Supplementary Information

High catalytic performance and sustainability of Ni/La$_2$O$_3$ catalyst for daily pre-reforming of liquefied petroleum gas under low steam/carbon molar ratio

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Experimental section

1. Preparation of LaNiO$_3$ perovskite

All reagents were analytical-grade, purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without purification.

LaNiO$_3$ perovskite was prepared by a precipitation-combustion method. In a typical process, citric acid (0.08 mol) and stoichiometric amounts of La(NO$_3$)$_3$·6H$_2$O (0.04 mol) and Ni(NO$_3$)$_2$·6H$_2$O (0.04 mol) were dissolved in 200 mL of deionized water at room temperature under stirring. 1 M (NH$_4$)$_2$CO$_3$ aqueous solution (1 mL/min) was dropped slowly into the above mixed solution to pH value of ca. 6.5 using a syringe pump at 40 $^{\circ}$C under vigorous stirring, when ca. 70 mL aqueous solution of (NH$_4$)$_2$CO$_3$ was consumed, and the increased pH induced the formation of precipitated product. The suspension solution was continuously stirred at 40 $^{\circ}$C for 2 h and then evaporated out at 80 $^{\circ}$C. The as-prepared solid was dried at 120 $^{\circ}$C overnight, and finally calcined at 400 $^{\circ}$C for 5 h and 600 $^{\circ}$C for 5 h, respectively, in air at a heating rate of 1 $^{\circ}$C/min. Caution! This process must be cautious to avoid the explosion of the ammonium nitrate.

For comparison, Ni/La$_2$O$_3$-imp containing 23.8 wt% Ni was prepared by the conventional impregnation method. 5 g of La$_2$O$_3$ support was added into 30 mL of an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O under stirring and kept at room temperature for 2 h. The mixture was evaporated out at 80 °C and then dried at 110 °C overnight, and finally the solid was calcined at 600 °C for 5 h under air.

2. Characterization

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Rigaku D/MAX-2200 apparatus using Cu Kα radiation (λ = 0.15418 nm) operated at a voltage of 40 kV and a current of 40 mA. N$_2$ adsorption was measured using a Micromeritics ASAP 2020 Sorptometer at liquid nitrogen temperature (–196 °C). Before the measurement, the sample was degassed at 300 °C for 8 h. The specific surface area was evaluated using the Brunauer–Emmett–Teller (BET) method in the P/P$_0$ range from 0.05 to 0.25. TEM micrographs were performed with JEOL JEM-2010F field emission microscope operating at 200 kV.

3. Catalysis reaction

The commercially available auto LPG, composed of C$_2$H$_6$ of 3.1 vol%, C$_3$H$_8$ of 84.0 vol% and C$_4$H$_{10}$ of 12.9 vol%, was purchased from Shanghai Auto Energy Co. Ltd and was used to study the catalytic behavior without further purification.

The steam reforming of LPG was performed under a steam/carbon (S/C) molar ratio of 1.0 without dilution gas under atmospheric pressure in a fixed-bed quartz tube reactor with an internal diameter of 10 mm and a length of 900 mm. A preheater filled with quartz balls with a set temperature of 300 °C was used to vaporize water and fully mix the reaction gases. The reaction gases and water were controlled using the mass flow controllers and a HPLC pump, respectively. The actual temperature of the catalyst was monitored using a thermocouple placed in the middle of the catalyst bed. 100 mg of catalyst (40–60 mesh) diluted with 900 mg of quartz particles (40–60 mesh) was placed between two layers of quartz wool in the center of the reactor. Prior to the reaction, the catalyst was first reduced in situ at 600 °C at a heating rate of 10 °C/min under a 60 mL/min flow of 15 vol% H$_2$/N$_2$ for 3 h, then cooled to the set reaction temperature

(400–550 ℃). Next, the reductive gas was switched to a gaseous mixture of N_2 (50 mL/min) and steam (the amount required in the reaction) for 5 min to avoid initial carbon deposition, followed by introducing LPG into the reaction system under atmospheric pressure and closing the N_2 valve. The effluent gas was cooled in a condenser at room temperature and passed a drierite bed to remove all water. Finally, the dried gas products were analyzed using an on-line GC-FID gas chromatograph with a CP–sil 5 CB column for hydrocarbons, followed by another GC-TCD gas chromatograph for CH_4, CO and CO_2 and H_2. The flow rate of outlet gas was measured by a soap flow meter. Other than H_2, CO, CO_2 and CH_4, no other products were observed in the exit gas. For XRD and TEM measurements, the reaction was terminated by closing the LPG and water valves, and cooled quickly by keeping the 100 mL/min N_2 flow and opening the furnace. The overall mass balance was more than 98% on the basis of carbon in the starting reactants.

In the daily start-up and shut-down (DSS) operation, the $LaNiO_3$ perovskite catalyst reduced at 600 ℃ was first performed for the 1st pre-reforming of LPG at 450 ℃ and gas hourly space velocity (GHSV) of 11000 mL/g_{cat} h with an S/C molar ratio of 1.0 for a longer time of 13 h so that the reaction system and the catalyst could be completely stable. After the 1st reaction, the LPG gas was switched into equivolumetric N_2 to provide a mixed steam purging gas. The used catalyst was in situ cooled from 450 ℃ to 200 ℃ within 2 h time and maintained for 4 h under steam purging condition. Then, the catalyst temperature was again elevated to 450 ℃ at a heating rate of 8 ℃/min under steam purging condition and the 2nd cycle reaction was started by switching N_2 to LPG and conducted for ca. 5.5 h under the identical reaction conditions for the 1st reaction, followed by steam purging. The following 3rd and 4th cycle reactions were performed in the same operation mode.

On the basis of the carbon balance in the effluent gas under the assumption of no carbon deposition, the conversion of LPG (X_{LPG}), which was defined as the percentage of the total molar flow rate of the carbon-containing products (CH_4, CO and CO_2) in the exit gas to the molar flow rate of carbon in the feed gas, and the selectivity of the product i (S_i), which was designated as the percentage of the molar flow rate of the carbon-containing product to the total molar flow rate of the carbon-containing products, were calculated with Eq. 1 and Eq. 2, respectively, shown as follows:

$$X_{LPG} = \frac{\sum N_i}{N_{carbon} \text{ in the feed}} \times 100\% \qquad (1)$$

$$S_i = \frac{N_i}{\sum N_i} \times 100\% \qquad (2)$$

Where N_i and N_{carbon} are the molar flow rate of product i (i = CO, CO$_2$, CH$_4$) and the molar rate of carbon in the feed gas, respectively.

H$_2$ selectivity, noted (S_{H2}) (Eq. 3), was defined as the percentage of the molar flow rate of H$_2$ in the effluent gas to the molar flow rates of all products containing hydrogen, multiplied with the proper factor, on the basis of hydrogen mass balance.

$$S_{H2} = \frac{N_{H2}}{(N_{H2} + 2 \times N_{CH4})} \times 100\% \qquad (3)$$
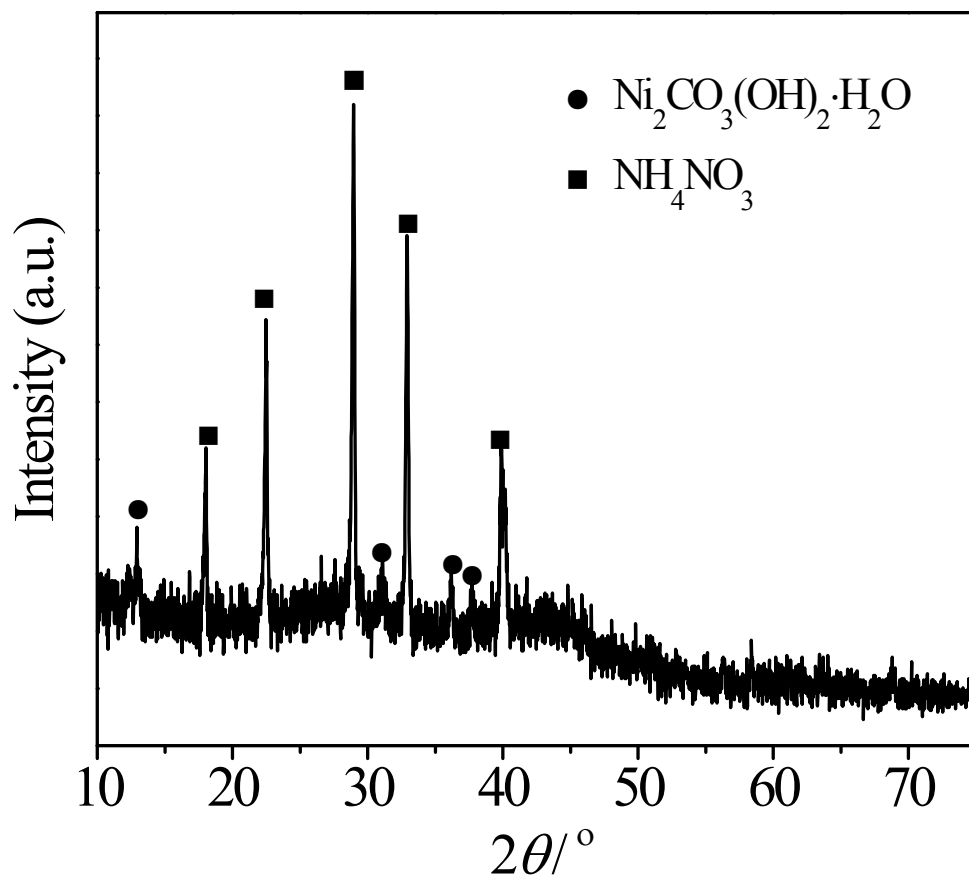
Supporting Figures

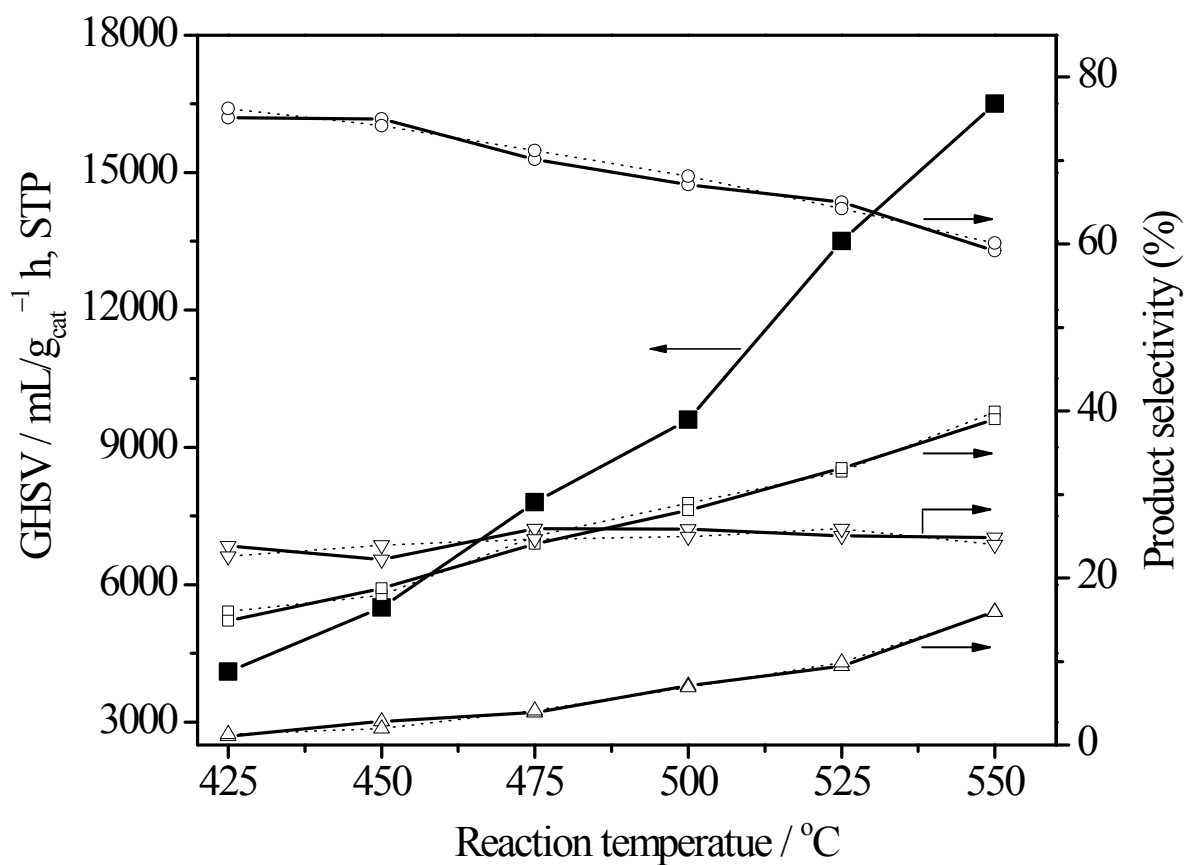**Fig. S1.** XRD pattern of the as-prepared material dried at 120 $^{\circ}$C

Fig. S2. The maximum gas hourly space velocities (■) of completely converting LPG and the product selectivities over the Ni/La$_2$O$_3$ catalyst at different reaction temperatures, and the corresponding equilibrium values of product selectivities (dot line). (□) H$_2$, (○) CH$_4$, (△) CO, and (▽) CO$_2$. Reaction conditions: catalyst, 100 mg; S/C = 1.0; reaction time, 20 h.
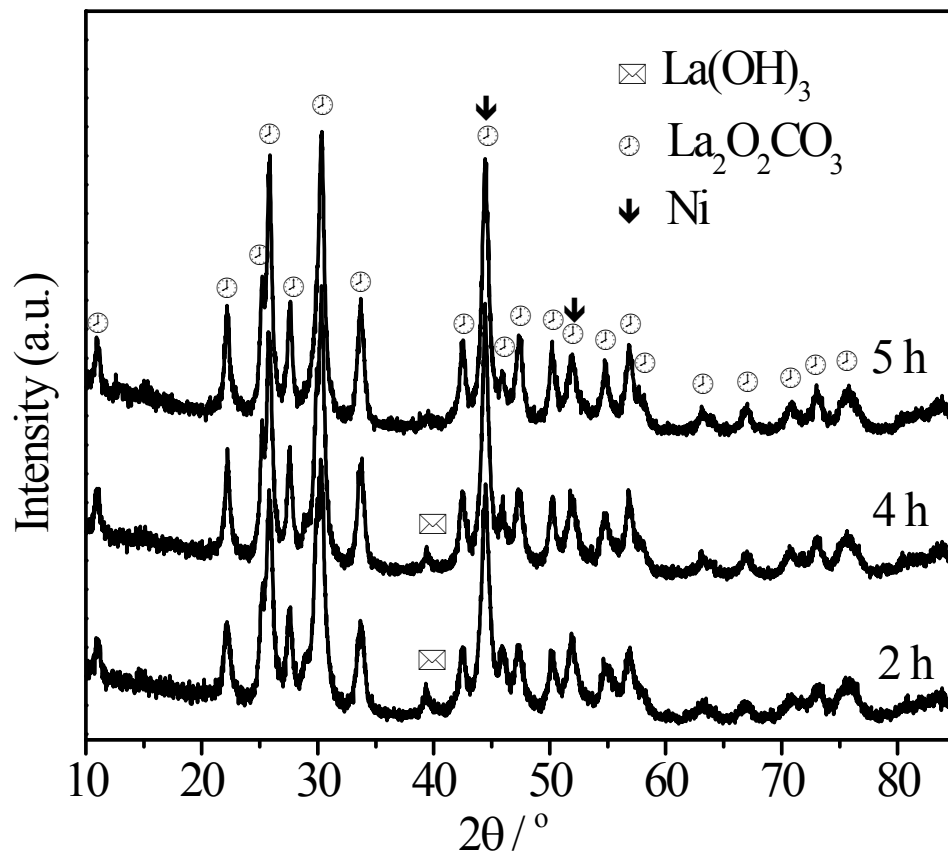
Fig. S3. XRD patterns of the Ni/La$_2$O$_3$ catalyst for the pre-reforming of LPG at different initial reaction periods. Reaction conditions: catalyst, 100 mg; GHSV = 11000 mL/g$_{cat}$ h; S/C = 1.0.