

## Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst for hydrogen production from steam reforming of acetic acid as a model compound of bio-oil

Ya-ping Xue<sup>\*,\*\*,\*</sup>, Chang-feng Yan<sup>\*,\*\*,\*</sup>, Xiao-yong Zhao<sup>\*,\*\*,\*</sup>,  
Shi-lin Huang<sup>\*,\*\*,\*</sup>, and Chang-qing Guo<sup>\*,\*\*,\*</sup>

<sup>\*</sup>Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>\*\*</sup>Key Laboratory of Renewable Energy, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>\*\*\*</sup>Guangdong Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, China

<sup>\*\*\*\*</sup>University of Chinese Academy of Sciences, Beijing 100039, China

(Received 28 June 2016 • accepted 6 October 2016)

**Abstract**—Hydrogen production from steam reforming of acetic acid was investigated over Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst. A series of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts were synthesized by sol-gel method coupled with wet impregnation, which was characterized by XRD, BET, TEM, EDS, TG, SEM and TPR. Catalytic activity of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> was evaluated by steam reforming of acetic acid at the temperature range of 550–750 °C. The tetragonal phase La<sub>0.1</sub>Zr<sub>0.9</sub>O<sub>1.95</sub> is formed through the doping of La<sub>2</sub>O<sub>3</sub> into the ZrO<sub>2</sub> lattice and nickel species are highly dispersed on the support with high specific surface area. H<sub>2</sub> yield and CO<sub>2</sub> yield of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst with 15%wt Ni reaches 89.27% and 80.41% at 600 °C, respectively, which is attributed to high BET surface area and sufficient Ni active sites in strong interaction with the support. 15%wt Ni supported on La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst maintains relatively stable catalytic activities for a period of 20 h.

**Keywords:** Hydrogen Production, Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> Catalyst, Steam Reforming, Bio-oil, Acetic Acid

### INTRODUCTION

Hydrogen is widely considered as a future transport fuel and clean energy carrier because of its cleanness and high gravimetric energy density. Nowadays, fossil fuels including natural gas, naphtha and coal are still main sources for hydrogen production [1]. With the depletion of fossil fuels and deterioration of environment from pollution, renewable resources for hydrogen production are of great interest, such as biomass, which is a renewable and CO<sub>2</sub> neutral clean resource. Hydrogen production from biomass includes two main thermal-chemical methods: direct gasification of biomass and steam reforming of bio-oil, which is produced by fast pyrolysis of biomass [2]. Bio-oil is higher gravimetric energy density than biomass, with easy storage and transportation in the application [3]. As a result, steam reforming of bio-oil is a promising and economical way to produce hydrogen. Bio-oil is a complicated mixture, including acids, aldehydes, alcohols, ketones and other oxygenate compounds with several inferior characteristics such as high viscosity, high oxygen and water content, low heating value, and low pH value [4,5]. Different compounds in bio-oil have distinct steam reforming reactivity. The different fractions can be applied more efficiently by the separation of bio-oil. Currently, column chromatography, solvent extraction, and distillation are main bio-oil separation methods [6]. Solvent extraction can achieve the enrichment of compounds with similar polarity and is one of the promising isolation methods of bio-oil. Among

many solvents, water is a cheap and efficient solvent, which can separate bio-oil into water-soluble and water-insoluble phases. The bio-oil water-soluble phase is widely applied for steam reforming to produce hydrogen. To design efficient catalysts for steam reforming of bio-oil, model compounds of bio-oil like acetic acid, ethanol, acetone and ethylene are already in use [7]. Several studies have been reported for steam reforming of acetic acid, which is regarded as the main component and representative model compound of bio-oil [8–10]. Steam reforming of acetic acid can be described as the following reactions [11],

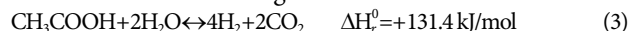
Steam reforming of acetic acid:



Water gas shift reaction:



The overall steam reforming of acetic acid is:



The influence of noble metal and nickel on steam reforming of acetic acid has been persistently investigated. Noble metal catalysts show high activities and good stability in steam reforming of acetic acid but they are rather expensive [12]. Nickel-based catalysts are low cost and have high C-C bond and C-H breaking activity and are widely studied in steam reforming of acetic acid. The type and features of catalyst support (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>) also play an important role in steam reforming of acetic acid. Bimela studied catalytic steam reforming of acetic acid over Ni/Al<sub>2</sub>O<sub>3</sub> and the catalyst with moderate nickel content showed the best performance because of good nickel dispersion and its stabiliza-

<sup>†</sup>To whom correspondence should be addressed.

E-mail: yancf@ms.giec.ac.cn

Copyright by The Korean Institute of Chemical Engineers.

tion in the reaction conditions [13]. Román Galdámez found that Ni/Al<sub>2</sub>O<sub>3</sub> modified with lanthanum did not increase the H<sub>2</sub> yield in steam reforming of acetic acid. A high content of lanthanum in the Ni/Al<sub>2</sub>O<sub>3</sub> could not favor metallic dispersion and Ni/Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> catalysts could be less reduced than the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst [14]. Medrano found that the addition of calcium as a promoter on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst did not result in an improvement in reforming activity and stability under the experimental conditions [15]. Medrano further chose calcium and magnesium as promoters to modify the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The catalysts with the Mg/Al molar ratio of 0.26 showed the best performance, while calcium modified catalysts showed lower carbon conversion; The addition of calcium generated an NiO phase with less interaction with the support [16]. Bimbela prepared a series of Ni/Al coprecipitated catalysts modified with magnesium and copper and tested in the catalytic steam reforming of model compounds. Copper as a promoter would induce a decrease in the initial reforming activity and an enhancement of the catalyst stability because of the Ni dilution effect and resistance to the formation of encapsulating coke, respectively [17]. Wang studied catalytic reforming of the water-rich distillation fraction from crude bio-oil molecular distillation over Ni/Al<sub>2</sub>O<sub>3</sub>; A slow decrease in H<sub>2</sub> content in the outlet gas was observed after 11 h, which was caused by coke deposits [18]. Wang further reported catalytic reforming of phenol, acetic acid and hydroxyacetone over an Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. They found that the nano-Al<sub>2</sub>O<sub>3</sub> acted as a more superior support and was beneficial in the formation of more active sites on the catalyst surface by compared with Ni/r-Al<sub>2</sub>O<sub>3</sub> [19].

Coke formation and sintering of particles are two main reasons of the deactivation of Ni-based catalysts [20]. A proper support is needed to improve the activity and stability because it affects the dispersion and stability of active metal, changes the electronic distribution and may participate in the reaction [21,22]. ZrO<sub>2</sub> is regarded as a promising support since ZrO<sub>2</sub> has proper acidic/basic features. The features can enhance the accumulation of steam and carbon oxides on the surface to improve hydrogen yield and prevent carbon deposition [23]. At the same time, the rare earth metal oxide La<sub>2</sub>O<sub>3</sub> can interact strongly with Ni active phase and enhance the interaction between Ni and support, which is beneficial to producing highly dispersed Ni species and avoiding particle coalescence [24,25]. La<sub>2</sub>O<sub>3</sub> also improves the stability of the catalysts by resisting and removing carbon deposited from metallic surface [26,27]. Therefore, the support ZrO<sub>2</sub> modified by adding a certain amount of La<sub>2</sub>O<sub>3</sub> is attractive and the mixture material may both have proper acidic/basic features and interaction with Ni active phase to prevent carbon deposition and avoid sintering of catalyst particles [28,29]. Moreover, oxygen vacancies may be created on the support La<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> by forming a solid solution, which is good for improving the redox property of support [30]. The Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> may be a promising catalyst for hydrogen production from steam reforming of acetic acid, but active sites, the interaction between Ni and supports and the structure-activity relationship need to be further explored.

In this paper, a series of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> with different Ni contents were prepared and evaluated in steam reforming reaction of acetic acid. The catalytic activities in the terms of H<sub>2</sub> selectivity and

CO<sub>2</sub> selectivity were related to the structural and chemical properties of the catalysts, indicating the interaction between Ni and support La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> played an important role on catalytic activities.

## EXPERIMENTAL

### 1. Catalyst Preparation

The mesoporous La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> support was prepared through a surfactant-directed sol-gel method by using hexadecyltrimethyl ammonium bromide (CTAB) as a template. First, tailored amounts of ZrOCl<sub>2</sub>·8H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were dissolved into the water. Second, CTAB was dissolved into the water and the PH was adjusted to 10 by adding NH<sub>4</sub>OH. The molar ratio of (ZrOCl<sub>2</sub>·8H<sub>2</sub>O+La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and CTAB was 1.4. Finally, the aqueous solution of ZrOCl<sub>2</sub>·8H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added slowly to the aqueous solution of CTAB and NH<sub>4</sub>OH and then kept for two hours under vigorous stirring at 60 °C. The white precipitate was filtered and washed with deionized water followed by ethanol, then dried at 100 °C for 12 h. Finally, the precursor of La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> support (10 wt% of La<sub>2</sub>O<sub>3</sub>) was put into the muffle furnace to calcine for 4 h at 600 °C.

A series of Ni catalysts supported on La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> were prepared via incipient wetness impregnation method. The mixtures were dried at 100 °C for 12 h, and then heated to 800 °C at a rate of 5 °C min<sup>-1</sup> and calcined for 6 h. NiO/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> obtained was pre-reduced at 800 °C in 5% H<sub>2</sub>/Ar for 4 hours. Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts with Ni loading of 5, 10, 15, 20 and 25 wt% were denoted as 5 Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, 10 Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, 15 Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, 20 Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and 25 Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, respectively.

### 2. Catalyst Characterization

XRD analysis was performed in PANalyticalX'Pert diffractometer (X'Pert PRO MPD, PW3040/60) with the 2θ ranging from 10° to 90° with Cu-Kα (λ=0.154060 nm) radiation (40 kV, 40 mA). N<sub>2</sub> adsorption-desorption tests were conducted in a Quantachrome Autosorb-1 instrument. Prior to measurement, the samples needed to be degassed at 250 °C for 12 hours. BET formula was used to calculate the surface area, and BJH method was applied to calculate the total pore volume and average pore size of catalysts. The morphology of catalyst was further characterized by transmission electron microscopy (TEM) on a JEM-2100 microscope followed by the energy dispersive spectrometer (EDS) analysis. H<sub>2</sub>-TPR characterization of the catalysts was executed in the following process: 30 mg of a powder sample was placed in a U quartz tube and then heated to 1,000 °C at a rate of 10 °C/min in the atmosphere of 10 vol% H<sub>2</sub>/Ar. The consumption of hydrogen was determined by a TCD detector. TG was performed in a thermal analyzer (STA409PC) to evaluate coke deposited during the reaction on reacted catalyst. The temperature was increased to 900 °C at a rate of 10 °C min<sup>-1</sup> and air flow was maintained at 80 ml min<sup>-1</sup>.

### 3. Catalyst Activity Tests

Steam reforming of acetic acid involved a bench-scale fixed-bed reactor at atmospheric pressure in the temperature range of 550-750 °C. Prior to the reforming reaction, 100 mg Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst was placed into a quartz tube reactor and pre-reduced at 800 °C in situ in a 5 vol% H<sub>2</sub>/Ar stream (120 ml min<sup>-1</sup>) for 4 hours. In the experiment, H<sub>2</sub>O and acetic acid with the molar ratio of

steam to HAC of 3 were vaporized in preheating zone and then fed into the reactor at a constant rate of  $0.78 \text{ g}_{\text{acetic acid}} \text{ h}^{-1}$  by a peristaltic pump. A thermocouple was placed into the center of the catalyst bed to detect reforming reaction temperatures, and a digital temperature controller was used to control the actual reaction temperature. The gaseous products consisting of H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> were analyzed online by the gas chromatograph (GC 7890II) equipped with a TCD detector and a TDX-01 column. After a reforming reaction of 2 hours, the collected liquid was detected by the gas chromatographs (GC 7890A) with a FID detector and a DB-FFAP column.

The stability of 15 Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst was evaluated for 20 h at 600 °C, H<sub>2</sub>O/HAC=3 and WHSV=7.8 g-acetic acid/g-cata·h<sup>-1</sup>.

#### 4. Data Analysis

The activity of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> in the steam reforming of acetic acid was measured by the acetic acid conversion and H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> selectivity. The calculation formulas are given as follows:

HAC conversion (%)

$$= \frac{\text{the moles of HAC in the feed} - \text{the moles of HAC in the effluent}}{\text{the moles of HAC in the feed}} \times 100\%$$

$$\text{H}_2 \text{ yield (\%)} = \frac{\text{the moles of H}_2 \text{ produced}}{4 \times \text{the moles of HAC in the feed}} \times 100\%$$

$$\text{CX yield (\%)} = \frac{\text{the moles of CX produced}}{2 \times \text{the moles of HAC in the feed}} \times 100\%$$

Where CX is CO, CH<sub>4</sub> and CO<sub>2</sub>, respectively.

## RESULTS AND DISCUSSION

### 1. Catalytic Characterization

The XRD patterns obtained for calcined catalysts are shown in Fig. 1(a). For 15Ni/ZrO<sub>2</sub>, the peaks of ZrO<sub>2</sub> are detected at about 2θ of 28.25°, 31.51°, 34.20°, 50.13° and 59.94°, which represent the monoclinic structure of (111), (−111), (002), (200) and (−131) planes, respectively. For Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, ZrO<sub>2</sub> monoclinic phase and La<sub>2</sub>O<sub>3</sub> phase are both not detected. La<sup>3+</sup> may be incorporated into the ZrO<sub>2</sub> lattice and a solid solution is formed. The peaks of La<sub>0.1</sub>Zr<sub>0.9</sub>O<sub>1.95</sub> are found at about 2θ of 30.25°, 35.00°, 50.27° and 60.05° corresponding to the tetragonal structure of (111), (200), (220) and (311) planes, respectively. As the solid solution of ZrO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> is formed, oxygen vacancies and lattice distortion are created because La<sup>3+</sup> (0.106 nm) has lower valence and larger ionic

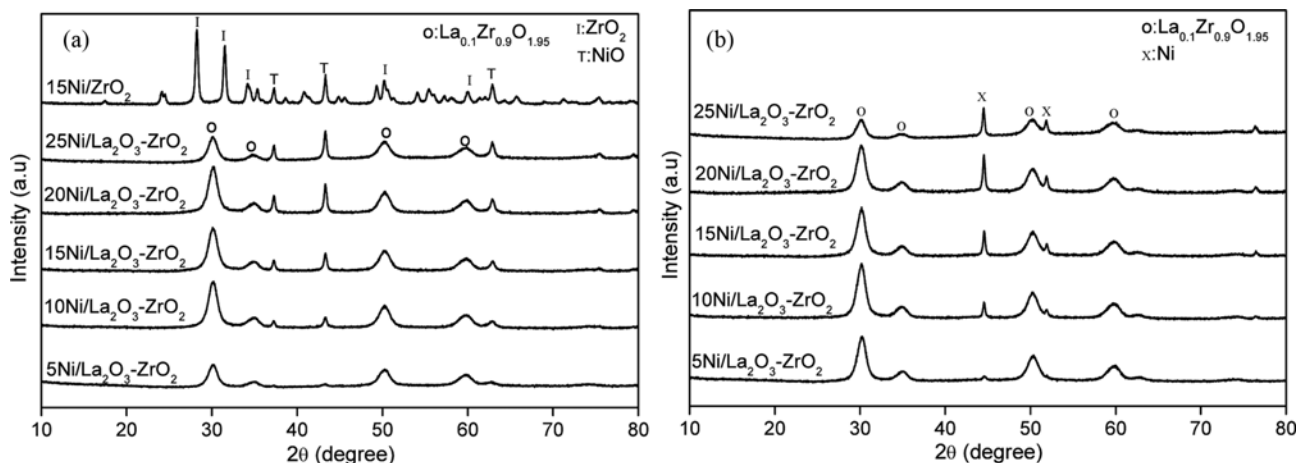


Fig. 1. XRD patterns of the calcined (a) and reduced (b) catalysts with different Ni content.

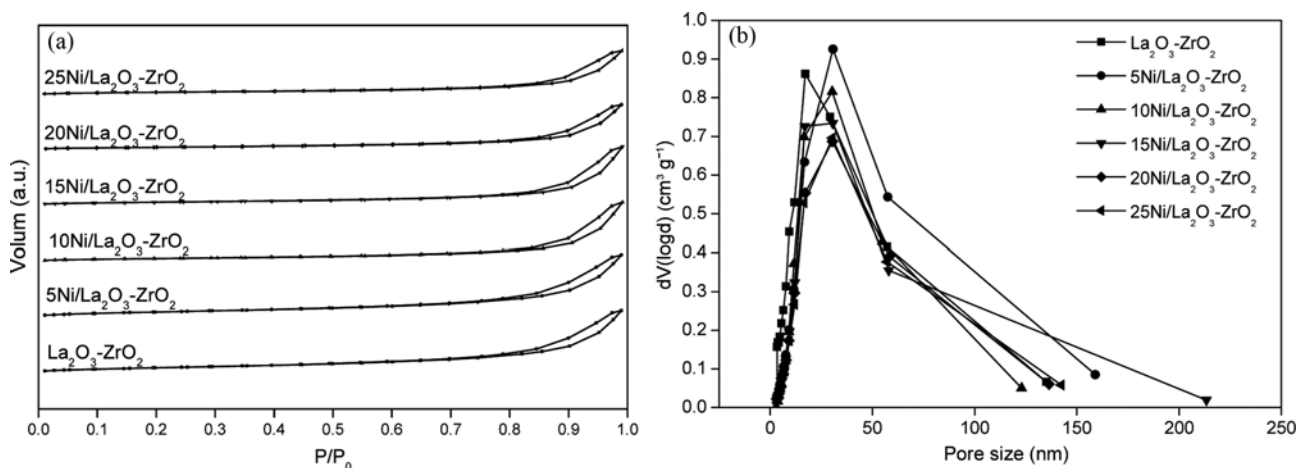


Fig. 2. N<sub>2</sub> physisorption isotherms (a) and pore size distribution curves (b) of reduced catalysts with different Ni content.

radius than the host ion  $\text{Zr}^{4+}$  (0.084 nm) [31]. The peaks of NiO phase are observed at  $37.25^\circ$ ,  $43.34^\circ$  and  $62.94^\circ$ , which is attributed to the rhombohedral structure of (101), (012) and (104) planes, respectively. The XRD patterns of catalysts reduced at  $800^\circ\text{C}$  for 4 h are shown in Fig. 1(b). Only the characteristic peaks of  $\text{La}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  and Ni are identified for reduced catalysts, indicating NiO is completely reduced to Ni, which is the active site in steam reforming of acetic acid. And the peaks of Ni phase are observed at  $44.49^\circ$ ,  $51.86^\circ$ ,  $76.36^\circ$ , belonging to the cubic structure of (111), (002), (022) planes, respectively.

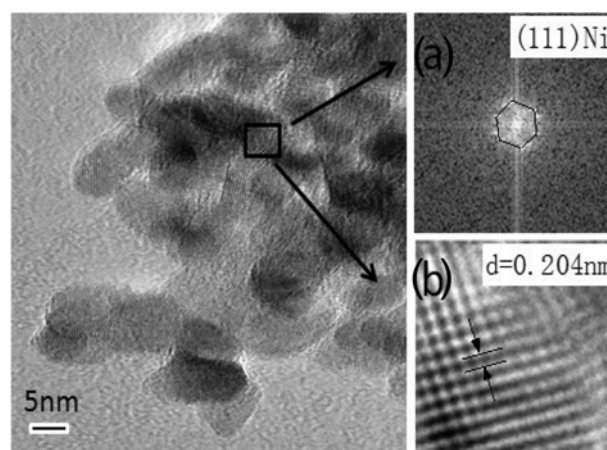
The adsorption-desorption isotherm obtained for  $\text{La}_2\text{O}_3\text{-ZrO}_2$  support and  $\text{Ni/La}_2\text{O}_3\text{-ZrO}_2$  catalysts shows type IV behavior with a well-developed hysteresis loop appearing in the relative pressure range from 0.7 to 1.0 as seen in Fig. 2. The hysteresis loop is not observed in low relative pressure region, indicating that all reduced catalysts possess large mesopores dimension [32,33]. Each curve shown in Fig. 2(b) has one narrow peak, suggesting that mesoporous  $\text{Ni/La}_2\text{O}_3\text{-ZrO}_2$  has uniform pore dimension. As expected, the specific surface area of the  $\text{La}_2\text{O}_3\text{-ZrO}_2$  support is high ( $176\text{ m}^2\text{g}^{-1}$ ) prepared as listed in Table 1, which can result in homoge-

neous distribution of nickel particles and provide sufficient active adsorption sites for reactant molecules. With Ni content increasing, both the surface area and pore volume of  $\text{Ni/La}_2\text{O}_3\text{-ZrO}_2$  gradually decrease, which possibly lies on the location of Ni particles inside the pores of  $\text{La}_2\text{O}_3\text{-ZrO}_2$  and blockage of pores of supports. The pore size (nm) of  $\text{Ni/La}_2\text{O}_3\text{-ZrO}_2$  decreases from 24.56 (Ni 5 wt%) to 22.90 (Ni 20 wt%) and increase from 22.90 (Ni 20 wt%) to 26.62 (Ni 25 wt%). 25 Ni/ $\text{La}_2\text{O}_3\text{-ZrO}_2$  possesses largest average pore size because bigger pores (150–200 nm) occur based on Fig. 2(b).

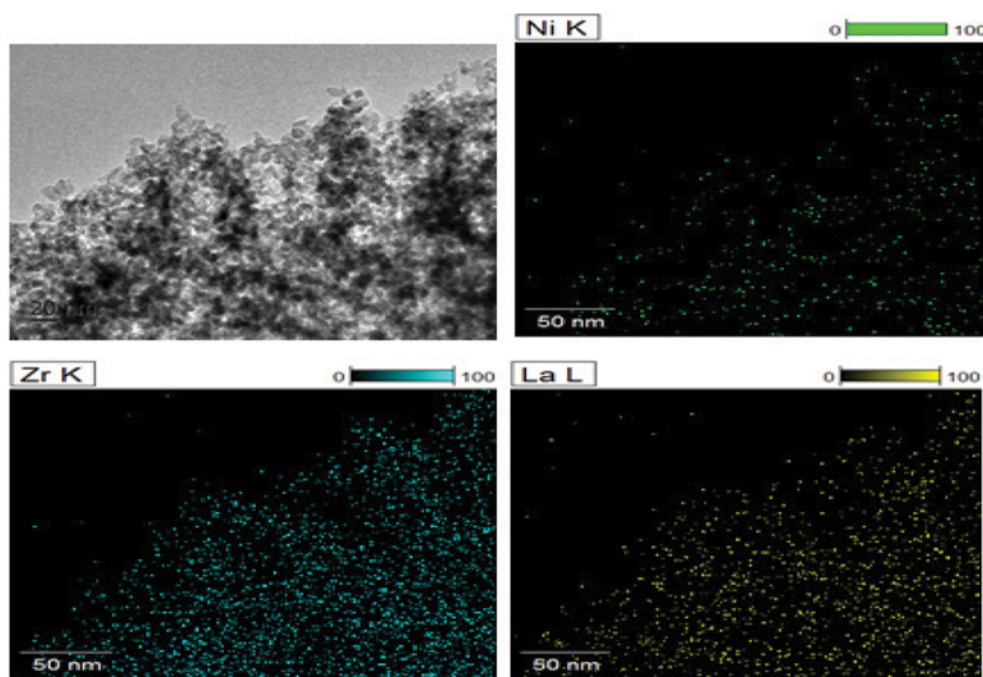
To explore the morphology and structural characterization, 15 Ni/ $\text{La}_2\text{O}_3\text{-ZrO}_2$  as a representative catalyst was further studied through HRTEM and electron diffraction pattern, and the interplanar spacing was obtained through Fourier transform as shown in Fig. 3. The pattern in Fig. 3(a) implies that the crystallite has

**Table 1. Specific surface area and pore structure of catalyst with different Ni content**

Ni/ $\text{La}_2\text{O}_3\text{-ZrO}_2$ Ni (wt%)	BET surface area ( $\text{m}^2\text{g}^{-1}$ )	Pore volume ( $\text{cm}^3\text{g}^{-1}$ )	Pore size (nm)
0	176.31	0.71	16.01
5	108.40	0.67	24.56
10	95.20	0.58	24.21
15	92.54	0.53	23.06
20	89.39	0.51	22.90
25	74.41	0.49	26.62



**Fig. 3. HRTEM images of  $\text{Ni/La}_2\text{O}_3\text{-ZrO}_2$  catalyst with 15%wt Ni.**



**Fig. 4. HRTEM images of  $\text{Ni/La}_2\text{O}_3\text{-ZrO}_2$  catalyst with 15% Ni.**

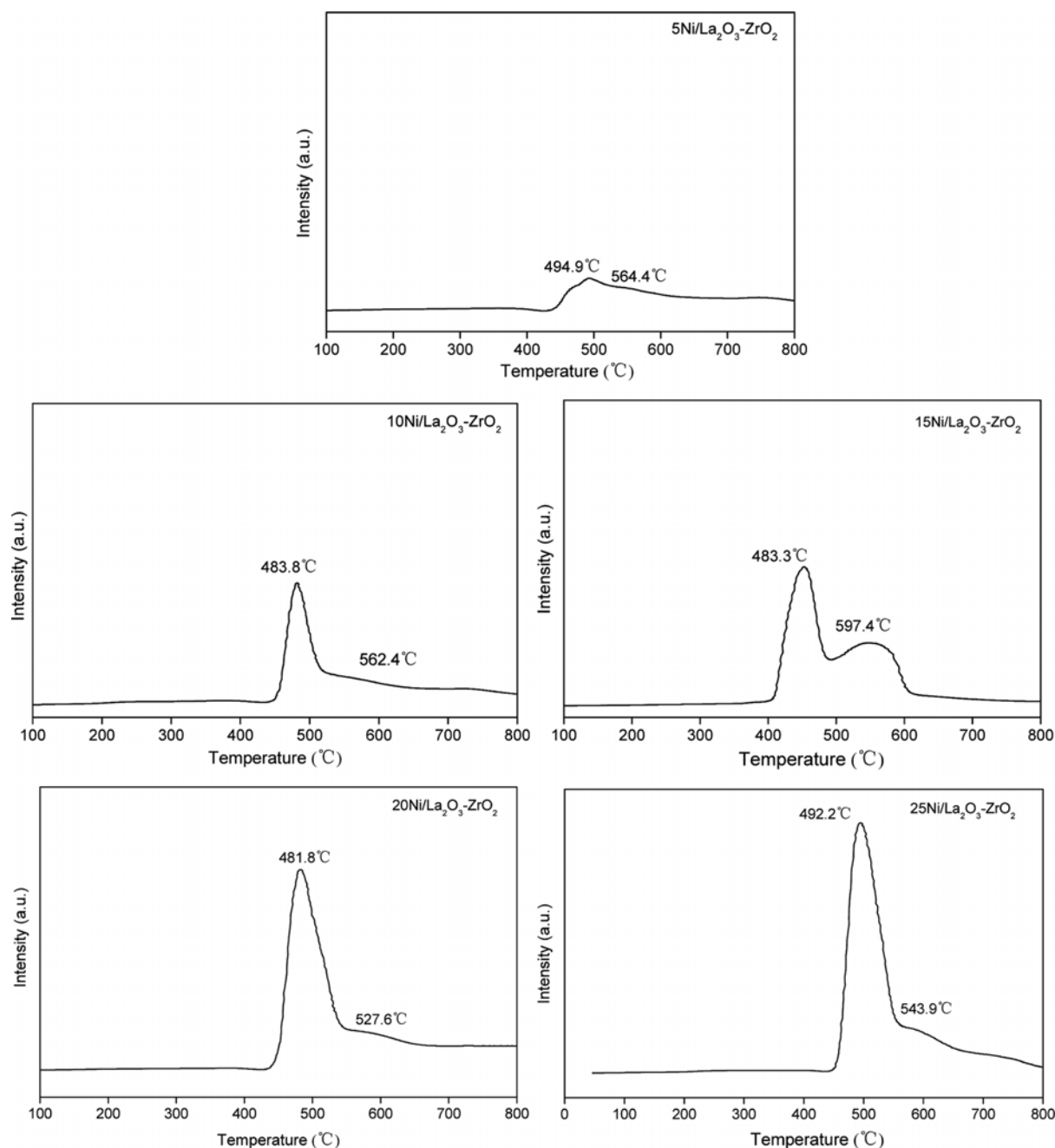


Fig. 5. H<sub>2</sub>-TPR profiles of catalysts with different Ni content.

cubic or hexagonal structure. The crystallite corresponds to cubic nickel nanocrystal, mainly because XRD characterization shows that only cubic Ni and tetragonal La<sub>0.1</sub>ZrO<sub>0.9</sub>O<sub>1.95</sub> are detected. Moreover, the corresponding interplanar spacing of nickel (111) crystal is 0.204 nm, which is very close to the interplanar spacing of 0.203 nm obtained by XRD analysis. Based on the analysis of 54 particles, the particle size of Ni-based catalyst is determined as 4–12 nm. Ni species are highly dispersed on the support as shown in Fig. 4, probably due to the good interaction between Ni and support La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> [34].

La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> support is not reduced under 900 °C and only reduction peaks of NiO species are observed in Fig. 5. The peaks at low

temperature (481–494 °C) are attributed to NiO with no or weak interaction with supports [35,36]. The peaks at high temperature (527–597 °C) are assigned to the NiO in strong interaction with support La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> [37]. The interaction between Ni and La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> can improve the dispersion of active component, change the active Ni electronic distribution and enhance the synergistic effect between Ni phase and the support, which has positive effects on the reforming reaction. The amount of H<sub>2</sub> consumption for first reduction peak increases with Ni loading. The phenomenon indicates that more Ni phases in no or weak interaction with the support are provided, as shown in Table 2. But the amount of H<sub>2</sub> consumption for the second peak shows a different trend. The

**Table 2. T<sub>max</sub> and H<sub>2</sub> consumption (mmol g<sub>cat</sub><sup>-1</sup>) of the TPR peaks obtained for the Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> with different Ni content**

Ni/La <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> Ni (wt%)	T <sub>max</sub> (°C)		Hydrogen consumption (mmol g <sub>cat</sub> <sup>-1</sup> )	
	1 <sup>st</sup> peak	2 <sup>nd</sup> peak	1 <sup>st</sup> peak	2 <sup>nd</sup> peak
5	492.2	543.9	0.42	0.43
10	481.8	527.6	0.92	0.59
15	483.3	597.4	1.19	1.18
20	483.8	562.4	2.49	0.84
25	494.9	564.4	2.98	0.87

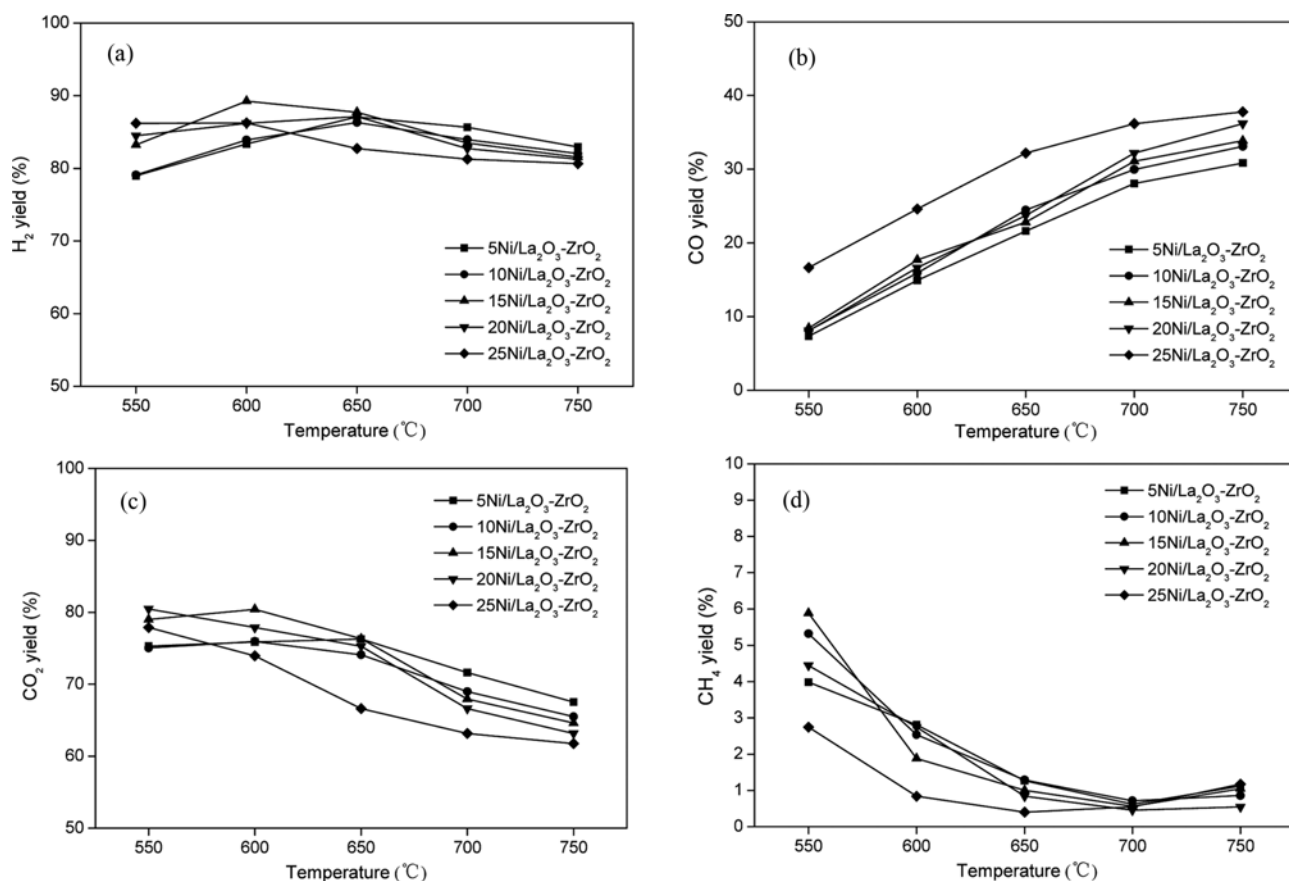
amount of H<sub>2</sub> consumption (mmol g<sub>cat</sub><sup>-1</sup>) for the second peak increases from 0.43 (Ni 5 wt%) to 1.18 (Ni 15 wt%) and decreases from 1.18 (Ni 15 wt%) to 0.87 (Ni 25 wt%). The 15 Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> has the largest hydrogen consumption for the second peak among all the catalysts, indicating that the catalyst possesses the most Ni sites interacting strongly with La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>.

## 2. Catalytic Performance

Catalytic activity of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts was evaluated in steam reforming of acetic acid in the temperature range of 550–750 °C as shown in Fig. 6. The conversion of acetic acid is near 100% at the temperature range of 550–750 °C. The yield of the gaseous products (H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub>) is low at 550 °C, mainly because of the occurrence of ketonization reaction (2CH<sub>3</sub>COOH→

CH<sub>3</sub>COCH<sub>3</sub>+CO<sub>2</sub>+H<sub>2</sub>O) and the formation of carbon, whereas the formation of acetone is limited to traces and the formation of gaseous products (mainly H<sub>2</sub>, CO and CO<sub>2</sub>) becomes predominant, and the yield of CH<sub>4</sub> for all catalysts is lower than 4% when the reaction temperature is above 550 °C.

With the increasing of reaction temperature from 600 °C to 650 °C, H<sub>2</sub> and CO<sub>2</sub> yield both follow the order of 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>>20Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>>10Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>~5Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, except that 25Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> shows the lowest yield of H<sub>2</sub> at 650 °C, probably due to the aggregation of Ni particles and the blocking of the pores of support, which will reduce the access of reactants to the active sites. 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> shows the best catalytic activity and the H<sub>2</sub> yield and CO<sub>2</sub> yield reaches 89.27% and 80.41% at 600 °C, respectively. Meanwhile, the yield of CO has contrary trends. The yield of H<sub>2</sub> and CO<sub>2</sub> for Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts is consistent with the number of nickel sites in strong interaction with support La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> based on the hydrogen consumption of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> in Table 2. The phenomenon means that Ni atoms strongly interacting with the support are the active sites and play a leading role on the steam reforming of acetic acid at low temperature of 600 °C and 650 °C. The strong interaction between active metal and support enhances the synergistic effect between Ni phase and the support, which further facilitates adsorption and dissociation of water and the formation of hydrogen. Moreover, the strong interaction between nickel and La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> may improve the dispersion and stability of nickel phases, which maintains sufficient Ni-support

**Fig. 6. The yield of gaseous products over Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> in the temperature range of 550–750 °C.**

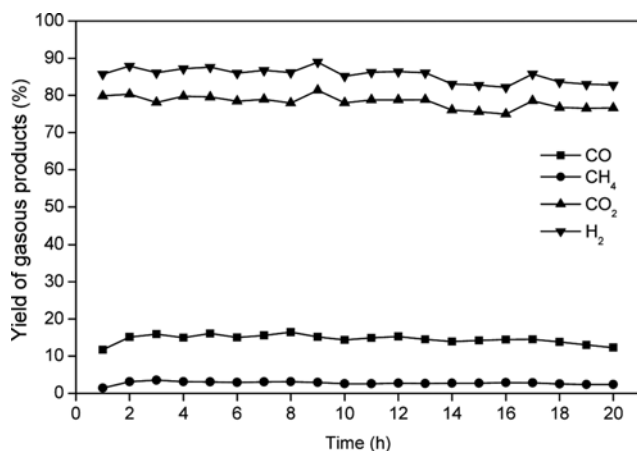


Fig. 7. The yield of gaseous products over 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> for 20 h at 600 °C.

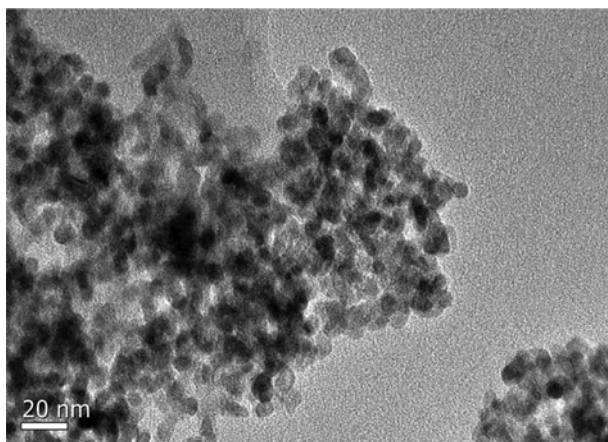


Fig. 8. HRTEM image of 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> after performing reforming reaction at 600 °C for 20 h.

interfacial areas where the reaction may occur. With the increasing of reaction temperature from 700 °C to 750 °C, the H<sub>2</sub> yield and CO<sub>2</sub> yield decrease with increase of Ni contents. And the amount of Ni atoms in no or weak interaction with supports increases with Ni content increase in Table 2. The phenomenon

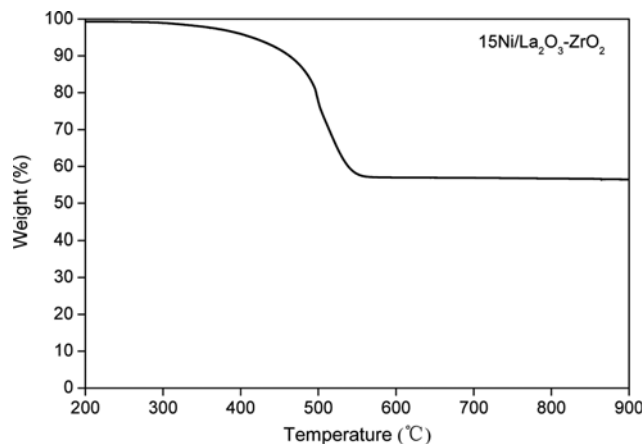


Fig. 10. TG image of 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> after performing reforming reaction at 600 °C for 20 h.

indicates that the Ni phases in no or weak interaction with supports play a dominate role at high temperature, but they are not conducive to steam reforming of acetic acid.

### 3. Stability Test

A stability test of 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> was conducted for 20 h at 600 °C, as shown in Fig. 7. The yield of H<sub>2</sub> for 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> maintains above 82.78% within 20 h, indicating the material has high activity and good stability in the steam reforming of acetic acid. To investigate properties and structures of the catalyst after reforming reaction of 20 h, SEM, TG and TEM characterization were used to analyze the used catalyst. The TEM observation shows that the used catalyst particles have no obvious sintering as shown in Fig. 8. The SEM observation finds that filamentous carbon is formed by comparison to the reduced catalyst, but the catalyst still possesses rich porous structure on the surface and the nickel sites are not blocked. Fig. 10 shows that the amount of coke deposited on 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> is 0.23 mmol C·h<sup>-1</sup>·g<sup>-1</sup><sub>-acetic acid</sub> at 600 °C, which is lower than the amount of coke deposited on Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> and Ni/MgO-Al<sub>2</sub>O<sub>3</sub> [38,36]. The amount of coke deposited on Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> and Ni/MgO-Al<sub>2</sub>O<sub>3</sub> was 0.71 mmolC·h<sup>-1</sup>·g<sup>-1</sup><sub>-acetic acid</sub> and 0.32 mmolC·h<sup>-1</sup>·g<sup>-1</sup><sub>-acetic acid</sub> respectively. To know how good the performance was of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, the catalysts were compared with

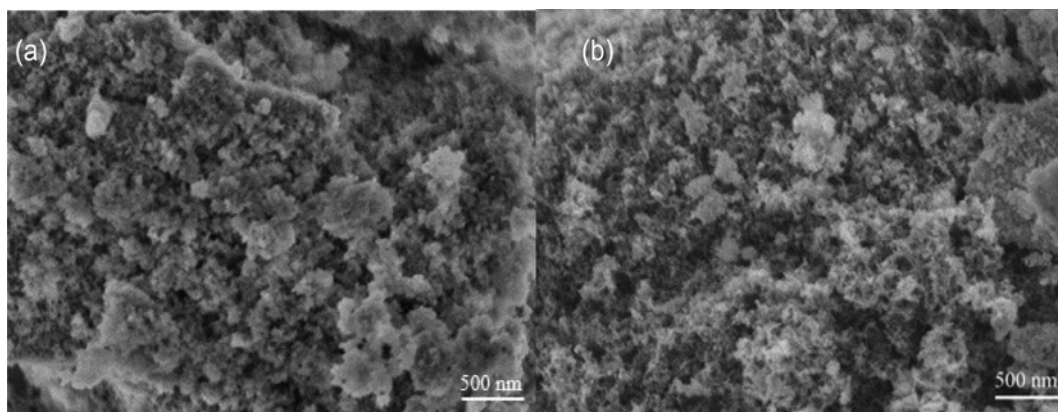


Fig. 9. SEM image of reduced 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (a) and 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> after performing reforming reaction at 600 °C for 20 h (b).



**Table 3. The H<sub>2</sub> yield and stability of catalysts in the steam reforming of acetic acid**

Catalyst	Temperature (°C)	H <sub>2</sub> O/HAc (mole/mole)	Y <sub>H<sub>2</sub></sub> (%)	Stability (h)	Reference
Ni/ZrO <sub>2</sub>	500	2	74	3	[23]
Ni/Al <sub>2</sub> O <sub>3</sub>	600	3	61	4	[39]
Ni/CeO <sub>2</sub> -ZrO <sub>2</sub>	650	3	78	25	[8]
Ni/La <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	600	5.7	20	---	[40]
Ni/MgO-Al <sub>2</sub> O <sub>3</sub>	600	2	69	20	[36]
Pd/HZM-5	600	18.4	60	--	[9]
Pt/ZrO <sub>2</sub>	600	10	87	2	[41]
Co/La <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	400	2	68	20	[27]
Ru/Mg(Al)O	700	6	70	20	[42]

similar catalyst system in the literature, as shown in Table 3. According to the characterization results, the superior performance of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> may be ascribed to high surface area, well-developed porosity and efficient Ni active sites. From this point, Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst is one promising candidate for industrial application in the future.

### CONCLUSION

Catalytic activity of Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> with different Ni content was evaluated by steam reforming of acetic acid in the temperature range of 550–750 °C in a fixed-bed quartz reactor. 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> showed good catalytic activities and H<sub>2</sub> yield and CO<sub>2</sub> yield reached 89.27% and 80.41% at 600 °C. 15Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst maintained relatively stable catalytic activities for a period of 20 h. The results show that the tetragonal structure of La<sub>0.1</sub>Zr<sub>0.9</sub>O<sub>2</sub> phase is formed and the Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts possess high surface area and uniform particle sizes. The Ni phases are the active sites in the reforming reaction, which are highly dispersed on the support. The interaction between Ni and support plays an important role in catalytic activities of the catalysts. Two types of Ni species were detected, which correspond to the Ni species in no interaction with supports and the Ni species strongly interacted with supports, respectively. The active Ni phase interacting with support La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> plays a dominant role in catalytic activity at low temperature of 600 °C and 650 °C, whereas Ni with no or weak interaction with the support plays a leading role at high temperature.

### ACKNOWLEDGEMENTS

The authors are grateful for the financial support of CAS Renewable Energy Key Lab., Natural Science Foundation of China (51576201), National Natural Science Foundation of Guangdong province (2015A030312007), Guangdong Science and Technology Project (2013B050800007), Guangzhou Science and Technology Project (2013J4500027).

### REFERENCES

- Y. Z. Lang, R. R. Arnepalli and A. A. Tiwari, *J. Nanosci. Nanotechnol.*, **11**, 3719 (2011).
- N. L. Panwar, R. Kothari and V. V. Tyagi, *Renew. Sust. Energy Rev.*, **16**, 1801 (2012).
- S. A. Chattanathan, S. Adhikari and N. Abdoulmoumine, *Renew. Sust. Energy Rev.*, **16**, 2366 (2012).
- P. M. Mortensen, J. D. Grunwaldt, P. A. Jensen, K. G. Knudsen and A. D. Jensen, *Appl. Catal. A*, **407**, 1 (2011).
- S. R. Wang, Y. R. Wang, Q. J. Cai, X. Y. Wang, H. Jin and Z. Y. Luo, *Sep. Purif. Technol.*, **122**, 248 (2014).
- S. R. Wang, Q. J. Cai, X. Y. Wang, L. Zhang, Y. R. Wang and Z. Y. Luo, *Energy Fuels*, **28**, 115 (2014).
- R. Trane, S. Dahl, M. S. Skjoth-Rasmussen and A. D. Jensen, *Int. J. Hydrogen Energy*, **37**, 6447 (2012).
- X. X. Zheng, C. F. Yan, R. R. Hu, J. Li, H. Hai, W. M. Luo, C. Q. Guo, W. B. Li and Z. Y. Zhou, *Int. J. Hydrogen Energy*, **37**, 12987 (2012).
- Q. Wang, S. R. Wang, X. B. Li and L. Guo, *Bioresources*, **8**, 2897 (2013).
- A. C. Basagiannis and X. E. Verykios, *Appl. Catal. A-Gen.*, **308**, 182 (2006).
- P. Mohanty, M. Patel and K. K. Pant, *Bioresour. Technol.*, **123**, 558 (2012).
- T. Montini, L. DeRogatis, V. Gombac, P. Fornasiero and M. Graziani, *Appl. Catal. B-Environ.*, **71**, 125 (2007).
- F. Bimbela, M. Oliva, J. Ruiz, L. García and J. Arauzo, *J. Anal. Appl. Pyrolysis*, **79**, 112 (2007).
- J. Román Galdámez, L. García and R. Bilbao, *Energy Fuels*, **19**, 1133 (2005).
- J. A. Medrano, M. Oliva, J. Ruiz, L. Garcia and J. Arauzo, *Int. J. Hydrogen Energy*, **33**, 4387 (2008).
- J. A. Medrano, M. Oliva, J. Ruiz, L. García and J. Arauzo, *J. Anal. Appl. Pyrolysis*, **85**, 214 (2009).
- F. Bimbela, D. Chen, J. Ruiz, L. Garcia and J. Arauzo, *Appl. Catal. B: Environ.*, **119–120**, 1 (2012).
- S. R. Wang, X. B. Li, F. Zhang, Q. J. Cai, Y. R. Wang and Z. Y. Luo, *Int. J. Hydrogen Energy*, **38**, 16038 (2013).
- S. R. Wang, Q. J. Cai, F. Zhang, X. B. Li, L. Zhang and Z. Y. Luo, *Int. J. Hydrogen Energy*, **39**, 18675 (2014).
- J. L. Lu, B. S. Fu, M. C. Kung, G. M. Xiao, J. W. Elam, H. H. Kung and P. C. Stair, *Science*, **335**, 1205 (2012).
- M. A. Khan and S. I. Woo, *Korean J. Chem. Eng.*, **31**, 1204 (2014).
- H. J. Lee, G. S. Shin and Y. C. Kim, *Korean J. Chem. Eng.*, **32**, 1267 (2015).
- Z. K. Li, X. Hu, L. J. Zhang, S. M. Liu and G. X. Lu, *Appl. Catal. a-*



- Gen.*, **417**, 281 (2012).
24. H. Z. Feng, P. Q. Lan and S. F. Wu, *Int. J. Hydrogen Energy*, **37**, 14161 (2012).
25. G. Pantaleo, V. LaParola, F. Deganello, P. Calatizzo, R. Bal and A. M. Venezia, *Appl. Catal. B-Environ.*, **164**, 135 (2015).
26. B. M. Guell, I. M. T. da Silva, K. Seshan and L. Lefferts, *Appl. Catal. B-Environ.*, **88**, 59 (2009).
27. X. Hu and G. X. Lu, *Catal. Commun.*, **12**, 50 (2010).
28. S. H. Park, B. H. Chun and S. H. Kim, *Korean J. Chem. Eng.*, **28**, 402 (2011).
29. W. Tao, G. W. Cheng, W. L. Yao, X. G. Lu, Q. H. Zhu, G. S. Li and Z. F. Zhou, *Int. J. Hydrogen Energy*, **39**, 18650 (2014).
30. T. F. Hou, B. Yu, S. Y. Zhang, J. H. Zhang, D. Z. Wang, T. K. Xu, L. Cui and W. J. Cai, *Appl. Catal. B-Environ.*, **168**, 524 (2015).
31. Y. Z. Chen, B. J. Liaw, C. F. Kao and J. C. Kuo, *Appl. Catal. A-Gen.*, **217**, 23 (2001).
32. A. Rumblecker, F. Kleitz, E. L. Salabas and F. Schuth, *Chem. Mater.*, **19**, 485 (2007).
33. M. M. Nair, S. Kaliaguine and F. Kleitz, *Acs Catal.*, **4**, 3837 (2014).
34. G. Wu, C. Zhang, S. Li, Z. Huang, S. Yan, S. Wang, X. Ma and J. Gong, *Energy Environ. Sci.*, **5**, 8942 (2012).
35. C. Jimenez-Gonzalez, Z. Boukha, B. de Rivas, J. J. Delgado, M. A. Cauqui, J. R. Gonzalez-Velasco, J. I. Gutierrez-Ortiz and R. Lopez-Fonseca, *Appl. Catal. A-Gen.*, **466**, 9 (2013).
36. F. G. E. Nogueira, P. G. M. Assaf, H. W. P. Carvalho and E. M. Assaf, *Appl. Catal. B-Environ.*, **160**, 188 (2014).
37. H. S. Roh, K. W. Jun, W. S. Dong, J. S. Chang, S. E. Park and Y. I. Joe, *J. Mol. Catal. A-Chem.*, **181**, 137 (2002).
38. R. R. Hu, C. F. Yan, X. X. Zheng, H. Liu and Z. Y. Zhou, *Int. J. Hydrogen Energy*, **38**, 6033 (2013).
39. P. G. M. Assaf, F. G. E. Nogueira and E. M. Assaf, *Catal. Today*, **213**, 2 (2013).
40. K. K. Pant, P. Mohanty, S. Agarwal and A. K. Dalai, *Catal. Today*, **207**, 36 (2013).
41. K. Takanabe, K. Aika, K. Seshan and L. Lefferts, *Chem. Eng. J.*, **120**, 133 (2006).
42. F. Bossola, C. Evangelisti, M. Allietta, R. Psaro, S. Recchia and V. Dal Santo, *Appl. Catal. B-Environ.*, **181**, 599 (2016).