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Glycerol steam reforming over hydrothermal synthetic Ni-Ca/attapulgite for green hydrogen generation



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ABSTRACT

Glycerol steam reforming (GSR) is one of the promising technologies that can realize renewable hydrogen production and efficient utilization of crude glycerol. To illuminate the functions of Ca content (3%, 6%, 9%, and 12%, by mass) and preparation method for Ni/ATP catalyst structure and its catalytic behaviors, the Ni-*x*Ca/ATP (*x* = 3%, 6%, 9%, and 12%, by mass) catalysts are prepared by co-impregnation (*ci*) and hydrothermal synthesis (*hs*) method and then tested in GSR. Characterization results of XRD, N₂ adsorption-desorption, H₂-TPR, HRTEM, XPS, and NH₃/CO₂-TPD demonstrate that the combined effect between appropriate Ca additive (6%, by mass) and *hs* enhance catalyst reducibility, uniform distribution of Ca additive and nickel species over ATP, and adsorption for CO₂. This attributes to *hs* method protects the ATP framework through suppressing the interaction of Ca with ATP and promotes the formation of Ni-CaO_x interface sites. Therefore, Ni-6Ca/ATP-*hs* exhibits the highest conversion (86.77%) of glycerol to gas product and H₂ yield (76.17%) and selectivity (58.56%) during GSR. Furthermore, XRD, HRTEM, TG-DTG and Raman analyses confirm that Ni-6Ca/ATP-*hs* also reveals outstanding anti-sintering and coke resistance. In addition, the structural evolution process of Ni/ATP catalyst with Ca introduction and *hs* method is presented. Considering the high performance, simple preparation process and low cost, the as-prepared catalyst providing new opportunities for utilization of glycerol derived from biodiesel industry.

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1. Introduction

Contemporarily, taking advantage of renewable energy resources such as biodiesel and biomass has become an imperative strategy to relieve the issues of fossil fuel depletion and environmental deterioration [1,2]. Biodiesel, before all, is a promising bio-fuel used for transportation because of its adaptability of manufacture by transesterification of not only conventional free fatty acids (FFAs) but also nonedible oils [3–5]. During the biodiesel production, crude glycerol as the main by-product accounts around 10% (mass) of total biodiesel [6,7]. Crude glycerol has inevitably increased and been perceived as an oversupplied waste along with the rapid consumption and manufacture of biodiesel. The management and utilization of crude glycerol waste that contains abundant water and other contaminants has been considered as

one of the central challenges for the biofuel industry due to the disposal and purification cost [8,9].

Glycerol steam reforming (GSR) for hydrogen production is a promising tactic for handling crude glycerol [10–16]. This process does not only to eliminate needlessly water but also capable of realizing sustainably produced hydrogen, which is perceived as a reasonable level of energy sources. It has well established that obtained high-purity hydrogen production from GSR is impacted obviously by multiple steps such as water-gas shift reaction (WGS), methanation, and intermediate species steam reforming (SR) reactions [6,10,11].

Generally, the development of applicable and cost-effective heterogeneous catalysts for GSR reaction is the significant important for determining glycerol conversion and H₂ selectivity/yield. This is a consequence of aforementioned complex reactions happened during GSR are tempestuously affected by the formulas, structure, morphologies and characters of catalysts [6,10,11,17–19]. Consequently, a myriad of efforts have been absorbed in developing catalysts based on precious and transition

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metals such as Pt [20,21], Ru [22,23], Ni [6,12,16,24,25], and Co [26,27]. Therein, nickel-based catalysts have been widely studied during SR of glycerol or other oxygenates since Ni metal sites have unique dehydrogenation capacity, high catalytic activity for cleaving C–C and C–H bonds and low cost [6,28–38]. However, the sintering of active nickel species and coke formation, which resulted from the carbophile of Ni metal phase and surface acidic sites, have been generally deemed to be the primary challenge of Ni-based catalysts for GSR [6,18,25,39,40].

To date the great deal of scientific attentions have been given to promote the efficiency and stability of Ni-based catalysts by revealing the reaction mechanisms of GSR [28,41], optimizing the dispersion/reducibility of active Ni species and textural structure [13–15,42–44], heightening metal-support interaction [6,42] and decreasing the surface acidic sites [45–47]. What calls for special attention is that these characters can be regulated synchronously through introducing promising promoters (La, Ce, Ca or Co), selecting peculiar supports (SBA-15, zeolite and attapulgite (ATP)) or employing applicable and convenient preparation process.

Wang *et al.* [6] found metal-modified Ni/ATP catalysts presented unique activity for GSR reaction and the characterization results demonstrated the addition of second metals obviously decreased the crystal size of Ni nanoparticles and improve the metal-support interaction, which strongly catalyzed the SR of glycerol and intermediates and enhanced WGS, where the maximized conversion of glycerol to gas product (79.7%) and H₂ yield (4.11 mol/mol glycerol) were achieved over Ni-Cu/ATP catalyst. Jing *et al.* [15] reported that addition of Ce into Ni-Al catalysts could promote the formation of Ni-Ce-O solid solution, leading to restrict the agglomeration of Ni species, create oxygen vacancies and improve the oxygen mobility, which further increased Ni dispersion and surface area and suppressed successfully carbon deposits. Among them, NiCe_{0.7}Al catalyst exhibited the 89.2% of glycerol conversion to gas and 82.9% of H₂ selectivity. Bizkarra *et al.* [48] selected CeO₂-modified zeolite L with different shape and size (nanocrystals and discs) as support to load Ni species and found that the catalysts with disc shape were the most active and produced superior hydrogen yields for SR of bio-oil/glycerol mixture. They attributed the unique performance to the optimized metal size and reducibility by zeolite disc shape. Additionally, the group of Yadav investigated hydrogen production *via* GSR process over Ni-Cu and Ni-Co supported on La-Mg based metal oxides prepared through coprecipitation and impregnation [40], and the results exhibited coprecipitation method was resultful for producing high H₂ yield (96.1% (mol)) attributing to better metal-support interaction and high surface area.

It is well established that basic promoters or additives including alkali metal and alkaline earth could not only neutralize the acid sites, but also favor steam adsorption and hydroxyl mobility on the catalyst surface [27,30,40,46,49]. These causes could alleviate dehydration/condensation reactions and facilitate the oxidation of carbonic intermediate to suppress carbon deposits. Calcium is a sixpenny metal with basic properties and has been tested as catalyst or promoter in various reactions including catalytic pyrolysis upgrading of biomass [50,51], dry reforming of methane [52], Fischer-Tropsch synthesis [53], dimethyl ether one-step synthesis [54] and SR reaction [55,56] in previous reports. Recently, CaO and its modified-substances as CO₂ absorbent to *in situ* enhance SR and WGS processes to increase the purity of hydrogen has been given considerable attentions during sorption-enhanced steam reforming (SESR) [57–60]. Although CaO as CO₂ absorbent could increase the purity of hydrogen during SESR, the issues of saturation adsorption and reactivation process (generally operated high temperature >700 °C) would lead to CaO sintering and increase the economic cost. Therefore, to further study the application of Ca as a promoter for Ni-based catalysts and reveal its effect

on SR reactions has crucial significance for developing hydrogen production *via* GSR.

Clay based materials, including attapulgite (ATP), sepiolite, and montmorillonite, have been identified as cost-effective and eco-friendly catalyst supports and given serious efforts in a variety of catalytic reactions/processes due to their special structure, superior absorption and structural stability [61–67]. According to our previous work [6,16,68–70], ATP employed as support to load various active metal had been studied in different SR reactions and presented excellent performance for dispersing active species, improving porousness and increasing reactant adsorption of catalyzed material. However, the composition characteristics of ATP framework containing Al/Mg and Si atoms make it have massive surface hydroxyl groups and acidic sites, which leading inevitably to active Ni species agglomeration and coke germination.

In this paper, therefore, the effect of Ca promoter on the Ni/ATP structure in microcosmic level is fully investigated, and comparing the impact of hydrothermal synthesis (*hs*) method on Ca-modified Ni/ATP catalyst structure with traditional impregnation method. In addition, the catalytic behavior of Ca-modified Ni/ATP catalyst for hydrogen production *via* GSR was evaluated and its resistibility for carbon deposits and sintering was revealed.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparing Ni-xCa/ATP-*ci* catalysts

The chemicals including Ni(NO₃)₂·6H₂O and Ca(NO₃)₂·4H₂O used as the precursors of active Ni metal and Ca promoter are analytically pure and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (Shanghai, China). Raw ATP clay was from Suzhou city of China and purified according to previous report [16].

Ni-xCa/ATP-*ci* catalysts, in which Ni content was fixed at 10% and *x* represented the Ca content is equal to 3%, 6%, 9%, 12% (mass) respectively, were fabricated by using traditional co-impregnation (*ci*) method. Taking Ni-6Ca/ATP-*ci* as an example, weighing 2.95 g Ni(NO₃)₂·6H₂O and 2.10 g Ca(NO₃)₂·4H₂O to place jointly into 250 ml beaker and then adding 100 ml absolute ethyl alcohol to dissolve fully above nitrate species. Next, 5.00 g purified ATP material was slowly poured into above mentioned precursor salt solution along with continuous agitation at 60 °C for 2 h under airtight condition. Then the obtained suspension denoted as **S** was heated steadily at 60 °C with continuous stirring until to outright evaporate and eliminate ethyl alcohol to produce solid product. The solid product was subsequently underwent dry (105 °C for 12 h), grind and sieving (80 mesh, 0.18 mm) processes to obtain the precursor of Ni-6Ca/ATP catalyst. With that, the precursor was calcined at 600 °C in tube furnace with a heating rate of 2 °C·min⁻¹ for 4 h under the air to prepare the calcined Ni-6Ca/ATP catalyst. Therefore, a series of calcined Ni-xCa/ATP-*ci* catalysts were synthesized following the above described steps by only changing the amount of Ni(NO₃)₂·6H₂O and Ca(NO₃)₂·4H₂O.

In order to compare, the calcined Ni/ATP sample was also prepared using aforementioned process without adding Ca(NO₃)₂·4H₂O.

2.1.2. Preparing Ni-6Ca/ATP-*hs* catalysts

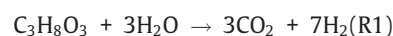
For the sake of comparing the influence of preparation method on the structures and characteristics of Ca-modified Ni/ATP catalysts, the hydrothermal synthesis (*hs*) method was employed. The process was similar to co-impregnation method except for adding the hydrothermal treatment technology. Concretely, before evaporation and elimination of ethyl alcohol the suspension **S** was

moved to high-pressure reaction vessel to hydrothermal treatment 16 h at 180 °C with 300 r·min⁻¹. After that, the following processes were same with co-impregnation method. It is worth mentioning that only Ni-6Ca/ATP-*hs* catalyst was prepared to reveal the impact of preparation methods.

The corresponding reduced catalysts mentioned in this work were the calcined counterpart activated at 700 °C in a 400 ml·min⁻¹ of 10% (vol) H₂/N₂ flow and holding on 2 h.

2.2. Catalytic tests for GSR

The evaluation of as-prepared catalysts for catalyzing GSR reaction was implemented in fixed bed stainless steel tubular reactor. The special parameters were reported in previous work [70]. Firstly, 1.50 g calcined catalyst was fixed at reactor middle by two-layer silica wool and activated *in situ* under 400 ml·min⁻¹ of 10% (vol) H₂/N₂ flow at 700 °C for 2 h. Then, the reactor cooled down to 600 °C and was purged by 400 ml·min⁻¹ of high-purity N₂ flow for 30 min. Subsequently, the reactants water and glycerol with the mole ratio of W/G = 3 were blended and imported into the preheater (280 °C) with a flow quantity of 13.71 g·h⁻¹ by using HL-2D constant flow pump (Shanghai Huxi Analysis Instrument Factory Co., Ltd, China) and then followed into reactor [6,16]. Meanwhile the carrier gas was 160 ml·min⁻¹ of N₂ flow. Generally, the effluent gas went through a cold trap and the non-condensable gas was collected by gasbag per 30 min. The gaseous products were analyzed on Huaai GC-9160 (Shanghai, China) by TCD equipped with TDX-01 column. Every experimental test was carried out three times using the same conditions and then used mean value to express the catalytic performance. Based on the theoretical stoichiometric reaction of GSR (R1), the conversion of glycerol to gas products, the yield and selectivity for H₂ and C1 species (such as CO, CO₂ and CH₄) were defined as following (Eqs. (1)–(5)).



Conversion of glycerol to gas products

$$= \frac{\text{Total mole of C in C1 species in outlet}}{\text{Total mole of C in feedstock}} \times 100\% \quad (1)$$

$$\text{H}_2 \text{ yield} = \frac{\text{The mole of H}_2 \text{ obtained in outlet}}{7 \times \text{mole of glycerol in feedstock}} \times 100\% \quad (2)$$

$$\text{H}_2 \text{ selectivity} = \frac{\text{The mole of H}_2 \text{ obtained in outlet}}{\text{C atoms obtained in gas product}} \times \frac{1}{r} \times 100\% \quad (3)$$

where *r* is the reforming ratio (7/3), defined as the ratio of moles of H₂ to CO₂ according to reaction R1.

$$\text{Yield of C1 product} = \frac{\text{The mole of C1 species obtained in outlet}}{\text{total C atoms in feedstock}} \times 100\% \quad (4)$$

$$\text{Selectivity to C1 product} = \frac{\text{The mole of C1 species in outlet}}{\text{Total mole of C1 species in outlet}} \times 100\% \quad (5)$$

C1 species represent CO, CO₂, CH₄, respectively.

2.3. Catalyst characterizations

XRD tests of the calcined/reduced/spent catalysts were conducted on a Rigaku Corporation SmartLab SE X-ray diffractometer (Japan) with the Cu K_{α1} X-ray source ($\lambda = 0.15406$ nm) and operated at 40 kV and 40 mA. XRD patterns were collected in the 2θ range of 5°–80° with 0.02° step size and analyzed in JADE 6 (Materials Data Inc., Livermore, CA) based on the International Centre for Diffraction Data database (ICDD) to determine crystalline structure and measure the particle size of Ni metal according to Debye-Scherrer formula. N₂ adsorption-desorption measurement was performed on a Multi-station automatic specific surface and porosity tester (BELSORP-mini II) of MicrotracBEL Japan, Inc. under liquid nitrogen atmosphere (–196 °C). Before testing, the sample was pretreated at 250 °C under vacuum for 4 h. The surface area was obtained using BET (Brunauer-Emmett-Teller) method, and the pore volume and diameter were obtained using BJH (Barrett-Joyner-Halenda) method based on the desorption isotherms. X-ray photoelectron spectroscopy (XPS) detection was operated on a Thermo Fisher Scientific ESCALAB250Xi (UK) with a monochrome Al K_α source (1486.68 eV) under the conditions of 150 W and 500 mm beam spots. XPS spectra were further fitted and analyzed using the Thermo Advantage v5.52 software (Thermo Fisher Scientific, Micro Focus Ltd). The catalyst surface morphologies were investigated using high-resolution transmission electron microscopy (HRTEM) under an FEI Tecnai G2 F20 (200 kV) transmission electron microscope (USA). H₂-temperature-programmed reduction (H₂-TPR) analysis was implemented in AutoChemII 2920 instrument (USA). Specifically, about 10 mg sample was pretreated in 40 ml·min⁻¹ of high-purity Ar flow at 200 °C for 2 h, then cooled down to room temperature. Next, 40 ml·min⁻¹ of 10% (vol) H₂/Ar flow was added into AutoChemII 2920 instrument to replace the high-purity Ar flow and then the instrument was heated from room temperature to 800 °C with a heating rate of 10 °C·min⁻¹. Meanwhile, the hydrogen uptake signals were collected and detected using TCD detector. NH₃/CO₂-TPD characterizations were also performed on the AutoChemII 2920 instrument (USA). Generally, the sample firstly experienced pretreatment process at 200 °C for 1 h in the 30 ml·min⁻¹ He flow, then the temperature was cooled down to 50 °C (100 °C for CO₂-TPD analysis) and adsorbed NH₃ using 50 ml·min⁻¹ of 5% (vol) NH₃/He flow or adsorbed CO₂ using 50 ml·min⁻¹ of CO₂ flow for 1 h to realizing sample saturation adsorption. Subsequently, the sample was heated to 650 °C with 10 °C·min⁻¹ speed in a 40 ml·min⁻¹ He flow and the desorbed signals of NH₃ and CO₂ were recorded. Raman test was conducted on a Renishaw Invia analyser (UK) and the corresponded spectra were collected in the range of 1000–2000 cm⁻¹. Thermal gravimetric (TG) and the derivative thermogravimetric analysis (DTG) was carried out on a STAR^e System instrument (Switzerland). 5 mg sample was placed in a platinum crucible and heated from ambient temperature to 800 °C with 10 °C·min⁻¹ heating rate under 50 ml·min⁻¹ of air flow.

3. Results and Discussion

3.1. Catalyst structure and character analysis

3.1.1. X-ray diffraction (XRD) analysis

Fig. 1 exhibits the XRD diffraction patterns of calcined and reduced Ca-modified Ni/ATP catalysts, showing the evolutions of crystalline structure of as-prepared catalysts with Ca content and preparation process. Obviously, in calcined Ni/ATP sample (Fig. 1 (A)), the diagnostic diffraction peaks of ATP appear at 8.5°, 13.7°, 19.8°, 27.8° and 34.7° based on previous report [47,70], and the peaks at 20.8° and 26.6° are assigned to SiO₂ substance [16]. In

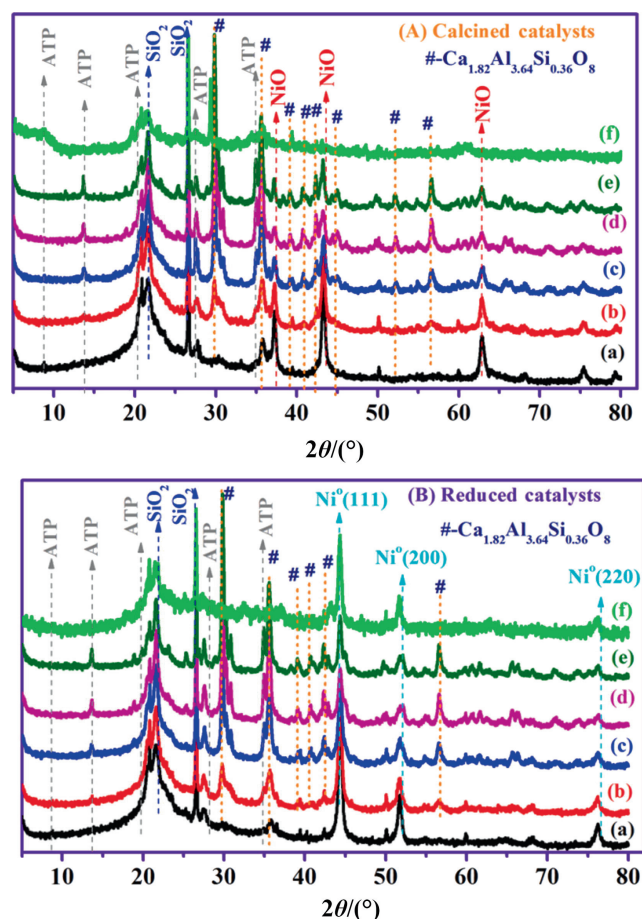


Fig. 1. XRD patterns of calcined and reduced catalysts. [(a) Ni/ATP, (b) Ni-3Ca/ATP-ci, (c) Ni-6Ca/ATP-ci, (d) Ni-9Ca/ATP-ci, (e) Ni-12Ca/ATP-ci, and (f) Ni-6Ca/ATP-hs.]

addition to that, it also finds some high-intensity peaks at 37.4° , 43.3° and 62.6° in calcined Ni/ATP, which attributing to the characteristic peak of NiO. After Ca introduction by co-impregnation method, the diffraction peaks of ATP, SiO_2 and NiO are observed clearly at their specific locations in calcined Ni-xCa/ATP-ci, but the intensities of ATP and NiO characteristic peaks are gradually decreased with Ca content. Furthermore, there are some neonatal peaks appear at 29.8° , 35.6° , 39.2° , 40.9° , 42.4° , 45.1° , 52.1° and 56.7° , owing to the specific diffractive peaks of calcium aluminum silicate species $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$. These results demonstrate that part of the Ca ions migrate into the framework of ATP and interact with Al/Si atoms of ATP to form $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ species, which then changing the interaction of NiO with ATP. Consequently, characteristic peak intensities of ATP and NiO are reduced with

Ca content, leading to the attenuation of their crystallization degree. Based on the Debye-Scherrer formula, the particle size of NiO shows an apparent decrease with Ca addition as the data listed in Table 1. The most noteworthy is that no NiO and $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ diffraction peaks are determined in calcined Ni-6Ca/ATP-hs prepared by hydrothermal synthesis and the peaks of ATP are weakened, but that of SiO_2 presents a slight increase in comparison with calcined Ni-6Ca/ATP-ci. These phenomena suggesting that the hydrothermal synthesis process inhibited the interaction of Ca with ATP framework, developed the dispersion of nickel oxides and enhanced the homogeneity among nickel species, Ca additive and ATP.

Went through reduction treatment, as shown in Fig. 1(B) the diffraction peaks of ATP, SiO_2 and $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ are clearly presented in reduced catalysts in comparison with the corresponding calcined counterpart. Notably, the characteristic peaks of NiO are disappeared and the emerging diffraction peaks at 44.4° , 51.8° and 75.1° ascribe to the (1 1 1), (2 0 0) and (2 2 0) lattice planes of Ni metal phase, respectively [32]. From the data in Table 1, the Ni size of reduced catalyst reduces from 18.0 nm in Ni/ATP to 13.1 nm in Ni-6Ca/ATP with Ca content, in the next moment it increases to 16.2 nm when the Ca content reaching to 12% (mass). This suggests that Ca addition by co-impregnation technique improves the dispersion of Ni, but superabundant Ca additive results in Ni metal reunion. The only difference is that hydrothermal synthesis technique leads to the significant increase of Ni particle size (19.4 nm for Ni-6Ca/ATP-hs). It may be attributed to the enhanced reducibility as revealed by H_2 -TPR analysis in the next section.

3.1.2. N_2 adsorption-desorption characterization

N_2 adsorption-desorption characterization is employed to further reveal the impact of Ca content and preparation method on the textural properties of as-prepared catalysts. Fig. 2(A) shows that all calcined samples have a III-type adsorption-desorption isotherms coupled with a well-defined H3-type hysteresis loops according to the IUPAC classification [16,47], suggesting calcined catalysts have abundant mesoporous channels consisted of the stacked lamellar nanorods of ATP. Clearly, upon increasing the Ca content, the hysteresis loops of Ni-xCa/ATP-ci rapidly shrunk in comparison with that of Ni/ATP. Furthermore, the surface area (S_{BET}) and pore volume (V_{pore}) significantly reduce from $115.62 \text{ m}^2\cdot\text{g}^{-1}$ and $0.265 \text{ m}^3\cdot\text{g}^{-1}$ of Ni/ATP to only $4.78 \text{ m}^2\cdot\text{g}^{-1}$ and $0.041 \text{ m}^3\cdot\text{g}^{-1}$ of Ni-12Ca/ATP-ci according to the data listed in Table 1, while the pore diameter (D_{pore}) increases from 8.8 nm to 18.4 nm. This indicative of Ca additive entered into ATP framework blocking the smaller pores and then they interacted with ATP framework during calcination process upon increasing Ca content, ultimately leading to the destruction of ATP and the generation of new species such as $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ that has confirmed by XRD. Therefore, the S_{BET} and V_{pore} exhibit the tremendous reduction.

Table 1

The particle sizes of Ni species and textural properties of samples

Samples	Particle size ^① /nm			Sinter degree ^② /%	Textural properties of calcined catalysts ^③		
	NiO	NiO of reduced catalysts	NiO of spent catalysts		$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{pore}}/\text{m}^3\cdot\text{g}^{-1}$	$D_{\text{pore}}/\text{nm}$
Ni/ATP	25.8	18.0	24.7	37.2	115.62	0.265	8.8
Ni-3Ca/ATP-ci	18.0	16.4	19.7	20.1	20.85	0.093	20.5
Ni-6Ca/ATP-ci	19.4	13.1	15.2	16.0	47.14	0.186	16.3
Ni-9Ca/ATP-ci	18.5	13.9	17.5	25.9	5.74	0.033	17.5
Ni-12Ca/ATP-ci	21.2	16.2	21.3	31.5	4.78	0.041	18.4
Ni-6Ca/ATP-hs	–	19.4	22.1	13.9	90.82	0.253	9.1

^① The data were obtained from the characteristic diffraction peaks of NiO at 43.3° and Ni metal at 44.4° in XRD results according to Debye-Scherrer formula.

^② The data were calculated based on the equation: $(\text{Ni}^0 \text{ particle size of spent catalyst} - \text{Ni}^0 \text{ particle size of reduced catalyst})/\text{Ni}^0 \text{ particle size of reduced catalyst} \times 100$.

^③ The data were calculated based on the results of N_2 adsorption-desorption analysis of calcined samples.

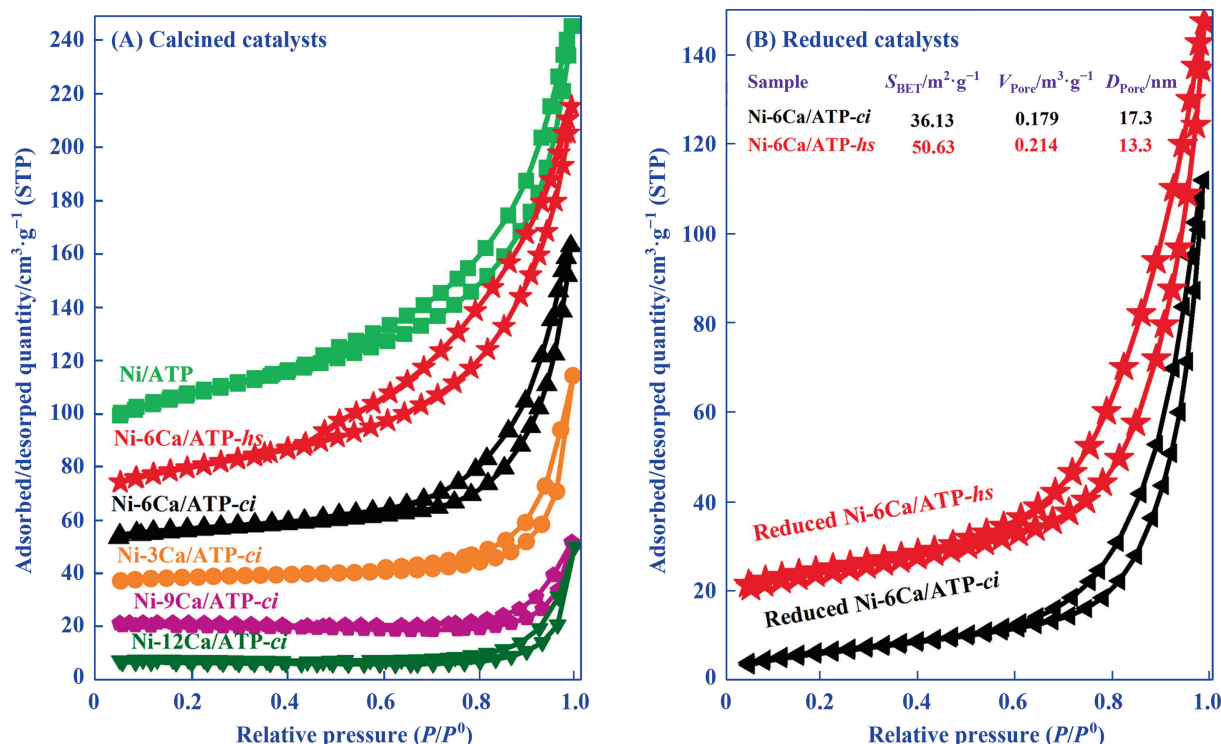


Fig. 2. The N_2 adsorption-desorption isotherms of nickel-based catalysts in different states.

Obviously, the hysteresis loop of Ni-6Ca/ATP-hs is larger than that of Ni-6Ca/ATP-ci and slightly smaller than that of Ni/ATP. Additionally, the S_{BET} and V_{pore} of Ni-6Ca/ATP-hs are $90.82 \text{ m}^2\cdot\text{g}^{-1}$ and $0.253 \text{ m}^3\cdot\text{g}^{-1}$ presenting a little lower than Ni/ATP. There causes imply that hydrothermal synthesis could inhibit the pore blocking and interaction of Ca promoters with ATP framework. It is possibly accepted that the inhibition of Ca migrated into ATP channel could promote the contact between Ca promoters and Ni species to form NiO-CaO_x interface.

In addition, the N_2 adsorption-desorption isothermal curves and textural properties of reduced Ni-6Ca/ATP-ci and Ni-6Ca/ATP-hs are presented in Fig. 2(B), revealing reduction or activation process makes the reduction of S_{BET} and V_{pore} reduce and the increase of D_{pore} in comparison with their calcined counterparts. This can be owing to the transformation of nickel oxide species into metallic nickel during reduction process, resulting in the disappearance of some smaller pores. Importantly, the S_{BET} and V_{pore} of reduced Ni-6Ca/ATP-hs are still larger than those of reduced Ni-6Ca/ATP-ci, implying further hydrothermal synthesis method fabricated NiO-CaO_x interface can transform into Ni-CaO_x interface sites during reduction process to improve its textural property. This is important for increasing the catalytic performance for GSR reaction.

3.1.3. XPS analysis

XPS spectra analysis technology is implemented to determine the metal-support and chemical states of calcined catalysts, and the XPS spectra of Ni 2p, Ca 2p, Al 2p, Mg 2p and Si 2p were shown in Fig. 3. Commonly, the Ni 2p XPS spectrum could be split into two major peaks at about 856 eV and 874 eV with two satellite peaks, respectively, which attributed to the Ni 2p_{3/2} and Ni 2p_{1/2} resulted from the spin splitting of Ni 2p orbit [6,52]. It had reported that the binding energy (BE) of Ni 2p_{3/2} of pure NiO located at about 854.4 eV [52,71]. In Fig. 3(A), after deconvolution, the conjugated fitting peaks at 854.2 eV and 871.8 eV in calcined Ni/ATP ascribed

to the bulk NiO or NiO species with weak interaction with ATP support, the other coupled peaks at 856.4 eV and 874.0 eV attributed to the Ni²⁺ species stronger interacted with ATP framework [13,15]. For Ni 2p XPS spectrum of Ni-6Ca/ATP-ci, it presented the similar fitting peaks with Ni/ATP, but the peak area of bulk NiO or NiO species weakly interacted with ATP significantly increased. This indicative of Ca additive clearly changed the nickel-ATP interaction. Ca migrated into the interior of ATP resulted in the generation of Ca_{1.82}Al_{3.64}Si_{0.36}O₈, so released more isolated bulk NiO species. Therefore, the fitted peak area of NiO species in Ni-6Ca/ATP-ci is higher than that in Ni/ATP, in consistent with the results of TPR (as shown in next section). However, when introduced Ca into Ni/ATP using hydrothermal synthesis method, the fitting paired peaks attributed to isolated Ni²⁺ species moved to higher binding energy of 854.8 eV and 872.4 eV, furthermore, the paired peak at 856.4 and 874.0 eV that ascribed to Ni²⁺ species strongly interacted with ATP or CaO_x are significantly heightened. This further suggests that hydrothermal synthesis method altered the interacting behavior of nickel species with ATP support or CaO_x.

For further uncovering the interaction changes among various compositions in Ca-modified Ni/ATP caused by hydrothermal synthesis method, the XPS spectra of Ca 2p and ATP-skeleton atoms including Al 2p, Mg 1s and Si 2p are also presented in Fig. 3(B)–(E). As disclosed in Fig. 3(B), the Ca 2p XPS spectrum of Ni-6Ca/ATP-ci exhibited a major peak at 347.5 eV along with a shoulder peak at 351.0 eV. It is due to the ionization of Ca 2p_{3/2} and Ca 2p_{1/2} electrons of the Ca²⁺ oxidation state [72]. In Ni-6Ca/ATP-hs, the peaks of Ca 2p_{3/2} and Ca 2p_{1/2} clearly shift to lower BE values, suggesting the electron concentration in the surrounding area of Ca became higher when used hydrothermal synthesis method introduced Ca into Ni/ATP. Furthermore, from the XPS spectra of Al 2p, Mg 1s and Si 2p, it could be observed that the addition of Ca promoter resulted in the peaks of Al 2p, Mg 1s and Si 2p migrated into lower values as compared those in Ni/ATP, but these peak centers in Ni-6Ca/ATP-hs and Ni-6Ca/ATP-ci were almost identical. It indicative

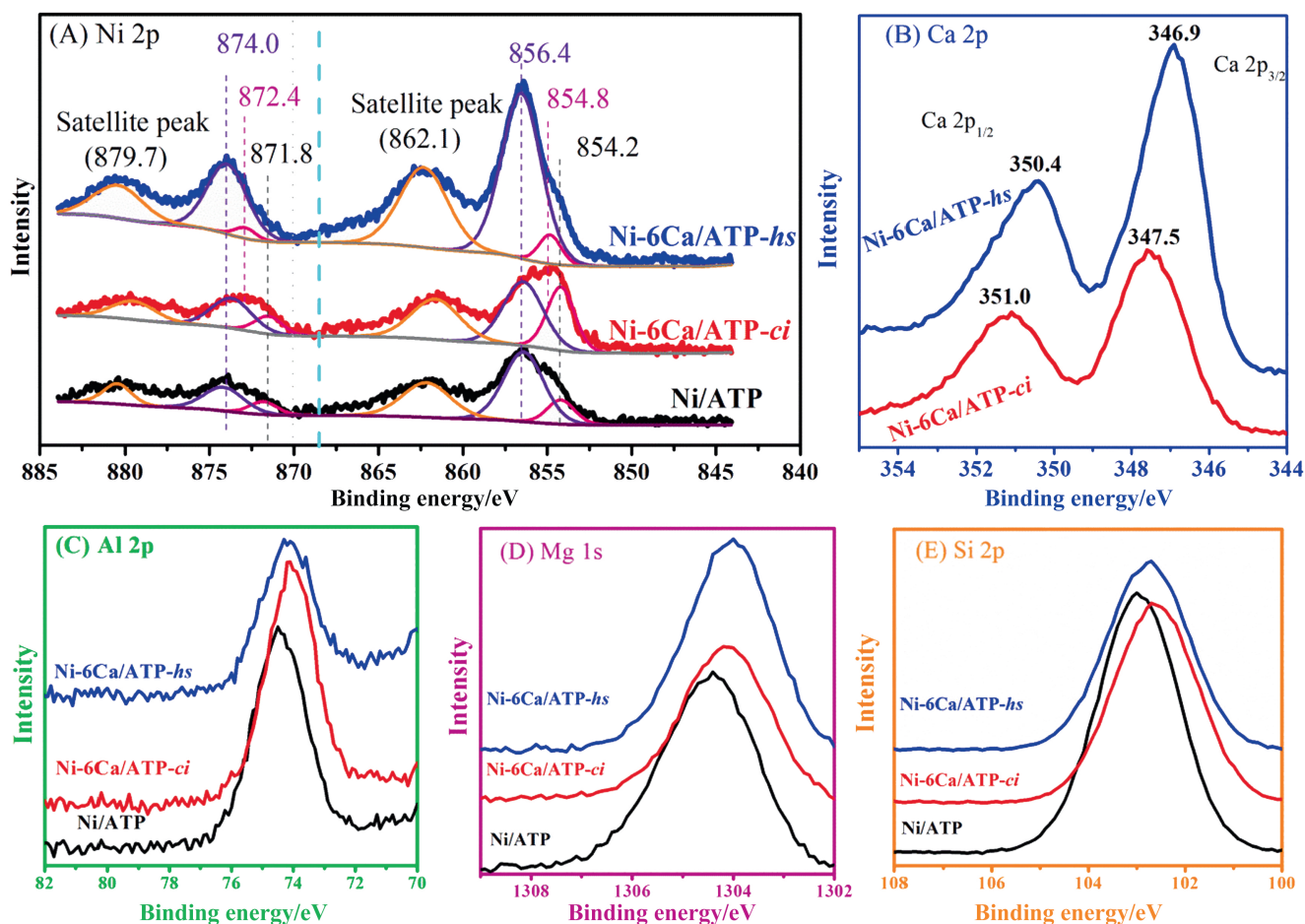


Fig. 3. The XPS spectra of Ni 2p, Ca 2p, Al 2p, Mg 1s and Si 2p of calcined catalysts.

of Ca additive changed the interaction between nickel species and ATP framework.

As confirmed by previous reports [47,68,70], the nickel species would interacted with the ATP framework in Ni/ATP catalyst to form abundant Ni-ATP interfaces, then improving the SR activity and stability. From XPS analysis, it found that Ca addition by utilizing co-impregnation method reduces the BE values of Al 2p, Mg 1s and Si 2p in comparison with those in Ni/ATP. Meanwhile, the peak of Ni 2p that attributed to isolated bulk NiO became more powerful in Ni-6Ca/ATP-ci. This cause demonstrated that Ca promoter altered the interaction of Ni^{2+} with ATP through the way that Ca interacted with ATP framework to form some new species $\text{Ca}_{1.82}\text{-Al}_{3.64}\text{Si}_{0.36}\text{O}_8$. However, it is noticed that employment of hydrothermal synthesis method to add Ca into Ni/ATP, the peak of Ni 2p shifted to higher BE and that of Ca 2p moved to lower BE, while the peaks of Al 2p, Mg 1s and Si 2p were similar to those of Ni-6Ca/ATP-ci. This could be owing to the newborn interaction of nickel species with CaO_x composition.

3.1.4. H_2 -TPR analysis

H_2 -TPR profiles are presented in Fig. 4 to exhibit the influences of Ca content and preparation method on the reducibility and metal-support interaction of Ca-modified Ni/ATP catalysts. For Ni/ATP sample, the reduction peak at low temperature (404 °C) is assigned to the reduction of NiO species had bulk phase or weakly interacted with ATP support. The peak at high temperature (651 °C) is ascribed to the reduction of Ni^{2+} species that had stronger interaction with ATP support or entrapped into the matrix of ATP framework [70,71]. Clearly, after the Ca induction by

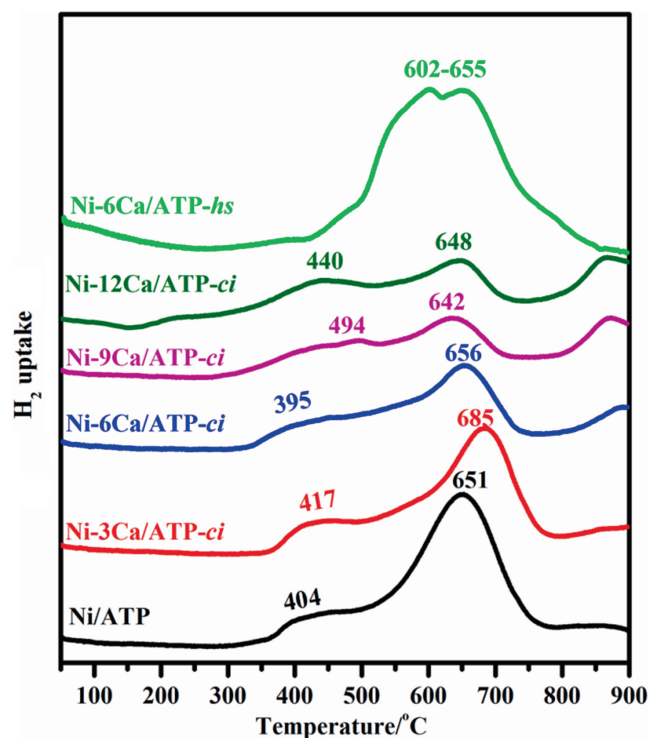


Fig. 4. The H_2 -TPR profiles of calcined nickel-based catalysts.

co-impregnation method, all Ni-xCa/ATP-*ci* catalysts have two major reduction peaks in line with Ni/ATP catalyst, but the reduction peaks of Ca-promoted Ni/ATP samples become weak and reveal a slight migration. It can be implied that Ca additive obviously changes the interaction of NiO species with ATP through interacting with ATP framework to produce some new species as presented by XRD analysis. Furthermore, the data listed in Table 2 reveal that the molar ratio of NiO species in Ni-xCa/ATP-*ci* displays increased tendency and their reduction degree of have a significant decrease with Ca content, which further indicative of Ca addition improves the interaction between NiO species and decreases the reduction degree, then causing the production of smaller Ni⁰ particle size. However, there is broad and symmetrical peak appears in the profile of Ni-6Ca/ATP-*hs*, in which its reduction degree reaches to 85.24%. This indicating hydrothermal synthesis method meaningfully changes the distribution of Ni species and enhances the reducibility of catalyst. It can be attributed that this strategy alter the interaction among Ca additives, NiO species and ATP support through forming new interface sites such as Ni-CaO_x and Ni-ATP.

3.1.5. HRTEM characterization

The surface configuration and particle size distribution of reduced catalysts influenced by Ca addition and synthetic method are investigated by HRTEM and the results show in Fig. 5. For all selected reduced sample, it observes that there are some black spheroidal particles as presented in (Fig. 5(A1), (B1) and (C1)), which are considered as Ni metal particles, which uniformly anchoring in the surface of support. Clearly, the Ni particle size distribution of Ni-6Ca/ATP-*hs* is more homogeneous and major concentrates in 17–28 nm with mean value of 22.5 nm (Fig. 5(C3)) in comparison with those of Ni/ATP and Ni-6Ca/ATP-*ci*, demonstrating hydrothermal synthesis optimizes the Ni metal distribution. In addition, stack-type rod-like fibres of ATP fundamental structure are well found in reduced samples. But for Ni-6Ca/ATP-*ci*, the rod-like fibres (Fig. 5(B1)) are out of shape and some eruciform species appeared (Fig. 5(B2)), which might be owing to the formation of Ca_{1.82}Al_{3.64}Si_{0.36}O₈ species as conformed by XRD analysis. Furthermore, in all reduced Ca-modified catalysts, the interplanar spacing (*d*) values are observed to be 0.204 nm, 0.176 nm and 0.125 nm (Fig. 5(B2) and (C2)), which are in good agreement with the (1 1 1), (2 0 0) and (2 2 0) planes of the Ni metal, respectively. However, a *d* values of 0.245 nm assigned to the (1 1 1) plane of NiO were found in all samples, suggesting some reduced Ni species were re-oxidized to form NiO species during *ex-situ* HRTEM characterization.

3.1.6. Surface acid/base analysis

The total acidity/basicity and relative strength over the surface of the different reduced catalysts were identified by NH₃/CO₂-TPD

and the resulted profiles are exhibited in Fig. 6. It observes that the NH₃ desorption of Ni/ATP catalyst showed two distinct peaks as displayed in Fig. 6(A), which assigned to the low-strength and moderate acid sites, respectively. These peaks attributed to the desorption of NH₃ adsorbed on Brønsted-acidic sites (OH groups) originated from the Al constituent in Ni/ATP, in agreement with the reports about the Al₂O₃-based materials [21,73]. Ca doping had a strong interplay on the NH₃ desorption peaks, consequently, on the distribution of acidic sites. The introduction of Ca by co-impregnation method resulted in the dramatic reduction of adsorbed amount of NH₃, which might be attributed to the Ca additive interacted with the framework of ATP to form new species led to the sharp decrease of surface Brønsted-acidic sites. It is noteworthy that the NH₃ desorption profile of Ni-6Ca/ATP-*hs* presented three distinguishable TCD peaks, which related to the low-strength, moderate and high-strength acid sites. The obtained amount of acid sites distribution over the reduced catalysts is exhibited in Table 3. It demonstrates that the weak and medium acid sites present the order of Ni/ATP > Ni-6Ca/ATP-*hs* > Ni-6Ca/ATP-*ci*, while Ni-6Ca/ATP-*hs* has 0.2132 mmol NH₃/(g cat)⁻¹ of strong acid sites. These causes confirm that Ca additive and preparation method have striking influence on the distribution of acidic sites. Calcium is a one of typical alkaline elements tend to neutralize the acid sites in solid catalyst surface [55]. Therefore, the addition of Ca significantly reduces the weak and medium acid sites of Ca-modified Ni/ATP. However, there are strong acid sites detect in Ni-6Ca/ATP-*hs*. This may be due to the hydrothermal synthesis method enhances the interaction between Ni and Ca additive and then inhibits Ca interacted with ATP to form more Ni-CaO_x interfaces in catalyst surface. Papageridis *et al.* [74] had reported that the peaks observed at temperatures higher than 500 °C in NH₃-TPD profiles might partially owing to NO_x species being produced for NH₃ reacted with the low coordination oxygen species of the catalyst. This further demonstrates the surface of reduced Ni-6Ca/ATP-*hs* is different from other two catalysts and has different oxygen species, which may in favor of suppressing carbon deposits during GSR reaction.

As shown in Fig. 6(B), CO₂ desorption profile of reduced Ni/ATP has two major peaks at 50–210 °C and 230–500 °C. Commonly, CO₂-TPD profile could identify the weak, medium and strong basic sites over the catalyst surface in line with the CO₂ desorption peaks at below 200 °C, between 230–500 °C and beyond 500 °C, respectively [72]. Therefore, most of basic sites presented in Ni/ATP are of weak and moderate strength, which might be attributed to the interaction of CO₂ with the basic surface OH— groups and Ni^{σ+}-O²⁻ acid-base pairs in Ni/ATP, respectively [74]. For Ni-6Ca/ATP-*ci*, there are two debilitated CO₂-desorption peaks appeared at similar temperature range in comparison with Ni/ATP. Generally, CaO is a promising CO₂ adsorbent and could increase CO₂

Table 2

The hydrogen consumption of different reduction peak, molar ratio of NiO and Ni²⁺ species, and reduction degree

Samples	Hydrogen consumption of peak at lower 500 °C/(mmol·(g cat) ⁻¹)	Hydrogen consumption of peak at higher 500 °C/(mmol·(g cat) ⁻¹)	Ratio of NiO/% (mol)	Ratio of Ni ²⁺ /% (mol)	Reduction degree ^① /%
Ni/ATP	0.035	0.784	4.23	95.73	48.15
Ni-3Ca/ ATP- <i>ci</i>	0.046	0.597	7.15	92.85	37.80
Ni-6Ca/ ATP- <i>ci</i>	0.032	0.354	8.29	91.71	22.69
Ni-9Ca/ ATP- <i>ci</i>	0.017	0.151	10.12	89.89	9.88
Ni-12Ca/ ATP- <i>ci</i>	0.054	0.150	26.47	73.53	11.97
Ni-6Ca/ ATP- <i>hs</i>	/	1.450	/	100	85.24

^① The theoretical H₂ uptake based on the reduction Ni loading was 1.701 mmol/(g cat)⁻¹.

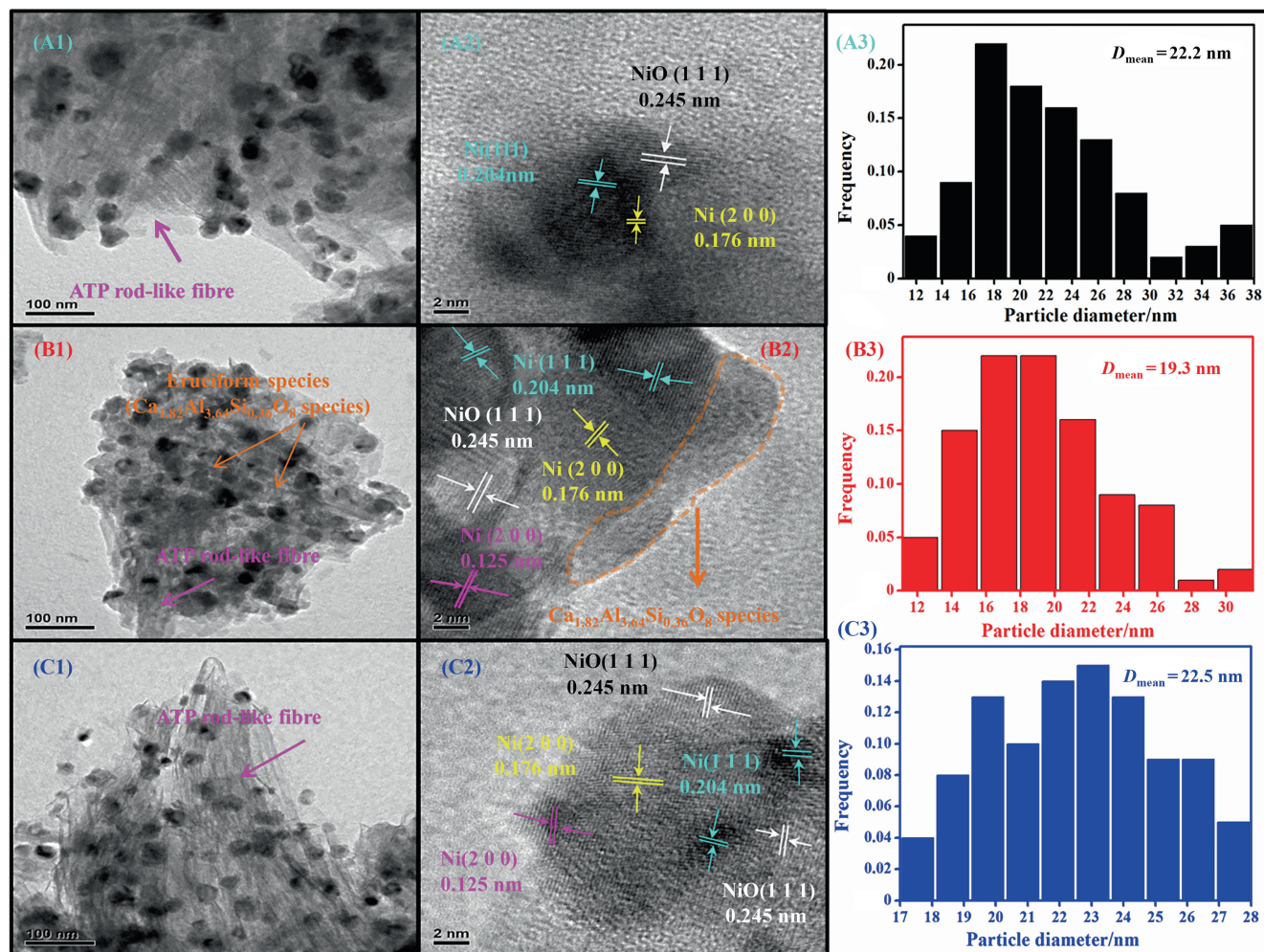


Fig. 5. HRTEM images and histograms of particle size distribution of representative reduced nickel-based catalysts, such as Ni/ATP (A1–A3), Ni-6Ca/ATP-ci (B1–B3) and Ni-6Ca/ATP-hs (C1–C3).

adsorbing capacity. This suggests co-impregnation method introduced Ca additive not exists as CaO phase but incorporates into ATP framework to form other structure, then reducing the content of surface basic surface OH— groups and $\text{Ni}^{\text{II}}-\text{O}^{2-}$ acid-base pairs. Therefore, the amounts of basic sites are decrease clearly as presented by the data in Table 3. Additionally, the CO_2 -desorption profile of Ni-6Ca/ATP-hs exhibits almost consistent peaks at temperature below 500 °C with Ni/ATP, but appears a robust peak at 500–600 °C, which attributing to the strong basic sites originated from the low coordinated O^{2-} anions. It also confirms that the different oxygen specie distribution in reduced Ni-6Ca/ATP-hs resulting from the newly generated Ni- CaO_x interfaces.

3.2. Catalytic performance evaluation

It well known that the activity of glycerol reforming can be generally influenced by the catalyst properties. To gain more insight about the effects of Ca additive and preparation method on hydrogen yield and gas product distribution, the GSR experiment is conducted over all as-prepared catalysts at the same reaction conditions: $T = 700$ °C, $P = 101325$ Pa, $\text{WHSV} = 9.14$ h^{-1} , $\text{W/G} = 3$, $\text{TOS} = 4$ h. The data about the conversion of glycerol to gas product, the yields and selectivities of H_2 , CO, CO_2 and CH_4 , and the molar ratios of H_2/CO and CO/CO_2 are obtained and displayed in Fig. 7. Firstly, the blank (none catalyst and only used ATP as catalyst) tests were performed at the same operating conditions. As

can be observed in Fig. 7(A), in the absence of the catalyst, the conversion of glycerol to gas product and yields of gas products are very low. The glycerol conversion into gas product is only 32.22% and the yields of CO, CO_2 , and CH_4 are only 22.31%, 4.03% and 5.89%, respectively. Among them, the selectivity to CO reaches to 71.20%, the highest value in all tests as presented in Fig. 7(B). Meanwhile, the values of H_2 yield and selectivity display the lowest and are 9.41% and 15.59%, respectively. This demonstrates that very small amount of glycerol is capable of transforming into H_2 via reacting with water and decomposition under high reaction temperature (700 °C). When only utilizing ATP as catalyst, it finds that the conversion of glycerol to gas product and H_2 yield exhibit obvious increase to 59.93% and 20.15%, respectively. Furthermore the yields of CO and CH_4 show distinct increase while there was little change in the terms of selectivity of these four kinds of gas products as compared with the blank test without catalyst. It confirms that ATP support only enhances the decomposition of glycerol and its reaction with water and does not affect the distribution of gas products, which perhaps because of the surface acid/basic sites and unique adsorption capacity of ATP support (the specific mechanism is not further discussed in this paper).

In the presence of nickel species, as shown in Fig. 7, Ni/ATP exhibits satisfactory 69.92% of glycerol conversion to gas product and 58.23% of H_2 yield, meanwhile its selectivity increases to 41.90%. Additionally, the yields of CO_2 and CH_4 present significant enhancement and CO yield reveals remarkable reduction in com-

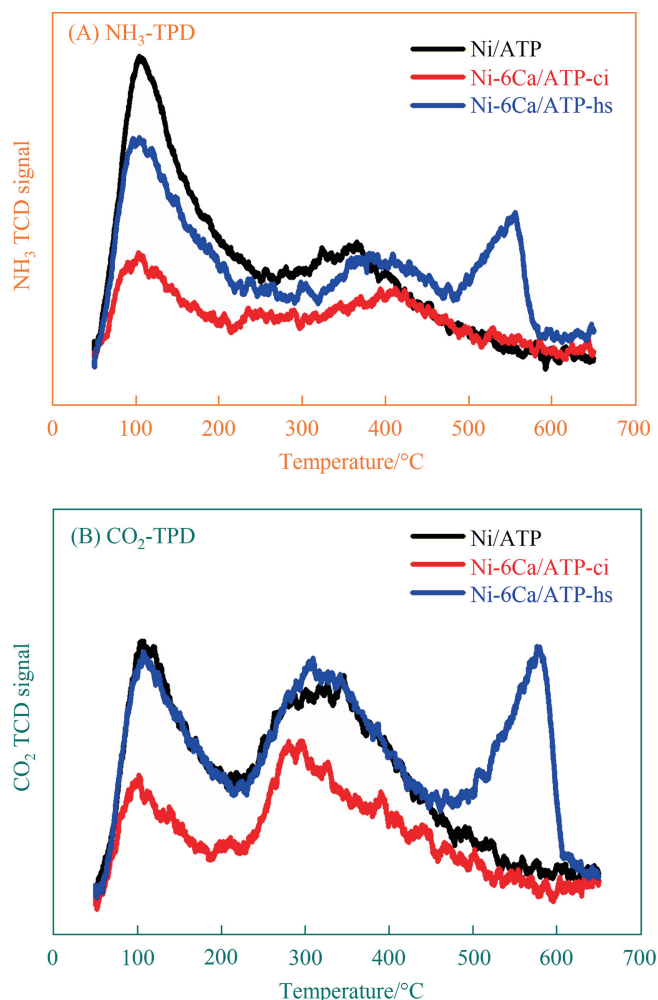


Fig. 6. The profiles of NH_3 -TPD (A) and CO_2 -TPD (B) of reduced nickel-based catalysts.

parison with those over ATP. The selectivity to the carbon-containing gas product exhibits same tendency with the corresponding yield. Notably, the yield and selectivity of CH_4 all reach to maximum values, 15.60% and 23.49% respectively. According to the reports [7,17,22], during the GSR the production of CH_4 was mainly from the decomposition of glycerol and methanation of CO and CO_2 . However, these methanation reactions were exothermic reactions and would be inhibited at 700 °C without employing catalysts. As a consequence, the result confirms that nickel species promote the decomposition of glycerol and CO/CO_2 methanation reactions, thus procuring higher both H_2 and CH_4 . In addition to these, the nickel metal also has unique performance for water–gas shift reaction (WGSR) due to the steep increase of H_2/CO molar ratio and rapid reduction of CO/CO_2 comparing with ATP. These two data are the key indicators for evaluating WGSR [6]. Recently, it had been confirmed that exsolved Ni nanoparticles (NPs) in perovskite oxide were the active sites for WGSR [75].

With the introduction of Ca into Ni/ATP by co-impregnation method, it plays a significant effect on the glycerol conversion, gas products yields and selectivity. Comparing with Ni/ATP, it can be found that the conversion of glycerol to gas product and the yield and selectivity of H_2 exhibit increase initially and decrease afterwards with Ca content and even lower than that over Ni/ATP when the Ca content exceeding 9%. Amongst, Ni-6Ca/ATP-ci demonstrates the superior conversion (78.51%) and the corresponding H_2 productivity and selectivity reaching to 72.90% and 51.08%, respectively. On the whole, Ca-modified Ni/ATP presents an obvious increase in terms of CO_2 yield and selectivity and a visible reduction tendency for CH_4 yield and selectivity. Furthermore, the molar ratios of H_2/CO and CO/CO_2 manifest the inversely changed direction with the Ca content. The H_2/CO ratio of Ca-modified Ni/ATP is significant higher than that of blank tests and Ni/ATP. Wherein, Ni-6Ca/ATP-ci has the highest H_2/CO ratio (2.27) and the lowest CO/CO_2 ratio (1.08) in Ni-xCa/ATP-ci catalysts. These causes explain that the Ca additive enhances both the glycerol decomposition and its reaction with water and the WGSR, meanwhile inhibits the formation of CH_4 . This mainly attributes to Ca promoter alters the internal structure of Ni/ATP and then influencing the interaction between nickel species and ATP and the surface and interface properties of Ni/ATP catalyst. It will be further discussed in Section 4.

For Ni-6Ca/ATP-hs catalyst, after simple hydrothermal treatment during its synthetic process, it surprisingly finds that the catalytic performance for GSR is further enhanced as shown in Fig. 7. The conversion of glycerol to gas product and H_2 yield enlarge to 86.77% and 76.17% over Ni-6Ca/ATP-hs catalyst, along with the maximal H_2 selectivity (58.56%). In addition, the CH_4 yield and selectivity achieve the lowest values 3.97% and 6.08% among all tests, and the ratio of H_2/CO reaches to 2.53, the maximum. This further demonstrates that Ni-6Ca/ATP-hs boosts the glycerol conversion and improves the transformation of intermediate species generated during GSR into target product H_2 . It mainly ascribes to the hydrothermal treatment further optimizes the spatial configuration structure and surface/interface sites of Ca-modified Ni/ATP catalyst, making them more suitable for GSR for hydrogen production. The specific reaction route is presented in Section 4.

3.3. Characterizations of spent catalysts

This was demonstrated in a number of studies that active metal sintering and coke of nickel-based catalysts were the key issues for realizing industrialization operation of hydrogen production from steam reforming of renewable oxygenates [10,18]. Therefore, to gain more insight about the effect of Ca additive and hydrothermal synthesis method, the spent catalysts after active test in Section 3.2 were collected and characterized using XRD, TG-DTG, Raman and TEM.

Fig. 8(A) shows the XRD patterns of the all spent catalysts and confirms that the presence of feeble ATP characteristic diffraction peaks at $2\theta = 8.5^\circ, 13.7^\circ, 19.8^\circ, 27.8^\circ$ and 34.7° in all catalysts in comparison with their reduced counterpart in Fig. 1(B). Meanwhile, the peaks of SiO_2 are also well observed. It illustrates that ATP crystalline structure has unique durability during GSR. However, the diffraction peaks of $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ presented in

Table 3
Acid and basic sites distribution over the reduced catalyst surface

Samples	Acid sites/mmol $\text{NH}_3 \cdot (\text{g cat})^{-1}$			Basic sites/mmol $\text{CO}_2 \cdot (\text{g cat})^{-1}$		
	Weak	Medium	Strong	Weak	Medium	Strong
Ni/ATP	0.3662	0.0552	0	0.0479	0.0482	0
Ni-6Ca/ATP-ci	0.1493	0.0237	0	0.0215	0.0263	0
Ni-6Ca/ATP-hs	0.2815	0.0493	0.2132	0.0464	0.0492	0.0513

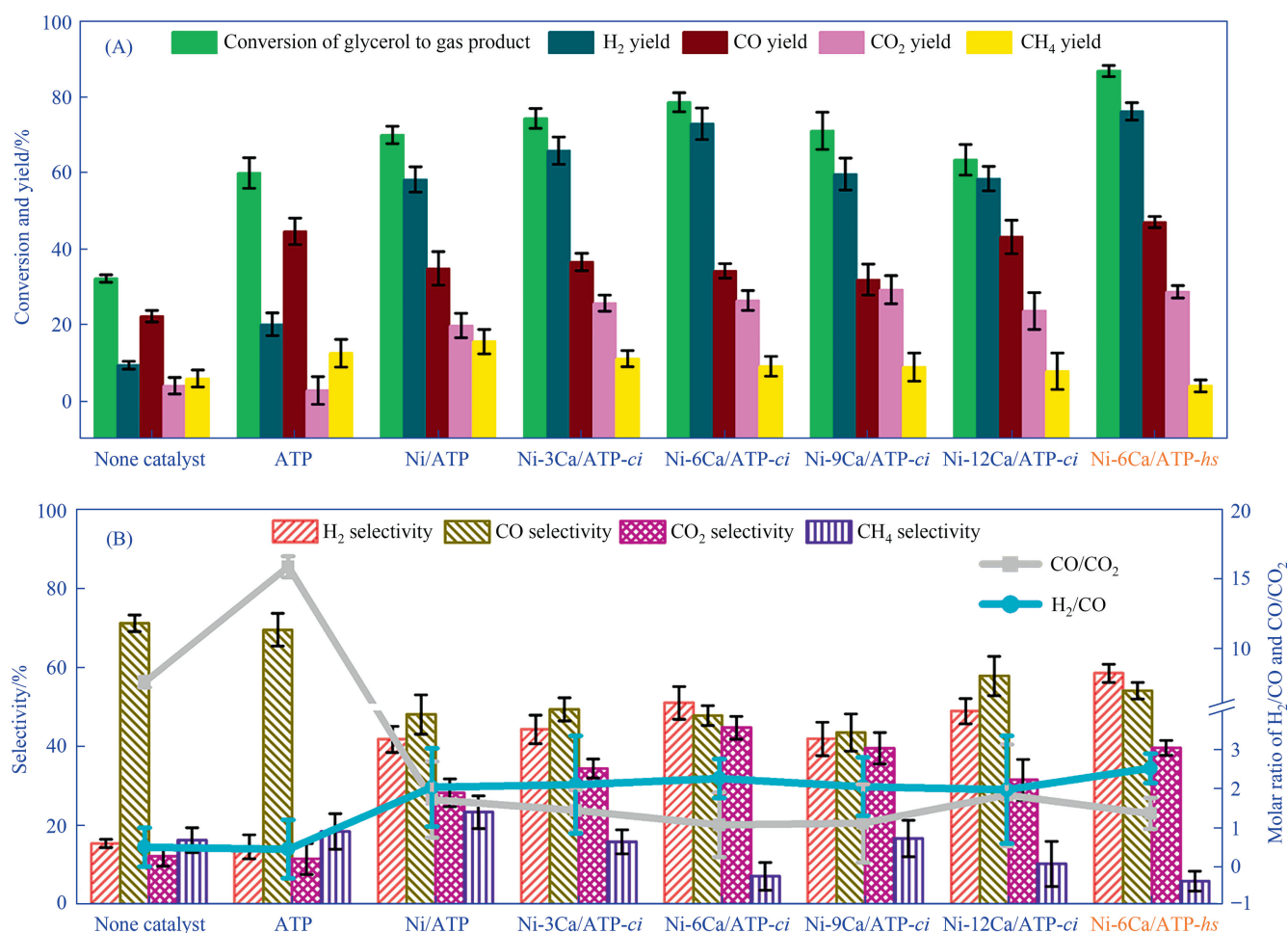


Fig. 7. Catalytic performances for GSR reaction over all as-prepared catalysts. [Reaction conditions: $T = 700\text{ }^{\circ}\text{C}$, $P = 101325\text{ Pa}$, $\text{WHSV} = 9.14\text{ h}^{-1}$, $\text{W/G} = 3$; $\text{TOS} = 4\text{ h}$].

reduced Ni- $x\text{Ca}/\text{ATP-ci}$ catalysts are not detected in corresponding spent sample, implying $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ species are not stable during GSR. The decomposition or transformation of $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ may result in the changes of catalyst crystalline structure, which further confirmed by the rougher XRD patterns of spent Ni- $x\text{Ca}/\text{ATP-ci}$ catalysts, and then affecting catalytic performance. The particle sizes of Ni metal of spent catalysts are also calculated and presented in Table 1. It exhibits that the Ni metal sizes of spent catalysts have an obviously increase compared with reduced catalysts.

For further illustrating the sintering incident of Ni metal, the values of sinter degree are also listed in Table 1 (the calculation method is also presented in footnote of Table 1). It clearly presents that Ca additive reduces the sinter extent, suggesting the addition of Ca inhibits the sintering of Ni metal particles. Wherein Ni-6Ca/ATP-ci shows the lower sinter degree (16.0%) among all Ni- $x\text{Ca}/\text{ATP-ci}$, manifesting Ni-6Ca/ATP-ci has superior anti-sinter ability during GSR. What is more important that Ni-6Ca/ATP-hs presents the lowest sinter degree (13.9%), which clearly demonstrates that hydrothermal synthesis method further enhances the sintering resistibility of Ni metal particles.

In addition, carefully comparing with the XRD patterns of reduced catalysts in the range of $2\theta = 23.9^{\circ}\text{--}27.5^{\circ}$, it obviously finds that the peaks become broad and weak in spent catalysts. This mainly results from the overlap of characteristic peaks of graphitized coke deposits with SiO_2 [76].

The types and amount of coke deposits formed on the spent Ni/ATP, Ni-6Ca/ATP-ci and Ni-6Ca/ATP-hs catalysts were detected

using a thermogravimetric (TG) analyzer under air flow. The obtained TG and DTG profiles are displayed in Fig. 8(B). It can be found that the amount of carbon deposits strings along the order of Ni-6Ca/ATP-hs (4.5%) < Ni-6Ca/ATP-ci (33.4%) < Ni/ATP (42.5%). This suggests that Ca additive and hydrothermal synthesis method significantly restrains the generation of coke, especially the Ni-6Ca/ATP-hs catalyst prepared by hydrothermal synthesis method. A good deal of advanced reports for understanding the burnup curves of carbon deposits over spent nickel-based catalysts are discussed in [6,7,29,43,44,76]. Generally, the burnout area at $460\text{--}600\text{ }^{\circ}\text{C}$ is related to the combustion of amorphous coke and that at above $600\text{ }^{\circ}\text{C}$ is corresponded to the burn of filamentous/nanorod-like and graphite-like coke. Consequently, one also observes that the carbon deposits over spent Ni/ATP catalyst have both the two kinds of coke, furthermore, Ca additive and hydrothermal synthesis method distinctly decrease the production of amorphous coke. The Ni-6Ca/ATP-hs catalyst presents the unique resistance to carbon deposition.

The characteristics of carbon deposition over spent catalysts are deeply investigated by Raman analysis technology and the obtained Raman spectra between $1000\text{--}2000\text{ cm}^{-1}$ are revealed in Fig. 8(C). Two representative peaks of carbon deposits are obviously observed in the three spent catalyst, which are considered as D band ($1250\text{--}1400\text{ cm}^{-1}$) and G band ($1510\text{--}1670\text{ cm}^{-1}$), respectively. Normally, the D band is corresponded to the Eigen vibrations of carbon in disordered sp^2 graphite structures, such as $-\text{CH}_3$ groups, olefin/aromatic species, which are collectively considered as amorphous coke [7,29,31,76,77]. G band is mainly

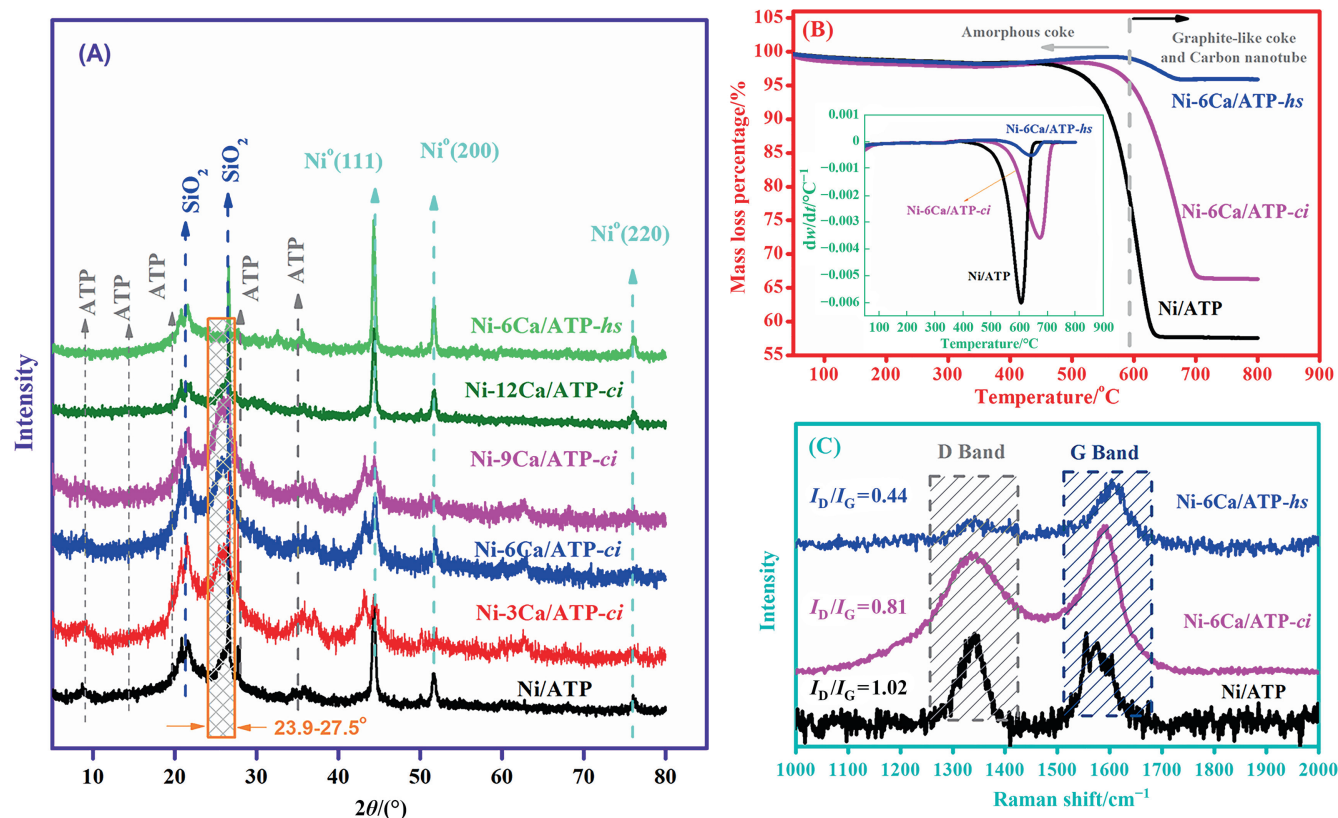


Fig. 8. The characterizations of spent catalysts: (A) XRD patterns, (B) TG (DTG in inset) profiles, and (C) Raman spectra. [Spent catalysts were obtained after reacting under $T = 700\text{ }^{\circ}\text{C}$, $P = 101325\text{ Pa}$, $\text{WHSV} = 9.14\text{ h}^{-1}$, $\text{W/G} = 3$ and $\text{TOS} = 4\text{ h}$.]

attributed to the overlapped stretching vibrations of $\text{sp}^2\text{ C}=\text{C}$ bonds of conjugated olefin and aromatic species with $\text{E}_{2g}\text{ C}=\text{C}$ inplane vibrations of graphite-like deposits, which are collectively regarded as filamentous/nanorod-like and graphite-like coke [7,29,76,77]. Therefore, the results in Raman spectra suggest that Ni-6Ca/ATP-hs significantly inhibits the formation of amorphous coke, due to it has very weak D band peak. This consequence is in accordance with TG-DTG result. Considering to the summarized reaction pathways in Ref. [14] and the involved parallel reactions affected significantly the gas product distribution in GSR [6,7,17,18], the coke production principally originates from the following two routes. One is the oligomerization of intermediate reactive substances such as acetaldehyde, ethylene, and acetone derived from glycerol dehydration at catalyst acidic sites to form conjugated olefin and aromatic species, which are regarded as amorphous coke [14,77]. The other is the decomposition of CH_4 and CO Boudouard reaction over Ni metal sites to form graphite-like coke in the form of carbon nanotubes or filamentous coke [77]. In addition, the intensity ratio of D band and G band (I_D/I_G) is commonly calculated to determine the distribution of amorphous and graphite-like carbon deposits. Consequently, I_D/I_G ratios of three spent catalysts present the following order Ni/ATP (1.02) > Ni-6Ca/ATP-ci (0.81) > Ni-6Ca/ATP-hs (0.44), implying hydrothermal synthesis method prepared Ni-6Ca/ATP-hs observably suppresses the generation of amorphous coke.

The HRTEM analysis is further executed to examine the morphology of spent catalysts. It can be found from Fig. 9 that the ATP rod-like fibres are clearly presented in the three spent catalysts, while the $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ species in reduced Ni-6Ca/ATP-ci is not observed in its spent counterpart, suggesting ATP morphologic structure is stable but the formed $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ species are easily transformation during GSR reaction, identifying

with the results of XRD analysis. The statistics of particle size distribution are also presented in Fig. 9. As compared with the results in Fig. 5, the particle size presents a clear increase after GSR reaction and the sintering degree of metal particle size shows the following order Ni/ATP (32.4%) > Ni-6Ca/ATP-ci (24.9) > Ni-6Ca/ATP-hs (12.4%), in consisted with the variation tendency that obtained by XRD analysis.

Additionally, a great deal of carbon deposits including amorphous coke, filamentous coke, and carbon nanotube are found in spent Ni/ATP and Ni-6Ca/ATP-ci catalysts, according to previous reports [21,39,42]. Furthermore, the diameter distribution of carbon nanotubes is consisted with that of Ni metal particle size. The carbon nanotube diameter ranges from 12 nm to 47 nm in spent Ni/ATP and that changes from 14 nm to 37 nm in spent Ni-6Ca/ATP-ci. Notably, the amount of amorphous and filamentous coke is distinctly reduced in comparison with other spent catalysts. In addition, it observes some eruciform deposits formed in the edge of spent Ni-6Ca/ATP-hs, which mainly attributed to the graphite-like carbon deposit. These findings are perfectly in accordance with those of TG and Raman.

Generally, the formation of filamentous coke ascribed to the carbonization of amorphous coke and carbon nanotube is attributed to the step-growth polymerization of absorbed CH_x^*/C^* fragments/species derived from the decomposition of CH_4 and CO Boudouard on metal sites [46,78,79]. Therefore, the size of carbon nanotube consists with size of active metal particle and closely attaches to the metal particle, resulting in lifting up the active metal and changing the catalyst structure if it does not have enough metal-support interaction and multiple metal-support/additive interfaces. For Ni/ATP, it has larger Ni metal particle size, more plentiful acid sites and weaker metal-support interaction as confirmed by above characterizations, improving the formation

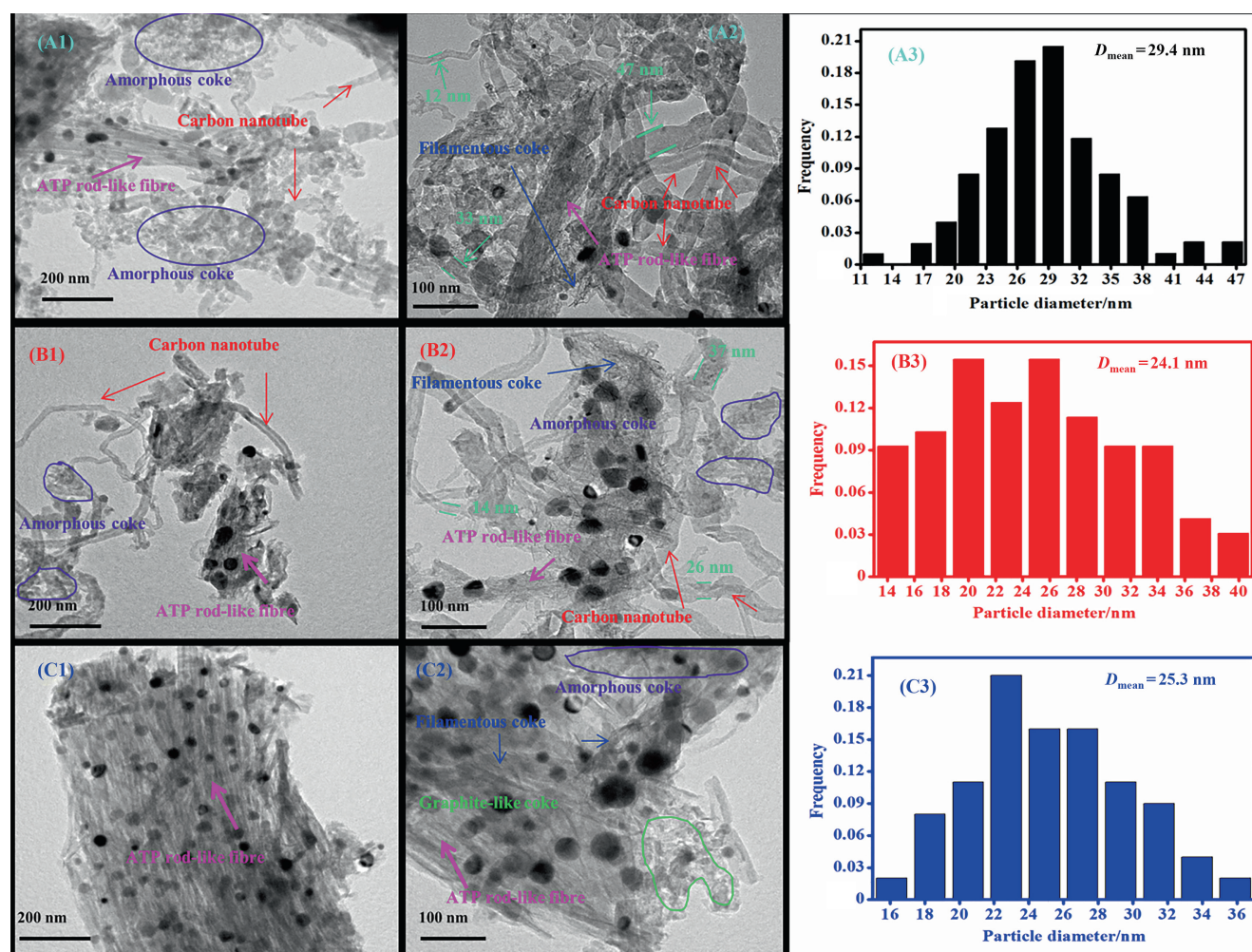


Fig. 9. HRTEM images and histograms of particle size distribution of spent catalysts including Ni/ATP (A1–A3), Ni-6Ca/ATP-ci (B1–B3) and Ni-6Ca/ATP-hs (C1–C3). [Spent catalysts were obtained after reacting under $T = 700\text{ }^{\circ}\text{C}$, $P = 101325\text{ Pa}$, $\text{WHSV} = 9.14\text{ h}^{-1}$, $\text{W/G} = 3$ and $\text{TOS} = 4\text{ h}$.]

of carbon deposits with various structure and morphology as shown in Figs. 8 and 9. While for Ni-6Ca/ATP-ci, the addition of Ca reduces the Ni metal particle size and surface acidic sites, so it presents a definite anti-carbon deposit. Meanwhile, the $\text{Ca}_{1.82}\text{-Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ decomposition changes the interaction or interface structure and leads to produce significant amount of carbon nanotube as displayed in Fig. 9, although it has higher metal-support interaction compared with Ni/ATP as revealed by H_2 -TPR. Considering to the Ni-6Ca/ATP-hs, it has been demonstrated presented larger metal particle size and surface acidic sites and even weaker metal-support interaction, furthermore had higher CO_2 adsorption capacity (as shown by CO_2 -TPD analysis). While it exhibits superior resistance for carbon deposits as confirmed by TG, Raman and HRTEM. This mainly reveals that the multiple Ni-ATP and Ni- CaO_x interfaces successfully inhibits the gasification of filamentous coke and absorbed CH_x^*/C^* fragments/species reacted with steam.

3.4. Analysis of catalyst structural evolution during GSR

On the grounds of above characterization results, the conceivable mechanism of Ni/ATP catalyst structural evolution affected by Ca additive and hydrothermal synthesis method during GSR reaction is put forward and mechanism diagram is revealed in Fig. 10. Considering the H_2 -TPR analysis, calcined Ni/ATP catalyst has two kinds of nickel species, consequently there are surface Ni nanoparticles, strong-interacted Ni metal with ATP and metallic Ni embedded into ATP distributed over ATP in reduced Ni/ATP cat-

alyst, as shown in Fig. 10. Furthermore, reduced Ni/ATP presents higher surface acid content as confirmed by NH_3 -TPD, promoting the dehydration/condensation of glycerol and its reactive derivatives to generate abundant amorphous coke, coating Ni metal sites. Meanwhile the CH_x^*/C^* fragments/species derived the splitting decomposition of glycerol, CH_4 and CO are formed around the Ni metal sites, then these fragments/species cumulating and growing into filamentous coke and carbon nanotube to boost up Ni metal particles weakly interacted with support to change the catalyst structure and even passivating catalyst. In addition, the surface Ni nanoparticles migrate and incorporate into other Ni metal to form sintering phenomenon during GSR. Therefore, Ni/ATP catalyst presents inferior catalytic performance during GSR and serious coke and sintering. Ca introduction partly alters the ATP framework and formed $\text{Ca}_{1.82}\text{Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ enhances the distribution of Ni metal and interaction between Ni and support, thus Ni-6Ca/ATP-ci exhibits superior performance for GSR. However, the $\text{Ca}_{1.82}\text{-Al}_{3.64}\text{Si}_{0.36}\text{O}_8$ species are not stable during GSR. Their destructions result in sintering of Ni metal and the formation of carbon nanotube. Additionally, Ca additive significantly reduces the acid sites as demonstrated by NH_3 -TPD, so there is small number of amorphous and filamentous coke formed in spent Ni-6Ca/ATP-ci catalyst as presented in Fig. 10. Hydrothermal synthesis method obviously modulates the interaction of Ca with ATP. The ATP framework is perfectly preserved in Ni-6Ca/ATP-hs and abundant Ni- CaO_x and Ni-ATP interfaces are formed as shown in Fig. 10. This makes the distribution of Ni metal particles become more uniform

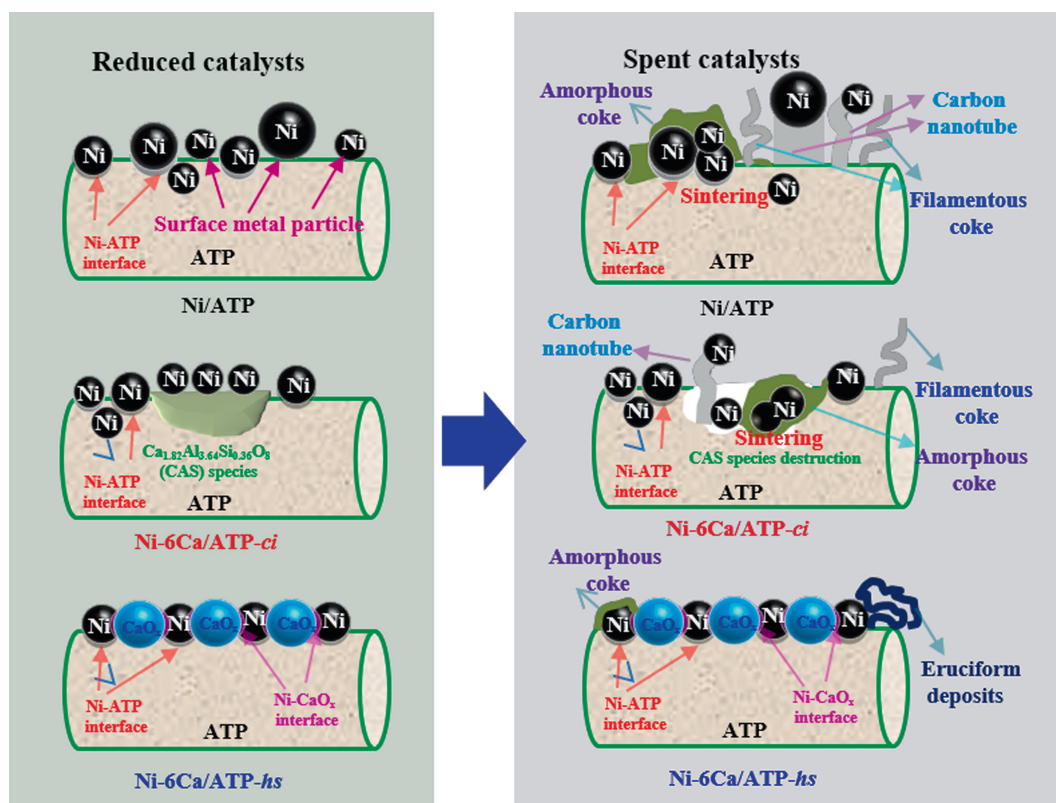


Fig. 10. Mechanism diagram of catalyst structural evolution underwent GSR reaction.

as compared with other two catalysts (conformed by HRTEM in Fig. 5). Consequently, Ni-6Ca/ATP-hs exhibits unique catalytic performance and outstanding anti-sintering and coke abilities during GSR test.

4. Conclusions

The influence of Ca additive and hydrothermal synthesis method on the structure of nickel-attapulgite catalysts and their activity and selectivity in the GSR was studied. Ca content and hydrothermal process had a significantly effect on the main characteristics of the Ni/ATP catalyst, including the size and distribution of Ni metal particles, Ni-support interaction and interface sites. Suitable amount of Ca content and hydrothermal synthesis method significantly enhanced the homogeneous distribution of Ni metal particle, catalyst reducibility, and surface strong acid/base sites due to the formation of Ni-CaO_x interface sites, which endowed Ni-6Ca/ATP-hs with unique glycerol conversion, H₂ yield and selectivity as well as outstanding resistances for metal sintering and carbon deposits during GSR. Furthermore, the reasonable mechanism of catalyst structural evolution with Ca additive and preparation method and reaction route of GSR over Ni-6Ca/ATP-hs catalyst were presented, in which the effect of interface sites on eliminating coke was clearly presented. This study demonstrated a possibility of fabricating promising reforming catalyst using green economic the support and metal species.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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