 450 °C), indicating that Pt/SiO_2 catalyst exhibited a promising ability for dehydrogenation reactions and C—C bonds cleavage and superior stability during 40 h of reaction. As has been taken into account in literature [44], Profeti and his co-workers conducted the GSR experiment over different noble metals (Pt, Ir, Pd and Ru) promoted Ni/CeO_2-Al_2O_3 catalysts, and their results demonstrated the addition of noble metals all increased the H_2 yield and glycerol conversion accompanied with the increase of CH_4 yield. Among them Ni-Pt/CeO_2-Al_2O_3 catalyst showed the highest H_2 yield and the lowest coke deposition rate. In spite of the noble-metal-based catalysts presented more active and more stable during GSR, their high expense virtually restrains their application on an industrial scale.

In order to realize the economical efficiency of catalysts applied for GSR reaction, the lion's share of researchers have shifted their interests to transition-metal-based catalysts, such as Ni-, and Co-based catalysts [8,21,33,46–53]. Among them, nickel-based catalysts were widely studied in GSR reaction and stand as one of the most investigated ones so far, which mainly due to its high capacity of breaking C—C bonds and lower cost. However, nickel species as active phase are easily sintered and Ni-based catalysts always present high carbon deposition rate, resulting in a dramatic deactivation on GSR process [21]. Wu et al. [48] prepared perovskite-derived nickel-based catalysts ($La_{1-x}Ca_xNiO_3$, x = 0.0, 0.1, 0.3, 0.5, 0.7 and 1.0) and investigated their catalytic performance on GSR reaction. The $La_{0.5}Ca_{0.5}NiO_3$ catalyst showed the highest H_2 yield and lower amount of coke deposition, owing to its strongest metal-support interaction (MSI) and best metal dispersion, while its stability significantly diminished after 15 h on steam. In addition, Ni/La_2O_3-Al_2O_3 catalysts presented the highest H_2 yield (47%) accompanied with the higher CO_2 yield (59%) in B_2O_3 and La_2O_3 modified Ni/Al_2O_3 catalysts during the GSR reaction at 400 °C, but it exhibited dramatic deactivation after 18 h of reaction and about 200 $mg/g_{cat.}$ of total carbon deposition [33].

So as to overcome these major drawbacks, some studies have been done to exploit and design more suitable nickel-based catalysts. Some supports with unique textural properties (such as higher surface area and larger pore volume) and meso-structure, e.g. SBA-15 [54], SiO_2 [55] and ZrO_2 [56], have been employed for preparing Ni-based catalysts. This is attributed to these distinctive properties are capable of highly dispersing active phase (Ni^o) and forming the strong interaction with nickel species, which are widely regarded as important for superior catalytic activity and stability [57]. Apart from that, the Ni-based catalysts usually combined with other second metals, such as Pt [58], Co [59,60], Cu [24,49,61], and Cr [62] have also been investigated during GSR reaction and the results according to literatures demonstrated Ni-based bimetallic catalysts effectively suppressed the sintering of nickel species by forming metal alloy, and then leaded to the long-term catalytic stability. Cheng and his co-works [59,60] investigated the nature of coke formation on bimetallic Co-Ni/Al_2O_3 catalyst during GSR reaction at 500 °C and 550 °C was attributed to the various glycerol dissociative adsorption and steam molecular chemisorption on two different sites of catalyst surface at different steam-to-glycerol ratios. This was related to the presence of both basic sites and Brönsted acid on the catalyst. The Ni-Cu/Al_2O_3 catalyst was prepared and applied into GSR by Wang et al. [61], it exhibited significantly higher H_2 selectivity (92.9%) and glycerol conversion (90.9%) at 650 °C in comparison with those of Ni/MgO. In addition, Carrero et al. [62] compared the catalytic performance of bimetallic Ni-(Cu, Co, Cr)/SBA-15 Silica catalysts on GSR reaction at 600 °C. It was observed that the glycerol conversions over different catalysts as the following order: Ni-Cr/SBA-15 > Ni-Co/SBA-15 > Ni/SBA-15 > Ni-Cu/SBA-15, and the corresponding H_2 distributions with the sequence: Ni-Cr/SBA-15 > Ni/SBA-15 > Ni-Co/SBA-15 > Ni-Cu/SBA-15. Additionally, the Ni-Cr/SBA-15 exhibited the excellent stability for 60 h on stream reaction and lowest carbon deposition rate (13 $mg_{coke}/(g_{cat}\,h)$). Therefore, the application of Ni-based bimetallic catalysts and supports with unique textural properties into catalytic systems for GSR reaction is a promising and potential technique to promote the product selectivities, glycerol conversions and catalytic stabilities of Ni-based catalysts.

Attapulgite (ATP, it is often called as palygorskite) is a kind of hydrated magnesium aluminum silicate clay mineral