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Intermediate hydrocarbon species for the CO_2–CH_4 reaction on supported Ni catalysts

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By using pulse surface reaction rate analysis (PSRA), the detailed structure of the intermediate hydrocarbon species was revealed by measuring the dynamic behavior of both CO and H_2 produced from the CO_2–CH_4 reaction on supported Ni catalysts. It was found that the number of hydrogen atoms involved in the intermediate was different from one catalyst support to another: 2.7 for MgO, 2.5 for ZnO, 2.4 for Al_2O_3, 1.9 for TiO_2, and 1.0 for SiO_2.

Keywords: CO_2–CH_4 reaction; pulse reaction; rate constant; reaction intermediate; supported Ni catalyst

1. Introduction

In order to avoid the warming of the globe, it is important to decrease the concentration of CO_2 in the atmosphere. For such purpose, many efforts have been devoted to the separation of CO_2 from exhaust gas and its utilization, especially by organizing international conferences [1]. The CO_2-reforming of CH_4 to produce syngas is a possible reaction for utilizing purified CO_2. Supported Ni is one of the most typical catalysts for this reaction [2]. To develop a high performance catalyst, it is necessary to elucidate the reaction mechanism. It has been proposed that the following steps are involved in this reaction [3]:

$$CO_{2\,gas} \rightleftharpoons CO_{ads} + O_{ads} \tag{1}$$

$$CH_{4\,gas} \rightleftharpoons CH_{x\,ads} + \tfrac{1}{2}(4-x)H_{2\,gas} \tag{2}$$

$$CH_{x\,ads} + O_{ads} \rightleftharpoons CO_{ads} + xH_{ads} \tag{3}$$

$$CO_{ads} \rightleftharpoons CO_{gas} \tag{4}$$

$$xH_{ads} \rightleftharpoons \tfrac{1}{2}xH_{2\,gas} \tag{5}$$

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Among the surface intermediates, hydrocarbon species, $CH_{x\,ads}$, are most important and the number of hydrogen atoms involved may change depending on the catalyst. The reactivity of the intermediate may also vary with the number of hydrogen atoms. However, it is difficult to reveal the detailed structure of the intermediate, or the number of hydrogen atoms involved in the intermediate, and also its reactivity.

Pulse surface reaction rate analysis (PSRA) enables us to measure the dynamics of reactant or product molecules: in this way the structure of a reaction intermediate can be revealed [4]. The purpose of the present study is to determine the number of hydrogen atoms involved in the intermediate hydrocarbon species and also to reveal their reactivity by measuring the dynamic behavior of both CO and H_2 produced from the CO_2–CH_4 reaction on supported Ni catalysts.

2. Experimental

Supported Ni catalyst (metal loading, 20 wt%) was prepared by impregnating an oxide support with an aqueous solution of $Ni(NO_3)_2$, followed by drying and subsequent calcination. As an oxide, MgO, ZnO, Al_2O_3, TiO_2, and SiO_2 were used. Before use, the catalyst was reduced at 773 K for 2 h. The PSRA apparatus was composed of a pulse microreactor equipped with a quadrupole mass spectrometer (Anelva, AGS-120). A small amount of CH_4 (0.1 ml) was pulsed onto the catalyst (200 mg) via the continuously flowing gas mixture of CO_2 and helium (ratio, 3/37; 40 ml min^{-1}). A small amount of the effluent gas was introduced to the mass spectrometer through a variable leak valve and the dynamic behaviors of reactant and product gases were monitored.

3. Results and discussion

Fig. 1 illustrates the responses for CO and H_2 produced from the reaction of the pulsed CH_4 with the carrier gas CO_2. A pronounced tailing was observed for both products. The pulse of CO, instead of the CH_4 pulse, yielded no tailing as shown by the dotted line in fig. 1. The H_2 pulse also yielded no tailing. Therefore, the observed tailings are understood by considering that the pulsed CH_4 is immediately adsorbed on the catalyst to form an intermediate and then the intermediate gradually reacts with oxygenated surface species to produce CO and H_2. Precise observation of the tailings in fig. 1 indicated that the H_2 tailing was less pronounced than the CO tailing, especially in the initial period of reaction. The tailing of this part was virtually the same as that for the H_2 pulse. This must be because different steps, like steps (2) and (5), are involved in H_2 production. According to the PSRA theory, the response (h) at a certain time (t) is proportional to the rate of production at t [4–7]. If the reaction is first order with respect to the number of

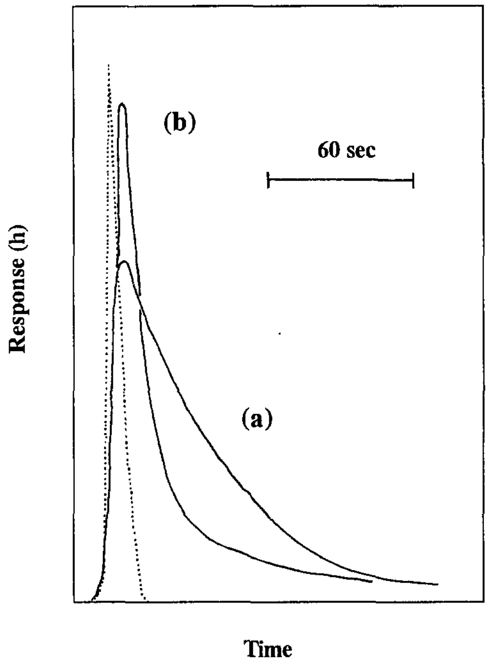

Fig. 1. Decays of CO (a) and H_2 (b) produced from CO_2–CH_4 reaction on Ni/Al_2O_3 catalyst at 723 K. The sharp dotted line is for the response of CO pulse.

adsorbed CH_4 molecules, the relationship between ln h and t should yield a straight line, the slope of which is the rate constant. It should be pointed out that the rate constant determined exhibited the intrinsic activity from which the influence of the number of active sites is excluded, because the reactivity of the adsorbed species is examined in PSRA. Fig. 2 shows the relationship between ln h and t both for CO and H_2 produced, where the response is normalized by dividing the highest one at $t = 0$. A good straight line was observed for the produced CO. Therefore, the first order rate constant can be determined and the results are summarized in fig. 3. As shown, TiO_2 was the best among the catalyst supports examined, although the difference in rate constant was not so marked.

For the dynamics of H_2 produced, a good straight line was also observed except in the initial period of reaction and the slope was almost the same as that for CO produced, as shown in fig. 2. Since CO_{ads} and H_{ads} are simultaneously produced from $CH_{x\,ads}$ to desorb CO and H_2 gases according to step (3), an equal rate constant observed between CO and H_2 productions is very natural and suggests that step (3) is rate-determining. The fast production of H_2 observed in the initial period of reaction must result from the dissociative adsorption of CH_4, which is accompanied by the rapid release of H_2 gas as shown by step (2).

For revealing the detailed structure of the intermediate, the number of hydrogen atoms involved was determined. As described above, two steps, namely steps (2) and (3), contribute to H_2 production. The amount of H_2 produced from step (3) was

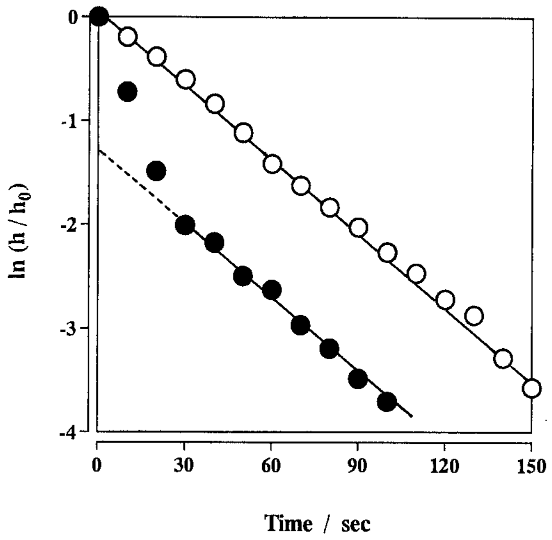

Fig. 2. Relationship between ln h and t for CO (○) and H_2 (●).

determined by extrapolating the straight line of ln h_{H_2} versus t to $t = 0$. Subtraction of this amount from the total amount of H_2 leads us to estimate the contribution of H_2 from dissociatively adsorbed CH_4. The number of hydrogen atoms involved in $CH_{x\,ads}$ can be determined from these two values as follows: under the present reaction condition, $x = 2.7$ for Ni/MgO, 2.5 for Ni/ZnO, 2.4 for Ni/Al_2O_3, 1.9 for Ni/TiO_2, and 1.0 for Ni/SiO_2. Except for Ni/SiO_2, x was not integer, which indi-

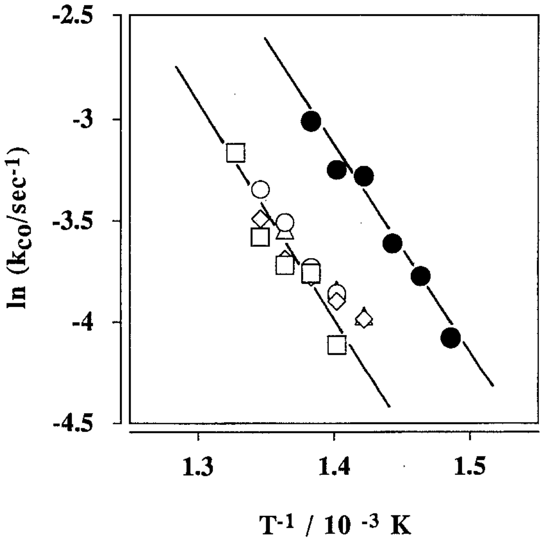

Fig. 3. Arrhenius plots of the rate constant for surface CO_2–CH_4 reaction. (○) Ni/MgO, (△) Ni/ZnO, (□) Ni/Al_2O_3, (◇) Ni/SiO_2, (●) Ni/TiO_2.

cated that more than one hydrocarbon species existed on the catalyst. However, it is evident that most hydrogen-deficient species were abundant on Ni/SiO_2 and least hydrogen-deficient ones were on Ni/MgO.

Steady-state CO_2–CH_4 reaction often accompanies carbon deposition, originating from deep dehydrogenation of $CH_{x\,ads}$. The easiness of carbon deposition may vary among catalysts. Indeed, Takita et al. [8] revealed that carbon deposition occurs at 773 K more easily for a support with larger acidity, i.e., most pronounced on Ni/SiO_2 and least pronounced on Ni/MgO. Fujimoto et al. [9] also reported that the basic property of a support was favorable for the suppression of carbon deposition. Our present finding is in accordance with the reported result by considering that more hydrogen-deficient $CH_{x\,ads}$ leads to easier carbon deposition. It should, however, be described that there is controversy about the easiness of carbon deposition: Turlier et al. [3] reported the reverse sequence on carbon deposition on supported Ni at 873 K. This discrepancy might be ascribed to the temperature, different in the two sets of experiments.

From analyzing the decay of products, the detailed structure of $CH_{x\,ads}$ was revealed and the number of hydrogen involved was found to vary from one catalyst support to another. However, it should be pointed out that there seems to be no correlation between the reactivity of $CH_{x\,ads}$ and the number of hydrogen involved in it. For clarifying the reason, further study is necessary.

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