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OLIGOMERIZATION OF THE ORGANIC LAYER IN THE SYSTEM GRAPHITE-Cs-ETHYLENE

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Abstract The peculiar behaviour of the system CsC_{24} - ethylene, is the ability for ethylene molecules to be oligomerized inside the host material, depending on the temperature. At low temperature, reversible intercalation occurs in two steps depending on the gas pressure, forming respectively a second stage ternary and a first stage ternary, whereas at temperature higher than ~250 K, only the second stage ternary is obtained and the reaction remains irreversible. By calorimetric measurement in the range 288 K to 308 K, two peaks were identified, corresponding for the first one to the heat of intercalation, and for the second one, to the oligomerization process. After exposure in air, a part of cesium is oxidised, but the ternary remains intercalated.

INTRODUCTION

Alkali metal binary graphite intercalation compounds are able to react with various organic molecules. The reaction with alkali metal graphitides is reversible for non-polar molecules, such as H_2, N_2, CH_4, rare gases (1) or n-alkanes (2), and the alkali metal graphitide can be characterised as a molecular sieve (1). In the case of molecules having 2p electrons such as THF (3), on the other hand, the reaction is irreversible, because of an affinity between the molecule and the alkali metal. Thus, because of the strong ion-dipole interaction, complexes are formed as in the case of the system THF-

CsC_{24} (3), or isomerization occurs as in the case of 1-butene or 1-pentene intercalated in KC_{24} (4). In the case of molecules having π electrons such as butadiene and styrene a irreversible polymerisation proceeds (5). In these systems, however, the formed ternary compounds remain unstable in air because of the very strong affinity of the alkali metal with oxygen or water, involving a complete decomposition of the graphite intercalation compounds (GICs). Taking into account the interaction between species, the case of ethylene presents an intermediate behaviour, since the reversibility depends on the temperature. The cause of the irreversibility at room temperature is due to the oligomerization of ethylene between the graphene planes (6). We investigated the conditions of oligomerization by using calorimetric experiment.

EXPERIMENTAL

Samples of 2nd stage cesium graphite-intercalation compounds, CsC_{24}, were prepared from graphite (Grafoil sheet, Union Carbide, GTA grade), cut into disks (diameter = 4 mm), and commercial cesium metal (purity 99.9%). Stoichiometric amount of graphite and cesium were introduced in a glass vessel inside a glove box under argon gas. The vessel was set under vacuum ($P = 10^{-5}$ Torr), and the Grafoil was outgassed at 900-950°C for 5-8 hours. Then, the mixture was allowed to react at 450°C for 1-2 days, resulting CsC_{24}. For the determination of C_2H_4 absorption, we used a classical volumetric device, set up on a calorimeter. The variations of pressure in the vessel were measured with a MKS Baratron gauge (in the range 0.1 to 1000 Torr), allowing to determine the intercalated amount of the gas.
Calorimetric measurements were made on a Multi Micro Calorimeter (MMC 5111, Tokyo Riko Co. Ltd).

RESULTS AND DISCUSSION

Isotherms of intercalation of C_2H_4 in CsC_{24} have been already established from 194 to 323 K (7). They presented two main plateaux at 1.1 and 2.1 C_2H_4/24 C, and identified by XRD as respectively, a second stage ternary (I_C = 10.1 Å, with a small amount of first stage binary), and first stage ternary (I_C = 6.85 Å). Each of these plateaux seems to be preceded by a small one at 1.85

C_2H_4/24 C, which corresponds to a mixture of second and first stage ternary compounds.

At 233 K, we checked the reversibility, by making several cycles of intercalation/de-intercalation by pumping. The reaction was reversible at low temperature, but after heating up to room temperature, the reaction became irreversible. We can conclude that heat treatment involves an irreversibility of the reaction. In other words, a reaction (such as oligomerization) occurs in the organic layer, by increasing the temperature. At low temperatures the organic layer is only constituted with monomer molecules (C_2H_4), while by heating up to room temperature, the oligomerization process of C_2H_4 occurs.

The solvent extrastion of organic molecules from the ternary compound was made using toluene with ultrasonic agitation at ~40°C. The extracts were carefully concentrated under N_2 gas flow at room temperature, and then analysed by GC/MS (gas chromatography/mass spectrometry) by JEOL JMS-AXSOSW, and by FDMS (field desorption mass spectrometry) using JEOL JMS-HX110) (8). The results showed a large distribution of oligomers was identified from C_{20} to C_{42}. In order to check the appearance of the oligomerization above room temperature, we investigated the intercalation of C_2H_4 in CsC_{24} by calorimetric measurements.

Calorimetric measurements during the intercalation

Calorimetry experiments were performed during the intercalation at 284, 288, 294, 298 and 309 K. At this temperature and for an initial pressure of 730 Torr, only the 1st plateau can be reached. The generation of heat occurs in 2 steps (Figure 1) : the 1st one, very fast, is representative of the heat of the intercalation, whereas the 2nd one (in inset), very slow, is representative of the secondary reaction, with an energy twice, with the same order of magnitude as the reaction of oligomerization of ethylene only. The heat released during intercalation is quite constant (Table 1), and is ~ -38 kJ/mol C_2H_4 in the temperature range of the experiment, while heat of oligomerization, -60 ~ -90 kJ/mol C_2H_4, shows some temperature dependence. If we consider that the rate of the global reaction is directly proportional to the slope of the integrated heat curve, we can assert that there is a dependence with the temperature (Figure 2). Then, the intercalation rate decreases when temperature increases, and oligomerization rate increases when temperature increases. Then at high

temperatures, there is a competition between intercalation and oligomerization, and where the ultimate stage is the reaction of an ethylene molecule with the others or oligomers, as soon as intercalated. Consequently, the formation of large molecules in the edges of the platelet, would hinder the complete filling. This is identified on isotherms for temperatures above 242 K, in which the intercalated amount at the first plateau decreases when the temperature increases.

Then, oligomerization occurs by forming molecules with chain length constituted with several tens of carbon atoms, such molecules would be in a 2D solid state, and consequently their mobility inside the substrate would be very weak. We can also suspect the formation of a network by oligomers, shielding the Cs^+ ions, and then would involve an increase of the stability after exposure to air.

T (K)	ΔH_{int} (kJ/mol C_2H_4)	ΔH_{oli} (kJ/mol C_2H_4)	ΔH_{oxi} (kJ/mol Cs)	C_2H_4/Cs
284	-36.2	-62.5	-91.8	1.29
288	-36.5	-68.3	- *	1.30
293	-42.4	-86.9	-98.8	1.10
298	-37.8	-81.2	-134.0	1.18
309	(-36.5)	(-87.7)	-122.5	1.07
CsC_{24} (288 K)	-	-	-217.6	0.00

TABLE 1 Thermodynamic data obtained by calorimetric measurements. (* failed to obtain the result).

Calorimetric measurements during exposure to air

By calorimetric measurement, we determined the heat evolved after exposure to air (Figure 3) at various temperature, compared with the oxidation of the starting binary, CsC_{24}. The calculated value of the heat released during oxidation for CsC_{24} is -243.5 kJ/mol Cs, taking into account the reaction Cs[s] + O_2[g] --> CsO_2[s] (9). The low experimental value in Table 1, -217.6 kJ/mol Cs, is due to the slowness of the reaction for reaching the equilibrium. Then in the case of CsC_{24}, we can consider that all cesium ions becomes oxidized after exposure to air. However, for the ternary, the oxidation corresponds 40 to 60% (depending on the temperature) of the one measured for the binary. Then, nearly half of cesium ions is oxidized. This

means that the "network" formed by the oligomeric chains shields only part of Cs^+ ions.

In a previous paper, we mentioned the stability of the ternary compound after the exposure to air of the sample $Cs(C_2H_4)_{1.8}C_{24}$, by XRD measurement at room temperature (7). The progress of XRD spectra shows that new lines attributed to α-CsO_2 and $CsOH$-H_2O appear, showing that a part of cesium in the ternary compound is oxidized. However, the sample is still intercalated, since the 00l lines of the 2nd stage ternary remains very strong.

Usually, with other organic molecules, the ternary compound exposed to air is decomposed, and both alkali metal and molecules are de-intercalated. On XRD pattern, this is shown by an increase of the stage with the time, finally reaching the graphite structure.

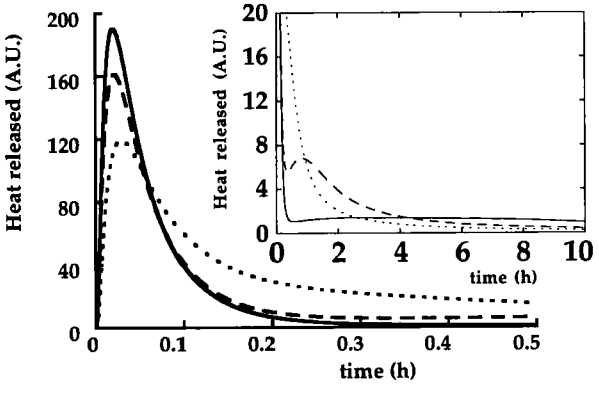

FIGURE 1 Measurement of the heat of sorption during the intercalation of C_2H_4 in CsC_{24} at (----) 288, (- - -) 298 and (...) 309 K.

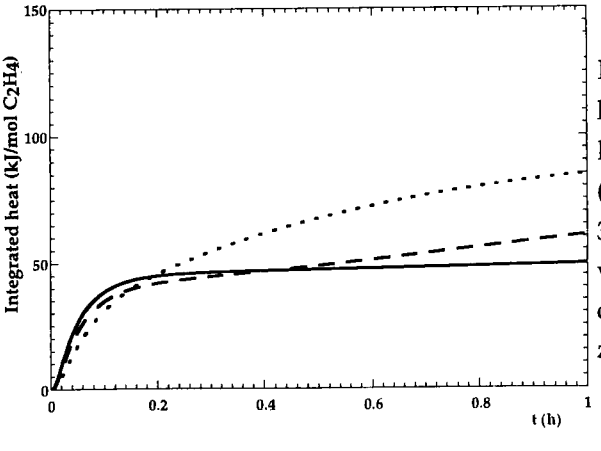

FIGURE 2 Integrated heat during the intercalation of C_2H_4 in CsC_{24} at (----) 288, (- - -) 298 and (...) 309 K : different behaviour between the intercalation and oligomerization rate.

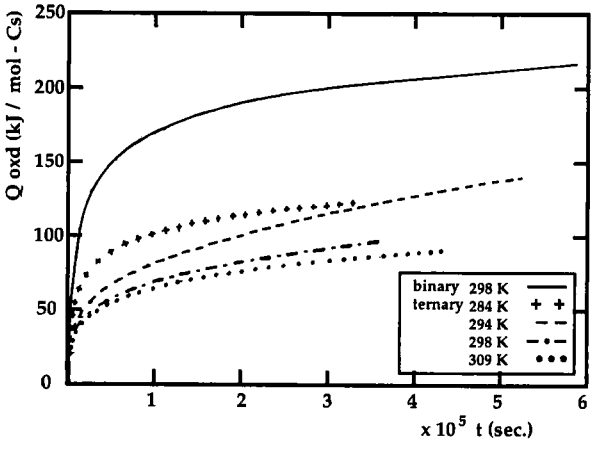

FIGURE 3 Measurement of the heat of oxidation during the exposure to air of the ternary compound at 284, 294, 298 and 309 K.

CONCLUSION

The intercalation of C_2H_4 in CsC_{24} occurs by forming a ternary compound in which the organic layer is oligomerized at temperature higher than ~250 K. This phenomenon involves a relative increase of the stability after exposure to air ; indeed the ternary compound globally remains intercalated. The consequences of this new process in GIC are under investigation, particularly in regards to the effects on the electrical conductivity on this compound.

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