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Investigation on reverse water–gas shift over La_2NiO_4 catalyst by cw-cavity enhanced absorption spectroscopy during CH_4/CO_2 reforming

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Reverse water–gas shift (RWGS) reaction over La_2NiO_4 catalyst was investigated during CH_4/CO_2 reforming by continuous wave cavity enhanced absorption spectroscopy, a sensitive absorption technique. The results indicated that the RWGS reaction promoted the conversion of CO_2 and decreased the partial pressure of hydrogen. By proper adjustment of the pressure of the reaction system, it is possible to suppress the occurrence of RWGS reaction and increase the selectivity of CH_4/CO_2 reforming. The intermediates of CH_4/CO_2 reforming such as CHO, OH and CH_3 were observed by means of the liquid-N_2 quenching technique, and a reaction step: $CH_x + [O] = CH_xO$ was primarily confirmed. In addition, XPS and XRD results verified that nickel over catalyst after CH_4/CO_2 reforming existed in elemental state. The HRTEM images of used catalyst indicated that the deactivation of catalyst was originated mainly from the formation of nanotubes and graphite carbon on active sites of nickel.

KEY WORDS: CH_4/CO_2 reforming; CEA spectra; reverse water–gas shift; La_2NiO_4 catalyst; intermediates.

1. Introduction

In recent years, there has been an increased interest on the catalytic transformation of CH_4/CO_2, both are greenhouse gases and cheap carbon-containing feed stock, into more useful or valuable chemicals. The synthesis gas (i.e. $CO + H_2$) with a H_2/CO ratio of 1:1 is more suitable for Fisher–Tropsch synthesis for the production of liquid hydrocarbons [1,2]. The CO_2/CH_4 reforming reaction has been studied over numerous supported metal catalysts, such as Ni-based [3–7] and noble metal catalysts [8,9]. However, it is more practical, from the industrial standpoint, to develop Ni-based catalysts that not only possess high stability and catalytic activity, but also are more economical than a catalyst of precious metal. A number of studies on CO_2/CH_4 reforming over supported Ni [5,10,11] catalysts indicated that they still did not meet the requirement for industrialization due to carbon deposition.

The carbon deposition over Ni-based catalysts has been considered to be originated mainly from CH_4 decomposition and CO disproportionation. The strong bonds in CH_4 (439 kJ mol^{-1} [12]) and the endothermic nature of reforming reactions require high temperatures and stable catalysts [13,14]. Therefore it is difficult to avoid the formation of coke over the catalyst and it can be partly removed in the presence of CO_2. The increase in CO concentration in the reaction system is the main cause of CO disproportionation. The coupling of catalytic reaction and membrane separation can reduce the partial pressure of CO and H_2 and suppress the occurrence of CO disproportionation, resulting in CH_4 and CO_2 conversions significantly higher than those observed over a common fixed-bed reactor. However, the practical outcome was not satisfactory due to separation efficiency of membrane (CH_4/H_2 and/or CO_2/CO separation was low) [15,16]. Therefore, no matter whether it is for the production of CO-free hydrogen gas suitable for fuel cell or the suppression of coke formation, it is necessary to probe the effect of RWGS on CH_4/CO_2 reforming.

High-resolution cavity enhanced absorption spectroscopy (CEAS) using a continuous wave (cw) narrow linewidth tunable diode laser (TDL) is a sensitive absorption technique for obtaining quantitative spectra of molecular species [17,18]. Since its introduction [18], CEAS has been applied to chemical problems ranging from surface phenomena to process measurements in plasmas and plumes, and in atmospheric studies and to a wide range of chemical kinetics studies. This novel type of long path-length measurement technique adopts an unstabilized ultra-high finesse optical cavity and records the intensity buildup inside the cavity. Laser radiation from the laser source is coupled into the cavity via accidental coincidences of the laser frequency with one of the multimodes of the cavity. The laser and the

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cavity are scanned and the absorption signal is extracted from a measurement recording the highest light intensity at a specified time period that leaks out of the cavity [19]. This high-resolution technique is capable of recording the vibration-rotational transitions of molecular species.

Recently, Goguet *et al.* [20,21] investigated the RWGS reaction over 2% Pt/CeO_2 catalyst and confirmed that in the course of the RWGS reaction carbon deposition was one of the major reasons for the slow deactivation of 2% Pt/CeO_2 catalyst. In general, the water produced from RWGS reaction in stream was removed only by the method of ice-water condensation [22]. In this work, using the CEAS technique, we investigated the effect of RWGS reaction over working La_2NiO_4 catalyst during CH_4/CO_2 reforming and resolved the problem ignored by most research groups. In the meantime, the mechanism of the reforming reaction under the condition was probed by means of the liquid-N_2 quenching technique. The performances of the catalyst before and after reaction were characterized by means of X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) techniques, respectively.

2. Experimental

2.1. *Preparation of catalyst*

According to literature [23], stoichiometric $Ni(NO_3)_2$ $6H_2O$ and La_2O_3 (molar ratio of Ni and La was 1:2) were dissolved completely in diluted nitric acid, and citric acid and ethylene glycol were added to the solution. The molar amounts of citric acid and ethylene glycol were 1.5 times that of the total metal ions. Then, the solution was heated to 60 °C with constant stirring. After the removal of water through evaporation, a translucent green gel was formed. Next, the cogel obtained was aged and dried in a beaker at room temperature (RT) for 3 days; subsequently, it was calcined at 500 °C for 3 h and at 800 °C for 5 h. This sol gel-generated catalyst will be referred to as 'La_2NiO_4' hereafter.

2.2. *Analysis of CH_4 and H_2O by means of CEAS technique*

CO_2/CH_4 reforming was carried out in a fixed-bed quartz reactor (i.d. 4 mm) and the feed rate of the reactant gas mixture was controlled by means of an automatic electronic pulsed valve. The catalyst was placed between two quartz-wool plugs in the reactor, and a thermocouple by which the reaction temperature was controlled was placed underneath the quartz reactor at the center of the catalyst bed. Typically, 50 mg of the catalyst was used, which was reduced in a flow of H_2/Ar mixture (1:3 V/V) at 750 °C for 1 h before the reaction. The effluent, CH_4 and H_2O spectra were monitored and analyzed by means of a sensitive CEAS technique. Figure 1 shows schematically the arrangement of optical components for CEAS. Experimental setup for performing CEAS has been reported

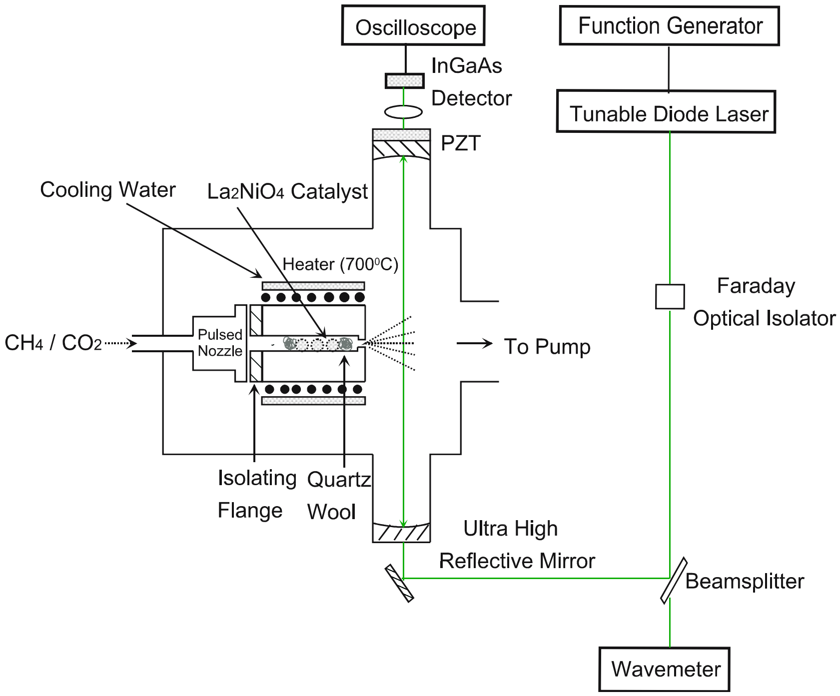

Figure 1. Schematic diagram of the cavity enhanced absorption (CEA) spectroscopy apparatus.

in previous publications [18,19,24]. Only a very brief description of the experimental conditions is given here. A cw TDL, operating in the 1279–1341 nm region with a 5 mW maximum power and a line width of about 5 MHz, was used as a light source. The laser radiation was coupled into a high finesse optical cavity formed by two plano-concave mirrors with a diameter of 20 mm (reflectivity of $R > 0.99995$), and the two mirrors were mounted on adjustable mirror-holders at a distance of 0.6 m apart. A piezoelectric translator (PZT) fixed to the end mirror modulated very slightly the cavity length. A Faraday isolator placed in the beam directly in front of the laser source minimized optical back reflection from the cavity mirrors to disturb the laser. The laser frequency was scanned with a voltage from a function generator at a slow rate (about 500–1000 s/1 cm^{-1}). A function generator was used to provide voltage to the PZT controller to sweep the cavity at a rate of 3–5 Hz. This modulation resulted in a CEAS cavity coverage of several longitudinal modes at a slow rate. The optical cavity used did not require any stabilization. An InGaAs detector was used to detect the laser light exited from the end mirror. The detected signal was amplified and displayed on a fast digital oscilloscope. The method of recording the highest light intensity signal received by the oscilloscope was used [19]. In this case, the data from the oscilloscope were transferred at a rate of 1 Hz via an interface bus to a computer for further processing. The laser frequency was measured directly by a wave-meter with an accuracy of about ± 0.002 cm^{-1}. During data processing, a procedure of averaging five adjacent points was applied for smoothing the spectrum.

2.3. Probation on intermediates of CH_4/CO_2 reforming

CH_4/CO_2 reforming reaction was carried out in a quartz U-type reactor. The La_2NiO_4 catalyst was heated to 700 °C and was reduced by flowing hydrogen through the reactor. A mixture with 1:1 ratio of CH_4/CO_2 was fed to the reactor. After the CH_4/CO_2 reforming reaction was allowed to occur for a short period of time, the reforming reaction was quenched by immersing quickly the hot tubular reactor (with the two ends sealed to prevent other gas from entering) into a flask containing liquid-N_2 (77 K). The trapped gas and molecular species were analyzed using mass spectrometry (MS). After the outlet of the reactor was connected to a mass spectrometer (HP G-1800A), helium gas was used as sweeping gas and flowed in continuously from the other end. The temperature of the reactor was gradually increased by slowly pulling the reactor out from the liquid-N_2 flask and stopped when it reached the RT (ca. 30 °C). The effluent from the reactor was monitored on-line using the MS. The reactor was eventually heated up to 750 °C in an oven to obtain the ad-species over La_2NiO_4.

2.4. Characterization of catalyst

XPS was adopted for surface analysis of catalyst. Each powder sample was pressed onto a piece of double-sided sticking tape and mounted on the sample stub; the sample was then outgassed (ca. 10^{-5} Torr) before being transferred into the analyzer chamber ($<710^{-9}$ Torr) for analysis. It was a VGX 900 spectrometer with a single channel detector coupled with Al K_α radiation. The effect of charging was corrected by calibration to contaminant carbon (C 1s binding energy = 284.6 eV). The powder XRD patterns of the catalysts were recorded on a BDX3300 diffractometer with a Cu $K\alpha$ radiation source at a voltage of 30 kV and a current of 20 mA. The average size of Ni particles was calculated using the Scherrer equation. The HRTEM images of catalyst surface were acquired with a Philip Tecnai G2 20 electron microscopy operating at 200 kV.

3. Results and discussion

3.1. Formation of H_2O over La_2NiO_4 catalyst during CH_4/CO_2 reforming

The high-resolution absorption spectrum of CH_4 near 7510 cm^{-1}, obtained by the CEAS technique is shown in figure 2. Methane is a spherical top molecule classified to have T_d point group symmetry, the 7510.59, 7510.88, 7510.96, 7511.10 and 7511.20 cm^{-1} absorption lines observed in figure 2 are the $\Delta J = 0$ (Q branch) rotational transitions of the 2_0^1 3_0^1 vibrational transition [25]. As for the H_2O absorption line at 7511.29 cm^{-1}, it is the $J = 5$, $K_a = 0$, $K_c = 5$ to $J = 6$, $K_a = 2$, $K_c = 4$ rotational transition of the 1_0^1 3_0^1 vibrational transition [26]. These absorption lines of CH_4 and H_2O in the 1.3 μm regions are also listed in the HITRAN database [27]. These molecular transition lines are chosen because they

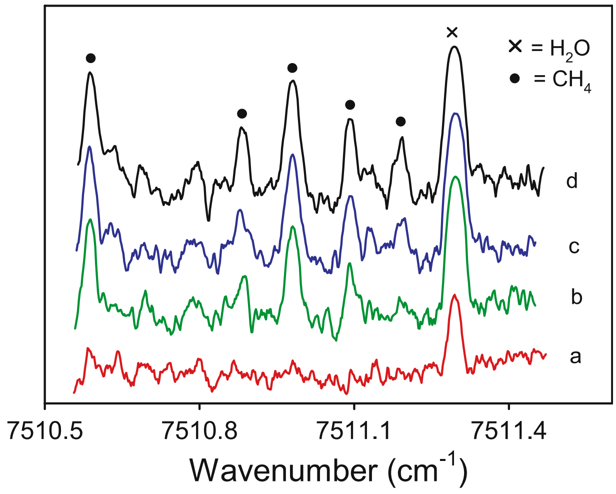

Figure 2. CEA spectra of CH_4 and H_2O obtained at different pulsing rate of CH_4/CO_2, respectively; (a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0 ms/2 Hz; reaction temperature = 700 °C.

are in the same wavelength region and under our experimental conditions their intensities are comparable so that simultaneous observation and monitoring of the two molecules are possible in one single scan. At the beginning of reaction (figure 2a), CH_4/CO_2 mixture was introduced by a pulsed valve with 0.50 milliseconds (ms) duration and at a rate of 2 Hz. In figure 2a, no absorption line of methane gas was found near 7510 cm^{-1}; only the weak absorption line of H_2O at 7511.29 cm^{-1} was observed. This means that CH_4/CO_2 reforming reaction is complete. When the pulsed duration of CH_4/CO_2 mixture was raised to 1.50 ms, the RWGS reaction increased significantly during CH_4/CO_2 reforming due to the enhancement of CO_2 partial pressure. Besides the absorption lines of CH_4, we observed that the water absorption line increased in intensity as shown in figure 2d. In our previous studies of the CH_4/CO_2 reforming [3,5], even though the feed ratio of CH_4 and CO_2 was the same, the CO_2 conversion were always 3–5% higher than that of CH_4, which indicates that the RWGS reaction promoted the conversion of CO_2. The observation is in good agreement with the results obtained under the condition of pulsed jet expansion by CEAS technique.

In addition, the effect of reaction temperature on RWGS is shown in figure 3. At 600 °C, the high-resolution absorption lines of CH_4 at 7510 cm^{-1} were observed and we also observed the presence of the absorption line of H_2O at CEA spectrum due to the occurrence of RWGS reaction. However, when reaction temperature reached 700 °C, the absorption lines of CH_4 decreased in intensity whereas the absorption line of H_2O was significantly enhanced as shown in figure 3. This demonstrated that with increasing temperature, the conversion of CH_4 over La_2NiO_4 catalyst increased gradually, and a large amount of CO and H_2 was formed. Under this situation, the rate of RWGS reaction accelerated due to the enhancement of partial pressure of hydrogen in the CH_4/CO_2 reforming. Mark *et al.* [28] has confirmed that the rate constants of RWGS reaction increased with increasing reaction temperature by examining the reaction kinetics of the CH_4/CO_2 reforming. They considered the RWGS reaction is an important network reaction; it significantly affected the H_2/CO product ratio, i.e. the selectivity of CH_4/CO_2 reforming.

According to earlier results [23], the conversion of CO_2 over La_2NiO_4 catalyst was nearly 8.0% higher than that of CH_4, which is attributable to the contribution of RWGS reaction:

$$CO_2 + H_2 = CO + H_2O \qquad \Delta H = +41\,\text{kJ/mol}.$$

The observation of H_2O line in the experiment was a clear indication of the occurrence of the RWGS reaction. We used the high resolution CEAS technique to investigate in detail the influence of time on-stream on the formation of H_2O. In figure 4a, the presence of the H_2O absorption line indicated that a certain amount of H_2O was formed during the reduction of La_2NiO_4. In this reduction reaction, the non-stoichiometric oxygen and structural lattice oxygen in the La_2NiO_4 catalyst reacted with hydrogen to form H_2O, La_2O_3 and Ni^o species, XRD results (figure 7) had verified the existence of Ni^o and La_2O_3 nanoparticles. Figure 4b illustrated that at the beginning of CH_4/CO_2 reforming, weak absorption lines of CH_4 and H_2O were observed, it implied that the RWGS reaction occurred. However, when the time on-stream was increased, although CH_4 conversion almost remained as a constant (the intensity of CH_4 adsorption lines slightly increased due to deactivation of catalyst) as shown in figure 4c and d, the water absorption line gradually increased in intensity.

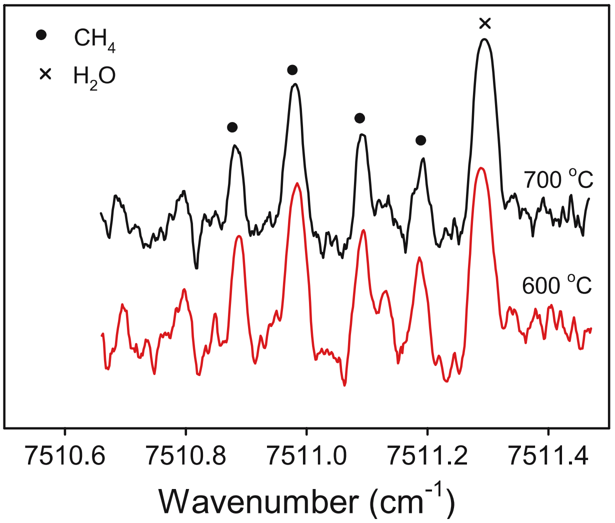

Figure 3. CEA spectra of CH_4 and H_2O obtained at different reaction temperature; (a) 600 °C (b) 700 °C; pulsing rate of CH_4/CO_2 is 2.0 ms/2 Hz.

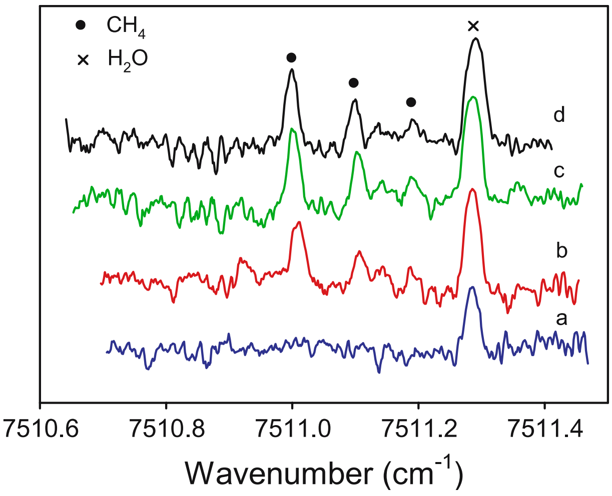

Figure 4. CEA spectra of CH_4 and H_2O obtained at different time on stream (a) H_2-reduced procedure, (b) 15 min, (c) 95 min, (d) 225 min; reaction temperature: 700 °C, pulsing rate of CH_4/CO_2 is 0.7 ms/2 Hz.

This suggested that RWGS reaction was favorably carried out under this condition, similar to the results analyzed by using gas chromatography. It is because when the time on-stream was increased further, a larger amount of coke had been deposited onto the surface of the catalyst, and the increase in pressure favored the RWGS reaction.

3.2. Investigation on intermediate of CH_4/CO_2 reforming

After CH_4/CO_2 reforming reaction was conducted at 700 °C for 2 h, the reactor was quickly inserted into a flask containing liquid-N_2 to quench the reaction and freeze the species produced. The trapped samples were analyzed using MS and the temperature of the reactor was slowly increased from 77 K to RT. It was found that besides CO_2, CH_4 and CO, the other most abundant species were H_2O, which also confirmed the existence of RWGS reaction during CH_4/CO_2 reforming. However, it was interesting to note that at the beginning when the reactor was still at low temperature, a strong MS signal at $m/z = 29$ (ca. 20 s) was observed, which suggested the existence of CHO radical as an intermediate of CH_4/CO_2 reforming. Stevens *et al.* [29] verified the existence of CHO species (2038–2019 cm^{-1} band) on Rh/Al_2O_3 catalyst by means of *in situ* IR spectroscopy technique. They considered that CH_4 reacted with ad-oxygen to form the ad-CH_xO species, and then CH_xO on the active sites further decomposed into adsorbed OH and CH_x species. Luo *et al.* [30] observed intermediates such as formate (HCOO) and formyl (HCO) over Ni-La_2O_3/5A by the method of CD_3I chemical trapping and MS measurement. They suggested that CO_2 reacted with ad-hydrogen to form formate (HCOO), and then the decomposition of HCOO produced HCO and oxygen species. This supported the phenomenon we observed by quenching the reaction and trapping the species by liquid-N_2. In addition, we found that for the MS signal of the other species, such as CH_3 and H_2O, the abundance of OH was always higher than that of H_2O except for the position of strong peaks. It indicated that OH fragment was partly produced from the ionization of other species instead of H_2O. Similarly, for the sample trapped in CH_4/CO_2 reforming for 40 min, the similar phenomenon was observed. The abundance of

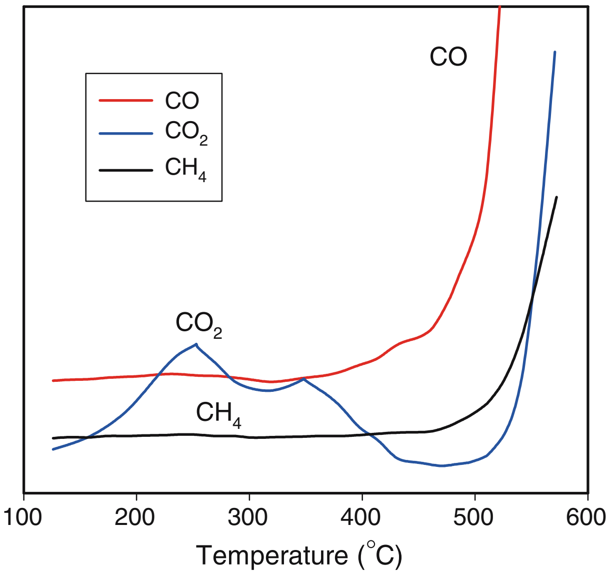

Figure 5. TPD spectra of CO_2, CH_4 and CO for the sample of CH_4/CO_2 reforming for 2h.

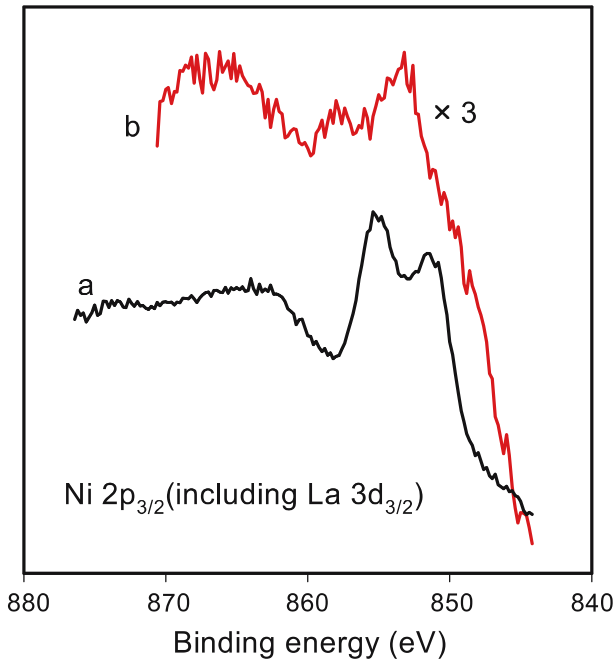

Figure 6. Nickel $2p_{3/2}$ XPS spectra (including La $3d_{3/2}$ contribution) of catalyst as-prepared (a) and exposed (b) to a CH_4/CO_2 mixture for 5h.

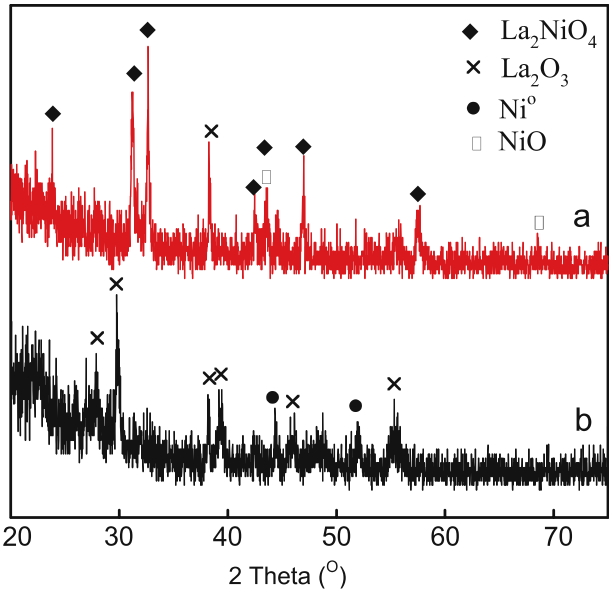

Figure 7. XRD patterns of La_2NiO_4 catalyst before and after reduction.

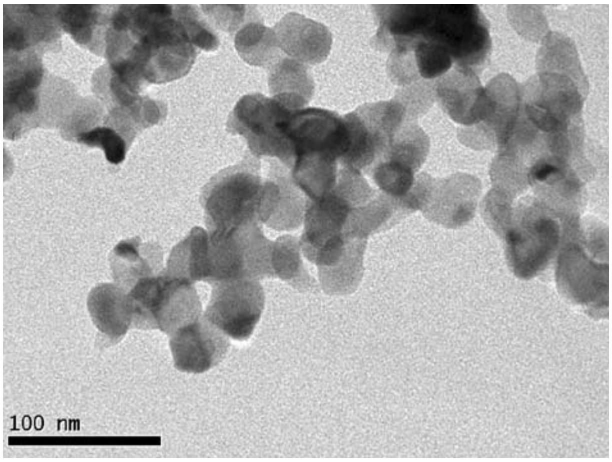

Figure 8. HRTEM images of as-prepared La_2NiO_4 sample.

H_2O is significantly lower compared to the sample trapped after CH_4/CO_2 reforming for 2 h. It suggested that the reaction rate of RWGS enhance with increasing time on-stream, similar to the result (figure 4) observed in the CEA spectra in CH_4/CO_2 reforming.

Furthermore, for the sample trapped in CH_4/CO_2 reforming for 40 min, a strong MS signal of CH_3 intermediate at ca. −60 °C was observed, which desorbed from the surface of catalyst and disappeared quickly within 40 s. Comparing to the MS signal of methane observed at the same time, the intensity of the MS signal of the intermediate species, CH_3 with $m/z = 15$, was higher. This demonstrated the existence of CH_3 intermediate species instead of the other fragments of CH_4 ionization. It is, therefore, possible to capture the intermediates such as, CH_x, OH and CHO during CH_4/CO_2 reforming using the liquid-N_2 quenching technique. To the best of our knowledge, no such result was reported before. Chskis [31] and Scherer *et al.* [32] observed reaction intermediates, such as CH_2, HCO and OH in low-pressure flames by means of the CEAS technique. We have work in progress to study reaction intermediates in CH_4/CO_2 reforming using CEAS and time-of-flight mass-spectrometry (TOF-MS) techniques in our laboratory. On the other hand, in order to probe further into the adsorbed species on the surface of La_2NiO_4 under the condition of high temperature, temperature-programmed desorption (TPD) experiment was carried out and the effluent was fed into a GC-MS. The result of this experiment is shown in figure 5, It indicated that the CO_2 ($m/z = 44$), CO ($m/z = 28$) and CH_4 ($m/z = 16$) were the most abundant adsorbed species, and no other intermediate was found.

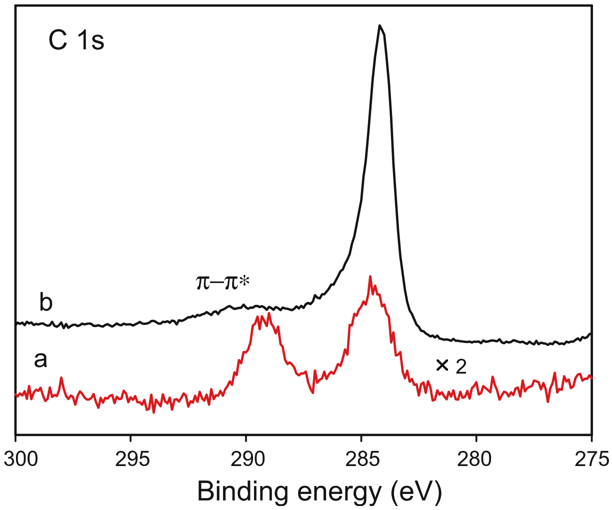

Figure 9. Carbon 1s XPS spectra for catalyst as-prepared (a) and exposed (b) to a CH_4/CO_2 mixture gas for 5h; $T = 700$ °C.

3.3. XPS and XRD characterization of La_2NiO_4 catalyst

In order to characterize the La_2NiO_4 catalyst used under the condition of supersonic jet expansion, the XPS technique was deployed to analyze the chemical state of the elements and the deposition of carbon. The Ni $2p_{3/2}$ spectra of the fresh and used La2NiO4 catalysts are displayed in figure 6. There were two components centered at ca. 852.5 and 855.6 eV. The former can be assigned to elemental Ni [33] whereas the latter to Ni_2O_3 [34] or Ni $(OH)_2$ [35], similar to the case of $NiAl_2O_4$ (855.8 eV) [36]. After exposure to a CH_4/CO_2 mixture for ca. 5 h, the catalyst surface was covered by deposited carbon, and there was attenuation of Ni $2p_{3/2}$ signal. The position of the Ni $2p_{3/2}$ peak indicated that most of the nickel had been reduced to metallic form (figure 6b). Owing to the overlapping of the Ni $2p_{3/2}$ and La $3p_{3/2}$ signals in XPS spectrum analysis, for the sake of confirming further the chemical state of nickel and avoiding the interference of lanthanum signals, XRD patterns of La_2NiO_4 sample before and after reduction were collected, as shown in figure 7. The result showed that for fresh La_2NiO_4 catalyst (figure 7a), the strong diffraction peaks at $2\theta =$ 23.8, 31.24, 32.76, 42.52, 43.62, 46.92 and 57.92°, attributable to a typical spinel structure of La_2NiO_4 was observed. This is in accordance with the XRD result reported by Rodriguez-Carvajal *et al.* [37]. In the meantime, we observed the existence of the diffraction lines of NiO at $2\theta = 43.62, 68.54°$ [38] and La_2O_3 at $2\theta =$ 38.4°, which related to diffraction of La_2O_3 {102} crystal face [39]. After La_2NiO_4 sample was reduced at the atmosphere of hydrogen, La_2NiO_4 was decomposed into microcrystallines of La_2O_3, and nickel nanoparticles of reduced states. Hence, there was the observation of diffraction lines of La_2O_3 (at 2θ = 29.82, 38.12, 39.36, 47.0 and 55.32°) and nickel (at 2θ = 44.44 and 52.02°) [40]. However, the broadness of the latter peaks indicated that the nickel particles after reduction were small and dispersed highly on the surface of catalyst. The size of nickel particles evaluated by Scherrer equation is 32.6 nm, similar to the outcome observed by HRTEM (figure 8). The C 1s spectra for fresh and used La_2NiO_4 catalysts are shown in figure 9. For fresh catalyst (figure 9a), there were two C 1s peaks, one at 284.6 eV and one at 289.3 ± 0.2 eV, attributable to contaminant carbon and carbon of CO_3^{2-} and/or $La_2O_2CO_3$, respectively. The concentration ratio of the two carbon species was approximately 1:1, remarkably higher than the results reported previously [5]. The result indicated that CO_2 adsorption was favorable on La_2NiO_4 catalyst, an important factor for the maintenance of catalyst stability. Figure 9b showed the C 1s spectra recorded after exposing the catalyst to a mixture of CO_2/CH_4 at 700 °C for 5 h. The C 1s peak was at a BE of 284.1 ± 0.2 eV and there was a shake-up line at ca. 291.5 eV, suggesting that there is a small but significant contribution of π–π* transition related to aromatics [41]. By HRTEM technique, we observed the formation of nanotube and graphite carbon on the active sites of metallic nickel over the used sample (figure 10), this is in accordance with the results observed by XPS.

4. Conclusion

The influence of pulsing rate, reaction temperature and time-on-stream on RWGS reaction during CH_4/CO_2 reforming was investigated by cw CEAS process, a sensitive adsorption technique applied extensively in molecular spectroscopy field. We proposed factors that would affect the selectivity of product. By a procedure of

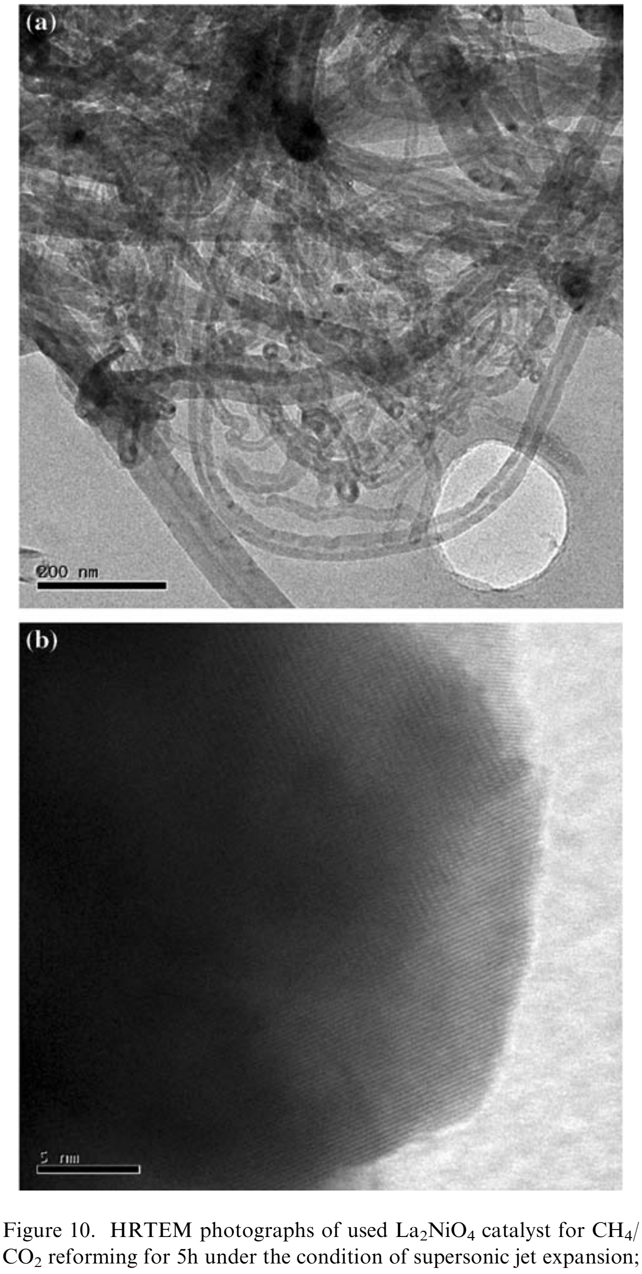

Figure 10. HRTEM photographs of used La_2NiO_4 catalyst for CH_4/CO_2 reforming for 5h under the condition of supersonic jet expansion; scale (a) 200 nm (b) 5 nm.

liquid-N_2 quenching, we observed reaction intermediates such as HCO, OH and CH_3 radicals that existed in the gas phase of CH_4/CO_2 reforming. Meanwhile, the properties of the catalyst used under the condition of supersonic jet expansion were characterized by means of XRD, XPS and HRTEM techniques. The results of the investigation are useful information for future mechanistic investigations using the CEAS technique.

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