Highly hydrogen-deficient hydrocarbon species for the CO_2-reforming of CH_4 on Co/Al_2O_3 catalyst

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The dynamics of produced CO and H_2, measured by pulse surface reaction rate analysis (PSRA), revealed that the intermediate hydrocarbon species for the CO_2-reforming of CH_4 was highly hydrogen-deficient ($CH_{0.75}$) on supported Co/Al_2O_3 catalyst. It was also found that the species was more reactive than the less hydrogen-deficient one ($CH_{2.4}$) on Ni/Al_2O_3 catalyst.

Keywords: CO_2-reforming; Co/Al_2O_3; pulse reaction; rate analysis; reaction intermediate

1. Introduction

It is well known that CO_2 is a greenhouse effect gas: increase in its amount in the atmosphere leads to the warming of the globe. Methane is also a greenhouse effect gas. The CO_2-reforming of CH_4 is an important reaction, because thereby these two harmful gases can be converted to useful synthesis gas [1–7]. It has been proposed that the following steps are involved in CO_2-reforming [8]:

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

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

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

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

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

By using pulse surface reaction rate analysis (PSRA), we confirmed the dissociative adsorption of CH_4 to release H_2 (step (2)) on supported Ni catalyst [9]. The detailed structure of $CH_{x\,ads}$, namely the number of hydrogen atoms involved in it, was also obtained from the reaction of adsorbed CH_4 with CO_2 (or O_{ads}) on supported Ni catalyst: about two hydrogen atoms were eliminated from CH_4 [9].

The structure of $CH_{x\,ads}$ may vary from one catalyst to another and its reactivity may also be different depending on the extent of the elimination of hydrogen from CH_4. We found that $CH_{x\,ads}$ was highly hydrogen-deficient on Co/Al_2O_3 catalyst and the resultant species exhibited higher reactivity. This paper describes the details.

2. Experimental

Supported Co catalyst was prepared by impregnating Al_2O_3 with an aqueous solution of $Co(NO_3)_2$, followed by drying at 383 K for 12 h and subsequent calcination at 773 K for 3 h. The metal loading was 20 wt%. Before use, the catalyst (200 mg) was reduced with flowing hydrogen (40 $dm^3\ min^{-1}$) at 773 K for 3 h.

The rate was measured with the PSRA apparatus at atmospheric pressure, in which a pulse microreactor was directly connected with a quadrupole mass spectrometer (Q-mass), in the same manner as described previously [9]. A small amount of CH_4 (0.1 dm^3) was pulsed onto the catalyst through the continuous flow of a mixture of CO_2 and helium (ratio, 3/37; 40 $dm^3\ min^{-1}$). A part of the effluent gas was introduced to the Q-mass and the dynamic behaviors of reactant and product gases were monitored.

3. Results and discussion

When a small amount of CH_4 was pulsed onto the catalyst through the continuously flowing gas mixture of CO_2 and helium, CO and H_2 were produced. The Q-mass responses for the products showed pronounced tailings, as shown in fig. 1.

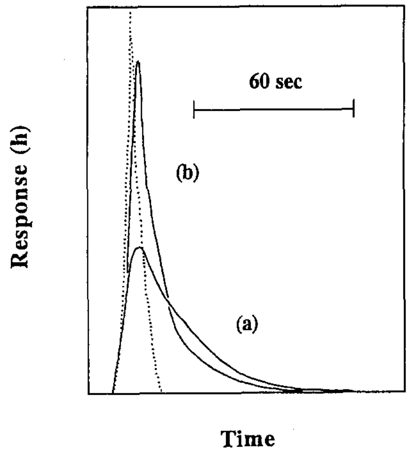


Fig. 1. Tailing curves of CO (a) and H_2 (b) produced from CO_2-reforming of methane on Co/Al_2O_3 catalyst at 723 K. The sharp dotted line indicates the response of CO (or H_2) injected at the inlet of the reactor instead of CH_4.

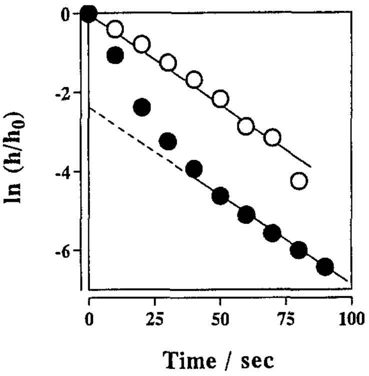


Fig. 2. Relationship between ln *h* and *t* for CO (○) and H_2 (●).

When CO, instead of CH_4, was pulsed onto the catalyst, it was immediately eluted from the catalyst as shown by the dotted line in fig. 1. The H_2 pulse also yielded no tailing, just as the CO pulse. Therefore, the observed tailings can be understood by considering that the pulsed CH_4 is immediately adsorbed on the catalyst and then gradually reacts with CO_2 to produce CO and H_2. Just like for the reaction on Ni catalyst [9], analysis of the decay in fig. 1 allows us to determine the rate constant of the reaction between the adsorbed CH_4 and CO_2. According to the PSRA theory [9], the Q-mass response is plotted in a logarithmic fashion in fig. 2 as a function of time. Since a good straight line obtained confirms the first order reaction with respect to the amount of adsorbed CH_4 molecules [9], the rate constant can be determined from the slope of the straight line. Fig. 3 summarizes the result together with that on Ni/Al_2O_3 catalyst. It is evident that the Co/Al_2O_3 catalyst was more active than the Ni/Al_2O_3 catalyst.

The rate analysis was also applied to the produced H_2 and the result is shown in fig. 2. Except in the initial period of reaction, the relationship between ln(Q-mass

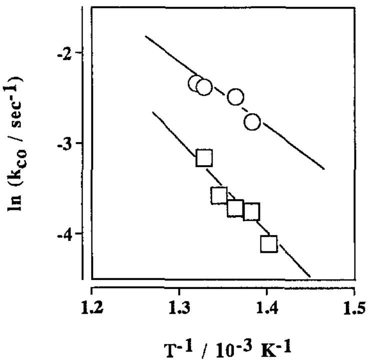
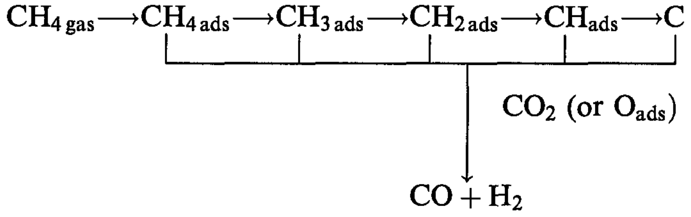


Fig. 3. Arrhenius plots of the rate constants for surface CH_4–CO_2 reaction on Co/Al_2O_3 (○) and Ni/Al_2O_3 (□).

response) and time gave a straight line and the slope was virtually the same as that for the produced CO. The reaction sequence from step (1) to (5) explains both the deviation from the line in the initial period of reaction and the fact that the rate constants are equal to each other: the pulsed CH_4 is dissociatively adsorbed on the catalyst to release a part of H_2 (step (2)) and the resultant hydrogen-deficient hydrocarbon species, $CH_{x\,ads}$, reacts with CO_2 (or O_{ads}) to simultaneously produce CO and H_2 (steps (3)–(5)). The dissociative adsorption of CH_4 followed by releasing H_2 is supported by the fact that the Q-mass response for the produced H_2 in the initial period of reaction was virtually the same as that for pulsed H_2. Separation of the amount of H_2 from the total amount of produced H_2 allows us to determine the number of hydrogen atoms involved in $CH_{x\,ads}$ [9]. Under the present reaction conditions, x was determined to be 0.75. Compared with Ni/Al_2O_3, on which $x = 2.4$ [9], a highly hydrogen-deficient hydrocarbon species was present on Co/Al_2O_3.

It is very natural to consider that the intermediate hydrocarbon species has a possible structure such as $CH_{4\,ads}$, $CH_{3\,ads}$, $CH_{2\,ads}$, or CH_{ads}. These adsorbed species should be produced from CH_4 by eliminating the hydrogen atom step by step followed by reacting with CO_2 (or O_{ads}) to produce CO and H_2, viz.



Our findings suggest that CH_{ads} abundantly produced on Co/Al_2O_3 is more reactive than $CH_{2\,ads}$, which is abundant on Ni/Al_2O_3 [9]. It is interesting to note that more hydrogen-deficient $CH_{x\,ads}$ exhibited higher reactivity under the condition of pulse reaction. During steady-state reaction between CO_2 and CH_4, carbon deposition sometimes occurs, by which the catalyst is deactivated. Highly hydrogen-deficient $CH_{x\,ads}$ may open easily a route to carbon deposition. Our preliminary experiment showed that carbon deposition was much more promoted on Co/Al_2O_3 catalyst than on Ni/Al_2O_3 catalyst, which may support the prediction described above. Therefore, the promotion of the reactivity of $CH_{x\,ads}$ should be compromised with the suppression of carbon deposition for developing a high performance catalyst. Further study is now in progress for such purpose.

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