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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



Yishuang Wang^{a,b}, Mingqiang Chen^{*,a,b}, Zhonglian Yang^b, Tian Liang^b, Shaomin Liu^b, Zhongshan Zhou^b, Xiaojing Li^b

^a School of Earth Science and Environmental Engineering, Anhui University of Science and Technology, 232001, Huainan, PR China
^b School of Chemical Engineering, Anhui University of Science and Technology, 232001, Huainan, PR China

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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, N₂ flow ratio = 0.16 L/min and GHSV = 9619 h^{-1} . The prepared calcined and/ or reduced samples were characterized by ICP-OES, N2 adsorption-desorption, XRD, TEM, FT-IR, XPS and H2-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 H₂ 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 H₂ 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 H₂ yield, while the increase rate of H₂/CO ratio was suppressed and CO/CO₂ 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, N₂ 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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^{*} Corresponding author at: School of Chemical Engineering, Anhui University of Science and Technology, 232001, Huainan, PR China. *E-mail address*: mqchen@aust.edu.cn (M. Chen).

pure glycerol in chemicals, pharmaceuticals and cosmetics, the reutilization 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-toethanol 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 watergas 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].

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

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

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

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

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

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

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

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

$$CO + H_2 \leftrightarrow H_2O + C \Delta H^0 = 131 \text{ kJ/mol}$$
(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 H₂ selectivity and lower CH₄ 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 SiO₂, γ -Al₂O₃, ZrO₂, and α -Al₂O₃ modified with Ce and Zr, respectively) for obtaining hydrogen/synthesis gas at low temperatures (< 450 °C), indicating that Pt/SiO₂ 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/CeO₂-Al₂O₃ catalysts, and their results demonstrated the addition of noble metals all increased the H₂ yield and glycerol conversion accompanied with the increase of CH₄ yield. Among them Ni-Pt/CeO₂-Al₂O₃ catalyst showed the highest H₂ 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 (La1-xCaxNiO3, 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}NiO₃ catalyst showed the highest H₂ 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/La₂O₃-Al₂O₃ catalysts presented the highest H₂ yield (47%) accompanied with the higher CO₂ yield (59%) in B₂O₃ and La₂O₃ modified Ni/Al₂O₃ catalysts during the GSR reaction at 400 °C, but it exhibited dramatic deactivation after 18h of reaction and about $200 \text{ mg/g}_{cat.}$ 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], SiO₂ [55] and ZrO₂ [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 longterm catalytic stability. Cheng and his co-works [59,60] investigated the nature of coke formation on bimetallic Co-Ni/Al₂O₃ 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/Al₂O₃ catalyst was prepared and applied into GSR by Wang et al. [61], it exhibited significantly higher H₂ 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 $(13 \text{ mg}_{coke}/(g_{cat} h))$. 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

[(H2O)4(Mg,Al,Fe)5(OH)2Si8O20.4H2O] with reactive hydroxy groups on its surface [63]. Its structure comprised the parallel double-strand Si-O tetrahedra, its upper and lower parts are contacted by a layer of octahedral magnesium/aluminum/iron atoms in 6-fold coordination, which leaded to the formation of lath or fibrous morphology [64]. This unique constitution leads to ATP possesses many excellent properties, such as the single rod-like crystal with nanometric dimension, the high specific surface area, the excellent thermal/mechanical stability, and the silanol-based chemistry of the surface [65]. In consequence, ATP is widely used into different heterogeneous catalysis, such as the lowtemperature NH₃-selective catalytic reduction over the Ce-MnO_x/ATP [66], the catalytic hydroconversion of model coal tar on microfiber ATP supported Ni species [67], and the low-temperature CO oxidation over CuO/ATP [68] and Pd-Cu/ATP [69]. At the same time, ATP is regarded as a catalytic support and gradually applied into SR reaction [70-72]. According to our previous studies [71-73], the Ni/ATP and Ni-Fe/ATP catalysts that prepared by different methods were used into SR of acetic acid and bio-oil model compound, they all showed excellent conversion of feedstock and H2 yield. However, the excellent catalytic support ATP is not yet used in GSR reaction for hydrogen up to now.

Considering the nickel-based bimetallic catalysts, such as Ni-Co, Ni-Cu, and Ni-Zn, were widely employed into other SR reaction in literatures [74–80], and obtained the excellent catalytic performance. In this paper, the ATP supported bimetallic Ni-M (M = Co, Cu, or Zn) catalysts were prepared by co-precipitation method. The calcined and/or reduced catalysts were characterized by ICP, N₂ adsorption-desorption, XRD, TEM, FT-IR, XPS and H₂-TPR. The catalytic performance of asprepared catalysts was investigated during GSR reaction for hydrogen production at 500–700 °C, W/G = 9, N₂ flow ratio = 0.16 L/min and GHSV (Gas Hour Space Velocity) = 9619 h⁻¹. In addition, the postreaction catalysts after long-term test were also characterized by XRD, TEM, TPO-MS and TG-DTG, for investigating the reasons that causing catalyst deactivation.

2. Experimental

2.1. Catalysts preparation

Natural attapulgite mineral clay, which produced from Anhui province of China, is purchased from Changzhou Bangding minerals technology Co., Ltd. (Jiangsu, China). In order to remove the impurities and increase the surface area, it was firstly acidulated by 5 mol/L nitric acid solution at 80 °C for 1 h, and then was filtered, dried, and ground and sieve to fine powder. After that the powder was calcined at 500 °C with for 2 h a heating rate of 2 °C/min to obtain modified attapulgite (ATP). The chemical materials of active metal precursors originated from the corresponding inorganic metal nitrates, such as nickel (II) nitrate hexahydrate [Ni(NO₃)·6H₂O], cobalt (II) nitrate hexahydrate [Co(NO₃)₂·6H₂O] and zinc (II) nitrate hexahydrate [Zn(NO₃)₂·6H₂O], which are analytically pure and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (Shanghai, China).

A series of 5%Ni-5%M/ATP (M = Co, Cu, and Zn) bimetallic catalysts were prepared by co-precipitation. 1.38 g of Ni(NO₃)·6H₂O and a certain amount of M(NO₃)·6H₂O were dissolved to absolute ethyl alcohol to form homogeneous solution, and then 5.00 g of ATP was added into this solution and magnetic stirred in water bath kettle at 60 °C for 4 h. After the 5 mol/L of aqueous ammonia was dropwisely introduced above turbid liquid until its pH reached about 9.0 \pm 0.5 to produce suspension. Soon afterwards, it was stirred intensely at 60 °C for 6 h and went on to age at 80 °C for 12 h. Consequently, experiencing a series of processes of filtration, drying (at 110 °C for 24 h) and calcinations (at 600 °C for 2 h with a heating rate of 2 °C/min), the three catalyst precursors were synthesized successfully and expressed as Ni-M/ATP (M = Co, Cu, and Zn). As comparison, the 10%Ni/ATP catalyst was also prepared by precipitation method, which experienced the same operations as mentioned above.

2.2. Catalytic performance measurements

The GSR reaction was carried out in a fixed bed reactor, which was consisted of stainless steel tube with the inner diameter of 30 mm and length of 300 mm, under ambient pressure at 500–700 °C and W/G = 9. The detailed information about the fixed-bed reactor was described in our previous study [73]. Typically, 1.5 g of as-prepared catalyst was loaded on porous flat plate, which was located at the one-third of the reactor. In advance of the reaction measurement, the catalyst was activated at 600 °C for 2 h under a 0.16 L/min of 10% H₂/N₂ flow. After that the reactor was rose to required temperature under N₂ flow (0.16 L/min) to completely eliminate the spare hydrogen. A glycerol solution with a given molar ratio of W/G was added into vapor generator at 280 °C and introduced into the reactor with a flow rate of 0.4 mL/min by using a HL-2D constant flow pump (Shanghai Huxi Analysis Instrument Factory Co., Ltd, China). The outlet mixer was passed though a condensing apparatus maintained at 0 °C and then separated into liquid and incompressible gaseous products. The gases were analyzed by off-line GC (Huaai GC-9160, Shanghai Huaai Chromatography Analysis Co., Ltd., China) equipped with 5 A molecular sieve column (detected H₂, CO, and CH₄) and Porapak R column (detected CO₂) by using TCD detector. The liquid products, included unreacted glycerol, methanol, ethanol, ethylene glycol, 2-propanol, 1,2propanediol were detected by using Aglient 6280 (USA) equipped with FID detector and a CP8843 capillary column.

The necessary data were calculated by using the following equations:

$$\% \text{ Glycerol conversion}_{(\text{global conversion})} = \left(\frac{\text{Glycerol}_{\text{in}} - \text{Glycerol}_{\text{out}}}{\text{Glycerol}_{\text{in}}}\right) \times 100$$
(1)

% Glycerol conversion_(gaseous products) =
$$\left(\frac{C \text{ atoms in gas products}}{\text{total C atoms in feedstock}}\right) \times 100$$
(2)

$$H_2 \text{ yield } = \left(\frac{H_2 \text{ moles produced}}{\text{ moles of glycerol in the feedstock}}\right)$$
(3)

% H₂ selectivity =
$$\left(\frac{H_2 \text{ moles produced}}{C \text{ atoms produced in the gas phase}}\right) \times \frac{1}{RR} \times 100$$
(4)

Where, RR is the reforming ratio (7/3), defined as the ratio of moles of H_2 to CO_2 formed.

% selectivity of i =
$$\left(\frac{C \text{ atmos in species i}}{C \text{ atoms produced in the gas phase}}\right) \times 100$$
 (5)

Where, species i refers to CO, CO₂, CH₄.

2.3. Catalyst characterizations

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed to obtain the actual metal content in calcined catalysts, which were conducted on a Varian 720-ES spectrophotometer (USA). Before measurements, every as-prepared was digested in acidic solutions.

 $\rm N_2$ adsorption-desorption was adopted to determine the textural properties of calcined catalysts using a ASAP2020 surface area and porosity analyzer (USA). The adsorption-desorption isotherms were acquired using static volumetric measurements at 77 K and room temperature. Prior to measurement, the sample was outgassed at 250 °C for 4 h under vacuum. The Brunauer-Emmett-Teller (BET) method based on the isotherms of adsorption-desorption was used to calculate the value of catalyst surface area (S_{BET}), the cumulative volume of pores (V_{pore}) and the average pore diameter (D_{pore}) were calculated using Barrett-

Joiner-Halenda (BJH) method.

X-ray diffraction (XRD) pattern measurements were performed on a Bruker-AXS D8 Advance diffraction instrument (Germany) using Cu Kα radiation ($\lambda = 0.154056$ nm) by filtering with the graphite at 40 mA and 40 kV, over a 20 rang of 5–80°, as well as the mean crystal diameter ($d_{\text{Ni-M}}$, nm) of the metallic particles was calculated by Scherrer's formula according to the characteristic peak. In addition, the active metal dispersion (D_m, %) was calculated from the equation: D_m (%) = 101/ $d_{\text{Ni-M}}$ based on the literatures [71,81,82]. It derived from the calculation for nickel dispersion (D_m (%) = 101/d), d was the crystallite size expressed in nm and the constant 101 was calculated assuming that the nickel particles have a spherical geometry and that the density of nickel particles in a poly crystalline surface is 1.54×10^{19} atoms Ni m⁻².

Transmission Electron Microscope (TEM) analysis was carried out on a FEI Tecnai G2 F20 (200 kV) transmission electron microscope (US) to measure the surface morphology of catalyst. After measure, the sample particle size was obtained by using the software of nano measurer 1.2 (Beijing Zhongke Baice Technology Service Co., LTD, Beijing, China) and the mean value of particle size was statistically calculated by the measurement of more than 100 uniform particles in several selected TEM images.

Fourier transform infrared spectroscopy (FT-IR) spectra was carried out on a Nicolet 3800 spectrometer (USA) in 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹, and the samples were diluted by using KBr powder.

X-ray photoelectron spectra (XPS) were recorded on a ThermoFisher Scientific ESCALAB250Xi (UK) using a monochrome Al Ka source (1486.68 eV) operating at 150 W and 500 μ m beam spot under a vacuum of mbar. Binding energies were made corrections by using the adventitious hydrocarbon C1s signal at 284.8 eV.

 $\rm H_2$ temperature-programmed reduction (H2-TPR) analysis was carried out to measure the reduction behavior of the calcined samples on a Tianjin Pengxiang PX200 chemical adsorption instrument (China). Typically, a sample (10 mg) was heated from room temperature to 800 °C at 10 °C /min in a 10% H2/Ar flow (40 mL/min). The signal of hydrogen consumption was detected by the thermal conductivity detector (TCD). Prior to experiment, the sample was pretreated by using Ar flow (40 mL/min) for 2 h at 200 °C to remove moisture and other impurities.

Thermogravimetric (TG) analysis was conducted to determine the amount of carbon deposition on the spent catalyst surface by using a TGA/DSC1 STAR^e System instrument (Switzerland). Typically, the spent samples (10 mg) were heated from ambient temperature to 900 °C at a ramp of 10 °C/min under air flow (50 mL/min). The mass loss as a function of temperature was measured in this process at experimental error about \pm 0.5%.

Temperature-programmed oxidation was also employed to investigate the types of carbon deposition on a Auto Chem II 2920 apparatus (USA) coupled with an Ametekquadrupolar mass spectrometer (TPO-MS). Typically, a sample (25 mg) was heated from room temperature to 800 °C with a heated rate of 10 °C/min under 3% O₂/He flow (50 mL/min), and using a mass spectrometry detector to monitor CO_2 signal (m/z = 44).

3. Results and discussion

3.1. Characterizations of calcined and reduced catalysts

The active metal contents (Ni, Co, Cu, and Zn) in calcined catalysts were determined by ICP-OES and the results were shown in Table 1, which confirmed that the metal contents of catalysts were almost similar to the given metal contents during catalyst preparation.

The N_2 adsorption-desorption technology was employed to estimate the textural properties of calcined catalysts (Fig. 1). According to the IUPAC classification, all catalysts exhibited type IV isotherms, indicative of the ATP support had typical mesoporous structure (Fig. 1A).
 Table 1

 The physical properties of different catalysts.

S _{BET} (m ² /g)	V _{pore} (cm ³ /g)	D _{pore} (nm)	Metal content ^a (wt.%)		d _{Ni-M} ^b (nm)		D _m ^c (%)	
			Ni	М	Reduced	Spent		
220.4	0.335	5.8	9.78	/	14.9	22.5	6.8	
150.8	0.326	9.6	4.69	4.91	8.6	14.3	11.7	
141.1	0.296	8.7	4.87	4.88	12.2	18.7	8.3	
134.0	0.310	9.4	4.91	4.68	10.3	11.2	9.8	
	S _{BET} (m ² /g) 220.4 150.8 141.1 134.0	$\begin{array}{ccc} S_{BET} & V_{pore} \\ (m^2/g) & (cm^3/g) \end{array}$	S_BET (m²/g) Vpore (cm³/g) Dpore (nm) 220.4 0.335 5.8 150.8 0.326 9.6 141.1 0.296 8.7 134.0 0.310 9.4	$ \begin{array}{c} S_{BET} \\ (m^2/g) \end{array} \begin{array}{c} V_{pore} \\ (cm^3/g) \end{array} \begin{array}{c} D_{pore} \\ (nm) \end{array} \begin{array}{c} Metal \\ (nm) \end{array} \\ \begin{array}{c} Metal \\ (nm) \end{array} \\ \begin{array}{c} Ni \end{array} \end{array} \\ \begin{array}{c} 220.4 \\ 150.8 \\ 150.8 \\ 141.1 \\ 0.296 \\ 141.1 \\ 0.310 \end{array} \\ \begin{array}{c} 9.6 \\ 8.7 \\ 9.4 \\ 4.91 \end{array} \end{array}$	$ \begin{array}{cccc} S_{BET} \\ (m^2/g) \end{array} \begin{array}{c} V_{pore} \\ (cm^3/g) \end{array} \begin{array}{c} D_{pore} \\ (nm) \end{array} \begin{array}{c} Metal \\ content^a \\ (wt.\%) \end{array} \\ \hline \\ \hline \\ Ni \end{array} \begin{array}{c} M \\ M \end{array} \\ \hline \\ 220.4 \\ 150.8 \\ 150.8 \\ 0.326 \\ 150.8 \\ 0.326 \\ 160 \\ 1$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	

^a Calculated from ICP data.

^b The crystal size was estimated by the peaks at near 43.1°.

 $^{\rm c}$ The dispersion of metal was calculated by using the equation of $D_{\rm m}=101/d_{\rm Ni\cdot M}$ in ref. [71,81,82].



Fig. 1. N_2 adsorption-desorption isotherms (A) and pore size distributions (B) of all alcined catalysts.

Additionally, all adsorption-desorption profiles shown the H₃-type hysteresis loops, suggesting all fresh catalysts possessed lamellar structure, which was a typical morphology for ATP [65,68]. It also can be found that the hysteresis loops were observed at the P/P_o range of 0.42–0.99 for Ni/ATP and 0.50–0.99 for all Ni-M/ATP samples, which showed the promoters (Co, Cu, and Zn) added into Ni/ATP catalyst to decrease its adsorbed and desorbed volumes. Therefore, the S_{BET} and V_{pore} of Ni/ATP were 220.4 m²/g and 0.335 cm³/g, respectively, and all decreased by the addition of promoters, such as 150.8 m²/g and 0.326 cm³/g for Ni-Co/ATP, 141.1 m²/g and 0.296 cm³/g for Ni-Cu/ATP, and 134.0 m²/g and 0.310 cm³/g for Ni-Zn/ATP, respectively (Table 1). In addition, the pore size distribution was determined from the N₂-desorption isotherm using BJH method and displayed in Fig. 1B.



Fig. 2. XRD profiles of calcined (A) and reduced (B) catalysts.

The pore size distributions of all calcined catalysts were narrow in a range of 2–15 nm, while the average pore diameter (D_{pore}) was 5.8 nm for Ni/ATP, 9.6 nm for Ni-Co/ATP, 8.7 nm for Ni-Cu/ATP, and 9.4 nm for Ni-Zn/ATP, respectively (Table 1). In summary, the introduction of promoters (Co, Cu, and Zn) decreased the S_{BET} and V_{pore} of Ni/ATP sample, while increased their D_{pore} . This was attributed to the smaller mesoporous in ATP were blocked by the smaller active metallic particles during calcinations. The results were also demonstrated and reported by Kousi and his co-workers [33].

The crystallinities of calcined and reduced catalysts were evaluated by XRD and the corresponding profiles were shown in Fig. 2. The peaks at $2\theta = 8.4^{\circ}$ and 35.5° in all samples are attributed to the characteristic peaks of ATP, which correspond to the lattice planes of (110) and (161), respectively [64]. On account of ATP is a kind of silicate, there are some silicon oxides with different crystallinity are formed during calcination and reduction. Hence, the peaks at $2\theta = 20.7^{\circ}$ and 26.6° are assigned to the lower crystalline of Si-O-Si layers in the clay and the higher degree of crystallinity of quartz (SiO₂), respectively [68]. The characteristic peaks of NiO (JCPDS 78-0643) at $2\theta = 37.3^{\circ}$, 43.3° and 62.6° in calcined samples (Fig. 2A) are not easily found in bimetallic catalysts, while a broad peak at 62.6° is observed in calcined Ni/ATP catalyst. It is demonstrated that the addition of second metal improved the dispersion of nickel species. As expected, this peak in Ni/ATP is disappeared after reduction process (Fig. 2B). In addition, from the diffraction patterns of calcined catalysts in Fig. 2A, except for the characteristic peaks of ATP support, it was unobserved the other unobvious peaks that attributed to metallic oxides of cobalt, copper or zinc and/or Ni-M alloy phases. This was mainly because these active metals particles were low crystallinity with undefined structure or highly dispersed on the ATP, which owed to the ATP support possessed superior textual properties that improved the dispersion of active metal, leading to them beyond out the detection of XRD. The similar results were also found in Lamodified ordered mesoporous Ni-based catalysts [83] and ceria-promoted Ni/SBA-15 catalysts [84], which all attributed to the unique textual properties of supports. As compared, the XRD patterns of reduced Ni/ATP and Ni-M/ATP samples, which were pretreated in 10% H₂/N₂ at 600 °C for 2 h, were displayed in Fig. 2B. For Ni/ATP catalyst, the peaks located at $2\theta = 44.5^{\circ}$ and 51.6° demonstrated the formation of the characteristics of nickel metal phase (JCPDS 01-1258), which related to the Niº crystal faces of (111) and (200), respectively. According to the reported in literatures [59,74,85], the characteristic peaks of Co° (JCPDS 01-1254) were at $2\theta = 44.2^{\circ}$ and 51.4° . As shown in Fig. 2B, the diffraction peaks at about 44.3° and 51.5° in Ni-Co/ATP catalyst are between the diffraction peaks of metallic Ni and Co, and their intensities were lower compared with those of metallic Ni diffraction peaks in Ni/ATP catalyst, indicating the addition of Co metal changed the crystalline structure of Ni^o, which may due to the formation of Ni-Co allov in reduced Ni-Co/ATP catalyst based the report in Ref. [86]. For Ni-Cu/ATP catalyst, it is obviously found the diffraction peaks of metal particles at near 44.5° and 51.6° are shifted into lower angles, additionally, the characteristics of Cuº (JCPDS 01-1242) were located at $2\theta = 43.3^{\circ}$ and 50.4° based on the report of Arbeláez et al. [87,88]. Therefore, the locations of metal diffraction peaks in Ni-Cu/ ATP catalyst were higher than those of Cu^o and lower than those of Ni^o, indicating that the formation of Ni-Cu alloy (JCPDS 47-1406) [76,87]. From the study about Zn-modified Ni/Al₂O₃ catalysts designed by Anjaneyulu et al. [89]. were used in SR of ethanol, the characterization result of XRD showed the diffraction peaks located at $2\theta = 43.6^{\circ}$, 46.8° and 51.0° were assigned to NiZn (JCPDS 06-0672) and Ni₄Zn (JCSDS 64-7139) phases. However, for reduced Ni-Zn/ATP catalyst, it has not found prominent peaks ascribed to Ni or Zn metal phase, except for the weak peak at 43.5°. This feeble peak may attribute to the interaction between nickel and zinc particles or the formation of Ni-Zn/ATP.

In order to further confirm the effect of second metals on the Ni/ATP crystalline structure, the crystal sizes of metal particles for all reduced catalysts were obtained and presented in Table 1. It can be seen that the metal particle sizes are as the following order: Ni-Co/ATP (8.6 nm) < Ni-Zn/ATP (10.3 nm) < Ni-Cu/ATP (12.2 nm) < Ni/ATP (14.9 nm), indicating the second metals obviously decreased the mean metallic particle sizes. Generally speaking, in XRD patterns, the catalysts have relative broad and weak diffraction peaks, suggesting whose metal particles were in highly dispersion state over the catalysts [74,90]. Consequently, the metal dispersions of catalysts with the following sequence Ni-Co/ATP > Ni-Zn/ATP > Ni-Cu/ATP > Ni/ATP, as shown in Table 1. Therefore, the addition of second metals undoubtedly changed the interaction between nickel particles and ATP support, which will be further discussed in the next section, and decreased the mean particle size and improved the metal dispersion.

The surface textures and morphologies of reduced catalysts were obtained from TEM images and the details were illustrated in Fig. 3. It was observed the principal surface textures of all reduced catalysts were bundles of fibrous structures that formed by the irregularly aggregate together of the ATP nano-fibers with long and narrow needle-like structure, which were in coincide with the results that reported by Li et al. [67]. and Cao et al. [68]. As shown in Fig. 3A, it can be seen that the metallic nickel particles are unevenly dispersed on the surface of Ni/ATP and they have somewhat sintering during reduction process. When the second metals (Co, Cu and Zn) added into Ni/ATP catalyst, the active species dispersion is obviously improved (Fig. 3B-C). Especially, for Ni-Co/ATP catalyst (Fig. 3B), the metallic particles become more uniform and smaller than other ones. In addition, the particle size distributions for all catalysts are also displayed in Fig. 3. It is observed that the mean particle size for reduced catalyst has the following order: Ni-Co/ATP (8.3 nm) > Ni-Zn/ATP (10.5 nm) > Ni-Cu/ATP (12.6 nm) > Ni/ATP (15.5 nm), which is almost consistent with that calculated for XRD data. These changes indicate the interaction of nickel specie and ATP particle is affected in different degree by other metals (such as Co, Cu and Zn). Based on the XRD analysis, we speculate that the introduction of other metal species into Ni/ATP to interactive with nickel specie, leading to suppress the agglomeration of nickel species and improve the metal dispersion [50,74,77].

The FTIR analysis was performed to investigate the structure



Fig. 3. TEM images and particle size distribution of reduced catalysts: (A) Ni/ATP, (B) Ni-Co/ATP, (C) Ni-Cu/ATP, and (D) Ni-Zn/ATP.

variations in calcined Ni-M/ATP bimetallic catalysts in comparison with raw ATP (was also calcined under the same conditions with calcined catalysts) and calcined Ni/ATP catalyst. The FTIR spectra of all samples are shown in Fig. 4, which demonstrates there are no significant differences for all samples, except for the weak changes between about 800 cm^{-1} and 600 cm^{-1} . According to the literatures [64,65,67] and the results in Fig. 4, the very broadband at 3700 cm^{-1} -3200 cm⁻¹ was combined vibration effects of (Mg, Al) –O units of the octahedral sheets and the randomly attached hydroxyl groups, such as Al³⁺-OH, (Fe, Mg) –OH and (Al, Mg) –OH, which were the major feature structure of ATP. In addition, the band around 1387 cm⁻¹ was also the –OH stretching variation in (Fe, Mg)–OH and (Al, Mg)–OH. The characteristic absorbance around 1633 cm⁻¹ was

attributed to the weakly bound hydroxyl groups that was transformed from the bond water (1650 cm⁻¹) after acid treatment process [64]. The bands around 1061 cm⁻¹ and 480 cm⁻¹ are ascribed to tetrahedral Si-O bending vibration mode, which was also demonstrated by XRD analysis. As compared with ATP, the weak variation bonds around 783 cm⁻¹ and 650 cm⁻¹ could be attributed to the stretching variation of Ni–M–O (M = Co, Cu and Zn) and Ni–O, respectively. Abdollahifar et al. [91]. prepared the bimetallic Ni-Co/Al₂O₃-MgO catalyst and used into CO₂ reforming of CH₄, from the FITR analysis for catalysts, they demonstrated the peaks below 1000 cm⁻¹ were related to metaloxygen-metal and metal oxides bonds. Consequently, the formation of metal-oxygen-metal and metal oxides bonds could improve the interaction between nickel species and second metals, and then would



Fig. 4. FTIR spectrum of calcined catalysts and raw ATP.

suppress the sintering of active metals during reduction.

To explore the effect of second metals on the catalysts surface properties, the XPS analysis was carried out for all reduced catalysts. Additionally, in order to illustrate the changes of chemical states of different metals that affected by the interaction between metal particles and support, the M/ATP (Co, Cu, and Zn) samples contented 5 wt.% M metal were prepared by the same process decreased in catalysts preparation section and then reduced at 600 °C for 2 h under the 10% H₂/ N2 flow, as well as they also were characterized by XPS. The XPS data for all samples were listed in Table 2. The XPS results of Ni2p spectra were presented in Fig. 5A, on the basis of the deconvolution of Ni2p spectra, the binding energies (B.E.s) at 852.3 eV (Table 2) in Ni2p_{3/2} spectra of reduced Ni/ATP catalyst is attributed to Ni(0) species, as shown in Fig. 5(A) [32,74,76]. As compared the XPS Ni2p spectra of 5% Ni/ATP was showed in Fig. S1, it presented almost the same information with Ni/ATP (Fig. 5(A)). However, the B.E.s that related to Ni(0) in Ni2p_{3/2} spectra in bimetallic catalysts are 853.6 eV for Ni-Co/ATP, 853.7 eV for Ni-Cu/ATP and 853.5 eV for Ni-Zn/ATP (Table 2), respectively. Notably, they all shifted to higher B.E.s in comparison with Ni/ATP. In addition, from the XPS spectra of Ni2p (Fig. 5A), it also can be observed that the two main peaks at about 856 eV and 874 eV, respectively with two low-intensity satellite peaks in Ni2p_{3/2} and Ni2p_{1/2} spectra for all reduced catalysts are assigned to Ni(II). Simultaneously, the B.E.s of main peaks attributed to Ni(II) (Ni2p_{3/2}) were also shifted to higher B.E.s (856.3 eV for Ni-Co/ATP, 856.6 eV for Ni-Cu/ATP and 856.2 eV for Ni-Zn/ATP (Table 2)) than that of Ni/ATP (855.7 eV) [24,32]. Consequently, the addition of metal M decreases the amount of Ni(0) species on the catalyst surface and the main oxidation state of Ni metal in bimetallic catalyst surface is Ni(II), suggesting Ni(0) in bimetallic catalyst surface is more easily reoxidized. It is may be inferred

Table 2

The BE of metals (Ni, Co, Cu and Zn) species in different chemical states in reduced samples.

Samples	B.E. Ni 2p _{3/2}		B.E. Co 2p _{3/2}		B.E. Cu 2p _{3/2}		B.E. Zn 2p _{3/2}		
	Ni(0)	Ni(II)	Co(0) Co (III)/ Co(II)		Cu (0)/ Cu(I)	Cu(II)	Zn(0)) Zn(II)	
Ni/ATP	852.3	855.7	_	_	-	-	-	-	
Ni-Co/ATP	853.6	856.3	778.2	781.6	-	-	-	-	
Ni-Cu/ATP	853.7	856.6	-	-	932.6	933.6	-	-	
Ni-Zn/ATP	853.5	856.2	-	-	-	-	1022.1	1022.4	
Co/ATP	-	-	-	781.7	-	-	-	-	
Cu/ATP	-	-	-	-	-	933.1	-	-	
Zn/ATP	-	-	-	-	-	-	-	1022.7	
Co/ATP Cu/ATP Zn/ATP	- - -	- -	- - -	781.7 - -	- - -	- 933.1 -	- - -	- - 1022.7	

from the addition of second metals changed the immediate surroundings of nickel species and the interaction between nickel nano-particles and ATP support (which will be further investigated by H_2 -TPR).

In additon, the XPS spectra of Co2p, Cu2p, and Zn2p were also shown in Fig. 5(B)-(D), respectively. As shown in Fig. 5(B), for reduced Ni-Co/ATP and Co/ATP, the B.E.s at ca. 781.7 eV and 797.9 eV, respectively, in Co2p3/2 and Co2p1/2 spectra were ascribed to the coexistence of Co(II) and Co(III) species, normally, they have the corresponding satellite peaks at *ca*.787.3 eV and 803.3 eV, respectively [74]. Whereas, there was a weak peak at 777.9 eV in $Co2p_{3/2}$ spectra after deconvolution that attributed to Co(0) species presents to the reduced Ni-Co/ATP [74]. For the XPS spectra of Cu2p in Fig. 5(C), only reduced Ni-Co/ATP sample exhibited the spectra with Cu2p_{3/2} the deconvolution peak locating at around 932.6 eV, indicating the co-existence of Cu (0) and Cu(I) species [88,92]. Moreover, the Cu2p spectra also with Cu2p_{3/2} and Cu2p_{1/2} had two main peaks at about 933.2 eV and 953.2 eV with a spin-orbit coupling energy of 20.0 eV, respectively with two lower satellite peaks at around 942.4 eV and 962.4 eV, suggesting the existence of Cu(II) species [76,92]. As can be seen from Fig. 5(D), the B.E.s at 1021.4 eV and 1044.5 eV in Zn2p_{3/2} and Zn2p_{1/2} spectra were assigned to Zn(0) species, respectively, only appear in reduced Ni-Zn/ATP catalyst [93]. Additionally, the peaks at 1021.7 eV and 1044.7 eV in $Zn2p_{3/2}$ and $Zn2p_{1/2}$ spectra that assigned to Zn(II) species, respectively, were found in reduced Ni-Zn/ATP and Zn/ATP samples [93]. In conclusion, it can be observed that there were some reduction state M (e.g. Co(0), Cu(0)/Cu(I) and Zn(0)) metal species appear on the surface of bimetallic catalysts based on the XPS data, while there were no metal species exist on monometallic M/ATP samples. This indicative of bimetallic catalysts suppress the reoxidized of second metals, which is mainly because the formation of interaction force between nickel metal and second metals. This interaction force make Ni(0) become more easily reoxidized and inhibit the reoxidation of second metals. In addition, the difference of the interaction between metal and support caused by the addition of second metals are also found by XRD, TEM and FT-IR. It was generally accepted that the superior interaction between was beneficial for inhibiting the sintering of Ni species and coke deposition at adjacent position of Ni metal, resulting in superior catalytic performance during steam reforming reaction [94-96].

H2-TPR experiment was conducted to investigate the reducibility of all calcined samples and the interaction between different metal particles and ATP support [20,48,56]. Their TPR profiles were presented in Fig.6, it is worthwhile mentioning that there was no obviously reduced peak in ATP support and there were two easily distinguishable peaks at below 750 °C in all calcined catalysts. According to the report of Maia et al. [20], the reduction profiles of NiO shown two main peaks, the one located at about 400 °C was attributed to the reduction of nickel oxide crystallites and the other located at about 600 °C was a shoulder peak that assigned to the reduction of bulk NiO particles. Much work so far had demonstrated that the reduction of nickel species that supported on various supports exhibited different peaks in TPR profiles [45,55,56,67], which resulted from the different aggregate states on support surface and/or interactions between nickel oxide and supports. These reduction peaks generally divided into the following categories, the one at 250-300 °C was the reduction of amorphous NiO with no interaction with support, the second one at a broad range of 350-750 °C was the reduction of crystal NiO species located on different positions of support, resulting in them had different interaction force (weak or strong contact) with support, and the third one at high temperature (> 750 °C) can be assigned to reduction of Ni²⁺ transported into lattice defects of support or Ni-based metal alloys formed with other metal. Consequently, for Ni/ATP catalyst, two peaks appear at 425 °C and 662 °C, respectively assigned to the reduction of nickel oxide particles had low contact with support and nickel oxide species exhibited intimate contact with supported or migrated into the interior of ATP [67,71].



Fig. 5. XPS spectra of samples reduced at 600 °C for 2 h. (A) Ni2p peaks of all reduced catalysts, (B) Co2p peaks, (C) Cu2p peaks, (D) Zn2p peaks.



Fig. 6. H₂-TPR profiles of all calcined catalysts.

In order to further explain the effect of second metals on the reducibility of bimetallic catalysts, the H₂-TPR experiment was also carried out on the calcined monometallic catalysts 5%M/ATP (the content of M is 5wt.%, and M = Ni, Co, Cu, and Zn). The TPR profiles and H₂ consumption were displayed in Fig. S2 and Table S1, respectively. All monometallic catalysts showed two main reduction peaks at low temperature and high temperature, respectively. It was attributed the reduction of different metal oxides that have weak and strong interaction with ATP. The reduction degree was 60% for 5%Ni/ATP, 58% for 5%Co/ATP, 99% for 5%Cu/ATP, and 45% for 5%Zn/ATP. For bimetallic Ni-Co/ATP and Ni-Zn/ATP catalysts, the two corresponding reduction peaks (Fig. 6) were all shifted to higher temperature in comparison with Ni/ATP and lower temperature than monometallic samples 5%Co/ATP and 5%Zn/ATP (Fig. S2), illustrating the second metals (Co and Zn) changed the reducibility of bimetallic catalysts

particles due to the addition of second metals [94]. Notably, there was a reduction peak at the highest temperature (ca. 840 °C) arose into the Ni-Zn/ATP catalyst that assigned to the reduction of Ni²⁺ and/or Zn²⁺ migrated into ATP lattice, suggesting the higher interaction between active phases and ATP support, which was generally accepted that the formation of higher interaction among metal species and support was conducive to the anti-sintering to improve the catalytic stability. For Ni-Cu/ATP (Fig. 6), it can be observed the two peaks: the one located at about 316 °C and the other located at ca. 648 °C with a shoulder peak at ca. 750 °C. Their central temperatures were higher than 5%Cu/ATP (Fig. S2) and lower than Ni/ATP (Fig. 6). In the light of previous reports [24,62,76,92], the presence of Cu in Ni-Cu/MWNT (multiwalled carbon nanotubes), Ni-Cu/SBA-15 And Ni-Cu/SiO2 catalysts decreased the reduction temperature of Ni(II), which was attributed to the Cu could produce spillover hydrogen in reduction conditions resulted in accelerating the nucleation of Ni metal and enhancing the reducibility of Ni (II) at lower temperature. This change also demonstrated the formation of Ni-Cu alloy in Ni-Cu/ATP based on the study of Rahman [24], which is consistent with the results of XRD. Additionally, the H₂ consumption of monometallic and bimetallic samples was also obtained from TPR results and showed in Table S1 and Table 3, respectively. It can be found that the reduced degree (Table 3) of bimetallic catalysts present the following order: Ni-Cu/ATP (74%) > Ni-Co/ATP (55%) > Ni-Zn/ ATP (36%), and they were all lower than Ni/ATP catalyst. Meanwhile, the monometallic catalysts showed the following sequence: 5%Cu/ATP (99%) > 5%Ni/ATP (60%) > 5%Co/ATP(58%) > 5%Zn/ATP(45%). Consequently, this demonstrated that second metals obviously decreased the reduced degree of catalyst. This was attributed to the interaction between nickel and ATP is improved by the addition of second metals, which is also demonstrated by the XPS analysis.

caused by improving the interaction metal oxides and ATP nano-

Therefore, from the comprehensive characteristic results, the

Table 3

H₂ consumption for the fresh catalysts obtained from TPR results.

Samples	Experimentally H ₂ consumption (mmol/g _{cat.})	Theoretically H ₂ consumption ^a (mmol/g _{cat})	% reduced degree		
ATP	-	-	-		
Ni/ATP	1.43	1.67	86		
Ni-Co/ATP	1.16	2.12	55		
Ni-Cu/ATP	1.18	1.60	74		
Ni-Zn/ATP	0.56	1.55	36		

^a The calculation of theoretical H₂ consumption based on the completely reduced of metal species (such nickel(II), cobalt(III), copper(II) and zinc(II)).

addition of second metals (e.g. Co, Cu and Zn) changed the surface textures and morphologies, improved the active metal dispersion and anti-sintering capacity of Ni/ATP by improving the interaction between active species and ATP nanoparticles (which have been proven by above mentioned characterization technologies). In addition, the effects of these changes of physicochemical properties in bimetallic catalysts on the catalytic performance during GSR reaction were investigated in the next section.

3.2. Catalytic performance test

3.2.1. The test of catalytic activity

The catalytic activities of the as-prepared catalysts for GSR reaction were investigated in fixed-bed reactor at 500-700 °C under the following conditions: W/G = 9, N_2 flow ratio = 0.16 L/min and GHSV = 9619 h⁻¹. The glycerol conversions, H_2 yields and the selectivities of gaseous products were summarized and listed in Table 4. It is found that the glycerol conversions to gaseous products are lower that 80% at 700 °C, while most studies reported almost complete to conversion to gas [33,37,43,46,56]. This is mainly because that the noble metal was used as catalysts [37,43] and the W/G in these studies were very higher (> 30) that in this paper. In addition, there was no denying that the GSR reaction was an endothermic reaction [8], suggesting that high temperature was beneficial for the cleavage of C-C, C-H and C-O bonds in the glycerol. Therefore, the global glycerol conversion and the glycerol conversion to gaseous products were increase with the temperature ranges from 500 °C to 700 °C (Table 4), such as 78.1%-90.2 % and 45.0%-65.3% for Ni/ATP, 82.1%-94.5% and 50.8%-78.0% for Ni-Co/ATP, 88.0%-98.1% and 66.6%-79.7% for Ni-Cu/ATP, and 77.5%-93.4% and 63.2%-73.1% for Ni-Zn/ATP, respectively. Obviously, the bimetallic catalysts (Ni-Co/ATP, Ni-Cu/ATP, and Ni-Zn/ATP) showed the both values of glycerol conversions were all higher than those of Ni/ATP. Because the bimetallic catalysts had smaller crystal sizes and higher metal dispersions (as demonstrated by XRD and TEM characterizations), which could provide more active sites for catalytic GSR reaction [37,74]. In addition, the glycerol conversion to gaseous product for bimetallic catalyst have an order: Ni-Cu/ATP (73.4%) > Ni-Co/ATP (70.4%) > Ni-Zn/ATP (67.6%) > Ni/ATP

(66.8%) at 600 °C (Table 4). (The reasons for selecting data obtained at 600 °C to compare the performance of catalysts as shown the following: (I) As reported in ref. [8]. and [20], above 600 °C, rising temperature would suppress the WGSR, which is beneficial for high H2 selectivity; (II) As we all known, the high temperature will significantly lead to the sintering of active metal species; (III) For the practical experiment, the low temperature (< 700 °C) is more practical value for the industrial application and more energy conservation; (IV) Analyzing the catalytic activity at 600 °C is corresponding to the results of stability test, which were also performed at 600 °C.). The H₂ yield of Ni-Cu/ATP (4.08) was also slightly higher than those of Ni-Co/ATP (3.85) and Ni-Zn/ATP (3.67) and significantly higher as compared with that of Ni/ATP (3.54) during GSR reaction at 600 °C. Consequently, Ni-Cu/ATP bimetallic catalyst exhibited the highest glycerol conversion and H₂ yield. It was commonly known that the conversion of feedstock in steam reforming reaction was not only affected by the crystal size of active metal, but also influenced by its reducibility [43,44,97,98]. The smaller crystal size and superior reducibility could improve the GSR reaction (Eq. (1)), WGSR (Eq. (3)) [88,99] and methane reforming reaction (Eq. (4) and Eq. (5)) [100]. Unfortunately, Ni-Cu/ATP catalyst showed the outstanding catalytic performance, but its particle size and reducibility were not show dominant advantages in comparison with other samples (as shown by all aforementioned characterizations). Hence, we may speculate that the crystal size and reducibility of catalyst all showed pivotal to impart suitable catalytic activity, as well as metal-support interaction could affect and change these physicochemical properties. As a consequence, these characteristics should have an optimal proportion for obtaining the outstanding catalytic performance.

In addition to the changes in terms of glycerol conversion and H₂ yield, the products selectivities were also affected by the addition of second metals. The H₂ selectivity during GSR reaction at 600 °C was changed from 57.4% for Ni/ATP to 65.3% for Ni-Co/ATP, 68.9% for Ni-Cu/ATP and 62.8% for Ni-Zn/ATP (Table 4), respectively. Whereas the CH_4 selectivity had a reverse trend with H_2 selectivity, suggesting the bimetallic catalysts effectively improved the steam reforming of methane produced from glycerol thermal decomposition, which was considered as an actively effect for increasing H₂ yield. Especially for Ni-Cu/ATP and Ni-Zn/ATP catalysts, there was almost no methane detected in gaseous products (Table 4). In addition, comparing to Ni/ATP catalyst, the CO selectivities for bimetallic catalysts were also significantly inhibited and the corresponding CO2 selectivities were dramatically increased for bimetallic catalysts. This may assign to bimetallic metal catalysts have an active effect on WGSR due to the reinforced interaction between active metal species and ATP nanoparticles that have been demonstrated by XPS and H2-TPR analysis. Apart from the effect of the characters of catalysts on gaseous products, the reaction temperature was also a major factor influenced the H₂ yield and gaseous products. As presented in Table 4, the H₂ and CO selectivities are increased with the temperature, such as 20.8%-61.8% and 45.5%-53.0% respectively for Ni/ATP, 50.9%-65.5% and 30.0%-43.3% respectively for Ni-Co/ATP, 44.4%-64.0% and

Table 4

The glycerol conversion, H_2 yield and the selectivities of gaseous products during GSR reaction for all catalysts at different temperatures (500 °C, 600 °C, and 700 °C) for 3 h. [Reaction conditions: W/G = 9, N₂ flow ratio = 0.16 L/min and GHSV = 9619 h⁻¹.].

Catalysts	Ni/ATP		Ni-Co/ATP			Ni-Cu/ATP			Ni-Zn/ATP			
Temperature (°C)	500	600	700	500	600	700	500	600	700	500	600	700
X _{Glycerol (global conversion)} (%)	78.1	81.3	90.2	82.1	93.7	94.5	88.0	98.5	98.1	77.5	90.9	93.4
X _{Glycerol to gaseous products} (%)	45.0	66.8	65.3	50.8	70.4	78.0	60.6	73.4	79.7	63.2	67.6	73.1
H ₂ yield (mole/mole of glycerol)	1.61	3.54	3.83	3.29	3.85	4.31	3.90	4.08	4.11	2.87	3.67	4.34
S _{H2} (%)	20.8	57.4	61.8	50.9	65.3	65.5	44.4	68.9	64.0	39.8	62.8	63.0
S _{CO} (%)	45.5	53.7	53.0	30.0	41.5	43.0	35.3	45.7	45.1	30.3	37.8	39.7
S _{CO2} (%)	39.2	37.2	38.2	64.9	55.7	54.5	62.8	53.5	54.3	65.9	61.8	59.5
S _{CH4} (%)	15.3	9.1	8.8	5.1	2.8	2.5	1.9	0.8	0.6	3.8	0.4	0.8



Fig. 7. The H_2 /CO (A) and CO/CO₂ (B) molar ratios of all catalysts at different temperature. [Reaction conditions: W/G = 9, N₂ flow ratio = 0.16 L/min and GHSV = 9619 h⁻¹.]

35.3%–45.1% respectively for Ni-Cu/ATP, and 39.8%–63.0% and 30.3%–39.7% respectively for Ni-Zn/ATP, while their selectivities for CO_2 and CH_4 exhibited an opposite trend. These changes are mainly attributed to the co-effect of WGSR (Eq. (3)), CH_4 steam reforming (Eqs. (4) and (5)) and dry reforming (Eq. (6)). The above discoveries were in good accordance with literature results, which had reported the formation of CH_4 was inhibited and the H_2 content was increased at high temperature and over the catalysts with high metal dispersion.

In order to further investigate the effects of catalysts' characters and reaction temperature on gaseous product, the functions of H₂/CO and the CO/CO₂ molar ratios, in which the value of every gaseous product was related to the molar content in the gaseous products' mixture, with temperature as shown in Fig. 7. It is notably observed that the H_2/CO values are significantly increased with temperature at the range of 500-600 °C over all samples, while the upward tendency of H₂/CO is obviously attenuated. The changes of CO/CO2 molar ratios show an opposite trend. The increasing of H_2/CO and the decreasing of CO/CO_2 molar ratios at 500-600 °C were attributed to the accelerated WGSR (Eq.(3)), resulting in an increase in CO₂ formation with increasing temperature [49], while they became descend at temperature higher than 600 °C, due to the reverse WGSR [8,20]. As compared with Ni/ATP catalyst, the bimetallic catalysts all showed higher H₂/CO and lower CO/CO₂ molar ratios in gaseous product, suggesting the addition of other metals promoted the WGSR (Eq. (3)) to increase the content of H₂. The positive effect of bimetallic catalysts on WGSR is mainly attributed the addition of second metals promote the crystal size and metal-support interaction.

3.2.2. The test of catalytic stability

Studying the stability of catalysts is one of the major issues in steam reforming process and has been intensively investigated [33,39,74]. To

obtain the stability of all as-synthesized catalysts, endurance experiments were performed at 600 °C, W/G = 9, $GHSV = 9619 h^{-1}$ for 30 h. The results were shown in Fig. 8. An obvious decrease in the activity of Ni/ATP catalyst could be observed for the whole steam reforming reaction, as values of glycerol total conversion and its conversion into gaseous products (Fig. 8A) rapid decreased from 89.5% to 65.0% and from 69.9% to 20.1%, respectively. On the contrary, the Ni-Cu/ATP catalyst seem to deactivate at a rather slower rate, such as the values of glycerol total conversion and its conversion into gaseous products drop from 95.3% to 78.2% and from 75.0% to 48.6%, respectively. While the Ni-Co/ATP and Ni-Zn/ATP catalysts almost keep unchanged in the whole reaction, as presented in Fig. 8A. For Ni/ATP catalyst (Fig. 8B), the H₂ vield was drastic decrease from 3.54 to 1.62 and H₂ selectivity was obvious increase from 57.4% to 83.0%. The changes about H₂ yield (from 4.08 to 2.65) and H_2 selectivity (from 55.0% to 73.2%) for Ni-Cu/ ATP catalyst (Fig. 8D) displayed a similar tendency with that for Ni/ ATP, while they showed a rather slower rate. Furthermore, the values of H₂ yield for Ni-Co/ATP (Fig. 8C) and Ni-Zn/ATP (Fig. 8E) catalysts were quite constant after about 30 h on steam, combined with their changes of glycerol total conversion and its conversion into gaseous products, implying the Ni-Co/ATP and Ni-Zn/ATP catalysts exhibited outstanding stability in the four catalysts. Apart from those, the glycerol conversion (Fig. 8A) and H₂ selectivity (Fig. 8E) over Ni-Zn/ATP showed the most stability during the endurance test. Additionally, CH₄ selectivity for Ni/ATP was very higher as compared with bimetallic catalysts and significantly increased during the stable test. The CO₂ selectivity for Ni/ATP was lower than CO selectivity, while it slightly became higher than CO selectivity for bimetallic catalysts. Therefore, the second metals addition promoted the catalytic stability, suppressed the formation of CH₄ and favored the WGSR. However, for bimetallic catalysts, the metal-support interaction (MSI) displayed the following order: Ni-Zn/ATP > Ni-Co/ATP > Ni-Cu/ATP, which was demonstrated by the H₂-TPR analysis (Fig. 6). While the MSI in Ni/ATP was higher than that in Ni-Cu/ATP catalyst, which because the reduction temperature of Ni/ATP was higher than that of Ni-Cu/ATP (Fig. 6), Cu metal interacted with nickel species to suppress the formation of coke (it was further demonstrated in the next section). Consequently, the stabilities of all catalysts during the long-term reaction as the following order: Ni-Zn/ATP > Ni-Co/ATP > Ni-Cu/ATP > Ni/ATP.

3.3. Deactivation analysis

The used catalysts after 30 h of stability experiment were characterized by different technologies to study the major factors leaded to catalyst deacivation.

TEM images and the relevant frequency distribution histogram of particle szie of all spent catalysts were shown in Fig. 9. It can be observed that fibrous structures were existed all spent catalysts in comparison with the relating reduced catalysts (Fig. 3) [67,73], suggesting the catalysts possessed promising hydrothermal stability, which leaded to the ATP supported catalysts were appropriate to apply into GSR. In addition, it can be found that there were different degree of coke deposition with fibrous structure (whisker) deposited on the surfaces of spent Ni/ATP, Ni-Co/ATP and Ni-Cu/ATP catalysts [48,50,54]. While there was few carbon deposited on the Ni-Zn/ATP (Fig. 9D) catalyst was found only after a much more detailed and meticulous analysis. Meanwhile, it also can be observed that the sintering of active metal was happened on the surface of spent Ni/ATP, Ni-Co/ATP and Ni-Cu/ ATP catalysts. According to the mathematical statistics of particle size for spent catalysts (Fig. 9), the mean particle size of spent catalysts showed the following order: Ni/ATP (22.9 nm) > Ni-Cu/ATP (18.2 nm) > Ni-Co/ATP (15.1 nm) > Ni-Zn/ATP (11.9 nm). The particle size of Ni-Zn/ATP catalyst almost kept unchanged in comparison with that of reduced Ni-Zn/ATP (Fig. 3), so it showed the highest antisintering during the toleration experiment. This is attributed to the highest MSI demonstrated by H2-TPR. Consequently, Ni-Zn/ATP



Fig. 8. Time on steam experiments (A) Total glycerol conversion and glycerol conversion into gaseous products and the changes of H_2 yield and gaseous products' selectivities during 30 h of GSR reaction for all catalysts: (B) Ni/ATP, (C) Ni-Co/ATP, (D) Ni-Cu/ATP, and (E) Ni-Zn/ATP. [Reaction conditions: W/G = 9, T = 600 °C, N₂ flow ratio = 0.16 L/min and GHSV = 9619 h⁻¹.]

showed the highest stability in long-term test (Fig. 8).

XRD patterns of used catalysts upon the stability test were displayed in Fig. 10. Diffraction peaks attributed to Si-O-Si crystalline and quarz phases and the characteristic peaks assigned to ATP (110) and (161) planes were shown in all spent catalysts, suggesting the crystalline structures of ATP supported catalysts had no changes as compared with the reduced ones (Fig. 2B), which indicated the ATP as catalyst support had promising hydrothermal durability. Comparing with the diffraction peaks at around 26.6° for all reduced catalysts in Fig. 2B, the peaks at about 26.5° for all spent catalysts in Fig. 10 became wider and their intensities were obviously weaker, especially for spent Ni/ATP and Ni-Cu/ATP catalysts. As it has been highlighted by many authors [50,54,59], the carbon deposited on the surface catalysts could make the characteristic peak at about 26° assigned to graphitic carbon (JCPDS 41-1487) appear in XRD patterns of spent catalysts upon GSR. Combining with the results of TEM images (Fig. 9), the peaks at about 26.6° (Fig. 10) turned into wider and weaker were attributed to the carbon deposition on used catalysts. The widths and intension of corresponding peaks of spent Ni/ATP and Ni-Cu/ATP catalysts were broader and weaker than those of spent Ni-Co/ATP and Ni-Zn/ATP catalysts, showing the carbon deposition-resistances of Ni-Co/ATP and Ni-Zn/ATP catalysts were superior compared to other two catalysts. In addition, the diffraction peaks assigned to the active species (Niº metal or Ni-M alloys) at 20 about 44° and 51° (Fig. 10) were not differed from those in reduced catalysts (Fig. 2B). While their intensities were evidently higher than those of reduced catalysts, except from the Ni-Zn

catalyst, whose intensities almost in accordance with the reduced Ni-Zn catalyst. For further investigating the crystal sizes of active species of spent catalysts, their values were calculated by Scherrer's formula based on the peaks at about 44° and the results were presented in Table 1. It can be seen that the crystal sizes of active particles in spent Ni/ATP, Ni-Co/ATP and Ni-Cu/ATP catalysts were significant increased in comparison with the corresponding reduced catalysts, while that for spent Ni-Zn/ATP sample had a slightly increased from 10.3 nm to 11.2 nm (Table 1). Additionally, the corresponding crystal sizes for all spent catalysts as the following order: Ni/ATP (22.5 nm) > Ni-Cu/ATP (18.7 nm) > Ni-Co/ATP (14.3 nm) > Ni-Zn/ATP (11.2 nm) (Table 1). This indicated the Ni-Zn catalyst exhibited outstanding anti-sintering ability, resulting in it shown a promising catalytic stability in long-term GSR reaction. For the XRD results of spent catalysts, it drew a conclusion that all catalysts shown some amount of coke deposited on spent catalysts. In order to further highlight the anti-carbon deposition of asprepared catalysts, the TG and TPO-MS technologies were also employed to analyze the spent catalysts.

The properties of the coke deposited on spent catalysts were analyzed by TG as depicted in Fig. 11. The TG profiles of all spent catalysts revealed a clearly decrease in the region of 450 °C to 700 °C, which was attributed the combustion of carbon deposition [41]. Furthermore, the mass loss percentage of catalysts reduced in the following sequence: Ni-Zn/ATP (15.7%) < Ni-Co/ATP (24.0%) < Ni-Cu/ATP (32.9%) < Ni/ATP (47.2%). TPO was also conducted to determine the amount of coke formation over spent catalysts as presented in Fig. 12. It considered that the



Fig. 10. XRD patterns of spent catalysts.

peak area of Ni/ATP catalyst in TPO profiles as a criterion of "1" [83]. By quantifying the CO2 peak areas after normalized, the peak area ratio o Ni/ATP, Ni-Co/ATP, Ni-Cu/ATP and Ni-Zn/ATP was 1:0.74:0.80:0.69, suggesting the addition of promote metals (such as Co, Cu and Zn) inhibited the coke accumulated on the surface of bimetallic catalysts. The trend was in accordance with that of TG result. From the DTG curves in Fig. 11, it shown oxidation of the formed carbonaceous species on ATP supported Nibased catalysts occurred at considerably broader temperatures range from 450 and 650 °C, which may be attribute to the burning of multiple carbon species that formed in different proportion over all spent samples [83,86]. In order to further investigate the carbon species, the TPO analysis was showed in the next text.

Fig. 9. Representative TEM images and particle size distributions of spent catalysts. (A) Ni/ATP, (B) Ni-Co/ATP, (C) Ni-Cu/ATP, and (D) Ni-Zn/ATP.

= 22.9 mm

= 15.1 nm

30 35

20 25

(nm)

15 size (nm)

18.2 nm

40

= 11.9 nm



It has been reported that the peaks in TPO profiles at blow 360 °C were attributed to the burning of carbon deposition with highly reactive carbon species closer to the metal particles or amorphous carbon [21]; the peaks at the range temperature from 450 °C to 550 °C assigned to the oxidation of amorphous carbon or carbon filaments with lower ordered graphitic nature [101] and the peaks at high temperature $(> 600 \degree C)$ were ascribed to the combustion of highly ordered graphitic filamentous carbon [101,102]. From the TPO profiles in Fig. 12, it obviously found that there were two types of carbon deposited on Ni/ ATP and Ni-Cu/ATP catalysts. According to TEM results (Fig. 9A and C), the peaks in Ni/ATP and Ni-Cu/ATP at lower temperature were assigned to the oxidation of filamentous carbon with lower ordered graphitic nature. The other peak at higher temperature in all samples may be attributed to combustion of more ordered graphitic filamentous carbon. However, the central temperature of TPO peaks of Ni-Co/ATP



Fig. 12. TPO profiles for all spent catalysts.

and Ni-Zn/ATP was obviously lower temperature comparing with those in Ni/ATP and Ni-Cu/ATP, implying the filamentous carbon deposited on Ni-Co/ATP and Ni-Zn/ATP had lower ordered graphitized nature. As found in the recent study [46], the larger Ni particles were easier leaded to growth of carbon deposition to form highly ordered graphitic carbon, which was mostly responsible for the catalyst deactivation because it acted like a shell on the catalyst covering the active sites layer by layer. Therefore, the stability on Ni-Co/ATP and Ni-Zn/ATP is superior to others. In addition, the TPO profile's area of Ni-Zn/ATP was slightly lower than that of Ni-Co/ATP (as shown in above section), suggesting the amount of coke deposition of Ni-Zn/ATP was lower. Meanwhile, Ni-Zn/ATP catalyst also showed higher anti-sintering ability of active metal in comparison with Ni-Co/ATP (demonstrated by XRD and TEM data.), resulting in it presented the excellent stability compared to other catalysts.

4. Conclusions

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 GSR reaction. It was concluded that the catalytic activity in terms of glycerol total conversion and its conversion into gaseous products increase with increasing of reaction temperature from 500 °C to 700 °C for all test catalysts. As expected, the bimetallic catalysts showed the higher glycerol conversions and H₂ yield, especially for Ni-Cu/ATP. It was attributed to that the crystal size and reducibility of catalysts, as well as its metal-support interaction were affected and changed by the addition of second metals, which had been demonstrated by XRD, XPS and H2-TPR characterizations, respectively. Furthermore, these changes of physicochemical properties showed pivotal to impart suitable catalytic activity. In addition, the addition of second metals also changed the reaction pathways, speculating from the changes of the H₂/CO and CO/CO₂ molar ratios obtained from GSR reaction. Obviously, bimetallic catalysts improved the methane reforming and water-gas shift reaction. Meanwhile, the stability test was also conducted out over all catalysts. The Ni-Zn/ATP catalyst exhibited the unique stability during 30 h of GSR reaction that related to the superior metal-support interaction, which could inhibit the formation of coke and suppress the sintering of active metal. Therefore, Ni-based bimetallic catalysts supported on attapulgite can be turned into a very promising candidate for glycerol steam reforming to produce H₂.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2017.11.014.

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