Chemical Modification of Carbon Hexagonal Plane by Ligand Exchange Reaction of Ferrocene

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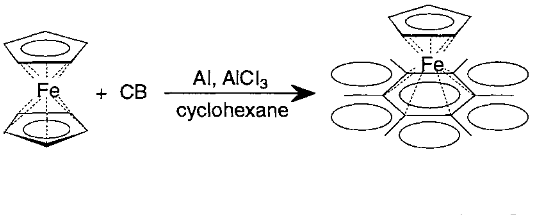
Introduction of the functional groups to the carbon hexagonal plane of the *sp*^{2}-carbon, which may provide the novel properties to carbon materials, proceeds by the ligand exchange reaction of ferrocene with the *sp*^{2}-carbon.

Surface conditions seriously affect performance of carbon materials, such as adsorptive,[1-6] disperse,[7-9] composite properties.[10] Surface modification of *sp*^{2} carbon makes us possible to design and to control surface properties and, furthermore, to provide the new functions, such as catalytic,[11] electronic,[12,13] and magnetic properties.[14] Introduction of functional groups is essential approach for such chemical modification. Functional groups can be easily introduced to the edges of constituent aromatic molecules by the aid of aromatic hydrogen.[15,16] On the other hand, carbon hexagonal planes have no reactive functional groups, so it is quite difficult to introduce functional groups by conventional organic reactions. No report appears yet about effective method to introduce functional groups to carbon hexagonal plane.

The sandwich compounds, e.g., ferrocene, are well known as the π complexes consisting of metal species sandwiched with two aromatic ligands, such as cyclopentadiene and benzene-derivatives.[17,18] Exchange reactions of one of aromatic ligands to another aromatic compound have been reported.[18,19] In this study, we have adopted such ligand exchange reaction of ferrocene to introduce functional groups to carbon hexagonal plane of *sp*^{2}-carbon (eq. 1) and demonstrate the validity of this approach for the chemical modification of *sp*^{2}-carbon surface.

Carbon black (CB, Hayashi Pure Chemicals Ind. Co., Ltd.), which expose the hexagonal planes to the surface, was mainly used as carbon sample. Highly oriented pyrolytic graphite (HOPG) was also used. The CB was sonicated in acetone for 1 h and dried under vacuum at 110 °C for 24 h prior to use. The HOPG was used after heat treatment at 1000 °C in Ar atmosphere. Typical procedures to synthesize the ligand-exchanged product (Cp-Fe-Arene complex, Cp:cyclopentadienyl, Arene:CB or HOPG) were as follows (eq 1): cyclohexane (200 ml) and carbon sample (0.5 g) were charged to a dried three-necked flask and agitated at r.t. for 10 min. Ferrocene (7.44 g, 40 mmol), $AlCl_3$ (13.33 g, 100mmol), and Al powder (0.68 g, 25 mmol) were added to the flask, and the mixture was refluxed for 8 h in N_2 atmosphere. After adding methanol to the mixture at 0 °C, the solid material was recovered by centrifugation, washed with methanol, acetone, and ether under ultrasonic irradiation, repeatedly (total sonication period : 2 h), and then dried at 60 °C under vacuum for 4 h. The butylation reaction was carried out by agitating the Cp-Fe-Arene complex of CB (0.3 g) with *n*-butyl lithium (20 mmol in 1.6 M *n*-hexane solution) in THF (200 ml) at 0 °C for 20 min.



(1)

The Cp-Fe-Arene complex obtained from CB by the ligand exchange reaction of ferrocene was analyzed by SEM/EDX. A peak corresponding to Fe appeared, which was not seen for the original CB. The Fe peak was observed even after washing in 1 M HCl aq. solution for 20 min. However, no Fe peak remained after an agitation in 0.1 M $KMnO_4$ aq. acetone solution. These results strongly indicate that ferrocene was not adsorbed on CB but chemically fixed on CB. Fe2p XPS spectrum of the complex is shown in Figure 1. The $Fe2p_{3/2}$ peak was observed at 707.95 eV.

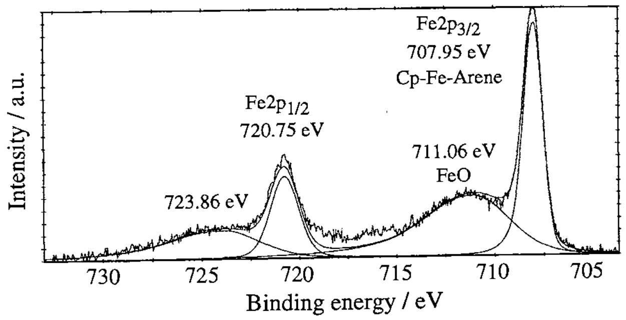


Figure 1. Fe2p XPS spectrum of the Cp-Fe-Arene complex of CB.

Compared with the reported $Fe2p_{3/2}$ value of ferrocene (707.7 eV),[20] it shifted to a high binding energy, suggesting the production of Cp-Fe-Arene complex. The H/C atomic ratio of the complex (0.208) estimated from elemental analysis is twice as high as that of the original CB (0.107) (Table 1). These results indicate fixation of Cp ligands on CB. The number of Cp introduced per 100 carbon atoms of CB was estimated to be 2.6 based on an increase in H/C value. This value roughly corresponds to one Cp per 15 benzene rings of carbon hexagonal plane.

Table 1. H/C ratios and the number of intruduced butyl groups of Cp-Fe-Arene complex of CB and the original CB

Sample	H/C ratio[a]	Bu / 100C[b]
Cp-Fe-Arene (CB)	0.208	-
Butylated product	0.297	1.13
CB	0.107	-
Butylated product	0.145	0.45

[a]Obtained from the elemental analysis. [b]The number of butyl groups introduced per 100 carbon atoms estimated by an increase in H/C value.

The Cp-Fe-Arene complex of HOPG was also synthesized in a similar manner, whose $Fe2p_{3/2}$ peak by XPS appeared at 709.6 eV. The complex was analyzed by using GCQMS with direct

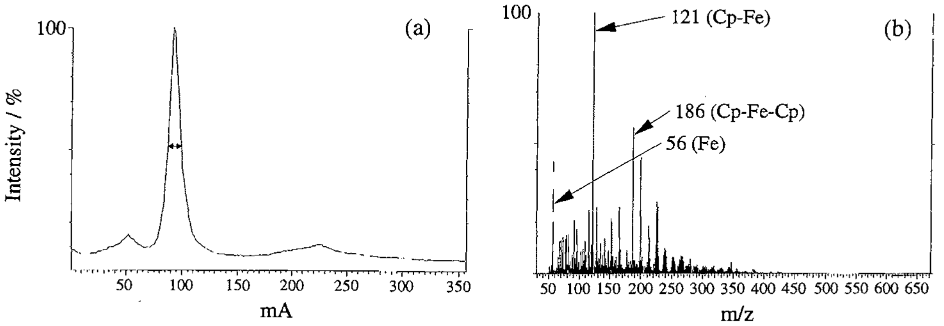


Figure 2. Total ion chromatogram (a) and GCQMS spectrum (b) of the Cp-Fe-Arene complex of HOPG. GCQMS spectrum was obtained by accumulating the region indicated with an arrow in (a). 5 mA corresponds to 5°C/s in horizontal axis of (a).

insertion probe to verify the ligand exchange reaction of ferrocene. The total ion chromatogram and mass spectrum of main peak of the chromatogram are shown in Figure 2. A parent ion peak was observed at m/z = 121 which corresponds to sum of the masses of Cp and Fe for the Cp-Fe-Arene complex. Although the molecular ion peak of ferrocene (m/z = 186) was also detected, the intensity was about half to that of m/z = 121 peak. Moreover, the peak corresponding to the atomic weight of Fe atom was also observed at m/z= 56. The physical mixture of HOPG and ferrocene gave the largest peak assigned to the molecular ion of ferrocene, while the peak intensities of m/z = 56 and 121 were small compared with those of the complex. These GCQMS results also indicate the formation of Cp-Fe-Arene complex.

Table 1 presents the H/C ratios and the number of introduced butyl groups for Cp-Fe-Arene complex and the original CB. After the butylation of the Cp-Fe-Arene complex of CB by using *n*-butyl lithium, H/C ratio increased to 0.297 from 0.208 of the complex. On the other hand, a moderate increase in H/C was observed when original CB was subjected to butylation ; H/C values of CB and its butylation product were 0.107 and 0.145, respectively. Such results may demonstrate a potential for the further functionalization of fixed Cp on CB.

In summary, to introduce the functional groups to the carbon hexagonal plane of *sp*^{2}-carbon, which has no reactive functional groups, a ligand exchange reaction of ferrocene in the presence of $AlCl_3$ and Al was carried out by using CB and HOPG as carbon samples. Fe species were detected from the reaction product by SEM/EDX (even after an agitation in 1M HCl solution). XPS and GCQMS indicate the formation of Cp-Fe-Arene complex of CB or HOPG. An increase in H/C ratio suggest fixation of Cp on CB and the fixed Cp was alkylated by using *n*-BuLi.

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