RESEARCH NOTE

Isotope Effect and Rate-Determining Step of the CO_2-Reforming of Methane over Supported Ni Catalyst

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In recent years, the CO_2-reforming of methane has received much attention from the viewpoint of utilizing greenhouse effect gases (1–3). The reaction of methane with carbon dioxide to produce syngas is an attractive way to reduce the emission of greenhouse effect gases. The syngas produced is a preferable feedstock for Fischer–Tropsch synthesis and for oxo-synthesis, because the CO_2-reforming produces low H_2/CO ratio syngas (4, 5). The CO_2-reforming is also considered a powerful candidate for chemical energy storage and energy transmission system (CETS) (6, 7). Supported Ni is the most commonly employed catalyst for this reaction. One of the main problems in this reaction is that the catalyst is often deactivated by coke formation. The reforming is operated in such a way that the catalyst is not deactivated with time on stream due to coking; for example, in Haldor Topsoe, a partly sulfur-passivated nickel catalyst is used to suppress the coking rate (8–11). To develop a high-performance catalyst, clarification of the reaction mechanism and the rate-determining step is important. Our interest in this reaction was generated from this aspect.

We have developed pulse surface reaction rate analysis (PSRA) for investigating the kinetics of the CO_2-reforming of methane (12–15). This rate analysis has enabled us to determine the reactivity of intermediate species with no information about the number of active sites. The following findings were revealed for CO_2-reforming over supported Ni catalysts: (1) Two steps are responsible for H_2 production, i.e., dissociative adsorption of CH_4 to produce $(4 − x)/2H_2$ and CH_x, and subsequent production of $x/2H_2$ together with CO by the surface reaction between CH_x species and atomic oxygen. (2) The number of hydrogen atoms involved in CH_x is dependent on the supports, although the reactivity is not correlated with the number of hydrogen atoms. (3) An isotope effect on the reaction of adsorbed hydrocarbon species with atomic oxygen is observed; the first-order rate constant for this reaction is 1.45 times larger for CH_4 than for CD_4 on Ni/Al_2O_3 at 723 K. (4) The surface reaction between CH_x and O to produce CO and H_2 is considered the rate-determining step.

In this paper, *ab initio* molecular orbital calculation of the surface reaction between CH_x and O to give CO and H_2 was carried out. The theoretical isotope effect was estimated from the transition-state theory and compared with the experimental one.

The surface reaction rate constant conducted by PSRA is ascribed to the reaction for producing final products from the most stable adsorbed species. The rate constant is obtained by assuming that the reaction rate is first order with respect to the concentration of adsorbed species. The surface reaction rate constant can be expressed in terms of the transition-state theory as (16)

$$\mathbf{k} = (\mathbf{k}T/\mathbf{h})(Q^{\ddagger}/Q^0) \exp(-E^0/RT). \quad [1]$$

Here, $\mathbf{k}$ is Boltzmann's constant, T is absolute temperature, $\mathbf{h}$ is Planck's constant, Q^0 and $Q^{\ddagger}$ are partition functions of adsorbed species and activated complex, respectively, E^0 is activation energy at 0 K, and R is the gas constant.

The right side of Eq. [1] includes many factors which may vary with the substitution of hydrogen atoms in the adsorbed species with deuterium atoms. However, the traditional transition-state theory has revealed that the kinetic isotope effect results mainly from the difference between the zero-point energy of hydrogen-containing species and that of deuterium-containing species participating in the reaction (16). Therefore, contribution from other factors is, as an approximation, negligible and only the value of E^0 in Eq. [1] should be considered for the variation of the adsorbed species when H is replaced by D; i.e., the following equation can be solved,

$$k_H/k_D = \exp\left[-\Delta E^0_{(H-D)}/RT\right] \quad [2]$$

$$\Delta E^0_{(H-D)} = E^0_{(H)} - E^0_{(D)}, \quad [3]$$

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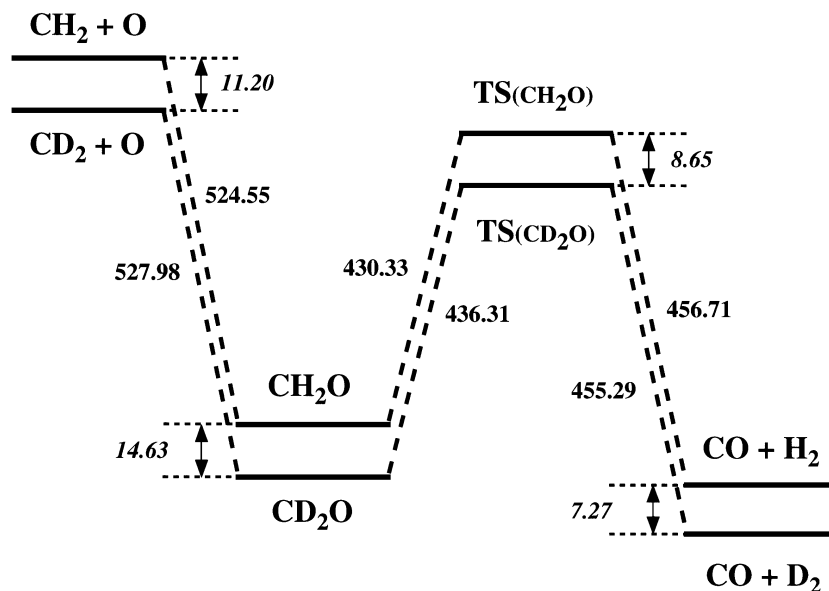nirin.go.jp.

FIG. 1. Schematic representation of energy profile for the reaction of CH$_2$ and O to CO and H$_2$ via CH$_2$O by *ab initio* molecular orbital calculation; unit, kJ mol^{-1}.

where k_H and k_D are the first-order rate constants for CH$_4$–CO$_2$ and CD$_4$–CO$_2$ reactions, respectively, and $E^0_{(H)}$ and $E^0_{(D)}$ are the activation energies for spontaneous decomposition of hydrogen-containing and deuterium-containing adsorbed species, respectively. $\Delta E^0_{(H-D)}$ is the activation energy difference between $E^0_{(H)}$ and $E^0_{(D)}$.

Among the individual steps in the CH$_4$–CO$_2$ reaction, a CH$_4$/CD$_4$ isotope effect is expected for (1) dissociative adsorption of methane to give adsorbed hydrocarbon species and (2) surface reaction between adsorbed hydrocarbon species and atomic oxygen to give the products. Since the former step proceeds rapidly as concluded from the sharp response of H$_2$ in the initial period of time by PSRA, this step is excluded from being rate determining. Therefore, the observed isotope effect strongly suggests that the latter step is rate determining for the CO$_2$-reforming of methane. Because no isotope effect is expected for an adsorbed carbon species which does not contain any hydrogen, the observed isotope effect clearly indicates that the adsorbed carbon species contains some hydrogen atoms, as concluded by the analysis of dynamic behavior of H$_2$. We reported for supported Ni catalysts that the number of hydrogen atoms involved in the intermediate hydrocarbon species differs from one catalyst support to another: 2.7 for MgO, 2.4 for Al$_2$O$_3$, 1.9 for TiO$_2$, and 1.0 for SiO$_2$ (12, 13). For the energy calculation of the surface reaction between CH$_x$ and O, a reasonable number of $x = 2$ is chosen for Ni/Al$_2$O$_3$ catalyst to reveal the *ab initio* dynamics. The calculation was carried out using a GAUSSIAN-94 program (17). A basis set of 6-31G(d) was used to calculate the energies of reactants, transition state, and products with zero-point energy

correction. A scaling factor of 0.8929 was used for the zero-point energy correction. Geometry optimization and vibration analysis were performed with a Hartree–Fock self-consistent field method.

In the calculation, more detailed steps are investigated: i.e., C–O bond formation between CH$_2$ and O to give CH$_2$O and subsequent dissociation of CH$_2$O to CO and H$_2$. Figure 1 shows the energy profiles for both steps by *ab initio* molecular orbital calculations. The dynamics for CD$_2$ + O is also shown. The former step, i.e., C–O bond formation between the radicals, is an exothermic reaction evolving the heat of 524.55 kJ mol^{-1} for CH$_2$ and O, while 527.98 kJ mol^{-1} for CD$_2$ and O. As for the latter step, i.e., dissociation of CH$_2$O to CO and H$_2$, the transition state, TS$_{(CH2O)}$, is found between CH$_2$O and CO + H$_2$ by the calculation. The energy is higher for TS$_{(CH2O)}$ than for TS$_{(CD2O)}$ as in the case of the reactants and the products. The activation energy for this step is 430.33 kJ mol^{-1} for CH$_2$O and 436.31 kJ mol^{-1} for CD$_2$O. The activation energy is higher for $E^0_{(D)}$ than for $E^0_{(H)}$. The difference between $E^0_{(H)}$ and $E^0_{(D)}$ is ascribable to the relatively small zero-point energy difference between TS$_{(CH2O)}$ and TS$_{(CD2O)}$ compared to that between CH$_2$O and CD$_2$O. The activation energy difference between $E^0_{(H)}$ and $E^0_{(D)}$ is calculated to be $\Delta E^0_{(H-D)} = -5.98$ kJ mol^{-1}. Experimental observation of unimolecular dissociation of CH$_2$O and CD$_2$O by electrical excitation also shows that the activation energy difference is ca. $\Delta E^0_{(H-D)} = -4.60$ kJ mol^{-1} (18), which is in good agreement with the calculated value. On the other hand, the transition state was not found by the calculation for CH$_2$O formation. Since simple elongation of a bond in a molecule

TABLE 1

Activation Energy Difference and Kinetic Isotope Effect

Method	$\Delta E^0_{(H-D)}$ (kJ mol^{-1})	k_H/k_D
Ab Initio MO calculation	−5.98	2.70
Electrical excitation[a]	−4.60	2.15
PSRA	−2.26	1.45

[a] From Ref. (18).

does not bring about a transition state, it is natural that a transition state was not found between $CH_2 + O$ and CH_2O in the calculation.

The theoretical isotope effect can be estimated from the activation energy difference according to Eq. [2]. The result is shown in Table 1. The value of k_H/k_D is estimated to be 2.70 for $\Delta E^0_{(H-D)} = -5.98$ kJ mol^{-1}, suggesting qualitative agreement with the experimental isotope effect ($k_H/k_D = 1.45$). The k_H/k_D is also estimated to be 2.15 for $\Delta E^0_{(H-D)} = -4.60$ kJ mol^{-1} in the unimolecular dissociation (18), which agrees more with the experimental isotope effect than that estimated from the calculation. Although perfect agreement is not obtained for k_H/k_D, the agreement between the calculated and observed values seems within the usual limit of variation of theoretical analysis by *ab initio* molecular orbital calculation, because the difference in $\Delta E^0_{(H-D)}$ is less than a few kJ mol^{-1}.

While a qualitative agreement between the experiment and the theory is observed for the isotope effect, it is also evident that there is a quantitative difference between them. The quantitative difference seems to result from the following: (1) For convenience of calculating theoretically, we assumed that the number of hydrogen atoms involved in the intermediate adsorbed species is 2 on Ni/Al$_2$O$_3$, although experimental observation of hydrogen number gives 2.4 (12, 13). This value is not an integer, which indicates that more than one adsorbed species should exist on the catalyst; however, we did not evaluate it in the calculation. (2) In the calculation, the influence of Ni on the CH_2O dissociation is not considered. The reforming reaction proceeds over an ensemble of three or four Ni atoms (8, 10), on the surface of which the C–H bond should be broken to give adsorbed hydrogen species on Ni, followed by gaseous H$_2$. We have tried to investigate the influence of the Ni atom (or Ni ensemble) on the dissociation of CH_2O in the calculation; however, we could not succeed at the present stage because of a poor basis set (LANL2DZ) applicable to the calculation for Ni. The activation energy difference evaluating the influence of Ni might give a more correlating k_H/k_D value. (3) As an approximation, we assumed that the kinetic isotope effect is mainly a result of the difference of zero-point energy of normal species and that of deuterio species participating in the reaction and that the contribution from

other factors such as partition functions is negligible. The difference in partition functions might also contribute to the isotope effect to some extent. Taking into account these assumptions described above and that there might be also some unavoidable experimental error in PSRA, we can consider that the theoretical k_H/k_D derived from the transition-state theory agrees closely with the isotope effect by PSRA, suggesting that ca. two hydrogen atoms are involved in the intermediate species and that the dissociation of CH_xO to CO and H$_2$ is rate determining for this reaction.

Some investigations have revealed an intermediate carbon species during the CH$_4$–CO$_2$ reaction. Kroll *et al.* (19, 20) and Zhang and Verykios (21) suggested that the surface carbon species is the intermediate for the CH$_4$–CO$_2$ reaction; however, Bradford and Vannice (22–24) recently suggested a hydrogen-containing intermediate species and determined the number of hydrogen atoms from a reaction kinetics model by proposing several reaction sequences. Interestingly, Bradford and Vannice suggested almost the same number as that observed by PSRA on supported Ni catalysts despite the difference in the two sets of experiments. A computational analysis of the CH$_4$–CO$_2$ reaction was performed using a hydrogen number of 2, giving a good correlation with the experimental kinetic behavior of the reaction. In the article, they proposed that a CH_xO decomposition to produce CO and H$_2$, rather than of a surface reaction between CH_x and O radicals to give CO and $x/2$H$_2$, seems more plausible for indicating the rate-determining step because radical reaction between CH_x and O occurs in the gas phase with no activation energy. They also indicated that a surface reaction between CH_x and O to give CO and $x/2$H$_2$ is difficult to differentiate from the decomposition of a subsequently formed CH_xO species. As shown in Fig. 1, no transition state is found for the surface reaction between CH$_2$ and O to CH$_2$O by the calculation, although it is natural as explained above. This step is an exothermic reaction, evolving heat of ca. 525–528 kJ mol^{-1} when the C–O bond is formed between the radicals. However, it should be noted that the radicals exist on Ni atoms (Ni ensemble) by adsorption, on the surface of which the C–O bond should be formed, presumably maintaining a chemical interaction between Ni and CH$_2$ and also between Ni and O. Considering that the radical species exist on the Ni surface by chemical adsorption, not that they exist in the gas phase, the transition state might exist in the surface reaction between the adsorbed species, suggesting the presence of activation energy. This step might also contribute to the deviation of the theoretical k_H/k_D from the experimental one to some degree, since contribution of this step is not considered for the theoretical analysis; on the other hand, this step seems to be included in PSRA. In fact, we obtain almost identical k_H and activation

energy for different Ni-supported catalysts except for Ni/TiO$_2$, in which the value of x in CH$_x$ varies (12, 13). This might indicate that the rate-determining step is related to the formation of the C–O bond due to a thermodynamic isotope effect on the concentration of CH$_x$/CD$_x$ intermediates. In the previous articles, we have proposed that the surface reaction between CH$_x$ and O to give CO and x/2H$_2$ is rate determining (12–15). However, contribution of C–O bond formation between the radicals to give CH$_2$O to the isotope effect does not seem major even if this step has an activation barrier. This is because: (1) the slope of ln h_{CO} vs t plot for PSRA curve, where h_{CO} is the response of CO at time t, is not influenced by methane pulse size and catalyst weight, which indicates that the reaction rate constant obtained from the slope is independent of the concentration of intermediate; and (2) the kinetic isotope effect is mainly due to cleavage of the C–H bond, and contribution of the secondary isotope effect, in this case the C–O bond formation between CH$_2$ and O to give CH$_2$O, to the kinetic isotope effect is considered minor. Therefore, the kinetic isotope effect observed by PSRA is ascribed to the dissociation of CH$_x$O to CO and H$_2$ on the Ni surface, suggesting the rate-determining step for this reaction.

To conclude, the theoretical isotope effect on the surface reaction between CH$_x$ and O was studied by *ab initio* molecular orbital calculation. The kinetic isotope effect calculated was qualitatively, although not quantitatively, in agreement with that observed by PSRA, suggesting that the intermediate species contains ca. two hydrogen atoms and that the step of CH$_x$O $\rightarrow$ CO + x/2H$_2$ is rate determining for this reaction. To obtain more precise k_H/k_D values from the theory, a more accurate calculation evaluating the influence of the Ni atom (or Ni ensemble) on CH$_x$O dissociation seems important. This will be achieved by using an advanced basis set for Ni calculation. The PSRA is an elegant technique to reveal a reaction mechanism and the rate-determining step in addition to the kinetics of the reaction without performing a conventional flow reaction. From the viewpoint of saving expensive reactants such as deuterio methane, the technique is also of great value.

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