JOURNAL OF CATALYSIS **86**, 280–288 (1984)

Mechanism of H_2–D_2 Equilibration on Potassium–Graphite Intercalation Compounds

N. TOMOTSU, I. KOJIMA,[1] AND I. YASUMORI*

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguroku, Tokyo 152, and
**Department of Applied Chemistry, Kanagawa University, Rokkakubashi, Yokohama 221, Japan*

Received August 1, 1983; revised September 27, 1983

H_2–D_2 equilibration reaction was investigated on the lamellar graphite intercalation compounds, C_8K and $C_{24}K$. The catalytic activity of these compounds did not depend on the stage number which was a measure of the extent of potassium intercalation, but was concerned with the area of the surface parallel to the c axis of the host graphite crystallites. A computer analysis of the reaction-time course by the nonlinear least-square fitting method revealed that the reactions proceeded via the exchange between chemisorbed atoms and gaseous (or physisorbed) molecules. By combining these findings with the data of catalyst deactivation by O_2 or CO, the structure of active site and the catalytic behavior like that of electron donor–acceptor complexes were discussed.

INTRODUCTION

Lamellar graphite intercalation compounds, C_nM, form ordered sequence of graphite and intercalation layers (for a review see Ref. (*1*)). The extent of the intercalation is characterized by the stage number which describes the number of graphite layers between two successive intercalated layers. Recently, graphite–alkali metal compounds have been noted as synthetic metals because of their high electrical conductivities and superconductivities like those of transition metals (*1*). The unique geometric and electronic properties of the lamellar compounds are of great importance with regard to their chemical properties such as the interaction with gas molecules and/or catalyses. The catalytic activity of $C_{24}K$ for the H_2–D_2 equilibration was found by Watanabe *et al.* (*2*). They also examined the molecular-sieve-like behavior of $C_{24}K$ for hydrogen sorption where the total number of molecules sorbed at saturation was about twice of that of potassium atoms (*3*). This amount of adsorbed hydrogen is compatible with that on $LaNi_5$. It is of interest that these chemical properties were not possessed by the individual components. Considerable efforts have been devoted to understanding the physical properties of alkali-metal graphite intercalation compounds, so far, however unsatisfactory in the field of their chemical and catalytic applications. Particularly, the role of the intercalated alkali metals in the chemical reactivity and the catalytic activity of the compounds still remains to be unraveled.

In the present study, H_2–D_2 equilibration reaction on the C_nK compounds was investigated. Attention was focused on the mechanism of the reaction and also on the structure of active sites responsible for the catalysis. With the aid of a computer, the reaction mechanism and the marked isotope effect were examined by simulating the reaction-time course. Further, the structure of site for hydrogen adsorption involved in the reaction process was discussed on the basis of the results of catalytic deactivation by poisoning and of the dependence of catalytic activity on crystal shape.

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[1] To whom correspondence should be addressed.

0021-9517/84 $3.00

TABLE 1

Structural Properties of Host Graphites and Potassium Intercalation Compounds

	G1	G2	C_8K[G1]	$C_{24}K$[G1]	C_8K[G2]
I_c (A)	3.35	3.35	5.35	11.80	5.35
d_{hkl} (A)					
(002)	187	192			
(004)	175	170			
(110)	389	239			
BET area (m^2 g^{-1})					
S	7.0	4.3	8.0	7.5	5.2
$S1$	0.8	0.6			
$S2$	6.2	3.7			

EXPERIMENTAL

The C_nK compounds were synthesized using the dual furnace method which requires the independent temperature control of a branching vessel containing graphite and potassium separately. C_8K (bronze in color) and $C_{24}K$ (blue) were prepared under different conditions as those used previously (*4*). The two kinds of used pure graphite, G2800 and G2200, were obtained from Toyo Carbon Company, they were graphitized at 2800 and 2200°C, respectively, and their code names were abbreviated as G1 and G2 hereafter. The intercalation compounds thus prepared were sealed in a thin Pyrex glass tube for use in the measurements of catalytic activity and gas adsorption or in a thin quartz glass capillary for use in X-ray diffraction study. The structural properties of the used graphites and the C_nK compounds are listed in Table 1. The identity periods, I_c, measured by X-ray diffraction for the graphites and the intercalation compounds agreed well with the reported ones (*4*). The surface area of the compound, S, was determined by the BET method using Kr adsorption at 78 K. The average size of the graphite crystallite was estimated by the thickness along the [*hkl*] direction, d_{hkl}, which was determined from the full width at half maximum (FWHM) of (*hkl*) diffraction line (*5*). By assuming that the shape of graphite crystallite is a hexagonal column, the total surface area, S, was divided into the side surface area of the column (S_1) and the area parallel to the carbon-network plane (S_2).

The H_2–D_2 equilibration reaction was carried out in a conventional closed circulation system of 410 ml in volume. The sealed glass tube containing the intercalation compound, C_nK, was put in the reaction cell and unsealed with a breaker operated by a magnet outside. The fractions of hydrogen isotopes in the reactant were determined by using a gas chromatograph connected to the reaction system (*6*). The reaction was studied in a pressure range of 5–50 Torr (1 Torr = 133.3 Pa) at temperatures between 78 and 335 K.

RESULTS

H_2–D_2 Equilibration

The equimolar mixture of H_2 and D_2 was contacted with the fresh catalyst at temperatures in a range of 253–324 K and the increase of HD fraction in the gas phase was followed with reaction time. The rate of HD formation during the equilibration could be well represented by

$$v_e = \frac{1}{t} \ln \frac{X_e - X_0}{X_e - X_t} \qquad (1)$$

where X_0, X_t, and X_e denote, respectively, the fractions of HD at the beginning of reaction, time t, and at equilibrium. Accordingly, the specific activity for HD formation, v_m (Torr s^{-1} g^{-1}) was given by

$$v_m = Pv_e/w_G \qquad (2)$$

where P is the total pressure of reactant and w_G is the net weight of the graphite contained in the catalyst.

Figure 1 shows the dependence of the specific activity, v_m, on the reaction temperature when the total pressure was kept constant at 8 Torr. The C_8K and $C_{24}K$ compounds prepared from G1 exhibited almost the same specific activity, whereas the C_8K derived from G2 gave a lower v_m value. The ratio of v_m of $C_{8,24}K$[G1] to that of C_8K[G2]

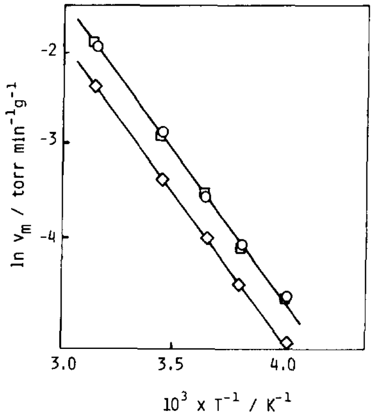


FIG. 1. Temperature dependence of v_m for H_2–D_2 equilibration. (○) C_8K[G1], (□) $C_{24}K$[G1], and (◇) C_8K[G2]. Solid lines are calculated by applying kinetic parameters listed in Table 2.

was constant at about 1.3 over the temperature range studied. The observed values of apparent activation energy of the equilibration were estimated to be 6.5 ± 0.3 kcal mol^{-1} for these catalysts.

The total pressure dependence of reaction rate was examined in a range of 6–40 Torr. The reaction order with respect to the total pressure was 0.8 ± 0.1 at 291 K. The dependence of the rate of HD formation on the partial pressures, P_H and P_D, was also examined at 291 and 253 K. The results are shown in Fig. 2 for C_8K[G1] and $C_{24}K$[G1]. A marked isotope effect was observed; the reaction orders with respect to P_H and P_D were, respectively, 0.2 ± 0.1 and 0.8 ± 0.1 at 291 K, whereas 0.0 ± 0.1 and 1.0 ± 0.1 at 253 K.

Reaction of Preadsorbed Species with Gaseous Molecules

In order to obtain more detailed information on the mechanism of the H_2–D_2 equilibration, the exchange reaction between the preadsorbed hydrogen and the gaseous deuterium and that between the preadsorbed deuterium and the gaseous hydrogen were investigated. The catalyst was, at first, exposed to H_2 (or D_2) of 10 Torr. After evacuation, the molecule in gas phase was quickly replaced by D_2 (or H_2). The amount of preadsorbed hydrogen was estimated from a study using a separated static system. Figures 3 and 4 show the behavior of hydrogen species during the course of these exchange reactions at 291 K. In both the cases, the rate of HD formation was appreciable at the beginning stage of reactions and, further, a small amount of the preadsorbed species itself desorbed into the gas phase as the reactions proceeded. It is noted that the HD formation was faster in the H (preadsorbed) + D_2 system than in the D (preadsorbed) + H_2 system. At a lower reaction temperature, 253 K, the desorption of the preadsorbed species became negligible during the course of reaction.

Poisoning of the Catalyst

Carbon monoxide and oxygen were found to adsorb strongly on the catalysts and to depress their activities. Thus, the

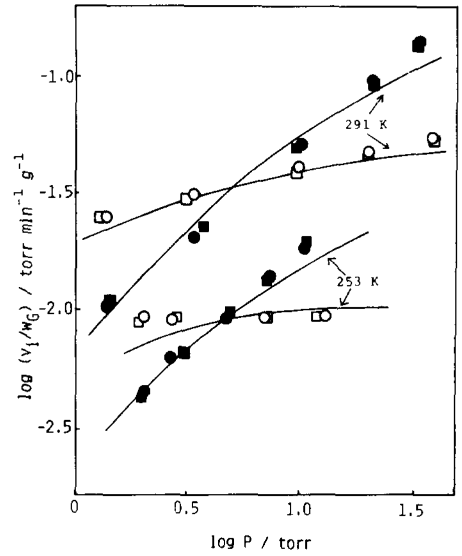


FIG. 2. Partial pressure dependence of initial rate at 291 and 253 K. v_i/w_G is the initial rate of HD formation per unit weight of graphite, and P is the initial pressure of H_2 or D_2. Open symbols exhibit the dependency on P_H, and shaded on P_D. (○) and (●) are taken on C_8K[G1], (□) and (■) are on $C_{24}K$[G1]. Initial pressure of D_2 (H_2) is chosen constant at 5 Torr for the experiments of open (shaded) symbols. Solid lines are calculated as those in Fig. 1.

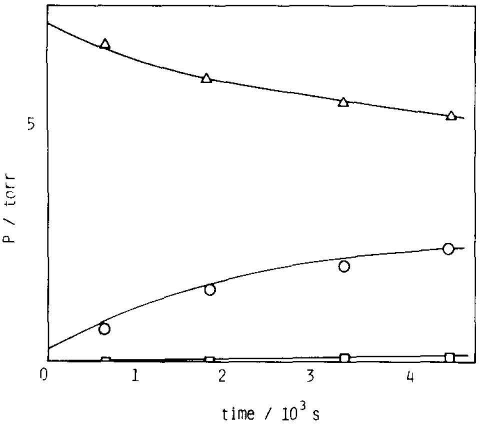


FIG. 3. Exchange reaction between preadsorbed hydrogen atom and D_2 at 291 K. (□) H_2, (○) HD, and (△) D_2. Solid lines are calculated as those in Fig. 1.

decreases in the activities of partially poisoned catalysts by these admolecules were examined to obtain information on the distribution and the structure of active sites. The catalysts were cooled at 78 K prior to the introduction of poisons, because the adsorption of these molecules on the C_nK compounds was exothermic. The catalytic activity for the H_2–D_2 equilibration was then examined by using the equimolar mixture of H_2 and D_2, 6 Torr in total pressure, at 273 K. The decrease of the activities as a function of the amounts of the adsorbed poisons are shown in Fig. 5. The catalytic activities were completely destroyed when the ratio of the amount of added O_2 molecules to that of contained potassium atoms in the catalyst reaches to unity. It is noted that this phenomenon is independent both of the stage number and of the kind of the host graphite. As for the poisoning by CO, however, the ratio of the amount of adsorbed CO molecules which destroyed the activities that of potassium atoms was 0.1 for the C_8K[G1] and $C_{24}K$[G2] catalysts. The X-ray diffraction measurement of the poisoned catalyst showed that the C_nK compounds poisoned with carbon monoxide retained its original structure, whereas those exposed to oxygen changed their structures to a graphite-like one.

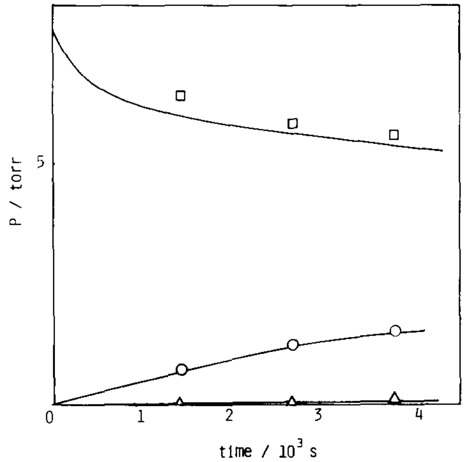


FIG. 4. Exchange reaction between preadsorbed D and H_2 at 291 K. (□) H_2, (○) HD, and (△) D_2. Solid lines are calculated as those in Fig. 1.

DISCUSSION

Reaction Mechanism

On the basis of the present kinetic data, we first discuss the mechanism of the H_2–

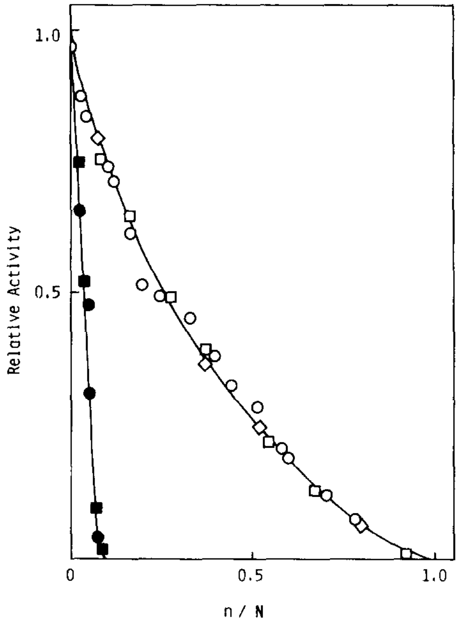


FIG. 5. Poisoning effect by O_2 (open symbols) and CO (shaded) adsorption. *n*/*N* is the ratio of the number of added poison to the number of potassium in catalyst. (○) and (●) C_8K[G1]; (□) and (■) $C_{24}K$[G1]; and (◇) C_8K[G2].

D_2 equilibration on the C_nK compounds. The marked isotope effects observed in the present study exclude the possibility of analysis by using the conventional approximations of rate-determining step and of steady state (*7*). Kiyomiya *et al.* (*8*) applied a least-square fitting method to the simulation of the H_2–D_2 equilibration on Cu surface to obtain optimum kinetic parameters such as the rate constants and the activation energies for adsorption and desorption. The parameters thus obtained were proved to be useful in understanding the feature of the overall reaction. Here, we extended the application of the method to the present nonlinear system which requires the use of more generalized technique, and analyzed the time course of H_2–D_2 equilibration on the C_nK compounds.

Two detailed mechanisms have been assumed to hold for the catalytic H_2–D_2 equilibration; one of them is the Rideal–Eley (RE) mechanism which involves a surface reaction between the chemisorbed hydrogen atom and the gaseous (or physically adsorbed) molecule (*9*). This mechanism was proposed for the equilibration at rather low temperatures on Pt (77–200 K) (*10*), Ni (77–300 K) (*11*), and MgO (78–113 K) (*12*). The other is the Bonhoeffer–Farkas (BF) mechanism (*13*) which consists of the reactions between adatoms and becomes predominant at higher temperatures on Pt (above 200 K) (*10*), Ni (330–440 K) (*11*), and Cu (313-363 K) (*8*). Accordingly, we took in the present study a generalized reaction scheme which involves both the BE and RE mechanisms as follows:

$$\mathrm{H_2} + 2s \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{H}s \qquad \text{(I)}$$

$$\mathrm{HD} + 2s \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{H}s + \mathrm{D}s \qquad \text{(II)}$$

$$\mathrm{D_2} + 2s \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2\mathrm{D}s \qquad \text{(III)}$$

$$\mathrm{H_2} + \mathrm{D}s + s \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{HD} + \mathrm{H}s + s \qquad \text{(IV)}$$

$$\mathrm{D_2} + \mathrm{H}s + s \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{HD} + \mathrm{D}s + s, \qquad \text{(V)}$$

where s denotes an adsorption site, and k_i and k_{-i} are, respectively, the forward and backward rate constants in the elementary step i. It is noted that the steps (IV) and (V) of the RE mechanism involve a vacant site adjacent to the site chemisorbed hydrogen atom. The material balance in the reaction system leads to a set of simultaneous differential equations, as follows:

$$\begin{aligned} KV\, dP_{\mathrm{H}}/dt = {} & -k_1 P_{\mathrm{H}} n_{\mathrm{v}}^2 + k_{-1} n_{\mathrm{H}}^2 \\ & - k_4 P_{\mathrm{H}} n_{\mathrm{D}} n_{\mathrm{v}} + k_{-4} P_{\mathrm{HD}} n_{\mathrm{H}} n_{\mathrm{v}} \qquad \text{(VI)} \end{aligned}$$

$$\begin{aligned} KV\, dP_{\mathrm{HD}}/dt = {} & -k_2 P_{\mathrm{HD}} n_{\mathrm{v}}^2 + k_{-2} n_{\mathrm{H}} n_{\mathrm{D}} \\ & + k_4 P_{\mathrm{H}} n_{\mathrm{D}} n_{\mathrm{v}} - k_{-4} P_{\mathrm{HD}} n_{\mathrm{H}} n_{\mathrm{v}} \\ & + k_5 P_{\mathrm{D}} n_{\mathrm{H}} n_{\mathrm{v}} - k_{-5} P_{\mathrm{HD}} n_{\mathrm{D}} n_{\mathrm{v}} \qquad \text{(VII)} \end{aligned}$$

$$\begin{aligned} KV\, dP_{\mathrm{D}}/dt = {} & -k_3 P_{\mathrm{D}} n_{\mathrm{v}}^2 + k_{-3} n_{\mathrm{D}}^2 \\ & - k_5 P_{\mathrm{D}} n_{\mathrm{H}} n_{\mathrm{v}} + k_{-5} P_{\mathrm{HD}} n_{\mathrm{D}} n_{\mathrm{v}}, \qquad \text{(VIII)} \end{aligned}$$

where V is the volume of the system, P_{H}, P_{HD}, and P_{D} are the partial pressures of H_2, HD, and D_2, respectively, and n_{H}, n_{D}, and n_{v} are the number of adsorbed H atoms, D atoms, and vacant sites, respectively, and K is a constant which converts PV value at the reaction temperature to the number of molecules. This set of equations was solved by a computer-aided calculation with the Runge–Kutta–Gill method. In the calculation, we used 90 data on the changes in partial pressures of gas-phase constituents during the course of reactions which did not satisfy the steady state conditions. A best fit between the observed and computed pressure values was obtained in a self-consistent manner by using nonlinear least-square method. In order to reduce the calculational complexity, the relations $k_1/k_{-1} = k_2/k_{-2} = k_3/k_{-3}$, $k_4 = 2k_{-4}$, and $k_5 = 2k_{-5}$ were assumed at the early stage of iteration. At the last stages, the former assumption was removed, then a satisfactory agreement was attained. The optimum rate constants thus determined are listed in Table 2. All of the solid lines shown in Figs. 1–4 were calculated by applying the rate constants obtained as stated above, and further the typical example of reaction time course was shown in Fig. 6. The activation energy

TABLE 2

Kinetic Parameters of Elementary Steps Optimized for H_2–D_2 Equilibration

Elementary step (i)	Rate constant (k_i)		Activation energy (E_i)[a] (kcal mol^{-1})	Frequency factor (ν_i)
	253 K	291 K		
1	1.09×10^{-25} [a]	5.12×10^{-25} [a]	6.0	1.5×10^{-20} [a]
2	6.24×10^{-26} [a]	3.80×10^{-25} [a]	7.0	6.4×10^{-20} [a]
3	1.16×10^{-27} [a]	1.16×10^{-26} [a]	8.9	5.2×10^{-20} [a]
−1	8.08×10^{-30} [b]	8.40×10^{-28} [b]	17.9	2.2×10^{-14} [b]
−2	4.64×10^{-30} [b]	5.32×10^{-28} [b]	18.3	2.7×10^{-14} [b]
−3	1.35×10^{-30} [b]	1.82×10^{-28} [b]	18.9	2.7×10^{-14} [b]
4	2.46×10^{-25} [a]	9.84×10^{-25} [a]	5.3	1.0×10^{-20} [a]
5	5.48×10^{-26} [a]	2.19×10^{-25} [a]	5.3	2.2×10^{-21} [a]

[a] Molecules g s^{-1} Torr^{-1} sites^{-2}.

[b] Molecules g s^{-1} sites^{-2}.

(E_i) and the frequency factor (ν_i) of the elementary reaction i were estimated from the Arrhenius equation,

$$k_i = \nu_i \exp(-E_i/RT), \qquad (3)$$

and given in Table 2. The small deviation of simulated curves from the observed values is mainly attributed to the use of simple dissociative adsorption of Langmuir type in the calculation and the neglect of surface heterogeneity.

It is easily seen that in the ordinary RE scheme consisting of elementary steps

$$H_2 + Ds \rightleftarrows HD + Hs \qquad (IV)'$$

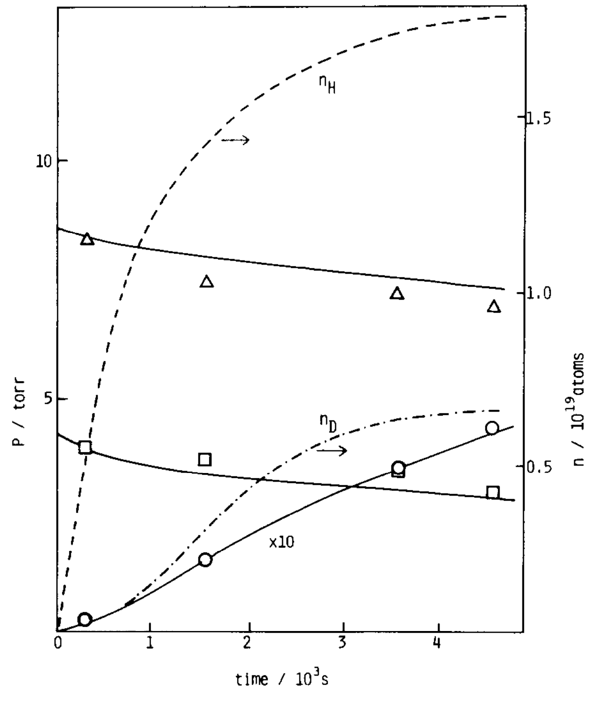


FIG. 6. An example of best fit for H_2–D_2 equilibration. (□) H_2, (○) HD, and (△) D_2. Dashed and dot-dashed curves are the numbers of adsorbed H and D atoms, respectively.

and

$$D_2 + Hs \rightleftharpoons HD + Ds, \qquad (V)'$$

the reaction order with respect to the total pressure is 1.0 or higher (*14*). However, since the mechanism proposed here involves a vacant site in the reaction steps (VI) and (V) and the number of the vacant site decreases as the pressure increases, the reaction order would be smaller than 1.0 in the case of stronger adsorption. The observed value in the present study, 0.8 ± 0.1, conforms with this trend. In fact, the RE scheme which consist of the steps (IV)′ and (V)′ was examined, but any effort to obtain a better fit was unsuccessful.

A preliminary thermal desorption study (unpublished information) showed that the spectrum of hydrogen desorption consisted of two peaks which appeared in the temperature range of 270–330 and above 350 K. The former peak obeyed the law of second-order desorption, and thus arose from the combination of dissociatively adsorbed hydrogen atoms. The activation energies of desorption of this low temperature peak were 18.2 and 20.3 kcal mol^{-1} for H_2 and D_2, respectively. These values are very close to those obtained in the present kinetic analysis.

From the present results, we can outline the kinetic feature of the equilibration on the C_nK compounds; the dissociative adsorption of hydrogen molecule is rather fast, whereas the desorption via atomic recombination is slow because of the fairly high activation energy of desorption. Accordingly, the equilibration proceeds mainly by the RE mechanism, and the contribution of the BF mechanism is expected to be less than 0.1% under the present experimental conditions. The marked isotope effect on the reaction orders which were zeroth and first for H_2 and D_2, respectively, at 253 K can be explained by the facts that the surface is mainly covered with adsorbed hydrogen atoms and thus the formation of HD occurred via the step (V) in the reaction scheme.

Structure of Active Sites

One of the interesting findings in the present work is that the catalytic activities of the C_nK compounds do not depend on the stage number but depend on the shape of the host graphite crystallite. The investigation of the surface poisoned by O_2 or CO with careful quantitative control is very useful to elucidate the structure of catalytically active sites. It was found that an O_2 molecule bonded with a potassium atom, perhaps in the form of $K^{\delta+} - O_2^{\delta-}$, and completely depressed the catalytic activity when the amount of added O_2 became equivalent to that of potassium in the catalyst. The X-ray diffraction measurement of C_nK compounds exposed to O_2 shows that the structural deformation occurred due to withdrawing of potassium atoms intercalated between the graphite layers. On the other hand, the introduction of CO molecule did not cause such structural change, but the catalytic activity was destroyed at the CO/K ratio of 0.1, which value was one-tenth of the required amount of O_2 poison. This phenomenon indicates that CO molecules selectively cover the catalytic active sites on surface. As shown in the previous section, the initiation of the H_2–D_2 equilibration is the activated dissociation of H–H and D–D bonds. Therefore, CO molecules may react only with potassium atoms exposed to surface, and thus inhibit the dissociative adsorption of hydrogen.

Of particular interest is that the ratio of the activity of the G1-catalyst to that of the G2-catalyst was about 1.3 and that this value is very close to the ratio of S1's estimated for the host graphite crystallites of the respective catalysts. These findings suggest that the reaction sites are present on the carbon chain of the outermost side plane. Figure 7 shows the structure of C_8K and $C_{24}K$ (*15*). The nearly identical behavior of deactivation as a function of CO/K ratio about C_8K and $C_{24}K$ suggest that the density of K atoms on C_8K surface is three times higher than that on $C_{24}K$ surface.

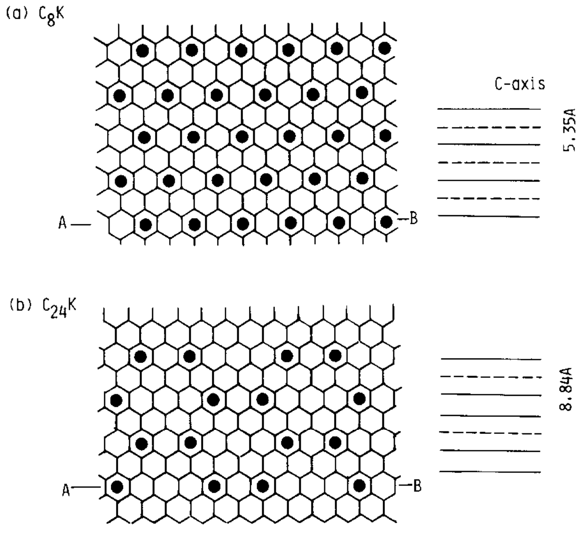
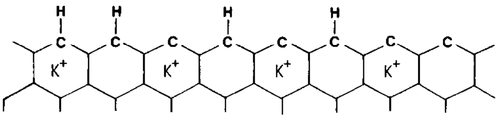


FIG. 7. Structures of (a) C_8K and (b) $C_{24}K$.

Thus, it is likely that the surface exposed at the section A–B and its equivalent as shown in Fig. 7 are mainly responsible for the catalysis.

Such catalytic active surfaces on the C_nK compounds are similar to those on the electron donor–acceptor (EDA) catalysts; for example, Tamaru and co-workers (*16*) found that the dissociative chemisorption of hydrogen slowly occurred on the stoichiometric complex of anthracene with sodium and that the chemisorbed hydrogen atoms could exchange with the gaseous deuterium molecules. The activity of the present C_nK compounds is much higher than that of the EDA complex, which would be attributed to the higher density of the chemisorption sites. A possible structure of active site is shown below.



All of the protruded carbon atoms on this surface would be equivalent as the chemisorption site of hydrogen atom.

It is known that the absorption of hydrogen by liquid potassium begins at about 200°C and that graphite does not react with hydrogen under ordinary conditions (*17*). Whereas, the dissociative chemisorption of hydrogen on the C_nK compounds occurs even at room temperature. It is certain that the potassium and carbon layers work cooperatively for the activated chemisorption of hydrogen and H_2–D_2 equilibration. The bonding energy of hydrogen atom on the C_nK compounds is estimated at about 60 kcal mol^{-1} from the activation energy values given in Table 2. This value is lower than the strength of single C–H bond, 98 kcal mol^{-1} (*18*). Such a difference in bond energy may be attributed to the change of electronic state of carbon atoms with excess electrons transferred from potassium atoms.

ACKNOWLEDGMENTS

The authors (I. K. and I. Y.) thank the Ministry of Education, Science, and Culture of Japan for the Grants-in-Aid (57740231 and 57112004) for Scientific Research.

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