Research Report

The First Application of Fullerene Polymer-like Materials, $C_{60}Pd_n$, as Gas Adsorbents

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ポリマー状フラーレン$C_{60}Pd_n$のガス吸着材としての最初の応用

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Abstract

$C_{60}Pd_n$ polymer-like materials were prepared and reacted with toluene, one of the harmful gases. Toluene was successfully adsorbed on $C_{60}Pd_n$ at ambient temperature without additional energy sources. This adsorptivity was retained even at low concentration of 1000 ppb, which is close to the actual toluene concentration in the environment. The strong adsorption of toluene molecules toward $C_{60}Pd_n$ was confirmed by IR, TG-IR, and cyclic voltammetry. The π- electrons of toluene are believed to adsorb on the partially positive Pd atoms of $C_{60}Pd_n$, and theoretical studies have suggested that the π-electrons of C_{60} and toluene overlap through the d-electron orbitals of the Pd atom, representing not just physical adsorption. This result should open the door to application of fullerene materials as adsorbents for harmful gases.

Keywords Fullerene, Polymer, $C_{60}Pd_n$, Gas adsorbent

要　　旨

ポリマー状フラーレンの$C_{60}Pd_n$を合成し，有害なガスの1つであるトルエンとの反応を調べた。トルエンは付加的なエネルギーを必要とせず室温で$C_{60}Pd_n$上に吸着された。この吸着性は，環境中の実際のトルエン濃度に近い1000ppbという低濃度でさえ保持された。$C_{60}Pd_n$へのトルエン分子の強い吸着は，IR，TG-IRおよびサイクリックボルタンメトリー解析によって確認された。トルエンのπ電子が$C_{60}Pd_n$の一部正に分極したPd原子上に吸着すると考えられ，理論的な研究により，Pd原子のd電子軌道を介してトルエンのπ電子とC_{60}のπ電子の軌道が重なり安定に吸着することを提案した。この結果はフラーレンの有害ガスの吸着材としての用途に道を開くものである。

キーワード　フラーレン，ポリマー，$C_{60}Pd_n$，ガス吸着性

1. Introduction

Since the first discovery of fullerenes[1] and the availability of synthetically useful amounts of C_{60} and higher fullerenes (C_{70}, C_{76}, C_{78} and C_{84}),[2] much work has investigated the physical properties and the reactivity of these stable molecules. C_{60} is the most abundant species, and considerations of the electronic structure of C_{60} have naturally focused on the surface π-electron orbitals. C_{60} has LUMOs which are triply degenerate t_{1u} orbitals. Since the LUMO is relatively low in energy, C_{60} is readily reduced. The highly interesting electronic properties of fullerenes have led to the possibility of using units of fullerenes in the formation of polymers. C_{60} can be polymerized into directly linked fullerenes by light, high pressure, or high temperature.[3-6] Fullerenes may be attached regularly to a polymeric backbone chain through fullerenating polystyrenes in type reactions.[7] Also, indirectly linked fullerenes including a spacer group are known. The polymers $C_{60}Pd_n$ or $C_{60}Pt_n$ are formed from C_{60} and $Pd_2(dba)_3{\cdot}CHCl_3$ or $Pt(dba)_2$, respectively (dba is dibenzylideneacetone).[8-11] These redox-active fullerene-based polymeric materials can be formed by electrochemical reduction of fullerenes under specific conditions.[12-15] These polymers have possible applications to catalysts, electronic devices, and other areas.

Volatile organic compounds (VOCs), found in residential environments due to emission from construction materials and paints, are problematic since they are harmful and odorous gases for human beings. Such gases are considered as one cause of Sick Building/House Syndrome.[16, 17] Some air purification systems are based on photocatalysts, adsorbents such as activated carbon, or ozone-promoted oxidants. Removing VOCs at room temperature without additional energy sources is challenging. Among the VOCs, the concentration of toluene, containing a benzene ring, is especially high in the living environment. It is emitted from paints and glues, and is hard to remove from the living environment. Materials able to successfully remove toluene have not been reported so far.

We believe fullerene polymers are possible candidates for the remover of toluene since the unique electronic properties of the polymers can lead to strong interaction between the benzene rings and the polymers. We have paid particular attention to indirectly linked fullerene polymers including a metal-spacer group because metal-sites would be good sites for adsorbing toluene. In addition, the electroactive characteristic of the polymers might result in the stabilization of toluene molecules on the polymers due to electron movements inside the polymer. In this paper, we report the first successful application of the fullerene polymeric materials, $C_{60}Pd_n$, as adsorbents.

2. Experimental section

2. 1 Materials

C_{60} (SES Research), $Pd_2(dba)_3$ (Aldrich), Benzene (WAKO), Acetonitrile (WAKO), and Tetra(*n*-butyl)ammonium perchlorate (WAKO) were obtained and used as received. Reaction gases (toluene, *p*-xylene, methyl mercaptan, formaldehyde, and acetaldehyde) were purchased from Takachiho Chemical Industrial Co., Ltd.

2. 2 Methods

The X-ray diffraction pattern was measured at an operation speed of 2°/min, a pipe voltage of 40 kV, and a pipe current of 30 mA using a RINT-2200 powder X-ray diffraction instrument (RIGAKU). The divergence slit, scattering slit, and receiving slit were 1/2°, 1/2°, and 0.15 mm, respectively.

The SEM images were obtained with the use of a S-4300 (HITACHI). The acceleration voltage for the electron beam was 7 keV.

Specific surface area was measured using the AUTOSORB-1 GAS SORPTION SYSTEM (Quantachrome) and was computed by the BET method. Dehydration of the sample was performed at 105 °C for 12 hours.

In the batch reaction to determine toluene adsorption, 0.1 g of adsorbent was placed in a 5-L aluminum bag, where 80 ppm of toluene and 20 % O_2 in N_2 was then pumped. Portions of the gas in the bag were taken for gas measurements during the reaction. The concentration of toluene was monitored versus the reaction time using a GC-14B model gas chromatograph (SHIMAZU). In batch reaction of *p*-xylene, methyl mercaptan, formaldehyde, and acetaldehyde adsorption, similar conditions were used. The concentrations of methyl mercaptan and formaldehyde were measured by Gas Detector Tubes (KITAGAWA), with a limit of detection of 1 ppm. The other gases were measured by GC. With GC, considering all possible error sources, the concentration (ppm) was measured to an accuracy of one decimal point. The initial concentrations in **Table 1** were measured from several reaction bags and averaged.

The infrared spectra (ATR method) were taken with the sample dispersed on a diamond tip using an Avatar 360 FTIR spectrometer (Nicolet).

For TG-IR analysis, a TG8120 thermogravimetric analyzer (Rigaku) was used at a heating rate of 10 °C/min under Argon atmosphere, in combination with a Magna 760 FTIR spectrometer equipped with a DTGS detector (Nicolet). The temperatures of the transfer line and cell were 240 °C and 250 °C, respectively.

Voltammetric experiments were performed on a HSV-100 Standard Voltammetric Tool (HOKUTO DENKO) with a three-electrode cell. A platinum disk covered with $C_{60}Pd_2$ was used as the working electrode. A silver wire immersed in 0.01 M silver nitrate and 0.09 M tetra(*n*-butyl)ammonium perchlorate in acetonitrile and separated from the working electrode by a ceramic tip (BAS) served as the reference electrode. With this electrode and solvent system, the ferrocene-ferrocenium redox couple occurs at +185 mV. The counter electrode was a platinum tab with an area of about 0.5 cm^2.

Table 1 Initial concentration and adsorption (%). The adsorptivity of $C_{60}Pd_2$ toward xylene, methyl mercaptan, formaldehyde, and acetaldehyde was tested. In the experiment, 0.1g of $C_{60}Pd_2$ was used and all the gases were air-balanced. The initial concentration and adsorption (%) after 24 hours of each gas are listed. Those of toluene are also listed for comparison. % each gas adsorption =[1- (concentration in bag containing sample/ concentration in bag without sample)] × 100

	Initial conc.	Adsorption after 24 h
Toluene	79.6 ppm	99 %
p-Xylene	50.0 ppm	95 %
Methyl mercaptan	80 ppm	32 %
Formaldehyde	300 ppm	43 %
Acetaldehyde	80.2 ppm	11 %

XPS spectra were obtained with PHI550MC spectrometer, which uses the magnesium K-α transition for X-rays (1253.6 eV).

3. Results

3. 1 Structural characterization of $C_{60}Pd_n$

C_{60} can form polymer-like materials having indirectly linked fullerenes with a metal-spacer group. One such group of polymer-like materials, $C_{60}Pd_n$, is synthesized through the reaction of C_{60} with $Pd_2(dba)_3$ in benzene.8-9) Depending on the stoichiometry and subsequent thermal treatment, the composition of these compounds varies (*n*=1, 2, 3, 3.5). These materials are proposed to contain a ... $PdC_{60}PdC_{60}Pd$ ... framework.

The $C_{60}Pd_n$ samples were analyzed to investigate their possible structures. $C_{60}Pd_n$ samples were analyzed by powder X-ray diffraction (XRD), but the powder XRD patterns showed very broad peaks and no clear structural information was obtained. However, the broad peak near $2\theta = 4^{o}$ indicates the formation of a mesoscopic structure from the interaction between the particles. During the synthetic process, Pd atoms are believed to bond to C_{60} at many possible sites and to form a network. Then, the particles are thought to aggregate and precipitate out. Considering this synthetic process and the powder XRD result, the $C_{60}Pd_n$ polymer-like materials prepared here have a more disordered structure than previously reported well-ordered structures.8) The particle size analyzed by SEM is 60-100 nm (**Fig. 1**), but the particles aggregate to form bulky materials. The specific surface area is around 380 m^2/g.

3. 2 Investigation of adsorptivity of $C_{60}Pd_n$ toward toluene

Toluene gas was chosen to investigate the adsorption ability of $C_{60}Pd_n$ toward VOCs, and a batch reaction was employed for the toluene adsorption. In this experiment, 0.1g of $C_{60}Pd_n$ (n = 0, 1, 2, 3) was introduced into a reaction bag (5 L) containing 80 ppm of toluene/ air-balanced. Toluene adsorption (%) was calculated in proportion to the concentration of toluene in the bag containing no adsorbent (blank), since the reaction bag itself adsorbs some toluene gas. The time courses of the toluene adsorption (%) at room temperature are shown in **Fig. 2**. C_{60} itself does not adsorb toluene gas at all. However, when C_{60} and Pd are combined together in polymer-like materials, they adsorb toluene well. $C_{60}Pd_2$ shows the best adsorptivity toward toluene. These polymeric materials also show good adsorptivity even at a low concentration of 1000 ppb, which is close to the actual toluene concentration in the environment.

Then, the adsorptivity of $C_{60}Pd_2$ toward other common VOCs in the living environment, such as xylene (*p*-xylene), methyl mercaptan, formaldehyde, and acetaldehyde, was tested in a similar way as described above. In these experiments, 0.1g of $C_{60}Pd_2$ was used and all the gases were air-balanced. The initial concentration and adsorption (%) after 24 hours of exposure to the adsorbent for each gas are listed in Table 1. $C_{60}Pd_2$ is a good adsorbent toward *p*-xylene as wells as toluene.

3. 3 Spectroscopic characterization of $C_{60}Pd_2$

The adsorption of toluene on $C_{60}Pd_2$ was confirmed by IR analysis using 0.2g of $C_{60}Pd_2$ remaining in a reaction bag filled with an initial concentration of 1000 ppm toluene and left for 24 hours. Comparing IR spectra before and after the reaction with toluene gas, the aromatic -CH absorption is observed at 3000-3200 cm^{-1} after the reaction. Therefore, the adsorption of toluene molecules on $C_{60}Pd_2$ was confirmed. For the $C_{60}Pd_2$ reacted with 80 ppm toluene, the aromatic -CH absorption is smaller than for $C_{60}Pd_2$ reacted with 1000 ppm toluene. In other words, the aromatic -CH absorption is more significant when $C_{60}Pd_2$ reacts with a higher concentration of toluene. According to TG-IR analysis, $C_{60}Pd_2$ itself is stable up to 310 ^{o}C in air. On the other hand, after 24-hour reaction of 0.2g of $C_{60}Pd_2$ and 1000 ppm toluene, TG-IR analysis showed the sample starts to lose weight at 50 ^{o}C and keeps losing weight gradually up to 250 ^{o}C in air. A total weight loss of 7.9 % is seen during this process. The material released during the temperature elevation was monitored and analyzed by IR. The released material was toluene only. This gradual weight loss indicates very strong toluene adsorption on the $C_{60}Pd_2$ polymer-like material. Based on the observed weight loss, 0.40 toluene molecules were adsorbed per Pd atom.

3. 4 Electrochemical studies of $C_{60}Pd_2$

Electrochemical studies of $C_{60}Pd_2$ were done. In a suspension of $C_{60}Pd_2$ in pyridine, a platinum disk electrode (working electrode) was dipped and then dried. The resulted $C_{60}Pd_2$-covered platinum electrode was placed in the reaction bag containing

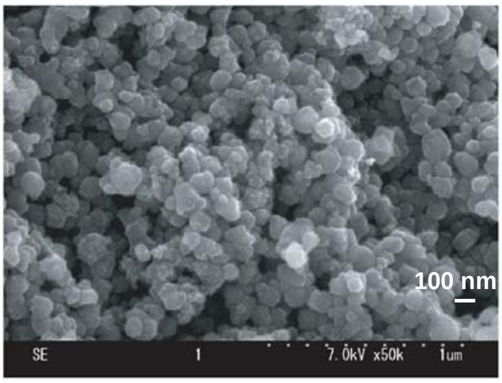


Fig. 1 SEM image of $C_{60}Pd_2$.
Spherical outcroppings in diameter from 60 to 100 nm are shown.

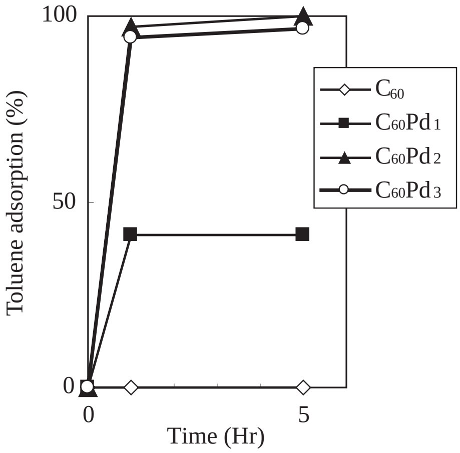


Fig. 2 Toluene adsorption (%) at room temperature.
0.1g of each sample was used and the concentration of toluene and O_2 were controlled at 80 ppm and 20 %, respectively. The time courses of the toluene adsorption (%) at room temperature are shown.
% toluene adsorption =[1- (toluene concentration in the bag containing sample/toluene concentration in the bag without sample)] × 100.

80 ppm of toluene/air-balanced. After 5 hours, the reaction bag was opened and the platinum electrode covered with $C_{60}Pd_2$ was taken out. Then, the electrochemical behavior of the $C_{60}Pd_2$ was studied in acetonitrile solution containing only a supporting electrolyte. Multicyclic voltammograms (10 cyc.) are shown in **Fig. 3**. It can be seen in Fig. 3a that $C_{60}Pd_2$ is electroactive and that its response to cycling in acetonitrile solution containing only supporting electrolyte (0.10 M tetra (*n*-butyl) ammonium perchlorate) is stable. The response is notably similar to electrochemically prepared C_{60}/Pd films.[14] During the reduction of $C_{60}Pd_2$, cation transport into and out of the material occurs. The electrochemical behavior of $C_{60}Pd_2$ after the reaction with toluene has changed (Fig. 3b). The electroactivity is unstable and the current diminishes with increasing cycling.

3. 5 XPS Studies of $C_{60}Pd_2$

XPS analysis was done to study the binding energy of Pd atoms in the $C_{60}Pd_2$. As seen in **Fig. 4**, the Pd peak is shifted toward a higher binding energy side than Pd(0) metal. This is probably because part of the $C_{60}Pd_n$ includes a chain of ... $PdC_{60}PdC_{60}Pd$ ..., where the electrons on the Pd are shifted toward C_{60}, which easily accepts and stabilizes electrons, resulting in partially positive Pd atoms. Therefore, the strong adsorption of toluene molecules on $C_{60}Pd_n$ is believed to come from the attraction of a π-cloud of toluene electrons toward the partially positive Pd (**Scheme 1**). If this is true, the Pd binding energy should be shifted toward the higher energy side after reaction with toluene. According to the NIST XPS database,[18] the binding energies of palladium metal, tetrakis (triphenylphosphine)palladium, dichlorobis (triphenylphosphine)palladium, and *cis*-dichloro((1,2-eta) cyclohexene)palladium are 335.1, 336, 337.8, and 338.6 eV, respectively. Based on those data, we expected that the binding energy would shift about 1 eV to the higher side after adsorption of toluene

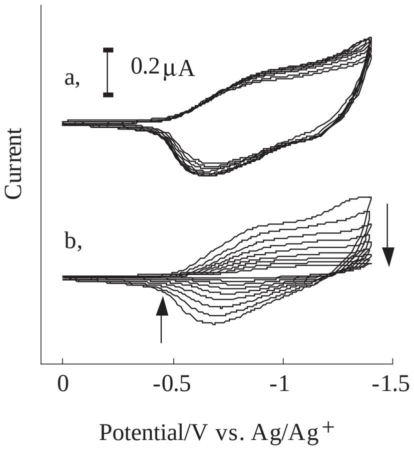


Fig. 3 Cyclic voltammograms of $C_{60}Pd_2$.
Multicyclic voltammograms (10 cyc.) showing electroactivity of $C_{60}Pd_2$ (a) before, (b) after reaction with toluene.

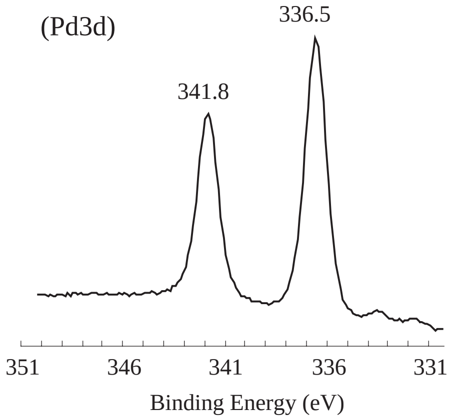
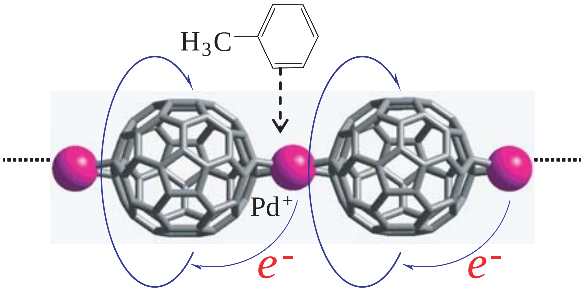


Fig. 4 XPS Spectrum of $C_{60}Pd_2$.
XPS Spectrum of $C_{60}Pd_2$ polymeric material showing Pd $3d_{5/2}$ and $3d_{3/2}$ doublet with binding energies of 336.5 and 341.8 eV, respectively. Typical values for Pd^0 are 335.1 eV and 340.4 eV, respectively.



Scheme 1 Proposed electron movement in chain of ... $PdC_{60}PdC_{60}Pd$ ... .
A π-cloud of toluene is attracted toward the partially positive Pd.

molecules onto Pd atoms. However, a difference in Pd binding energies before and after the reaction was not observed at all. It might occur that during the XPS analysis under high vacuum (2×10^{-9} torr), toluene gas molecules were released from the Pd sites of $C_{60}Pd_2$, and so the difference in Pd binding energies was not observed. This idea was proven by IR analysis. The aromatic -CH absorption at 3000-3200 cm^{-1} was observed to disappear for the sample after the XPS analysis. Therefore, the shift in Pd binding energy when toluene was adsorbed could not be measured by XPS at room temperature.

3. 6 Theoretical analyses of adsorption mechanism

To investigate the toluene adsorption mechanism, theoretical analyses were done using the semiempirical MOPAC2002/AM1 method.19) When toluene is adsorbed on a Pd site of C_{60}-Pd-C_{60} (**Fig. 5**a), the π-electrons of C_{60} and toluene overlap through the *d*-electron orbitals of the Pd atom. A surface electron density plot and an example of orbital surface plots for toluene adsorption on Pd for C_{60}-Pd-C_{60} are shown in Fig. 5b and 5c, respectively. Based on calculations using the above method, toluene adsorption on Pd is stabilized with an energy of -9.69 kcal/mol, which is more than just physical adsorption. On the other hand, when toluene adsorbs on the C_{60} site of C_{60}-Pd-C_{60}, the adsorption energy is only -0.07 kcal/mol. Therefore, toluene adsorbs on the Pd site and not on the C_{60} site of $C_{60}Pd_n$ polymeric materials.

3. 7 Toluene adsorptivity of fullerene polymer-like materials containing other metals

To further study the toluene adsorption mechanism, fullerene polymer-like materials containing other metals were tested for adsorption. A $C_{60}Ru_3$ polymer-like material was prepared by literature methods.20-21) $C_{60}Ru_3$ (0.1g) was introduced into a reaction bag containing 80 ppm of toluene (air-balanced), and the concentration of toluene in the bag was monitored by GC. In contrast to $C_{60}Pd_n$, $C_{60}Ru_3$ did not adsorb toluene at all. Based on the IR spectrum, CO molecules from the starting material were still attached to Ru. These COs are believed to prevent toluene adsorption on the Ru site. $C_{60}Pt_1$,10-11) which has a similar structure to $C_{60}Pd_n$, was tested for toluene adsorption under the same conditions as the Ru material. $C_{60}Pt_n$ also showed good adsorptivity toward toluene. After 24 hours, there was 95% toluene adsorption.

4. Discussion

Fullerene polymer-like materials, $C_{60}Pd_n$, showed good adsorptivity toward toluene. Even at a low concentration of 1000 ppb, which is close to the actual toluene concentration in the environment, the adsorptivity is retained. Among $C_{60}Pd_n$ materials, $C_{60}Pd_2$ shows the best adsorptivity toward toluene. Adsorption of other VOCs, such as *p*-xylene, methyl mercaptan, formaldehyde, and acetaldehyde, was also tested. The experimental results showed good adsorptivity for $C_{60}Pd_2$ toward gases containing a benzene ring.

The strong adsorption of toluene molecules on $C_{60}Pd_2$ is confirmed by IR and TG-IR. Further, electroactivities of $C_{60}Pd_2$ before and after adsoption

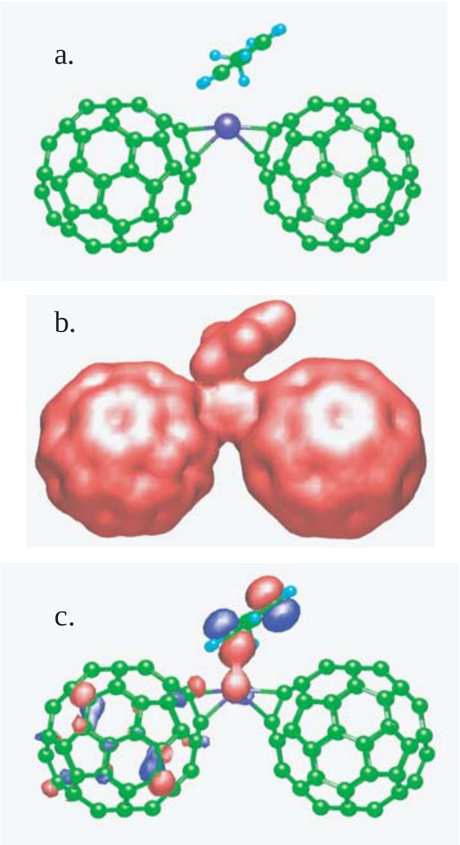


Fig. 5 Computed structures of toluene adsorbed on C_{60}-Pd-C_{60} using the semiempirical MOPAC2002/AM1 method. (a) Idealized structures of C_{60}-Pd-C_{60} + toluene.
(b) A surface electron density plot.
(c) An example of orbital surface plots.

of toluene were analyzed. $C_{60}Pd_2$ itself is electroactive and cation transport occurs in and out of the material during reduction-oxidation of $C_{60}Pd_2$. However, the electroactivity is unstable and the current diminishes with increasing cycling after the adsorption of toluene. The details of electrochemical studies of C_{60} /Pd films have been reported by Winkler et al.[22-23] The redox behavior of the C_{60} /Pd film involves both electron and ion transport within the film, and the ion transport depends on the nature of solvent and supporting electrolyte. In the case of small solvent molecules, the C_{60} /Pd film exhibits reversible redox behavior. For larger solvent molecules, the reversibility is lost. The reduction of the film is accompanied by changes in its morphology allowing for solvent swelling of the film. When the solvent molecule is too large, the film cannot tolerate the solvent transport and loses its reversible redox activity. The redox behavior also similarly depends on the size of the cation of the supporting electrolyte. In our case, the same solvent and supporting electrolyte were used throughout the experiments, so the diminishment of current is not because of the effects of the solvent or supporting electrolyte. Instead, this is probably due to changes in the morphology of the material by adsorption of toluene molecules with the material not strong enough to allow the cation to transport in and out repeatedly.

Fullerene polymer-like materials are not porous materials, but the formation of a mesoscopic structure from interaction between the particles is confirmed by XRD. The distance between the particles is about 2-3 nm, and the gas molecules can be adsorbed. In this case, the adsorption is just physical adsorption and is not very strong. This type of adsorption probably occurs during the reaction, but the strong adsorption of toluene cannot be explained by this mechanism only. The mechanism of such a strong adsorption is believed to come from attraction between the π-cloud of toluene toward the partially positive Pd. The partially positive Pd exists, probably because part of $C_{60}Pd_n$ includes a chain of ... $PdC_{60}PdC_{60}Pd$ ..., and the electrons on the Pd are shifted toward C_{60}, which easily accepts and stabilizes electrons. As a result, the Pd binding energy is shifted to higher energy as compared to Pd(0) in XPS. We expected that the binding energy would be shifted to higher energy when a toluene molecule is adsorbed. However, the shift is not observed by XPS at room temperature because, under a high vacuum (2×10^{-9} torr), toluene gas molecules are desorbed from the Pd site of $C_{60}Pd_2$. XPS analysis at lower temperature is probably necessary to see the shift, and this condition is still under study. This mechanism is also supported by theoretical calculations. Theoretical studies have suggested that π-electrons of C_{60} and toluene overlap through the *d*-electron orbitals of the Pd atom, which results in more than just physical adsorption.

Adsorption of toluene on the metal (M) sites of fullerene polymer-like materials is also supported by experimental results. Both $C_{60}Pd_n$ and $C_{60}Pt_1$ adsorb toluene molecules very well. On the other hand, $C_{60}Ru_3$ does not adsorb toluene at all. The difference in structures of these three materials is the availability of metals sites. Both $C_{60}Pd_n$ and $C_{60}Pt_1$ have metal sites open for adsorption of toluene molecules, but $C_{60}Ru_3$ does not since CO molecules from the starting material remain attached to the Ru, as was confirmed by IR. Therefore, the metal (M) sites of $C_{60}M_n$ polymeric materials are important to adsorb toluene. Moreover, the interaction between C_{60} and M is important to promote the adsorption reaction. The adsorption process should be supported by the easy movement of electrons between C_{60} and M in the polymeric network.

Steric hindrance also influences the adsorption of toluene. As stated before, only 0.4 toluene molecules were adsorbed per Pd atom. Moreover, structural differences probably account for why $C_{60}Pd_2$ has higher adsorptivity than other $C_{60}Pd_n$ polymeric materials. These structural differences are still under study currently.

This is the first application of fullerene polymers as gas adsorbents at ambient temperature without additional energy sources. The adsorptivity is retained even at low gas concentration. This result should open the route to using fullerene materials to remove harmful gases from the living environment.

Acknowledgements

We thank H. Kadoura, E. Sudo, and N. Takahashi for their experimental support.

In addition, we would like to thank the Royal Society of Chemistry for their permission to reprodude this paper.[24)]

References

1) Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. and Smalley, R. E. : Nature, **318**(1985), 162-163
2) Kratschmer, W., Lamb, L. D., Fostiropoulos, K. and Huffman, D. R. : Nature, **347**(1990), 354-358
3) Rao, A. M., Zhou, P., Wang, K. A., Hager, G. T., Holden, J. M., Wang, Y., Lee ,W. T., Bi, X. X., Eklund, P. C., Cornett, D. S., Duncan, M. A. and Amster, I. J. : Science, **259**(1993), 955-957
4) Iwasa, Y., Arima, T., Fleming, R. M., Siegrist, T., Zhou, O., Haddon, R.C., Rothberg, L. J., Lyons, K. B., Carter, H. L., Hebard, A. F., Tycko, R., Dabbagh, G., Krajewski, J. J., Thomas, G. A. and Yagi, T. : Science, **264**(1994), 1570-1572
5) Wang, G. W., Komatsu, K., Murata, Y. and Shiro, M. : Nature, **387**(1997), 583-586
6) Komatsu, K., Wang, G. W., Murata, Y., Tanaka, T., Fujiwara, K., Yamamoto, K. and Saunders, M. : J. Org. Chem., **63**(1998), 9358-9366
7) Liu, B., Bunker, C. E. and Sun, Y. P. : Chem. Commun., (1996), 1241-1242
8) Nagashima, H., Nakaoka, A., Saito, Y., Kato, M., Kawanishi, T. and Itoh, K. : J. Chem. Soc. Chem. Commun., **4**(1992), 377-379
9) Nagashima, H., Yamaguchi, H., Kato, Y., Saito, Y., Haga, M. A. and Itoh, K. : Chem. Lett., 12(1993), 2153-2156
10) Nagashima, H., Kato, Y., Yamaguchi, H., Kimura, E., Kawanishi, T., Kato, M., Saito, Y., Haga, M. and Itoh, K. Chem. Lett., (1994), 1207-1210
11) van Wijnkoop, M., Meidine, M. F., Avent, A. G., Darwish, A. D., Kroto, H. W., Taylor, R. and Walton, D. R. M. : J. Chem. Soc. Dalton. Trans., (1997), 675-677
12) Fedurco, M., Costa, D. A., Balch, A. L. and Fawcett, W. R. : Angew. Chem. Int. Ed., **34**(1995), 194-196
13) Winkler, K., Costa, D. A., Fawcett, W. R. and Balch, A. L. : Adv. Mater., **9**(1997), 153-156
14) Balch, A. L., Costa, D. A. and Winkler, K. : J. Amer. Chem. Soc., **120**(1998), 9614-9620
15) Hayashi, A., de Bettencourt-Dias, A., Winkler, K. and Balch, A. L. : J. Mater. Chem., **12**(2002), 2116-2122
16) Jones, A. P. : Atmos. Environ., **33**(1999), 4535-4564
17) Kostiainen, R. : Atmos. Environ., **29**(1995), 693-702
18) available from <http://srdata.nist.gov/xps/index.htm>
19) Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. and Stewart, J. J. P. : J. Am. Chem. Soc., **107**(1985), 3902-3909
20) Braun, T., Wohlers, T., Belz, T., Nowitzke, G., Wortmann, G., Uchida, Y., Pfander, N. and Schlogl, R. : Catal. Lett., **43**(1997), 167-173
21) Braun, T., Wohlers, M., Belz, T. and Schlogl, R. : Catal. Lett., **43**(1997), 175-180
22) Winkler, K., de Bettencourt-Dias, A. and Balch, A. L. : Chem. Mater., **11**(1999), 2265-2273
23) Winkler, K., de Bettencourt-Dias, A. and Balch, A. L. : Chem. Mater., **12**(2000), 1386-1392
24) Hayashi, A., Yamamoto, S., Suzuki, K. and Matsuoka, T. : J. Mater. Chem., **14**(2004), 2633-2637

(Report recieved on Nov. 30, 2004)

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