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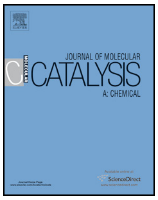

Studies of the dissociation activities of methane and carbon dioxide over supported nickel catalyst

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ABSTRACT

Pulse experiments for testing the dissociation activity of CH_4 and CO_2 were carried out on supported Ni catalysts (Ni/Al_2O_3, Ni/La_2O_3, and Ni/CeO_2) with or without pre-adsorbed species on the catalysts. The CO_2 pulse on Ni/Al_2O_3 produced a small amount of CO without pre-adsorbed species, while a CO_2 pulse produced more CO in the presence of CH_x species on Ni/Al_2O_3. The CH_x species on Ni/Al_2O_3 promote the dissociation of CO_2 on the catalyst. The production of CO by the CH_4 pulse was low on Ni/Al_2O_3 regardless of the presence of adsorbed species by the pre-pulse of CO_2, while both H_2 and CO were effectively produced on Ni/CeO_2.

1. Introduction

The use of natural gas has been attracting much attention for producing synthesis gas, a mixture of H_2 and CO, or a process for hydrogen production. Synthesis gas is a major feedstock for important processes, such as the Fisher–Tropsch synthesis, methanol synthesis, and ammonia synthesis [1,2]. The carbon dioxide reforming of methane is appropriate for these processes, because it produces low H_2/CO ratios [3,4]. Furthermore, the carbon dioxide reforming of methane is attractive for environmental concerns, because it uses two major greenhouse gases. Many types of metals have an activity for the carbon dioxide reforming of methane. Although novel metal catalysts show a low coke deposition activity, application of these catalysts to an industrial process is limited because of their high cost and limited availability. Nickel-based catalysts are preferable for industrial practices from an economical view point and availability, but they have a high activity of coke deposition [5,6]. Therefore, the development of a nickel catalyst with a high coke resistance is a crucial issue for the industrial use of nickel catalysts for the carbon dioxide reforming of methane. The following elementary reactions of the carbon dioxide reforming of methane has been proposed by Erdohelyi et al. and Rostrup-Nielsen et al. [7,8].

$$CH_4 + 2^* \rightarrow CH_3{}^* + H^*$$

$$CH_3{}^* + (3-x)^* \rightleftarrows CH_x{}^* + (3-x)H^*$$

$$CO_2 + H^* \rightleftarrows CO + HO^*$$

$$2HO^* \rightleftarrows H_2O + O^* + {}^*$$

$$CH_x{}^* + O* + (x-2)^* \rightleftarrows CO + xH^*$$

$$2H* \rightleftarrows H_2 + 2^*$$

For effectively producing CO and H_2 from CO_2 and CH_4, the dissociative adsorption of methane and carbon dioxide on a catalyst surface, and an effective reaction between $CH_x{}^*$ species and O^* should be needed. When the value of x in $CH_x{}^*$ is low, $CH_x{}^*$ would form deposited carbon before reacting with O^* [9]. Therefore, the catalyst without an activity for producing deposited carbon should have an appropriate degree of dissociative adsorption of CH_4 and CO_2. In this study, the ability of dissociation of CH_4 and CO_2 was investigated over δ-Al_2O_3, La_2O_3, CeO_2, and Ni on these oxide supports for evaluating the features of these materials. These supports are often used for the carbon dioxide reforming of methane, and especially, the addition of CeO_2 as a promoter has been reported to reduce the amount of deposited carbon [10–16]. In order to reveal the features of the effects of the support types on the activity and the amount of deposited carbon, H/D exchange reactions and dissociation reactions of CO_2 were carried out. We also carried out pulse experiments of (i) CO_2 and (ii) that of CH_4, and the two consecutive pulse experiments, i.e., (iii) three CO_2 pulses, then CH_4 pulse,

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and (iv) three CH_4 pulses, then CO_2 pulse. The pulse experiment would be a good technique for analyzing a fresh catalyst surface, because the fresh surface of the catalyst not adsorbed and covered by the reactant can be observed. Furthermore, the pulse experiment would also be appropriate for analyzing the reaction between the substrate and the specified adsorbed species on the surface.

2. Experimental

2.1. Materials

CH_4 (99.99%), D_2 (99.995%), H_2 (99.99%), CO_2 (99.95%), O_2 (99.9%), Ar (99.995%), and He (99.995%) were obtained from the Takachiho Trading Co., Ltd., Japan. δ-Al_2O_3 (Showa Light Metals Co., Ltd.) was used after treatment under an Ar atmosphere at 1173 K for 6 h. La_2O_3 (Wako Pure Chemical Co., Ltd.) and CeO_2 (JRC-CEO-1, Catalysis Society of Japan) were used as received.

2.2. Preparation of supported nickel catalyst

A 5 wt% nickel catalyst was prepared by the impregnation method. δ-Al_2O_3 (surface area: 69 m^2), La_2O_3 (5 m^2), or CeO_2 (157 m^2) (2.0 g) was immersed in an aqueous solution of $Ni(NO_3)_2$ (0.521 g of $Ni(NO_3)_2{\cdot}6H_2O$ in 40 cm^3 of H_2O) and stirred at 353 K for 2 h. The resulting solid was dried at 373 K for 18 h. The dried sample was calcined under O_2 (20 $cm^3\ min^{-1}$) at 623 K for 1 h and at 1173 K for 24 h to obtain the precursor. The particle size of the precursor was adjusted between 24 and 35 mesh.

2.3. Hydrogen-deuterium (H/D) exchange of methane

A continuous gas-flow fixed bed glass reactor (14 mm id) was used for the catalytic test. The measurement without an exchange reaction was first carried out by a CH_4 pulse (0.6 cm^3) without a catalyst in a He (50 $cm^3\ min^{-1}$) stream. The precursor (0.05 g) was placed in the reactor and treated with a D_2 stream (mixture of D_2 (3 $cm^3\ min^{-1}$) and He (50 $cm^3\ min^{-1}$)) at atmospheric pressure for 1 h at 1173 K. The H/D exchange reaction was carried out in the same reactor by a CH_4 pulse (0.6 cm^3) under a continuous gas flow of a mixture of D_2 (3 $cm^3\ min^{-1}$) and He (50 $cm^3\ min^{-1}$) at 1173 K. A small amount of the outlet flow was continuously leaked through a silica capillary tube (0.05 mm id × 2.5 m) into a Q-mass spectrometer (PFEIFFER Vacuum Prisma QMS 200) for isotopic analysis. The data set of the ion current (m/z = 12–20) was collected every 0.7 s. Background corrections of the observed spectra were made (H_2O at m/z = 18) [17].

2.4. Quantitative determination of the exchanged species by the correction of the methane isotopologues

When the determination of the isotopologues of methane was carried out by quadrupole mass spectroscopy, the methane isotopologues CH_xD_{4-x} (x = 0–4) have their own characteristic fragmentation patterns, which overlap each other. Therefore, to obtain the pure molecular ion peaks of the methane isotopologues, corrections have to be made for the observed ion peaks. In the present study, to determine each of the isotopologues in the pulse experiment, the pulse areas of the ion current were calculated by our proposed method. The correction was based on the ratios of the ion current of each daughter fragment peak to the parent peak for every data point. The fragment patterns were obtained by CH_4 pulse and CD_4 pulse without catalyst. The detailed correction method is described elsewhere [18].

The percentage of the exchanged species was expressed by the following (Eq. (1)) using the peak area $S(CH_xD_{4-x})$ (x = 0−4) of its corrected ion current of the intrinsic parent ion.

$$\frac{\text{Exchanged species}}{\%} = 100 \times \frac{\left\{S\langle CH_3D\rangle + S\langle CH_2D_2\rangle + S\langle CHD_3\rangle + S\langle CD_4\rangle\right\}}{S_{sum}} \tag{1}$$

$$S_{sum} = S\langle CH_4\rangle + S\langle CH_3D\rangle + S\langle CH_2D_2\rangle + S\langle CD_4\rangle$$

The average value of x in CH_xD_{4-x} was obtained using the following (Eq. (2)). The x value would represent the degree of the production of deposited carbon from the adsorbed species. The lower the value x in CH_x^*, the more easily the deposited carbon is produced.

$$\begin{aligned} Q(CH_xD_{4-x}) &= \frac{S(CH_xD_{4-x})}{\{S(CH_3D) + S(CH_2D_2) + S(CHD_3) + S(CD_4)\}} \\ x(\text{average}) &= 3 \times Q(CH_3D) + 2 \times Q(CH_2D_2) + 1 \times Q(CHD_3) \\ &\quad + 0 \times Q(CD_4) \end{aligned} \tag{2}$$

2.5. Dissociation reaction of CO_2

The dissociation reaction of CO_2 was carried out using the same reactor for the hydrogen-deuterium exchange reaction. The precursor (0.05 g) was placed in the reactor and treated with a mixture of H_2 (3 $cm^3\ min^{-1}$) and He (50 $cm^3\ min^{-1}$) at atmospheric pressure for 1 h at 1173 K. The dissociation reaction of CO_2 was carried out in the same reactor by a CO_2 pulse (0.6 cm^3) at 1173 K. The ion current (m/z = 2, 12, 28, and 44) was collected every 0.7 s using a Q-mass spectrometer (PFEIFFER Vacuum Prisma QMS 200).

2.6. Quantitative determination of the dissociated species of CO_2

When the outlet gas of the dissociation reaction of CO_2 was introduced to the quadrupole mass analyzer, the fragments of CO (m/z = 28) and C (m/z = 12) as well as CO_2 (m/z = 44) were observed. In order to obtain the pure molecular ion peaks of CO_2 (CO_{2out}) and CO (CO_{out}) at the outlet of the reactor, corrections have to be made for the observed ion peaks. The observed ion currents of CO_2 (CO_{2obs}, m/z = 44), CO (CO_{obs}, m/z = 28), and C (C_{obs}, m/z = 12) were expressed by the following (Eq. (3)), where x and y are the ratio of the dissociation of CO_2 to CO and to C, respectively, and z is the ratio of the dissociation of CO to C in the analysis chamber. The x and y were determined by the introduction of CO_2 without catalyst, and z was determined by the introduction of CO without catalyst to the analysis chamber.

$$\begin{aligned} CO_{2obs} &= (1 - x - y)CO_{2out} \\ CO_{obs} &= xCO_{2out} + (1 - z)CO_{out} \\ C_{obs} &= yCO_{2out} + zCO_{out} \end{aligned} \tag{3}$$

The ratio of the production of CO, the ratio of the adsorbed carbon on the catalyst, the activity of the dissociation of CO_2 were express by the following (Eq. (4)) using the peak areas of CO_{2out}, CO_{out}, C_{ad}, and CO_{2in} ($S(CO_{2out})$, $S(CO_{out})$, $S(C_{ad})$, and $S(CO_{2in})$,