CHEMISTRY LETTERS, pp. 1531-1534, 1989.

Isotopic Studies on Oxidative Methane Coupling over Samarium Oxide

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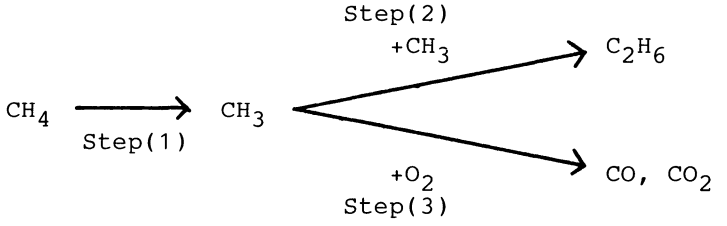
The evident kinetic isotope effect was observed for the formations of ethylene and ethane through the oxidative coupling of methane on Sm_2O_3, when CH_4 and CD_4 were used as the reactants. Ethanes formed in the reaction of a mixture of CH_4, CD_4, and O_2 were C_2H_6, $C_2H_3D_3$, and C_2D_6 as major products. These results indicate that the rate-determining step of the reaction is abstraction of hydrogen from methane and that ethane is formed through the coupling of methyl intermediate.

Oxidative coupling of methane on solid catalysts has been intensively investigated from view points of chemical interest in activation of C-H bond of saturated hydrocarbons and of industrial utilization of natural gas as chemical resources instead of petroleum.1) Although many effective catalysts for the reaction have been reported1,2) there have been only a few direct evidences for the reaction mechanism and reaction intermediate. It is generally believed that coupling of methyl radicals in the gas-phase or of methyl groups on the surface produces ethane.3) On the other hand, Mirodatos and Martin have proposed that coupling of methane proceeds via carbene intermediate on Li-doped MgO.4) Otsuka and Jinno have proposed a mechanism of the reaction on Sm_2O_3 on the basis of kinetic investigations that ethane is formed by coupling of methyl intermediate and carbon oxides (CO, CO_2) are produced by further oxidation of the methyl intermediate.5) The abstraction of hydrogen from methane forming methyl intermediate is a rate-determining step.5) The mechanism is demonstrated as follows,



(1)

This paper reports an evidence supporting the above mechanism on the basis of isotopic studies of the reaction using CH_4 and CD_4.

Methane and oxygen were used after passing through a cold trap at 77 K. CD_4 purchased from Cambridge Isotope Laboratories (purity>99%) was used without further purification. Samarium oxide (Sm_2O_3, purity>99.9%, surface area 0.72 m^2g^{-1}) was supplied from Asahi Chemical Industry Co. A conventional glass-made gas circulation system connected to a vacuum system was used for pretreatment of the catalyst and the reaction experiments. Sm_2O_3 was pretreated in oxygen gas at 1023 K for 1 h in the system. Water produced during the pretreatment was collected by a cold trap at 77 K. Oxygen was evacuated after the catalyst was cooled to reaction temperatures. A mixture of reactants such as CH_4, CD_4, and O_2 will be denoted as $CH_4/CD_4/O_2$, hereafter. Compositions of the mixtures of the reactants and the products were determined by gas chromatography. The isotopic distribution in reactants and products was determined by mass spectrometry after separating methane, ethane, and ethylene by gas chromatography.

The reactions on Sm_2O_3 were carried out using the reactants of CH_4/O_2 and CD_4/O_2. Figure 1 shows the conversions of methanes along the reaction time at 923 K. The rate of conversion of CH_4 was higher than that of CD_4. The initial

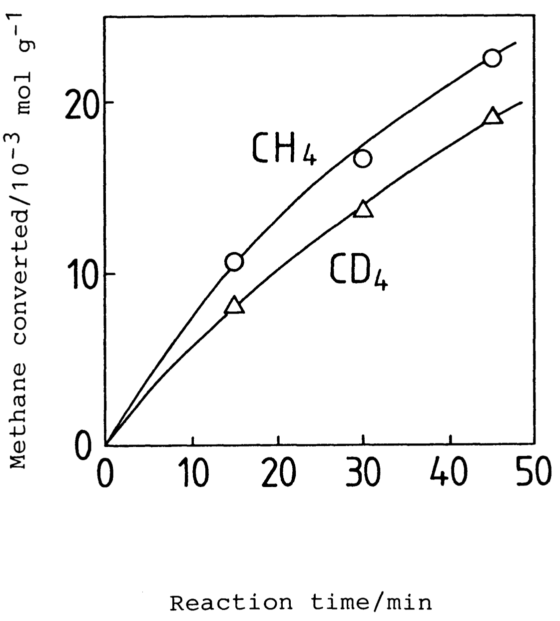


Fig.1. Conversions of CH_4 and CD_4 on Sm_2O_3.

(○)CH_4, (△)CD_4. Reaction temperature, 923 K;Sm_2O_3, 2.1 mg;P(CH_4)=P(CD_4)=2.7 kPa, P(O_2)=1.3 kPa.

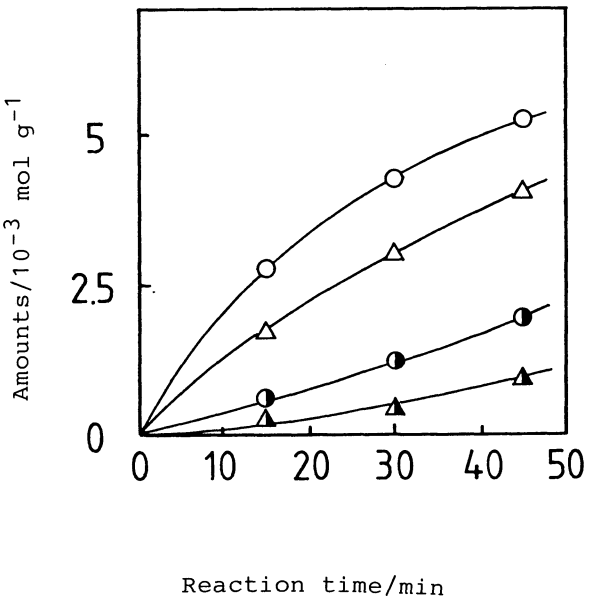


Fig.2. Formations of ethane and ethylene.

(◑) C_2H_4, (○) C_2H_6+C_2H_4, (▲)C_2D_4 (△)C_2D_6+C_2D_4. All the reaction conditions were the same as those described in Fig.1.

conversion rates of methanes calculated from the conversions at 15 min were 7.3×10^{-4} and 5.5×10^{-4} mol $g^{-1}min^{-1}$, for CH_4 and CD_4, respectively. The kinetic isotope effect was determined as 1.3 from these initial rates. The kinetic isotope effects evaluated in the similar way at lower temperatures were 1.4 (873 K) and 1.7 (823 K). These evident isotope effects support the assumption that the C-H breakage is the rate-determining step in the overall reaction.

Figure 2 shows the kinetic curves of the formations of C_2 products, ethane and ethylene, in the same experiments as those in Fig.1. The delay observed for the formation of ethylene supports the idea that ethylene is formed through oxidative dehydrogenation of ethane.5) The kinetic isotope effect for the formation of the C_2 compounds (ethane and ethylene) was 1.6. The larger isotope effect for the formation of the C_2 compounds than that for the total conversion of methane (1.3) can be ascribed to the second order dependence of the formation of ethanes on the concentration of methyl intermediate which is determined by the abstraction rate of H or D from methanes, i.e., the isotope effect in the formation rates of CH_3 and CD_3 is amplified in the formation rates of C_2H_6 and C_2D_6. The apparent isotope effect observed for the formation rates of ethylenes (C_2H_4, C_2D_4) was 2.3. This largest isotope effect can be ascribed to the overlap of the isotope effect in the formation rates of ethanes with that in the rates of

Table 1. Isotopic distribution in ethane formed in the reaction of a mixture of $CH_4/CD_4/O_2$

Ethane	m/e	Obsd.a)	Cald.b)
C_2H_6	30	48	65
C_2H_5D	31	1	
$C_2H_4D_2$	32	0	
$C_2H_3D_3$	33	100	100
$C_2H_2D_4$	34	2	
C_2HD_5	35	1	
C_2D_6	36	35	38

Reaction temperature, 923 K;Sm_2O_3, 3.4 mg;$P(CH_4)=P(CD_4)=P(O_2)=1.3$ kPa.
a)Relative amounts observed.
b)Relative amounts calculated using the isotope effect observed.

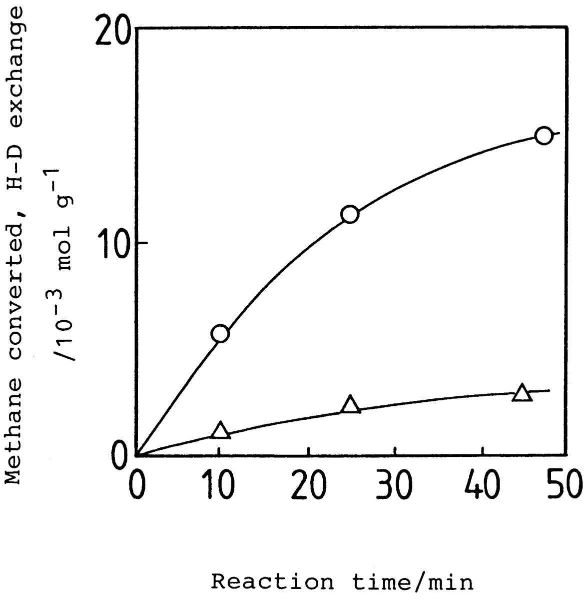


Fig.3. H-D exchange between CH_4 and CD_4 during the reaction of $CH_4/CD_4/O_2$.

(○)methane conversion, (△)H-D exchange; reaction temperature 923 K;Sm_2O_3, 2.1 mg; $P(CH_4)=P(CD_4)=P(O_2)=1.3$ kPa.

dehydrogenation of ethanes to ethylenes.

The isotope distribution in the ethane formed in the reaction of the mixture, $CH_4/CD_4/O_2$, is shown in Table 1. The main products were C_2H_6, $C_2H_3D_3$, and C_2D_6 and the other deuterated ethanes were much less than the main ones. This experimental result strongly supports the above assumption that ethane is formed through coupling of methyl species, i.e., CH_3 and CD_3. A possibility of carbene species as an intermediate is excluded from the results above. The relative composition of the three main deuterated ethanes was calculated by assuming that the isotope effect in the concentrations of methyl intermediates was the same as that observed in the conversion rates of CH_4 and CD_4 ($[CH_3]/[CD_3]=1.3$). These calculated values coincided with the observed ones relatively well.

Figure 3 shows the kinetic curves for the conversion of methanes to the C_2 compounds and carbon oxides and for the amount of exchanged hydrogen and deuterium between CH_4 and CD_4. The rate of the exchange was 1/6 of that of the methane conversion, suggesting that the recombination of CH_3 and H (backward reaction of step 1 in Eq.1) is slower than the coupling (step 2) and the complete oxidation (step 3). These suggestions are consistent with the idea that step 1 in Eq.1 is the rate-determining step.

In conclusion, the mechanism of the reaction proposed in Eq.1 has been approved from the results described above. However, whether the methyl intermediate described above is methyl radical in the gas-phase or methyl group adsorbed on the surface is still an open question.

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(Received May 27, 1989)