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Title: Carbon dioxide methanation over Ni catalysts supported on various metal oxides

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Keywords: carbon dioxide methanation; nickel catalyst; basic property; in situ infrared spectroscopy

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Abstract: Carbon dioxide methanation is well known to offer some advantages and be catalyzed by Ru, Rh, Pd, and Ni. In this study, Ni catalysts supported on various metal oxides were fabricated and their catalytic activity for CO₂ methanation was evaluated. The CO₂ conversion for most of catalysts drastically increased at 225–250 °C and reached a maximal value at 300–350 °C. The order of CH₄ yield at 250 °C was as follows; Ni/Y₂O₃ > Ni/Sm₂O₃ > Ni/ZrO₂ > Ni/CeO₂ > Ni/Al₂O₃ > Ni/La₂O₃. The catalytic activity could be partly explained by the basic property of the catalysts. Moreover, the chemical species formed on the catalyst surface during CO₂ methanation were examined by in situ infrared spectroscopy. From the obtained results, the difference in the activity depending on the support material of Ni catalysts was discussed.

July 11, 2016

Dear Prof. Christophe Copéret,

We are sending herewith the response to editor comment and revised manuscript entitled “Carbon dioxide methanation over Ni catalysts supported on various metal oxides” by H. Muroyama *et al.*, which we should like to submit for publication as a research paper in Journal of Catalysis: Catalytic CO₂ conversion processes to fuels and other small molecules.

Please let me know of your decision at your earliest convenience.

Yours sincerely,

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Editor:

The authors would like to appreciate your fruitful comments. We modified the manuscript with red-letter.

After reading the revised manuscript, it may become suitable for publication in J. Catal. However, the manuscript presents mainly light-off curve and hardly any data regarding testing the catalysts under constant temperature regime. To become suitable for J. Catal. one expect to see additional test regarding the performance of the catalyst (conv. vs. time but also selectivity vs. time; it is also essential that the catalyst tests under kinetic regime have to be included as they provide information about the catalyst and the catalyst life time).

A. The durability tests for the Ni/Al₂O₃ and Ni/Sm₂O₃ catalysts were also carried out at 300 °C and 20,000 l kg⁻¹ h⁻¹. The time courses of CO₂ conversion, and CH₄ and CO yields over the Ni/Al₂O₃, Ni/Y₂O₃, and Ni/Sm₂O₃ catalysts are shown in the revised manuscript. The performance of Ni/Al₂O₃ was stable within 48 h. The CO yields were quite higher than those for Ni/Y₂O₃. In contrast, the CO₂ conversion over Ni/Sm₂O₃ catalyst significantly decremented accompanied by the decreases in CH₄ and CO yields. It is well-known that the degradation of catalysts is derived from the carbon deposition and the sintering of Ni particles. Then, the fresh (reduced) and spent samples for each catalyst were examined by Raman spectroscopy and XRD. No Raman band assigned to deposited carbon was confirmed for all the samples. Moreover, no specific enlargement of Ni crystallite during the durability test was observed for each catalyst from XRD analysis. Thus, the obvious degradation factors are not identified at the present stage, and further investigation is required.

The holding time in the evaluation of catalytic performance against temperature was added to the experimental part in the revised manuscript because it was revealed that the catalyst performance was not stable for Ni/Sm₂O₃.

Research highlights

Nickel catalysts supported on various metal oxides were prepared.

The activity of nickel catalysts for CO₂ methanation was evaluated.

The Ni/Y₂O₃ catalyst exhibited the highest activity.

The reaction mainly proceeded via the formation of formate over Ni/Y₂O₃.

Carbon dioxide methanation over Ni catalysts supported on various metal oxides

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Abstract

Carbon dioxide methanation is well known to offer some advantages and be catalyzed by Ru, Rh, Pd, and Ni. In this study, Ni catalysts supported on various metal oxides were fabricated and their catalytic activity for CO₂ methanation was evaluated. The CO₂ conversion for most of catalysts drastically increased at 225–250 °C and reached a maximal value at 300–350 °C. The order of CH₄ yield at 250 °C was as follows; Ni/Y₂O₃ > Ni/Sm₂O₃ > Ni/ZrO₂ > Ni/CeO₂ > Ni/Al₂O₃ > Ni/La₂O₃. The catalytic activity could be partly explained by the basic property of the catalysts. Moreover, the chemical species formed on the catalyst surface during CO₂ methanation were examined by *in situ* infrared spectroscopy. From the obtained results, the difference in the activity depending on the support material of Ni catalysts was discussed.

Keywords: carbon dioxide methanation, nickel catalyst, basic property, *in situ* infrared spectroscopy

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1. Introduction

At present, human beings globally face serious energy and environmental issues. They have produced an enormous energy with a use of fossil fuel accompanied with a significant development of industries. The human activities, however, have induced several climate changes on the earth. The global warming originates from the greenhouse effect gases such as carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄), fluorocarbons, and chlorofluorocarbons. The CO₂ concentration in the atmosphere has increased rapidly since the Industrial Revolution, and achieved ca. 400ppm. At the same time, the depletion of fossil fuel has been concerned due to its huge consumption. Then, the utilization technologies of renewable energy such as solar, wind power, and biomass have been developed strenuously so as to break the heavy reliance on fossil fuel. Among them, hydrogen produced from the renewable energy has attracted much attention as a promising energy medium in the sustainable energy society. Especially, the recent development of fuel cells has enhanced the importance of hydrogen. However, the low volume density and the difficulty in storage and transportation obstruct the practical utilization of hydrogen. Thus, reactions of CO₂ and hydrogen to form hydrocarbons and alcohols have been extensively investigated to overcome the above-mentioned issues. These processes correspond to the recycling of carbon source and the utilization of synthesized fuels makes no contribution to the increase in CO₂ emission amount. Furthermore, the synthesized fuels serve as hydrogen storage media and are utilized in order to produce hydrogen at consuming areas.

Methane is an important chemical feedstock as well as a fuel for the power generation by gas turbines. Because it is a major component of natural gas, the handling and infrastructure for storage and transportation of methane are well established. The methanation reaction of CO₂, which is also called as the Sabatier reaction, proceeds as:

Although this process is thermodynamically favorable, there are significant kinetic limitations to reduce the fully-oxidized carbon to methane [1, 2]. Thus, various catalysts have been developed for the promotion of CO₂ methanation. Metal catalysts of Ru, Rh, Pd, and Ni are well known to be active in this reaction [3–23]. These metal catalysts are supported on metal oxides (e.g. Al₂O₃, SiO₂, zeolites, TiO₂, CeO₂, and CeO₂–ZrO₂) [3–18]. The precious metal catalysts possess better activity than Ni one. Thampi et al. reported the CH₄ formation over

the Ru/TiO₂ catalyst at room temperature and atmospheric pressure [3]. However, they are not suitable for the industrial application due to their high cost. Thus, it is necessary to find Ni catalysts with high activity and durability for CO₂ methanation.

Considerable effort has been also devoted to elucidating CO₂ methanation mechanism [4, 5, 9, 14–21]. Although the methanation reaction over metal catalysts has been studied for a long time, discussion on the mechanism has not yet reached a clear conclusion. The proposed reaction mechanisms are classified into two main categories from experimental and theoretical calculation studies. In one reaction pathway, carbon dioxide is converted to CO as an intermediate followed by CO methanation [5, 9, 14, 15, 19, 20]. The other mechanism involves the formation of formate species as the main intermediate during the direct hydrogenation of CO₂ [4, 16–18, 21].

The present study focused on Ni catalysts supported on various metal oxides for CO₂ methanation. Although a number of studies have been performed for the development of highly-active Ni catalysts and the clarification of reaction mechanism, there are not many reports relating the catalytic activity to intermediates and species formed on Ni catalysts to the best of our knowledge [14, 16, 17]. In this study, therefore, we aimed to investigate the correlation between the catalytic activity and the species formed on Ni catalyst surface during CO₂ methanation. Ni catalysts supported on various metal oxides were fabricated and their catalytic activities for the methanation reaction were examined. Moreover, the species formed in the reaction were compared for some catalysts.

2. Experimental

(i) Sample preparation

Nickel catalysts supported on metal oxides were synthesized by the impregnation method. Commercial Ni(NO₃)₂·6H₂O (Wako Pure Chemical Industries, Ltd.) was applied as a nickel source. The following oxides were employed as support materials: Al₂O₃ (AKP G-015, Sumitomo Chemical Co., Ltd.), Y₂O₃ (Wako Pure Chemical Industries, Ltd.), ZrO₂ (Daiichi Kigenso Kagaku Kogyo Co., Ltd.), La₂O₃ (Shin-Etsu Chemical Co., Ltd.), CeO₂ (JRC-CEO1, The Catalytic Society of Japan), and Sm₂O₃ (Wako Pure Chemical

Industries, Ltd.). The nickel nitrate was dissolved in pure water at room temperature. The support material was added into the aqueous solution. The mixture was kept on a steam bath at 80 °C until the solution was evaporated. The resulting powder was calcined at 600 °C for 2 h in air. The Ni loading amount was fixed at 10 wt%.

(ii) Characterization

The crystal structure of the samples was analyzed by X-ray diffraction (XRD, Rigaku, Ultima IV X-ray diffractometer) equipped with high-speed detector (D/tex Ultra). The typical working condition was 40 kV and 40 mA with a scanning rate of $20^\circ \text{ min}^{-1}$. The volume per unit weight of as-prepared samples was evaluated by Archimedes' method (Quantachrome Instruments, Ultrapycnometer 1000). The morphology of Ni particles in catalyst was observed by using a transmission electron microscope (TEM, JEOL, JEM-2100F) equipped with an energy dispersive X-ray spectrometer (EDS, JEOL JED-2300T). Prior to the TEM observation, the sample was reduced at 600 °C for 3 h with a supply of 10% H_2 –90 % N_2 at a flow rate of 100 ml min^{-1} . The basic property of the sample was examined by CO_2 temperature programmed desorption (CO_2 -TPD, BEL Japan, BELCAT-A). After reducing at 600 °C for 2 h in H_2 (30 ml min^{-1}) and cooling to 50 °C in He, carbon dioxide was supplied. Subsequently, the sample was heated to 600 °C in He and the desorbed CO_2 was detected by a thermal conductivity detector. The reduction behavior of catalysts was evaluated by temperature-programmed reduction (TPR, BEL Japan, BELCAT). The sample was fixed in a quartz tube reactor, and then a gaseous mixture of 4% H_2/Ar was fed to the reactor. The temperature was raised at a rate of $10^\circ \text{C min}^{-1}$ from 50 to 1000 °C, and the rate of hydrogen consumption was measured by a thermal conductivity detector (TCD). The species formed over catalysts was analyzed with the diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. A reaction cell capped with ZnSe window was used for *in situ* measurement. First, the powder sample was set in the reaction cell and reduced at 600 °C for 1.5 h in 5% H_2 –95% N_2 (100 ml min^{-1}). After cooling to 200 °C in N_2 , a reaction gas was fed to the sample at a rate of 100 ml min^{-1} . Gaseous mixtures of 4% CO_2 –96% N_2 , 4% CO_2 –16% H_2 –80% N_2 , and 5% H_2 –95% N_2 were supplied as reaction gases. After measuring a background spectrum at 200 °C in N_2 , the sample was held sequentially (i) in the CO_2 – N_2 atmosphere for 30 min, (ii) in the CO_2 – H_2 – N_2 atmosphere for 30 min, and (iii) in the H_2 – N_2 atmosphere for 2 h. The spectra were recorded 50

scans at a resolution of 4 cm⁻¹ using an infrared spectrometer equipped with an MCT detector (NICOLET 8700, Thermo Fisher Scientific). Difference spectra corresponding to the formed species were collected by subtracting those recorded in the reaction gas to that obtained in N₂.

(iii) Catalytic activity

The prepared powder was pelletized and pulverized to 10–18 mesh. Prior to the evaluation of catalytic test, the sample was reduced at 600 °C for 3 h with a supply of 10% H₂–90 % N₂ at a flow rate of 100 ml min⁻¹. The catalytic test was conducted with a use of a fixed-bed reactor under atmospheric pressure. The temperature dependence of catalytic performance was examined with a supply of 10% CO₂–40% H₂–50% N₂ at space velocities of 20,000 and 30,000 l kg⁻¹ h⁻¹ in the heating process. **At each temperature, the sample was kept for 30 min.** The durability of catalyst was evaluated at 300 °C by feeding 10% CO₂–40% H₂–50% N₂ at 20,000 l kg⁻¹ h⁻¹. The composition of outlet gas was analyzed by on-line gas chromatograph with a thermal conductivity detector (VARIAN, CP-4900). The CO₂ conversion, and CH₄ and CO yields were defined as follows:

$$\text{CO}_2 \text{ conversion (\%)} = \frac{[\text{CH}_4] + [\text{CO}]}{[\text{CH}_4] + [\text{CO}] + [\text{CO}_2]} \times 100 \quad (2)$$

$$\text{CH}_4 \text{ yield (\%)} = \frac{[\text{CH}_4]}{[\text{CH}_4] + [\text{CO}] + [\text{CO}_2]} \times 100 \quad (3)$$

$$\text{CO yield (\%)} = \frac{[\text{CO}]}{[\text{CH}_4] + [\text{CO}] + [\text{CO}_2]} \times 100 \quad (4)$$

where [X] (X = CH₄, CO, CO₂) represents the molar fraction of X component in the outlet gas.

3. Results and discussion

The crystal structure of samples was examined before and after reducing at 600 °C for 3 h in 10% H₂–90% N₂. Before the reduction treatment, the diffraction lines of NiO and support material were confirmed for the Ni/Al₂O₃, Ni/ZrO₂, and Ni/CeO₂ catalysts, while the patterns of the Ni/Y₂O₃ and Ni/Sm₂O₃ catalysts were attributed to those of metal oxide support. The Ni/La₂O₃ catalyst was composed of La(OH)₃ and LaNiO₃. The La(OH)₃ phase may be formed via the reaction between La₂O₃ and water at the preparation step. Fig. 1 shows the XRD patterns of reduced Ni catalysts. The metallic Ni phase was detected for all the catalysts other than

Ni/Sm₂O₃. The pattern of Ni/La₂O₃ catalyst revealed that the LaNiO₃ phase was decomposed to form the Ni metal by the reduction treatment. The Ni particles of reduced catalysts were examined by TEM observation. The Ni particles over the respective support materials were observed in the following size range; Ni/Al₂O₃: 6.0–18 nm, Ni/Y₂O₃: 4.9–18 nm, Ni/ZrO₂: 18–210 nm, Ni/La₂O₃: 5.3–23 nm, Ni/CeO₂: 8.1–68 nm, and Ni/Sm₂O₃: 4.3–16 nm. Some agglomerated Ni particles were located over the support material for the Ni/ZrO₂ and Ni/CeO₂ catalysts.

The H₂-TPR profiles of the Ni catalysts are shown in Fig. 2. Most of Ni species in Ni/Y₂O₃, Ni/ZrO₂, Ni/CeO₂, and Ni/Sm₂O₃ catalysts was reduced up to 600 °C, indicating that the Ni species was in the metallic state at the beginning of activity test. In contrast, the Ni/Al₂O₃ catalyst was continuously reduced over 1000 °C, and the reduction of Ni/La₂O₃ needed high temperature of 750 °C. It is known that the composite oxides such as NiAl₂O₄ and LaNiO₃ are readily formed in these catalysts at the calcination process in air. Thus, hydrogen would be consumed for the reduction of nickel species in such composite oxides at high temperatures.

Fig. 3 shows the CO₂ desorption behavior of the Ni catalysts after the reduction at 600 °C for 2 h. The profile of Ni/ZrO₂ exhibited only a small amount of desorbed CO₂. This catalyst scarcely possessed basic sites. The CO₂ desorption was observed at 50–180 °C for Ni/CeO₂, indicating the existence of weak basic sites. A large amount of desorbed CO₂ was detected in the wide temperature range for Ni/Al₂O₃. The large specific surface area of this material (141 m² g⁻¹) should be one of the reasons for a number of basic sites. As in the case of the Ni/Al₂O₃ catalyst, carbon dioxide was desorbed from Ni/La₂O₃ in the wide temperature region, implying that the basic sites with several strengths were widespread on the catalyst surface. Especially, the CO₂ desorption at 400–500 °C was more remarkable for Ni/La₂O₃ than for the other samples. In contrast, no strongly-adsorbed CO₂ was confirmed for the Ni/Y₂O₃ and Ni/Sm₂O₃ catalysts.

CO₂ methanation reaction over the Ni catalysts was investigated at 200–450 °C in the heating process. The CO₂ conversion, and CH₄ and CO yields over the Ni catalysts supported on metal oxides at a low space velocity of 20,000 l kg⁻¹ h⁻¹ are plotted in Fig. 4. The dashed lines in Figs. 4(a) and (b) correspond to the equilibrium value from the thermodynamic calculation. The CO₂ conversion drastically increased at 225–250 °C and then reached a maximal value at 300–350 °C under this condition for most of the catalysts investigated. Subsequently, the value gradually decreased as elevating the reaction temperature. The CH₄ yield also showed

similar temperature dependence to the CO₂ conversion (Fig. 4(b)). In the low temperature region, the CO₂ conversion and CH₄ yield were mostly coincident at each temperature for all the respective catalysts, indicating that CO₂ methanation was highly selective to the CH₄ formation. In Fig. 4(c), the CO yield significantly incremented above 350 °C accompanied with the decrease in CH₄ yield. This phenomenon was mainly attributed to the reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$), which dominantly proceeds at higher temperatures. When the catalytic activity test was conducted with a constant weight of sample, the Ni/Y₂O₃ catalyst exhibited the highest activity for the CH₄ formation in the wide temperature range among the catalysts investigated and provided the CH₄ yield of 80% at 300 °C. On the other hand, the catalysts of Ni/Al₂O₃ and Ni/La₂O₃ were inferior in performance to the others, especially at low temperatures. Their low activities were partly attributable to the difficulty in the reduction of some nickel species in these catalysts at the reduction treatment, which was indicated in the H₂-TPR measurements (see Fig. 2). Table 1 summarizes the volume per unit weight of as-prepared samples obtained based on the Archimedes' principle. Due to the fixed sample weight in the performance test, the contact time between the catalyst and the reactant gas was different from each other. The volume per unit weight of Ni/Y₂O₃ was ca. 1.4 times larger than that of Ni/CeO₂, which had the lowest value of all. Then, the activity test of Ni/Y₂O₃ was carried out at the low contact time to confirm its high catalytic performance (gray square symbols in Fig. 4). The space velocity was set at 30,000 l kg⁻¹ h⁻¹, which corresponded to the lowest contact time among all the conditions investigated. The CO₂ conversion and CH₄ yield over Ni/Y₂O₃ decreased with an increase in the space velocity. However, compared with the others, the higher or comparable performance was obtained even at the higher space velocity. Thus, it could be concluded that the Ni/Y₂O₃ catalyst possessed the superior activity for CO₂ methanation. Note that there was a rough relationship between the CH₄ yield and the basic property of the catalysts. For Ni/Y₂O₃ and Ni/Sm₂O₃ with the relatively high CH₄ yield at 225 and 250 °C, most of adsorbed CO₂ was desorbed below 400 °C in the CO₂-TPD measurement. In contrast, only a small amount of CO₂ was converted to CH₄ over the Ni/Al₂O₃ and Ni/La₂O₃ catalysts at these temperatures. Considering that these materials possessed the strong basic sites, the strongly-adsorbed CO₂ may inhibit the progress of CH₄ formation. Accordingly, the moderate basic sites would be one of the desired properties of Ni catalyst for the CH₄ production from CO₂ methanation. On the other hand, the CO yield of Ni catalysts was not related with this property.

The durability tests for the Ni/Al₂O₃, Ni/Y₂O₃, and Ni/Sm₂O₃ catalysts were carried out at 300 °C and 20,000 l kg⁻¹ h⁻¹. Fig. 5 shows the time courses of CO₂ conversion, and CH₄ and CO yields over the Ni/Al₂O₃, Ni/Y₂O₃, and Ni/Sm₂O₃ catalysts. The performance of Ni/Al₂O₃ was stable within 48 h. For Ni/Y₂O₃, the CO₂ conversion slightly dropped from 77.0% to 74.2% with time. The CO yields were within 0.05% throughout this test, which were quite lower than those for Ni/Al₂O₃. As a result, carbon dioxide could be selectively converted to CH₄ in this durability test. In contrast, the CO₂ conversion over Ni/Sm₂O₃ catalyst significantly decremented accompanied with the decreases in CH₄ and CO yields. It is well-known that the degradation of catalysts is derived from the carbon deposition and the sintering of Ni particles [22, 23]. Then, the fresh (reduced) and spent samples for each catalyst were examined by Raman spectroscopy and XRD. No Raman band assigned to deposited carbon was confirmed for all the samples. Moreover, no specific enlargement of Ni crystallite during the durability test was observed for each catalyst from XRD analysis. Thus, the obvious degradation factors are not identified at the present stage, and further investigation is required.

The species formed on the Ni catalyst during CO₂ methanation was examined by *in situ* DRIFT spectroscopy to elucidate the reason for the difference in catalytic activity depending on the sample. The Ni/Y₂O₃, Ni/Al₂O₃, and Ni/La₂O₃ catalysts were selected because these materials provided the significantly different catalytic performance as shown in Fig. 4. Fig. 6 displays the infrared spectra of species formed on Ni/La₂O₃, Ni/Al₂O₃, and Ni/Y₂O₃ recorded at 200 °C after sequential holding (a) in the CO₂-N₂ atmosphere for 30 min, (b) in the CO₂-H₂-N₂ atmosphere for 30 min, and (c) in the H₂-N₂ atmosphere for 1 min. The assignment of adsorption bands was conducted by reference to the infrared spectra of species formed on Y₂O₃, CeO₂-ZrO₂, Al₂O₃, Ni/CeO₂-ZrO₂, and Ni/Al₂O₃ under CO₂-containing atmospheres or CO₂ methanation conditions reported in the previous literatures [9, 16–18, 24]. In the spectra for Ni/La₂O₃, the formed species was independent of the measurement atmospheres. Furthermore, no change in the spectra was confirmed during holding in H₂-N₂ for 2 h. The bands centered at 1570, 1504, 1423, and 1315 cm⁻¹ were assigned to carbonates on La₂O₃. Thus, the carbonate species were quite stable over Ni/La₂O₃ under this condition. Six bands clearly appeared in the spectrum obtained under the CO₂ atmosphere for Ni/Al₂O₃. The broad bands at 2021 and 1851 cm⁻¹ are attributed to linear CO species and two-fold bridged CO species located on Ni, respectively [9]. This implied that carbon dioxide was readily dissociated to form CO on the Ni particles. Hydrogen carbonates (1653, 1534,

and 1230 cm^{-1}) and carbonates (1443 cm^{-1}) on the Al_2O_3 support were also detected [9, 17]. As hydrogen was introduced to the CO_2 atmosphere, the bands of hydrogen carbonates and carbonates disappeared accompanied with the band formation of formate species on Al_2O_3 at 1595 , 1392 , and 1377 cm^{-1} [9]. The adsorption bands of CO species (2021 and 1832 cm^{-1}) became more remarkable, which would indicate that the reverse water gas shift reaction was promoted by the water generated from CO_2 methanation. Moreover, the band at 1906 cm^{-1} newly appeared, which has not been assigned specifically so far. Hu et al. observed an adsorption band at ca. 1912 cm^{-1} under H_2 -CO co-adsorption condition at 150 – $250\text{ }^\circ\text{C}$, which was ascribable to nickel carbonyl hydride [25]. It was also suggested that rhodium carbonyl hydride was formed on Rh catalysts under H_2 - CO_2 atmosphere [26]. Thus, in this study, considering that the hydrogen introduction resulted in the band at 1906 cm^{-1} , this might originate from nickel carbonyl hydride. The spectra scarcely changed for 1 min from the beginning of the supply of 5% H_2 -95% N_2 . The spectra for $\text{Ni}/\text{Y}_2\text{O}_3$ mainly exhibited two broad bands in the 1700 – 1200 cm^{-1} range under the three conditions. In the CO_2 atmosphere, the spectrum was composed of the bands of several carbonate-like species (carbonates and hydrogen carbonates) formed on Y_2O_3 [24]. Then, the subsequent supply of CO_2 - H_2 - N_2 mixture resulted in the strong band of formate species at 1595 cm^{-1} accompanied with the disappearance of hydrogen carbonates (1670 and 1221 cm^{-1}) [16, 17, 24]. As compared with the carbonate-like species, the intensity of absorption band of formate slightly decreased even in 1 min after stopping CO_2 supply. The extremely small bands attributable to CO species were also detected at 2100 – 1800 cm^{-1} and seemed to show the same behavior against the atmospheres as in the case of $\text{Ni}/\text{Al}_2\text{O}_3$.

Subsequently, the variation of band intensity in the H_2 atmosphere was compared for $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Y}_2\text{O}_3$. Fig. 7 shows the infrared spectra of species formed on $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Y}_2\text{O}_3$ in the H_2 - N_2 atmosphere for 2 h during the series of infrared spectroscopic analysis in Fig. 6. Two adsorption bands of formate species were observed at 2906 and 2767 cm^{-1} for $\text{Ni}/\text{Al}_2\text{O}_3$ and at 2852 and 2728 cm^{-1} for $\text{Ni}/\text{Y}_2\text{O}_3$ in addition to the wavenumber range shown in Fig. 6. In the spectra for $\text{Ni}/\text{Al}_2\text{O}_3$, the bands of CO formed on Ni disappeared within 20 min from the stop of CO_2 supply, indicating that the CO species were desorbed and/or converted in the H_2 atmosphere. In contrast, a slow decrease in the band intensity of formate species was confirmed. The previous literatures proposed that CO_2 methanation over the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst proceeds via the formation of CO intermediate. In that case, the CO species are dissociated into carbon and oxygen species, and these species are

hydrogenated to form CH₄ and water, respectively [9, 20]. Because the dissociation of CO was reported to be the rate-determining step on CO₂ methanation via the formation of CO intermediate [20], the stable CO species formed on Ni were observed by the infrared spectroscopic analysis in this study. On the contrary, at the present stage, it could not be judged whether the formate species contributed to the methanation reaction. For Ni/Y₂O₃, the formate species were rapidly decomposed within 2 h relative to the carbonate-like species. The weak bands of CO species formed on Ni vanished within 20 min as observed for Ni/Al₂O₃. Considering the more rapid decomposition of formate species and the higher catalytic activity for CO₂ methanation, the formate species should serve as an intermediate in the reaction over the Ni/Y₂O₃ catalyst. In the previous studies, the supported metal catalysts containing CeO₂ and CeO₂-ZrO₂ materials promoted the decomposition of formate species, giving rise to high catalytic activity for CO₂ methanation [5, 16, 17]. Accordingly, in this study, the support effect of Y₂O₃ on the decomposition of formate species would be responsible for the superior catalytic performance of Ni/Y₂O₃. In contrast, the CO species may slightly contribute to the methanation reaction as an intermediate because their behavior over Ni/Y₂O₃ was the same as that over Ni/Al₂O₃. Over the less-active Ni/La₂O₃ catalyst, hydrogen carbonates and formate species were not formed even in the presence of H₂ and CO₂ (see Fig. 6). This should be related to the CO₂-TPD result, which showed the CO₂ desorption at high temperatures. The *in situ* infrared spectroscopic analysis suggested that strong basic sites on Ni catalysts would have a negative effect on the activation of carbonates in CO₂ methanation. Consequently, these results revealed that there was a possibility for the dependence of the support material on the dominant reaction path and the formed intermediate in CO₂ methanation.

4. Conclusions

Various Ni catalysts supported on metal oxides were investigated for the activity of CO₂ methanation and the species formed on their surface in the reaction. The Ni/Y₂O₃ catalyst exhibited the highest CH₄ yield below 350 °C among all the samples studied, while methane was scarcely produced over Ni/La₂O₃ at 250 °C. The CO₂ desorption behavior of Ni catalysts suggested that the moderate basic sites should have a positive effect on the catalytic activity for CO₂ methanation. The species formed on the surface during CO₂ methanation was

compared for Ni/Y₂O₃, Ni/Al₂O₃, and Ni/La₂O₃. For Ni/Al₂O₃, the CO species on Ni surface was specifically confirmed, indicating that CO₂ methanation should proceed via the formation of CO intermediate. Only carbonates were formed over Ni/La₂O₃ even under the methanation condition. In contrast, over Ni/Y₂O₃ the carbonate-like species were converted to formate species by introducing H₂ to the CO₂ atmosphere, followed by the decomposition of formate species in the H₂ atmosphere. The promotion of the decomposition of formate species over the Ni/Y₂O₃ catalyst would be responsible for its high catalytic activity. Although the reaction mechanism of CO₂ methanation over Ni catalysts has not been elucidated sufficiently, the mechanism should be different depending on the catalysts. Thus, further investigations on the reaction mechanism as well as the search for new materials are requested for the development of highly-active catalysts.

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Table 1 Volume per unit weight of as-prepared 10wt.% Ni/metal oxide catalysts (Al₂O₃, Y₂O₃, ZrO₂, La₂O₃, CeO₂, Sm₂O₃)

Sample	Ni/Al ₂ O ₃	Ni/Y ₂ O ₃	Ni/ZrO ₂	Ni/La ₂ O ₃	Ni/CeO ₂	Ni/Sm ₂ O ₃
Volume per unit weight / cm ³ g ⁻¹	0.202	0.174	0.150	0.166	0.126	0.143

Figure captions

Fig. 1 XRD patterns of 10wt.% Ni/metal oxide catalysts (Al_2O_3 , Y_2O_3 , ZrO_2 , La_2O_3 , CeO_2 , Sm_2O_3) after reducing at 600 °C for 3 h in 10% H_2 –90% N_2 .

Fig. 2 H_2 –TPR profiles of 10wt.% Ni/metal oxide catalysts (Al_2O_3 , Y_2O_3 , ZrO_2 , La_2O_3 , CeO_2 , Sm_2O_3). Atmosphere: 4% H_2 /Ar. Heating rate: 10 °C min^{-1} .

Fig. 3 CO_2 desorption rates over 10wt.% Ni/metal oxide catalysts (Al_2O_3 , Y_2O_3 , ZrO_2 , La_2O_3 , CeO_2 , Sm_2O_3). Atmosphere: He. Heating rate: 10 °C min^{-1} .

Fig. 4 (a) CO_2 conversion, and (b) CH_4 and (c) CO yields in CO_2 methanation over 10wt.% Ni/metal oxide catalysts (Al_2O_3 , Y_2O_3 , ZrO_2 , La_2O_3 , CeO_2 , Sm_2O_3). Reaction gas: 10% CO_2 –40% H_2 –50% N_2 . Low S.V.: 20,000 $\text{l kg}^{-1} \text{h}^{-1}$. High S.V.: 30,000 $\text{l kg}^{-1} \text{h}^{-1}$.

Fig. 5 Time courses of (a) CO_2 conversion, and (b) CH_4 and CO yields in CO_2 methanation over 10wt.% Ni/ Al_2O_3 , Ni/ Y_2O_3 , and Ni/ Sm_2O_3 . Reaction gas: 10% CO_2 –40% H_2 –50% N_2 . S.V.: 20,000 $\text{l kg}^{-1} \text{h}^{-1}$.

Fig. 6 Infrared spectra of species formed on (A) Ni/ La_2O_3 , (B) Ni/ Al_2O_3 , and (C) Ni/ Y_2O_3 at 200 °C after holding (a) in the CO_2 – N_2 atmosphere for 30 min, (b) in the CO_2 – H_2 – N_2 atmosphere for 30 min, and (c) in the H_2 – N_2 atmosphere for 1 min. These spectra were recorded with sequential supply of (a), (b), and (c).

Fig. 7 Infrared spectra of species formed on (A) Ni/ Al_2O_3 and (B) Ni/ Y_2O_3 under the prolonged exposure to H_2 – N_2 atmosphere for 2 h in the series of infrared spectroscopic analysis in Fig. 5.

Fig. 1 H. Muroyama et al.

Fig. 2 H. Muroyama et al.

Fig. 3 H. Muroyama et al.

Fig. 4(a) H. Muroyama et al.

Fig. 4(b) H. Muroyama et al.

Fig. 4(c) H. Muroyama et al.

Fig. 5(a) H. Muroyama et al.

Fig. 5(b) H. Muroyama et al.

Fig. 6(A) H. Muroyama et al.

Fig. 6(B) H. Muroyama et al.

Fig. 6(C) H. Muroyama et al.

Fig. 7(A) H. Muroyama et al.

Fig. 7(B) H. Muroyama et al.