K-doped LaNiO$_3$ perovskite for high-temperature water-gas shift of reformate gas: Role of potassium on suppressing methanation

Thawatchai Maneerung, Kus Hidajat, Sibudjing Kawi*

Department of Chemical & Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 119260, Singapore

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**Abstract**

LaNiO$_3$ perovskite has been successfully used as a catalyst precursor for high temperature water-gas shift (HT-WGS) reaction of reformate gas to produce additional hydrogen from the hydrocarbon reforming. The Ni$_0$ nanoparticles with the particle size of ca. 21 nm obtained after reduction of LaNiO$_3$ perovskite can effectively suppress CO methanation during HT-WGS reaction using pure CO/H$_2$O gas. However, for HT-WGS reaction of reformate gas (including CO, H$_2$O, CO$_2$ and H$_2$), LaNiO$_3$ perovskite exhibits lower catalytic activity with significant CH$_4$ formation predominantly via CO$_2$ methanation. In this work, the CO$_2$ methanation during HT-WGS reaction of reformate gas was suppressed by the addition of potassium onto LaNiO$_3$ perovskite. This is due to the adsorption of H$_2$O on the potassium which is located at the interface between La$_2$O$_3$ and Ni$_0$ nanoparticle (as deduced from XPS and HRTEM results) that forms stable K–OH, blocking the methanation of CO$_2$ adsorbed on the La$_2$O$_3$ with H$_2$ adsorbed on the Ni$_0$ nanoparticles. Moreover, the formation of stable K–OH also promotes the formation of formate (HCOO) – a key intermediate for WGS reaction over the reduced LaNiO$_3$ perovskite – even at high reaction temperature by continuously supplying hydroxyl group to react with CO adsorbed on the Ni$_0$ nanoparticle, which helps to maintain the catalytic activity for WGS reaction at high reaction temperature.

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**Introduction**

Hydrogen (H$_2$) is envisioned as a viable clean energy carrier in the near future which is capable of reducing the dependency on fossil fuels as an energy source. Industrially, reforming reactions (i.e. partial oxidation, steam reforming and CO$_2$ dry-reforming of hydrocarbons) have been intensively employed for hydrogen production [1–7]. However, the major problem of H$_2$ production from the hydrocarbon reforming reactions is the co-production of carbon monoxide (CO) in the gaseous product (that is called “reformate gas”) which can poison the Pt-catalyst used in the fuel cell as well as create an environmental issue [8].

In order to circumvent this problem, downstream processes such as water-gas shift (WGS) and selective CO oxidation reactions are widely employed to oxidize CO in the product stream [9–12]. Conventionally, WGS reaction is
performed in two stages which involves a high temperature shift (350–450 °C) over an iron-based catalyst followed by a low temperature shift (200–250 °C) over a copper-based catalyst [13,14]. In the high temperature shift reaction, Fe3O4/Fe2O4 catalyst is commonly doped with Cr2O3 to prevent thermal agglomeration of the catalyst and hence enhance its catalytic stability at high reaction temperatures [15]. However, the usage of chromium poses ecological and environmental safety issues [16]; thus, these concerns have generated much research interests to develop novel catalysts with high catalytic performance to replace the conventional Fe–Cr–O catalyst. Nickel-based catalyst has been found to be a potential candidate for the high temperature water gas shift (HT-WGS) reaction as it exhibits a promising catalytic performance in terms of CO conversion and catalytic stability [17]. However, the major problem of nickel-based catalyst is the formation of methane via CO methanation (Eq. (3)) during the HT-WGS reaction. This undesired side reaction significantly consumes the H2 produced, and hence decreases the reaction efficiency. Nevertheless, it has been reported by Takenaka [18] that the small particle size of Ni catalyst has a significant effect not only towards suppressing methane formation, but also the enhancement of CO conversion during HT-WGS reaction. In our previous work [19], LaNiO3 perovskite has been successfully used as a catalyst precursor for the rapid decomposition of methane into carbon nanotubes and CO2-free H2. The main advantages of using LaNiO3 perovskite as a catalyst precursor are found to be: (1) the formation of uniform and small particle size of metallic Ni0 nanoparticles (<20 nm) after H2 reduction, and (2) the strong interaction between metallic Ni0 particles and La2O3 support can prevent the thermal agglomeration of the catalyst, both of which contribute to the excellent catalytic performance of LaNiO3 perovskite. This is in good agreement with the literature [20,21] which have employed perovskite-type oxides as catalyst precursors for reforming reactions of light alcohols.

Another problem needs to be considered is that the gaseous product streams from industrial reforming processes usually contain large amounts of CO2 apart from CO and H2. Therefore, it is very important to develop catalyst for the WGS reaction that can handle reformate gas, not only by providing high catalytic activity and stability, but also by suppressing undesirable reactions. In the presence of CO2 and H2, several side reactions may take place other than the WGS reaction of CO/H2O [22]:

\[
\text{CO}_2 \text{ methanation: } \text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{Reverse water-gas shift: } \text{CO}_2 + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{CO} \quad (2)
\]

\[
\text{CO methanation: } \text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (3)
\]

The formation of methane from any of these side reactions significantly lowers the activity and selectivity of the catalyst for WGS. The addition of promoters such as alkali metals has been employed to modify the catalytic properties in order to prevent those undesired side reactions. Hwang et al. [48] reported that Ni (111) catalyst doped with alkali metal can significantly enhance both catalytic activity and product selectivity for the WGS reaction of pure CO/H2O gas. Davis et al. [23] and Panagiotopoulou [24] also reported that the addition of alkali metal to Pt/ZrO2 catalysts leads to weakening of the C–H bond of the carbon-containing intermediate compound which can enhance its decomposition rate into H2 and CO2 product.

In this study, LaNiO3 perovskite was used as a catalyst precursor for the HT-WGS reaction of both pure CO/H2/O gas and reformate gas (CO, H2/O, CO2, and H2) mixtures. Moreover, the effect of potassium (K) doping onto LaNiO3 perovskite on its catalytic performance in terms of methane suppression and CO conversion during the HT-WGS reaction was also studied. Finally, in situ DRIFTS studies were carried out in order to shed light on the mechanistic pathway of the WGS reaction over the reduced LaNiO3 and K-doped LaNiO3 perovskite as well as to investigate the role of potassium doping on suppressing CO2 methanation.

### Experimental

#### Catalyst preparation

LaNiO3 perovskite were prepared by the citrate sol–gel method. La(NO3)3·6H2O (Sigma–Aldrich) and Ni(NO3)3·6H2O (Strem Chemicals) served as the metal precursors. They were first dissolved in distilled water. Citric acid (Sigma–Aldrich) which was used as a chelating agent, was then added to the aqueous solution of metal nitrates at a 1:1 M ratio of total cations (La3+ and Ni2+) to citric acid. The resulting solution was continually stirred at 55 °C for 6 h until the greenish gel was obtained. This gel was then dried at 100 °C for 24 h. The obtained solid precursor was milled and decomposed in air at 200 °C (2 °C/min) for 1 h and, subsequently, calcined in air at 850 °C for 6 h using a heating rate of 2 °C/min.

LaNiO3 perovskite was doped with potassium (K) promoter in different weight percents. Respective amounts of KNO3 were weighed and mixed with LaNiO3 in 10 ml of deionized water. The mixtures were stirred continuously at 70 °C to evaporate the water and placed in an oven at 100 °C overnight to dry. The obtained precursor was milled and finally calcined in air at 600 °C for 4 h using a heating rate of 2 °C/min. Finally, the dried fresh K-doped LaNiO3 perovskite was ground and kept in a plastic container with a sealed cap for further use.

NiO/La2O3 as a reference supported catalyst, containing the same Ni amount as LaNiO3 perovskite catalyst (ca. 24 wt%), was prepared by the wet impregnation method. Ni(NO3)3·6H2O was weighted and dissolved in the distilled water. The solutions were stirred continuously at room temperature. The resulting solution was then heated up to 70 °C to evaporate water. The residue was dried at 100 °C for 24 h. The obtained solid precursor was milled and finally decomposed in air at 400 °C for 1 h using a heating rate of 2 °C/min and subsequently calcined in air at 850 °C for 6 h using a heating rate of 2 °C/min.
Catalyst characterization

X-ray diffraction was carried out to investigate the structural features of all fresh, reduced, and used catalysts by using a SHIMADZU XRD-6000 diffractometer. The Cu Ka radiation was used at λ = 0.154 nm and settings were at 40 KV and 30 mA. A counting time of 5 s per step in the 2θ range of 20°−80° was utilized to obtain the data at 0.02° per step.

Reduction behavior of the fresh catalysts was studied by H2 temperature programmed reduction (H2-TPR) using a Chem-BET™ 3000. The sample, about 50 mg of catalyst, was placed in the U-shaped quartz tube. The sample was first degassed at 150 °C for 3 h with a helium flow rate of 50 ml/min and then cooled to room temperature under flowing helium. Reduction profiles were recorded using 5 vol. % hydrogen in nitrogen, with a heating rate of 10 °C/min, from room temperature to 800 °C. Hydrogen consumption was obtained from the integrated peak area of the reduction profiles relative to the calibration curve.

Metallic Ni surface area of the reduced catalyst precursors was determined by H2 chemisorption method using a Chem-BET™ 3000. The sample, about 50 mg of catalyst, was placed in the U-shaped quartz tube. The sample was first degassed at 150 °C for 3 h with a helium flow rate of 50 ml/min and then reduced in flow H2 at 20 ml/min at 600 °C for 1 h. The system was then purged with nitrogen and cooled down to 50 °C. The H2 chemisorption was started by injecting 0.5 ml of 5 vol. % hydrogen in nitrogen and repeated at 10 min intervals until hydrogen peaks became identical. The amount of hydrogen consumption was measured with a thermal conductivity detector (TCD). Metallic Ni surface area was finally calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni = 1).

Transmission electron microscopy (TEM, JEOL JEM-2010) was performed to examine the structure and size features of the catalysts. The samples were ultrasonically dispersed in ethanol in order to obtain a homogeneous dispersion. A droplet of the dispersion was placed in a carbon coated copper grid before undergoing a drying process at 60 °C for 15 min. TEM was operated under the settings of 100−150 kV acceleration voltage and 10,000−100,000 × magnification range.

The BET surface areas of catalysts were measured by using N2 physisorption (Quantachrome Autosorb-6B). Prior to the analysis, the samples were degassed for 24 h at 200 °C under vacuum to remove the adsorbed moisture on the catalyst surface. Analysis was conducted with nitrogen gas as the adsorbate.

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS, using a monochromatized Al Ka X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and pass energy of 40 eV. All binding energies were referenced to the C 1s hydrocarbon peak at 284.8 eV.

In situ DRIFTS analysis

CO, H2O and CO2 adsorption
A Perkin Elmer Spectrum 2000, equipped with a DTGS detector and a high temperature DRIFTS cell (Harrick, Praying Mantis) fitted with ZnSe windows, were used to record, in an in situ manner, infrared spectra under reaction conditions and during gas adsorption. The spectra were taken at a resolution of 4 to give a data spacing of 1 cm⁻¹ in the 400−4000 cm⁻¹ range. 100 scans were taken to improve the signal to noise ratio. Moreover, the DRIFTS spectra were smoothed when necessary to minimize the frequency noise level and further using the software Spectrum® for Windows. Initially, 100 mg of catalyst precursor was reduced in-situ in flow H2 at 20 ml/min at 600 °C for 1 h. After that, the DRIFTS cell was cooled to 50 °C in flowing He to remove remaining H2 for 30 min. CO adsorption was performed in a mixture of 5 mol. % CO (balance He) from 50 °C to 500 °C in the flowing gas, while DRIFTS spectra were recorded at each temperature with an interval temperature of 50 °C. The adsorption of H2O and CO2 were performed under the same flow condition of 5 mol. % H2O and 5 mol. % CO2, balance He, respectively.

Water-gas shift reaction

For in situ DRIFTS analysis of the WGS reaction, the feed gas lines connected to the DRIFTS cell and outlet of the cell were heat traced and insulated with insulating tape to prevent condensation of water along the gas lines. Brooks 5850 series E mass flow controllers were used to control the flow rates of the feed gases. The sample, about 100 mg of catalyst, was first reduced in-situ in flowing H2 at 20 ml/min at 600 °C for 1 h. Subsequently, DRIFTS cell was cooled to 50 °C in flowing He to remove the remaining H2. The reactant gases [pure CO/H2O mixture and reformate (CO2, CO, and H2) mixture] with the desired composition were flowed into the saturated water bath to vaporize the water into the DRIFTS cell during the water gas shift reaction. At each temperature, 100 scans were taken to improve the signal to noise ratio and to ensure the reproducibility of the steady state condition.

Catalytic activity for the HT-WGS reaction

The WGS reaction was conducted in a fixed-bed plug flow reactor using a ¼” OD quartz tube reactor. Deionized water was supplied into the flowing gas stream by a calibrated Shimadzu HPLC pump and vaporized in a heated gas line, which was maintained at 150 °C before entering the reactor. The feed gas lines were heat traced and insulated with insulating tape to avoid condensation of water vapor. A cooling jacketed condenser was installed at the reactor exit to remove any remaining moisture. The sample, about 50 mg of catalyst, was first reduced in H2 (20 ml/min) at 600 °C for 1 h and then purged with 20 ml/min of He. For WGS of pure CO/H2O mixture, the feed gas consists of 5 mol. % CO, 25 mol. % H2O, and He balance gas at a total flow rate of 50 ml/min. In the reformate gas, the reactant mixture consists of 5 mol. % of CO, 10 mol. % of CO2, 40 mol. % H2, 25 mol. % of H2O and a balance of He. The reaction studies were performed in a temperature range of 350−550 °C. The effluent was u ring on-line using a HP6890 Series GC equipped with a thermal conductivity detector.

Catalyst performance was evaluated by total conversion of CO and methane selectivity. The total conversion of CO (XCO) was calculated according to the following equation:

$$X_{CO} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\%$$
On the other hand, methane selectivity (%) is calculated according to the following equation [32]:

\[
\text{Methane selectivity} = \frac{\left[ \text{CH}_4 \right]_{\text{out}}}{\left[ \text{CO}_2 \right]_{\text{out}} + \left[ \text{H}_2 \right]_{\text{out}} + \left[ \text{CH}_4 \right]_{\text{out}}} \times 100\%
\]

For the turnover frequency (TOF) calculations, the catalytic activity testing was performed with diluted catalysts (diluted with powder quartz) with a total flow rate of 75 ml/min in order to maintain a total CO conversion of below 10%. The diluted catalysts were reduced in pure H₂ with a flow rate of 20 ml/min at 600 °C for 1 h followed by a pretreatment at the standard WGS conditions (6.8% CO, 21.9% H₂O, 8.5% CO₂, 37.4% H₂, and balance He) with a flow rate of 75.4 ml/min at 360 °C for 20 h. In order to ensure that the conversion was below 10%, the temperature was maintained at 400 °C the catalytic activity testing for both LaNiO₃ and K-doped LaNiO₃ perovskite. The TOF (s⁻¹) was calculated using the following equation [39]:

\[
\text{TOF} = \frac{\text{mol of CO converted}}{\text{mol of surface metal} \times \text{time (s)} \times 100\%}
\]

**Results and discussion**

**Catalyst characterization**

**Physical properties of catalysts**

Table 1 shows some important physical properties of catalysts which include specific catalyst surface area, total pore volume, and metallic Ni⁰ surface area. The specific surface area of LaNiO₃ perovskite is approximately 16 m²/g (with a corresponding pore volume of about 2 × 10⁻³ cm³/g), which is in agreement with the general trend of perovskite structures synthesized by the sol–gel method. Moreover, a significant decrease in the specific surface area and pore volume of LaNiO₃ perovskite can be observed after potassium doping, probably due to the covering of LaNiO₃ perovskite by potassium. Similarly, the surface area of metallic Ni⁰ nanoparticles obtained after H₂ reduction of K-doped LaNiO₃ perovskite was significantly decreased with increasing potassium content, which can significantly affect catalytic performance.

**XRD analysis — structural properties**

Fig. 1 shows the XRD patterns of fresh and reduced K-doped LaNiO₃ perovskite catalyst precursors. As shown in Fig. 1a, the characteristic diffraction peaks of perovskite-type structures (2θ = 23.2, 32.6, 40.5, 46.9 and 58.7°) (PDF 00-033-0710) without the presence of additional peaks, are observed in the XRD pattern of LaNiO₃ perovskite, showing the formation of a homogenous solid solution of La and Ni in the perovskite structure. In addition, a splitting of the diffraction peak at 2θ = 32.6° indicates that LaNiO₃ perovskite is of rhombohedral symmetry [25].

After H₂ reduction at 600 °C for 1 h, the characteristic diffraction peaks attributed to the rhombohedral perovskite structure of LaNiO₃ disappeared, while the characteristic diffraction peaks attributed to La₂O₃ (2θ = 29.2, 30.0, 39.6, 46.2, and 55.5°) (PDF 01-074-1144) and metallic Ni⁰ (2θ = 44.7, 52.1, and 76.5°) (PDF 01-071-4655) appeared, as shown in Fig. 1b. This result shows that LaNiO₃ perovskite was completely collapsed after the H₂ reduction, forming metallic Ni⁰ nanoparticles dispersed on the La₂O₃ support. This observation is in good agreement with the literature [19].

In addition, the characteristic diffraction peaks of K₂O (2θ = 25.3, 29.3, 41.9, and 52.0°) (PDF 01-077-2176) can also be observed in the XRD patterns of both fresh and reduced K-doped LaNiO₃, indicating the existence of K-doping in the form of potassium oxide (K₂O) on both the fresh and reduced K-doped LaNiO₃. This is also in good agreement with the literature [26], which have reported that K₂O is the major species formed when the K-doped catalyst was calcined and reduced at high temperature.

Fig. 2 shows the TEM image characterizing the formation of metallic Ni⁰ nanoparticles after the H₂ reduction of the NiO-supported La₂O₃, LaNiO₃ perovskite and 5 wt. % K-doped LaNiO₃ perovskite at 600 °C for 1 h. The TEM image of the reduced LaNiO₃ perovskite shows that the metallic Ni⁰ nanoparticles obtained after the H₂ reduction have a smaller particle size (ca. 24 nm) as compared to those obtained from the reduced NiO-supported La₂O₃ (ca. 41 nm). This can be attributed to the strong interaction between nickel and lanthanum oxide in the framework of perovskite which not only promotes the dispersion of metallic Ni⁰ nanoparticles on the La₂O₃ support during H₂ reduction but also prevents the thermal agglomeration of metallic Ni⁰ nanoparticles [27]. Moreover, it
was also found that the particle size of metallic Ni\textsuperscript{0} nanoparticles is even smaller and more uniform (ca. 21 nm) after the addition of potassium onto the LaNiO\textsubscript{3} perovskite. This result suggests that the addition of potassium can prevent the thermal agglomeration of metallic Ni\textsuperscript{0} nanoparticles.

**XPS analysis — surface properties**

Fig. 3a and b, respectively, show the La 3d and Ni 2p XPS spectra for the reduced K-doped LaNiO\textsubscript{3} perovskite. The binding energies of Ni 2p and La 3d significantly decreased with increasing potassium content. On the other hand, the K 2p XPS spectra of the reduced K-doped LaNiO\textsubscript{3} perovskite (Fig. 3c) show that the binding energy of K 2p significantly increased with increasing potassium content. These results suggest that there was a significant electron transfer from K to both Ni and La, indicating a strong interaction between potassium oxide (K\textsubscript{2}O) with both metallic Ni\textsuperscript{0} particles and La\textsubscript{2}O\textsubscript{3}. This strong interaction can significantly prevent the thermal agglomeration of metallic Ni\textsuperscript{0} nanoparticles \[24,26,36\], resulting in the smaller metallic Ni particles, which is in line the TEM results. Furthermore, the decrease in the intensity of La 3d and Ni 2p XPS spectra after the addition of potassium doping also indicates the coverage of the metallic Ni\textsuperscript{0} particles and the La\textsubscript{2}O\textsubscript{3} support by K\textsubscript{2}O. Based on these XPS results and the HR-TEM observation (Fig. 2e), it can be reasonably concluded that K\textsubscript{2}O is located at the interfacial site between the metallic Ni\textsuperscript{0} particle and the La\textsubscript{2}O\textsubscript{3} support after H\textsubscript{2} reduction of K-doped LaNiO\textsubscript{3} perovskite. It will be shown later that the presence of this interfacial K\textsubscript{2}O not only helps to enhance CO conversion but also suppress CO\textsubscript{2} methanation.

**Catalyst performance for the HT-WGS reaction**

The high-temperature water-gas shift (HT-WGS) reaction of two different feeding gases was performed over the reduced LaNiO\textsubscript{3} perovskite, K-doped LaNiO\textsubscript{3} perovskite and NiO-supported La\textsubscript{2}O\textsubscript{3} (as a reference catalyst) in the fixed-bed plug flow reactor at different temperatures ranging from 350 °C to 550 °C. Two different types of feeding gas consist of: (1) a pure CO/H\textsubscript{2}O gas which contains 5 mol. % CO, 25 mol. % H\textsubscript{2}O and the balanced He; and (2) a reformate gas which contains 5 mol. % CO, 25 mol. % H\textsubscript{2}O, 10 mol. % CO\textsubscript{2}, 40 mol. % H\textsubscript{2} and the balanced He.

The CO conversion and CH\textsubscript{4} selectivity during HT-WGS reactions of the pure CO/H\textsubscript{2}O gas and the reformate gas as a function of reaction temperature are shown in Figs. 4 and 5, respectively. With the presence of CO\textsubscript{2} and H\textsubscript{2} in the reformate gas, many undesired side reactions may take place other than WGS reaction as shown in the following:

\[ \text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O} \]  
\[ \text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O} \]  
\[ 2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CO}_2 + \text{CH}_4 \]  
\[ \text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \]  
\[ \text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \]

These side reactions produce either methane or carbon as undesired side-product. However, there was no carbon formation observed on the catalyst surface after WGS reaction. On the other hand, the formation of methane was detected during HT-WGS reaction, especially the HT-WGS reaction of reformate gas. These results suggest that methane formation
via the methanation reactions of CO and CO$_2$ (Eqs. (7) and (8)) are the main side reactions which take place simultaneously with HT-WGS over all catalysts. However, methanation of CO$_2$ has been reported to proceed with much lower activation energy (21.2 kJ/mol) [45] than methanation of CO (103.4 kJ/mol) [26] over the same Ni-catalyst. Therefore it can be concluded that the formation of methane during HT-WGS, especially with the abundance of CO$_2$ and H$_2$ in the reformate gas, can be mainly attributed to methanation of CO$_2$ (Eq. (8)).

As shown in Fig. 4, the reduced NiO-supported La$_2$O$_3$ catalyst exhibited the lowest CO conversion with a detectable amount of methane during HT-WGS reaction even without CO$_2$ and H$_2$ in the feed stream, whereas there was no methane formation observed over the reduced LaNiO$_3$ and K-doped LaNiO$_3$ perovskite during HT-WGS reaction under the same reaction conditions. This result suggests that the methanation of CO takes place simultaneously with the HT-WGS reaction over the reduced NiO-supported La$_2$O$_3$ catalysts. It was found in our previous study [19] that the larger Ni$^0$ nanoparticle the more lattice oxygen on the La$_2$O$_3$ support was obtained after the H$_2$ reduction of the NiO-supported La$_2$O$_3$. This larger Ni$^0$ nanoparticle can probably be responsible for the lower HT-WGS activity of the reduced NiO-supported La$_2$O$_3$. Moreover, Jacobs et al. [23] reported that the lattice oxygen on the support is capable of weakening the C$-$O bond strength of CO (gas), and hence increasing the methanation rate of CO during WGS reaction which is due to the C atom in the weakened C$-$O bond of CO reacts with H$_2$ rather than with H$_2$O [49] and subsequently forms methane. Furthermore, it has also been reported that the Ni catalysts having larger Ni metal particles are more active for the methanation of CO than those having smaller particles [18,28]. Fig. 4a shows the CO conversion during HT-WGS reaction of pure CO/H$_2$O gas over the reduced LaNiO$_3$ and K-doped LaNiO$_3$ perovskite. Both of the reduced catalyst precursors exhibited almost the same catalytic behavior during the HT-WGS reaction of pure CO/H$_2$O gas. However, the significant difference in the catalytic activities of these two catalysts can be clearly observed at low reaction temperatures. In particular, about 90% of CO conversion was obtained from the reduced K-doped LaNiO$_3$ perovskite, whereas only 64.3% of CO conversion was obtained from the reduced LaNiO$_3$ perovskite at 350 °C. Moreover, it can also be observed that the CO conversion increased with increasing reaction temperature from 350 °C to 450 °C, but it decreased when the temperature was further increased beyond 450 °C. This is mainly due to the exothermic nature of the WGS reaction.

On the other hand, the CO conversion and CH$_4$ selectivity during HT-WGS of reformate gas (containing 5 mol. % CO, 25 mol. % H$_2$O, 10 mol. % CO$_2$, 40 mol. % H$_2$, balance of He) over these three different catalyst precursors are presented in Fig. 5. Similarly, the reduced NiO-supported La$_2$O$_3$ still exhibited the lowest CO conversion during HT-WGS reaction.

Fig. 2 – TEM images and Ni$^0$ particle size distributions of the reduced (a) NiO/La$_2$O$_3$, (b) LaNiO$_3$, (c) 5 wt. % K-doped LaNiO$_3$, (d) and (e) HR-TEM images of the reduced LaNiO$_3$ perovskite and 5 wt. % K-doped LaNiO$_3$ perovskite, respectively.
of reformate gas and at the same time much higher amount of CH₄ (~100 times) was produced during HT-WGS reaction of reformate gas. This is mainly due to the methanation reactions of both CO and CO₂ can take place together over the reduced NiO-supported La₂O₃. It can also be observed that with the presence of CO₂ and H₂ in the reformate gas, a dramatic decrease in the CO conversion accompanied with high methane formation can be observed during HT-WGS reaction for the entire reaction temperature range.

Denkwitz et al. [29] studied the effect of CO₂ on the conversion of CO during WGS reaction of the idealized and realistic reformate and a similar observation was reported. This is probably due to the fact that with the presence of CO₂ and H₂ in the reformate gas, both two main side reactions including the hydrogenation of CO₂ (Eq. (2)) and methanation of CO₂ (Eq. (9)) can take place along with WGS reaction, forming CO and methane as the main products, respectively. This subsequently leads to the decrease in the overall CO conversion and a high methane formation rate. However, the reduced K-doped LaNiO₃ perovskite still exhibited higher CO conversion. For example at 400 °C, about 64% CO conversion was obtained from the reduced K-doped LaNiO₃ perovskite, whereas only 42% and 35% CO conversions were obtained from the reduced LaNiO₃ and NiO-supported La₂O₃ catalysts, respectively. In addition, the reduced K-doped LaNiO₃ perovskite exhibited lower methane formation as compared to both the reduced LaNiO₃ and NiO supported La₂O₃ catalysts (Fig. 5b). These results clearly show that the addition of potassium onto the LaNiO₃ perovskite not only helps to enhance CO conversion during HT-WGS reaction but also effectively suppresses the formation of methane. Interestingly, the results show that the CO conversion at high temperature is above the equilibrium CO conversion. This is mainly due to the contributions from the methanation reactions of both CO and CO₂ taking place concurrently during HT-WGS of reformate gas in the presence of H₂ and CO₂. This phenomenon has also been reported in the literature [30,31]. Moreover, it was also found that LaNiO₃ perovskite with 5 wt. % of potassium doping exhibited the best catalytic performance for HT-WGS reaction in terms of the highest CO conversion and less methane formation. However, further increase in potassium content led to a drastic decrease in CO conversion, which can be explained by the coverage of metallic Ni⁰ nanoparticles with excessive potassium doping, as described previously.

Fig. 6 shows the stability study of the three prepared catalysts for the HT-WGS of reformate gas for a continuous 45 h run-time. It can be seen that the reduced NiO-supported La₂O₃ catalyst showed a gradual decrease in the catalytic activity after 20 h. In contrast, both of the reduced LaNiO₃ and 5 wt. % K-doped LaNiO₃ perovskite were almost stable throughout the entire reaction period. This can be attributed to the strong interaction between metallic Ni⁰ nanoparticle and lanthanum oxide of the reduced LaNiO₃ perovskite, preventing the thermal agglomeration of metallic Ni⁰ nanoparticles, which is in good agreement with literature [50,51].

In addition, catalytic activity of the reduced 5 wt. % K-doped LaNiO₃ perovskite was also compared with other catalysts reported in the literature. The calculated TOF values and the various operating conditions used in testing of different catalyst systems were tabulated in Table 3. It was found that the reduced 5 wt. % K-doped LaNiO₃ perovskite has a lower TOF value than the Pt-based catalyst as reported by Zhu et al. [52] that was tested at 300 °C. However, it has higher TOF value as compared to other Ni-based catalysts [39,47] which have been reported in the literature. Therefore, the 5 wt. % K-doped LaNiO₃ perovskite can be considered as a promising Ni-based catalyst which can be utilized for the HT-WGS reaction.

In situ DRIFTS analysis — adsorption and surface WGS reaction studies

In order to clearly elucidate the mechanism of the WGS reaction over the reduced LaNiO₃ and K-doped LaNiO₃ perovskite, in situ DRIFTS analysis on the adsorption of reactant gases (i.e. CO, H₂O, and CO₂) and during the WGS reaction were conducted. As a reference for the interpretation of the in situ DRIFTS spectra presented in this section, the relevant vibrational frequencies of possible gaseous and adsorbed species are summarized in Table 2.

CO adsorption

The in situ DRIFTS spectra of CO adsorption on the reduced LaNiO₃ and K-doped LaNiO₃ perovskite catalyst precursors are
presented in Fig. 7. There are four absorption bands at 2170, 2110, 2060, and 1910 cm\(^{-1}\) observed during the CO adsorption on both reduced catalyst precursors. The absorption bands observed at 2170 and 2110 cm\(^{-1}\) can be assigned to the stretching of CO (gas phase) which should typically be observed at 2143 cm\(^{-1}\). The superimposition of rotational levels contributes to the appearance of these two absorption bands. On the other hand, the absorption bands at 2060 cm\(^{-1}\) (strong) and 1910 cm\(^{-1}\) (weak) can be assigned to the linear and bridging forms of CO adsorbed on the sites of metallic Ni\(^0\), respectively [32]. This result clearly indicates that CO (gas) was adsorbed on the sites of metallic Ni\(^0\) nanoparticles. The intensity of the absorption bands of CO adsorbed on the metallic Ni\(^0\) in the reduced K-doped LaNiO\(_3\) perovskite (Fig. 7b) were significantly lower than those of the reduced LaNiO\(_3\) perovskite (Fig. 7a), which is mainly due to the coverage of metallic Ni\(^0\) nanoparticles by potassium as discussed earlier in Section CO adsorption.

H\(_2\)O adsorption

The in situ DRIFTS spectra of adsorbed H\(_2\)O on the reduced LaNiO\(_3\) and K-doped LaNiO\(_3\) perovskite catalyst precursors are presented in Fig. 8. From the assigned vibrational frequencies shown in Table 2, the strong absorption bands observed at
3750 cm\(^{-1}\) in Fig. 8 can be attributed to the O–H stretching modes of H\(_2\)O. On the other hand, the absorption bands observed at 3675 and 3710 cm\(^{-1}\) during H\(_2\)O adsorption on the reduced LaNiO\(_3\) perovskite indicated the formation of hydroxyl (–OH) groups on the La\(_2\)O\(_3\) surface in the form of La(OH)\(_3\). This is consistent with the literature\,[33] which has reported that lanthanum oxide (La\(_2\)O\(_3\)) is highly hygroscopic and it readily forms La(OH)\(_3\) on the surface when it is exposed to water vapor (Eq. (9)).

\[
\text{La}_2\text{O}_3 + 3\text{H}_2\text{O} \leftrightarrow 2\text{La(OH)}_3 \tag{9}
\]

However, La(OH)\(_3\) species can easily decompose to its original oxide form when it is exposed to high temperature (higher than 300 °C)\,[34]. This can be a reasonable explanation for the decrease in the intensity of the absorption bands at 3675 and 3710 cm\(^{-1}\) corresponding to the surface –OH groups of La(OH)\(_3\) species upon increasing temperature.

Similar absorption bands at 3675 and 3710 cm\(^{-1}\), which correspond to the surface La–OH groups, can also be observed on the reduced K-doped LaNiO\(_3\) perovskite. However, there is an additional strong absorption band observed at 3570 cm\(^{-1}\). This additional band can be assigned to the O–H stretching of the new hydroxyl species formed on the site of potassium. There are two additional absorption bands observed at 1367 and 879 cm\(^{-1}\) on the reduced K-doped LaNiO\(_3\) perovskite (as shown in Fig. 8d and f, respectively). The first absorption band at 1367 cm\(^{-1}\) can be assigned to the KOH bending mode whereas the second absorption band at 879 cm\(^{-1}\) can be assigned to the K–O stretching mode (Table 2). This indicates that potassium hydroxide (KOH) complex is formed when H\(_2\)O is adsorbed on the surface of potassium in the reduced K-doped LaNiO\(_3\) perovskite. This result is consistent with the literature\,[35,36] which has reported that the addition of the electropositive alkali metals (e.g. K, Na, Li, and Cs, etc.) promotes the formation of the active –OH species which has relatively high thermal stability. For example, K–OH complex formed on the surface of potassium can only be decomposed into K, O, and H (Eq. (10)) at temperatures of above 350 °C\,[37].

\[
\text{KOH} \rightarrow \text{K} + \text{O} + \text{H} \tag{10}
\]

This phenomenon can be a reasonable explanation for the observation in Fig. 8b that there is slightly decrease in the intensities of the absorption bands corresponding to the surface K–OH complex with increasing temperature. As a result,
it can be concluded that the H2O adsorption on the reduced K-doped LaNiO3 perovskite catalysts leads to the formation of two different surface hydroxyl groups including: (1) the La2O3 support; and (2) the stable K−OH group which is formed on the surface of potassium.

As will be discussed later, the decrease in the concentration of surface La−OH groups on the reduced LaNiO3 perovskite at high temperature leads to a lowering in the catalytic activity; on the other hand, the formation of stable surface K−OH groups on the reduced K-doped LaNiO3 perovskite can significantly enhance the catalytic activity during HT-WGS reaction even at high temperature.

Adsorption of CO2 and CO2/H2O mixture

Fig. 9a and b, respectively, show the in situ DRIFTS spectra of CO2 adsorption on La2O3 and K2O (as references) at different temperatures ranging from 200 °C to 550 °C. The in situ DRIFTS spectra of CO2 adsorption on La2O3 (Fig. 9a) exhibits the main absorption bands at 1550, 1490, 1460, and 1410 cm−1, corresponding to the carbonate species of La2O2CO3 formed through the reaction of CO2 with La2O3 (Eq. (11)). More specifically, the absorption band at 1550 cm−1 is attributed to the bidentate carbonate, whereas the absorption bands at 1490, 1460, and 1410 cm−1 are associated with the bridge, linear, and unidentate carbonate species, respectively.

Table 2 – Assignment of the observed vibration frequencies from the in-situ DRIFT spectra.

<table>
<thead>
<tr>
<th>Wavenumber (cm−1)</th>
<th>Vibration mode</th>
<th>Molecule</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>2060</td>
<td>ν (C−O)</td>
<td>CO(ads)</td>
<td>Linear CO chemisorbed on NiO2</td>
</tr>
<tr>
<td>1910</td>
<td>ν (C−O)</td>
<td>CO(ads)</td>
<td>Bridge CO chemisorbed on NiO2</td>
</tr>
<tr>
<td>1370</td>
<td>ν (C−O)sym</td>
<td>HCOO(ads)</td>
<td>Formate intermediate</td>
</tr>
<tr>
<td>1585</td>
<td>ν (C−O)asym</td>
<td>HCOO(ads)</td>
<td>Formate intermediate</td>
</tr>
<tr>
<td>2845</td>
<td>δ (C−H)</td>
<td>CH4(gas)</td>
<td></td>
</tr>
<tr>
<td>3014</td>
<td>ν (C−H)</td>
<td>CH4(gas)</td>
<td></td>
</tr>
<tr>
<td>1045</td>
<td>ν (C−O)sym</td>
<td>CO2(ads)</td>
<td>Bidentate carbonate</td>
</tr>
<tr>
<td>1295</td>
<td>ν (C−O)asym</td>
<td>CO2(ads)</td>
<td>Bidentate carbonate</td>
</tr>
<tr>
<td>1585</td>
<td>ν (C−O)asym</td>
<td>CO2(ads)</td>
<td>Unidentate carbonate</td>
</tr>
<tr>
<td>1390</td>
<td>ν (C−O)asym</td>
<td>CO2(ads)</td>
<td>Unidentate carbonate</td>
</tr>
<tr>
<td>1475</td>
<td>ν (C−O)asym</td>
<td>CO2(ads)</td>
<td>Unidentate carbonate</td>
</tr>
<tr>
<td>3710</td>
<td>ν (O−H)</td>
<td>−OH(ads)</td>
<td>Surface germinal OH</td>
</tr>
<tr>
<td>3650</td>
<td>ν (O−H)</td>
<td>−OH(ads)</td>
<td>Surface germinal OH</td>
</tr>
<tr>
<td>3570–3620</td>
<td>ν (O−H)</td>
<td>−OH(ads)</td>
<td>Surface germinal OH</td>
</tr>
<tr>
<td>1340–1500</td>
<td>δ (O−H)</td>
<td>−OH(ads)</td>
<td>Surface germinal OH</td>
</tr>
<tr>
<td>200–880</td>
<td>ν (K−O)</td>
<td>K−O</td>
<td>K−OH</td>
</tr>
<tr>
<td>3750</td>
<td>ν (O−H)</td>
<td>H2O(gas)</td>
<td></td>
</tr>
</tbody>
</table>

Note: ν is a stretching vibration; δ is a bending vibration.

Table 3 – Comparison of the TOF of the 5 wt. % K-doped LaNiO3 with the literature values.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>conditions</th>
<th>T (°C)</th>
<th>TOF (S−1)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt. % K-doped LaNiO3</td>
<td>7% CO, 22% H2O, 8.5% CO2, 37% H2, balance He</td>
<td>400</td>
<td>0.46</td>
<td>This work</td>
</tr>
<tr>
<td>Ni/2Na/CeO2</td>
<td>7% CO, 22% H2O, 10% CO2, 20% H2, balance He</td>
<td>400</td>
<td>0.46</td>
<td>[32]</td>
</tr>
<tr>
<td>5Ni5Cu/GeO2</td>
<td>7% CO, 22% H2O, 10% CO2, 20% H2, balance He</td>
<td>350</td>
<td>0.013</td>
<td>[47]</td>
</tr>
<tr>
<td>5Ni5Cu/SiO2</td>
<td>7% CO, 22% H2O, 8.5% CO2, 37% H2, balance Ar</td>
<td>350</td>
<td>0.002</td>
<td>[39]</td>
</tr>
<tr>
<td>Pt−4Na/TiO2</td>
<td>2.83% CO, 5.66% H2O, 37.7% H2, balance He</td>
<td>300</td>
<td>3.82</td>
<td>[52]</td>
</tr>
</tbody>
</table>

Fig. 7 – The in situ DRIFTS spectra of CO adsorption on the reduced (a) LaNiO3 perovskite and (b) 5 wt. % K-doped LaNiO3 perovskite as a function of temperature.
Fig. 8 – The in situ DRIFTS spectra of H₂O adsorption on the reduced (left) LaNiO₃ perovskite and (right) 5 wt. % K-doped LaNiO₃ perovskite as a function of temperature at different wavenumber ranges of: (a) and (b) 3500–3800 cm⁻¹; (c) and (d) 1300–1500 cm⁻¹; (e) and (f) 700–950 cm⁻¹.
1460, and 1410 cm$^{-1}$ are attributed to the unidentate carbonate [38].

La$_2$O$_3$ + CO$_2$ $\leftrightarrow$ La$_2$O$_3$CO$_3$  \hspace{1cm} (11)

On the other hand, the in situ DRIFTS spectra of CO$_2$ adsorption on K$_2$O (Fig. 9b) exhibits the main absorption bands at 1490 and 1375 cm$^{-1}$, corresponding to the surface carbonate species of K$_2$CO$_3$ formed through the adsorption of CO$_2$ on the surface of K$_2$O. This result suggests that CO$_2$ can be adsorbed on both La$_2$O$_3$ and K$_2$O. However, it has been reported that the surface K$_2$CO$_3$ species has low thermal stability, hence enabling CO$_2$ to be desorbed from the surface of potassium at temperatures above 175 °C [26], especially in the presence of H$_2$O, as illustrated in Eq. (12).

K$_2$CO$_3$ + H$_2$O $\leftrightarrow$ 2KOH + CO$_2$  \hspace{1cm} (12)

In order to investigate the thermal stabilities of these two carbonate species in the presence of H$_2$O, the in situ DRIFTS spectra of the adsorption of CO$_2$/H$_2$O mixture on the reduced LaNiO$_3$ and K-doped LaNiO$_3$ perovskite were therefore recorded, as presented in Fig. 10. It was found that CO$_2$ and H$_2$O are competitively adsorbed on the La$_2$O$_3$ support for the entire range of temperature to form La$_2$O$_3$CO$_2$ and La(OH)$_3$ species, respectively (Fig. 10a). This result suggests that the density of surface La–OH groups on the surface of La$_2$O$_3$ support can be dramatically decreased due to the formation of La$_2$O$_3$CO$_3$, hence decreasing the WGS activity of the catalyst, to be discussed.

Fig. 10b also shows that CO$_2$ and H$_2$O are competitively adsorbed on the surface of K$_2$O on the reduced K-doped LaNiO$_3$. However, it was found that the main absorption band of K$_2$CO$_3$ (1490 cm$^{-1}$) is decreased upon increasing the temperature beyond 300 °C, whereas the main absorption band of KOH (3570 cm$^{-1}$) is drastically increased. This result implies that K$_2$O in the reduced K-doped LaNiO$_3$ perovskite preferentially adsorbs H$_2$O to form the KOH species at temperatures above 300 °C.

WGS reaction of pure CO/H$_2$O gas

In order to elucidate the mechanism of the HT-WGS reaction over the reduced LaNiO$_3$ perovskite, in situ DRIFTS analysis was carried out during the HT-WGS reaction of pure CO/H$_2$O gas (5 mol. % CO, 25 mol. % H$_2$O, balance He) over the reduced LaNiO$_3$ perovskite at different reaction temperatures ranging from 200 °C to 550 °C, and the obtained in situ DRIFTS spectra are shown in Fig. 11.

Typically, there are two different mechanisms proposed for the WGS reaction including: (1) the regenerative (redox) mechanism that involves the oxidative and reductive reactions of CO and H$_2$O over the catalyst surface, with corresponding changes in the oxidation state of the support for each step [33,39]; and (2) the adsorptive (non-redox) mechanism, where CO and H$_2$O have been proposed to adsorb on the catalyst surface to form the surface carbon-containing intermediate that subsequently decomposes to form the gaseous products of H$_2$ and CO$_2$ [40,41]. There are three main surface carbon-containing intermediates which have been extensively proposed for the adsorptive mechanism during WGS reaction including: (1) formate (HCOO); (2) carbonates (CO$_3$)$^-$; and (3) carboxylate (HOCO) species [42]. However, these three surface intermediates have different life-times on the catalyst surface depending on their thermal stabilities [43]. The carboxylate intermediate has been reported to have very low thermal stability, making it an ideal transient intermediate for the WGS reaction [44]. In addition, this intermediate can only be observed under steady state conditions. On the other hand, it has been reported that the formate intermediate has greater stability than the carbonate intermediate. The former has a higher desorption temperature of up to about 700 K, whereas the latter can only survive on the surface with temperatures of up to about 300 K [45]. Since the WGS reaction was performed in this study at temperatures up to 823 K, formate (HCOO) is expected to be the key surface intermediate over the reduced LaNiO$_3$ perovskite.

It can be seen from the in situ DRIFTS spectra during the WGS reaction of pure CO/H$_2$O gas that the strong C–H stretching bands at 2875 cm$^{-1}$ (symmetric mode) and 2950 cm$^{-1}$ (asymmetric mode) are observed along with the OCO stretching bands at 1370 cm$^{-1}$ (symmetric mode) and 1630 cm$^{-1}$ (asymmetric mode). This suggests the formation of the formate (HCOO) species as the surface intermediate rather than the carbonate (CO$_3$)$^-$ species. Moreover, the decrease in the intensity of formate bands at 2875 cm$^{-1}$ (bridged) and 2950 cm$^{-1}$ (bridged) coupled with the increase of the IR band at 2346 cm$^{-1}$ which correspond to the CO$_2$ (gas) indicates that the decomposition of the surface formate intermediate toward the gaseous products of CO$_2$ and H$_2$ upon increasing reaction temperature from 200 °C to 450 °C. Further increase in reaction temperature leads to a remarkable decrease in the intensity of formate. At the same time, it was also observed that the in situ DRIFTS spectra in the region of hydroxyl groups (3600–3800 cm$^{-1}$) corresponds to the overall intensity of the surface La–OH absorption bands (3675 cm$^{-1}$ and 3710 cm$^{-1}$) significantly decreases when the reaction temperature is increased to higher than 400 °C, indicating that the surface La–OH groups on La$_2$O$_3$ support have a relatively low thermal stability as mentioned previously. Therefore, it can be concluded that the significant decrease in the intensity of the formate bands (2875 and 2950 cm$^{-1}$) is caused by the decrease of the surface La–OH groups on the La$_2$O$_3$ support at high reaction temperatures due to its relatively low thermal stability, leading to the lower catalytic activity at high reaction temperatures. This result also implies that the HT-WGS activity of the reduced LaNiO$_3$ perovskite is mainly controlled by the formation of the surface –OH groups. Furthermore, no IR band is observed at around 3014 cm$^{-1}$ which corresponds to the C–H stretching of CH$_4$ (gas). This result implies that no methane is formed over the reduced LaNiO$_3$ perovskite during HT-WGS reaction of pure CO/H$_2$O gas, which is in a good agreement with the catalytic activity results shown earlier.

Based on the different thermal stabilities of intermediates and the above in situ DRIFTS results, the formate (HCOO) could be the key surface intermediate, which subsequently decomposes to form gaseous products of H$_2$ and CO$_2$ during the WGS reaction. Thus, it can be concluded that the WGS reaction over the reduced LaNiO$_3$ perovskite catalyst undergoes a
similar pathway of “formate mechanism” which has been intensively proposed in the literature [40,44,46,47] as follows:

\[
\begin{align*}
\text{CO}_\text{gas} & \leftrightarrow \text{CO}_{\text{ads}} \quad (13) \\
\text{H}_2\text{O}_\text{gas} & \leftrightarrow \text{H}_2\text{O}_{\text{ads}} \quad (14) \\
\text{H}_2\text{O}_{\text{ads}} & \leftrightarrow \text{OH}_{\text{ads}} + \text{H}_{\text{ads}} \quad (15) \\
\text{CO}_{\text{ads}} + \text{OH}_{\text{ads}} & \leftrightarrow \text{HCOO}_{\text{ads}} \quad (16) \\
\text{HCOO}_{\text{ads}} & \leftrightarrow \text{CO}_2\text{gas} + \text{H}_{\text{ads}} \quad (17) \\
2\text{H}_{\text{ads}} & \leftrightarrow \text{H}_2\text{gas} \quad (18)
\end{align*}
\]

From the in situ DRIFTS spectra of adsorbed CO and H2O shown in Figs. 7 and 8, respectively, it can be concluded that the CO (gas) adsorbs on the metallic Ni0 nanoparticles forming the CO_{ads} (Eq. (13)); while the adsorption and dissociation of H2O (forming the OH_{ads}) takes place on the oxide (i.e., the La2O3 support) (follows Eqs. (14) and (15)). Therefore, it is possible to assume that the formate intermediate (HCOO_{ads}) is formed at the interface between metallic Ni0 nanoparticles and La2O3 support (Eq. (16)) as a consequence of the reaction between the CO adsorbed on the metallic Ni0 nanoparticles and the surface OH groups on the La2O3 support (Fig. 13).

WGS reaction of reformate gas – role of potassium
In order to further elucidate the WGS mechanism of reformate gas and to investigate the role of potassium, the in situ DRIFTS analysis was carried out during WGS reaction of reformate gas (which contains 5 mol. % CO, 25 mol. % H2O, 10 mol. % CO2, 40 mol. % H2, balance He) over both the reduced LaNiO3 and K-doped LaNiO3 perovskite at different reaction temperatures ranging from 200 °C to 550 °C. These in situ DRIFTS spectra results are shown in Fig. 12a and b, respectively.

Similar to the in situ DRIFTS spectra during WGS reaction over the reduced LaNiO3 perovskite of pure CO/H2O gas, the strong absorption bands (C–H stretching at 2875 and 2950 cm⁻¹, OCO stretching at 1370 and 1630 cm⁻¹) of the formate intermediate can be observed for the entire reaction temperature range. It is also observed that the intensity of the absorption bands of formate intermediate dramatically decreases upon increasing temperature, this is mainly due to the decrease in the surface La–OH group at high temperature as can be seen in the in situ DRIFTS spectra in the region of hydroxyl groups (3650–3800 cm⁻¹) (as presented in the inset of Fig. 12a).

For this reaction system, there is a strong absorption band of CH4 (gas) (C–H bond stretching at 3014 cm⁻¹) observed in the in situ DRIFTS spectra (Fig. 12a) for the entire temperature range. This indicates that the methanation of CO2 also takes place concurrently with the WGS reaction; this result is in agreement with the observed catalytic activity results shown earlier. With the observations from the in situ DRIFTS spectra of CO2 and CO2/H2O adsorptions on the reduced LaNiO3 perovskite shown in Figs. 9 and 10, respectively, it can be concluded that methane can easily be produced via the methanation reaction of CO2 adsorbed on the La2O3 support with H2 adsorbed on the metallic Ni0 nanoparticles during the WGS reaction of reformate gas, as schematically shown in Fig. 13a.

On the other hand, the in situ DRIFTS spectra characterizing the WGS reaction of reformate gas over the reduced K-doped LaNiO3 perovskite are shown in Fig. 12b. Similarly, the strong absorption bands (C–H stretching at 2875 and 2950 cm⁻¹, OCO stretching at 1370 and 1630 cm⁻¹) of the formate intermediate are observed for the entire reaction temperature range. However, only a slight decrease in the...
intensity of the absorption bands of formate intermediate is observed upon increasing reaction temperature. The in situ DRIFTS spectra in the region of two different hydroxyl groups (i.e. La–OH group at 3650–3800 cm⁻¹, K–OH group at 3450–3650 cm⁻¹) as presented in the inset of Fig. 12b shows that the overall intensities of the surface La–OH absorption bands at 3675 and 3710 cm⁻¹ are significantly decreased upon increasing temperature to higher than 400 °C. On the other hand, there is only a slight decrease in the intensity of the surface K–OH absorption band at 3575 cm⁻¹ observed for the entire reaction temperature range. These results suggest that the abundance of stable K–OH groups on the potassium surface helps to promote the formation of “formate intermediate” even at high reaction temperature by supplying the surface – OH group to react with the CO adsorbed on metallic Ni⁰. Hence, this results in the improved catalytic activity of LaNiO₃ perovskite for the WGS reaction even at high reaction temperature; this result is in good agreement with the catalytic activity results discussed earlier. At the same time, the absorption band of CH₄ (gas) (at 3014 cm⁻¹) can be observed only at high reaction temperature (>400 °C), indicating that the addition of potassium to the LaNiO₃ perovskite helps to significantly suppress the methanation of CO₂ at low reaction temperature, which is also in good agreement with the catalytic activity results. This is probably due to the fact that the K–OH groups on the surface of potassium dopant (which is located between the La₂O₃ support and the metallic Ni⁰ nanoparticle) block the methanation reaction of H₂ adsorbed on metallic Ni⁰ nanoparticles with the CO₂ adsorbed on the La₂O₃ support (as schematically shown in Fig. 13b), hence resulting in less methane formation during the WGS reaction of reformate gas over the reduced K-doped LaNiO₃ perovskite.

The above results clearly indicate that the addition of potassium onto the LaNiO₃ perovskite catalyst precursor not only helps to enhance the WGS activity of LaNiO₃ perovskite at high reaction temperature by promoting the adsorption and dissociation of H₂O – which help to supply the surface hydroxyl groups to react with the CO adsorbed on the metallic

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Fig. 10 – The in situ DRIFTS spectra of H₂O/CO₂ mixture adsorption on the reduced (a) LaNiO₃ perovskite and (b) 5 wt. % K-doped LaNiO₃ perovskite as a function of temperature at the wavenumber ranges of 3500–3800 cm⁻¹ and 1300–1500 cm⁻¹.
Fig. 11 – The in situ DRIFTS spectra during HT-WGS reaction of pure CO/H$_2$O gas over the reduced LaNiO$_3$ perovskite.

Fig. 12 – The in situ DRIFTS spectra during HT-WGS reaction of reformate gas over the reduced (a) LaNiO$_3$ perovskite and (b) 5wt. % K-doped LaNiO$_3$ perovskite as a function of temperature.
Ni nanoparticles and subsequently form the “formate intermediate” even at high reaction temperature—but also helps to suppress the formation of methane by blocking the methanation reaction of the CO₂ adsorbed on the La₂O₃ support with the H₂ adsorbed on the metallic Ni nanoparticles during WGS reaction.

Fig. 13 — Schematic diagrams of the proposed WGS mechanism of reformate gas over (a) the reduced LaNiO₃ perovskite and (b) the reduced K-doped LaNiO₃ perovskite catalyst precursors.

Conclusions

LaNiO₃ perovskite has been successfully used as a catalyst precursor for the high temperature water-gas shift reaction of reformate gas. The Ni nanoparticles with small particle size
perature water-gas shift of pure CO/H2O gas, whereas CO2 can effectively suppress CO methanation during high temperature gas shift of reformate gas can be suppressed by the addition of potassium onto LaNiO3 perovskite. This is due to the adsorption of H2O on potassium which is located at the interface between La2O3 and Ni2+ nanoparticle, forming stable K–OH species to block the methanation of CO2 adsorbed on La2O3 with H2 adsorbed on Ni2+ nanoparticles. Moreover, the formation of K–OH species with relatively high thermal stability also promotes the formation of formate (HCOO−) intermediate even at high reaction temperature by continuously supplying hydroxyl groups to react with CO adsorbed on the Ni metal nanoparticle, hence enhancing the catalytic activity of LaNiO3 perovskite.

Acknowledgments

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References


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