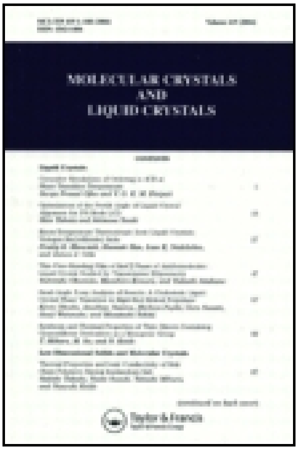

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Hydrogen Adsorption of Alkali Metal Complexes of Polycyclic Aromatic Hydrocarbon and Graphite, and Their Solid State Properties

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HYDROGEN ADSORPTION OF ALKALI METAL COMPLEXES OF POLYCYCLIC AROMATIC HYDROCARBON AND GRAPHITE, AND THEIR SOLID STATE PROPERTIES

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Abstract The hydrogen adsorption in alkali metal complexes of graphite and triphenylene has been investigated by means of ESR and electrical resistivity under hydrogen atmosphere. In the first stage graphite compound C_8Rb, hydrogen molecules are dissociated into atoms which are stabilized in graphite gaps. C_8K has a two stage hydrogen adsorption process: dissociation and charge transfer. For C_8Cs, the catalytic activity for hydrogen comes from the surface. The second stage compounds $C_{24}M$ (M=K, Rb, and Cs) show weaker activities for hydrogen than the first stage ones. Triphenylene-potassium complex has a two stage process for hydrogen adsorption.

INTRODUCTION

Polycyclic aromatic hydrocarbons form charge transfer complexes of alkali metals with various compositions. The complexes of graphite, which is an extreme of polycyclic aromatic hydrocarbons, are called graphite-alkali metal intercalation compounds. It is known that the complexes have catalytic activities for hydrogen, i.e. ortho-para-hydrogen conversion and the hydrogen-deuterium exchange reaction.[1-5] The physisorption of hydrogen takes place at low temperatures below about 200K, which is correlated with ortho-para-hydrogen conversion, while the chemisorption takes place at higher temperatures, and it is examined by hydrogen-deuterium exchange reaction. The activities for hydrogen in these aromatic hydrocarbon complexes have not been well studied, compared with those in transition and rare earth metals. The present authors have been investigating the chemisorption of hydrogen and the static and dynamic behavior of the absorbed hydrogen in the polycyclic aromatic hydrocarbon-alkali metal complexes.[6-8] In this paper, the authors present the chemisorption mechanism of hydrogen in graphite-alkali metal intercalation compounds C_nM (M=K, Rb and Cs, n=8,24) and triphenylene-potassium complexes(TpK_x) studied by means of ESR and electrical conductivity under hydrogen atmosphere.

EXPERIMENTAL

Graphite-alkali metal intercalation compounds C_nM (M=K, Rb, and Cs) were prepared with a double furnace method presented by Nixon and Parry.[9] The first stage compounds C_8M have alkali metal arrays in every graphite gap, while the second stage ones $C_{24}M$ have arrays in every two gaps. The first and second stage compounds with potassium, rubidium and cesium were used in this experiment. Triphenylene-potassium complexes TpK_x were prepared as follows. Triphenylene, purified through sublimation, was dissolved in distilled and deoxidized tetrahydrofuran in a vacuum glass tube. After distilled potassium metal was introduced in the tetrahydrofuran solution of triphenylene, the solution was stirred for about three hours. The powdered samples were obtained through the evaporation of the solvent. The composition of the complex was determined to be $TpK_{1.46}$ by chemical analysis.

The hydrogen gas was purified through a Pd-Ag thimble and was introduced to samples in the vacuum glass tube.

The ESR measurements were carried out using a conventional X-band spectrometer to obtain the time dependence of the spectra just after introduction of hydrogen. Temperature dependence of ESR spectra was measured with a continuous-flow liqiud helium cryostat in the temperature range between liqiud helium and room temperatures.

The electrical resistivity was measured by means of a two or a four probe method under hydrogen atmosphere.

RESULTS

All of the graphite-alkali metal intercalation compounds are metallic and show dysonian ESR signals with asymmetry,[10] which results from the spins of conduction electrons within the skin depth.

The time dependence of the ESR signal under 1 atm hydrogen gas at room temperature is shown for C_8K in Fig.1. The intensity I(t) steeply increases just after introduction of hydrogen, reaches a maximum of $I(t)/I(0)\sim1.19$ at around $t\sim14$ min, and then decreases gradually to a steady state value which is about 48% of the initial value at 150h. The maximum value varied between 1.1 and 1.6 times of I(0) depending on samples. The resistivity increased to about twice the initial one in the steady state around 50 h under hydrogen atmosphere. The color of C_8K changed from gold to blue during hydrogen absorption.

Figure 2 shows the ESR signal of the hydrogen-absorbed C_8Rb at room temperature as well as that of the original C_8Rb. For the original C_8Rb in vacuo, the line shape is

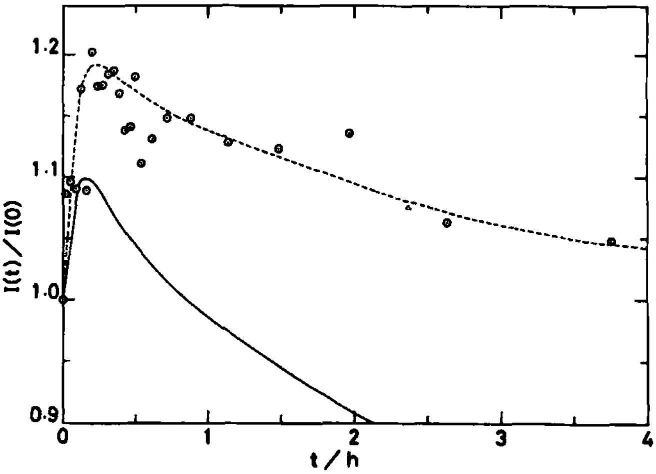

FIGURE 1. The time dependence of the ESR intensity for C_8K after introduction of hydrogen at T=293 K and P_{H_2}=9.0 x 10^4 Pa. The solid line denotes the intensity corrected for the skin depth.

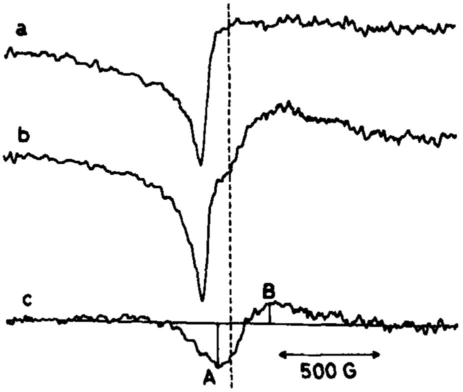

FIGURE 2. ESR signal of C_8Rb and the hydrogen-absorbed C_8Rb at 297 K, (a) C_8Rb signal, (b) the hydrogen-absorbed C_8Rb signal at 36 min after introduction of hydrogen (P_{H_2}= 8.9x10^4 Pa), (c) the difference signal (b)-(a).

asymmetric to a great degree, which results from the fast diffusion of the conduction electrons.[10] The center of the signal (g=2.072) deviates from the position of free electron spin (g_o=2.0023), because of the spin-orbit interaction due to heavy Rb atoms. When hydrogen is introduced, no change is observed for about 10 min and then the line shape appears to be changed in such manner that another broad signal around g_o is superposed upon the initial signal of the conduction electron spins. After a steady state is achieved in about 40 min, the change becomes small. In order to extract the new signal generated under hydrogen atmosphere, the difference signal is obtained by means of the subtraction of the signal of the original C_8Rb from that of the hydrogen-absorbed C_8Rb, as shown in Fig.2(c). The temperature dependence of the difference signal was measured between liquid helium and room temperatures, and the intensity was found to obey the Curie-Weiss law. X-ray diffraction proved that the lattice spacing of C_8Rb was not changed during the hydrogen absorption. It is an interesting feature that the hydrogen absorption was found to leave the color of C_8Rb unchanged in contrast with the case of C_8K. The resistivity increased by about 13% during the hydrogen absorption at room temperature.

For C_8Cs, the ESR signal and the resistivity were not changed under hydrogen atmosphere.

In the case of the second stage compound, $C_{24}K$, as hydrogen was introduced, the ESR intensity decreased monotonically depending on time and reached a steady state in about 150 h. The intensity at the steady state is about 61% of the initial value in vacuo. For $C_{24}Rb$, the intensity of the signal was very slightly lowered with time under a hydrogen atmosphere. The ESR signal of $C_{24}Cs$ was not changed under a hydrogen atmosphere. The changes in the ESR signals of the second stage compounds were rather weaker than those of the first stage ones.

Figure 3 shows the time dependence of the conductivity

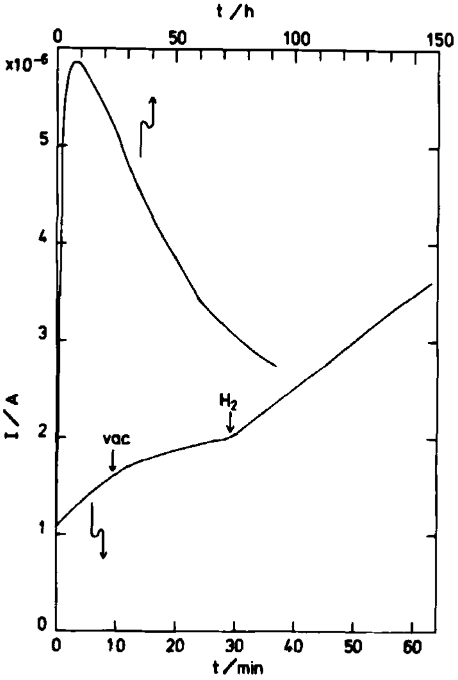

FIGURE 3. The time dependence of the current for the conductivity measurement of a $TpK_{1.46}$ complex film at 295 K after introduction of 1 atm hydrogen gas. The applied voltage is 1 V. The arrows shown by vac and H_2 mean the times of the evacuation and the reintroduction of hydrogen, respectively.

of $TpK_{1.46}$ just after introduction of 1 atm hydrogen gas at room temperature. The conductivity has a steep increase until about 8 h and then it decreases gradually. Thus, we find two stages for the conductivity change. As shown in Fig.3, it becomes clear that the ejection of hydrogen cannot cause the conductivity to recover. This fact suggests that the conductivity change due to the hydrogen absorption takes place irreversibly at room temperature.

Figure 4 shows the ESR intensity as a fuction of time

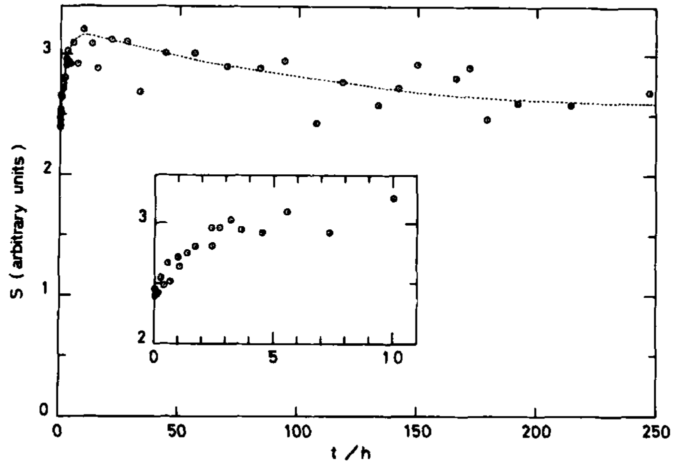

FIGURE 4. The time dependence of the ESR intensity at 297 K for $TpK_{1.46}$ after introduction of hydrogen.

just after introduction of 1 atm hydrogen gas. The time dependence of the intensity has two stages. At the first stage, the intensity increases abruptly and has a maximum at about 10 h where the increment reaches about 32%, and it is gradually lowered tending to reach a steady state value at the second stage. The intensity at 250 h after introduction of hydrogen is about 1.1 times as large as the initial one.

DISCUSSION

Graphite-alkali metal intercalation compounds

In the case of the first stage compound C_8Rb, the new ESR signal generated under hydrogen atmosphere at room temperature shows the following features. The line width is about 200G and the g-value is between 2.001 and 2.003, which is around the g-value of free electron spins, while the signal of conduction electron spins deviates from the position of the free electron spins. This means that the

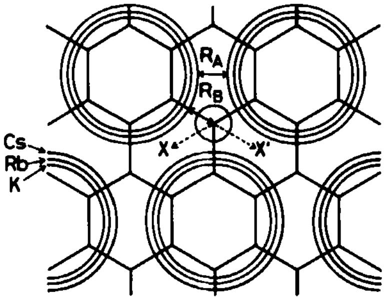

FIGURE 5. The structure of the first stage compounds C_8M. The radii of alkali metal atoms are drawn for the valence state $M^{+0.5}$. The small circle shows a hydrogen neutral atom with the diameter of 1.06Å. R_A is 1.57Å, 1.28Å or 0.88Å, and R_B 1.16Å, 1.02Å or 0.82Å for K, Rb or Cs, respectively.

spins observed in the new signal are far from the rubidium atoms with large spin-orbit interaction. The asymmetry parameter A/B is about 2. Following the ESR theory of metals,[10] this value of A/B suggests that the spins are localized in the metallic compounds where the internal field is fluctuating. The Curie-Weiss behavior of the signal intensity supports the localization of the spins. It is known that the H-D exchange reaction takes place at room temperature in/on the graphite-alkali metal intercalation compounds through the dissociation of hydrogen molecules. Therefore, it is supposed that dissociated hydrogen atoms with localized spins are generated during the hydrogen absorption of C_8Rb. Figure 5 shows the structure of the first stage graphite-alkali metal intercalation compounds. The alkali metal atoms with partial charge of +0.5 form a triangular lattice in the gaps of graphite layers. The number of interstitial sites among alkali metal atoms is twice the number of alkali metal atoms. Hydrogen atoms with 1.06Å diameter can be easily accommodated in these interstitial sites of C_8Rb as shown in Fig.5. The number of the absorbed hydrogen atoms in C_8Rb is estimated, comparing the ESR signal intensity of hydrogen spins to that of the conduction electron spins that show Pauli paramagnetism. Using the density of states at the Fermi level $N(E_F)=0.55/eV$ per C atom,[11] we estimate the content of the absorbed hydrogen as $C_8RbH_{0.3}$.

In the case of C_8K, we have a two stage hydrogen absorption process as shown in Fig.3. In the first stage of hydrogen absorption, the enhancement of the ESR signal intensity is deduced to be enhanced by the generation of dissociated hydrogen atoms with localized spins. In the second stage, the intensity is decreased. The ESR intensity of the conduction electron spins is proportional to the density of states at the Fermi level $N(E_F)$ because of Pauli paramagnetism. Ionization potentials of C_8K and hydrogen are 3.3[12] and 13.6eV, respectively. This will cause the charge transfer from C_8K to hydrogen. The theoretical study suggests that the charge transfer results in the decrease of $N(E_F)$.[13] Therefore, in the second stage of hydrogen absorption, hydride ion H^- is stabilized in the gaps of graphite layers through the charge transfer from C_8K to hydrogen. Hydride ion, 3.06Å in diameter, is too large to be accommodated in the interstitial sites of the first stage structure for C_8K as shown in Fig.5. Thus, in order to accommodate H^-, the structure must be changed. Meanwhile, the metal-metal distance in the first stage graphite-alkali metal intercalation compounds is 4.92Å and larger than the distances in the pure metals. For rubidium, the distance increases by 14% through intercalation, while, for potassium, it increases by 21%. The Debye temperature of C_8K is lower than that of C_8Rb.[11] The triangular lattice of potassium atoms in the graphite gaps is weaker than that of rubidium atoms.

Therefore, the hydrogen absorption induces the structure change through the displacement of potassium atoms which results in accommodating large hydride ions.

For C_8Cs, there are no changes in ESR signal and resistivity under hydrogen atmosphere, though we have the H-D exchange reaction. This finding suggests the catalytic activity of C_8Cs is due to the surface properties. Small volume of the interstitial site among Cs atoms, as shown in Fig.5, may inhibit the activity inside C_8Cs.

In the case of the second stage compound $C_{24}K$, the decrease of the ESR intensity during hydrogen absorption is considered to relate to the generation of hydride ion H^- through the charge transfer from $C_{24}K$ to hydrogen. At room temperature, alkali metals are in liquid state in the two dimensional graphite gaps. Moreover, the structure of the second stage compounds in which the density of alkali metal atoms is 2/3 of that of the first stage compounds is favorable for accommodation of large hydride ions. This might cause the absence of the stability of dissociated hydrogen atoms in the gaps of graphite layers. $C_{24}Rb$ behaves like $C_{24}K$ under hydrogen atmosphere, but the activity of $C_{24}Rb$ is much weaker than that of $C_{24}K$. The ESR signal of $C_{24}Cs$ is not changed by introduction of hydrogen gas. The activity of $C_{24}Cs$ is considered to be due to the surface properties.

Triphenylene-potassium complex

$TpK_{1.46}$ shows a two stage hydrogen absorption as shown in Figs.3 and 4, similar to the graphite-potassium intercalation compound C_8K. In the first stage of hydrogen absorption, the conductivity and the spin concentration are enhanced, while the both decrease as a function of time in the second stage. The H-D exchange reaction of triphenylene complex also has a two stage behavior depending on time.[3] The reaction is fast in the first stage and slow in the second stage. The generation of dissociated hydrogen atoms will contribute to the enhancement of the spin concentration as the case of C_8K. The fast reaction is deduced to come from the presence of the dissociated hydrogen atoms. The formation of hydride ion H^- through the charge transfer from $TpK_{1.46}$ to hydrogen depresses the spin concentration. The reduction of the dissociated hydrogen atoms makes the H-D exchange reaction slow in the second stage of hydrogen absorption.

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