A study on the stability of a NiO−CaO/Al₂O₃ complex catalyst by La₂O₃ modification for hydrogen production

H.Z. Feng [b], P.Q. Lan [b], S.F. Wu [a,b,*]

[a] *Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Zhejiang University, Hangzhou 310027, China*
[b] *Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China*

ARTICLE INFO

ABSTRACT

This paper details the study of La₂O₃ modifications and their effect on the stability of a NiO−CaO/Al₂O₃ sorption complex catalyst used in the ReSER (reactive sorption enhanced reforming) process of hydrogen production. The La₂O₃-modified NiO−CaO/Al₂O₃ sorption complex catalyst was prepared by isometric impregnation. The microstructure, morphology and reducibility of the La₂O₃-modified sorption complex catalyst were characterized by means of BET, TEM, XRD and TPR. The stability of the catalyst used in the ReSER process was evaluated on a laboratory-scale fixed-bed reactor. Our results showed that modifying the sorption complex catalyst with La₂O₃ improved its stability up to 30 cycles of the ReSER process for hydrogen production, while only seven cycles were obtained without La₂O₃ modification. We showed that the source of the stability improvement that the La₂O₃ in the catalyst not only functioned to restrain the decrease of the support surface area and reduce the sintering of nano-CaCO₃, which could limit the decay of the sorption capacity and stability of the catalyst, but also increased the interaction between nickel oxide and the support, which improved the stability of the catalyst by increasing the dispersion of nickel grains and inhibited the growth of nickel grain size.
Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen is used in petroleum, chemical engineering, energy, metallurgy, medicine, aerospace and other industrial areas. Because of its high combustion value and its non-pollution nature when used as a fuel, hydrogen is one of the most clean and efficient secondary energy sources. Currently 96% of hydrogen for industrial use is produced from fossil fuels such as coal, oil, natural gas and other sources [1]. Steam methane reforming (referred to as SMR) is one of the most widely used methods of hydrogen production as a result of its relatively simple process, low cost, and high efficiency [2−4]. To overcome the disadvantage of high energy consumption as the reforming reaction itself is strongly endothermic, reactive sorption enhanced reforming [5](ReSER) is a promising technology that can reduce the temperature of the reforming reaction, and get as high as 95% v/v hydrogen concentration with a CO₂ adsorption-enhanced reforming reaction [6,7].

The study of sorption complex catalysts is a crucial technology of the ReSER process for hydrogen production. He and Wu [8] studied a NiO−CaO/Al₂O₃ sorption complex catalyst prepared by mechanical mixing of the precursors NiO, CaO and Al₂O₃, and showed that the outlet hydrogen concentration was more than 95% in a fixed-bed reactor. However, the stability of the complex catalyst is insufficient for industrial application. Wu and Wang [9] added ZrO₂ to prepare a ZrO₂-

modified NiO–CaO/Al$_2$O$_3$ sorption complex catalyst using a cycle of 600 °C reforming reaction and 800 °C regeneration of CaCO$_3$ to evaluate the stability of the catalyst. Their data showed that the ZrO$_2$-modified catalyst could be used for 20 cycles in the ReSER process of hydrogen production.

To improve the stability of the catalyst, some researchers have found that La$_2$O$_3$ performed better in reducing the carbon deposition of the Ni catalyst [10,11]. Lanthanum is a rare earth metal used to modify catalysts by an interaction that inhibited the Al$_2$O$_3$ support sintering rate caused by surface diffusion and increased the stability of the support [12]. Subsequently, La$_2$O$_3$ was studied alone as a support. Zhang et al. [13–15] found that a Ni/La$_2$O$_3$ catalyst had good performance in methane and ethanol reforming reactions. More detailed research on the effects of preparation condition and procedure, such as impregnation order, impregnation time, and others have also been previously studied [16–20].

As the stability of the complex catalyst is much insufficient for industrial application, it is important to study how to improve its stability. In this paper we used La$_2$O$_3$ as an additive to a modified NiO–CaO/Al$_2$O$_3$ complex catalyst prepared by isometric impregnation, and studied La$_2$O$_3$ effect on the Ni crystal size and formation of NiAl$_2$O$_4$ under the mass quantity of CaO exist in ReSER hydrogen produce process.

2. Experiment

2.1. Preparation of catalysts

About 50 g of nano-CaCO$_3$ (70 nm, >95% purity, Hu Zhou Ling Hua Ltd., China) was dispersed in distilled water, and then ultrasonically dispersed for 5 min. Aluminum sol, with a mass ratio of CaCO$_3$ and Alumina 1:0.7, was added to the above solution and the mixed slurry was fully stirred. The slurry was dried, extruded and calcined at 550 °C for 2–4 h. Finally, 1.3–1.5 mm diameter particles were obtained as a support.

The catalyst was prepared by two-step isometric impregnation using La(NO$_3$)$_3$·6H$_2$O (44% purity (La$_2$O$_3$ weight), Sinopharm Chemical Reagent Co., Ltd., China) and Ni(NO$_3$)$_2$·6H$_2$O (98% purity, Shanghai HengXin Chemical Reagent Co., Ltd., China) as the precursors of La$_2$O$_3$ and NiO, respectively. First, the water absorption of the support was measured, and then the support was impregnated in 16.4% mass concentration lanthanum nitrate for 12 h. After drying, the sample was calcined at 500–550 °C for 2–5 h. The sample was then impregnated in a mass concentration 53.72% nickel nitrate solution, which was adjusted to a pH 5–6 with ammonia, for about 12 h. As described previously, the sample was again dried and calcined at 500–550°C for 2–5 h. The obtained catalyst was a La$_2$O$_3$-modified NiO–CaO/Al$_2$O$_3$ complex catalyst and named "LNCA". The catalyst prepared without La$_2$O$_3$ modification in the above process was a NiO–CaO/Al$_2$O$_3$ complex catalyst and referred to as "NCA".

2.2. Catalyst characterization

The microstructure of the catalyst was determined by BEL-SORP-miniII instrument (Japan). The surface area was measured by N$_2$ adsorption at 77 K and calculated with BET formula. The sorption capacity and sorption stability of the catalyst were measured through thermo-gravimetric analysis (TGA, PYRIS 1 produced by Perkin Elmer Corporation, America). The Ni particle mean diameter was examined by X-ray diffraction (XRD) on the D/MAX-RA X-ray diffractometer made in Japan with a copper anode under the following experimental conditions: voltage 40 kV, current 40 mA. TPR was tested by the TP-5000III adsorption instrument made in Tianjin. 50 mg of catalyst were loaded into the trap joining with N$_2$ mixed with 5% H$_2$, and the temperature was increased from 373 K to 1123 K at a rate of 10 K min^{-1}. In this study, TEM instrumentation was a JEM-1230 transmission electron microscope produced by Japanese Electronics Corporation with 95% ethanol used as a dispersant and an accelerating voltage of 80 kV.

2.3. Evaluation of ReSER hydrogen production

To test the catalysts, evaluation of the sorption complex catalysts in the ReSER process was carried out in a fixed-bed reactor as shown in Fig. 1. The reactor was produced from a stainless steel reactor tube with a size of Φ 500 × 15 mm. Before the experiment, 5 g of complex catalyst particles were filled into the constant-temperature zone of the reactor tube. Methane provided by the cylinder and water from the evaporator were mixed, preheated and conducted into the reactor. To remove the effects of internal and external diffusion on reactions, the reactions were carried out under the following operation conditions: a reaction temperature of 600 °C, space velocity 257 h^{-1}, a steam-carbon mole ratio of 4, and a regeneration temperature of 800 °C. The reaction and regeneration temperature could be automatically detected and controlled by a programmable temperature controller for the furnace. The concentration data of H$_2$, CH$_4$, CO and CO$_2$ from the reforming reaction were detected and analyzed by an on-line gas chromatography detector. The conversion of methane was calculated according to the Eq. (1) where X_{CH_4} (%) is the conversion of methane, F_{CH_4} (mL/min) is the flow rate of methane, F_{out} (mL/min) is the effluent flow rate of the product gas, and y_{CH_4} (%) is the methane content. The stability of the
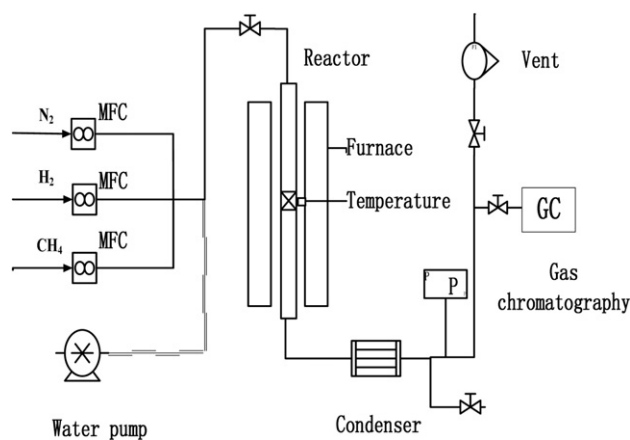

Fig. 1 – The diagram of the fixed-bed reactor for hydrogen production.

Table 1 – Pore structure properties of LNCA and NCA.

Number	Name	Surface area [$m^2 \, g^{-1}$]	Pore size (nm)	Pore volume [$cm^3 \, g^{-1}$]
1	LNCA	29.18	4.6	0.15
2	NCA	33.37	4.02	0.1977

catalyst was evaluated by repeated cycles of the reforming reaction and regeneration process.

$$X_{CH_4} = \frac{F_{CH_4} - F_{out} \times y_{CH_4}}{F_{CH_4}} \qquad (1)$$

3. Results and discussions

3.1. Microstructure characteristics of a La₂O₃-modified NiO−CaO/Al₂O₃ catalyst

The microstructure of a catalyst can greatly influence its catalytic performance. The amount of the reforming active component (NiO) and the reaction sorption component (CaO) of the catalyst affect the specific surface area of catalyst. The use of La$_2$O$_3$ as an additive will affect the microstructure of the catalyst, so we measured the specific surface area, pore size, pore volume and morphology of the sorption complex catalyst with and without La$_2$O$_3$. The results are listed in Table 1.

Table 1 shows the BET test results of LNCA and NCA. The specific surface area and pore volume of LNCA decreased by 12% and 20%, respectively, when compared to NCA. However, the pore size of LNCA was increased 15% over that of NCA. One possible reason was that the preparation of LNCA had one more step of impregnation and high temperature calcination than that of NCA, and some small pores of LNCA collapsed

which might have increased the mean pore size. Meanwhile, La$_2$O$_3$ dispersed on the support surface and pore of the support could decrease the specific surface area and pore volume of the complex catalyst.

Fig. 2(a–e) show the TEM results of LNCA and NCA during each of the preparation steps.

Fig. 2(a) shows the flocculent state of Al$_2$O$_3$ calcined from the alumina sol. The flocculent Al$_2$O$_3$ distributed on the surface of CaCO$_3$ particles when the mixture of the alumina sol and nano-CaCO$_3$ was calcinated as shown in Fig. 2(b). Compared Fig. 2(b) with Fig. 2(a), we could know that the cubic one was CaCO$_3$. Fig. 2(c) shows the surface morphology of the support after it was impregnated with La(NO$_3$)$_3$ and calcinated. It was clear that the particle of La$_2$O$_3$ was cylindrical with a length of 100 nm and diameter of 10 nm, and it played a sustaining role in the connection between two CaCO$_3$ particles. Fig. 2(d) shows the surface morphology of LNCA which was impregnated with Ni(NO$_3$)$_2$ and calcinated based on the state shown in Fig. 2(c). Then the cylindrical La$_2$O$_3$ disappeared as a result of calcination. Similarly, Fig. 2(e) shows the surface morphology of NCA, which was impregnated with Ni(NO$_3$)$_2$ based on the support and calcinated as shown in Fig. 2(b). Obviously the point with deep color is NiO in Fig. 2(d) and Fig. 2(e). Comparing Fig. 2(d) with Fig. 2(e), the catalyst modified with La$_2$O$_3$ had smaller nickel size and uniformly dispersed nickel particles.

3.2. The reducibility of La₂O₃-modified NiO−CaO/Al₂O₃ catalyst

The reducibility of the LNCA and NCA catalysts, which determined the amount of the Ni active component was measured by a TPR test as shown in Fig. 3.

It can be seen from Fig. 3 that there were two peaks on the reduction curve of fresh LNCA, and the reduction peak points
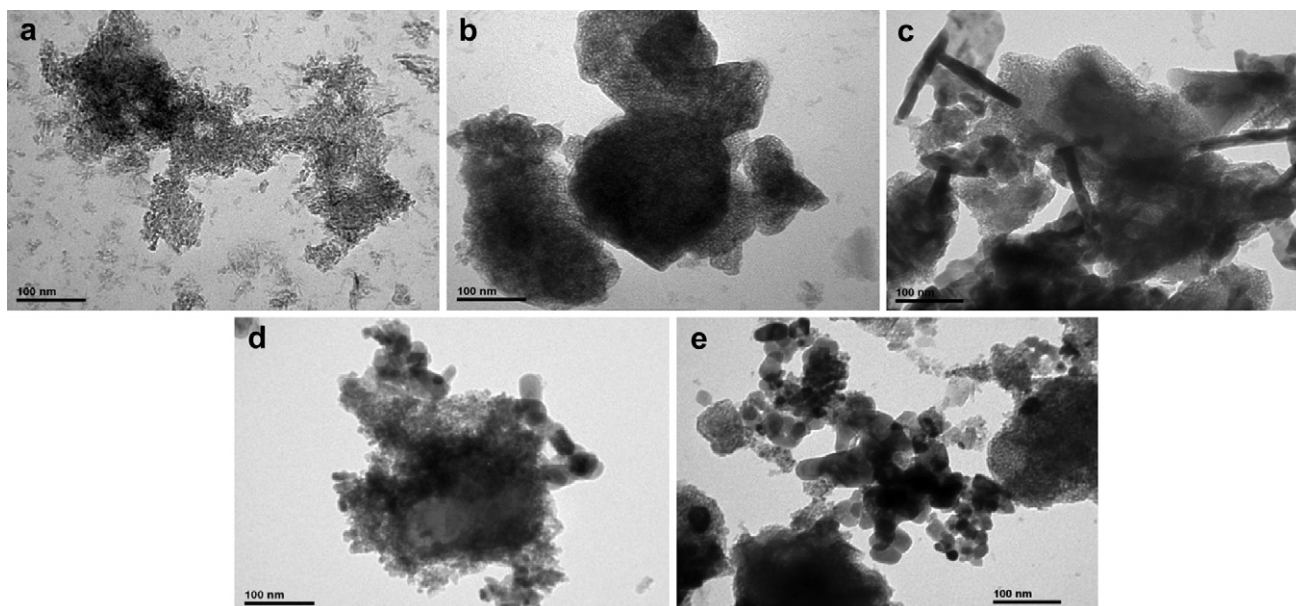

Fig. 2 – (a) Support (Al₂O₃), (b) Support and sorbent (Al₂O₃ and CaCO₃), (c) Impregnation with La(NO₃)₃(Al₂O₃, CaCO₃ and La₂O₃), (d) LNCA(NiO−CaO/La₂O₃/Al₂O₃), (e) NCA(NiO−CaO/Al₂O₃).
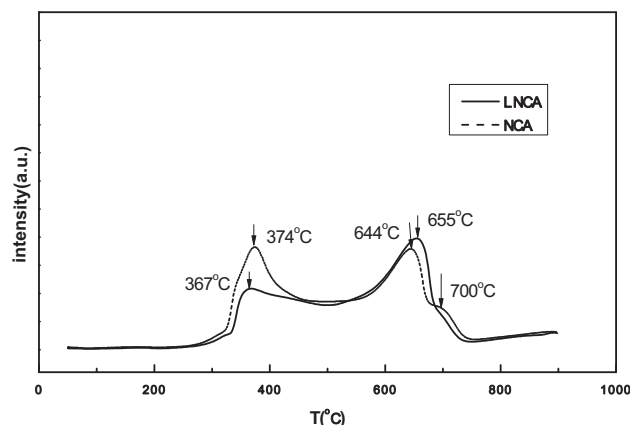
Fig. 3 − TPR test result of LNCA and NCA.

Fig. 4 − The sorption capacity of fresh LNCA and NCA.

were 367 °C and 655 °C. NCA has one more reduction peak at high temperature. The first peak temperature is 374 °C and is regarded as the free NiO reduction peak. The second one is 644 °C and regarded as the NiOx group which has a strong interaction with the support. The third is 700 °C and it should be a peak of $NiAl_2O_4$ since NiO easily reacts with Al_2O_3 to yield $NiAl_2O_4$. The figure obviously showed that the initial reduction temperature of the catalyst increased after La_2O_3 modification. The peak area at lower temperature as well as total peak area are less; this explains that the amount of reducible nickel oxide decreases by addition of La_2O_3. In short, La_2O_3 modification raised the reduction difficulty of nickel oxide in the catalyst and, thus, decreased the degree of reduction. The increasing reduction peak area at high temperature demonstrated that La_2O_3 modification enhanced the interaction between nickel oxide and the support. This interaction is not strong enough to produce $NiAl_2O_4$. There was a $NiAl_2O_4$ reduction peak at 700 °C on the reduction curve of NCA only, which showed that the addition of La_2O_3 inhibited the formation of $NiAl_2O_4$.

3.3. The sorption capacity of La_2O_3-modified NiO−CaO/Al_2O_3 catalyst

Sorption capacity affects the hydrogen production efficiency directly and is an important indicator of the sorption complex catalyst in ReSER hydrogen production. The carbonation−calcination cycles were carried out in TGA. About 2 mg of catalyst complex was placed in the platinum basket. The temperature increased from 150 °C to 725 °C, and maintained for 10 min to make the catalyst decompose completely. Then the carbonation−calcination cycles were going on. Temperatures for the carbonation and calcination reactions were set at 600 °C and 725 °C, respectively. And both their durations were 10 min. The reactive gas flow rate was 50 mL/min with a CO_2 concentration of 20% (N_2 balance) during the carbonation stage and the gas flow rate was kept unchanged in calcination stage with N_2 only. Fig. 4 shows the influence of La_2O_3 modification on the sorption capacity of the complex catalyst.

In Fig. 4, the data shows that the sorption capacity of fresh LNCA increased by 49% compared to NCA. As the number of
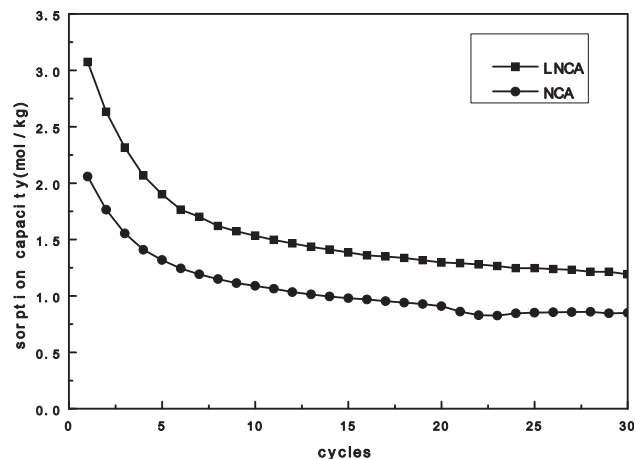
carbonation−calcination cycles increased, the sorption capacity of both LNCA and NCA decreased. It could also be seen from Fig. 4 that the sorption capacity of the LNCA catalyst was higher than NCA's, which must be the result of CO_2 adsorption by La_2O_3. Furthermore both of the catalysts were much more durability after 15 cycles.

3.4. Evaluation of a La_2O_3-modified NiO−CaO/Al_2O_3 catalyst for ReSER hydrogen production

The influence of La_2O_3 modification on the stability of LNCA and NCA during ReSER hydrogen production in a fixed-bed reactor was determined by the method described in Section 2.3. The results are shown in Fig. 5.

Fig. 5 shows that more than 92% of hydrogen concentration can be obtained by both the LNCA and NCA catalysts. The highest hydrogen concentration obtained by using the LNCA catalyst was 95%. Compared with ZrO_2-modified complex catalyst proposed by Wu and Wang (2010) [9], the La_2O_3-modified NiO−CaO/Al_2O_3 catalyst had 10 more cycles of hydrogen production under the same operation conditions. The conversion of methane with LNCA in ReSER hydrogen production cycles was higher than that of NCA. From the product concentration of NCA as shown in Fig. 6, we can see
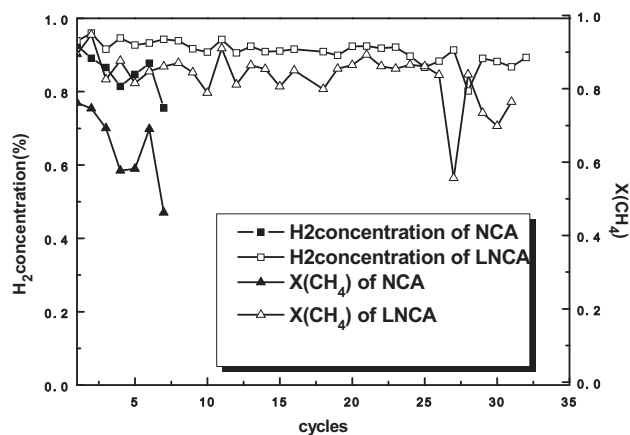

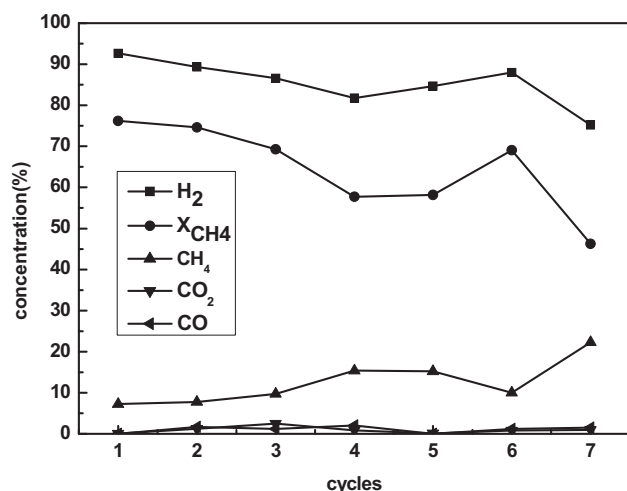**Fig. 5 − The hydrogen production result of LNCA and NCA.**

Fig. 6 – The product concentration of NCA.

Table 3 – The microscopic structure and adsorption properties of sorption complex catalyst.

Name	Surface area	Pore size	Pore volume	Sorption capacity ($mol \cdot g^{-1}$)	
	$[m^2\ g^{-1}]$	(nm)	$[cm^3\ g^{-1}]$	0 cycle	10th cycle
LNCA-r-30	14.0	1.64	0.0616	1.34	0.91
NCA-r-7	10.7	1.64	0.0550	1.05	0.89

The characterizations of microscopic structure and adsorption properties of sorption complex catalyst after evaluation are shown in Table 3.

Tables 1 and 3 and Fig. 2 show that the specific surface area of LNCA dropped by 52% after 30 reaction cycles, while that of NCA diminished by 67.9% after 7 cycles. The final specific surface area of LNCA was still larger than that of NCA. The stability improvement from La_2O_3 modification of the catalyst likely derives from the microscopic structure stability of the support, especially withstanding the temperature fluctuations between 600 °C and 800 °C. H. Schaper et al. (1984) [12] also proved that the addition of La_2O_3 inhibited the support sintering rate and diminished the decreasing extent of the support surface area.

Another potential source of LNCA catalyst stability improvement over NCA catalyst is that the sorption capacity proved to be more stable over 30 cycles. In addition, our previous study showed the characteristics of using a nano-$CaCO_3$ as a CaO precursor had a fast reactive sorption [23]. The catalyst LNCA had higher sorption capacity in first surface reaction of CaO with CO_2 in short time. This will cause higher methane conversion than an NCA catalyst under the same reaction conditions.

that as the hydrogen production cycles increase, the X_{CH_4} decreases. But the concentration of CO_2 keeps in a relatively low value. It means that the main reason of the decline in methane conversion is the decrease of catalytic activity, not because of sorption capacity of the catalyst. These results indicated that La_2O_3 modification not only increased the conversion of methane in ReSER, but also significantly improved the stability of the sorption complex catalyst.

3.5. Analysis of the improvement in catalyst stability

The sorption complex catalysts before and after ReSER hydrogen production were characterized by XRD to study the influence of La_2O_3 modification on the nickel grain size of the NiO–CaO/Al$_2$O$_3$ catalyst. After 30 runs of ReSER hydrogen production, LNCA was referred to as LNCA-r-30, and NCA was referred to as NCA-r-7 after 7 runs. The nickel grain size was calculated by the Scherrer formula and is shown in Table 2 [21,22].

It can be seen from the data in Table 2 that the NiO grain size of fresh LNCA was smaller than that of fresh NCA, and the Ni grain size of LNCA increased to 107.7 nm after 30 cycles, while the Ni grain size of NCA was 256 nm after 7 cycles. This could indicate that the sorption complex catalyst modified by La_2O_3 inhibited the growth of the Ni grain during the reaction cycles. The activity of the catalyst was obviously decreased as demonstrated by the Ni grain size increasing to about 250 nm. The TPR result from Fig. 4 showed that the La_2O_3-modified NiO–CaO/Al$_2$O$_3$ catalyst improved the interaction between nickel oxide and the support, which led to increasing dispersion of nickel grains and reduction in nickel size.

4. Conclusions

In this paper, a La_2O_3-modified NiO–CaO/Al$_2$O$_3$ complex catalyst was prepared by isometric impregnation with lanthanum nitrate. The sorption complex catalyst was tested in a fixed-bed reactor which showed that La_2O_3-modified NiO–CaO/Al$_2$O$_3$ catalyst had 30 cycles of ReSER process of hydrogen production, while the catalyst without La_2O_3 modification yielded only 7 cycles. The La_2O_3-modified catalyst also yielded 10 more cycles than a ZrO_2-modified NiO–CaO/Al$_2$O$_3$ complex catalyst. Our analysis of different catalysts showed how La_2O_3 modification improved catalyst stability: the formation of $NiAl_2O_4$ was inhibited, and Ni particle and surface area were kept more stable after multiple 600 °C–800 °C temperature cycles.

Table 2 – The nickel and nickel oxide grain size of the sorption complex catalyst.

	LNCA	NCA	LNCA-r-7	NCA-r-30
NiO grain size	18.14	25	89.55	/
Ni grain size	21	32.4	107.7	256

REFERENCES

[1] Hufton JR, Mayorga S, Sircar S. Sorption-enhanced reaction process for hydrogen production. AIChE J 1999;45:248–56.

[2] Harrison DP. Sorption-enhanced hydrogen production: a review. Ind Eng Chem Res 2008;47:6486–501.

[3] Yang XC, Wei YN. Research progress in methane reforming catalyst for the production of hydrogen. Mater Rev 2007;21:49–52.

[4] Li WB, Qi ZP. Progress on technical study for production of hydrogen from methane. Nat Gas Industry 2005;25:165–8.

[5] Wu SF, Li LB, Zhu YQ, Wang XQ. A micro-sphere catalyst complex with nano CaCO₃ precursor for hydrogen production used in ReSER process. Eng Sci 2010;8:22–6.

[6] Barelli L, Bidini G, Gallorini F, Servili S. Hydrogen production through sorption-enhanced steam methane reforming and membrane technology: a review. Energy 2008;33:554–70.

[7] Ding Y, Alpay E. Adsorption-enhanced steam-methane reforming. Chem Eng Sci 2000;55:3929–40.

[8] He J, Wu SF. The characteristics of sorption enhanced steam methane reforming for hydrogen production on a complex catalyst. Chem React Eng Technol 2007;23:470–3.

[9] Wu SF, Wang LL. Improvement of the stability of a ZrO₂-modified Ni-nano-CaO sorption complex catalyst for ReSER hydrogen production. Int J Hydrogen Energy 2010;35:6518–24.

[10] Xu Z, Li YM, Zhang JY, Zhang Y, H F. Performance of supported nickel catalyst for reforming of CH₄ with CO₂ to syngasII. Effect of basic promoters. Chin J Casis 1997;18:364–7.

[11] Wu DX, Zhu H, Guo SD. Effects of rare-earth oxides on nickel dispersion and activities of nickel catalysts for co methanation. Chin J Ca 1987;8:138–43.

[12] Schaper H, Amesz DJ, Doesburg EBM, Van Reijen LL. The influence of high partial steam pressures on the sintering of lanthanum oxide doped gamma alumina. Appl Catal 1984;9:129–32.

[13] Zhang ZL, Zhang Xenophon E, Susan M, Stanley A. Comparative study of carbon dioxide reforming of methane to synthesis gas over Ni/La₂O₃ and conventional nickel-based catalysts. J Phys Chem 1996;100:744–54.

[14] Zhang LF, Li W, Liu J, Guo CL, Wang YP, Zhang JL. Ethanol steam reforming reactions over Al₂O₃ center dot SiO₂-supported Ni–La catalysts. Fuel 2009;88:511–8.

[15] Zhang BC, Cai WJ, Li Y, Xu YD, Shen WJ. Hydrogen production by steam reforming of ethanol over an Ir/CeO₂ catalyst: reaction mechanism and stability of the catalyst. Int J Hydrogen Energy 2008;33:4377–86.

[16] Yu XH, Zhang SC, Wang LQ, Jiang Q, Li SG, Tao Z. Hydrogen production from steam reforming of kerosene over Ni–La and Ni–La–K/cordierite catalysts. Fuel 2006;85:1708–13.

[17] Yang ZB, Zhang YY, Ding WZ, Zhang YW, Shen PJ, Zhou YD. Hydrogen production from coke oven gas over LiNi/gamma-Al₂O₃ catalyst modified by rare earth metal oxide in a membrane reactor. J Nat Gas Chem 2009;18:407–14.

[18] Seo JG, Youn MH, Jung JC, Song IK. Effect of preparation method of mesoporous Ni–Al₂O₃catalysts on their catalytic activity for hydrogen production by steam reforming of liquefied natural gas (LNG). Int J Hydrogen Energy 2009:5409–16.

[19] Liu YX, Chen JX, Zhang JY, He F. Effect of La₂O₃ promoter on structure and hydrogenation performance of Ni/SiO₂ catalyst. J Chem Ind and Eng (Chinese) 2005;56:2114–8.

[20] Deng C. Influence of promoters on the catalytical performance of supported-Ni catalysts. J of Nanchang University (Natual Science) 2000;12:120–6.

[21] Shi NH, Liu LG, Zhu W, Yu Q, Liu ZY. Method of determination of the crystallite size distribution of active component of catalyst and its application. Chin J Ca 1982;3:268–75.

[22] Pan HF, Zhou SX, Zhang ZL, Xiao CZ. The relation between the size of primary crystallites and the catalytic activity -the optimum dispersion. J China Univ Petrol (Ed Nat Sci) 1985;2:54–8.

[23] Wu SF, Li QH, Kim JN, Yi KB. Properties of nano CaO/Al₂O₃ CO₂ sorbent. Ind Eng Chem Res 2008;47:180–4.