CH_4 / CD_4 isotope effect on the reaction of adsorbed hydrocarbon species in CO_2-reforming over Ni / Al_2O_3 catalyst

Toshihiko Osaki *, Tatsuro Horiuchi, Kenzi Suzuki and Toshiaki Mori

National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan

Received 13 August 1996; accepted 4 December 1996

By replacing CH_4 with CD_4, the isotope effect on the reaction of adsorbed hydrocarbon species with CO_2 over Ni / Al_2O_3 catalyst was studied using pulse surface reaction rate analysis (PSRA). The first-order rate constant for this step was 1.45 times larger for CH_4 than for CD_4. The observed isotope effect suggests that the reaction of adsorbed hydrocarbon species with CO_2 (or adsorbed oxygen) is rate-controlling for the reforming of CH_4.

Keywords: CH_4 / CD_4 isotope effect, CO_2-reforming, methane, pulse reaction, Ni / Al_2O_3

1. Introduction

Reforming of CH_4 with CO_2 is an attractive reaction from the points of view that (i) syngas with low H_2 / CO ratios for alcohol synthesis or oxo-synthesis can be obtained therefrom [1–3] and (ii) both harmful greenhouse effect gases CH_4 and CO_2 can be converted to useful chemicals. Supported Ni is known as one of the typical catalysts for this reaction [4]. To develop a high performance catalyst, it is of great importance to unravel the reaction mechanism. However, the unambiguous reaction mechanism has not been revealed yet for this reforming reaction.

Concerning the elucidation of the reaction mechanism, measuring the isotope effect is very informative. Wang and Au recently found that CH_4 conversion in the reaction of CH_4 and CO_2 was larger than CD_4 conversion in the reaction of CD_4 and CO_2 on Ni / SiO_2 catalyst, while such acceleration was not observed for the CO_2 conversion [5]. On the basis of their finding, they discussed that two different pathways existed for the formation of CO, i.e., the oxidation of CH_x species and the dissociation of CO_2. Since CO_2-reforming consists of several steps including the dissociative adsorption of both CH_4 and CO_2, surface reaction between the resultant hydrocarbon species and oxygen atoms, and the desorption of CO and H_2, it would be more informative to examine the isotope effect on a specified step than on the overall reaction.

We found previously that the rate of reaction between adsorbed hydrocarbon species and CO_2 (or adsorbed oxygen) can be determined by applying pulse surface reaction rate analysis (PSRA) to the CH_4–CO_2 reaction [6–8]. This paper describes the CH_4 / CD_4 isotope effect on such a specified step involved in the CH_4–CO_2 reaction by replacing CH_4 with CD_4.

2. Experimental

Ni / Al_2O_3 catalyst (metal loading, 20 wt%) was prepared by impregnating a commercially obtainable Al_2O_3 (surface area, 112 $m^2\,g^{-1}$) with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ followed by drying and subsequently calcining at 773 K for 3 h. PSRA experiments were performed in the same manner as described previously [6–8]: a small amount of CH_4 or CD_4 was pulsed onto the catalyst via the CO_2–Ar carrier gas, and the effluent gases were monitored by a quadrupole mass spectrometer.

3. Results and discussion

CD_4 pulsed onto the catalyst via the carrier gas reacted with CO_2 to produce CO and D_2. The dynamic behaviors of the produced CO and D_2 are shown in fig. 1. A pronounced tailing was observed in the mass spectroscopic signal for the produced CO. When CO was pulsed instead of CD_4 no tailing could be observed (dotted line in fig. 1). The produced D_2 also showed a tailing in the later period of reaction after a sharp response. The authors found similar dynamic behavior for CO and H_2 produced from the reaction of CH_4 with CO_2 and concluded that the pulsed CH_4 was dissociatively adsorbed on the catalyst to release gaseous H_2 and the resultant adsorbed hydrocarbon species gradually reacted with CO_2 (or adsorbed oxygen atoms) to produce CO and H_2 [6–8]. The rate analysis for the dynamics of the products, CO and D_2, also enabled us to determine the first-order rate constant of the reaction of adsorbed hydrocarbon

---

* To whom correspondence should be addressed.

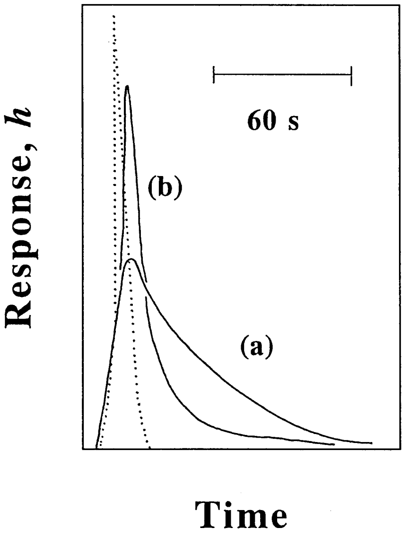

Fig. 1. Tailing curves of CO (a) and D_2 (b) produced from CD_4–CO_2 reaction on Ni/Al_2O_3 catalyst at 703 K. The sharp dotted line is the response for CO pulsed instead of CD_4.

species, CD_x, with CO_2 (or adsorbed oxygen atoms). Assuming that the rate of CO production is proportional to the concentration of adsorbed species, the following equation is obtained [6–8]:

$$\ln h_{CO} = -k_D t + \text{constant},$$

where h_{CO} is the response of the produced CO at time t. The relationship between $\ln h_{CO}$ and t should give a straight line, the slope of which is the first-order rate constant, k_D. As shown in fig. 2, the $\ln h_{CO}$ vs. t plot gives a straight line, indicating that the equation is valid for the kinetic analysis as in the case of the CH_4–CO_2 reaction [6–8].

In fig. 2, $\ln h_{D_2}$ is also plotted as a function of t. Here, h_{D_2} is the response of the produced D_2. Although deviation from the straight line is observed in the initial period of reaction, a good straight line is also obtained and the slope is almost the same as that of $\ln h_{CO}$ vs. t. The almost equal rate constant should result from simultaneous productions of CO and D_2 from the reaction between adsorbed hydrocarbon species and CO_2 (or adsorbed oxygen atoms), which provides evidence for involving deuterium atom(s) in the adsorbed hydrocarbon species. The deviation of $\ln h_{D_2}$ vs. t from the straight line in the initial period of reaction must result from D_2 released from dissociative adsorption of CD_4.

Fig. 3 shows the comparison of the first-order rate constant between the reactions of CH_4 and of CD_4. The rate constant of the reaction between CH_4 and CO_2 was 1.45 times larger than that between CD_4 and CO_2, indicating a CH_4/CD_4 isotope effect on the surface reaction between adsorbed hydrocarbon species and CO_2 (or adsorbed oxygen atoms). The activation energy was ca. 71 kJ mol^{-1}, which was comparable to that on Rh/Al_2O_3 (66 kJ mol^{-1}) or on Pd/Al_2O_3 (87 kJ mol^{-1}) [9]. Among the steps involved in the CO_2-reforming of CH_4, the dissociative adsorption of CH_4 and the surface reaction between adsorbed hydrocarbon species and CO_2 (or adsorbed oxygen atoms) are the steps in which hydrogen atom(s) are concerned and therefore the isotope effect is expected. Since the former step proceeds rapidly as described above, this step is excluded from being the rate-determining step. Therefore, the observed isotope effect strongly indicates that the surface reaction between adsorbed hydrocarbon species and CO_2 (or adsorbed oxygen atoms) is rate-controlling for the CO_2-reforming of CH_4. Since no isotope effect is expected for the adsorbed carbon species which does not contain any hydrogen, the observed isotope effect also clearly indicates that the adsorbed species contains some hydrogen atom(s), as concluded by the analysis of the dynamics of the produced D_2.

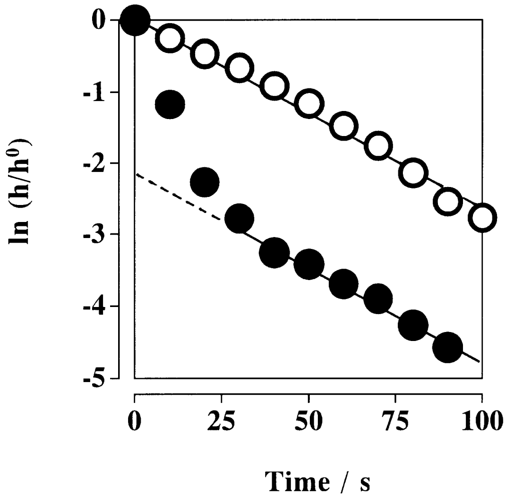

Fig. 2. $\ln h_{CO}$ vs. t (○) and $\ln h_{D_2}$ vs. t (●). The responses are respectively normalized by dividing the highest ones, h^0, at $t = 0$.

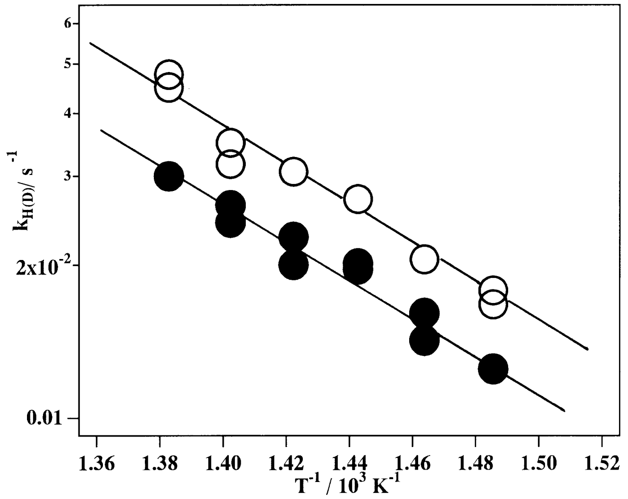

Fig. 3. Arrhenius plots of the rate constants, k_H (○) and k_D (●) for CH_4–CO_2 reaction and for CD_4–CO_2 reaction, respectively, on Ni/Al_2O_3 catalyst determined by PSRA.

References

[1] J.R. Rostrup-Nielsen, *Catalytic Steam Reforming*, Catalysis, Science and Technology, Vol. 5, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1984) p. 1.

[2] J.A. Stal, D.C. Hanson, J.-H. Bak Hansen and N.R. Udengaard, Oil and Gas J. 90 (1992) 62.

[3] H.J. Topfer, Gas Wasserfach 117 (1976) 412.

[4] T. Sodesawa, A. Dobashi and F. Nozaki, React. Kinet. Catal. Lett. 12 (1979) 107.

[5] H.Y. Wang and C.-T. Au, Catal. Lett. 38 (1996) 77.

[6] T. Osaki, H. Masuda and T. Mori, Catal. Lett. 29 (1994) 33.

[7] T. Osaki, H. Masuda, T. Horiuchi and T. Mori, Catal. Lett. 34 (1995) 59.

[8] T. Osaki, T. Horiuchi, K. Suzki and T. Mori, J. Chem. Soc. Faraday Trans. 92 (1996) 1627.

[9] F. Solymosi, Gy. Kutsan and A. Erdöhelyi, Catal. Lett. 11 (1991) 149.