Mechanistic studies of CO_2/CH_4 reforming over Ni–La_2O_3/5A

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The mechanism of CO_2/CH_4 reforming over Ni–La_2O_3/5A has been studied. The results of the CO_2-pulsing experiments indicated that the amount of CO_2 converted was roughly proportional to the amount of H present on the catalyst, implying that CO_2 activation could be H-assisted. Pulsing CH_4 onto a H_2-reduced sample and a similar sample pretreated with CO_2, we found that CH_4 conversion was higher in the latter case. Hence, the idea of oxygen-assisted CH_4 dissociation is plausible. The fact that the amount of CO produced in 10 pulses of CO_2/CH_4 was larger than that produced in 5 pulses of CO_2 followed by 5 pulses of CH_4, indicated that CO_2 and CH_4 could activate each other synergistically. In the chemical trapping experiments, following the introduction of CD_3I onto a Ni–La_2O_3/5A sample pretreated with CH_4/CO_2, we observed CD_3COOH, CD_3CHO, and CD_3OCD_3. In the *in situ* DRIFT experiments, IR bands attributable to formate and formyl were observed under working conditions. These results indicate that formate and formyl are intermediates for syngas generation in CO_2/CH_4 reforming, and active O is generated in the breaking of a C–O bond. Based on these results, we suggest that during CO_2/CH_4 reforming, CO_2 activation is H-promoted and surface O species generated in CO_2 dissociation reacts with CH_x to give CO. A reaction scheme has been proposed.

Keywords: CO_2/CH_4 reforming reaction, molecular sieve, nickel catalyst, lanthanum oxide

1. Introduction

The catalytic reforming of CH_4 with CO_2 is industrially attractive because it yields syngas with H_2/CO ratio suitable for Fischer–Tropsch synthesis [1]. The conversion of CH_4 and CO_2 into fuels cannot by itself ameliorate the emission of greenhouse gases; the process, however, is environmentally friendly [2–5]. Supported Group VIII metals have been studied as catalysts for CO_2/CH_4 reforming. Compared to the precious metals, nickel is more economical to use as a catalyst. To generate a stable and active nickel catalyst for the reaction has been the goal of many researchers [6–8]. As far as the reaction mechanism is concerned, there are issues which are still under dispute [8–18]. It is generally accepted that both CH_4 and CO_2 adsorb dissociatively:

$$CH_{4,g} \rightarrow CH_{x,s} + (4-x)H_s \tag{1}$$

$$CO_{2,g} \rightarrow CO_s + O_s \tag{2}$$

Solymosi et al. [14–16] and Basini et al. [17] observed that the dissociation of CO_2 could be aided by hydrogen species present on the catalyst surface:

$$CO_{2,s} + H_s \rightarrow CO_s + OH_s \tag{3}$$

Solymosi et al. [14] reported that surface CH_x species could react with CO_2 to form CO:

$$CH_{x,s} + CO_2 \rightarrow 2CO_g + xH_s \tag{4}$$

However, Efslathiou et al. [18] found no evidence to support reaction steps (3) and (4).

In this paper, we report the performance of a new catalyst, viz. Ni–La_2O_3/5A. We used 5A molecular sieve as a support because of its great affinity to CO_2. It is known that lanthanum and nickel oxides react to form thermally stable perovskite-like La_2NiO_4. We envision that by using La_2NiO_4 as a precursor, the Ni^0 particles formed in hydrogen reduction would be well separated. For mechanistic investigation, we performed *in situ* DRIFT investigation as well as pulsing and chemical trapping experiments. A scheme has been proposed for the reaction.

2. Experimental

Ni–La_2O_3/5A catalyst was prepared by adopting the citric acid complexing method. We added 6.3 g of 5A molecular sieve to a mixed solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 M, 18.8 ml), $La(NO_3)_3 \cdot 6H_2O$ (0.5 M, 37.6 ml) and citric acid (6 g). The resultant gel was heated and stirred continually until a viscous syrup was formed. The residue was calcined in air at 500 °C for 4 h and then at 850 °C for 6 h. The Ni loading of the catalyst was 7.8 wt%. For performance testing, the catalyst was first reduced *in situ* at 500 °C in H_2 (20 ml min^{-1}) for 1 h.

The catalysts were tested in a fixed-bed continuous-flow quartz microreactor (i.d. = 4 mm) at atmospheric pressure. In each test, 50 mg of the catalyst was used. The flow rate of the reactant mixture (CO_2/CH_4 molar ratio = 1) was 40 ml min^{-1}. The effluents were analyzed on-line by a TCD gas chromatograph (Shimadzu-8A) with Spherocarb and Porapak Q columns. The CH_4 and CO_2 conversions

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were calculated according to the following formulas:

$$X_{CH_4} = \left(1 - \frac{2}{1 + R_{CO_2/CH_4} + R_{CO/CH_4}}\right) \times 100,$$

$$X_{CO_2} = \left(1 - \frac{2}{1 + R_{CH_4/CO_2} + R_{CO/CO_2}}\right) \times 100,$$

where $R_{i/j}$ is the molar ratio of i to j in the product.

The specific surface area was measured by the BET method on a NOVA-1200 instrument. Phase compositions of catalysts were determined by using a X-ray diffractometer (XRD, Rigaku D-MAX). The Ni particle size was estimated according to the width at half height of the Ni(111) peak obtained in XRD studies. CO chemisorption was performed on a pulse quartz reactor (i.d. = 4 mm) connected on-line with a mass spectrometer (HP G-1800A). The catalyst (50 mg) was pre-reduced by H_2 at 500 °C for 1 h, then cooled to room temperature in He for CO pulsing. The volume of each CO pulse was 67.5 μl. We kept on pulsing CO until there was no observable decrease in CO-pulse intensity after passing the catalyst. The total amount of CO adsorbed was estimated. The uptake of CO was then used to calculate Ni metal dispersion and particle size, assuming that each surface Ni site chemisorbs one CO molecule, i.e., $CO/Ni_{surface} = 1$.

For the pulsing experiments, 50 mg of the catalyst was placed in a quartz microreactor and was treated at 500 °C in a H_2 flow (10 ml min^{-1}) for 1 h, followed by heating to 600 °C in a flow of He (10 ml min^{-1}). Pulses (67.5 μl) of CO_2, CH_4 or CO_2/CH_4 (in 1/1 molar ratio) would then be pulsed into the system. The effluent gases were monitored on-line by a mass spectrometer (HP G-1800A). For the measurement of the CO signal, the contribution of the CO_2 fragment was subtracted and accounted for.

For the chemical trapping experiments, the H_2-reduced (20 ml min^{-1}, 600 °C, 1 h) sample was treated with CO_2/CH_4 (in 1/1 molar ratio) pulses until a steady state was reached. The sample was then kept in a flow of He (20 ml min^{-1}) and 10 μl CD_3I was introduced. The effluent products were analyzed on-line by mass spectrometry (HP G-1800A). The contributions due to isotopes and fragments were carefully eliminated for product identification.

A Nicolet Magna 550 FT-IR spectrometer was used for the DRIFT experiments. The catalyst sample was crushed to a particle size less than 100 mesh and fixed in the DRIFT cell (Spectra Tech.). The sample was purged with He (10 ml min^{-1}) and reduced in H_2 (10 ml min^{-1}) for 2 h at 600 °C, respectively, and a spectrum was recorded as background. Such a background would be subtracted from the spectra obtained in the experiments that followed.

3. Results and discussion

3.1. Catalytic performance

The catalytic performance over Ni–La_2O_3/5A versus reaction temperature is shown in table 1. At 600 °C, a significant amount of syngas was formed. With the increase in temperature, the conversions of CO_2 and CH_4 increased. At 800 °C, the CH_4 and CO_2 conversions were 92.1 and 79.7%, respectively. Considering the stoichiometric CH_4/CO_2 reforming reaction and unity molar ratio of reactant gases, the CH_4 and CO_2 conversions should be equal. However, this was not the case (table 1); the CH_4 and CO_2 conversions were not equal. At temperatures below 700 °C, CH_4 conversions were lower than that of CO_2, while at temperatures higher than 700 °C, it was the other way round. The difference in CH_4 and CO_2 conversions indicated that the main reaction was accompanied by several secondary processes. The higher CO_2 conversion could be due to the RWGS reaction (reverse water–gas shift reaction, i.e., $CO_2 + H_2 \rightarrow CO + H_2O$) as indicated by Bradford and Vannice in their review article [19]. Water was indeed detected in the reaction products. Chen and Ren [20] reported that CH_4 conversion was higher than CO_2 conversion over Ni/Al_2O_3 at 800 °C. Wang and Au [21] attributed such results to CO_2 complete dissociation, i.e., $CO_{2,s} \rightarrow CO_s + O_s$, $CO_s \rightarrow C_s + O_s$. The extent of CO_2 dissociation would be much larger at higher temperature. Kim et al. [22] have pointed out that the dissociative reduction of CO_2 would lead to the formation of CO or surface carbon and surface oxide. Since we detected no higher hydrocarbons such as ethane or ethene in the effluent, we deduce that CH_4 conversion was enhanced by the oxygen adspecies generated from CO_2 complete dissociation. Our recent ^{13}C results indicated that at 800 °C, most of the deposited carbon were from CO_2 in a CH_4/CO_2 reforming reaction over the Ni–La_2O_3/5A catalyst [23].

The stability of the Ni–La_2O_3/5A catalyst at 800 °C was investigated. The conversions of CH_4 and CO_2 decreased only moderately with time. Over a period of 48 h, CH_4 and CO_2 conversions decreased gradually from the initial values of 92.1 and 79.7%, respectively, to 80.2 and 75.0%. Under similar reaction conditions, a nickel catalyst using Al_2O_3, SiO_2, or CaO as support deteriorated much faster, possible due to the accumulation of carbon on the surface [6,24,25]. These results reveal that compared to Al_2O_3, SiO_2, and CaO, La_2O_3-5A is a better material to support nickel for CO_2/CH_4 reforming.

Table 1
The performance of Ni–La_2O_3/5A for the production of syngas in CO_2/CH_4 reforming.[a]

Temp.	Conv. (%)		TOF (s^{-1})			
(°C)	CH_4	CO_2	CH_4	CO_2	CO	H_2
600	29.02	30.31	1.88	1.96	3.84	3.02
650	42.61	44.33	2.76	2.87	5.63	4.83
700	63.25	59.02	4.09	3.82	7.91	7.15
750	80.71	72.86	5.22	4.71	9.94	9.24
800	92.12	79.74	5.96	5.16	11.12	10.44

[a] Reaction conditions: feedstock CH_4/CO_2 molar ratio = 1; GHSV = 48,000 ml h^{-1} g^{-1}.

3.2. Catalyst characterization

Figure 1 shows the phase compositions of Ni–La_2O_3/5A. There were La_2NiO_4 and 5A phases, but very little Al_2O_3 and SiO_2 phases in the fresh catalyst. After reduction in H_2 at 500 °C, nickel existed mainly as Ni^0 in Ni–La_2O_3/5A; the diameter of Ni^0 particles was estimated to be about 9 nm. Some physico-chemical properties of the catalyst are listed in table 2. It can be seen that the diameter of nickel particles estimated by CO chemisorption was 29 nm, about three times that (9 nm) estimated according to the Scherrer's equation. Over a 17 wt% Ni/La_2O_3 catalyst, Verykios et al. [24,25] observed that the nickel particle size (110–324 nm) deduced from H_2 and CO chemisorption was up to 3–10 times that (33 nm) estimated according to the XRD line broadening results. They attributed this to the decoration of the nickel particle by LaO_x originating from the La_2O_3 support. According to the XRD results, there was perovskite-like La_2NiO_4 in the fresh Ni–La_2O_3/5A catalyst. It is reasonable to speculate that during H_2-reduction, the aggregation of nickel atoms would be hindered by La_2O_3. Compared to the estimation of XRD results, the bigger size of nickel particles deduced from CO chemisorption might be due to the suppression of CO chemisorption [25], a result of the isolation effect of La_2O_3 on nickel particles in the Ni–La_2O_3/5A catalyst.

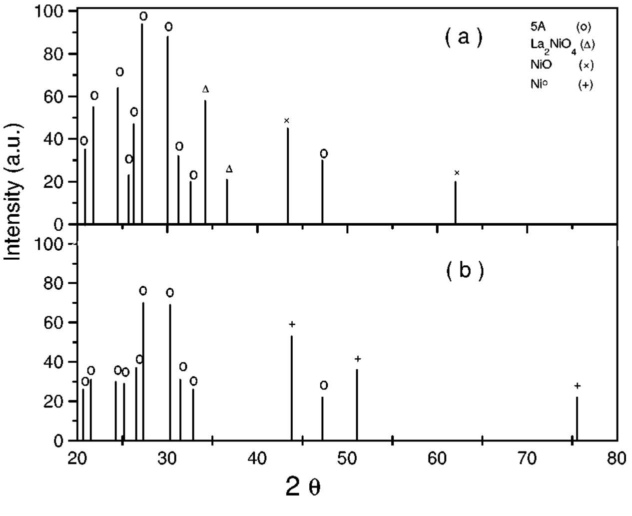

Figure 1. XRD patterns of Ni–La_2O_3/5A: (a) fresh and (b) after H_2 reduction at 500 °C for 1 h.

Table 2
Physico-chemical properties of the Ni–La_2O_3/5A catalyst.

Specific surface area (m^2/g)	CO uptake (μmol/g)	Ni dispersion (%)	Ni particle size (nm)	
			a	b
157	46	3.4	29	9

[a] Based on CO chemisorption data.
[b] Based on XRD results.

3.3. Pulse experiments

Tables 3 and 4 show the results of CH_4, CO_2, and CH_4/CO_2 pulsing experiments. The amount of CH_4 converted in 5 pulses of CH_4 at 600 °C over a H_2-reduced Ni–La_2O_3/5A sample was 1.3 μl (table 3) and there was no generation of C_2H_6, C_2H_4 or CO_x. It indicates that the carbon generated in CH_4 dissociation remained entirely on the catalyst. When CH_4 was pulsed onto a H_2-reduced sample pretreated with 5 pulses of CO_2 at 600 °C (table 4), CO was detected, indicating that there was interaction between CH_4 and the oxygen released in CO_2 dissociation. Taking into consideration that the amount of converted CH_4 (8.8 μl) over the CO_2-treated catalyst was much larger than that (1.3 μl) over the reduced catalyst, we propose that surface oxygen species such as O and OH promote the decomposition of CH_4. Similar trends were observed at 700 and 800 °C. Hence, we advocate the idea of oxygen-assisted CH_4 dissociation.

When CO was pulsed over a H_2-reduced Ni–La_2O_3/5A sample at or above 600 °C, we detected CO_2 and CH_4 in the effluent. The generation of CH_4 was due to CO methanation, a result of CO interaction with the hydrogen adsorbed during the reduction of the catalyst. We envisioned that the amount of CH_4 generated should be proportional to the amount of H species present. In order to vary the concentration of H adspecies, we purged the H_2-reduced sample with He for 10 min at 600, 700, and 800 °C, respectively. We then cooled the sample to 600 °C in He and pulsed CO onto the catalyst until there was no observable change in CO peak intensity. Table 5 shows the amount of CH_4 produced during CO pulsing. One can observe that with the rise in purging temperature, the amount of CH_4 generated decreased. Similarly, we observed that the amount of CO_2 consumption during CO_2 pulsing at 600 °C over the He-purged samples decreased with the rise in purging

Table 3
The amounts of converted CH_4 and CO_2 and that of CO generated in first 5 pulses of CH_4 followed by 5 pulses of CO_2 over a H_2-reduced Ni–La_2O_3/5A sample.

Temp.	CH_4 pulse		CO_2 pulse	
(°C)	CH_4 (μl)	CO (μl)	CO_2 (μl)	CO (μl)
600	1.3	0.0	13.0	14.0
700	67.5	0.0	101.2	114.8
800	113.4	4.2	303.8	336.8

Table 4
The amounts of converted CO_2 and CH_4 and that of CO generated in first 5 pulses of CO_2 followed by 5 pulses of CH_4 over a H_2-reduced Ni–La_2O_3/5A sample.

Temp.	CO_2 pulse		CH_4 pulse		CH_4/CO_2 pulse[a]
(°C)	CO_2 (μl)	CO (μl)	CH_4 (μl)	CO (μl)	CO (μl)
600	8.1	6.0	8.8	1.4	280
700	58.7	55.3	114.3	36.5	480
800	293.0	283.5	308.5	219.4	614

[a] Produced in 10 pulses of CO_2/CH_4 (molar ratio = 1/1).

Table 5
The amounts of CH_4 produced in CO-pulsing and that of CO_2 consumed in CO_2-pulsing at 600 °C over a H_2-reduced Ni–La_2O_3/5A sample He-purged at various temperatures.

	He purging temperature (°C)		
	600	700	800
Amount of CH_4 formed (μl)	4.7	2.7	0.5
Amount of CO_2 consumed (μl)	9.0	5.2	2.0

temperature. It was a clear indication that surface hydrogen promoted the dissociation of CO_2.

From table 2, it can be seen that the total amount of CO (7.4 μl) formed in the first 5 pulses of CO_2 and in the following 5 pulses of CH_4 was much smaller than that (280 μl) generated in 10 pulses of CO_2/CH_4 at 600 °C. Similar trends were obtained at 700 and 800 °C. Therefore, we suggest that CH_4 and CO_2 can activate each other mutually.

3.4. Chemical trapping experiments

The nature and fate of the reacting intermediates arising form CO_2 and CH_4 remain an open fundamental question for CH_4/CO_2 reforming [26]. Solymosi et al. [14–16] and Ross et al. [27] proposed that the dissociation of CO_2 could be aided by the hydrogen species generated in CH_4 decomposition. They gave no further explanation and reported no observation of intermediate species such as formate (HCOO) and formyl (HCO).

Adding an alkylation reagent to convert surface formyl or formate species into the corresponding aldehyde or carboxylic acid is a common method of chemical trapping. Methyl iodide, a highly effective methanation reagent, is widely used as a trapping agent. Following a pulse of CD_3I onto a catalyst at working conditions, CD_3COOH ($m/z = 63$), CD_3OCD_3 ($m/z = 52$), CD_3CHO ($m/z = 47$) as well as CD_4 ($m/z = 20$), DCO_2D ($m/z = 48$), and D_2CO ($m/z = 32$) were observed. Figure 2 shows the intensities of these molecules. When COOH, O, and CHO are trapped by CD_3 radicals, the expected products are CD_3COOH, CD_3OCD_3, and CD_3CHO, respectively; the products CD_4, DCO_2D, and D_2CO are less expected. It is apparent that the CD_3 radical generated in CD_3I dissociation could further decompose to give D which reacted with surface CD_3, CO_2, and CO to produce, respectively, CD_4, DCO_2D, and D_2CO. Although with much lower intensities, some isotopic H/D-exchanged formic acid ($m/z = 46$) and formaldehyde ($m/z = 30$) were also detected. The presence of CD_3COOH, CD_3OCD_3, and CD_3CHO implied that there were COOH, O, and CHO on the catalyst. In other words, COOH, CHO, and O are intermediates in CO_2/CH_4 reforming.

3.5. In situ DRIFT studies

3.5.1. Interaction of CO_2 with Ni–La_2O_3/5A

Figure 3 shows the DRIFT spectra obtained when CO_2 was passed over a H_2-reduced Ni–La_2O_3/5A catalyst at 600 °C. After 5 min (figure 3(a)), there were IR bands within the 1800 to 1300 cm^{-1} range; a small band was also observed at 2040 cm^{-1}. The bands stretching from 1800 to 1300 cm^{-1} are likely to be due to signals of surface carbonate species [27,28]. The weak band at 2040 cm^{-1} is attributable to linearly adsorbed CO [12,28]. This weak band disappeared after 10 min of CO_2 exposure (figure 3(b)). The observation of the CO band is a clear evidence for CO_2 dissociation. The disappearance of surface CO after prolonged CO_2 exposure may be linked to the oxidation of Ni^0 by the oxygen generated in CO_2 dissociation. With the increase in surface oxygen concentration, CO existence became unfavorable.

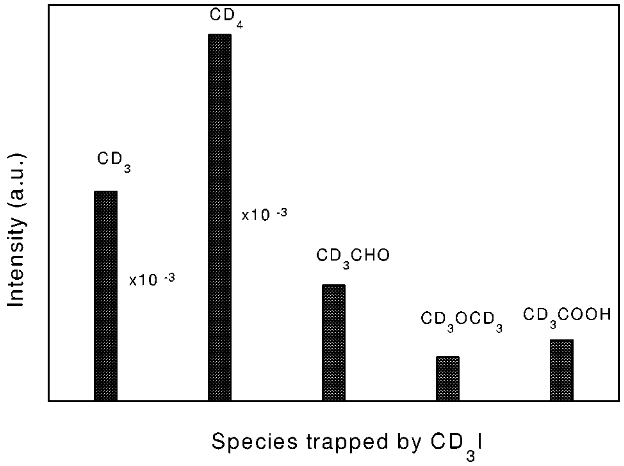

Figure 2. Patterns of CHO, O, and COOH trapped by CD_3I over Ni–La_2O_3/5A. For comparison, the patterns of CD_3 and CD_4 are also shown.

3.5.2. Interaction of CO_2/CH_4 on Ni–La_2O_3/5A

The IR spectrum recorded after keeping the Ni–La_2O_3/5A sample in a flow of CO_2/CH_4 for 10 min at 600 °C is shown in figure 4; spectra obtained at various intervals between 5 and 60 min are rather similar to this one. The narrow bands at 3016 and 1304 cm^{-1} are due to gaseous CH_4 and the weak ones at 2170 and 2110 cm^{-1} are due to the gaseous CO generated in CO_2/CH_4 reforming. The band at 2040 cm^{-1} can be assigned to linearly adsorbed CO; the intensity of this band is much greater than that obtained in the CO_2 adsorption experiments (figure 3(a)). The results indicate that as more surface oxygen was consumed by the carbon species generated from CH_4, more CO could be retained on the surface.

We also observed that within the 60 min of reaction time, the intensities of the two bands centered at 2918 and 2844 cm^{-1} were rather constant. For better assignment of these bands, we introduced formic acid and formaldehyde, respectively, onto a Ni–La_2O_3/5A sample freshly H_2-reduced at 600 °C. In both cases, bands were observed at similar positions. It should be noted that due to the overlapping of bands in the carbonate region (1300–1800 cm^{-1}), it is difficult to make unequivocal assignment of the bands. We tentatively attribute the IR signals at 2918 and 2844 cm^{-1} to C–H asymmetric and symmetric

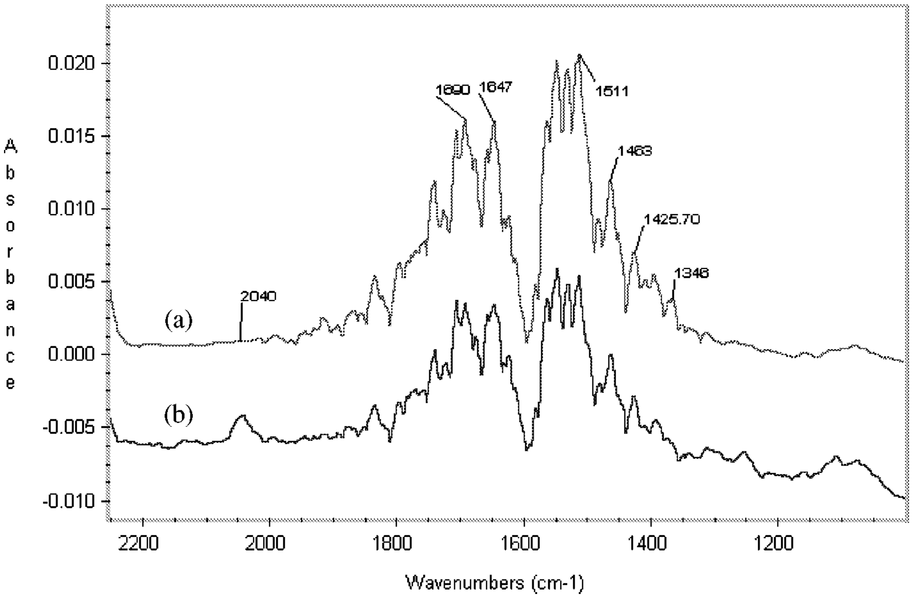

Figure 3. IR spectra of a H_2-reduced Ni–La_2O_3/5A sample exposed to CO_2 at 600 °C for (a) 5 and (b) 10 min.

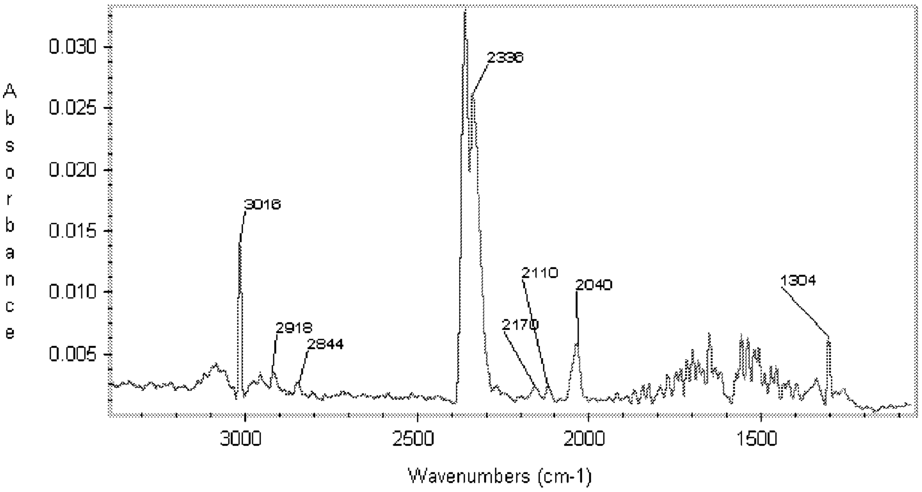

Figure 4. IR spectrum of a H_2-reduced Ni–La_2O_3/5A sample exposed to a flow of CO_2/CH_4 (1 : 1 in molar) for 10 min at 600 °C.

vibrations of formate and formyl. Such an assignment is in accord with that of [29]. As both HCOO and HCO were detected in the CD_3I-trapping experiments, we suggest that both formate and formyl were formed on the surface. The results indicate that the H species generated in CH_4 decomposition could react with CO_2. In other words, the dissociation of CO_2 over Ni–La_2O_3/5A was H-assisted. In the IR studies of CO_2/CH_4 reforming, bands attributable to surface formate and formyl were not detected over Ni/La_2O_3 [24,25] and Pt/TiO_2 [23], while over Ni/Al_2O_3 [24,25] and Rh/TiO_2 [19], they were detected. It is apparent that the presence of formate or formyl is closely related to the nature of the catalyst. The La_2O_3-5A support in the Ni–La_2O_3/5A catalyst exhibited large specific surface area (158 $m^2\,g^{-1}$) and good affinity to CO_2. These are favorable factors for the production of surface formate and formyl species.

3.6. A model for reaction mechanism

Based on the above results, we propose a model for the CO_2/CH_4 reforming reaction. As suggested by Osaki et al. [11] and Bradford et al. [12,19], CH_4 could first adsorb on Ni^0 and dissociate to give CH_x ($x = 0$–3) species. In the reaction scheme, we suggest that there are CH_x and H on the surface. The adsorbed CO_2 reacts with H to form HCOO which decomposes to give HCO and O. Syngas formation is a result of both HCO decomposition and CH_x interaction with O. The reaction steps are:

$$CH_{4,g} \rightarrow CH_{4,s} \tag{5}$$

$$CO_{2,g} \rightarrow CO_{2,s} \tag{6}$$

$$CH_{4,s} \rightarrow CH_{x,s} + (4 - x)H_s \tag{7}$$

$$CO_{2,s} + H_s \rightarrow HCOO_s \tag{8}$$

$$HCOO_s \rightarrow HCO_s + O_s \tag{9}$$

$$HCO_s \rightarrow CO_s + H_s \tag{10}$$

$$CH_{x,s} + O_s \rightarrow CO_s + xH_s \tag{11}$$

$$2H_s \rightarrow H_{2,g} \tag{12}$$

$$CO_s \rightarrow CO_g \tag{13}$$

(s: surface, g: gas phase).

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