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HYDROGEN-DEUTERIUM INVERSE ISOTOPE EFFECT MEASURED FOR THE C-O BOND DISSOCIATION PROCESS IN THE METHANATION ON SUPPORTED NICKEL CATALYSTS

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A hydrogen-deuterium inverse isotope effect was found for the C-O bond dissociation process in the methanation of adsorbed CO on a Ni catalyst using a pulse technique; the average value of k_H/k_D was 0.75. Such an effect (0.77) was also found for the steady-state reaction of the CO methanation. It was shown that the adsorbed CO molecule is partially hydrogenated before the C-O bond dissociation.

Much attention has been given to the methanation of CO from the view point of the utilization of coal1). Although it is relatively a simple reaction, its mechanism has not been established unambiguously: It is now well known that an adsorbed CO species is readily formed when CO comes into contact with a metal2). One of the most important problems remained unsolved for the mechanism of methanation is therefore whether the adsorbed CO species is partially hydrogenated before the C-O bond dissociation or not3). In order to solve this kind of problems, the data of hydrogen-deuterium isotope effect would be relevant4): If hydrogen plays an important role in the C-O bond dissociation, the isotope effect should appear for the rate constant of that process. If hydrogen does not play any important role, the isotope effect does not appear for the rate constant5). Although the data of the isotope effect have been obtained for the hydrogenation of CO on several catalysts6), these have not lead to a definitive conclusion of the reaction mechanism. This seems to be due to insufficient information about the step responsible for the observed isotope effect7). In the present study, by using pulse surface reaction rate analysis (PSRA), we have succeeded to observe an inverse isotope effect for the rate constant of the C-O bond dissociation process of the adsorbed CO molecule in the methanation on a Ni catalyst.

A Ni/SiO_2 or $Ni/\alpha\text{-}Al_2O_3$ catalyst was prepared by impregnating silica gel or α-alumina with an aqueous solution of nickel nitrate; the mixture was then dried and calcined. The content of nickel was 20 wt% for both catalysts. Before use it was reduced in a purified hydrogen stream at 773 K for 2.5 hr. Continuous flow experiment was carried out using a conventional flow reactor. Particular care was taken to the control of the reaction temperature, and pressures of CO, H_2 (or D_2), and N_2 (an internal standard). PSRA experiments were carried out under atmospheric pressure:

A small amount of CO was injected at the inlet of the pulse reactor into flowing purified hydrogen (40 cm^3-STP/min). It was immediately adsorbed on the surface of the catalyst, and the adsorbed CO was gradually hydrogenated by H_2 to CH_4 and H_2O; the methanation took place selectively. The rate of formation of CH_4 at time t, r(t), was continuously measured using a flame ionization detector (FID) located at the outlet of the reactor; the FID response, h, is proportional to r(t)8). Figure 1(a) shows an example of such r(t)-t profiles. As shown, the h or r(t) decreased gradually with time from the top of the curve. This is because the number of the adsorbed CO molecules is gradually decreased by the methanation. Therefore, the first order rate constant for the surface reaction can be determined from the slope of the linear relationship between log h and t [Fig. 1(b)]8). The total amount of H_2O produced up to a given time was determined by trapping the reaction product at 77 K, followed by its analysis using a gas chromatograph - a Porapak Q column was used. The amount of CH_4 was determined from integration of its chromatographic peak. Figure 2 shows the total amounts of CH_4 and H_2O produced by the hydrogenation of the adsorbed CO on Ni/α-$Al_2O_3$9). At any time, the amount of CH_4 produced was almost equal to that of H_2O produced. Similar results were obtained for the reaction at 483 K. When CH_4 instead of CO was injected into the flowing hydrogen, a quick response of CH_4 was observed [dotted line in Fig. 1(a)]. When air instead of CO was injected into the flowing hydrogen, H_2O was immediately produced. These results indicate that the C-O bond dissociation process of the adsorbed CO is rate controlling in this experiment, but rule out the idea10) that the hydrogenation of surface carbon species is the rate-determining step. If the C-O bond dissociation takes place quickly and the hydrogenation of the resultant carbon species is rate-limiting, H_2O should be produced more rapidly than CH_4. Therefore, the rate constant determined from the slope of the straight line in Fig. 1(b) represents the rate constant for the C-O bond dissociation process of the adsorbed CO in H_2, k_H. The values of k_H at various temperatures were similarly determined and the results are shown in Fig. 3. These are formulated as

$$k_H = 5.4 \times 10^6 \exp(-19000/RT),\ \mathrm{sec}^{-1}.$$

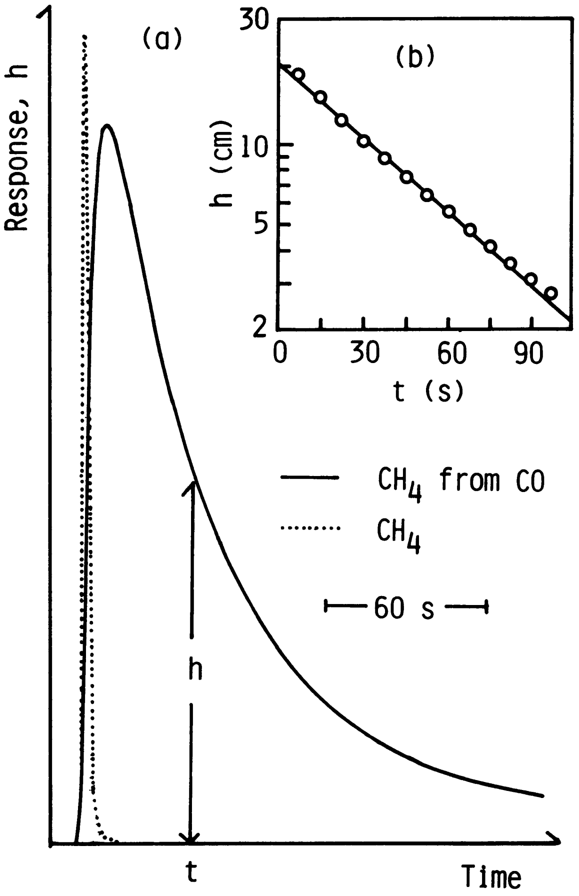

Fig. 1 (a) The FID response of CH_4 produced by the hydrogenation of adsorbed CO molecules on Ni/SiO_2 catalyst in flowing H_2 (atmospheric pressure) at 473 K. The sharp dotted line indicates the FID response of CH_4 injected instead of CO at the inlet of the reactor.
(b) Relationship between log h and t

It should be noted that the value of the pre-exponential factor is much smaller than that for usual unimolecular decompositions (ca. $kT/h \approx 10^{13}$)[11].

From the data of the PSRA experiments in flowing D_2 (40 cm^3-STP/min; atmospheric pressure), the first order rate constant for the C-O bond dissociation process of the adsorbed CO molecule in D_2, k_D, was determined at various temperatures. The results are also shown in Fig. 3. As shown, k_D is considerably larger than k_H, indicating an inverse isotope effect on the rate constant of the C-O bond dissociation of the adsorbed CO molecule. The average value of the inverse isotope effect, k_H/k_D, was 0.75. Since simple dissociation of the C-O bond of the adsorbed CO molecule to adsorbed carbon and oxygen atoms leads to the absence of the isotope effect, the results shown in Fig. 3 indicate that hydrogen atoms play an important role in the dissociation of C-O bond. The inverse isotope effect is usually caused by a thermodynamic effect on the concentration of a reaction intermediate[4]. The k_H or k_D measured by PSRA is the rate constant with respect to an adsorbed CO molecule and consequently independent on the concentration of the adsorbed CO molecule. Therefore, the inverse isotope effect in the C-O bond dissociation process of the adsorbed CO molecule suggests the presence of an adsorbed intermediate state before the C-O bond dissociation and a higher concentration of the intermediate in D_2 than in H_2. It is then evident that the intermediate on the catalyst contains hydrogen atoms in addition to carbon and oxygen atoms, indicating the presence of a partially hydrogenated CO species.

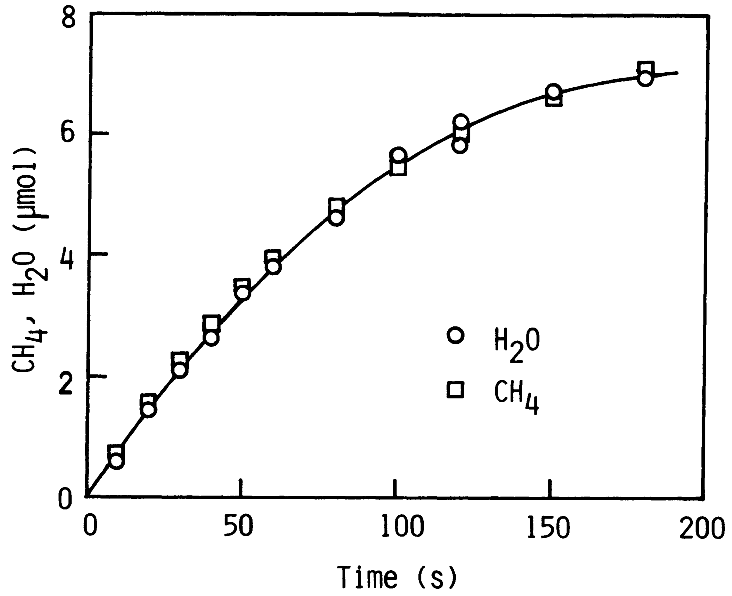

Fig. 2 The amount of CH_4 and H_2O produced by the hydrogenation of adsorbed CO molecule on Ni/α-Al_2O_3 at 473 K up to various times.

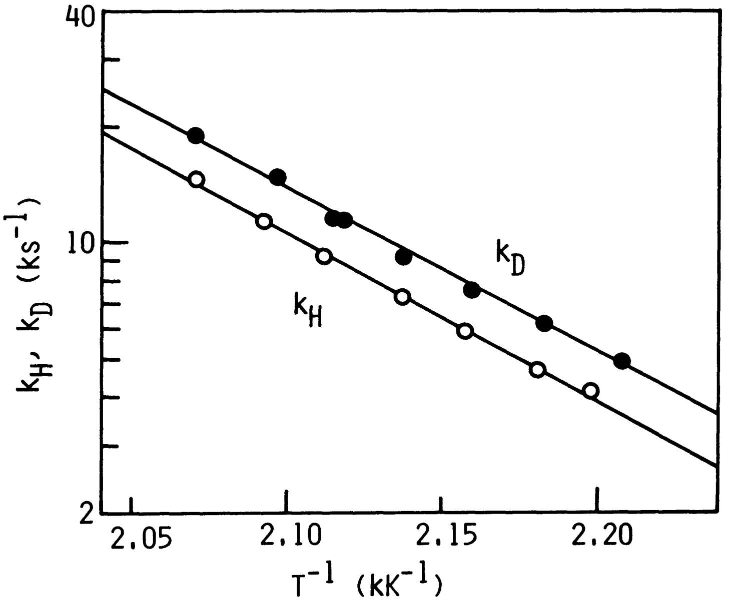

Fig. 3 Arrhenius plot for the first order rate constant of the methanation on Ni/SiO_2 catalyst in H_2 (○) and in D_2 (●).

The inverse isotope effect was also found for the steady-state reaction of the CO methanation. Fig. 4 shows the turnover frequency for the CO-H_2 and CO-D_2 reactions measured using the continuous flow reaction technique. The turnover frequency for the CO-D_2 reaction was larger than that for the $CO-H_2$ reaction. The average value of the isotope effect was calculated from the data in Fig. 4 to be 0.77 at 476 K, meaning the inverse isotope effect. The inverse isotope effect (0.78) was similarly observed for the reaction at 521 K. It should be noted that the extent of the inverse isotope effect measured using the flow technique is almost the same as that measured using PSRA. According to Ho and Harriott[3)], the rate-determining step of the steady-state methanation on Ni/SiO_2 catalyst is also the C-O bond dissociation process of the adsorbed CO molecule. Therefore, it is concluded that hydrogen atoms play an important role in the C-O bond dissociation process of the adsorbed CO molecule not only in the non-steady state methanation using the pulse technique but also in the steady-state methanation using the flow technique.

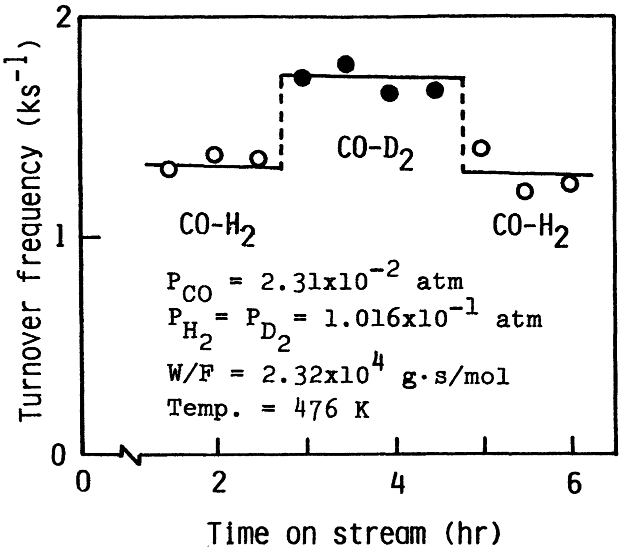

Fig. 4 Turnover frequency for $CO-H_2$ and $CO-D_2$ reactions on Ni/SiO_2 catalyst using the continuous flow technique.

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