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Exchange Reaction of Methane with Deuterium over Solid Base Catalysts

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The exchange reaction of CH_4 with D_2 was carried out over 13 kinds of metal oxide catalysts. Among them, a series of alkaline earth metal oxides (MgO, CaO, SrO, and BaO) and La_2O_3 exhibited activity at 300°C. The variations of the activities of these catalysts as a function of the pretreatment temperature of the catalysts were measured. The pretreatment temperatures to give maximum activity were 700°C for MgO and CaO prepared from $Ca(OH)_2$, 800°C for CaO prepared from $CaCO_3$ and for BaO, 1000°C for SrO, and 650°C for La_2O_3. The reaction rate of $CH_4 + D_2$ was higher than that of $C_2H_6 + D_2$ and equal to that of $CH_4 + CD_4$ over alkaline earth metal oxides. In the exchange reaction of iso-C_4H_{10} with D_2, a methyl H exchanged faster than a methyne H. It is suggested that the reaction of $CH_4 + D_2$, as well as $C_2H_6 + D_2$ and iso-$C_4H_{10} + D_2$, is initiated by the abstraction of an H^+ by basic sites on the catalysts.

INTRODUCTION

Catalytic exchange reactions of alkanes with D_2 have been extensively investigated in connection with isomerization, hydrogenation, and hydrocracking. Most catalysts used for exchange reactions are metal catalysts, while only a few kinds of oxide catalysts have been studied. Among oxide catalysts, Al_2O_3 shows extremely high activity for exchange of alkanes with D_2. Larson and Hall (*1*) reported that the CH_4–D_2 exchange proceeded even at room temperature and showed that the active sites involved only a small fraction of the OH groups on Al_2O_3. On the other hand, Flockhart *et al.* (*2*) measured surface properties of Al_2O_3 and found that the amount of oxidizing sites correlated best with the activity for the C_3H_6–D_2 exchange, though poisoning of reducing sites also resulted in deactivation of the catalyst.

Robertson *et al.* (*3*) showed that the reaction intermediates in the exchange of alkanes with D_2 over Al_2O_3 were carbanionic in character. This conclusion was based on a comparison of reactivities of different alkanes and on the easy exchangeability of methyl H compared with methyne H in iso-C_4H_{10}. The carbanion intermediates have been also postulated by Burwell *et al.* (*4*) in exchange of alkanes with D_2 over Cr_2O_3 on the basis of the differences in reactivities of different kinds of alkanes.

Since alkaline earth metal oxides exhibit basic properties and possess an ability to abstract an H^+ from olefins when they are properly pretreated (*5*), it is expected that they are also active for exchange of alkanes with D_2 if an abstraction of an H^+ from alkanes is an important step. Actually Flockhart *et al.* (*2*) reported that MgO and CaO pretreated at 570°C catalyzed the exchange of propane with D_2 at 300°C.

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Only one pretreatment temperature was used in this study, but the nature of the active sites on alkaline earth metal oxides are quite dependent on pretreatment condition. For instance, BaO exhibits the activity for the isomerization of butenes by the evacuation at temperatures above 400°C but does not show any activity for the exchange reaction of butene with D_2 until evacuated at the temperatures above 550°C (*6*). For the hydrogenation of olefins, a much higher evacuation temperature is required (*7*, *8*).

In this paper, the activities of various kinds of metal oxides for the CH_4–D_2 exchange were tested. For a series of alkaline earth metal oxides and La_2O_3 which exhibited relatively high activity, the dependencies of the activities on pretreatment temperature were measured and the reaction mechanisms are discussed.

EXPERIMENTAL METHODS

The magnesium oxide, CaO(I), CaO(II), SrO, and BaO catalysts were prepared from $Mg(OH)_2$ (Kanto Chem. Co.), $Ca(OH)_2$ (Kanto Chem. Co.), $CaCO_3$ (Kanto Chem. Co.), $SrCO_3$ (E. Merk Co.), and from granular BaO (E. Merk Co.) by evacuation at different temperatures for about 3 hr. Lanthanum oxide, CeO_2, TiO_2, and ZrO_2 were obtained by hydrolysis of aqueous solutions of $La(NO_3)_3$ (Nakarai Chem. Ltd.), $Ce(NO_3)_3$ (Nakarai Chem. Ltd.), $TiCl_4$ (Wako Pure Chem. Ind.), and $ZrOCl_2$ (Wako Pure Chem. Ind.), respectively, followed by evacuation at various temperatures. Thorium oxide and WO_3 were prepared by pyrolysis of $Th(NO_3)_4$ (Wako Pure Chem. Ind.) and $(NH_4)_{10}W_{12}O_4$, (Wako Pure Chem. Ind.) at 500°C in air followed by evacuation. Praseodymium oxide and Tb_2O_3, which were kindly supplied by Professor T. Sato of Yamagata University, were prepared by pyrolysis of the oxalate forms and evacuated before use.

Methane, C_2H_5, and iso-C_4H_{10} were purified by passage through 4A molecular sieves at −78°C after a vacuum distillation. Perdeuterio methane (CD_4) was purchased from CEN-Saclay-Dry in a glass ampule and used without further purification. Deuterium and O_2 were purified by passage through 13X molecular sieves at −196 and −78°C, respectively, and they were stored over a well-degassed mixture of 13X molecular sieves and MgO.

All reactions were carried out in a closed recirculation reactor that had a total volume of ca. 400 ml. For the CH_4–D_2 exchange, a mixture of 5 Torr of CH_4 and 45 Torr of D_2 was used. In the experiments to determine the reaction order, pressures of CH_4 and D_2 were varied between 5 and 90 Torr. For the C_2H_6–D_2 exchange and the iso-C_4H_{10}–D_2 exchange, a mixture of 5 Torr of C_2H_6 and 45 Torr of D_2 and 40 Torr of iso-C_4H_{10} and 200 Torr of D_2 was used, respectively, For the CH_4–CD_4 scrambling, about 25 Torr of a mixture containing 1:4 ratio of CH_4 to CD_4 was reacted. In the poisoning experiments, BaO evacuated at 800°C was exposed to 10^{16} molecules cm^{-2} of O_2 at 300°C or at room temperature for 10 min and, then, evacuated to 2×10^{-5} Torr at each poisoning temperature.

TABLE 1

Specific Surface Areas of Catalysts (m^2/g)

Catalyst	Evacuation temperature (°C)					
	500	600	700	800	900	1000
MgO	145	135	117	93	—	—
CaO(I)	71	72	52	36	32	—
CaO(II)	5	22	17	17	—	17
SrO	—	9	—	10	—	10
BaO	0.1	0.1	0.2	0.2	0.2	—
La_2O_3	43	39	27	21	15	—
CeO_2	—	—	11	—	—	—
Pr_2O_3	—	—	10	—	—	—
Tb_2O_3	—	—	26	—	—	—
TiO_2	85	—	—	—	—	—
ZrO_2	—	30	—	—	—	—
ThO_2	—	59	—	—	—	—
ZnO	3	—	—	—	—	—
WO_3	—	31	—	—	—	—

The reaction was monitored by sampling a small quantity of a reaction mixture for mass spectrographic analysis. NEVA NAG-515 Mass Filter was operated with the ionization valtage of 95 eV. The isotopic methanes were followed by scanning m/e peaks 12 to 20. The isotopic composition was calculated by using the cracking patterns inferred from the available data (*9*). Relative sensitivities of isotopic ethanes were followed by scanning m/e 26 to 36 and the cracking patterns were cited from the reported data (*10*). Corrections of the observed spectra to background were made.

Two different rate constants, k_ϕ and k_x, were determined from each experiment, by using the following equation (*11*),

$$\frac{d\phi}{dt} = k_\phi \cdot W \cdot \left(\frac{\phi_\infty - \phi}{\phi_\infty}\right),$$

$$\frac{dx}{dt} = -k_x \cdot W \cdot \left(\frac{x - x_\infty}{x_0 - x}\right),$$

where ϕ represents the average number of D atoms in 100 alkane molecules at time t, ϕ_0 for $t = 0$ and ϕ_∞ for $t = \infty$, x is the percentage of nondeuterio alkane at time t, x_0 for $t = 0$ and x_∞ for $t = \infty$, and W is the weight of catalyst. The rate constant k_ϕ is the number of D atoms that enter 100 alkane molecules per unit weight of catalyst in unit time at the start of the reaction, and k_x is the decreasing number of the nondeuterio alkane per 100 molecules per unit weight of catalyst in unit time. The value of k_ϕ/k_x, multiplicity of the exchange reaction (M), means the average number of D atoms that entered one exchanged alkane molecule at the initial stage of the reaction. The values of ϕ_∞ and x_∞ were calculated by neglecting an isotope effect on the equilibrium.

RESULTS

Specific surface areas of catalysts are given in Table 1.

TABLE 2

Catalytic Activities of Various Oxides for $CH_4 + D_2$ Reaction

Catalyst	Evacuation temperature (°C)	Reaction temperature (°C)	Activity ($10^3 k_\phi$, $\% s^{-1} g^{-1}$)	M value
MgO	700	300	35.5	1.16
CaO(I)	700	300	42.6	1.19
SrO	1000	300	17.3	1.07
BaO	800	300	1.76	1.05
La_2O_3	650	300	27.8	1.20
CeO_2	700	500	20.1	1.06
Pr_2O_3	700	500	5.9	1.48
Tb_2O_3	700	500	0.0	—
TiO_2	500	500	0.0	—
ZrO_2	600	400	0.6	1.07
ThO_2	600	400	0.6	1.03
ZnO	500	400	0.5	1.18
WO_3	600	500	0.0	—

The activities of various oxides for the $CH_4 + D_2$ reaction are included in Table 2. A series of alkaline earth metal oxides and La_2O_3 showed catalytic activities at 300°C when they were properly pretreated, though the activities were not so high as that of Al_2O_3 which catalyzes the reaction at room temperature. Zirconium oxide, ThO_2, and ZnO did not show measurable activities at 300°C but became active at 400°C. Cerium oxide and Pr_2O_3 showed activities only at 500°C, and TiO_2, Tb_2O_3, and WO_3 hardly showed any activities even at 500°C.

For all catalysts, the M values were close to unity and the distributions of D atoms were binomial. The reaction orders were 1.0 and 0.2 with respect to CH_4 and D_2, respectively, for MgO evacuated at 700°C, and 1.1 and −0.1 with respect to CH_4 and D_2, respectively, for CaO(I) evacuated at 700°C.

The variations of the activities as a function of evacuation temperature are plotted in Fig. 1 for MgO and BaO, in Fig. 2 for two kinds of CaO, and in Fig. 3 for SrO and La_2O_3. The activity is expressed by the rate constant, k_ϕ, on the unit weight base. The maximum activities were obtained when evacuated at 650°C for La_2O_3, at 700°C for MgO and CaO(I), at 800°C for CaO(II) and BaO, and over 1000°C for

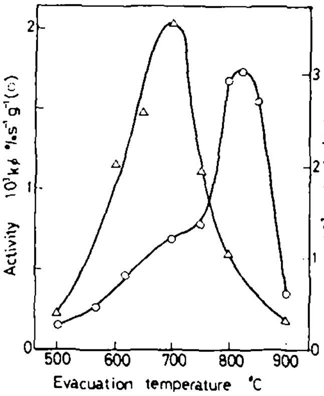

FIG. 1. Variations of activities of MgO (△) and BaO (○) for the CH_4-D_2 exchange at 300°C as a function of evacuation temperature.

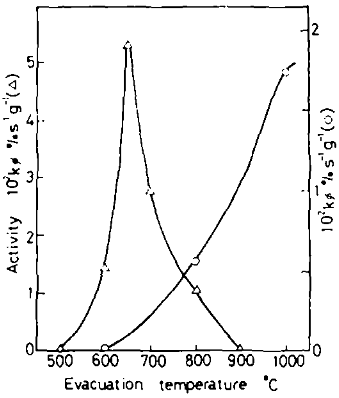

FIG. 3. Variations of activities of SrO(○) and La_2O_3 (△) for the CH_4-D_2 exchange at 300°C as a function of evacuation temperature.

SrO. On comparing the maximum activities among alkaline earth metal oxides on unit surface area base, the activities are in the following order: BaO > SrO > CaO(II) > CaO(I) > MgO.

The poisoning effects by O_2 adsorption on BaO are listed in Table 3. The activity was completely lost by the adsorption of O_2 at 300°C, and it was reduced to $\frac{1}{10}$ of its original activity when O_2 was adsorbed at room temperature.

The rate constants for the C_2H_6-D_2 exchange are compared with those for the CH_4-D_2 exchange in Table 4. With all catalysts, CH_4 exchanged its H atoms more readily than C_2H_6.

The reaction rates of the CH_4-CD_4 exchange over MgO, CaO(I), and SrO are also compared with those of the CH_4-D_2 exchange in Table 4. The rates of the two kinds of reactions on an oxide were within a factor of two of each other. When a mixture of CH_4, H_2, and D_2 was reacted at 300°C over CaO that had been evacuated at 700°C, the H_2-D_2 equilibrium was virtually instantaneous.

The iso-C_4H_{10}-D_2 exchange over CaO(I) and La_2O_3 that had been evacuated at 700°C was followed by recording the NMR spectrum of the sampled isobutane in the course of reaction. In Fig. 4 the intensity ratios of the methyl hydrogen to methyne hydrogen against reaction time are plotted. The ratio decreased with reaction time.

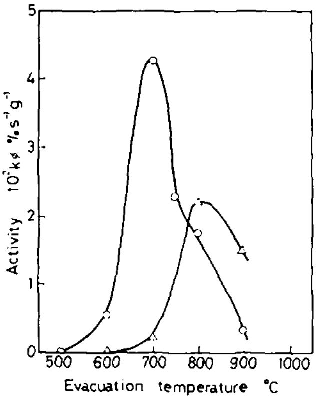

FIG. 2. Variations of activities of CaO(I) (○) and CaO(II) (△) for the CH_4-D_2 exchange at 300°C as a function of evacuation temperature.

TABLE 3

Poisoning Effect with O_2 on the Activity of BaO Evacuated at 800°C

Treatment	Activity (10^3 k_ϕ, %s^{-1} g^{-1})
Unpoisoned	1.76
Poisoned at room temperature	0.27
Poisoned at 300°C	0.00

TABLE 4

Comparison of the Reaction Rates for $CH_4 + D_2$, $C_2H_6 + D_2$, and $CH_4 + CD_4$[a]

Catalyst	Evacuation temperature (°C)	Activity ($10^3 k_\phi$, % $s^{-1} g^{-1}$)		
		CH_4+D_2	$C_2H_6+D_2$	CH_4+CD_4
MgO	700	35.5	4.7	21.0
CaO(I)	700	42.6	2.1	20.8
SrO	1000	17.3	1.8	34.0

[a] Reaction temperature, 300°C. [D]/[H] = 4.5.

This indicates that the methyl hydrogens are more labile than the methyne hydrogen to the exchange with D_2.

DISCUSSION

In the previous paper (*12*), it is suggested that two different types of sites exist on CaO(I) and BaO and that the appearance of these sites is dependent on the evacuation temperatures. One of them (Site I) is active only for the isomerization of butenes and the other (Site II) is active both for the isomerization and the exchange of butenes with D_2. The generation of Site II needs higher evacuation temperature than that of Site I. Site II is poisoned by O_2, while Site I is not. Two types of active sites may also exist on MgO and SrO.

The maxima in the activity for the CH_4–D_2 exchange with evacuation temperature are in a higher evacuation temperature range than those for the isomerization of 1-butene (*5*). In addition, the CH_4–D_2 exchange over BaO was almost entirely poisoned by the adsorption of O_2. Therefore, it is suggested that the active sites for the CH_4–D_2 exchange are Site II type.

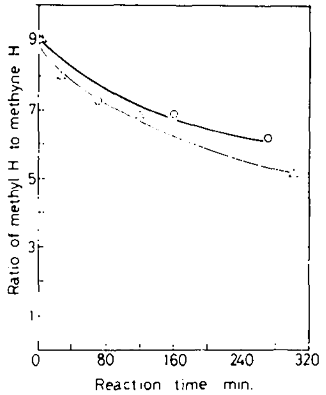

FIG. 4. Changes of the ratios of methyl H to methyne H of iso-C_4H_{10} with reaction time in the iso-C_4H_{10}–D_2 exchange over CaO(I) (○) and La_2O_3 (△). The CaO(I) and La_2O_3 were pretreated at 700 and 650°C, respectively.

The C–H bond energy for CH_4 is greater than for C_2H_6. If the reaction intermediates were radical and the slow step involves a homolytic cleavage of the C–H bond, C_2H_5 would undergo exchange faster than CH_4. The observed sequence was just the inverse. On the other hand, the pK_a value of CH_4, 40, is lower than that of C_2H_6, 42 (*13*). Should the reaction be initiated by the abstraction of an H^+ to form the carbanion, CH_4 would react faster than C_2H_6. This is the observed result. The greater exchangeability of a methyl hydrogen than a methyne hydrogen in the iso-C_4H_{10} also suggests that the intermediates are carbanionic character.

A similar rate constant for the CH_4–CD_4 scrambling to that for the CH_4–D_2 exchange and a fast equilibration of the H_2–D_2 imply that the slow step is either the abstraction of an H^+ from CH_4 to form

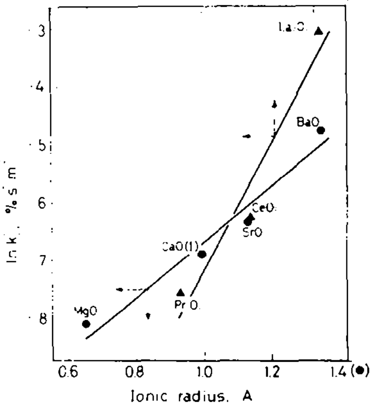

FIG. 5. Variations of activities with ionic radii. The value of k'_ϕ represents the activity on a unit surface area basis.

a carbanion or the addition of an H^+ to the carbanion to form CH_4. Since the multiplicity (M value) is close to unity, the desorption step of the adsorbed CH_4 must be fast.

In Fig. 5, logarithms of the maximum activities of each alkaline earth metal oxide per unit surface area are plotted against ionic radii of metal cations of the oxides. A linear relation was obtained. The basic strength is expected to increase as the ionic radius increases within a certain group. Although the numbers of active sites per unit surface area may be different for each oxide, the correlation suggests that the reaction rate increases with increase in the basic strength of the sites, which coincides with the idea that a slow step involves the abstraction of an H^+. The same relation between the activities and the ionic radii also holds for a series of the lanthanide oxides. In this figure, the ionic radius of Ce^{3+} is plotted instead of that of Ce^{4+}, because CeO_2 was reduced to Ce_2O_3 on evacuation at 700°C (*14*). Lanthanum oxide that had been properly pretreated exhibits high activity for the isomerization of butenes, and the reaction proceeds via carbanion (*15*). The reaction mechanism for the CH_4–D_4 exchange and the nature of active sites on La_2O_3 are considered to be same as those of alkaline earth metal oxides.

Although TiO_2, ZrO_2, ThO_2, and ZnO have a basic property on their surfaces and an ability to abstract H^+ from olefins, the strengths of their basic sites seem not to be sufficient to be acting as active sites for the CH_4–D_2 exchange at 300°C.

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