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## Nickel-Supported on La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> Pyrochlores for Methane Steam Reforming: Insight into the Difference between Tin and Zirconium in the B Site of the Compound

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La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, two pyrochlore compounds with different B-site cations, were prepared and used as supports for Ni in methane steam reforming. Compared with Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, both Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> show very stable reaction performance. Whereas Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> also displays reasonably high activity for the reaction, the activity of Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> is extremely low. It was found that severe coking occurred with Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, but no coke formation was observed on the two pyrochlore catalysts. On the reduced and spent Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalyst, the

### Introduction

With energy shortage and environmental pollution becoming serious global problems, the search for novel green energy is currently an urgent and pressing issue. Hydrogen, as a clean energy source, offers an alternative to fossil fuels.<sup>[1]</sup> Although other methods such as photocatalytic splitting of water and biomass conversion are under intensive study by many chemists, these processes are not mature enough for industrial hydrogen production for the present needs. Multistep processing of hydrocarbon fuels is still the most practical approach to efficient hydrogen production, and steam reforming of hydrocarbons has been widely employed in the chemical industry for this purpose. In particular, the reforming of natural gas with water steam is the leading method for the production of hydrogen around the world<sup>[2–5]</sup> owing to the abundant storage of natural gas.

The major reactions of methane steam reforming are described in Equations (1) and (2):

$$CH_4 + H_2O = CO + 3 H_2$$
  $\Delta H^{\circ}_{298} = 206.2 \text{ kJ mol}^{-1}$  (1)

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$$CO + H_2O = CO_2 + H_2$$
  $\Delta H^{\circ}_{298} = -41.2 \text{ kJ mol}^{-1}$  (2)

It is clear that this process is highly endothermic and it is usually performed at approximately 800 °C and 1.5–3.0 MPa.<sup>[6]</sup> Although noble metal catalysts have been reported to be more active and less sensitive to carbon deposition, their use in reforming is confined by their high cost and limited availability.<sup>[7-9]</sup> In contrast, owing to abundant sources and their low price. Ni-based catalysts are still the most appropriate catalysts for this reaction.<sup>[10,11]</sup> However, some potential problems can arise from the high temperature required for the reaction, including sintering of the Ni active sites and supports. Therefore, thermal stability of the catalyst is a critical issue, because low thermal stability will not only induce deactivation of the catalysts, but it will also crush the catalyst pellets, increase the pressure drop, and eventually block the reactor.<sup>[12]</sup> Moreover, a good support with strong thermal resistance and reasonable surface area can stabilize the size of Ni even at high temperature, which will effectively inhibit carbon deposition and maintain the initial activity. Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are two traditional supports for Ni catalysts for various reforming reactions. Coke-resistant Ni-based catalysts have attracted great interest. Recently, various strategies involving confinement effects and crystal facet effects have been developed to suppress coking and to maintain the high activity of the catalyst.<sup>[13-16]</sup> To obtain catalysts with more potent coke resistance and higher efficiency, some other composite oxide supports with a stable structure, such as perovskite and spinel, have been investigated.<sup>[17-19]</sup>

Pyrochlores have the empirical formula  $A_2B_2O_7$ , in which "A" is typically a rare-earth element with a +3 valence state and "B" is generally a transition element with a +4 valence state.

Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn alloys were detected; these alloys suppressed coke formation but also decreased the activity of the catalyst. In comparison, a large amount of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was formed on the used Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalyst; these species reacted with the carbon deposits formed on the Ni particles and continuously restored the Ni sites. Thus, coking was effectively suppressed and the initial high activity of the catalyst was maintained. Thus, Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> is a superior catalyst having the potential for industrial use.

Pyrochlores exhibit high chemical stability and catalytic activity at high temperatures in the oxidative coupling of methane.<sup>[20,21]</sup> The application of pyrochlores as combustion catalysts was also recently suggested, as reasonable surface area and catalytic activity were observed despite the high temperature required for the formation of the pyrochlore structure.<sup>[22]</sup> Over the past five years, pyrochlore compounds have also been investigated as catalysts for different reforming reactions. Spivey and co-workers studied La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> in which part of the Bsite Zr was substituted by Ru, Rh, Pt, or Ni for methane dry reforming, and they found that the substitution led to the formation of more mobile oxygen species.[23-29] As a result, the reforming activity of the catalysts was improved and carbon deposition was suppressed.<sup>[30,31]</sup> Catalysts substituted by a suitable amount of Ru or Rh display performance that is improved relative to that of unsubstituted La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, and thus they have the potential to be used in industrial applications.<sup>[23-29]</sup> Upon studying Ru-pyrochlore catalysts for the autothermal reforming of volatile organic compounds, Peppley and co-workers found that Ru-substituted La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> was a very active and stable catalyst for the target reactions. The reason was ascribed to the uniform dispersion of Ru into the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore matrix.<sup>[32]</sup> Bussi and co-workers investigated Ni-, Co-, and Cu-modified La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> for ethanol steam reforming. They found that both Ni- and Co-modified catalysts showed very high reforming activity. However, the addition of Cu into Nimodified La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> decreased the activity of the catalyst. Upon preparing Ni-modified La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> with both co-precipitation and impregnation methods, the highest H<sub>2</sub> yield and stability were obtained with the former method.[33-35] For ethanol steam reforming on La2Ce2-xRuxO7 pyrochlore solid solution catalysts, Lee and co-workers observed metal-metal interaction between La and Ru, which thus resulted in catalysts with high activity and stability.<sup>[36]</sup>

Apparently, these reports mainly focused on using substituted pyrochlores as catalysts directly for reforming reactions. Given that pyrochlores generally have good chemical and thermal stabilities and reasonable surface areas, they could also be good candidates as supports for Ni or other metals to prepare reforming catalysts. However, only a few publications can be found on this topic. For instance, Hu and co-workers revealed that NiO supported on La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore was an active and stable catalyst for methane dry reforming as a result of the fine and uniform dispersion of NiO on the pyrochlore support surface.<sup>[37]</sup> In comparison, by using X-ray photoelectron spectroscopy (XPS) Spivey and co-workers found the presence of NiO and Ni<sub>2</sub>O<sub>3</sub> on the surface of Ni-substituted La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore.<sup>[23]</sup> They observed that the Ni-substituted catalyst deactivated severely because of fast coking. In spite of this discrepancy, to the best of our knowledge, Ni supported on a pyrochlore other than La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> as a catalyst for reforming reactions has not been reported. Therefore, with the expectation to obtain a catalyst with potent coke resistance, high activity, and applicable stability for methane steam reforming, in this study, both La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlores were prepared by the co-precipitation method, and they were subsequently used as supports for Ni to prepare catalysts for methane steam reforming. For comparison, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, a traditional industrial reforming catalyst, was also prepared by using the impregnation method with commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the support. Compared with Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, both Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> showed much more potent coking resistance. However, high and stable activity for the reforming reaction was only found for Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>. With different characterization methods, reasons leading to these differences in performance were elucidated.

### **Results and Discussion**

#### Activity evaluation of the catalysts

The reaction performance of the catalysts for methane steam reforming at different temperatures is shown in Figure 1. Notably, all the data shown herein were collected after stabilization for only 30 min at the corresponding temperature; therefore, the data reflect the initial activity of the catalysts. On all of the catalysts, both CH<sub>4</sub> conversion and H<sub>2</sub> yield increased with an increase in the reaction temperature. As a result of the strong endothermic effect of the reaction, the increase in the conversion of methane was very evident, as shown in Figure 1a. In comparison, the increase in the yield of H<sub>2</sub> was much slower, which could be due to the inhibition of the water-gas shift reaction, a mild exothermic reaction, at higher temperatures, as shown in Figure 1b. Among all of the catalysts, Ni/γ-Al<sub>2</sub>O<sub>3</sub> displayed the highest initial CH<sub>4</sub> conversion and the highest H<sub>2</sub> yield, but these values dropped very quickly because of the deactivation of the catalyst, as shown in Figure 2. In contrast, Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> showed an unexpected low conversion of CH<sub>4</sub> and a low yield of H<sub>2</sub>; consequently, it may not be applicable to real industrial use. In contrast, Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> had a much higher initial conversion of CH<sub>4</sub> and a higher initial yield of H<sub>2</sub> than Ni/La2Sn2O7, but these values were lower than those of Ni/Y- $AI_2O_3$ .

For the purpose of H<sub>2</sub> production by steam reforming, achieving a high H<sub>2</sub>/CO ratio is of great importance. Therefore, the H<sub>2</sub>/CO ratios of the catalysts at different temperatures are compared in Figure 1 c. To a certain extent, the H<sub>2</sub>/CO ratios are controlled by the second step in the water–gas shift reaction involved in the steam reforming reaction. Increasing the operating temperature clearly reduced the H<sub>2</sub>/CO ratios gradually for all of the catalysts, because of the exothermic properties of the second step in the water–gas shift reaction. Among the three catalysts, the highest H<sub>2</sub>/CO ratio was achieved on the Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalyst. However, the difference in the H<sub>2</sub>/CO ratio between the Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts is negligible. Although Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> displayed the highest H<sub>2</sub>/CO ratio, its use could be limited by its low activity, as mentioned above.

For the steam reforming reaction, it is always a big challenge and a major objective to find a stable catalyst having potent resistance to coke formation and Ni crystallite size growth during the high-temperature process. Therefore, to study the properties of the catalysts further, they were subjected to long-term stability tests at 800 °C, and the results are shown in Figure 2. As shown in Figure 2 a, although Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited



**Figure 1.** Reaction performance of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> for methane steam reforming: a) methane conversion, b) H<sub>2</sub> yield, and c) H<sub>2</sub>/CO ratio. Reaction conditions: H<sub>2</sub>O/CH<sub>4</sub>=2:1, WHSV=18000 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>.

the highest initial conversion of  $CH_4$  among the three catalysts, over the first 80 h, the conversion of  $CH_4$  decreased from 94 to 78%, which indicates that the catalyst deactivates quickly. However, the yield of  $H_2$  remained stable. On the contrary, the conversion of  $CH_4$  on Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> increased over the first inducing period of 120 h and eventually stabilized at 98% after



**Figure 2.** Long-term stability test: a) methane conversion, b) H<sub>2</sub> yield, and c) H<sub>2</sub>/CO ratio. Reaction conditions: H<sub>2</sub>O/CH<sub>4</sub>=2:1, T=800 °C, WHSV = 18000 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>.

180 h. Furthermore, after an inducing period of 80 h, this catalyst exhibited a yield of H<sub>2</sub> that was similar to that exhibited by Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Similar to Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> also showed an inducing period of approximately 20 h, after which the conversion of CH<sub>4</sub> remained stable at approximately 30%. Apparently, the stable activity of Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and the yield of H<sub>2</sub> on this

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catalyst are much lower than that observed on Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. As shown in Figure 2c, Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> have the same stable H<sub>2</sub>/CO ratio, which is slightly lower than that of Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. Taking into account all of the aspects of the three studied catalysts, it is clear that Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> is the most promising catalyst for the target reaction in this study, which has the potential for industrial use.

#### Thermogravimetric analysis and differential scanning calorimetry of coke formation on the spent catalysts after long-term stability tests

To clarify the reasons leading to the reaction performance difference, thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) were used to analyze the catalysts after long-term stability tests; the results are shown in Figure 3. For



Figure 3. a) TGA and b) DSC profiles of long-term used Ni/ $\gamma$ -Al\_2O\_3, Ni/ La\_2Sn\_2O\_7, and Ni/La\_2Zr\_2O\_7 catalysts

Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, a 21.5% weight loss stage was observed between 400 to 700 °C in the TGA curve, which was accompanied by two strong exothermic peaks at 554 and 576 °C in the DSC profile; this indicates the presence of two types of carbon deposits with different chemical environments, perhaps graphitic carbon atoms.<sup>[38]</sup> Apparently, severe coking of this catalyst oc-

curred during the steam reforming process, which could be one of the major causes for the quick decrease in activity. Besides this, a minute weight loss stage with approximately 1.8% weight loss between 300 and 400 °C that was accompanied by a small exothermic peak at 318°C was also observed for Ni/y-Al<sub>2</sub>O<sub>3</sub>; this could be attributed to the combustion of a small amount of a very active carbon deposit, such as absorbed atomic carbon or Ni carbide species.[39,40] Interestingly, for both the Ni/La2Sn2O7 and Ni/La2Zr2O7 catalysts, no evident weight loss was observed, which indicates the lack of deposited carbon species. On the contrary, after 300°C, a small amount of weight gain was detected, which was due to the reoxidation of the reduced metallic Ni back into NiO species on the two catalysts. The two small exothermic peaks at 285 and 393 °C in the DSC profile of Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and the small exothermic peak at 488 °C in the DSC profile of Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> further confirm this. Clearly, by using the two pyrochlore compounds as the support for Ni, coke formation was effectively suppressed. After all, we believe this explains the stable reaction performance of these two pyrochlore-supported Ni catalysts.

## Scanning electron microscopy analysis of coke formation on the spent catalysts after long-term stability tests

Scanning electron microscopy (SEM) was used to investigate the morphology and surface changes of the catalysts before and after long-term stability tests. For convenient comparison, the SEM images of freshly reduced Ni/y-Al<sub>2</sub>O<sub>3</sub>Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and  $Ni/La_2Zr_2O_7$  are shown in Figure 4a-c, whereas those after the long-term stability tests are shown in Figure 4a'-c' in sequence. As presented in Figure 4a, the surface of the freshly reduced Ni/y-Al<sub>2</sub>O<sub>3</sub> catalyst is very clean and consists mainly of fine fibrous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. After a reaction time of 80 h at 800 °C, whisker-like carbon fiber deposits with an average diameter of 50 nm can be clearly observed, as shown by Figure 4a'. This is in line with the TGA-DSC results, which indicated that severe coking occurred to the catalyst during the reaction. The SEM images of the freshly reduced Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalysts show that the two samples are made up of small round particles that are 25-30 nm in size. After long-term reaction, no significant change occurred to Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, but a slight aggregation was observed for Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> However, the clean surfaces of both spent catalysts testify to the absence of any carbon deposit, and this indicates that coking can be completely suppressed by using the two pyrochlores as supports for Ni.

In summary, the SEM images of the catalysts further testify to the fact that on Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, severe coking takes place during the methane steam reforming reaction, and this could be one of the major reasons why the catalyst deactivates so quickly. However, on the Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalysts, no coke formation was observed. As a consequence, both catalysts show stable reaction performance for methane steam reforming.

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Figure 4. SEM images of freshly reduced a) Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, b) Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, and c) Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and those of spent a') Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, b') Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, and c') Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>.

## N<sub>2</sub> adsorption-desorption study on the freshly calcined supports and the corresponding Ni catalysts

To elucidate the reasons leading to the different reaction performance, the texture properties of the freshly calcined supports and the corresponding Ni catalysts before and after use were measured by  $N_2$  adsorption–desorption, and the results are compared in Figure 5 and Table 1. As exhibited in Figure 5 a, all the supports show a typical type IV adsorption feature, which indicates the presence of mesopores that are generally larger than 5 nm. The presence of H3 hysteresis loops in the nitrogen adsorption–desorption isotherms of all the samples further confirm this. In comparison with the supports, all

Table 1. Physicochemical properties of the freshly calcined and spent catalysts measured by $N_{\rm 2}$ adsorption–desorption.						
Catalysts	BET surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore volume [m <sup>2</sup> g <sup>-1</sup> ]	Pore size [nm]			
γ-Al <sub>2</sub> O <sub>3</sub>	84.4	0.513	13.2			
$La_2Sn_2O_7$	22.3	0.281	36.9			
$La_2Zr_2O_7$	21.8	0.116	14.1			
$Ni/\gamma$ - $Al_2O_3^{[a]}$	55.6	0.366	12.6			
Ni/La <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub> <sup>[a]</sup>	8.9	0.092	41.6			
Ni/La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> <sup>[a]</sup>	4.4	0.057	13.6			
Ni/γ-Al <sub>2</sub> O <sub>3</sub> <sup>[b]</sup>	40.3	0.279	11.2			
Ni/La <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub> <sup>[b]</sup>	7.0	0.063	50.9			
Ni/La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> <sup>[b]</sup>	2.1	0.020	32.1			
[a] Freshly calcined catalyst. [b] Spent catalyst.						





Figure 5.  $N_2$  adsorption-desorption isotherms of a) the supports, b) the freshly calcined Ni catalysts, and c) the spent Ni catalysts.

of the catalysts with 12% supported Ni display no large difference in their adsorption-desorption behavior. However, after long-term stability tests, the hysteresis loops became smaller than those of the fresh catalysts, and this indicates that the structure changed during the reaction. It is clear, however, that the spent catalysts still retain their mesoporous structures.

For comparison, the BET surface areas, pore volumes, and pore sizes of the samples are also listed in Table 1.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has the largest BET surface area and pore volume among the three

supports, as a result of its well-known porous structure. Although  $La_2Sn_2O_7$  and  $La_2Zr_2O_7$  have similar surface areas, the pore volume and pore size of the latter is much smaller.  $La_2Sn_2O_7$  has the largest pore size among all of the supports. Considering the results shown in Figure 4b,b', this suggests that some mesopores could be formed among the particles. After Ni loading, the surface areas and pore volumes of all the samples decreased, and this indicates possible blockage of part of the pores by NiO. In addition, all of the supported Ni catalysts were recalcined in air at 800 °C for another 6 h after Ni loading, which could be another reason for their lower surface areas and pore volumes. After long-term reaction at 800 °C for more than 50 h, the surface areas as well as the pore volumes of all the samples decreased, and this indicates the impact of high temperature on the pore structure.

### X-Ray diffraction analysis of phase composition and texture properties of the freshly calcined supports and the corresponding Ni catalysts

The X-ray diffraction (XRD) patterns of the freshly calcined supports and the corresponding Ni catalysts are displayed in Figure 6. As shown in Figure 6a, commercial Al<sub>2</sub>O<sub>3</sub> used in this study shows diffraction peaks at  $2\theta = 37.5$ , 46.8, and 66.7°, which is typical for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase. Both La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and  $La_2Zr_2O_7$  display the typical intense diffraction peaks of the pyrochlore structure at  $2\theta = 28.74$ , 33.31, 47.83, and 56.76°, which confirms that the solid-state reaction between La2O3 and SnO<sub>2</sub> or ZrO<sub>2</sub> took place during calcination at 800 °C thus to produce the La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore compounds. However, in the XRD pattern of La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, a minute peak at  $2\theta = 26.6^{\circ}$ , which is attributed to the strongest diffraction peak of the tetragonal rutile SnO<sub>2</sub> phase, can still be detected. Although a stoichiometric La/Sn ratio of 1:1 was intentionally selected for sample preparation, it seems that the reaction between La<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> was not complete, perhaps as a result of limitations imposed by the reaction equilibrium. Therefore, in this catalyst, part of the free SnO<sub>2</sub> is still present.

After Ni loading and recalcination, all of the catalysts exhibited diffraction features that were essentially the same as those of the corresponding supports, except that all the diffraction peaks become more intense. This better crystallization is in line with the lower surface areas of the supported Ni catalysts. Nevertheless, NiO microcrystallites can be evidently observed for both Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, as indicated by the specific diffraction peaks of NiO spinel at (111) 37.68° and (20 0) 43.66°. In contrast, no diffraction peaks related to Ni species can be detected for Ni/\gamma-Al<sub>2</sub>O<sub>3</sub>, because of the reaction between NiO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to form a new compound, spinel NiAl<sub>2</sub>O<sub>4.</sub><sup>[41,42]</sup> Indeed, our H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) results in the following section also provide strong evidence to testify to the formation of spinel NiAl<sub>2</sub>O<sub>4</sub> compounds in this catalyst, which escapes detection by XRD as a result of its low crystallization. Notably, the diffraction peaks of the SnO<sub>2</sub> phase become more intense in the pattern of Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, which further confirms the presence of free  $SnO_2$  in this catalyst.



Figure 6. XRD patterns of a) the freshly calcined supports and b) the corresponding Ni catalysts.

# H<sub>2</sub>-TPR study on the freshly calcined supports and the corresponding Ni catalysts

The H<sub>2</sub>-TPR profiles of the freshly calcined supports and corresponding Ni catalysts are presented in Figure 7. Both the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> supports display no reduction below 900  $^{\circ}$ C; this indicates that these two supports are nonreducible. However, in the profile of the La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> support shown in Figure 7a, a reduction peak at 618°C, which is assigned to the reduction of SnO<sub>2</sub> in the support, is clearly observed.<sup>[43]</sup> This is in agreement with the XRD results in Figure 6 and further confirms the presence of a small amount of free SnO<sub>2</sub> in this sample. The quantification results of the amount of H<sub>2</sub> consumed by the samples are listed in Table 2. The La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> support has a  $H_2$  consumption of 0.8 mmol g<sup>-1</sup>, which is equal to an O/Sn atomic ratio of 0.25. If all of the  $Sn^{4+}$  in the sample is reduced to metallic Sn, the H<sub>2</sub> consumption amount should be 6.4 mmol g<sup>-1</sup>. Therefore, it is reasonable to deduce that only approximately 12.5% Sn<sup>4+</sup> is present in the sample as free SnO<sub>2</sub>. The remaining 87.5% Sn<sup>4+</sup> is present in the crystal matrix of La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlore. Owing to the stable structure of



Figure 7.  ${\rm H_2-TPR}$  profiles of a) the freshly calcined supports and b) the corresponding supported Ni catalysts.

Table 2. Quantification results of $\rm H_{2}\mathchar`-TPR$ for the freshly calcined catalysts.						
Catalysts	$H_2$ consumption [mmol g <sup>-1</sup> ]	O/M atomic ratio O/Sn O/Ni				
γ-Al <sub>2</sub> O <sub>3</sub>	-	-	-			
$La_2Sn_2O_7$	0.8	0.25	-			
$La_2Zr_2O_7$	-	-	-			
Ni/γ-Al <sub>2</sub> O <sub>3</sub> <sup>[a]</sup>	1.7	-	0.80			
Ni/La <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	2.8	0.24	1.00			
Ni/La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	2.0	-	1.00			
[a] The reduction of $NiAl_2O_{4}$						

pyrochlore compounds, a much higher temperature is needed to reduce this part of  $Sn^{4+}$  into metallic Sn.

To clarify this, the  $La_2Sn_2O_7$  sample was subjected to  $H_2$ -TPR experiments with different ending temperatures; the results are shown in Figure S1 (Supporting Information). For clarification, Figure S1 a plots the  $H_2$  consumption versus the reduction temperatures, whereas Figure S1 b plots the  $H_2$  consumption versus the reduction time. Notably, for each experiment, the sample was always held at the ending temperature for 30 min

to achieve more complete information. All of the profiles show a reduction peak at approximately 610 °C, which is assigned to the reduction of the free SnO<sub>2</sub> to metallic Sn. Apparently, with the reduction stopped at 700 °C, even with an extended time, no further reduction took place, as shown by Figure S1 b. However, if the reduction temperature was improved to 900 and 1000 °C, a high temperature reduction peak, which is attributed to the reduction of Sn<sup>4+</sup> in the pyrochlore La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> phase, can be clearly observed.

To gain a deeper understanding of the reduction process, the phase composition of the reduced samples after reduction at each ending temperature were also analyzed by XRD. As shown by Figure S2, after reduction at 700 °C, the original 12.5% of free SnO<sub>2</sub> in the calcined sample disappeared, whereas metallic Sn was observed. The pyrochlore phase remained intact. For clarification, the part of the XRD patterns between 43 and  $47^{\circ}$  are enlarged and are plotted beside the major figure to show the metallic Sn and La<sub>2</sub>O<sub>3</sub> signals more clearly. By increasing the ending temperature to 900 and 1000 °C, the intensity of the metallic Sn peaks became larger, and the La<sub>2</sub>O<sub>3</sub> phase started to show at 900 °C. On the contrary, the intensity of the peaks of pyrochlore La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> decreased and eventually disappeared at 1000 °C, which is indicative of the collapse of the pyrochlore structure. These results demonstrate that Sn<sup>4+</sup> in the lattice of pyrochlore La2Sn2O7 can only be reduced at temperatures higher than 700°C and that the reduction is complete at 1000 °C. In summary, these results strongly prove the high chemical stability of the pyrochlore structure, which impedes the reduction of the Sn<sup>4+</sup> cations in the crystal matrix.

The H<sub>2</sub>-TPR profiles of the supported Ni catalysts are listed in Figure 7b. Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a reduction peak at 806 °C, which is attributed to the reduction of spinel NiAl<sub>2</sub>O<sub>4</sub>.<sup>[41,42]</sup> This indicates the presence of a strong interaction between NiO and Al<sub>2</sub>O<sub>3</sub>, which leads to the solid-state reaction between the two during the high-temperature calcination. The quantified O/Ni atomic ratio in Table 2 is 0.8, which is lower than the theoretical value of 1.0. Apparently, owing to the formation of the NiAl<sub>2</sub>O<sub>4</sub> structure, part of the Ni species becomes more difficult to reduce. However, it was reported that a mixture of Ni cations in the matrix of spinel NiAl<sub>2</sub>O<sub>4</sub> can hinder growth of the Ni particles during prereduction of the catalysts, which has a positive effect on the activity and stability of the catalysts.<sup>[44]</sup>

The profile of Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> shows two reduction peaks at 400 and 500 °C. The 400 °C peak is assigned to the reduction of NiO to metallic Ni, which was confirmed by the quantified O/ Ni atomic ratio of 1.0 in Table 2. The 500 °C peak is assigned to the reduction of free SnO<sub>2</sub> in the sample. Compared with the La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> support, the reduction temperature is 100 °C lower because of the H<sub>2</sub> spillover effect induced by metallic Ni from the reduction of NiO in this sample. The deconvolution and integration results show that the O/Sn atomic ratio based on this peak is 0.24. If all the Sn<sup>4+</sup> in the sample is reduced to metallic Sn, the theoretical O/Sn ratio should be 2.0. Therefore, in this Ni-containing sample 12% Sn<sup>4+</sup> is present as free SnO<sub>2</sub>. Within experimental error, this amount is the same as the 12.5% free SnO<sub>2</sub> achieved on the La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> support without Ni. Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> also displays two major reduction peaks at 343 and 461 °C. As mentioned above, the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> support itself shows no reduction in the studied temperature region. Therefore, the reduction peaks can be safely assigned to the reduction of Ni oxides. As listed in Table 2, the overall H<sub>2</sub> consumption gives an O/Ni atomic ratio of 1.0; this implies that the Ni species are present solely as NiO in the sample, but with different chemical environments. The NiO species with the higher reduction temperature clearly have a stronger interaction with the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> support.<sup>[27]</sup> After all, the presence of multiple NiO species with different properties could be an important reason for the superior reaction performance of the Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalyst.

## XRD analysis of phase composition and texture properties for the freshly reduced and spent catalysts

The XRD patterns of the reduced and spent catalysts are shown in Figure 8. As shown in Figure 8a, metallic Ni was detected in both the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalysts after reduction at 800 °C for 2 h in 10% H<sub>2</sub>/Ar flow. However, for the



Figure 8. XRD patterns of a) the freshly reduced catalysts and b) the spent catalysts.

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Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalyst, not metallic Ni but the Ni<sub>3</sub>Sn<sub>2</sub> alloy was observed, which indicates that NiO reacts with the 12% free SnO<sub>2</sub> on the La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> support during the reduction process. For elucidation, the  $2\theta$  values of the typical diffraction peaks of the Ni<sub>3</sub>Sn<sub>2</sub> alloy are listed in Table S1. Notably, several minute diffraction peaks of La2O3 were detected for the reduced Ni/  $La_2Sn_2O_7$  catalyst, and this testifies to the fact that the  $La_2Sn_2O_7$ pyrochlore phase could start to be reduced at this temperature to release La<sub>2</sub>O<sub>3</sub> species originally in the pyrochlore structure. After long-term stability tests, there was no significant change in the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalysts, except that a new graphite diffraction peak was observed in the pattern of Ni/y-Al<sub>2</sub>O<sub>3</sub>, which provides evidence in addition to the TGA-DSC and SEM data that severe coke formation occurs on this catalyst during the reaction. Interestingly, after a reaction time of 60 h, the original Ni<sub>3</sub>Sn<sub>2</sub> alloy phase in Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> disappeared, and a new Ni<sub>3</sub>Sn alloy was formed. Former studies have proved that the presence of a Ni-Sn alloy in the Ni-based catalysts can suppress coke formation but at the expense of reforming activity.<sup>[42,45-47]</sup>

The crystallite sizes of the pyrochlore supports, metallic Ni, and Ni–Sn alloys are compared in Table 3. After the reaction,

Table 3. Crystallite sizes of the reduced and spent catalysts measured by XRD.							
Catalyst		Pyrochlore crystallites size [nm]		Metal crystallite size [nm]			
		$La_2Sn_2O_7$	$La_2Zr_2O_7$	Ni	Ni–Sn alloy		
Ni/γ-Al <sub>2</sub> O <sub>3</sub>	reduced <sup>[a]</sup>	-	-	24.5	-		
	spent <sup>[b]</sup>	-	-	33.6	-		
Ni/La <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	reduced <sup>[a]</sup>	33.8	-	-	14.4		
	spent <sup>[b]</sup>	31.7	-	-	10.7		
Ni/La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	reduced <sup>[a]</sup>	-	30.2	12.3	-		
	spent <sup>[b]</sup>	-	34.5	16.7	-		
[a] Reduced at 800 °C for 2 h. [b] Ni/Al <sub>2</sub> O <sub>3</sub> obtained after 70 h, Ni/La <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub> obtained after 60 h, and Ni/La <sub>2</sub> Tr.Q. obtained after 250 h							

the crystallite size of La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> decreased by approximately 2 nm, but that of  $La_2Zr_2O_7$  increased by approximately 4 nm. The SEM image in Figure 4c also demonstrates that the  $La_2Zr_2O_7$  support has a slight aggregation after 250 h. This small change indicates that both of the pyrochlore supports have high chemical and thermal stability. For both the Ni/y-Al<sub>2</sub>O<sub>3</sub> and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalysts, the Ni crystallite size increased after long-term reaction. However, the Ni size growth rate of  $Ni/\gamma$ -Al<sub>2</sub>O<sub>3</sub> is clearly larger than that of Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, which could be another reason for the quick deactivation of Ni/y-Al<sub>2</sub>O<sub>3</sub>. This could be one of the reasons why Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> has a high reaction stability. Former studies indeed indicate that coking on Ni is closely related to its size. Generally, the larger the Ni size, the easier it is to form coke.<sup>[48,49]</sup> Notably, the relatively smaller Ni crystallite size on Ni/La $_2$ Zr $_2$ O $_7$  could be an important reason for its high activity. It is not very meaningful to compare the crystallite sizes of the two Ni-Sn alloys, because of phase and chemical composition changes from Ni<sub>3</sub>Sn<sub>2</sub> to Ni<sub>3</sub>Sn during the reaction. However, the crystallite sizes of both Ni–Sn alloys are below 15 nm.

Upon studying carbon formation for the reforming reaction over Ni-based catalysts, Nikolla and co-workers found that the formation of a Ni-Sn alloy can increase coke resistance of the catalysts at the expense of activity.<sup>[45-47]</sup> On the basis of DFT calculations and scanning transmission electron microscopy (STEM) experiments, they found that Sn displaced some Ni from the carbon nucleation sites by alloy formation, which lowered the binding energy of the surface carbon. Consequently, the overall rate of oxidation of surface carbon was improved significantly, and it was much greater than the rate of C-C bond formation; thus, coke deposition was suppressed effectively. On the other hand, the addition of Sn to form a Ni-Sn alloy increases the activation energy for the CH<sub>4</sub> dry reforming reaction, which indicates that the presence of Sn has a negative effect on the activity. The inherent reason was ascribed to blockage of part of the low-coordinate Ni sites on the Ni particles by Sn, which are actually the active sites for C-H activation, the rate-determining step for CH<sub>4</sub> reforming. The same phenomenon was observed by us for methane dry reforming on Sn-modified Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>[42]</sup>

In the present study, the formation of Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn intermetallic compounds on the Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalyst was directly observed by XRD analysis. Apparently, the presence of Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn alloys should be a major reason for the low reforming activity and strong coke resistance of the catalyst.

## FTIR spectroscopy study on the surface properties and adsorbates of the reduced and spent catalysts

FTIR spectroscopy was used to monitor the surface composition of both the reduced and spent catalysts. The FTIR spectra of the reduced and spent Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalysts are compared in Figure 9a. Both spectra show a band at  $\tilde{\nu} = 570 \text{ cm}^{-1}$ , which is assigned to vibration of the Sn–O bonds.<sup>[50]</sup> Compared with the reduced sample (Figure 9a, ----), several new IR bands appeared at  $\tilde{v} = 916$ , 992, 1459, and 1504 cm<sup>-1</sup> for the spent sample. According to the literature, the band at  $\tilde{\nu} = 1504 \text{ cm}^{-1}$ can be assigned to formate species, whereas that at  $\tilde{\nu} =$ 1459 cm<sup>-1</sup> can be assigned to La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species, which could come from the reaction between La<sub>2</sub>O<sub>3</sub> and CO<sub>2</sub> in the reaction flow.<sup>[51,52]</sup> The FTIR spectra of the reduced and spent Ni/ La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalysts are compared in Figure 9b. After long-term reaction, formate and lanthanum oxycarbonate La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species can also be observed, as evidenced by the bands at  $\tilde{v} =$ 1512 and 1467 cm<sup>-1</sup>, respectively. Compared with spent Ni/ La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the signal for La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> in this sample is much stronger, which indicates the formation of more lanthanum oxycarbonate.

Upon studying dry reforming of natural gas on Ni/La<sub>2</sub>O<sub>3</sub>, Shirsat and Verykios and also found the formation of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species on the catalysts.<sup>[51-53]</sup> In their opinion, this La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species plays a critical role in maintaining the activity and stability of the Ni/La<sub>2</sub>O<sub>3</sub> catalysts. In detail, the La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species can react with carbon deposits on the Ni particles at the interface between Ni and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. Therefore, the initial Ni sites



Figure 9. FTIR spectra of the reduced and used catalysts: a) Ni/La\_2Sn\_2O\_7 and b) Ni/La\_2Zr\_2O\_7.

deactivated by coking can be clean up with restoration of the activity. In this way, coke formation of the catalysts is impeded, and thus the catalysts exhibit good stability and activity. In this study, the La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species was formed on both the Ni/  $La_2Sn_2O_7$  and Ni/ $La_2Zr_2O_7$  catalysts, which clearly improved their coking resistance and benefitted their reaction performance. As shown in Figure 2, these two Ni-pyrochlore catalysts showed very stable reforming activity during the longterm test. Indeed, the presence of  $La_2O_2CO_3$  species could be the inherent reason for this. Notably, the FTIR results demonstrate the formation of much more La2O2CO3 species on Ni/ La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> than on Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, which explains the reason why Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> has much higher reforming activity than Ni/ La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. In addition, as we mentioned above, the formation of Ni-Sn alloys on Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> can decrease the activity of the Ni sites, and as a consequence, coke formation on this catalyst is suppressed at the expense of reforming activity.

In conclusion, all of these reasons make Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> a superior catalyst for methane steam reforming; it shows much better reaction performance than Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. With further optimization, Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> could be developed and used in industrial applications.

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### Conclusions

In this study, La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, two pyrochlore compounds with different B-site cations, were prepared by the coprecipitation method and were used as supports for Ni to prepare catalysts for methane steam reforming. Compared with the traditional Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, both Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ni/ La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> showed very stable reaction performance. Whereas Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> also displayed high activity for the reaction, the activity of Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> was extremely low. TGA-DSC and SEM results revealed that severe coking occurred on Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, but no carbon deposition was found on either of the pyrochlore catalysts, which indicates that coking can be effectively suppressed with the two pyrochlores as supports for Ni. XRD analysis of the reduced and spent Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> catalysts provided direct evidence to demonstrate the formation of Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn intermetallic compounds, respectively, which can deactivate the Ni active sites. As a consequence, coke formation on the catalyst was significantly inhibited but at the expense of reforming activity. In comparison, FTIR spectroscopy indicated that a large amount of La2O2CO3 species was formed on the Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalyst, and it can react with the carbon deposits formed on the Ni particles to restore the Ni active sites continuously; this thus effectively suppresses coking and maintains the initial high activity of the catalyst. In addition, Ni supported on  $La_2Zr_2O_7$  has much smaller crystallite sizes than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is also believed to be beneficial to the activity and stability of the Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalyst. In conclusion, with further optimization, the Ni/La2Zr2O7 catalyst could be developed for industrial use.

### **Experimental Section**

#### **Catalyst preparation**

The La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore supports were prepared by the co-precipitation method from the corresponding chemicals. Typically, the calculated amount of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9%) and SnCl<sub>4</sub>·5H<sub>2</sub>O (99.9%) was mixed into a uniform aqueous solution, and then NH<sub>3</sub>·H<sub>2</sub>O was added dropwise under constant stirring until the pH value of the mixture was adjusted to approximately 10. Afterwards, the mixture was separated by centrifuging. The achieved solid was then washed completely with distilled deionized water until the total dissolved solids of the outflow liquid was less than 20 ppm. After thoroughly drying, the solid was calcined at 800 °C for 4 h in air to obtain the final La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlore support. The above method and procedure was also used to prepare the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> support by using La(NO<sub>3</sub>)<sub>3</sub>·6 H<sub>2</sub>O (99.9%) and ZrOCl<sub>2</sub>·8 H<sub>2</sub>O (99.9%) as precursors.

Ni(NO<sub>3</sub>)<sub>3</sub> (99.9%) solution was impregnated onto the pyrochlore supports with the incipient wetness method. After impregnation, the samples were place under ambient conditions for 24 h, then dried at 80 °C, and calcined at 800 °C for 4 h in air to obtain the Ni/ La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> catalysts. For comparison, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, a traditional reforming catalyst, was also prepared by using the impregnation method with commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the support. The Ni loading for all the prepared catalysts was 12 wt %.

#### **Catalyst characterization**

The specific surface areas of the samples were measured by nitrogen adsorption–desorption at 77 K with an ASAP2020 instrument. Specific surface areas were calculated by using the Brunauer– Emmett–Teller (BET) method in the relative pressure ( $P/P_0$ ) range of 0.05–0.25. The pore size distribution of the samples was calculated with the Barrett–Joyner–Halenda (BJH) method, and the average pore sizes were obtained from the peak positions of the distribution curves. Total pore volume was accumulated at relative pressure  $P/P_0 = 0.99$ .

The powder X-ray diffraction (XRD) patterns were recorded with a Bruker AXS D8 Focus diffractometer operating at 40 kV and 30 mA, with CuK<sub>a</sub> irradiation ( $\lambda = 1.5405$  Å). Scans were taken in the  $2\theta$  range from 10 to 90° with a step of 2° min<sup>-1</sup>. To keep the data comparable, all of the samples were tested continuously. The mean crystallite sizes of the samples were calculated with the Scherrer equation on the basis of the three strongest peaks of the pyrochlores, La<sub>2</sub>O<sub>3</sub>, and Ni.

Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were performed with a FINESORB 3010C instrument in a 10% H<sub>2</sub>/Ar gas mixture flow with a rate of 30 mL min<sup>-1</sup>. The temperature was increased from room temperature to 1000°C at a ramp rate of 10°C min<sup>-1</sup>. Generally, 50 mg of the catalyst was used for the test. A thermal conductivity detector was employed to monitor H<sub>2</sub> consumption. For H<sub>2</sub> consumption quantification, CuO (99.99%) was used as the calibration standard sample.

Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images were taken with a Tecnai F30 transmission electron microscope.

Thermogravimetric analysis differential scanning calorimetry (TGA-DSC) was used to monitor the amount of coke deposited on the spent catalysts. The experiments were performed with approximately 10 mg of the spent catalyst on a TAQ600 instrument at a ramping rate of  $10 \,^{\circ}\mathrm{C\,min^{-1}}$  from 25 to  $800 \,^{\circ}\mathrm{C}$  in an air flow of  $100 \,\mathrm{mL\,min^{-1}}$ .

FTIR spectra were collected with a Nicolet Avatar 360 spectrometer. The spectra were recorded by accumulating 64 scans at a spectral resolution of 2 cm<sup>-1</sup>. The sample was pressed into a self-supported wafer (18 mm diameter,  $\approx 0.05 \text{ g}$ ) and introduced into a cell equipped with KBr windows.

#### Activity evaluation

Evaluation of the activity of the catalysts was performed in a fixedbed microreactor made of a quartz tube with an inner diameter of 8 mm. The catalyst (400 mg) was reduced in 10%  $H_2/Ar$  at 800  $^{\circ}C$ for 2h in situ. Deionized water with a flow rate of 0.064 mL min<sup>-1</sup>, which gave a steam/methane ratio of 2:1, was fed through a pump into a heated chamber controlled at 200 °C to evaporate the liquid water completely. Afterwards, steam and CH<sub>4</sub> were mixed in a gas mixer at a stoichiometric ratio of 2:1. Notably, the flow rate of pure CH<sub>4</sub> (99.99%) was 40 mLmin<sup>-1</sup> and that for water steam was 80 mL min<sup>-1</sup>, which corresponds to a weight hourly space velocity (WHSP) of  $18\,000\,\text{mL}\,\text{h}^{-1}\,\text{g}_{\text{cat}}^{-1}$ . The outlet gas passed through a cold water trap to condense the excess amount of water in the reaction flow, and it was then analyzed on-line with a GC9310 gas chromatograph equipped with a TDX-01 column and a thermal conductivity detector by using Ar as the carrier gas to monitor hydrogen, carbon monoxide, methane, and carbon di-

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oxide. After the reaction, the spent catalyst was analyzed by TGA-DTA in an air flow to measure the amount of carbon deposition.

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- L. Barreto, A. Makihira, K. Riahi, Int. J. Hydrogen Energy 2003, 28, 267– 284.
- [2] S. Ayabe, H. Omoto, T. Utaka, R. Kikuchi, K. Sasaki, Y. Teraoka, K. Eguchi, *Appl. Catal. A* 2003, 241, 261–269.
- [3] E. Kikuchi, Y. Nemoto, M. Kajiwara, S. Uemiya, T. Kojima, Catal. Today 2000, 56, 75-81.
- [4] D. L. Trimm, *Catal. Today* **1999**, *49*, 3–10.
- [5] S. Freni, G. Calogero, S. Cavallaro, J. Power Sources 2000, 87, 28-38.
- [6] V. V. Chesnokov, V. I. Zaikovskii, R. A. Buyanov, V. V. Molchanov, L. M. Plyasova, *Catal. Today* 1995, 24, 265–267.
- [7] A. T. Ashcroft, A. K. Cheetham, M. L. H. Green, P. D. F. Vernon, *Nature* 1991, 352, 225–226.
- [8] J. R. Rostrupnielsen, J. H. B. Hansen, J. Catal. 1993, 144, 38-49.
- [9] J. H. Bitter, K. Seshan, J. A. Lercher, J. Catal. 1997, 171, 279-286.
- [10] K. Sutthiumporn, S. Kawi, Int. J. Hydrogen Energy 2011, 36, 14435– 14446.
- [11] S. Damyanova, B. Pawelec, K. Arishtirova, J. L. G. Fierro, Int. J. Hydrogen Energy 2012, 37, 15966–15975.
- [12] J. Sehested, Catal. Today 2006, 111, 103-110.
- [13] X. Du, D. Zhang, L. Shi, R. Gao, J. Zhang, J. Phys. Chem. C 2012, 116, 10009-10016.
- [14] X. Du, D. Zhang, R. Gao, L. Huang, L. Shi, J. Zhang, Chem. Commun. 2013, 49, 6770-6772.
- [15] X. Du, D. Zhang, L. Shi, R. Gao, J. Zhang, Nanoscale 2013, 5, 2659-2663.
- [16] T. Xie, L. Shi, J. Zhang, D. Zhang, *Chem. Commun.* 2014, *50*, 7250–7253.
   [17] N. Sahli, C. Petit, A. C. Roger, A. Kiennemann, S. Libs, M. M. Bettahar, *Catal. Today* 2006, *113*, 187–193.
- [18] S. O. Choi, S. H. Moon, *Catal. Today* **2009**, *146*, 148–153.
- [19] M. Simões, S. Baranton, C. Coutanceau, Appl. Catal. B 2010, 93, 354– 362.
- [20] C. Petit, J. L. Rehspringer, A. Kaddouri, S. Libs, P. Poix, A. Kiennemann, Catal. Today 1992, 13, 409–416.
- [21] A. K. C. A. T. Ashcroft, M. L. H. Green, C. P. Grey, P. D. F. Vernon, J. Chem. Soc. Chem. Commun. 1989, 1667 – 1669.
- [22] J. M. Sohn, M. R. Kim, S. I. Woo, Catal. Today 2003, 83, 289-297.
- [23] S. Gaur, D. J. Haynes, J. J. Spivey, Appl. Catal. A 2011, 403, 142-151.
- [24] S. Gaur, D. Pakhare, H. Wu, D. J. Haynes, J. J. Spivey, Energy Fuels 2012, 26, 1989-1998.

- [25] D. Pakhare, D. Haynes, D. Shekhawat, J. Spivey, Appl. Petrochem. Res. 2012, 2, 27–35.
- [26] D. Pakhare, C. Shaw, D. Haynes, D. Shekhawat, J. Spivey, J. CO<sub>2</sub> Utilization 2013, 1, 37–42.
- [27] V. Abdelsayed, D. Shekhawat, J. A. Poston, J. J. Spivey, Catal. Today 2013, 207, 65–73.
- [28] D. Pakhare, H. Wu, S. Narendra, V. Abdelsayed, D. Haynes, D. Shekhawat, D. Berry, J. Spivey, Appl. Petrochem. Res. 2013, 3, 117–129.
- [29] D. Pakhare, V. Schwartz, V. Abdelsayed, D. Haynes, D. Shekhawat, J. Poston, J. Spivey, J. Catal. 2014, 316, 78–92.
- [30] S. Q. Chen, H. Wang, Y. Liu, Int. J. Hydrogen Energy 2009, 34, 7995-8005.
- [31] R. B. Duarte, M. Olea, E. Iro, T. Sasaki, K. Itako, J. A. V. Bokhoven, Chem-CatChem 2014, 6, 2898–2903.
- [32] A. Qi, C. Thurgood, B. Peppley, Energy Procedia 2012, 29, 503-512.
- [33] J. Bussi, N. Bespalko, S. Veiga, A. Amaya, R. Faccio, M. C. Abello, *Catal. Commun.* 2008, 10, 33–38.
- [34] N. Bespalko, A. C. Roger, J. Bussi, Appl. Catal. A 2011, 407, 204-210.
- [35] J. Bussi, M. Musso, S. Veiga, N. Bespalko, R. Faccio, A. C. Roger, *Catal. Today* 2013, 213, 42–49.
- [36] S. Weng, Y. Wang, C. Lee, Appl. Catal. B 2013, 134-135, 359-366.
- [37] H. Meng, R. S. Hu, X. F. Zhang, G. Q. Lu, H. Q. Su, J. Chin. Rare Earth Soc. 2006, 24, 62–67.
- [38] J. A. Torres, J. Llorca, A. Casanovas, M. Domínguez, J. Salvadó, D. Montané, J. Power Sources 2007, 169, 158–166.
- [39] J. J. Guo, H. Lou, H. Zhao, D. F. Chai, X. M. Zheng, Appl. Catal. A 2004, 273, 75–82.
- [40] D. P. Liu, R. Lau, A. Borgna, Y. H. Yang, Appl. Catal. A 2009, 358, 110– 118.
- [41] J. K. Xu, W. Zhou, Z. J. Li, J. H. Wang, J. X. Ma, Int. J. Hydrogen Energy 2009, 34, 6646–6654.
- [42] J. J. Liu, H. G. Peng, W. M. Liu, X. L. Xu, X. Wang, C. Q. Li, W. F. Zhou, P. Yuan, X. H. Chen, W. G. Zhang, H. B. Zhan, *ChemCatChem* **2014**, *6*, 2095–2104.
- [43] X. L. Xu, R. B. Zhang, X. R. Zeng, X. Han, Y. C. Li, Y. Liu, X. Wang, Chem-CatChem 2013, 5, 2025–2036.
- [44] N. Muradov, F. Smith, A. T-Raissi, Int. J. Hydrogen Energy 2008, 33, 2023– 2035.
- [45] E. Nikolla, J. W. Schwank, S. Linic, Catal. Today 2008, 136, 243-248.
- [46] E. Nikolla, J. Schwank, S. Linic, J. Am. Chem. Soc. 2009, 131, 2747-2754.
- [47] E. Nikolla, J. Schwank, S. Linic, J. Catal. 2009, 263, 220-227.
- [48] X. L. Zhu, P. P. Huo, Y. P. Zhang, D. G. Cheng, C. J. Liu, Appl. Catal. B 2008, 81, 132–140.
- [49] C. J. Liu, J. Ye, J. Jiang, Y. Pan, ChemCatChem 2011, 3, 529-541.
- [50] K. Li, T. Zhang, H. Wang, H. Yan, J. Solid State Chem. 2006, 179, 1029– 1034.
- [51] A. N. Shirsat, M. Ali, K. N. G. Kaimal, S. R. Bharadwaj, D. Das, *Thermochim. Acta* 2003, 399, 167–170.
- [52] X. E. Verykios, Int. J. Hydrogen Energy 2003, 28, 1045-1063.
- [53] A. C. Basagiannis, X. E. Verykios, Appl. Catal. A 2006, 308, 182-193.

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