

Articles

Kinetic Investigation of CO₂-CH₄ Reaction over Ni/La₂O₃ Catalyst using Photoacoustic Spectroscopy

Hyun-Jin Oh, Jin-Gyu Kang, Eil Heo,[†] Sung-Han Lee,^{†,*} and Joong-Gill Choi^{*}

Department of Chemistry, Yonsei University, Seoul 120-749, Korea. *E-mail: jgchoi@yonsei.ac.kr

[†]Department of Chemistry, Yonsei University, Wonju 220-710, Korea. *E-mail: shl2238@yonsei.ac.kr

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Ni/La₂O₃ with a high dispersion was prepared by reduction of LaNiO₃ perovskite oxide to examine the catalytic activity for the CO₂-CH₄ reaction. The Ni/La₂O₃ catalyst was found to be highly active for the reaction. The ratios of H₂/CO were measured in a flow of the reaction mixture containing CO₂/CH₄/Ar using an on-line gas chromatography system operated at 1 atm and found to be varied with temperature between 0.66 and 1 in the temperature range of 500-800 °C. A kinetic study of the catalytic reaction was performed in a static reactor at 40 Torr total pressure of CO₂/CH₄/N₂ by using a photoacoustic spectroscopy technique. The CO₂ photoacoustic signal varying with the concentration of CO₂ during the catalytic reaction was recorded as a function of time. Rates of CO₂ disappearance in the temperature range of 550-700 °C were obtained from the changes in the CO₂ photoacoustic signal at early reaction stage. The plot of ln rate vs. 1/T showed linear lines below and above 610 °C. Apparent activation energies were determined to be 10.4 kcal/mol in the temperature range of 550-610 °C and 14.6 kcal/mol in the temperature range of 610-700 °C. From the initial rates measured at 640 °C under various partial pressures of CO₂ and CH₄, the reaction orders were determined to be 0.43 with respect to CO₂ and 0.33 with respect to CH₄. The kinetic results were compared with those reported previously and used to infer a reaction mechanism for the Ni/La₂O₃-catalyzed CO₂-CH₄ reaction.

Key Words : Kinetic study, CO₂ reforming of CH₄, Ni/La₂O₃ catalyst, Photoacoustic spectroscopy

Introduction

The CO₂ reforming of CH₄, CO₂ + CH₄ → 2CO + 2H₂, has received of great attention because it converts green house gases into a synthesis gas. This reaction produces a synthesis gas with a H₂/CO molar ratio close to 1, which is suitable for the production of oxygenated hydrocarbons like methanol and aldehyde. Nickel has been proven to be one of the active catalysts for the CO₂ reforming of CH₄. A major problem of a nickel catalyst is to deposit carbon species on the surface during the reaction, resulting in the deactivation of catalyst. It has been reported that the tendency of the carbon deposition is closely related to the type of a support used and the dispersion and size of nickel particles on support.^{1,2} To develop a coke-resistant nickel catalyst various metal oxides have been examined as the support of the Ni catalyst. Lanthanum sesquioxide as a support of a nickel catalyst is known to be a particularly effective component in reducing the carbon deposition.^{3,4} It has been reported that La₂O₃ can suppress the carbon deposition on the surface and the aggregation of nickel crystallites during the reforming reaction, leading to the enhancement of the catalyst stability.⁵⁻⁸

Supported metal catalysts are generally prepared by the conventional impregnation method. However, this method often fails to reproduce the catalyst and may give rise to the

poor dispersion of metal particles on the support. One promising method for the preparation of well-dispersed nickel particles has been proposed by Takehira group,^{9,10} called "solid phase crystallization method". In this method, metal-containing complex oxides are utilized as metal precursors. In recent, well-dispersed nickel particles on La₂O₃ have been successfully prepared by using LaNiO₃ or La₂NiO₄ perovskite oxide as a starting material and the resulting Ni/La₂O₃ catalyst has been proved to be highly active and stable in the reforming reaction.^{4,11}

Catalytic performances of Ni/La₂O₃ for the reforming reaction have been largely studied.¹²⁻¹⁴ However, little kinetic data for the catalytic reaction have been reported so far.^{8,15} Although empirical kinetic data do not directly provide the accurate information of the reaction mechanism, kinetic information about the catalytic reaction is essential to understand the reaction mechanism. The most important consideration in the kinetic study is to monitor the concentration of reactants and/or products of interest as a function of time. We have shown previously that photoacoustic spectroscopy (PAS) is a suitable technique for *in situ* monitoring of the initial stage reaction processes.^{16,17} Since the PAS technique provides highly selective detection and extremely low molecular gas level detection, the signals with enough intensity can be obtained for even time-resolved experiments.^{18,19}

The photoacoustic signals are directly related to the concentration of samples of interest, which allows this method to measure a temporal variation in concentration at short period of reaction times where rates are high.

In this work, LaNiO₃ perovskite-type oxide was synthesized by a citrate sol-gel method. The oxide was reduced in a flow of H₂ to form nickel metal particles dispersed on lanthanum oxide particles, so that the resulting product was examined as a catalyst for the CO₂ reforming of CH₄. A CO₂ laser-based photoacoustic technique with a differential photoacoustic cell was employed to analyze kinetically the CO₂-CH₄ reaction over Ni/La₂O₃ catalyst. The photoacoustic experiments were performed using a static reactor in the temperature range of 550-700 °C at various partial pressures of CO₂ and CH₄. The changes in the concentration of CO₂ during the catalytic reaction were measured as a function of time. Rates of CO₂ consumption in early reaction stage were obtained from the CO₂ photoacoustic data. The apparent activation energy and reaction orders were determined from the initial rates of CO₂ consumption. The conversion of reactants and the ratio of H₂/CO were also measured in a flow reactor in the temperature range of 500-800 °C using an on-line gas chromatography system. The kinetic data obtained in this work were compared with others reported previously. A reaction mechanism of the CO₂-CH₄ reaction over the Ni/La₂O₃ catalyst was then discussed from the kinetic results.

Experimental

Catalyst Preparation. LaNiO₃ perovskite-type oxide was prepared from La(NO₃)₃·6H₂O (> 99.99%, Aldrich-Sigma) and Ni(NO₃)₂·6H₂O (> 99.99%, Aldrich-Sigma). Both the lanthanum nitrate and nickel nitrate were weighed to yield the desired mole ratio of La/Ni and were then dissolved in deionized water. The resulting solution was mixed with an aqueous solution of citric acid to have the same amount of equivalents. Water was slowly evaporated from the mixed solution at 70 °C in vacuum until a viscous gel was formed. The viscous gel was kept at 100 °C overnight to produce a solid amorphous mixture. The resultant amorphous mixture was ground and calcined at 400 °C. Further calcination was made at 600 °C to eliminate carbon species remaining in the sample and then cooled to room temperature at 60 °C/h rate. The product was reduced in a flow of H₂ at 700 °C for 3 h and further heated at 700 °C for 1 h in a flow of He, which was followed by cooling to room temperature and ground in an agate mortar. These processes were then repeated three times to form nickel metal particles. X-ray powder diffraction analyses for the samples were conducted by using a Bruker D2 Phaser diffractometer with Cu-K_α radiation at room temperature. EDX (energy dispersive X-ray) analyses were performed for the LaNiO₃ perovskite oxide using an Oxford Link ISIS 300 spectrometer. FE-SEM (Field emission-scanning electron micrograph) images of catalyst were obtained with a Hitachi SU70.

Kinetic Measurements. The catalytic reaction rate in the

reforming reaction was measured by using the CO₂ laser-based photoacoustic technique. The experimental arrangement for the photoacoustic detection method was described in previous paper.^{17,19} The catalytic reaction was carried out in a closed-circulating reactor system, where the reactor was made of a quartz tubing with a volume of 21 cm³. The reactor was placed in an electric furnace and directly connected to a differential photoacoustic cell by an adjoining tube. The differential photoacoustic cell consisted of a sample cell and a reference cell, separated from each other by a ZnSe window. Each photoacoustic cell was a Helmholtz resonator of 1.9 cm in diameter and 3.3 cm in length with an adjoining tube of 1.1 cm in diameter and 2.8 cm in length, where microphones were located at the ends of the adjoining tubes. The output beam of a cw CO₂ laser (Synrad Series 48-1-28) operating in multilines of 10.6 μm was modulated at the nonresonance condition of 25 Hz. The signals were detected by the microphones in both the sample (signal A) and reference (signal B) cells and amplified by a lock-in amplifier (EG & G Princeton Applied Research Model 5210). The signal ratio (A/B) was then recorded as a function of time by using a personal computer. The total pressure of gaseous reactants in the reactor was maintained at 40 Torr filled with N₂ as a buffer gas. The reference cell (signal B) was filled with a mixture of CO₂ (0.2 Torr) and N₂ (39.8 Torr) and the sample cell (signal A) was connected to the reactor loaded with the catalyst (200 mg). The gaseous reaction mixture (CO₂/CH₄/N₂) was introduced into the reactor at a given temperature. The purity of gases was greater than 99.99% and the gases were dehydrated with suitable filters.

Conversions of reactants and ratio of H₂/CO in the CO₂-CH₄ reaction over the Ni/La₂O₃ catalyst were measured in a fixed-bed type flow reactor in the temperature range of 500-800 °C at atmospheric pressure. The reactor was quartz tubing with a 0.8-cm-i.d. and 3-cm-long tube sealed to 0.4-cm-i.d. tubes on two ends. The catalyst (200 mg) was well dispersed on a fused-silica bed placed in the middle of the reactor which was kept in an electric furnace. The feed flow rate at ambient conditions was 5/5/20 cm³/min (CH₄/CO₂/Ar) and the flow rates of gases were controlled by electronic mass flow controllers. The gaseous reactants and products were analyzed by using an on-line gas chromatography with a thermal conductivity detector. A cold trap was placed at the reactor exit to remove water vapor from the gaseous mixture. CH₄, CO₂, and CO gases were analyzed by a gas chromatography using He carrier gas and H₂ gas was separately analyzed by a gas chromatography using Ar carrier gas. The CO₂ and CH₄ conversions were calculated on the basis of the formula; conversion (%) = 100 × [F_{in} - F_{out}]/F_{in}, where F_{in} and F_{out} were inlet and outlet flow rate of each reactant, respectively. The conversions were typically compared at 0.5 h time-on-stream.

Results and Discussion

The XRD pattern of the LaNiO₃ sample synthesized by the citrate sol-gel method is displayed in Figure 1(a). The

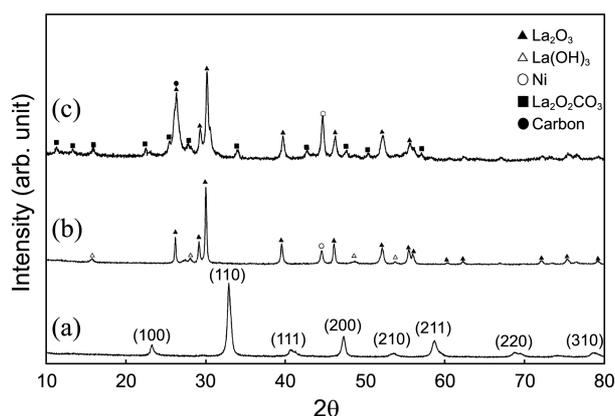


Figure 1. XRD patterns of (a) LaNiO₃ prepared by citrate sol-gel method, (b) Ni/La₂O₃ catalyst obtained by reduction of LaNiO₃, and (c) Ni/La₂O₃ catalyst after activity test at 700 °C.

LaNiO₃ was found to be monophasic perovskite-type oxide possessing a rhombohedra structure (JCPDF 33-0711). Ni/La atomic ratio in LaNiO₃ was determined to be 1.02 from the K-lines obtained by EDX analysis. The XRD pattern of the H₂-reduced LaNiO₃ is shown in Figure 1(b), in which La₂O₃ (JCPDF 5-0562) and Ni metal with (111) preferential plane of a cubic structure (JCPDF 87-0712) are observed as a major phase and La(OH)₃ (JCPDF 36-1481) as a minor phase. This result indicates that the LaNiO₃ oxide is completely decomposed into La₂O₃ and Ni⁰ under the reducing conditions. Accordingly, the H₂-reduced LaNiO₃ sample corresponds to 26.5 wt % Ni/La₂O₃. Figure 1(c) shows the XRD pattern of the Ni/La₂O₃ catalyst after the activity test for the reforming reaction at 700 °C in a flow reactor, which reveals the presence of carbon solid (JCPDF 75-1621) and La₂O₂CO₃ (JCPDF 37-0804 and 48-1113) phases. A FE-SEM image of the Ni/La₂O₃ catalyst is displayed in Figure 2, showing well-dispersed nickel metal crystallites and lanthanum oxide particles.

The rates of the CO₂ consumption in early reaction stage for the reforming reaction were measured by the CO₂ laser-based photoacoustic technique. As mentioned above, the PAS technique is applicable to the quantitative analysis by

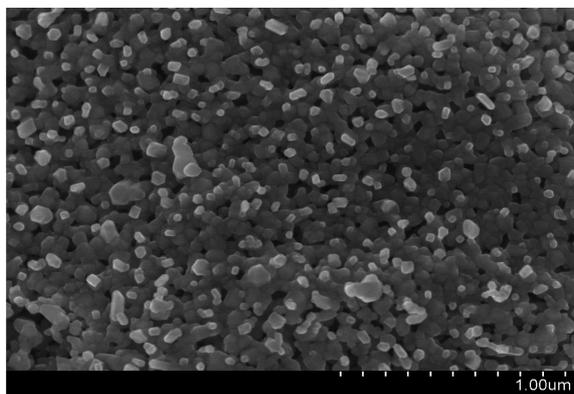


Figure 2. FE-SEM image of Ni/La₂O₃ sample obtained by reduction of LaNiO₃.

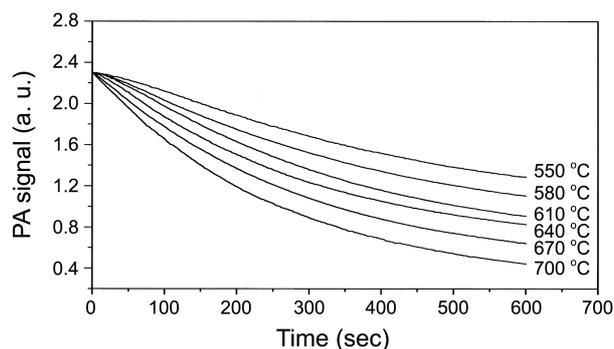


Figure 3. Variations of CO₂ photoacoustic signal with time at various temperatures for CO₂-CH₄ reaction over Ni/La₂O₃ catalyst: CO₂/CH₄/N₂ = 7/7/26 in Torr, catalyst weight = 200 mg.

monitoring the progress of the reaction because the photoacoustic signal is directly proportional to the concentration of reaction analytes under a given conditions. The CO₂ photoacoustic signal was found to show an optimal linearity and response of the signal under conditions of CO₂ laser power ranging of 1-8 W and CO₂ partial pressures below 10 Torr. Accordingly, the PAS measurements were conducted under CO₂ partial pressure below 10 Torr at a CO₂ laser power of 1.5 W. A blank test, performed with a CO₂/CH₄/N₂ (5/5/30 in Torr) mixture in the absence of catalyst, showed no variations of the CO₂ photoacoustic signal in the temperature range of 550-700 °C. Thus, the effect of temperature on the rate of CO₂ consumption for the CO₂-CH₄ reaction over the Ni/La₂O₃ was investigated using CO₂/CH₄/N₂ (5/5/30 in Torr) mixture in the temperature range of 550-700 °C. In Figure 3 is displayed the variations of the CO₂ photoacoustic signal with time for the reforming reaction at various temperatures. As observed in Figure 3, the CO₂ photoacoustic signals gradually decrease with time in the reaction period up to 600 s. The rates of the CO₂ consumption were estimated from the photoacoustic signal data in the early reaction period of 0-50 s. The rates were then plotted as a function of reciprocal temperature according to the Arrhenius-type equation. As displayed in Figure 4, the curve shows linear lines below and above 610 °C. The apparent activation energies for the CO₂ consumption, calculated from the slope of each curve, were 10.4 kcal/mol for the low temperature

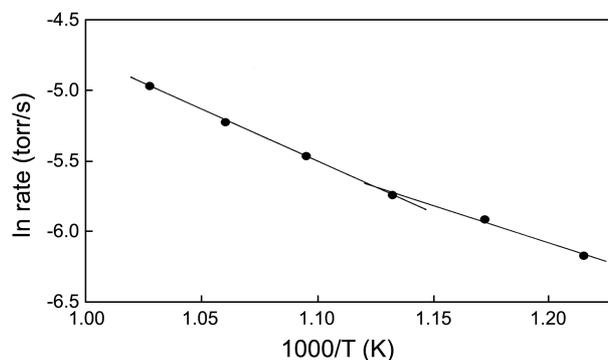


Figure 4. Influence of temperature on rate of CO₂ disappearance for CO₂-CH₄ reaction over Ni/La₂O₃ catalyst: CO₂/CH₄/N₂ = 7/7/26 in Torr, catalyst weight = 200 mg.

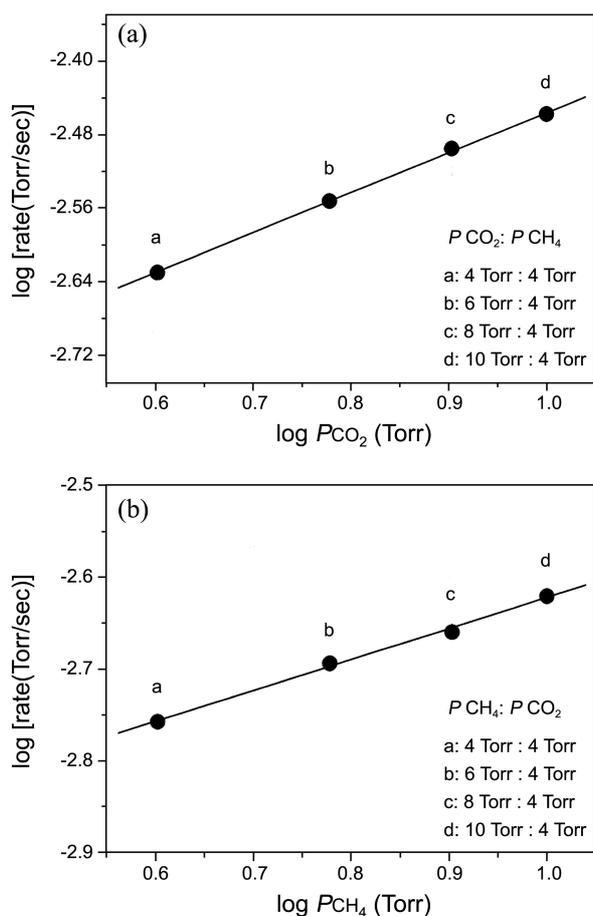


Figure 5. (a) P_{CO_2} dependence and (b) P_{CH_4} dependence of CO_2 disappearance rate at 640 °C for CO_2 - CH_4 reaction over $\text{Ni}/\text{La}_2\text{O}_3$ catalyst.

region (550-610 °C) and 14.6 kcal/mol for the high temperature region (610-700 °C). To investigate the pressure dependence of the CO_2 consumption rate for the reforming reaction, the CO_2 photoacoustic signals were recorded under various partial pressures of CO_2 and CH_4 , P_{CO_2} and P_{CH_4} , at 640 °C. The initial rates obtained from the CO_2 photoacoustic data were plotted as a function of P_{CO_2} and P_{CH_4} , respectively, according to the power rate law, $\text{rate} = k(P_{\text{CO}_2})^m(P_{\text{CH}_4})^n$. Figure 5 shows the P_{CO_2} and P_{CH_4} dependences of the rate of CO_2 consumption for the reforming reaction. The reaction orders, determined from the slope of the curves, were 0.43 with respect to CO_2 and 0.33 with respect to CH_4 .

Figure 6 shows the variations of conversions and the ratio of H_2/CO with temperatures for the CO_2 - CH_4 reaction over $\text{Ni}/\text{La}_2\text{O}_3$ catalyst in the temperature range of 500-800 °C, which was measured in a flow of $\text{CH}_4/\text{CO}_2/\text{Ar}$ (5/5/20 cm^3/min) mixture at 1 atm. As shown in Figure 6, the CO_2 conversion is nearly equal to the CH_4 conversion below 550 °C, but in the temperature range of 600-750 °C the CO_2 conversion is somewhat lower than the CH_4 conversion. Note that at 800 °C both the conversions reach to almost 100%. The ratios of H_2/CO were found to vary with temperature between 0.66 and 1.0; less than 1 at 500 °C and 550 °C, close to 1 at 600 °C and 650 °C, and less than 1 above

700 °C.

Because only limited kinetic data for the rates of the CO_2 consumption have been reported previously, it is difficult to compare the present data directly with others. According to the kinetic results reported previously for the nickel-catalyzed CO_2 - CH_4 reaction,²⁰ the apparent activation energies for the CO_2 consumption, varying with the supports used, are in the range of 8-22 kcal/mol, noting that our values fall in the range. Tsipouriari and Vergyios¹⁵ measured the rates of the CO formation for the CO_2 - CH_4 reaction over 17 wt % $\text{Ni}/\text{La}_2\text{O}_3$ catalyst in a flow reactor in the temperature range of 650-750 °C. They determined the apparent activation energy to be 13.2 kcal/mol of which value is close to the one in the present experiment, 14.6 kcal/mol, obtained in the temperature range of 610-700 °C. In the previous work,¹⁶ we performed kinetic studies of the reforming reactions over Ni/TiO_2 and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts using a PAS technique. From the CO_2 consumption rates measured in the temperature range of 400-650 °C, the apparent activation energies were determined to be 14.3 kcal/mol for Ni/TiO_2 catalyst and 15.4 kcal/mol for $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. These values are close to 14.6 kcal/mol obtained in the temperature range of 610-700 °C in this work. Figure 5 shows that the CO_2 consumption rate depends on the P_{CO_2} and P_{CH_4} , in which the reaction order to CO_2 , 0.43, is somewhat higher than the reaction order to CH_4 , 0.33. The reaction orders are also difficult to compare directly with others because partial orders determined from the CO_2 consumption rates for the $\text{Ni}/\text{La}_2\text{O}_3$ -catalyzed reforming reaction have not been reported. According to Tsipouriari and Vergyios,¹⁵ the rate of the CH_4 consumption for the CO_2 - CH_4 reaction over $\text{Ni}/\text{La}_2\text{O}_3$ catalyst in the temperature range of 650-750 °C is more sensitive to P_{CO_2} than to P_{CH_4} at low partial pressures below 75 Torr, which is considered to be in agreement with our results.

The CO_2 - CH_4 reforming reaction is highly endothermic and is favored by low pressure and high temperature. Various reaction models for the reforming reaction have been suggested during the last twenty years. Although there are some disagreements in the reaction mechanism, it is generally accepted that both CH_4 and CO_2 are dissociatively chemisorbed on nickel metal surface. Erdöhelyi *et al.*²¹ and Rostrup-Nielson *et al.*²² have suggested that methane is dissociatively adsorbed on nickel surface, $\text{CH}_4(\text{g}) \rightleftharpoons \text{CH}_x(\text{ads}) + (4-x)\text{H}(\text{ads})$, and the CO_2 dissociation can be promoted by the $\text{H}(\text{ads})$. Bradford and Vannice²⁰ have proposed that surface $\text{CH}_x(\text{ads})$ fragments react with either oxygen atoms or hydroxyl groups to form a formate-type CH_xO intermediate which subsequently decomposes into CO and H_2 products. Zhang *et al.*²³ have suggested from the FT-IR and XPS results for $\text{Ni}/\text{La}_2\text{O}_3$ -catalyzed CO_2 - CH_4 reaction at 750 °C that a formate-type HCOO^- intermediate is initially formed and subsequently reacts with $\text{H}^+(\text{ads})$ to yield H_2O and CO .

If formate-type species are intermediates in the reaction mechanism, the rate of the CO_2 consumption should be closely related to the adsorption of CH_4 on the surface.^{22,23} As is observed in the current study, the CO_2 consumption

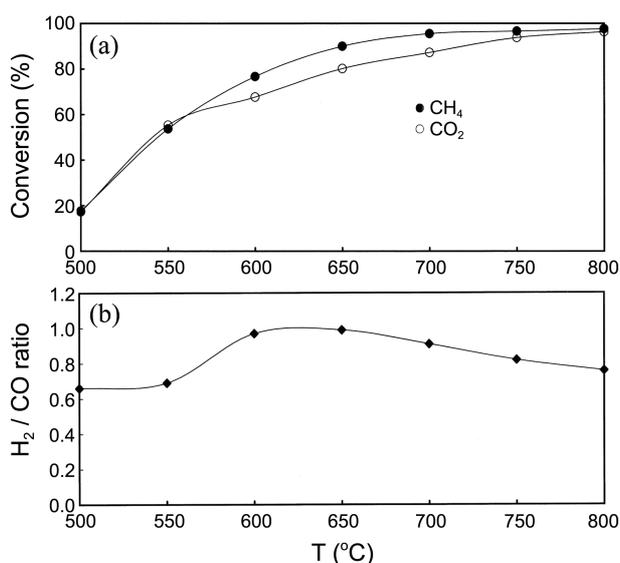


Figure 6. (a) Conversions and (b) ratio of H₂/CO at various temperatures for CO₂-CH₄ reaction over Ni/La₂O₃ catalyst: CO₂/CH₄/Ar = 5/5/20 cm³/min, catalyst weight = 200 mg.

rate is dependent on the P_{CH_4} . In order to form formate-type intermediates, oxygen atoms must be provided from CO₂ acting as a potential oxidant. It is well known that CO₂ participates in the reaction mechanism through the reverse water-gas shift reaction to form surface OH groups which react with CH_x(ads) to form formate-type intermediates.¹⁵ Note that the reverse water-gas shift reaction, $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$, occurs below 820 °C. If the reverse water-gas shift reaction is favorable as a side reaction, the ratio of H₂/CO would be lower than 1. In Figure 6, the H₂/CO ratios at 500 and 550 °C, measured in a flow reactor with CH₄/CO₂/Ar mixture (5/5/20 cm³/min), are lower than 1, where the CO₂ conversion is nearly equal to the CH₄ conversion. This result suggests the occurrence of the reverse water-gas shift reaction as a side reaction at these temperatures.

On the other hand, the H₂/CO ratios measured at 600 and 650 °C are close to 1, where the conversion of CO₂ is lower than CH₄ as shown in Figure 6. The result implies that other side reactions may occur at the temperatures. Under the conditions of stoichiometric CO₂-CH₄ reaction, both the CO disproportionation ($2\text{CO}(\text{g}) \rightarrow \text{C}(\text{s}) + \text{CO}_2(\text{g})$) and the methane cracking ($\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 2\text{H}_2(\text{g})$) can be considered as side reactions. From the viewpoint of thermochemistry, the CO disproportionation occurs below 700 °C at 1 atm and the methane cracking occurs above 560 °C at 1 atm. When both the reactions as side reactions favorably occur in the temperature range of 600–650 °C, the CO₂ conversion would be lower than the CH₄ conversion and then the H₂/CO ratios would increase with temperature. As observed in Figure 6, the H₂/CO ratios at 600 °C and 650 °C are greater than those below 550 °C. Both the CO disproportionation and the methane cracking produce carbon species, which can give rise to the catalytic deactivation. In Figure 1, the XRD pattern of the Ni/La₂O₃ catalyst after the activity test at 700 °C exhibits the presence of carbon phase, indicating that carbon is

deposited during the reforming reaction. The CO disproportionation reaction is exothermic ($\Delta H^\circ = -41.2$ kcal/mol), while the methane cracking is endothermic ($\Delta H^\circ = +17.9$ kcal/mol). Accordingly, it is expected that the methane cracking is more favorable at higher temperatures. When the methane cracking occurs favorably at higher temperatures, the catalyst would be rapidly deactivated by the carbon deposition during the reforming reaction.

Carbon species deposited on the surface of Ni catalyst, which can serve as intermediates in the reforming reaction, are known to be highly reactive.^{24,25} The surface carbon can readily react with H₂O(g) and CO₂(g) to form H₂, CO, and CO₂ according to the following processes; $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$, $\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2(\text{g})$, $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$. These reactions, called the gasification of carbon solid, can occur above 700 °C at 1 atm and can be promoted by nickel.^{26,27} In Figure 6, the H₂/CO ratio is found to be less than 1 above 700 °C and decreases with increasing temperature. This suggests that the CO₂ gasification of carbon solid may be more favorable. The CO₂ consumption in the side reaction, $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$, would give rise to larger change in the total CO₂ photoacoustic signal during the reforming reaction, resulting in the observation of higher apparent activation energy for the CO₂ consumption. It is also notable that the C(s)-CO₂(g) reaction is expected to be more favorable at lower pressures. As shown in Figure 4, the apparent activation energy obtained for the high temperature region, 14.6 kcal/mol, is higher than that for the low temperature region, 10.4 kcal/mol, which is enable us to consider that the C(s)-CO₂(g) reaction occurs at high temperatures.

La₂O₃ oxide is known to be strongly basic and it is easily hydrated and carbonated when it is exposed to air.²⁸ In Figure 3, the XRD pattern of the Ni/La₂O₃ catalyst after the activity test at 700 °C shows the presence of lanthanum dioxycarbonate, indicating that La₂O₃ is carbonated to La₂O₂CO₃ phase during the reforming reaction. When La₂O₃ is exposed to a mixture of water vapor and CO₂, La₂(OH)₄CO₃ phase is formed and subsequently decomposes to La₂O₂CO₃ around 460 °C, which have been also identified as intermediate phases in the decomposition of lanthanum carbonate.²⁸ Since La₂O₂CO₃ phase decomposes around 630 °C at 1 atm, La₂O₃ support is expected to be carbonated at surface levels during the reforming reaction at temperatures above 630 °C. The carbonation of La₂O₃ by CO₂(g) can be represented as $\text{La}_2\text{O}_3 + \text{CO}_2(\text{g}) \rightleftharpoons \text{La}_2\text{O}_2\text{CO}_3$ or $\text{La}_2\text{O}_3 \cdot (\text{CO}_2)_{\text{ads}}$, which means that there is an equilibrium between CO₂(g) and CO₂(ads). Rivas *et al.*¹¹ and Zhang *et al.*²⁹ have suggested that La₂O₂CO₃ species at the interfacial area react with the carbon species deposited on the surface of nickel particles to produce two CO molecules. This indicates that the La₂O₂CO₃ phase can play a major role in the catalytic stability. The carbon species can react with CO₂ molecules adsorbed on La₂O₃ or released from La₂O₂CO₃ to produce CO. It is shown in Figure 6 that the H₂/CO ratio decreases with temperature above 700 °C. When the reaction between carbon and CO₂(g)/or CO₂(ads) favorably occurs during the reforming reaction, the ratio of

H₂/CO would be lower than 1. In the early work of Ni/Al₂O₃- and Ni/TiO₂-promoted CO₂-CH₄ reactions,¹⁶ the reaction orders determined from initial rates of the CO₂ consumption at 600 °C were found to be 0.48 for CH₄ and 0.45 for CO₂ for the Ni/Al₂O₃-promoted process, and 0.38 for CH₄ and 0.32 for CO₂ for the Ni/TiO₂-promoted process. This indicates that the reaction orders to CH₄ are somewhat higher than to CO₂. However, the dependence of the CO₂ consumption rate to CO₂, determined from initial rates of the CO₂ consumption at 640 °C in this work, was observed to be somewhat higher than that to CH₄. This result is considered to be due to the C(s)-CO₂(g) reaction (the reverse Boudouard reaction).

Conclusion

In this work, well-dispersed Ni/La₂O₃ catalyst was prepared by the reduction of perovskite-type LaNiO₃ and examined for the CO₂ reforming of CH₄. The CH₄ and CO₂ conversions measured in a flow reactor under atmospheric pressure showed the catalyst to be highly active for the reaction. The catalytic reaction was kinetically investigated in the temperature range of 550-700 °C at various partial pressures of CO₂ and CH₄ (40 Torr total pressure of CO₂/CH₄/N₂) in a static reactor system with the differential photoacoustic cell. Rates of CO₂ disappearance were obtained by *in situ* monitoring the concentration changes of CO₂ during the catalytic reaction. The apparent activation energy and the reaction orders were determined from the rates of the CO₂ disappearance in the early reaction stage. A reaction mechanism for the Ni/La₂O₃-catalyzed CO₂-CH₄ reaction could be deduced from the kinetic results in conjunction with the catalytic data obtained in a flow reactor. The kinetic data obtained for early reaction stages characterized by high reaction rates may be different from those for the later stages showing a constant catalytic activity. In addition, the kinetic measurement at high pressure could be more advantageous to the integrated kinetic analysis for the catalytic reaction because the reaction rate is directly linked to the surface coverage depending on the pressure of reaction gases. Nevertheless, it should be pointed that the CO₂ photoacoustic signal linearly varies with the concentration of CO₂ in low molecular level detection at a low pressure environment and can be recorded as a function of time-on-stream during the catalytic process. This allows that the photoacoustic technique is considered as a suitable one for the molecular level study of the reaction kinetics at the early reaction stage in the catalytic CO₂-CH₄ reaction.

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