Chemical Modification Method of Diamond Surface for Preparation of New Type Intelligent Hybrid Materials

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PREFACE

Diamond is one of the most promising materials for industrial applications because of its excellent properties such as high hardness, large band gap, and transparency over a wide wavelength region. Diamond as a bulk material is inert to chemical reagents. This is one of the reasons why diamond is a promising industrial material. However, this inertness prevents diamond from forming composites with other materials. If a technique for chemical modification of diamond surface were to be established, diamond composite materials would be easy to develop. Diamond as a bulk material has various specific properties. On the other hand, organic functional groups also possess various functions. If functional groups were controllably introduced on the diamond surface, we could develop new types of organic-inorganic hybrid materials. Therefore, the study of chemical modification of diamond surface is very important.

In this study, we carried out the chemical reaction of diamond surface using various chemical reagents for preparation of new type intelligent hybrid materials.

Chapter 1 Introduction

In this chapter, the general background of chemical modification of diamond surface, general properties of diamond, synthesis method of diamond, and aim of the present study are described. The content of this chapter is party based on the following papers:

Toshiki Tsubota, Shintaro Ida, Naoki Okada. Masanori Nagata, Yasumichi Matsumoto, Nobumitsu. Yatsushiro
"CVD diamond coating on WC-Co cutting tool by using ECR MPCVD apparatus via electrophoretic seeding pretreatment"
Surface and Coatings Technology, 169-170, 262-265, (2003)

Toshiki Tsubota, Shintaro Ida, Naoki Okada, Masanori Nagata, Yasumichi Matsumoto, Nobumitsu Yatsushiro

"CVD diamond synthesis on WC-Co cutting tool via electrophoretic seeding process"
Materials Research Society Symposium Proceedings, 697, 159-164, (2002).

Toshiki Tsubota, Masanori Nagata, Naoki Okada, Shintaro Ida, Yasumichi Matsumoto, Nobumitsu Yatsushiro
"CVD diamond coating on WC cutting tool using electrophoresis" (in Japanese)
Journal of the Ceramic Society of Japan, 109, 782-788, (2001).

Chapter 2 Hydrogen abstraction reaction on hydrogenated diamond surface using benzoyl peroxide

The chemical reaction of hydrogenated diamond surface using benzoyl peroxide is described. The dependences of reaction time, added benzoyl peroxide and solvent are discussed. The content of this chapter is based on the following papers:

Toshiki Tsubota, Osamu Hirabayashi, Shintaro Ida, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto
"Abstraction reaction of hydrogenated diamond surface with benzoyl peroxide as a radical initiator" (in Japanese)
Journal of The Surface Science Society of Japan, 22(12), 822-826, (2001).

Toshiki Tsubota, Osamu Hirabayashi, Shintaro Ida, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto
"Abstraction of hydrogen atoms on diamond surface using benzoyl peroxide as radical initiator"
Diamond and Related Materials, 11, 1374-1378, (2002).

Toshiki Tsubota, Osamu Hirabayashi, Shintaro Ida, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto
"Chemical modification of hydrogenated diamond surface using benzoyl peroxide"

Physical Chemistry Chemical Physics, 4, 806-811, (2002).

Chapter 3 Reactivity of the hydrogenated diamond surface with various radical initiators

The reactivity of hydrogenated diamond surface with various radical initiators is described. Benzophenone, azo compounds, dialkyl peroxides and diacyl peroxides are used as the radial initiator. The reaction mechanism between hydrogenated diamond surface and racial initiators is discussed. The content of this chapter is based on the following papers:

Toshiki Tsubota, Osamu Hirabayashi, Shintaro Ida, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto, Katsuki Kusakabe, Seiji Morooka
"Hydrogen abstraction reaction of hydrogenerated diamond surface in liquid phase by radical initiators used in polymer synthesis" (in Japanese)
Journal of Chemical Society of Japan, 11, 631-636, (2001).

Toshiki Tsubota, Osamu Hirabayashi, Shintaro Ida, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto
"Reactivity of hydrogen atoms on diamond surface with various radical initiators in mild condition"
Diamond and Related Materials, 11, 1360-1365, (2002).

Toshiki Tsubota, Osamu Hirabayashi, Shintaro Ida, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto
"Reactivity of hydrogenerated diamond surface with radical initiators generating oxygen radical species" (in Japanese)
Journal of the Ceramic Society of Japan, 110, 669-675, (2001).

Shintaro Ida, Toshiki Tsubota, Osamu Hirabayashi, Masanori Nagata, Yasumichi Matsumoto
"Chemical modification of diamond surface for creating new type functional organic-inorganic hybrid materials"

Proceedings of the 19^{th} Korea-Japan International Seminar on Ceramics, 412-416, (2002).

Shintaro Ida, Toshiki Tsubota, Osamu Hirabayashi, Masanori Nagata, Yasumichi Matsumoto, Akira Fujishima
"Chemical reaction of hydrogenated diamond surface with peroxide radical initiators"
Diamond and Related Materials, 12, 601-605 (2003)

Chapter 4 Chemical modification of diamond surface using diacyl peroxide and CN group containing compounds for the introduction of the CN group

The chemical modification method for preparation of CN-terminated diamond surface is described. The characterization of diamond surface is demonstrated. The reaction mechanism among hydrogenated diamond surface, racial initiators and CN group containing compounds is discussed. The content of this chapter is based on the following papers:

Toshiki Tsubota, Shintaro Ida, Osamu Hirabayashi, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto
"Chemical modification of diamond surface using a diacyl peroxide as radical initiator and CN group-containing compounds for the introduction of the CN group"
Physical Chemistry Chemical Physics, 4, 3881-3886, (2002).

Toshiki Tsubota, Shintaro Ida, Osamu Hirabayashi, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumoto
"Chemical modification of diamond surface with CN Group in asetonitrile and Benzonitrile solutions containing benzoyl peroxide"(in Japanese)
The Surface Finishing Society of Japan, 53 (8), 530-534, (2002).

Chapter 5 Chemical modification of diamond surface with $CH_3(CH_2)_nCOOH$ using benzoyl peroxide

The chemical modification method of diamond surface using benzoyl peroxide and $CH_3(CH_2)_nCOOH$ described. The characterization of diamond surface is demonstrated. The reaction mechanism among hydrogenated diamond surface, racial initiators and $CH_3(CH_2)_nCOOH$ is discussed. The content of this chapter is based on the following papers:

Toshiki Tsubota, Shunsuke Tanii, Shintaro Ida, Masanori Nagata, Yasumichi Matsumoto
"Chemical modification of the diamond surface with $CH_3(CH_2)_nCOOH$ using benzoyl peroxide"
Physical Chemistry Chemical Physics, 5, 1474-1480, (2003).

Toshiki Tsubota, Shunsuke Tanii, Shintaro Ida, Masanori Nagata, Yasumichi Matsumoto
"Chemical modification of diamond surface with long alkyl chaining carboxylic acid in benzoyl peroxide containing organic solution"
Journal of The Surface Finishing Society of Japan, 54(11), 758-763, (2003).

Toshiki Tsubota, Shunsuke Tanii, Shintaro Ida, Masanori Nagata, Yasumichi Matsumoto
"Chemical modification of diamond surface with various carboxylic acids by radical reaction in liquid phase"
Diamond and Related Materials. in press.

Chapter 6 Preparation of HOOC-terminated diamond surface using benzoyl peroxide and dicarboxylic acid

Chemical modification of hydrogenated diamond surface using benzoyl peroxide and dicarboxylic acid is described. The characterization of diamond surface is demonstrated. The reaction mechanism among hydrogenated diamond surface, racial initiators and dicarboxylic acids is discussed. The content of this chapter is based on the following papers:

Shintaro Ida, Toshiki Tsubota, Shunsuke Tanii, Masanori Nagata, Yasumichi Matsumoto
"Chemical modification of diamond surface using benzoyl peroxide and dicarboxylic acids"
Langmuir, 19, 9693-9698, (2003).

Shintaro Ida, Toshiki Tsubota, Shunsuke Tanii, Masanori Nagata, Yasumichi Matsumoto
"New method for introducing the -COOH groups onto hydrogenated diamond surface"
Proceedings of the 20th Korea-Japan International Seminar on Ceramics, 317-320, (2003).

Chapter 7 Oxygenation of hydrogenated diamond surface in liquid phases

The reactivity of hydrogenated diamond surface with inorganic acid and basis is demonstrated. The characterization of diamond surface is demonstrated. The reaction mechanisms for the oxygenation of hydrogenated diamond surface in liquid phase are discussed. The content of this chapter is based on the following papers:

Shintaro Ida, Toshiki Tsubota, Shunsuke Tanii, Toshihito Ishida, Masanori Nagata, Yasumichi Matsumoto
"The reactivity of the hydrogenated diamond surface in the liquid phase"
Diamond and Related Materials, to be submitted.

Chapter 8 Chemical reaction of carbonyl groups of diamond surface with $LiAlH_4$

The reactivity of oxygenated diamond surface with LiAlH4 is demonstrated. The chemical reaction between carbonyl groups on oxygenated diamond surface and $LiAlH_4$ is discussed. The content of this chapter is based on the following papers:

Shintaro Ida, Toshiki Tsubota, Masanori Nagata, Yasumichi Matsumoto, Masato Uehara, Junichi Hojo
"Chemical reaction of carbonyl group on diamond surface with $LiAlH_4$"
Journal of The Surface Finishing Society of Japan, 54(11), 764-768. (2003).

Chapter 9 Surface modification of the oxygenated diamond surface with silane coupling reagents

Chemical modification of oxygenated diamond surface reforming using various silane coupling reagents is demonstrated. The mechanism of organic reaction on diamond surface is discussed. The content of this chapter is based on the following papers:

Toshiki Tsubota, Shintaro Ida, Osamu Hirabayashi, Sanpei Nagayama, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumo
"Surface reforming of the oxidized diamond surface with silane coupling reagents"
Journal of the Ceramic Society of Japan, 110, 904-910, (2002).

Toshiki Tsubota, Takahiro Kawahara, Shintaro Ida, Osamu Hirabayashi, Sanpei Nagayama, Shoji Nagaoka, Masanori Nagata, Ysasumichi Matsumo
"Surface reforming of diamond powder using silane coupling reagents" (in Japanese)
The Surface Finishing Society of Japan, 53(6) 413-418, (2002).

Chapter 10 General Conclusion

In this chapter, the general conclusions of present thesis are described.

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1.1. General Background

Diamond is one of the most well-known crystalline inorganic materials as jewels. Diamond is also one of the most promising substances for industrial material because diamond as a massive material possesses several specific physical properties, such as hardness, large band gap, transparency over a wide wavelength region, high thermal conductivity and so on. Therefore, so far a lot of research works have been performed for the synthesis of diamond and diamond's new application in the various fields [1].

Diamond is a crystalline inorganic material comprising sp^3-hybridised carbon atoms bonded to each other. Organic compounds also contain carbon atoms. Diamond surface is stabilized by bonding to elements other than carbon atoms, for example oxygen atoms or hydrogen atoms. The diamond surface terminated by hydrogen atoms or oxygen atoms may be regarded as the elongation of organic compounds because organic functional groups such as $-CH_x$ (x=1-3), -COOH, -CO-, -OH and so on are present on the diamond surface. Organic functional groups display various useful functions such as ion exchange and molecular recognition. If these functional organic compounds can be introduced onto diamond surface, the intelligent organic-diamond composite materials having chemical function of organic compounds and physical property of diamond will be able to be synthesized. Although the information of chemical reactivity of diamond surface is necessary to introduce organic compounds onto diamond surface, little is known about reactivity between organic regents and diamond surface. The purpose of this study is to investigate the chemical reactivity of diamond surface adopting the theory and techniques of organic chemistry and to suggest chemical modification method of diamond surface.

In this chapter, aim of chemical modification of diamond surface, general property of diamond, diamond growth overview and application of diamond are described. In the section of application of diamond, the outcome of our study on diamond's application for cutting tool is also described.

1.2. Aims of the chemical modification of diamond surface

Diamond consists of only carbon atoms which combine with sp^3 hybrid orbital each other. Diamond as a massive material is very stable against chemical reagents. However, it is known that diamond surface cannot terminate with carbon atom and is covered with heteroatoms such as oxygen atoms and hydrogen atoms, and diamond consists of carbon atoms, which is a prime constituent atom in organic compounds.

All organic compounds contain carbon atoms in the chemical structure. Organic chemistry, which deals with the properties of organic compounds, is one of the most basic academic fields in chemistry. Therefore, the theory, the technology, and the knowledge of organic chemistry have been considerably established. We believe that chemical modification of the diamond surface is possible using techniques of organic chemistry. However, the theory of organic chemistry may not be adopted directly because diamond is a true inorganic material. The study of chemical modification of diamond surfaces using organic chemistry is therefore quite interesting from an academic point of view.

At first glance, hydrogen terminated diamond surface is regarded as a huge alkane from the viewpoint of organic chemistry. However, the theory of organic chemistry cannot be directly applied to the hydrogenated diamond surface. So far, a few papers have reported that hydrogenated diamond surface is chlorinated by radical reaction [2-4], and that diamond surface is chemically modified with the NH_2 group via chlorinated surface as an intermediate [5, 6]. The chemical reaction mechanism of the diamond surface via chlorinated surface condition must be quite different from that of alkyl chloride. There are only two chemical reaction mechanisms of the substitution reaction for alkyl chloride, that is, the S_N1 mechanism and the S_N2 mechanism. In the case of the S_N1 mechanism, alkyl chloride separates into cation (carbocation) and anion (chloride ion), and then nucleophilic reagent reacts with carbocation. On the other hand, in the case of the S_N2 mechanism, nucleophilic reagent attacks the carbon atom combined with Cl atom from the opposite side of the Cl atom. If the chemical reaction mechanism of chlorinated diamond surface is the S_N1 mechanism, the intermediate must be multicharged cation because there are a number of chlorine atoms on a chlorinated surface diamond particle. However, it must be difficult for Cl^- ion to separate from the multichaged cation. If the chemical reaction mechanism of chlorinated diamond surface is the S_N2 mechanism, nucleophilic reagent must attack the carbon atom combined with Cl atom from the opposite side of the Cl atom. However, it is impossible for nucleophilic reagent to attack the diamond surface carbon atom from the opposite side of the Cl atom. Therefore, as for the substitution reaction, chlorinated diamond surface cannot be regarded as alkyl chloride at all. However, chlorinated diamond surface chemically reacts in practice. This reactivity of the chlorinated diamond surface is explained as follows [2]. The bond between the diamond surface carbon atom and the chlorine atom is unstable because of the steric hindrance of chlorine atom. Therefore, chlorinated diamond surface is easy to release chlorine atom, and results in the highly reactivity. This explanation is quite different form the reaction mechanism for alkyl chloride. Therefore, new theory for the chemical reaction of diamond surface must be established to explain the chemical reactivity of diamond surface. So far, there have been reported several research works related to chemical modification of diamond surface [2-11]. However, most of the experiments in these research works were performed in vapor phase. Moreover, very few papers reported the organic chemical reaction of diamond surface [5, 6], and there have been no study for the elucidation of the organic chemical reactivity of diamond surface, except for our papers [12-15].

It is known that most of organic functional groups have various functions such as ion exchange, molecular recognition, DNA immobilization, formation of covalent bonding and so on. Most of these functions are chemical properties. Both diamond as a massive material and organic functional group possess the unique and useful properties, and the properties of diamond as a massive material are quite different from those of organic material. Therefore, if diamond surface is controllably modified with organic functional groups, we can make quite a new organic-inorganic functional material, which possesses physical function of diamond as a massive material and chemical function of organic functional group.

For example, if high thermal conductivity (physical property of diamond as a massive material) and DNA immobilization (chemical property of organic functional group) are combined, PCR micro reactor will be established on diamond chip. p-Type conductive diamond as a massive material is easily synthesized by boron doping. Moreover, it is known that as grown CVD diamond surface has p-type conductivity. However, because of the reproducibility, it is difficult to synthesize n-type conductive diamond as a massive material although there are a few papers about the synthesis of n-type conductive diamond [17-21]. Moreover, so far there has been no report about n-type conductive diamond surface. If n-type conduction of diamond surface is realized by means of the chemical modification of diamond surface, electronic device will be fabricated on diamond surface by the combination of the n-type conduction and the known p-type diamond surface conduction.

So far, most of the research works related to diamond surface were performed from a physical standpoint, that is, the theory and the technique of surface physics [22-33]. The concept of these studies is that diamond should be explained by the expanded theory of silicon single crystal because diamond has the same crystal structure as silicon single crystal and carbon, which constitutes diamond, is the same group in periodic table as silicon. High expensive equipments (high vacuum apparatus, high sensitive spectroscopy, and high purity materials etc.), which are used in the research works for silicon as electronic material, have been used in these studies. However, it is a disadvantage to use these high expensive equipments for industrial application. In contrast, the reactions of organic chemistry are generally carried out under mild conditions (mild atmosphere, mild temperature, poor purity, and so on). Scale-up and mass production are facilitated in the case of reactions in the liquid phase. In general, the cost for the apparatus of liquid-phase chemical reactions is less than that of vacuum systems. Moreover, the technology of chemical engineering, which is the academic system for chemical plants, can be applied when chemical reactions were adopted for chemical modification of diamond surface. The technique of chemical modification of the diamond surface using organic chemistry is therefore quite interesting from an industrial point of view.

In this study, we carried out the chemical reaction of diamond surface using various chemical reagents for preparation of new type intelligent hybrid materials.

1.3. General property of diamond

Diamond is a crystalline inorganic material comprising sp^3-hybridised carbon atoms bonded to each other. Each carbon atom is bonded to four neighbors, and these tetrahedra are arranged in such a way that eight atoms it in a cube whose edge is the lattice constant (3.567 □). The distance between C-C bond is 1.54 □.

Diamond provides an impressive combination of chemical, physical and mechanical properties. For example, diamond has special properties, such as high hardness, wide bandgap, chemical inertness and so on. Typical physical and mechanical properties are listed in Table 1.1 [34]. With regard to the special surface properties of diamond surface, there are extreme chemical inertness, low surface energy, low friction coefficients, negative electron affinity and biological inertness.

Diamond react with strong carbide forming metals (i.e. tungsten, tantalum and zirconium). It dissolves in iron, cobalt, manganese, nickel, chromium and the platinum-group metals.

Table 1.1 Typical physical and mechanical properties for diamond.

Density (g/cm^3)	3.50
Young's Modulus (GPa)	1050
Bend Strength (MPa)	850
Fracture Toughness K_{Ic} (MPa.m $^{0.5}$)	3.5
Hardness (GPa)	45
Thermal Expansion Coefficient (x 10^{-6}/°C)	1.1
Coefficient of Friction	0.02
Electrical Resistivity (ohm.cm)	$>10^{13}$
Thermal Conductivity (W/mK)	400
Decomposition Temperature in nitrogen (°C)	1500

1.4. Diamond growth overview [1]

Naturally occurring diamond; about 20 tones of diamond are mined each year. Half are gem quality and half are industrial quality. Synthetic single crystal diamond; about 90 tones of diamond are made annually by the high-pressure and high temperature method. Most industrial diamond is made from graphite at pressures of 4.5 to 6.0 GPa and temperatures of 1400 to 1600°C with the aid of a molten transition metal catalyst. These diamonds are considerably cheaper than natural diamond. Polycrystalline diamonds are formed usually by either cementing diamond grains together using metal as a bonding agent or sintering using Boron Carbide as a sintering aid. Vapor phase deposition. Both chemical vapor deposition (CVD) and physical vapor phase deposition (PVD) produce thin diamond films. About 10 tones of vapor phase grown diamond films are produce annually. Their cost is more than four times that of naturally occurring diamond. However, their application can be justified economically as they are used in thin film form and make a significant difference to component properties.

Diamond is one of the most stable chemical structures in nature, but graphite has an even more favorable free energy of formation than diamond under normal ambient pressures and temperatures. The Gibbs free energy of formation at room temperature and 1 atm is 2.9 kJ/mol more negative for graphite than for diamond. When carbon condenses under other than extreme pressures, the formation of graphite is thermodynamically favored instead of the growth of diamond. If one were to try to transform graphite to diamond at room temperature, a pressure of at least 16,000 atm would be required, although the kinetics of transformation would of course be vanishingly slow at this temperature. However, at higher temperatures the pressure stability region of graphite expands even further, and even higher pressures are required to favor the growth of diamond. At 1700 K in excess of 50 kbar are required to reach the diamond stability region, which creates a serious technical barrier to the growth of synthetic diamond by high pressure processes.

Despite these barriers, synthetic diamond is now grown on a large scale in high pressure presses under diamond stable conditions by dissolution of graphite in metal "solvent-catalysts" and precipitation of diamond. This process was developed in the mid 1950s and commercialized by General Electric, followed soon after by De Beers and others. The worldwide market for synthetic super abrasives, including diamond and cubic boron nitride grit, polycrystalline diamond and cubic boron nitride (manufactured under high pressures and high temperatures), and diamond and cubic boron nitride powder, is approximately one billion US dollars per year and continues to expand significantly.

Questions remain concerning how diamond forms in nature. Conventional models have diamond growing over geological eons, 200 or more kilometers below the surface of the earth under high temperatures and pressures, and subsequently being transported to the surface by primary volcanic intrusions. In South Africa, the type of volcanic rock commonly associated with diamonds is called kimberlite, after the area where it was first discovered. In the 1970s, in Australia, diamonds were also discovered in a significantly different type of volcanic intrusion known as lamproite. More recently, it has also been proposed that diamond can form in the interior of large planets such as Uranus and Neptune, whose atmospheres contain CH_4, water, and ammonia, through the conversion of methane to diamond at pressures in the range of 10–50 GPa and 2000–3000 K. The authors propose that this process of conversion to diamond even produces enough energy to contribute to the observed energy budget of these planets.

1.5. Applications

The use of diamond has grown enormously since World War 2, exploiting the unique combination of properties and the increased availability of the material as synthesis methods developed. The following applications are covered in more detail below [35, 36]

1.5.1 Thermal Management in Substrates, Heat Spreaders and Heat Sinks

Diamond provides the unique combination of high thermal conductivity with electrical insulation. Applications include hybrid circuit packages, heat sinks for laser diodes and small microwave power device, integrated circuit substrates and printed circuit boards. The use of diamond enables higher operating speed as devices can be more tightly packed without overheating. Further reliability improvements should be expected, as the junctions in the devices will be operating at lower temperature when mounted on diamond.

1.5.2. Semiconductor Devices

The electronic structure of diamond has a wide band gap giving it the potential for use as a semiconductor. However, there are a number of issues that must be overcome before diamond coatings are widely exploited in this area. Prime concerns are effectively doping the material and the growth of single crystal or highly oriented films. Active devices have been made from boron doped (p-type) films grown on diamond substrates. The devices are capable of operating at temperatures > 500°C compared with a maximum operating temperature of 200°c for silicon and gallium arsenide devices. Potential applications include very high power transistors, high temperature integrated circuits, piezoelectric devices and radiation hardened integrated circuits.

1.5.3. Optical Components

Diamond is starting to be used in optical components, particularly as a protective coating for infrared optics in harsh environments. A thin layer of CVD diamond can protect Infra Red windows made from ZnS, ZnSe, and Ge, which are brittle and easily damaged. Future applications may use freestanding polycrystalline film, provided optical flatness can be achieved.

1.5.4. Cutting Tools

The properties exploited by cutting tools are hardness, strength, low thermal expansion coefficient, low friction coefficient and chemical inertness. The cutting tool products, for example, include oil drilling bits, rock drill cutters, wire drawing dies, extrusion dies, cutting tool inserts, optical grinding tools, coatings for computer hard discs and coatings for ball bearings. Diamond-cutting tools are separated from two types. One is cutting tool used single crystal diamond, the other is cutting tool used polycrystalline diamond. In the case of cutting tool used polycrystalline diamond, diamond film are coated onto cutting tool by CVD. When using coatings, manufacturers must pay attention to coating adhesion and ensure the coating is uniform.

In this section, we report preparation method of CVD diamond films on WC-Co substrates via electrophretic deposition.

First of all, background of this study is described. It is well known that the nuclei density of CVD diamond synthesized on a non-diamond substrate is insufficient for forming a diamond film without an appropriate pretreatment. For the purpose of synthesizing a diamond film, several techniques have been developed for enhancing the nuclei density. Scratching pretreatment is one of the most popular methods for increasing the nuclei density. Yugo et al. [37] found that a bias enhanced nucleation (BEN) method was effective for increasing the nucleation density. It is known that the diamond surface dispersed in solvent has electrical charge. Using this phenomenon, diamond particles could be deposited on a substrate. This method is called electrophoresis. Several researchers have attempted to utilize electrophoretic deposition as the seeding process for CVD diamond synthesis [38-41]. Zhitomirsky [39] reported that diamond particles were electrophoretically deposited on a cathode by using keto-enol reaction. Lee et al.[40] tried to synthesize (111) oriented diamond films with electrophoretic deposition. Schaller et al.[41] analyzed the surface properties of electrophoretically deposited nano-size diamond particles on a Si(100) substrate.

A number of research works into CVD diamond coating on cutting tools [42-59] have been carried out in order to utilize the highest hardness of diamond. Cutting tools made of cobalt-doped tungsten carbide (WC-Co) are suitable as the substrate for CVD diamond because of the hardness. In the case of CVD diamond coating on WC-Co cutting tools, the abrasion force between the WC-Co substrate and the CVD diamond is the most important factor for improving the performance. To date, the adhesion force has been insufficient to make full use of the performance of diamond. It is known that the cobalt on the WC-Co cutting tool causes weakness of the adhesion force. Cobalt acts as a sintering agent in WC-Co cutting tools. However, carbon, which is the constituent atom of diamond, dissolves in cobalt. In general, for the purpose of removing the cobalt on the WC-Co substrate surface, the WC-Co substrate is treated with mineral acid before CVD diamond synthesis. Murakami reagent, a solution of potassium ferricyanide and potassium hydroxide in water (1:1:10), is used for removing the cobalt on the WC-Co substrate [60]. The adhesion force of CVD diamond increased with the acid pretreatment to some extent, but was insufficient for application as a cutting tool. So far, a great number of works regarding the adhesion force of CVD diamond [42-59] have been performed in several laboratories. Peter et al. [53] reported that pretreatment with Murakami reagent was effective in enhancing the adhesion force of diamond on WC-Co substrate. Decarburization of the WC-Co surface prior to the diamond deposition was also carried out [44-46] to enhance the adhesion force. Saito et al. [47] proposed that a heat treatment for creating an interlayer be adopted as one of the steps in pretreatment. Oles et al. [48] reported that heat treatment prior to the CVD process strengthened the adhesion force of the CVD diamond on the WC substrate. Singh et al. [53] found that treatment with multiple nanosecond laser pulses before diamond deposition is effective in enhancing the adhesion force. Murakawa et al, [50] reported that the diamond made from ethanol had a good adhesion force on WC-Co substrate. Nesladek et al. [51] reported that the development of a complex interlayer on WC-Co substrate improved the adhesion force of CVD diamond. As mentioned above, there are numerous studies related to the diamond coating on WC-Co cutting tools, or related to the electrophoretic deposition of diamond. However, no researcher has used an electrophoretic deposition for the seeding process of CVD diamond in the case of the diamond coating on a WC-Co cutting tool. The reason for this is that the adhesion force between the electrophoretically deposited diamond particles and the substrate is supposed to be weak. Nevertheless, electrophoretic deposition is one of the most promising seeding methods. Electrophoretic deposition is electrically controlled, so the deposition condition can be controlled precisely. Therefore, in this study we attempted to synthesize CVD diamond films on WC-Co substrates via electrophretic deposition, and the improve the strength of the adhesion force between CVD diamond and WC-Co substrate.

Experimental was performed as following, Commercial WC-Co cutting tools, (JIS standard: K-10), were used as the substrate for CVD diamond films in this study. In order to eliminate the cobalt on the WC-Co surface, the substrate was immersed in dilute HNO_3 solution for 5 minutes, and then rinsed with distilled water. Diamond powder (average diameter = 250 nm) was suspended in acetone at a concentration of 0.1 g l^{-1}. This suspension was agitated with ultrasonic cleaner. A Si(100) substrate or a WC-Co substrate was dipped in the acetone containing diamond powder, and used as an electrode. A Pt plate was also dipped in this solution as a counter electrode. The diamond particles were electrophoretically deposited on the electrode. After this electrophoretic deposition, the WC-Co substrate was heated in an Ar atmosphere at 500□ for 2 hours. CVD diamond was synthesized on these substrates using an ECR-MPCVD apparatus.

The reason why the substrate was immersed in dilute HNO_3 solution is because cobalt on the surface of the WC cutting tool prevented CVD diamond from depositing on the WC cutting tool. Scratching with diamond particles on the surface of the WC cutting tool, which is one of the most popular pretreatments for enhancing the nuclei density of CVD diamond, were ineffective on the WC cutting tool without removing surface cobalt. On the other hand, electrophoresis treatment was effective for increasing the diamond nuclei density on the WC cutting tool without removing the surface cobalt. However, when elecrophoresis was adopted as a pretreatment, the CVD diamond films synthesized on the WC cutting tools with no surface cobalt separated from the surface of the WC cutting tool. To improving the adhesion force between CVD diamond film and the WC cutting tool, heat treatment was performed after the electrophoresis pretreatment. The heat treatment condition was 500□ for 2 hours in Ar flow. The heat treatment after electrophoresis treatment was effective for improving the adhesion force between WC surface and CVD diamond film. The Vickers hardness test was carried out for estimating the adhesion force. The Vickers hardness of the CVD diamond film made with electrophoresis-heat pretreatment was as hard as that of the CVD diamond film made with scratch pretreatment, a conventional pretreatment. From the result of the Vickers hardness test, it was concluded that the heat treatment after electrophoresis was effective for improving the strength of the adhesion force.

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Chapter 2

Hydrogen abstraction reaction on hydrogenated diamond surface using benzoyl peroxide

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2.1. Introduction

Diamond as a solid state material has many specific properties such as high hardness, large band gap, stability against chemical reagents, transparency over a wide wavelength region, high thermal conductivity, and so on. Therefore, many researchers have regarded diamond as one of the most promising industrial materials in various fields.

It has been reported that the diamond surface reacts with chemical materials [1-16]. Ando et al. [1-7] and Miller et al. [8] attempted chlorination of the hydrogenated diamond surface using Cl_2 in the gas phase. They utilized a radical reaction process for this surface reforming. Ohtani et al. [9] reported that functional groups were introduced on boron-doped CVD diamond surfaces. This CVD diamond was exposed to Cl_2 gas and simultaneously subjected to UV irradiation, and then treated with boiling pyridine. Kuo et al. [10] utilized a boron-doped diamond substrate as a cathode for the electrochemical reaction of phenyl diazonium in acetonitrile. Saito et al. [11-13] and Tsubota et al. [14, 15] attempted to chlorinate the hydrogenated diamond surface in the liquid phase. Recently, Fujishima et al. [16] have examined the potential of surface modified diamonds for use as electrochemical electrodes.

It is known that Cl radical abstracts the hydrogen atoms on a diamond surface [1-9, 11-15]. However, there has been no report of hydrogen abstraction reactions of a diamond surface with the other radical species. Benzoyl peroxide is one of the most popular radical initiators in polymer science. In this study, we carried out hydrogen abstraction reaction on hydrogenated diamond surface using benzoyl peroxide as radical initiator. The reaction rates for the abstraction of hydrogen atoms on diamond surface were calculated from the experimental results.

2.2. Experimental

Commercial diamond powder (Tomei diamond MD500; average diameter = 500 nm) was used as the substrate in this study. The diamond powder was washed with mixed acid (HF + HNO_3) at room temperature for 4 hours, and then rinsed with distilled water. After drying, the diamond powder was washed with mixed acid (H_2SO_4 + HNO_3) at 80℃ for 4 hours, and then rinsed with distilled water. After re-drying, the treated diamond powder was heated in an H_2 gas flow at 900℃ for 5 hours. This latter powder ("hydrogenated diamond") was used as the starting material.

Figure 2.1 shows a diagram of the reaction apparatus used in this study. Benzoyl peroxide was employed as a radical initiator. Both the hydrogenated diamond powder and benzoyl peroxide were suspended in a solvent; i.e. toluene, acetonitrile, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), cyclohexane, or *n*-hexane. Argon gas was bubbled into the suspensions while these were heated at 75℃ to activate the radical initiator. After this radical reaction process, the diamond powders were washed a few times with chloroform then dried in a vacuum dryer.

The surfaces of the diamond powder were characterized by diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy (JASCO FT/IR-700). A field emission type scanning electron microscope (FE-SEM) (HITACHI S-4000) was used for the observation for the microstructure of the diamond particles. BET measurements (QUANTACHROME AUTOSORB-1) were carried out to evaluate the specific surface area of the diamond powder.

2.3. Results and discussion

2.3.1. Hydrogenated diamond

The IR spectrum of the hydrogenated diamond powder used in this study as the starting material is shown in Figure 2.2. In this spectrum, there are two large peaks at *ca.* 2840 cm^{-1} and *ca.* 2930 cm^{-1}. These peaks are assigned to the C-H bonds. The appearance of this bond is similar to that of the spectra reported previous by [1-7, 11-15]. Ando et al.[7] reported that the larger peak at *ca.* 2840 cm^{-1} and the smaller peak at *ca.* 2930 cm^{-1} are assigned to the C-H stretching vibration and the C-H asymmetric vibration, respectively.

The SEM image of the hydrogenated diamond powder used in this study is shown in Figure 2.3. The shape of these diamond particles is not spherical but multi faceted surface.

The specific surface area of this hydrogenated diamond powder was 9.94 m^2 g^{-1}.

The specific surface areas, S m^2 g^{-1}, of a spherical particle and a cubic particle are calculated as follows,

$S = 6/r\rho$ (spherical particle) (1)

$S = 6/r\rho$ (cubic particle) (2)

where r [m] is the diameter of the spherical particle or the length of the side for the cubic particle, and ρ g m^{-3} is the density of the spherical particle or the length of the side for the cubic particle. The ρ value is reported to be 3.515×10^6 g m^{-3}. When the r value is 500 nm, the S values are as follows,

$S = 3.41$ m^2 g^{-1} (spherical particle)

$S = 3.41$ m^2 g^{-1} (cubic particle)

These calculated values are rather smaller than the measured S value in this study. As shown in Figure 2.3, the diamond particle used in this study has a rough surface, the presence of which must the reason for the larger specific surface area.

A few researchers [4, 7, 14, 15] reported the specific surface area of hydrogenated diamond powders that have 500 nm average diameter. The values reported Ando et al. were 20.3 m^2 g^{-1} [4] and 22.1 m^2 g^{-1} [7], and that reported Tsubota et al.[14, 15] was 21.0 m^2 g^{-1}. These previously reported values are rather larger than the value obtained in this study. In this study, we utilized diamond powder that has a narrow particle size distribution. We can consider that the difference in the distribution of the particle size must be the reason for the differences in the specific surface areas.

2.3.2 Reaction with benzoyl peroxide

Benzoyl peroxide decomposes on heating (60-80 °C) and generates radical species as follows,

$C_6H_5\text{-}COO\text{-}OOC\text{-}C_6H_5 \rightarrow 2\ C_6H_5\text{-}COO\cdot$ (3)

In order to investigate the reactivity of the hydrogenated diamond surface with the radical species generated from benzoyl peroxide, we reacted the hydrogenated diamond powder with benzoyl peroxide in the various solvents.

The IR spectra of the diamond powders after reaction are shown in Figure 2.4. In all cases, the intensities of the peaks attributed to the C-H bonds on the diamond surface decreased following reaction with benzoyl peroxide. Hydrogen atoms on the diamond surface, therefore, must be abstracted by the radical species generated from benzoyl peroxide.

The peak intensity of the C-H bands after the reaction process depended on the solvent used. For the solvent dependence of the C-H peak intensity after the reaction process, we can consider the solvent dependence of the chain transfer constant and the solvent dependence of the rate of the induced decomposition of benzoyl peroxide

It is known that THF and DMF have large chain transfer constants. This could be the reason why the diamond powders reacted in THF or DMF have larger peaks assigned to C-H bonds.

The peak positions and the number of the additional peaks appearing after the reaction were independent of the solvent, except for acetonitrile. The diamond surface after reaction with benzoyl peroxide, therefore, must be in the same state, regardless of the nature of the solvent. The peak at ca. 2280 cm^{-1} in the IR spectrum after reaction in acetonitrile must be assigned to the presence of the C≡N bond. The functional group produced containing the C≡N bond most probably is derived from acetonitrile.

After radical reaction, a small peak appeared at 3072 cm^{-1} in the IR spectra of all the samples. This peak may correspond to the phenyl group reacting with the diamond surface.

As shown in Figure 2.4, the intensity of the peaks assigned to the C-H bond after the reaction process depended on the species of the solvent. To quantitatively evaluate the degree of hydrogen abstraction from the diamond surface, we carried out normalization of the peak intensities of the C-H bands. The small peak at *ca.* 2160 cm^{-1} was assigned to the absorption for the two-phonon of diamond. The intensity of the peak assigned to the C-H stretching vibration, $I_{C\text{-}H}$, at ca. 2840 cm^{-1}

was divided by the intensity of the peak assigned to the two-phonon peak, $I_{\text{two-phonon}}$. We used only the peak heights only. Table 2.1 shows the value of this ratio depended on the solvent.

The radical species generated from benzoyl peroxide dissolves as follows when the radical species does not react with another molecule.

$$C_6H_5\text{-}COO^{\cdot} \rightarrow C_6H_5^{\cdot} + CO_2 \qquad (4)$$

The chemical reaction indicated in Eq. (4) is called induced decomposition. It is well known that in the case of peroxide compounds the reaction rate of the induced decomposition depends on the solvent. The induced decomposition, therefore, could be the reason for the difference of the reaction rate shown in Table 2.1.

In order to examine the chemical reaction of the hydrogenated diamond surface with benzoyl peroxide more thoroughly, further experiments were performed. Using toluene as the solvent, we investigated the reaction time dependence of the diamond surface condition. The IR spectra for the diamond powders treated with benzoyl peroxide are shown in Figure 2.5. The peaks assigned to the C-H bonds decreased with increasing reaction times which decreased on increasing the amount of benzoyl peroxide. The peak positions and the number of peaks produced were independent of the reaction time.

The reaction time dependences of the ($I_{\text{C-H}}/I_{\text{two-phonon}}$) values are shown in Figure 2.6. Although the ($I_{\text{C-H}}/I_{\text{two-phonon}}$) value decreased with increasing reaction time, the decrement per unit time of this decreased with increasing the reaction time.

In order to reveal the limit of the hydrogen abstraction by benzoyl peroxide, we performed the experiment under the following conditions: amount of added benzoyl peroxide 2 g; reaction time 8 hours. The ($I_{\text{C-H}}/I_{\text{two-phonon}}$) value of this sample was 2.8.

In the case of the following chemical reaction,

$$A + B \rightarrow C \qquad (5)$$

where A and B are reactants and C is a product, C is not affected by the reaction rate. The reaction rate is as follows,

$$-r_A = k\,C_A^{n}\,C_B^{m} = k'\,C_A^{n} \qquad (6)$$

$$k' = k\,C_B^{m} \qquad (7)$$

where r_A is the reaction rate of this reaction, k and k' are the reaction rate constants, and C_A and C_B are the concentrations of the reactants.

In this study, we used the $(I_{C\text{-}H}/I_{two\text{-}phonon})$ values as the C_A value, and adopted the slope of the curved line in Figure 2.6 as the r_A value.

From Eq. (6),

$$\log(-r_A) = n \log C_A + \log k' \qquad (8)$$

The graph of log C_A vs. log $(-r_A)$ is shown in Figure 2.7. From the lines in Figure 2.7, the values of k' and n were determined and are shown in Table 2.2.

Therefore,

$$r_A = (5.75\times10^{-8})\ C_A^{5.62} \qquad (9)$$

$$r_A = (1.25\times10^{-3})\ C_A^{2.81} \qquad (10)$$

The k' values are the product of corresponding k and C_B values. C_B is the amount of benzoyl peroxide instantaneously present, and depends on both the amount of added benzoyl peroxide and the reaction time. Therefore, the difference in the k' values for these two samples is reasonable. The n value was affected by the amount of added benzoyl peroxide but the reason for this difference is unclear.

After reaction with the benzoyl peroxide, several new peaks appeared in the IR spectra. Two small peaks appeared at just above 3000 cm^{-1}. These peaks could be attributed to the C-H bond in aromatic compounds and the peaks at 700-1450 cm^{-1} assigned to an ester group. The peak at 1718 cm^{-1} must be assigned to a C=O bond. Ando et al.[7] reported that the peak assigned to a C=O bond on diamond surface shifted to a higher wavenumber with the increasing degree of oxidation of the diamond surface. However, in this study the peak position of the C=O bond was constant in the IR spectra of all the diamond powders reacted with benzoyl peroxide.

From this data, we can conclude that the C=O bond in the reacted diamond powders was not bound directly with the diamond surface.

From the IR data, we believe that the chemical reaction at the diamond surface abstracted the hydrogen atoms to give bound benzoate,

$$(\text{diamond})\cdot + C_6H_5\text{-}COO\cdot \rightarrow (\text{diamond})\text{-}OOC\text{-}C_6H_5 \qquad (11)$$

2.3.3. Dependence of the amount of the added benzoyl peroxide

The IR spectra for the diamond powders treated with benzoyl peroxide are shown in Figure 2.8. The peak intensities of the diamond C-H bonds decreased with increasing amounts of added benzoyl peroxide. The peak position and the number of peaks appearing after the reaction process were independent of the amount of added benzoyl peroxide up to 0.5 [g].

The dependence of the ($I_{C\text{-}H}/I_{\text{two-phonon}}$) value on the amount of benzoyl peroxide added is shown in Figure 2.9. It decreased rapidly with increasing amounts of added benzoyl peroxide up to 0.005 g, and was approximately constant thereafter.

Saito et al. estimated the number of hydrogen atoms on the hydrogenated diamond surface at 5.95×10^{-4} mol g^{-1}.[13] The specific surface area of the diamond powder used by Saito et al. was 21.0 m^2 g^{-1}. If this estimate reported by Saito et al. is correct, then the density of the hydrogen atoms on the diamond surface used in this study is 2.82×10^{-4} mol g^{-1}. The mol numbers of hydrogen atoms on diamond, toluene used as the solvent, and added benzoyl peroxide are summarized in Table 2.3.

The hydrogen abstraction reaction of the diamond surface with the radical species generated from benzoyl peroxide should be as follows,

$$(\text{diamond})\text{-}H + C_6H_5\text{-}COO\cdot$$
$$\rightarrow (\text{diamond})\cdot + C_6H_5\text{-}COOH \qquad (12)$$

In this study, the reaction was performed in toluene. The hydrogen abstraction reaction of toluene with the radical species generated from benzoyl peroxide should also be considered,

$$C_6H_5\text{-}CH_3 + C_6H_5\text{-}COO\cdot \rightarrow C_6H_5\text{-}CH_2\cdot + C_6H_5\text{-}COOH \quad (13)$$

As shown in Table 2, the number of toluene molecules is much larger than that of hydrogen atoms on the diamond surface. If the reaction of Eq. (13) is more dominant than that of Eq.(12), then the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value does not decrease with increasing amounts of added benzoyl peroxide when the amount of added benzoyl peroxide is small. Therefore, the rapid reduction of the C-H peak up to 0.005 g indicates that most of the radical species generated from benzoyl peroxide abstract the hydrogen atoms on the diamond surface.

Given the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value was approximately constant at more than 0.005 g, we can conclude that not all of the hydrogen atoms on the diamond surface are abstracted by the radical species generated from benzoyl peroxide.

The maximum peak after the reaction with benzoyl peroxide is at 1275 cm^{-1}. The intensity of this peak, I_{max}, was estimated and the ($I_{max}/I_{two\text{-}phonon}$) value was calculated, as shown in Figure 2.10. The ($I_{max}/I_{two\text{-}phonon}$) value increased with increasing added benzoyl peroxide up to 0.005 g, and gently decreased with added benzoyl peroxide more than 0.005 g.

As shown in Table 2.3., when the amount of added benzoyl peroxide was 0.005 g, the amount of added benzoyl peroxide was nearly equal to the numbers of the hydrogen atoms on the diamond surface. We think that an excess radical species derived from benzoyl peroxide would then attack the functional groups produced on the diamond surface.

2.4. Conclusion

The reactivity of a hydrogenated diamond surface with benzoyl peroxide was investigated. It was found that the radical species derived from benzoyl peroxide reacts with the hydrogenated diamond surface and abstracts the hydrogen atoms on the diamond surface. The degree of this hydrogen abstraction was quantitatively discussed. The reaction rate of the hydrogen abstraction reaction was calculated from the experimental data.

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Table 2.1 The $I_{\text{C-H}}/I_{\text{two-phonon}}$ values of the IR spectra for the diamond powder treated in various solvents

	toluene	acetonitrile	THF	DMF	cyclohexane	n-hexane
$I_{\text{C-H}}/I_{\text{two-phonon}}$	4.8	5	14	7	4.3	3.2

Table 2.2 Values of the coefficients for the reaction in toluene

Amount of added benzoyl peroxide [g]	log K	K [min^{-1}]	n
0.001	-7.24	5.75×10^{-8}	5.62
0.05	-2.90	1.25×10^{-3}	2.81

Table 2.3 Amounts of reagents used in this study

Diamond	Hydrogen atoms on diamond	Toluene		Benzoyl peroxide	
[g]	[10^{-5} mol]	[ml]	[10^{-2} mol]	[g]	[mol]
0.1	2.82	5	4.70	0.001	4.13×10^{-6}
0.1	2.82	5	4.70	0.005	2.07×10^{-5}
0.1	2.82	5	4.70	0.01	4.13×10^{-5}
0.1	2.82	5	4.70	0.05	2.07×10^{-4}
0.1	2.82	5	4.70	0.1	4.13×10^{-4}
0.1	2.82	5	4.70	0.3	1.24×10^{-3}
0.1	2.82	5	4.70	0.5	2.07×10^{-3}

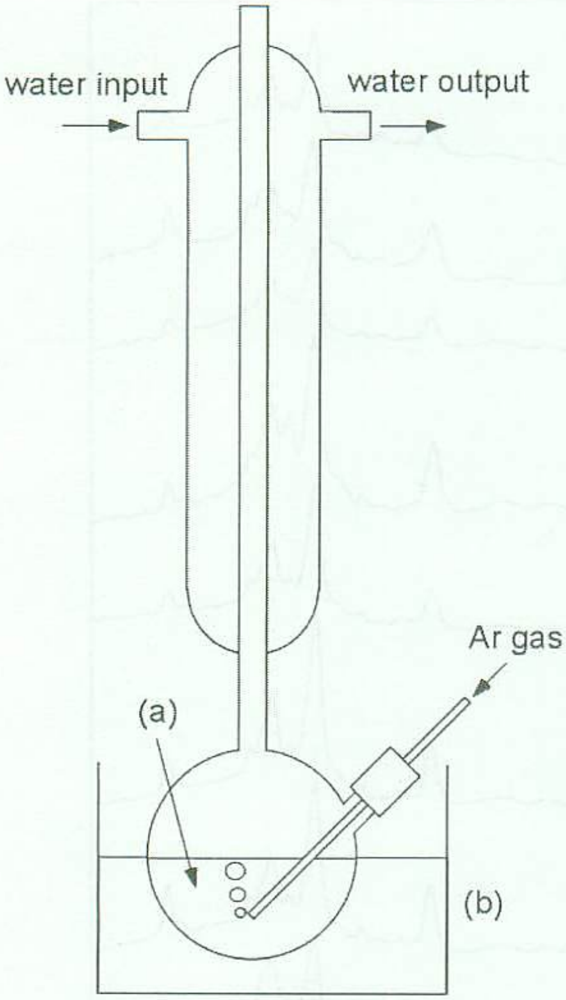

Figure 2.1 Reaction apparatus used in this study.

(a) suspension; (b) oil bath.

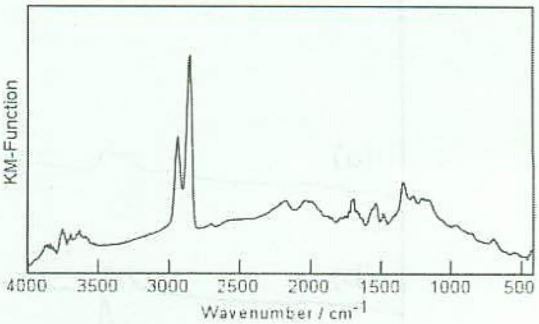

Figure 2.2 IR spectrum for hydrogenated diamond powder used in this study.

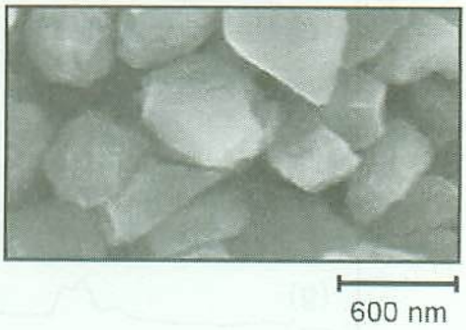

Figure 2.3 SEM image of the hydrogenated diamond powder used in this study.

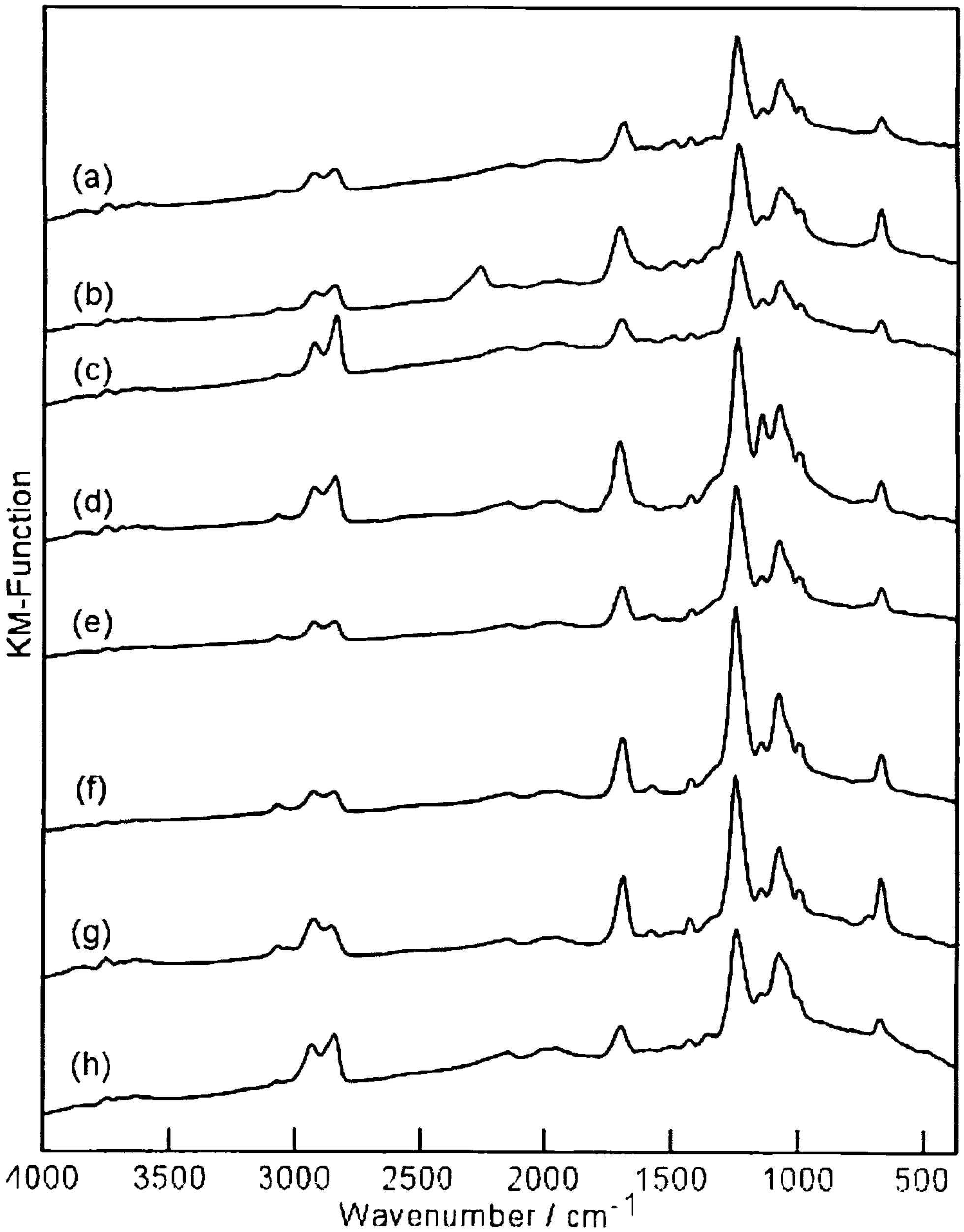

Figure 2.4 IR spectra for the diamond powders reacted with benzoyl peroxide in (a), toluene; (b), acetonitrile; (c), tetrahydrofuran (THF); (d), N,N-dimethylformamide (DMF); (e), cyclohexane; (f), n-hexane; (g), styrene; (h), ethanol.

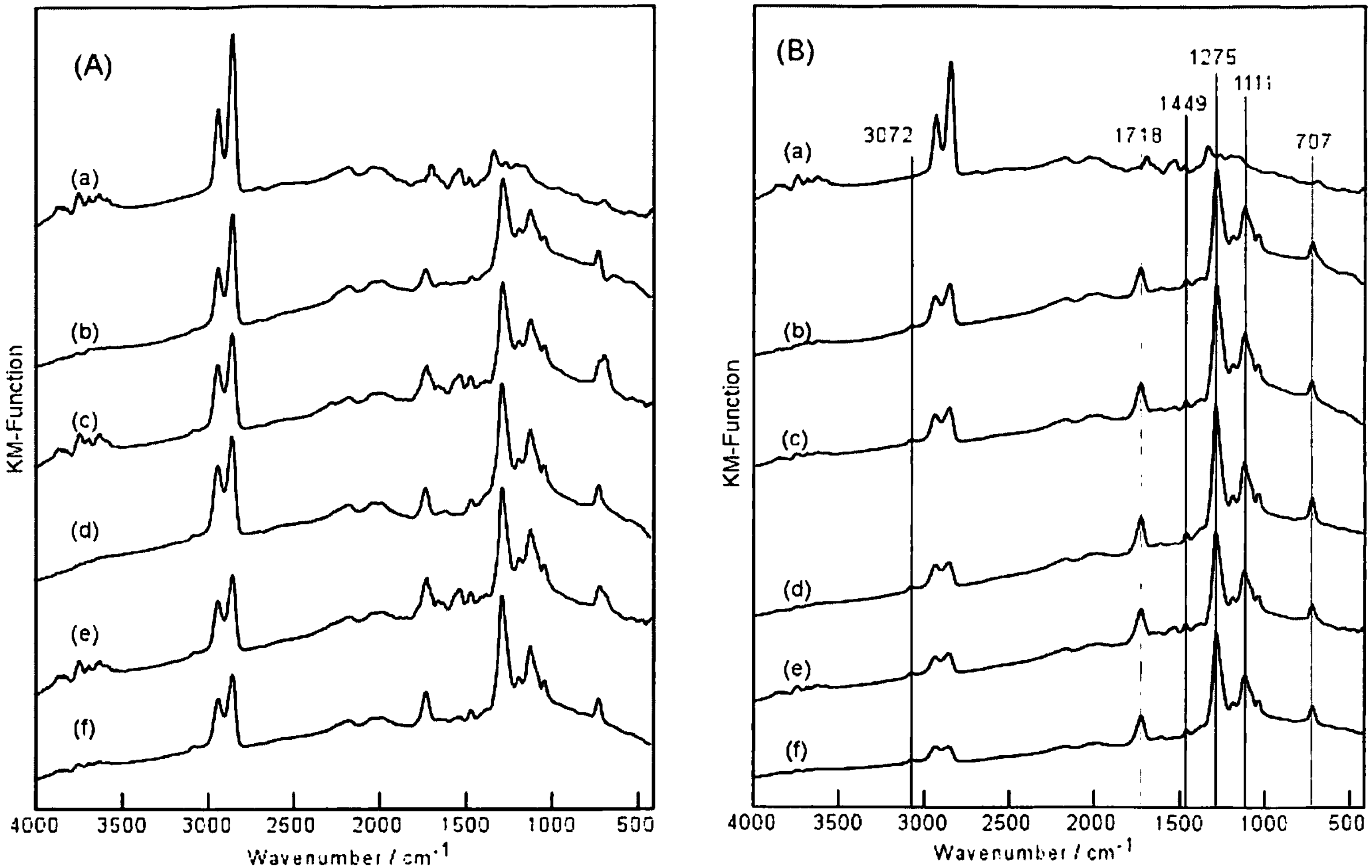

Figure. 2 5 IR spectra for the diamond powders treated with benzoyl peroxide in toluene
(A) the amount of the added benzoyl peroxide is 0.001 g,
(B) the amount of the added benzoyl peroxide is 0.05 g,
(a) reaction time = 0 min, (b) 5 min, (c) 15 min, (d) 30 min (e) 60 min, (f) 120 min

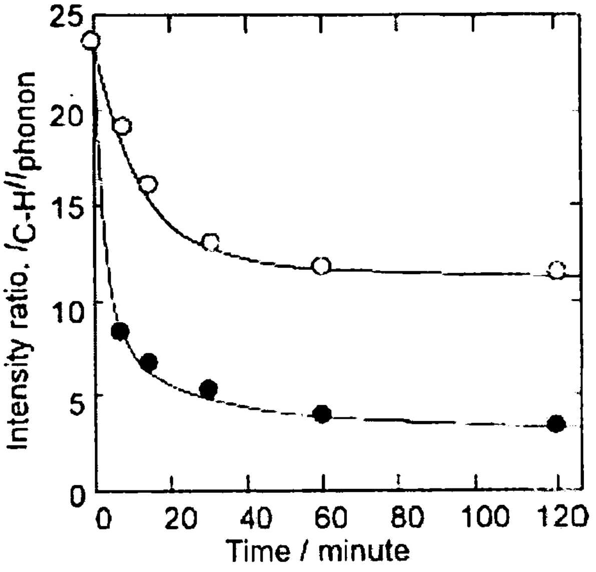

Figure 2.6 Reaction time dependence of the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) values.o, 0.001[g; •, 0.05 g.

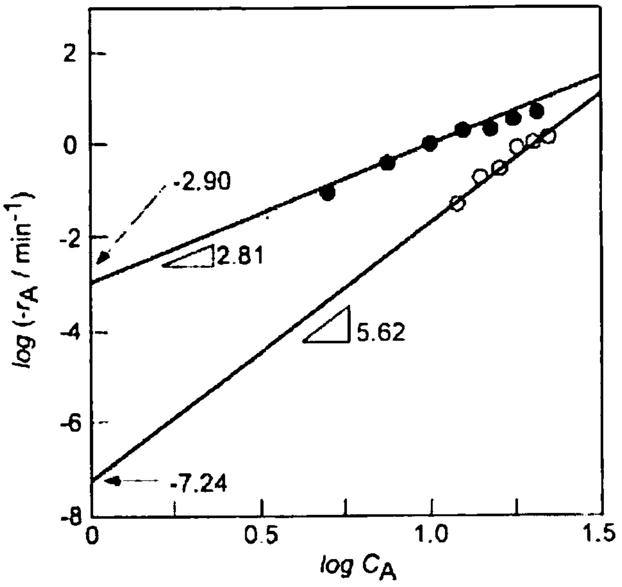

Figure 2.7 Plots of log C_A vs. log ($-r_A$). o, 0.001 [g]; •, 0.05 [g].

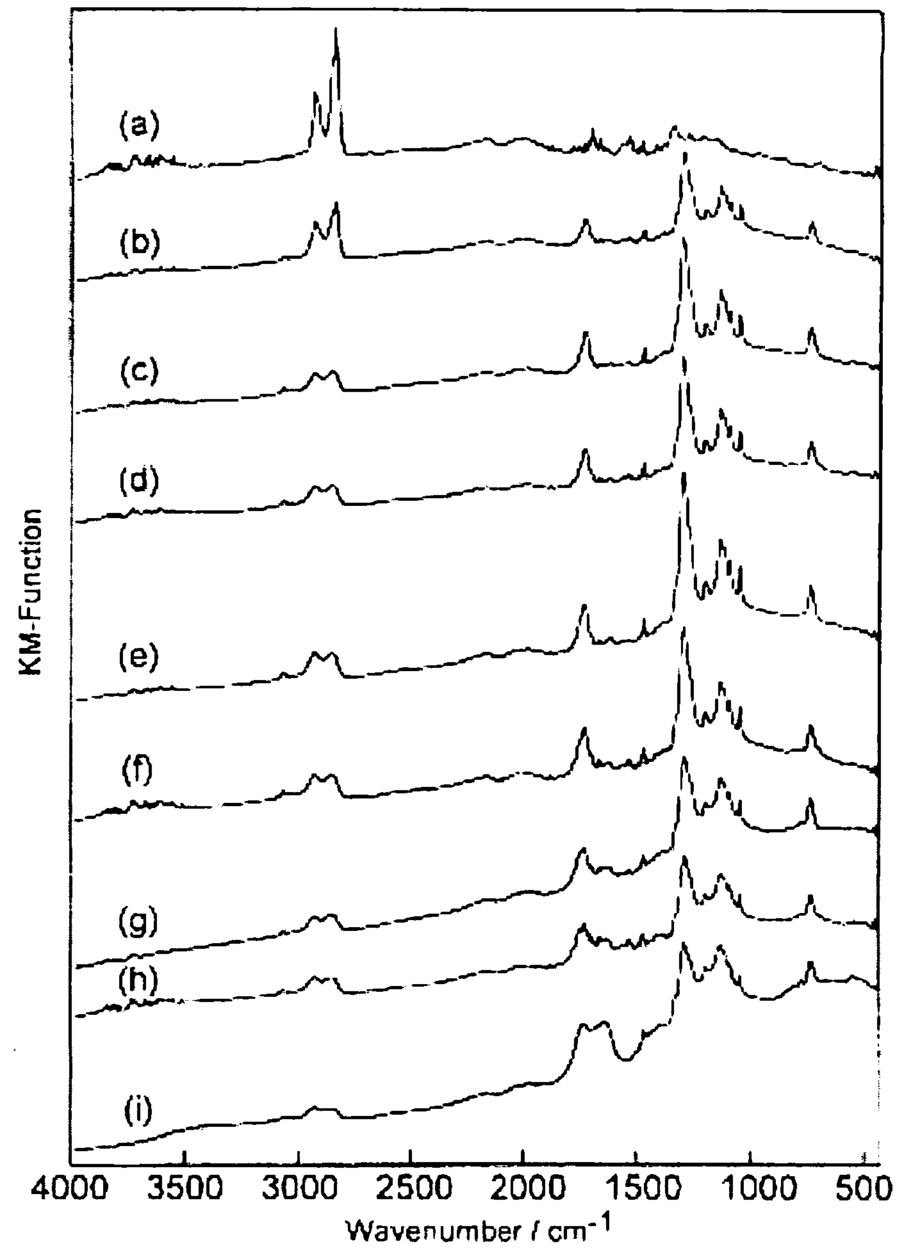

Figure 2.8 IR spectra for the diamond powders reacted with benzoyl peroxide.
(a), 0 g; (b), 0.001 g; (c), 0.005 g; (d), 0.01 g; (e), 0.005 g; (f), 0.1 g; (g), 0.3 g; (h), 0.5 g.

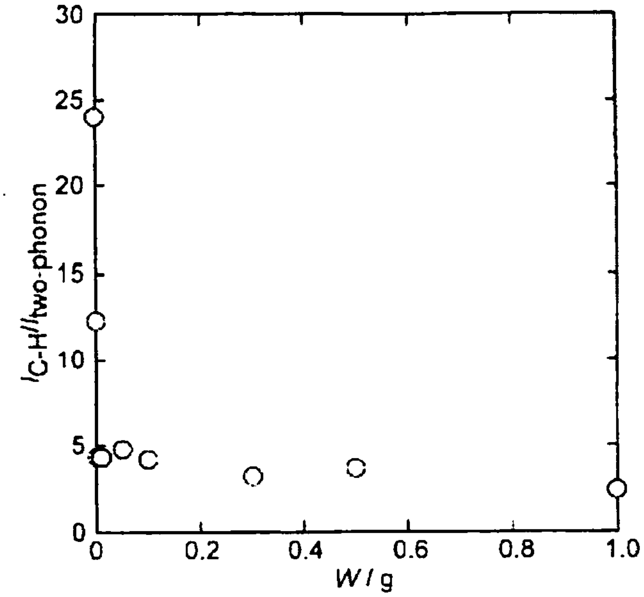

Figure 2.9 Dependence of the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) values on the amount of added benzoyl peroxide.

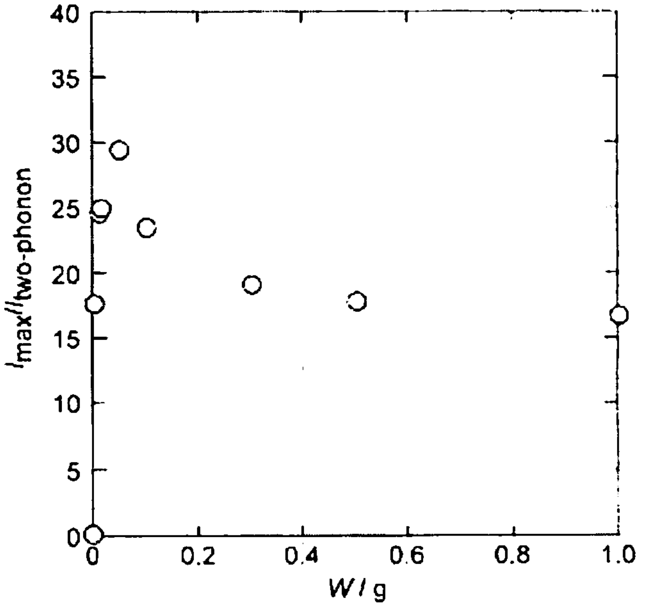

Figure 2.10 Dependence of ($I_{max}/I_{two\text{-}phonon}$) values on the amount of added benzoyl peroxide.

Chapter 3

Reactivity of the hydrogenated diamond surface with various radical initiators

Chapter 3

Reactivity of the hydrogenated diamond surface with various radical initiators

3.1. Introduction

Diamond surface reactivity has been covered in several publications [1-18]. So far, studies have focused on interactions between diamond surface and functional groups, such as fluorinated compounds, amino groups, and thiol groups [4-8]. These studies were performed in the vapor or solid phase.

In the vapor phase, Cl radicals are known to abstract the hydrogen atoms on a hydrogenated diamond surface [7, 9]. However, until now, no reports of hydrogen abstraction of a diamond surface by organic radical species have been made. In chapter 1, it is demonstrated that the radical species derived from benzoyl peroxide abstracts hydrogen atoms on a hydrogenated diamond surface. In the present study, we investigated the chemical reactivity of hydrogenated diamond surface with radical initiators such as benzophenone, azo compounds, dialkyl peroxides and diacyl peroxides in organic solvents.

3.2. Experimental

3.2.1. Pretreatment of diamond powder

Commercial diamond powder (Tomei diamond MD500; average diameter 500 nm, 9.94 $m^2 g^{-1}$ specific surface area) and diamond film deposited on a silicon substrate were used as diamond substrate. The diamond powder was washed with mixed acid ($HF + HNO_3$) at room temperature for 4 hours, and rinsed with distilled water. After drying, the diamond powder was washed with mixed acid ($H_2SO_4 + HNO_3$) at 80℃ for 4 hours, and then rinsed with distilled water. As-grown diamond film was treated mixed acid ($H_2SO_4 + HNO_3$) at 80℃ for 4 hours, and then rinsed with distilled water. After drying, the treated diamond powder and diamond film were heated in a H_2 gas flow at 900℃ for 5 hours. The resultant hydrogenated diamond powder was used as the starting material.

3.2.2. Photoexcitation of benzophenone

A drawing of the reaction apparatus for Photoexcitation of benzophenone is shown in Figure 3.1. Hydrogenated diamond powder (0.1 g) and benzophenone (0.05 g) were suspended in solvent (5 ml). The solvent was irradiated with ultraviolet light from a high pressure mercury lamp (USHIO INC., UM-102) in Ar atmosphere. The illumination area of this lamp was 4 cm. Reaction process was performed at room temperature.

3.2.3 Thermal activation of radical initiators

Hydrogenated diamond powder (0.1 g) and a radical initiator (0.05 g) were suspended in solvent (5 ml) using apparatus shown in Figure 3.1. Argon gas was bubbled into the suspensions while this suspension was heated for activating the radical initiator. After this radical reaction process, the diamond powders were washed with chloroform a few times. The washed diamond powders were dried in a vacuum dryer. In this study, α, α'-azobisisobutyronitrile (AIBN) and 2,2'-Azobis(2,4-dimethylvaleronitrile) (V-65) were employed as the radical initiators of azo compound, di-*t*-butyl peroxide and dicumyl peroxide were employed as the radical initiators of dialkyl peroxide, benzoyl peroxide and lauroyl peroxide were employed as the radical initiators of diacyl peroxide.

3.2.4 Characterization

The surface conditions of diamond powder were characterized by diffuse reflectance infrared Fourier-transformed (FT-IR) spectroscopy (JASCO FT/IR-700) and X-ray photoelectron spectroscopy (XPS; VG scientific Σ-probe).

3.3. Results and discussion

3.3.1. Radical reaction with benzophenone

We attempted to abstract the hydrogen atoms on diamond surface using benzophenone excited by UV light.

It is known that benzophenone is a photosensitizer that acts as a hydrogen abstraction type. Benzophenone is efficiently excited by UV light, and attains the excited triplet state. This excited triplet ketone abstracts a hydrogen atom from another molecule as shown in Eq. (1).

$$C_6H_5COC_6H_5(T_1) + RH \rightarrow C_6H_5C\cdot(OH)C_6H_5 + R\cdot \qquad (1)$$

We regarded hydrogenated diamond as "RH" in Eq. (1), and attempted to perform the chemical reaction indicated in Eq. (1). However, the hydrogen atoms on diamond surface were not abstracted with this reaction as shown in Figure 3.2. From the results of this experiment, it is concluded that the hydrogen atoms on diamond surface are not abstracted by the reaction mechanism indicated in Eq. (1).

It is known that alcohols act as good hydrogen donors. When the hydrogen atoms in alcohols are abstracted by photoexcited benzophenone, radical species form as follows.

$$C_6H_5COC_6H_5 + R'CH_2(OH) \rightarrow C_6H_5C^{\cdot}(OH)C_6H_5 + R'C^{\cdot}H(OH) \qquad (2)$$

$$R'C^{\cdot}H(OH) + RH \rightarrow R'CH_2(OH) + R\cdot \qquad (3)$$

We regarded hydrogenated diamond as "RH", and attempted to perform the chemical reactions indicated in Eq. (2) and Eq. (3). However, the hydrogen atoms on hydrogenated diamond surface were not abstracted with this reaction as shown in Figure 3.2(b). From the results of this experiment, it is concluded that the hydrogen atoms on diamond surface are not abstracted by the reaction mechanism indicated in Eq. (2) and Eq. (3).

When benzophenone mixed with tertiary amine is irradiated with light, these compounds form a triplet exciplex. As shown in Eq. (4), the exciplex efficiently generates a ketyl radical and an amine radical via electron-proton transfer.

$$C_6H_5COC_6H_5 + RCH_2CH_2NR'_2$$

$$\rightarrow [(C_6H_5)_2C^{\cdot}(\text{-}O^{-}) \cdot\cdot\cdot N^{\cdot +}R'_2\text{-}CH_2CH_2R]$$

$$\rightarrow (C_6H_5)_2C^{\cdot}\text{-}OH + RCH_2C^{\cdot}HNR'_2 \qquad (4)$$

We performed the experiment used triethylamine as a solvent. The IR spectrum of the sample after this experiment is shown in Figure 3.2(c). From the result of Figure 3.2(c), it was confirmed that the hydrogen atoms on diamond surface were not abstracted in the reaction mechanism.

In order to estimate the diamond surface condition quantitatively, we used the peak assigned to the absorption of the two-phonon. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value after the reaction with benzophenone was calculated and listed on Table 3.1. The calculated value were the same as that of hydrogenated diamond.

From the experimental results described above, it was confirmed that hydrogen atoms on hydrogenated diamond surface cannot be abstracted with the radical reaction of the photoexcited benzophenone in the experimental condition in this study.

3.3.2. Radical reaction with azo compounds

AIBN decomposes on heating (45-65 ℃), and generates radical species as follows,

$$(CH_3)_2(CN)C\text{-}N{=}N\text{-}C(CN)(CH_3)_2 \rightarrow 2(CH_3)_2(CN)C\cdot + N_2 \qquad (5)$$

The generated radical species attacks other molecules. We attempted to utilize AIBN for abstracting the hydrogen atoms on diamond surface in various solvents. In this study, we heated these solvents at 60 ℃. The IR spectra of the samples after the experiments are shown in Figure 3.3. All the samples treated with AIBN were unchanged from the hydrogenated diamond in the IR spectrum. In order to estimate the diamond surface condition quantitatively, the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value was calculated and listed on Table 3.2. The intensities of the peaks assigned to the C-H bond remained large after the reaction process. It was obvious, therefore, that the hydrogen atoms on diamond surface cannot be abstracted with the radical reaction of AIBN in the experimental condition in this study.

2,2'-Azobis(2,4-dimethylvaleronitrile) (V-65) decomposes on heating (60-80 ℃), and generates radical species as shown in Eq. (6),

$$(CH_3)_2CHCH_2(CH_3)(CN)C\text{-}N{=}N\text{-}C(CN)(CH_3)CH_2CH(CH_3)_2$$
$$\rightarrow 2(CH_3)_2CHCH_2(CH_3)(CN)C\cdot + N_2 \qquad (6)$$

The generated radical species ($(CH_3)_2CHCH_2(CH_3)(CN)C\cdot$) can react with other molecules. Hydrogen abstraction reaction of the hydrogenated diamond surface was carried out using this chemical reaction. Various organic solvents were used as the solvent for this experiment. The suspension containing hydrogenated diamond powder and V-65 was heated at 60 ℃ for 2 hours for activating V-65. The IR spectra of the diamond powders after the reaction process are shown in Figure 3.4. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value was calculated and listed on Table 3.3. The intensities of the peaks assigned to the C-H bond remained large after the reaction process. It was confirmed from these experimental results that the radical species generated from V-65 has low reactivity with the hydrogen atoms on diamond surface at least on the experimental condition in this study.

3.3.3. Radical reaction with dialkyl peroxides

Di-*t*-butyl peroxide decomposes on heating (>80℃), and generates radical species as shown in Eq. (7),

$$(CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \rightarrow 2(CH_3)_2C\text{-}O\cdot \qquad (7)$$

The generated radical species ($(CH_3)_2C\text{-}O\cdot$) can react with other molecules. Hydrogen abstraction reaction of the hydrogenated diamond surface was carried out using this chemical reaction. Various organic solvents were used as the solvent for this experiment. The suspension containing hydrogenated diamond powder and di-*t*-butyl peroxide was heated at 100 ℃ for 2 hours for activating di-*t*-butyl peroxide. The IR spectra of the samples after the reaction process are shown in Figure 3.5. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value was calculated and listed on Table 3.4. The intensities of the peaks assigned to the C-H bond remained large after the reaction process. It was confirmed from these experimental results that the radical species generated from di-*t*-butyl peroxide has low reactivity with the hydrogen atoms on diamond surface at least on the experimental condition in this study.

Dicumyl peroxide decomposes on heating (>70℃), and generates radical species as shown in Eq. (8),

$$C_6H_5(CH_3)_2C\text{-}O\text{-}O\text{-}C(CH_3)_2C_6H_5 \rightarrow 2\ C_6H_5(CH_3)_2C\text{-}O\cdot \qquad (8)$$

The generated radical species ($C_6H_5(CH_3)_2C\text{-}O\cdot$) can react with other molecules. Hydrogen abstraction reaction of the hydrogenated diamond surface was carried out using this chemical reaction. Various organic solvents were used as the solvent for this experiment. The suspension containing hydrogenated diamond powder and dicumyl peroxide was heated at 80 ℃ for 2 hours for activating dicumyl peroxide. The IR spectra of the samples after the reaction process are shown in Figure 3.6. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value was calculated and listed on Table 3.5. The intensities of the peaks assigned to the C-H bond remained large after the reaction process. It was confirmed from these experimental results that the radical species generated from dicumyl peroxide has low reactivity with the hydrogen atoms on diamond surface at least on the experimental condition in this study.

3.3.4. Radical reaction of with diacyl peroxides

Benzoyl peroxide decomposes on heating (60-80 ℃), and generates radical species as shown in Eq. (9),

$$C_6H_5COO\text{-}OOCC_6H_5 \rightarrow 2C_6H_5COO\cdot \qquad (9)$$

The generated radical species ($C_6H_5COO\cdot$) can react with other molecules. Hydrogen abstraction reaction of the hydrogenated diamond surface was carried out using this chemical reaction. Various organic solvents were used as the solvent for this experiment. The suspension containing hydrogenated diamond powder and benzoyl peroxide was heated at 75 ℃ for 2 hours for activating benzoyl peroxide. The IR spectra of the samples after the reaction process are shown in Figure 3.7. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value was calculated and listed on Table 3.6. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) values rather decreased with the reaction process. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value depended on the kind of the solvent. The reaction rate, therefore, must depend on the kind of the solvent. We have already reported the hydrogen abstraction reaction from hydrogenated diamond surface using benzoyl peroxide in chapter 2. The chemical reaction scheme should be as follows,

$$C_6H_5COO\cdot + (\text{diamond})\text{-}H \rightarrow C_6H_5COOH + (\text{diamond})\cdot \qquad (10)$$

Lauroyl peroxide decomposes on heating (60-80 ℃), and generates radical species as shown in Eq. (11),

$$C_{11}H_{23}COO\text{-}OOCC_{11}H_{23} \rightarrow 2C_{11}H_{23}COO\cdot \qquad (11)$$

The generated radical species ($C_{11}H_{23}COO\cdot$) can react with other molecules. Hydrogen abstraction reaction of the hydrogenated diamond surface was carried out using this chemical reaction. Various organic solvents were used as the solvent for this experiment. The suspension containing hydrogenated diamond powder and benzoyl peroxide was heated at 75 ℃ for 2 hours for activating lauroyl peroxide. The IR spectra of the samples after the reaction process are shown in Figure 3.8. The order of the intensities for the two peaks assigned to the C-H bond was reversed after the treatment of lauroyl peroxide. Moreover, several peaks appeared at the lower wavelength region after the treatment of lauroyl peroxide. The hydrogen atoms on diamond surface, therefore, must be abstracted by the radical species generated from lauroyl peroxide. We can presume that the chemical reaction of lauroyl peroxide with hydrogenated diamond surface is similar to that of benzoyl peroxide.

$$C_{11}H_{23}COO\cdot + (\text{diamond})\text{-}H \rightarrow C_{11}H_{23}COOH + (\text{diamond})\cdot \qquad (12)$$

Further experiments were carried out to investigate this hydrogen abstraction reaction on diamond surface with lauroyl peroxide in detail. We used toluene as a solvent, and examined the reaction time dependence of the hydrogen abstraction reaction. The IR spectra of the samples after the reaction process are shown in Figure 3.9. The ratios between the ($I_{two\text{-}phonon}$) value and the peaks assigned to the C-H bond were estimated to understand the reaction process quantitatively. The peak intensities at 2837 cm^{-1} and 2936 cm^{-1} are $I_{C\text{-}H}$ and $I_{C\text{-}H}$, respectively. The reaction time dependences of the ($I_{C\text{-}H} / I_{two\text{-}phonon}$) value and the ($I_{C\text{-}H} / I_{two\text{-}phonon}$) value are shown in Figure 3.10. The ratio of the intensities for the two peaks assigned to the C-H bond depended on the reaction time. On the other hand, the kinds of the generated peaks after the reaction were independent of the reaction time. We can consider from this result that the same chemical reaction proceeded in all the solvents, and that no side reaction proceeded when the reaction time was prolonged.

Next, the amount of the added lauroyl peroxide dependence was investigated.

The results of these experiments are shown in Figure 3.11. The shape of the IR spectrum depended on the amount of lauroyl peroxide. The amount dependences of the added lauroyl peroxide of the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value and the ($I_{C\text{-}H}$ / $I_{two\text{-}phonon}$) value are shown in Figure 3.12. The intensity of the peak assigned to the C-H bond at higher wavelength increased with increasing the amount of the added lauroyl peroxide. The absolute values of $I_{C\text{-}H}/I_{two\text{-}phonon}$ and $I'_{C\text{-}H}/I_{two\text{-}phonon}$ do not have chemical or physical meanings. However, the fluctuation of these values means the change of the diamond surface condition. The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value and the ($I_{C\text{-}H}$ / $I_{two\text{-}phonon}$) value depended on the amount of the added lauroyl peroxide up to 0.1 g, and then are independent of the amount of the added lauroyl peroxide. However, the shape of the IR spectrum at the lower region depended on the amount of the added lauroyl peroxide. We can consider from the results that side reaction proceeded with increase of the amount of the added lauroyl peroxide.

3.3.5. Surface condition of diamond surface after the reaction with benzoyl peroxide or lauroyl peroxide.

In the case of treatment by benzoyl peroxide, the area under the peaks assigned to the C-H bond decreased with increasing treatment time and amount of benzoyl peroxide. Several peaks emerged in the IR spectra after the reaction. The small peak at 3072 cm^{-1} could be attributed to the stretching vibration mode of C-H bonds of aromatic compounds. The peaks between 700-1450 cm^{-1} could be attributed to the ester group. The peak at 1718 cm^{-1} is most likely attributable to the C=O group. The C=O peak reportedly shifts to higher wavenumbers as oxidation proceeds during the treatment of hydrogenated diamond surface with O_2 gas in the vapor phase [16]. In the present study, the C=O peak in the IR spectra for diamond powders treated with benzoyl peroxide did not shift, indicating that the condition of the C=O bond was independent of the extent of the reaction.

With lauroyl peroxide as the radical initiator, the area under the peaks assigned to the C-H bond increased with treatment time and amount of lauroyl peroxide. With increasing treatment time, the intensity of the peak at 2936 cm^{-1} increased, while the intensity of the peak at 2837 cm^{-1} decreased. The peak at 1726 cm^{-1} is assigned to the C=O bond. The peak position was independent of the extent of the reaction.

In order to quantify the amount of hydrogen on the diamond surface, we normalized the area under the C-H peaks (2780-3010 cm^{-1}). The peak at 2157 cm^{-1} was ascribed to the diamond two-phonon absorption, and was used as a reference. The area of the C-H peaks (2780-3010 cm^{-1}) was divided by the area of the two-phonon absorption peaks (2100-2230 cm^{-1}). The ratio was denoted by $S_{C\text{-}H}$. In order to normalize $S_{C\text{-}H}$, the $S_{C\text{-}H}$ value for the diamond powders treated with radical initiators was divided by the $S_{C\text{-}H}$ value for hydrogenated diamond powder. The ($S_{C\text{-}H}$ / $S_{C\text{-}H(hydrogenated)}$) value is shown as a function of treatment time in Figure 3.13 The value reflects the reaction extent on diamond surface. In the case of the diamond powder treated with benzoyl peroxide, $S_{C\text{-}H}$ / $S_{C\text{-}H(hydrogenated)}$ decreased with increasing reaction time, while in the case of lauroyl peroxide, it increased with increasing reaction time. These results suggest that a free-radical substitution reaction occurred on the diamond surface treated with benzoyl or lauroyl peroxide. After treatment with benzoyl or lauroyl peroxide, the presumed condition of the diamond surface is as follows:

(Diamond)- $OOC\text{-}C_6H_5$ (13)
(Diamond)- $OOC\text{-}C_{11}H_{23}$ (14)

Upon treatment with benzoyl peroxide, the hydrogen atoms on the hydrogenated diamond surface are abstracted by the radical species. Subsequently, another organic radical bonds to the radical sites on the diamond surface through a termination reaction. As these reactions proceed, the ($S_{C\text{-}H}$ / $S_{C\text{-}H(hydrogenated)}$ value is expected to decrease, which fits with experimental observations. The peaks at 3072 cm^{-1}, 1718 cm^{-1}, 1449 cm^{-1}, 1275 cm^{-1}, 1111 cm^{-1} and 707 cm^{-1} can be assigned to the ($C_6H_5\text{-}COO$) group. The radical species derived from lauroyl peroxide should be capable of abstracting hydrogen atoms from the diamond surface. However, the C-H peak area increased with reaction time. This is because the ($C_{11}H_{23}\text{-}COO\text{-}$) groups introduced on the diamond surface.

If diamond surfaces treated with benzoyl and lauroyl peroxide have the structures shown in Eq. 13-14, the ester bonds could be broken through hydrolysis reaction. Diamond powders treated with diacylperoxide were maintained in 1 M HCl at 80 ℃ for 3 h, and then rinsed with distilled water. The intensities of C=O peaks in IR spectra decreased as a result of treatment. The amount of oxygen on the diamond surface (Eq. 13 & 14) should decrease as a result of hydrolysis. In order to determine the extent of the hydrolysis reaction, the diamond surface was analyzed under X-ray photoelectron spectroscopy. Diamond film was used as substrate. Figure 3.14 shows XPS spectra of hydrogenated diamond surface treated with benzoyl peroxide or lauroyl peroxide. After treatment with benzoyl or lauroyl peroxide, O(1s) peaks appeared. The ratio of the area under the O(1s) XPS signal to the area under the total C(1s) signal was 6.31 (benzoyl peroxide) and 4.52 (lauroyl peroxide). After hydrolysis, the intensity of the O(1s) peak decreased (Figure 3.14A(b), Figure 3.14B(b)). The O/C ratios were 4.45 (benzoyl peroxide) and 4.23 (lauroyl peroxide). These results confirmed hydrolysis reaction occurred on the diamond surface. However, the extent of the hydrolysis reaction depended on the chemical condition on diamond surface.

3.3.6 Reactivity of hydrogenated diamond surface with organic radical species

The radical initiators used in this study generated the organic radical species. However, the reactivity of the radical species with hydrogenated diamond surface depended strongly on the type of radical initiator. Reactivity is likely determined by the radical species' structure. The radical species' structures derived from benzophenone, azo compounds, dialkyl peroxides or diacyl peroxides are different, respectively. For example, The radicals derived from diacyl peroxide have a planar structure, while the radical species derived from dialkyl peroxide has a tetrahedral structure (Figure 3.15). The difference of steric hindrance should be one of the reasons for difference of the reactivity.

3.4. Conclusion

Using various radical initiators used in polymer science, we attempted to abstract the hydrogen atoms on a diamond surface for investigating the chemical reactivity of the hydrogenated diamond surface. When benzophenone was used for the reaction process, most of the hydrogen atoms on diamond surface were not abstracted. The radical species derived from azo compounds and from dialkyl peroxides also cannot abstract most of the hydrogen atoms on diamond surface. On the other hand, the radical species derived from diacyl peroxides such as benzoyl peroxide and lauroyl peroxide can abstract the hydrogen atoms on diamond surface. This study revealed that the reactivity for the hydrogen abstraction reaction with organic radical reagents depends on the kind of the radical species. The radical species derived from benzoyl and lauroyl peroxide was found to react with hydrogenated diamond surface (introducing (C_6H_5-COO) and ($C_{11}H_{23}$-COO) groups on the surface, respectively), while those derived from dicumyl and di-*t*-butyl peroxide did not react sufficiently.

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Table 3.1 The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value of the diamond treated with benzophenone.

	hydrogenated diamond	acetone	ethanol	triethylamine
$I_{C\text{-}H}/I_{two\text{-}phonon}$	20.1	18.6	16.5	17.2

Table 3.2 The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value of the diamond treated with AIBN in various solvents.

	hydrogenated diamond	toluene	acetonitrile	THF	DMF	cyclohexane	n-hexane	ethanol
$I_{C\text{-}H}/I_{two\text{-}phonon}$	20.1	13.0	13.4	12.5	14.8	14.3	13.6	14.0

Table 3.3 The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value of the diamond treated with V-65 in various solvents.

	hydrogenated diamond	toluene	acetonitrile	THF	DMF	cyclohexane	n-hexane	ethanol
$I_{C\text{-}H}/I_{two\text{-}phonon}$	20.1	13.3	12.5	14.0	14.0	14.1	14.1	14.4

Table 3.4 The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value of the diamond treated with di-t-butyl peroxide in various solvents.

	hydrogenated diamond	toluene	acetonitrile	THF	DMF	cyclohexane	n-hexane	ethanol
$I_{C\text{-}H}/I_{two\text{-}phonon}$	20.1	15.0	15.3	13.6	16.3	15.9	16.8	16.8

Table 3.5 The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value of the diamond treated with dicumyl peroxide in various solvents.

	hydrogenated diamond	toluene	acetonitrile	THF	DMF	cyclohexane	n-hexane	ethanol
$I_{C\text{-}H}/I_{two\text{-}phonon}$	20.1	14.9	15.3	14.9	14.8	15.1	14.6	14.8

Table 3.6 The ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value of the diamond treated with benzoyl peroxide in various solvents.

	hydrogenated diamond	toluene	acetonitrile	THF	DMF	cyclohexane	n-hexane	ethanol
$I_{C\text{-}H}/I_{two\text{-}phonon}$	20.1	2.7	2.4	2.6	3.2	1.8	2.9	5.0

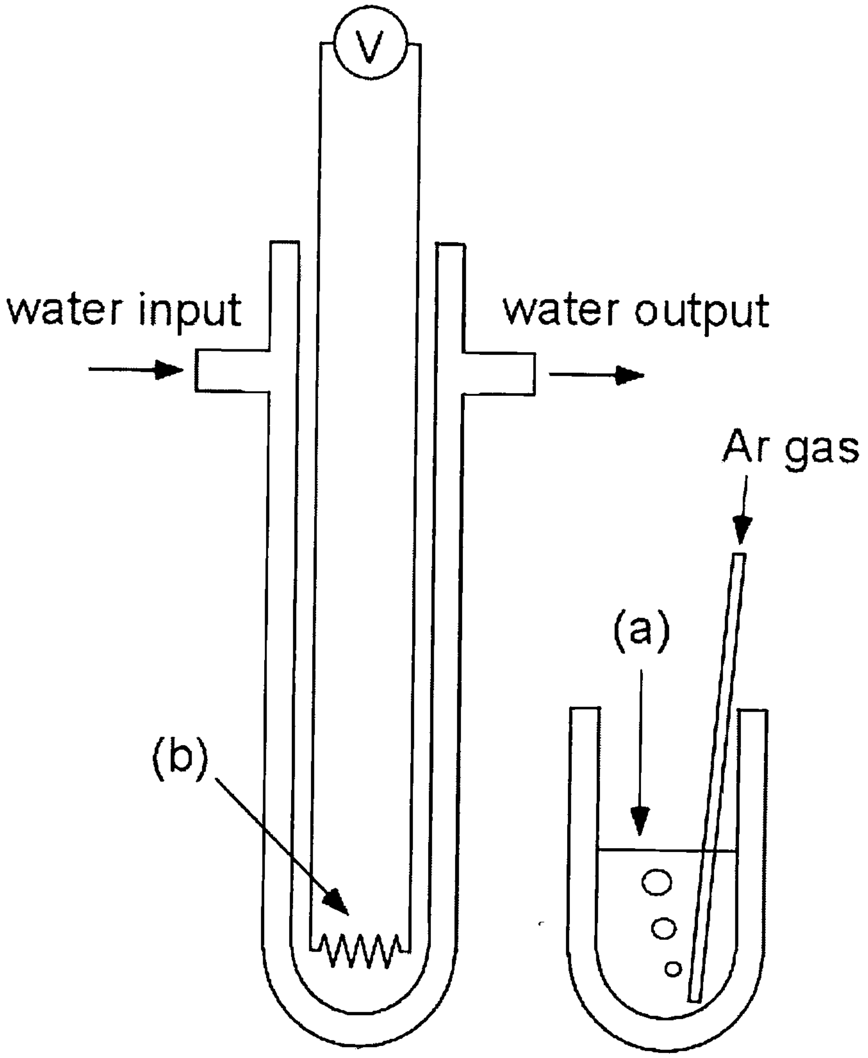

Figure 3.1 Reaction apparatus for UV irradiation (a) suspension, (b) UV lamp.

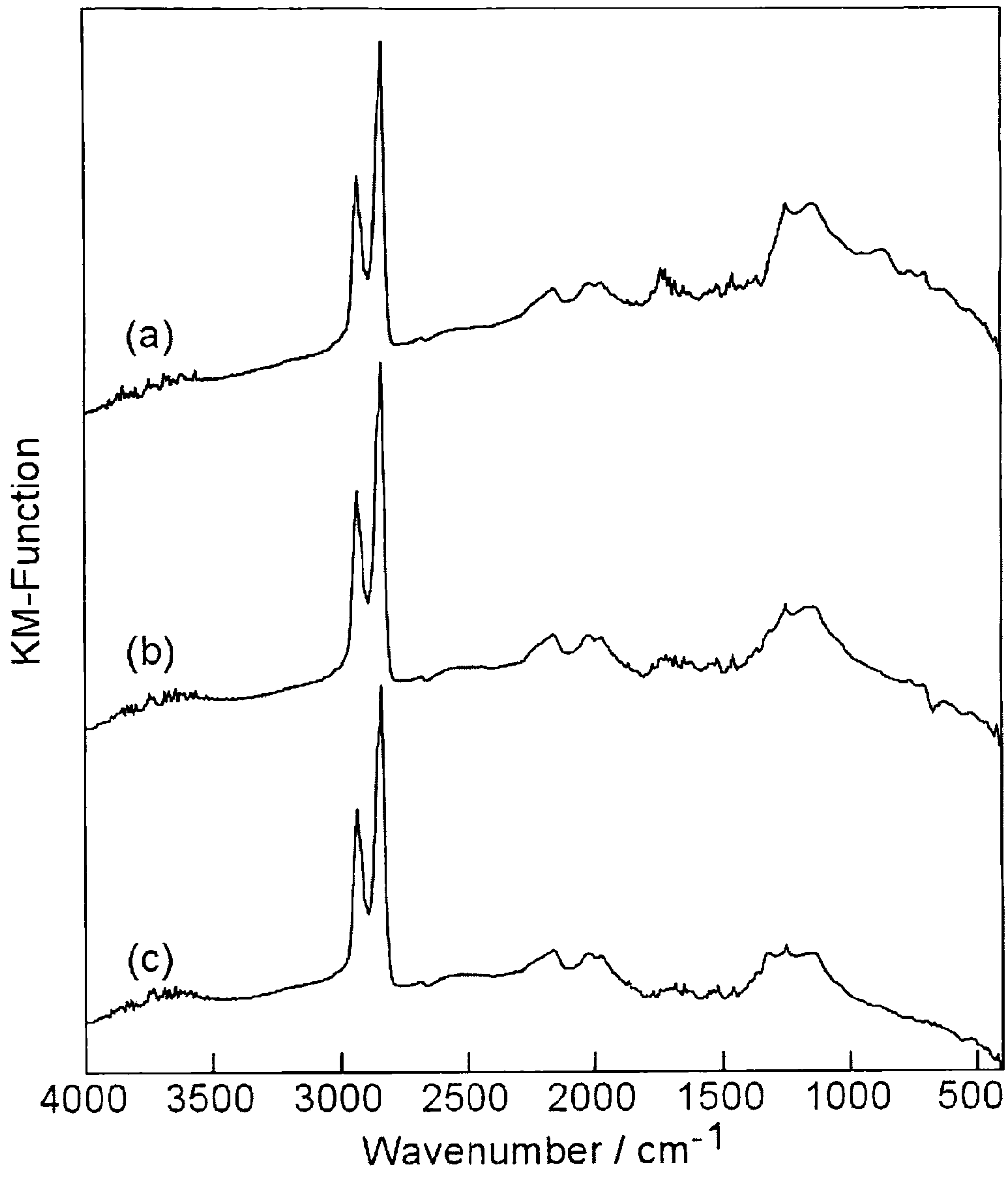

Figure 3.2 IR spectrum of diamond powder after reaction with benzophenone. (a) in toluene, (b) in ethanol, (c) in triethylamine

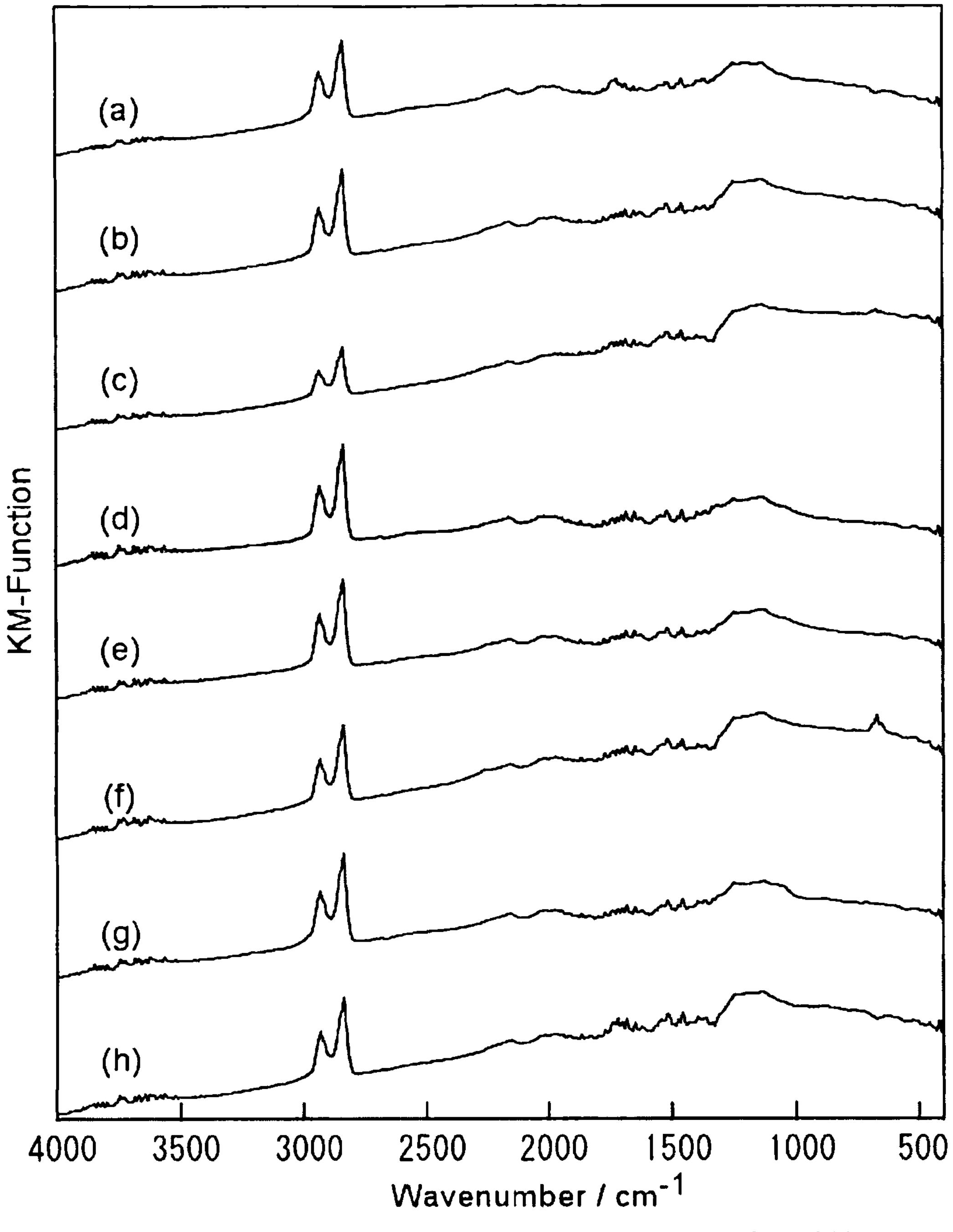

Figure 3.3 IR spectra of diamond powder after reaction with AIBN in various solvents. (a) toluene, (b) acetonitrile, (c) tetrahydrofuran (THF), (d) *N,N*-dimethylformamide (DMF), (e) cyclohexane, (f) *n*-hexane, (g) ethanol, (h) chloroform.

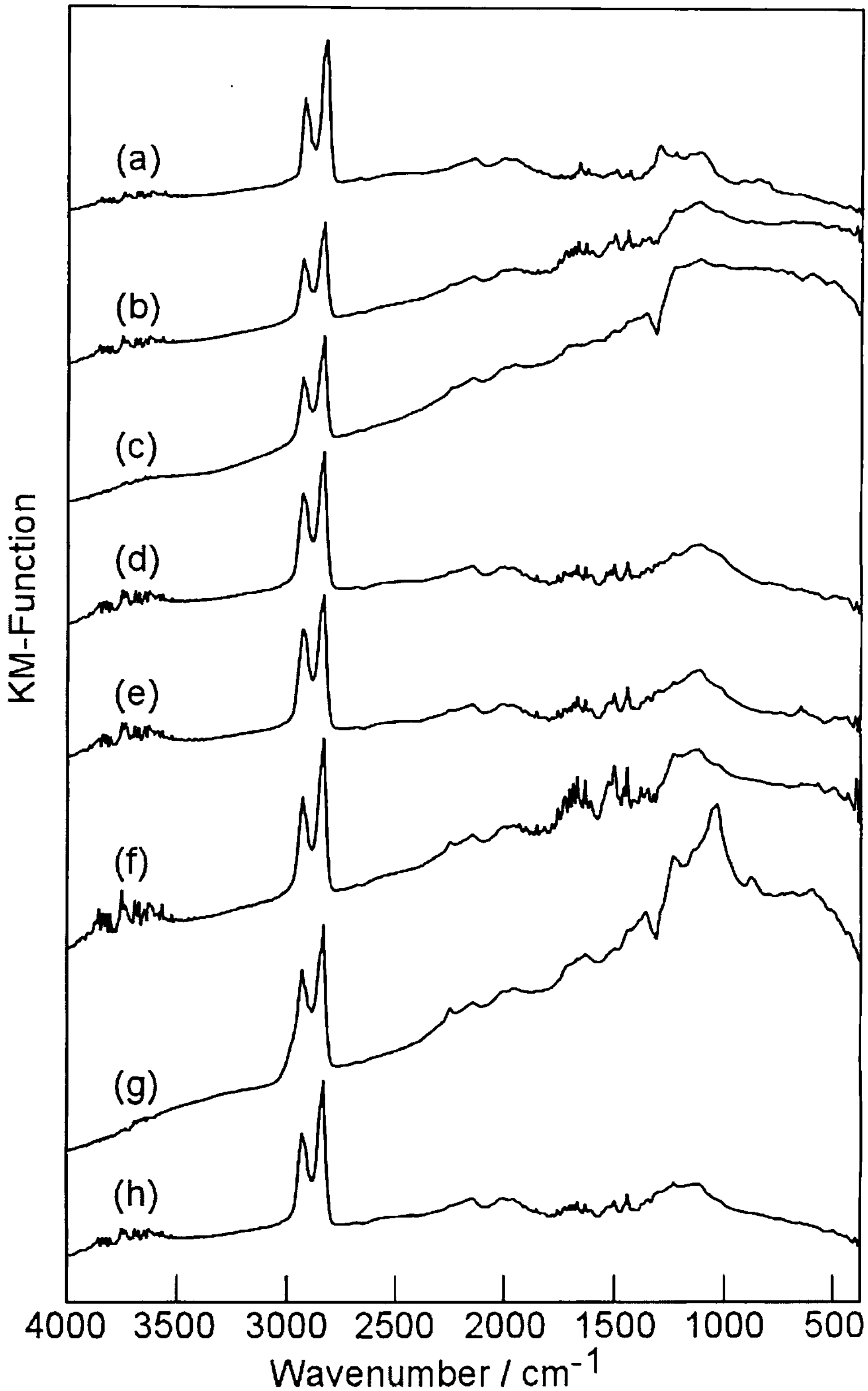

Figure 3.4 IR spectra of diamond powder after reaction with V-65 in various solvents. (a) hydrogenated diamond (starting material), (b) toluene, (c) acetonitrile, (d) tetrahydrofuran (THF), (e) *N,N*-dimethylformamide (DMF), (f) cyclohexane, (g) *n*-hexane, (h) ethanol.

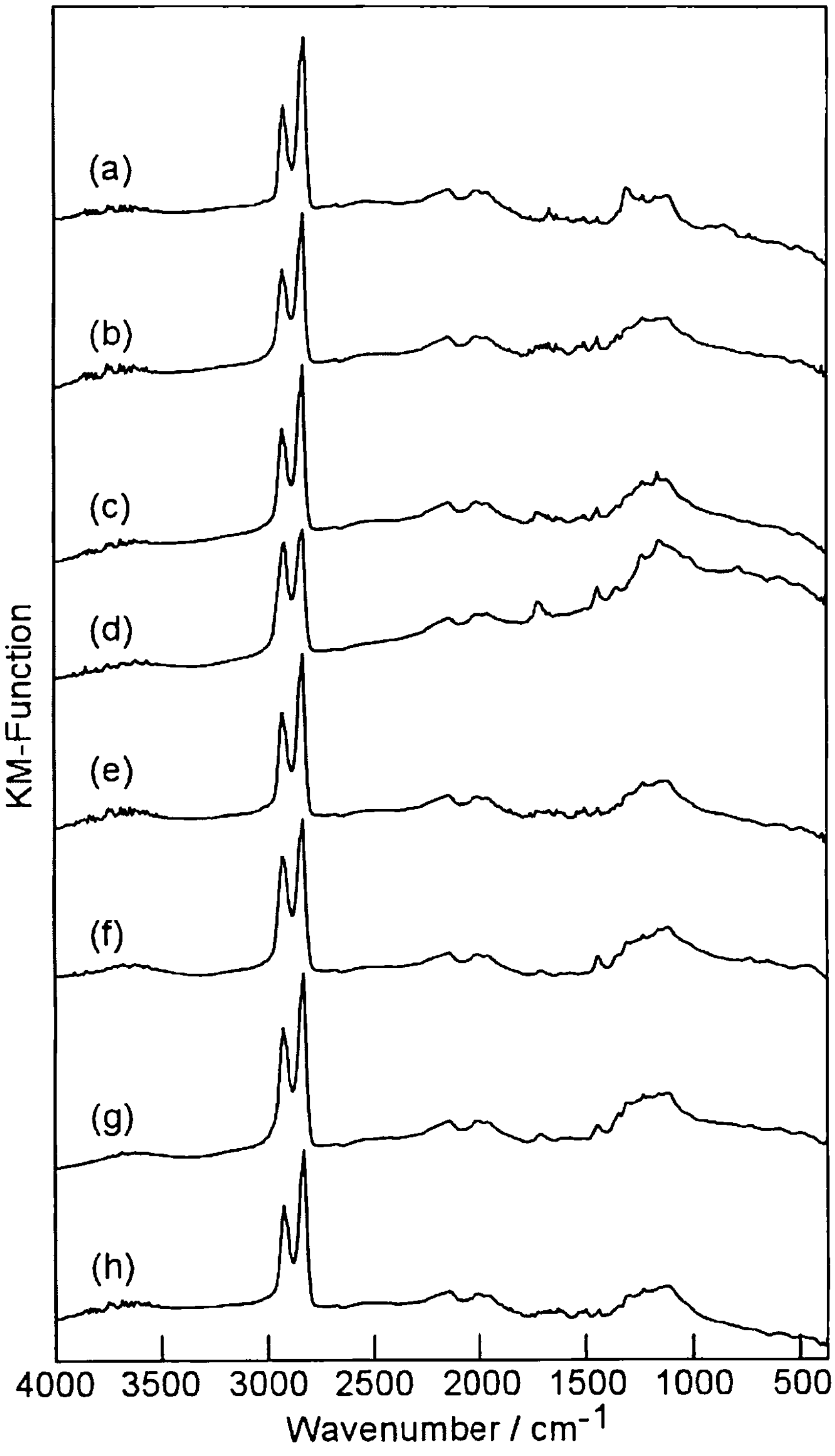

Figure 3.5 IR spectrum of diamond powder after reaction with di-*t*-butyl peroxide in various solvents.(a) hydrogenated diamond (starting material), (b) toluene, (c) acetonitrile, (d) tetrahydrofuran (THF), (e) *N*,*N*-dimethylformamide (DMF), (f) cyclohexane, (g) *n*-hexane, (h) ethanol.

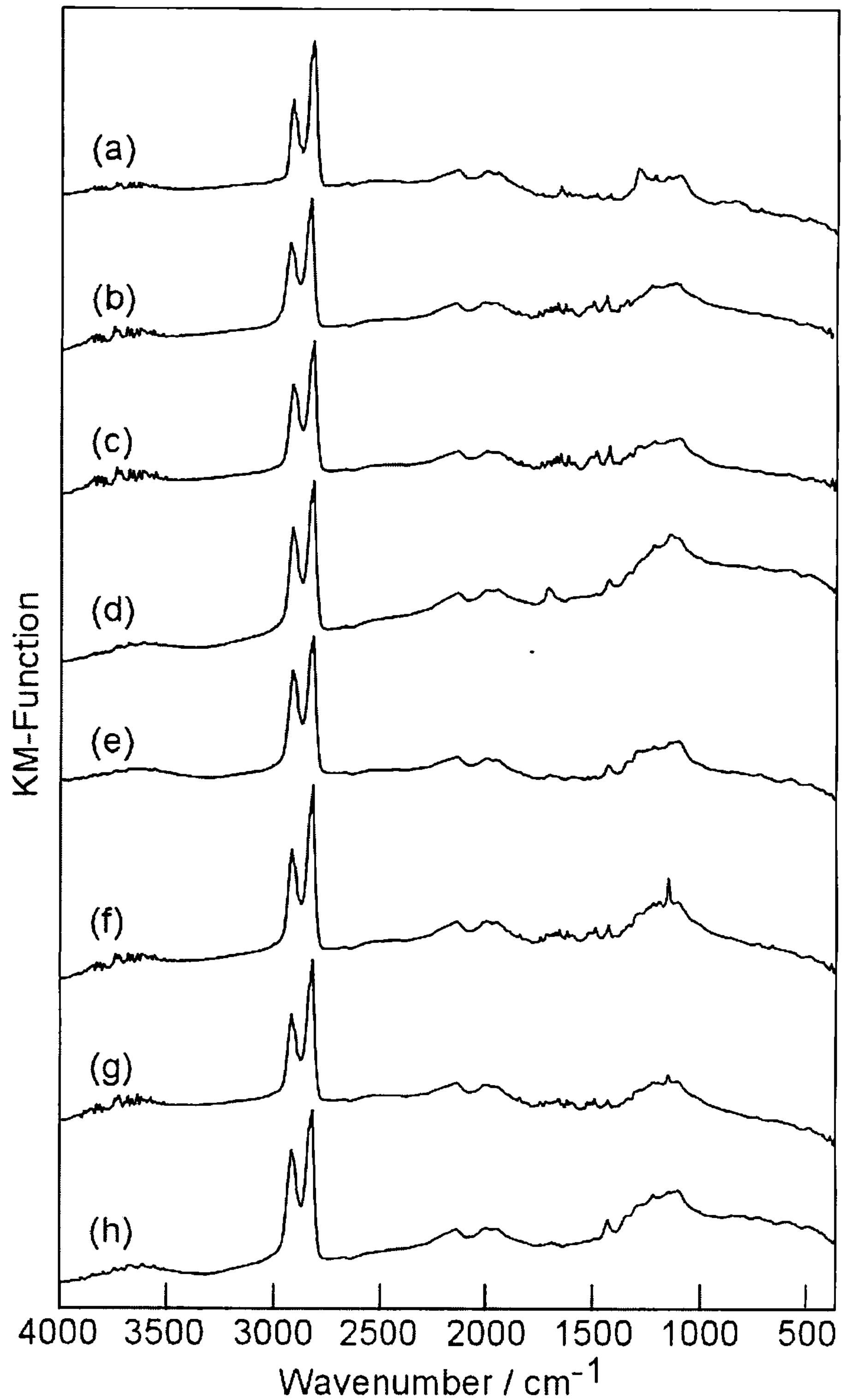

Figure 3.6 IR spectrum of diamond powder after reaction with dicumyl peroxide in various solvents. (a) hydrogenated diamond (starting material), (b) toluene, (c) acetonitrile, (d) tetrahydrofuran (THF), (e) *N,N*-dimethylformamide (DMF), (f) cyclohexane, (g) *n*-hexane, (h) ethanol.

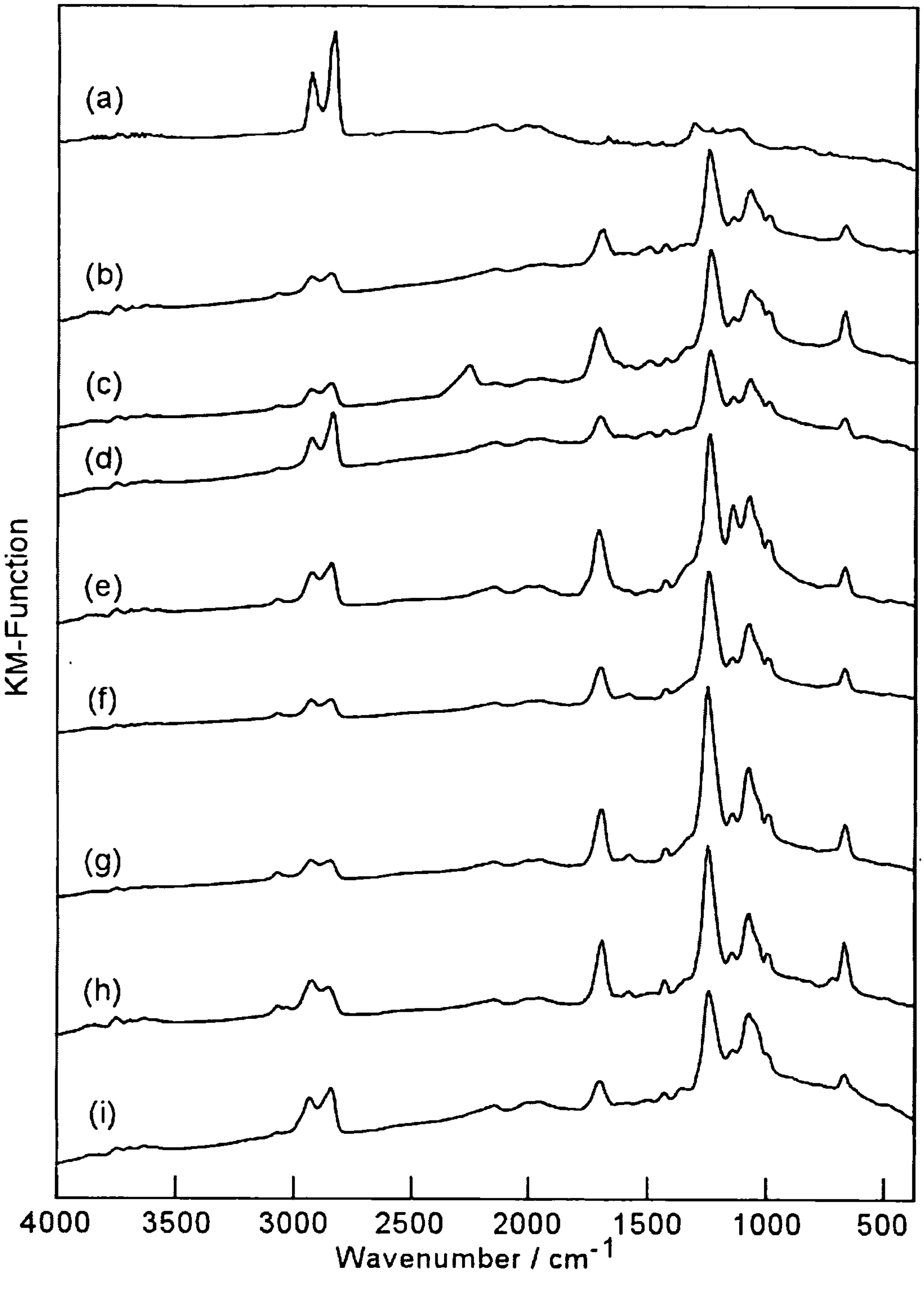

Figure 3.7 IR spectra of diamond powder after reaction with benzoyl peroxide in various solvents.(a) hydrogenated diamond (starting material), (b) toluene, (c) acetonitrile, (d) tetrahydrofuran (THF), (e) *N*,*N*-dimethylformamide (DMF), (f) cyclohexane, (g) *n*-hexane, (h) ethanol, (i) chloroform.

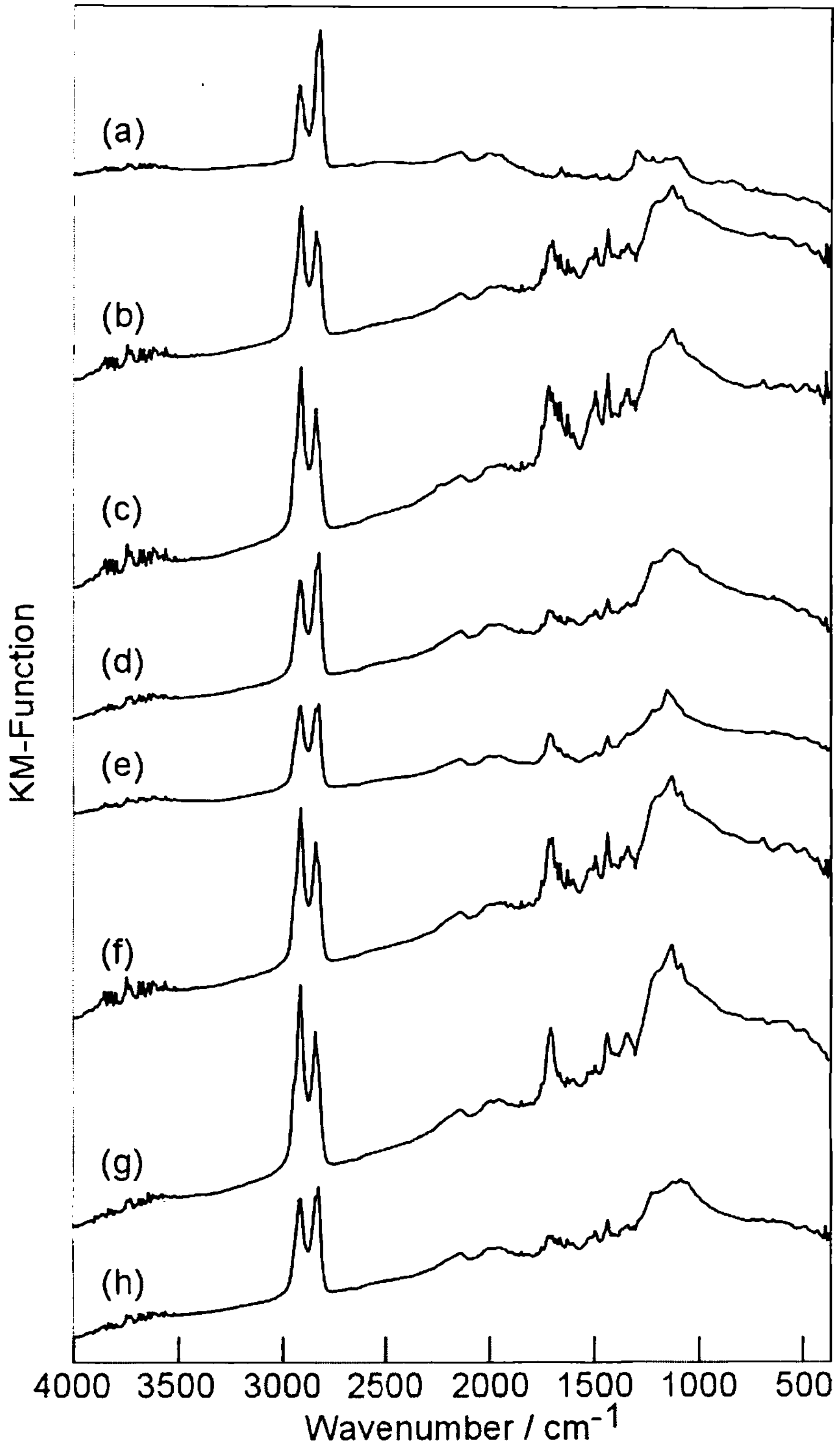

Figure 3.8 IR spectrum of diamond powder after reaction with lauroyl peroxide in various solvents. (a), hydrogenated diamond; (b), toluene; (c), acetonitrile; (d), tetrahydrofuran (THF); (e), *N,N*-dimethylformamide (DMF); (f), cyclohexane; (g), *n*-hexane; (h), ethanol.

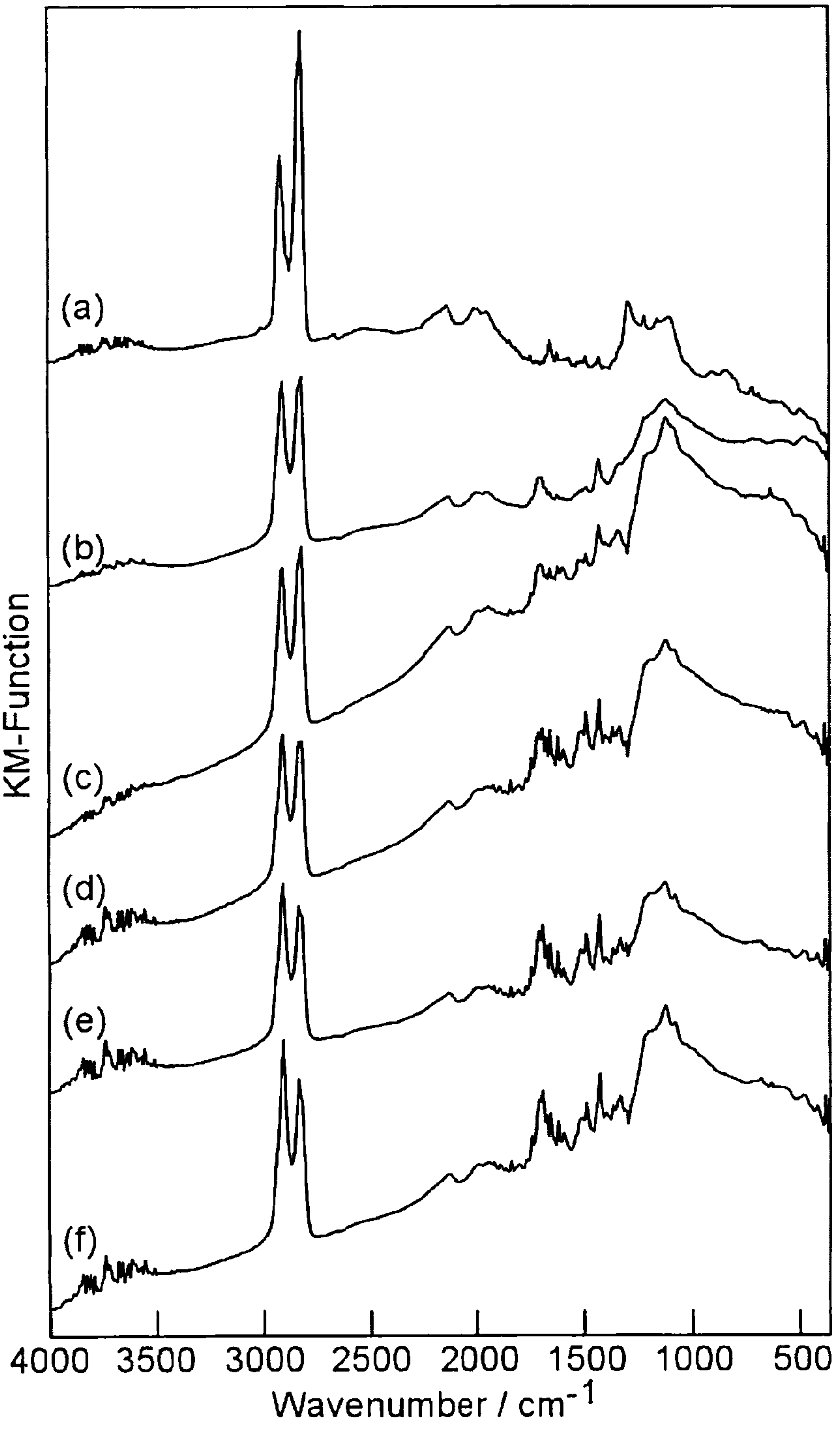

Figure 3.9 IR spectrum of diamond powder after reaction with lauroyl peroxide in toluene. (a) reaction time = 0 min, (b) 5 min, (c) 15 min, (d) 30 min, (e) 60 min, (f) 120 min.

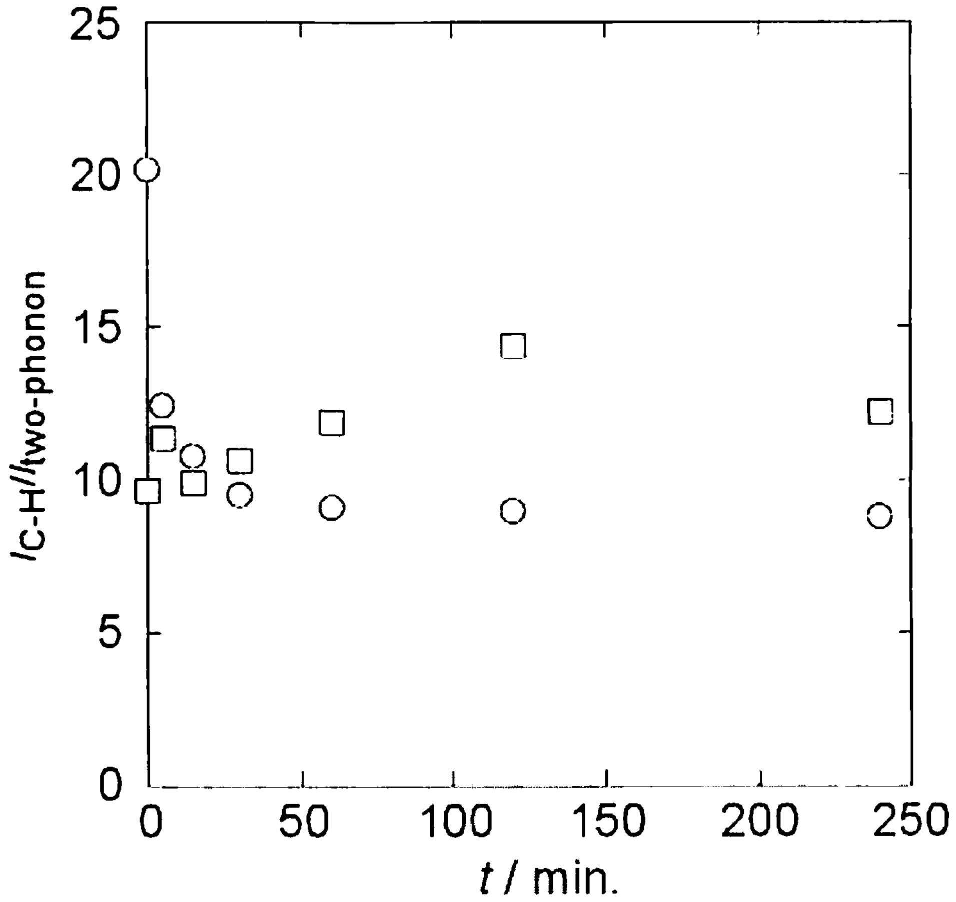

Figure 3.10 Reaction time dependence of the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value and the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value. ○ $I_{C\text{-}H}/I_{two\text{-}phonon}$, □ $I_{C\text{-}H}/I_{two\text{-}phonon}$.

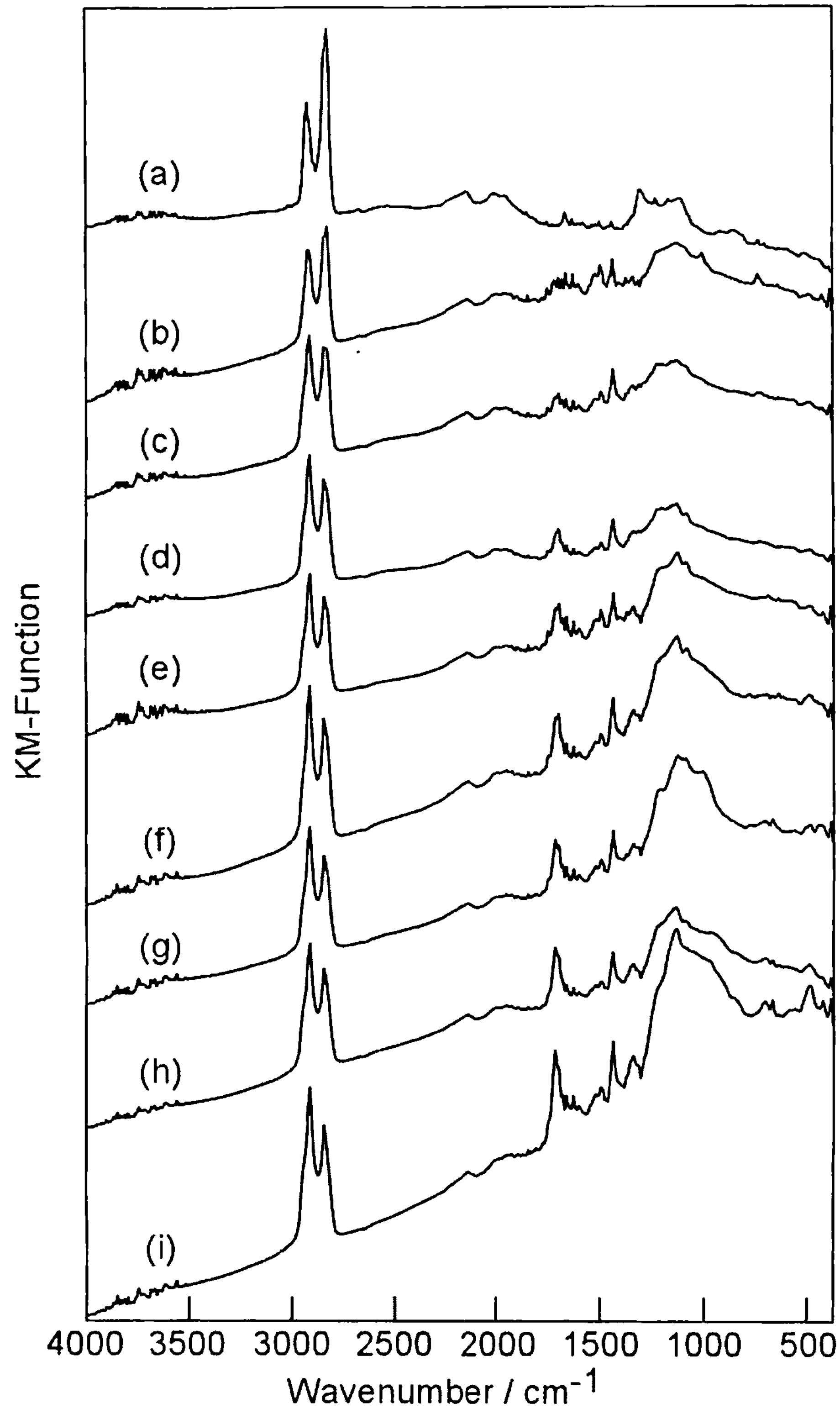

Figure 3.11 IR spectrum of diamond powder after reaction with lauroyl peroxide in toluene. (a) 0 g, (b) 0.001 g, (c) 0.005 g, (d) 0.01 g, (e) 0.05 g (f) 0.1 g, (g) 0.3 g, (h) 0.5 g, (i) 1.0g.

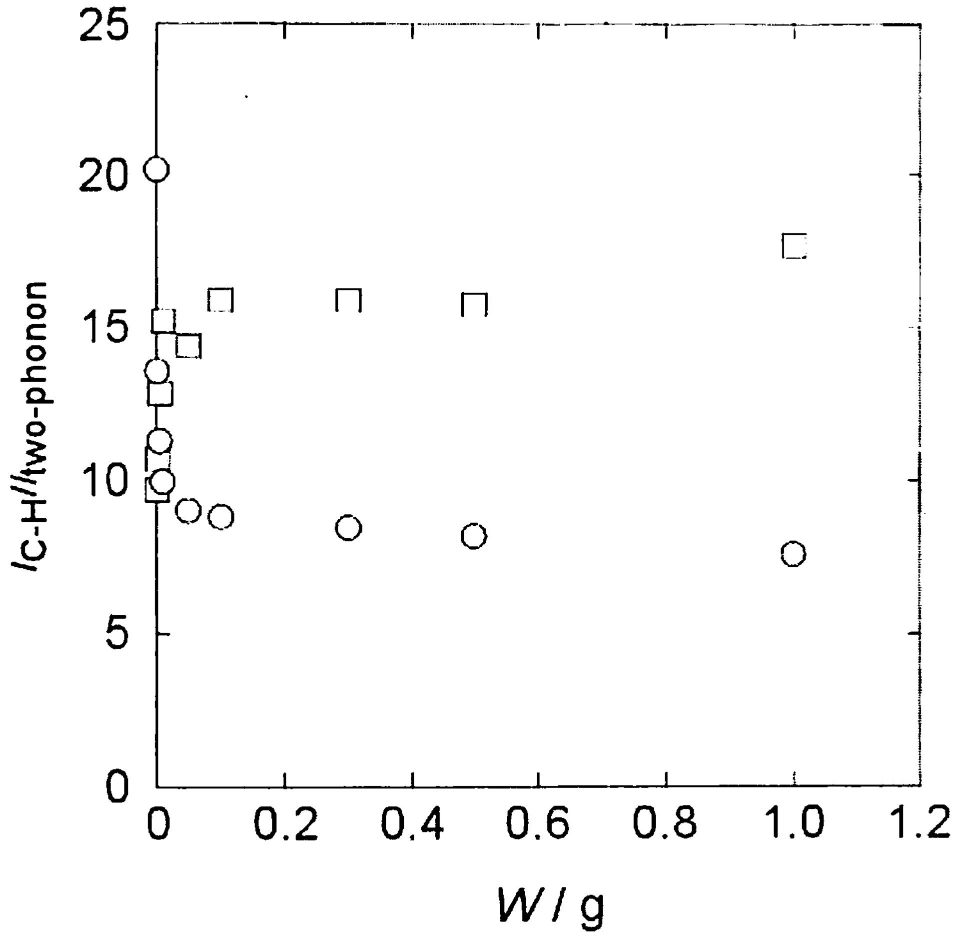

Figure 3.12 Amount dependence of the added lauroyl peroxide of the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value and the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value.○ $I_{C\text{-}H}/I_{two\text{-}phonon}$, □, $I_{C\text{-}H}/I_{two\text{-}phonon}$.

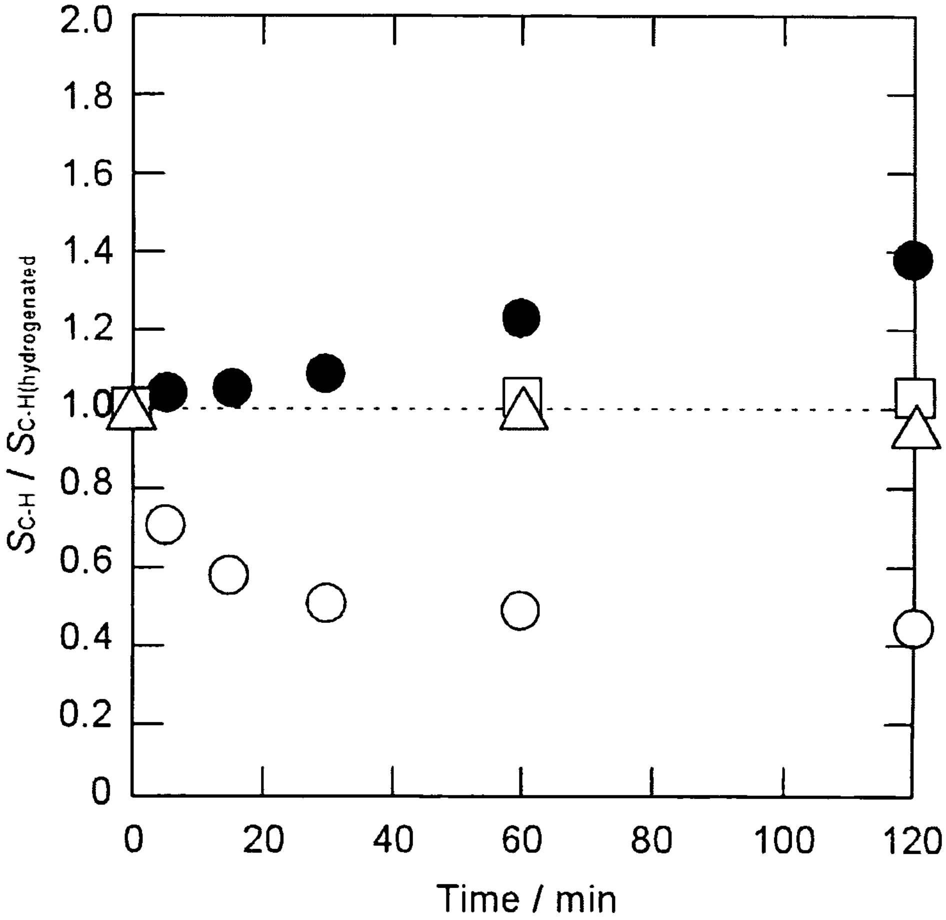

Figure 3.13 $S_{C\text{-}H}$ / $S_{C\text{-}H(hydrogenated)}$ vs. reaction time for diamond powder treated with radical initiator. ○ benzoyl peroxide, ● lauroyl peroxide, △ di-*t*-butyl peroxide, □ dicumyl peroxide.

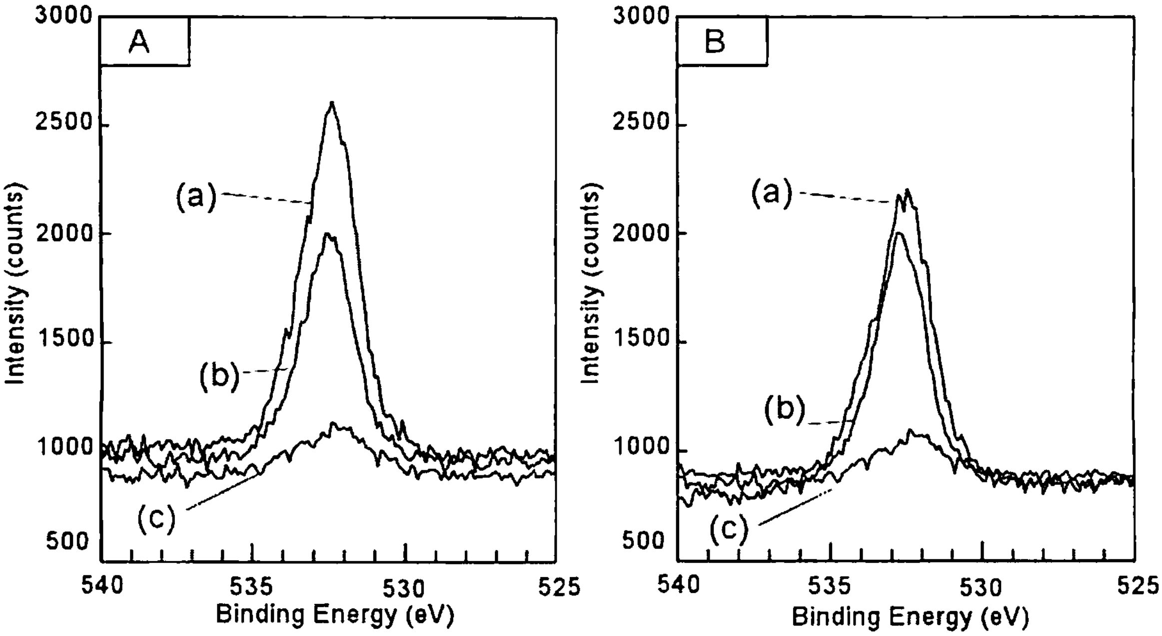

Figure 3.14 XPS spectra for the diamond films treated with benzoyl peroxide or lauroyl peroxide. (A) treated with benzoyl peroxide, (B) treated with lauroyl peroxide, (a) treated with radical initiator, (b) treated sample (a) with HCl, (c) hydrogenated diamond.

Chapter 4

Chemical modification of diamond surface using diacyl peroxide and CN group containing compounds for the introduction of the CN group

Chapter 4

Chemical modification of diamond surface using diacyl peroxide and CN group containing compounds for the introduction of the CN group

4.1. Introduction

The surface conditions of diamond have been studied primarily for the purpose of elucidating the diamond growth mechanism in CVD synthesis [1–3] and therefore most experiments have therefore been carried out in a vacuum system in the gas phase. In contrast, the reactions of organic chemistry are generally carried out under mild conditions (mild atmosphere, mild temperature, poor purity, and so on). Scale-up and mass production are facilitated in the case of reactions in the liquid phase. In general, the cost of the apparatus for liquid-phase chemical reactions is less than that of vacuum systems. The technique of chemical modification of the diamond surface using organic chemistry is therefore quite interesting from an industrial point of view.

There have been only a few reports on chemical reactions of the diamond surface in the liquid phase.[4–8] Thus investigations of the reactivity of the diamond surface in the liquid phase are quite important. Thus far, we have reported that the hydrogenated diamond surface reacts with the radical species derived from diacyl peroxide. When acetonitrile is used as the solvent for the reaction process, the peak assigned to the CN group appears in the IR spectrum. In the present study, to elucidate the chemical reactivity of the diamond surface, we investigated the introduction of the CN group onto the diamond surface using diacyl peroxides and CN group-containing compounds.

4.2. Experimental

Commercial diamond powder (tomei diamond, average diameter: 500 nm) was adopted as the diamond substrate for surface reactions. The diamond powder was washed with mixed acid (HF + HNO_3) at room temperature for 4 hours and rinsed with distilled water. After drying, the diamond powder was washed with mixed acid (H_2SO_4 + HNO_3) at 80℃ for 4 hours, and then rinsed with distilled water. After drying, the treated diamond powder was heated in a H_2 gas flow at 900℃ for 5 hours. This diamond powder heated in H_2 gas ("hydrogenated diamond") was utilized as the starting material for the chemical reaction.

The hydrogenated diamond powder was suspended in the C ≡ N group-containing compound (acetonitrile or benzonitrile) with diacyl peroxide (benzoyl peroxide or lauroyl peroxide). These suspensions were heated to activate the radical initiators in an Ar atmosphere.

After the reaction process, the treated diamond powder was washed with chloroform, then dried in a vacuum dryer.

Diffuse reflectance infrared Fourier-transform (FT-IR) spectroscopy (JASCO FT/IR-700) was used to characterize the surface condition of the diamond powder.

4.3. Results and discussion

4.3.1 Reaction with benzoyl peroxide in acetonitrile (CH_3-C≡N)

We have previously reported that hydrogenated diamond treated with benzoyl peroxide in acetonitrile has a peak corresponding to the CN bond in its IR spectrum.[Chapter 2] In the present study, several experiments were carried out to confirm that the CN group is introduced onto the diamond surface not by physical adhesion but by chemical bonding.

The reaction process was allowed to take place in acetonitrile without the addition of benzoyl peroxide. The IR spectrum of this sample is shown in Figure 4.1(c). It is known that the peak assigned to the CN bond of aliphatic nitriles appears at 2240-2260 cm^{-1}. The small peaks at 2300-2350 cm^{-1} in the IR spectra in this study can be assigned to the absorption of CO_2. The peaks assigned to the C-H bond remained large, and no peak corresponding to the CN bond appeared in the IR spectrum, indicating that the addition of benzoyl peroxide is necessary to introducing the CN group onto the diamond surface.

Diamond treated in toluene and washed with acetonitrile was also prepared. The IR spectrum of this sample is shown in Figure 4.1(d). There is no peak assigned to the CN bond in Figure 4.1(d), with the spectrum appearing similar to that of the diamond treated in toluene and washed with chloroform (Figure 4.1(b)). The adsorbed acetonitrile on the diamond surface can therefore not explain the appearance of the peak assigned to the CN bond in Figure 4.2. Thus, we should consider that the functional group containing the CN group was introduced onto the diamond surface during the reaction process.

The reaction time-dependence of the surface condition for the diamond treated in acetonitrile was investigated. The IR spectra of the diamond powders treated in acetonitrile are shown in Figure 4.2. An obvious peak appears at 2271 cm^{-1} in the IR spectra. It is known that the peak assigned to the CN bond of aliphatic nitrile appears at 2240-2260 cm^{-1}, however, we can assign the peak at 2271 cm^{-1} to the CN bond, as there is no candidate functional group. The peak assigned to the CN bond in the IR spectrum appeared after 5 min of treatment. Introduction of the CN bond onto the diamond surface must therefore start early in the reaction process. The peaks appearing after treatment were independent of the reaction time. No side reactions were observed to proceed when the treatment time was prolonged.

Thus far, the peak assigned to the absorption of two-phonons, which appears at ca. 2160 cm^{-1}, has been used for quantitative estimation of the diamond surface condition.[9,10,12] In the present study, the background subtracted peak intensity at 2158 cm^{-1}, $I_{\mathrm{two\text{-}phonon}}$, the background subtracted peak intensity at 2271 cm^{-1}, I_{CN} , and the background subtracted peak intensity at 2834 cm^{-1}, $I_{\mathrm{C\text{–}H}}$, were used to evaluate the relative amount of the CN group introduced onto the diamond surface and the decrease in the amount of C–H bond on the diamond surface. The reaction-time dependences of the ($I_{\mathrm{CN}}/I_{\mathrm{two\text{-}phonon}}$) and ($I_{\mathrm{C\text{–}H}}/I_{\mathrm{two\text{-}phonon}}$) values shown in Figure 4.3. The ($I_{\mathrm{CN}}/I_{\mathrm{two\text{-}phonon}}$) value increased with increases in the reaction time up to 30 min, and was independent of reaction time, hence, the chemical reaction introducing the CN group must be complete in less than 30 min. In contrast, the ($I_{\mathrm{C\text{–}H}}/I_{\mathrm{two\text{-}phonon}}$) value decreased with increases in the reaction time up to 30 min and was then independent of the reaction time. These experimental results indicate that both the chemical reaction introducing the CN bond and the chemical reaction abstracting the hydrogen atoms on the diamond surface proceed simultaneously.

In order to discuss the peak positions in detail, the IR spectra in the region of 400-2000 cm^{-1} are shown in Figure 4.4. As shown in Figure 4.1, the kinds of peaks of the diamond treated in toluene are the same as those of the diamond treated in acetonitrile, except for the presence of the peak assigned to the CN bond. However, the peak positions of the sample treated in toluene are different from those of the diamond treated in acetonitrile, as shown in Figure 4.4. When acetonitrile was used as a solvent (Figure 4.4(b)), the peaks at 1714 cm^{-1}, 1278 cm^{-1} and 704 cm^{-1} shifted to 1726 cm^{-1}, 1268 cm^{-1}, and 711 cm^{-1}, respectively. In contrast, when acetonitrile was used as the solvent for washing (Figure 4.4(c)), the peak at 1278 cm^{-1} shifted to 1271 cm^{-1}. The peak shifts to

1726 cm^{-1} and 711 cm^{-1} are not due to the adsorption of acetonitrile molecules.

The presumed reaction scheme for the diamond surface treated in toluene is as follows,

$$\text{(diamond)-H} + C_6H_5COO\cdot \rightarrow \text{(diamond)}\cdot + C_6H_5COOH \qquad (1)$$

$$\text{(diamond)}\cdot + C_6H_5COO\cdot \rightarrow \text{(diamond)-}OOCC_6H_5 \qquad (2)$$

The radical species derived from benzoyl peroxide ($C_6H_5COO\cdot$) abstracts the hydrogen atoms on the diamond surface, and the abstracted diamond surface then combines with another radical species derived from benzoyl peroxide ($C_6H_5COO\cdot$). When acetonitrile was utilized as the solvent for the reaction process, the same peaks, appeared, although the positions of these peaks differed slightly from those of the peaks for the diamond treated in toluene. The chemical reaction of Eq. (1) and Eq. (2), therefore, must proceed in the acetonitrile. Moreover, another chemical reaction introducing the C≡N group onto the diamond surface must proceed simultaneously because of the appearance of the peak assigned to the CN bond.

If the diamond surface activated by the radical species generated from benzoyl peroxide reacts with a molecule of acetonitrile, the chemical reaction is as follows,

$$\text{(diamond)}\cdot + CH_3\text{-}C\equiv N \rightarrow \text{(diamond)-H} + \cdot CH_2\text{-}C\equiv N \qquad (3)$$

Reaction of Eq. (3) does not introduce the CN group onto the diamond surface. The presumed chemical reaction introducing the CN group onto the diamond surface is as follows,

$$CH_3\text{-}C\equiv N + C_6H_5COO\cdot \rightarrow \cdot CH_2\text{-}C\equiv N + C_6H_5COOH \qquad (4)$$

$$\text{(diamond)}\cdot + \cdot CH_2\text{-}C\equiv N \rightarrow \text{(diamond)-}CH_2\text{-}C\equiv N \qquad (5)$$

Based on the experimental results, we should consider that the chemical reactions of both Eq. (2) and Eq. (5) proceeded on the diamond surface.

Next, the dependence of the added benzoyl peroxide was examined. The IR spectra of the diamond powder treated in acetonitrile are shown in Figure 4.5. The shape of the IR spectrum changed with increases in the amount of the added benzoyl peroxide, particularly at the lower wavelength region. Moreover, the wavenumber for the peak of the CN bond depended on the amount of the added benzoyl peroxide.

The dependencies of the ($I_{CN}/I_{two\text{-}phonon}$) and ($I_{C\text{-}H}/I_{two\text{-}phonon}$) values on the added benzoyl peroxide are shown in Figure 4.6. The ($I_{CN}/I_{two\text{-}phonon}$) value increased with increased in the amount of added benzoyl peroxide up to 0.05 g, and then decreased when the amount of the added benzoyl peroxide exceeded 0.05 g. In contrast, the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value decreased rapidly up to 0.05 g, and then remained constant with more than 0.05 g. When acetonitrile was used as a solvent for the reaction process, the heavily benzoyl peroxide-doped solvents colored, with the degree of coloration increasing with increases in the amount of the added benzoyl peroxide. The same trend was observed in the case of the reaction in toluene. We can therefore consider that the radical species generated from benzoyl peroxide attacks another radical species as well as the modified diamond surface in the case of excessive doping of benzoyl peroxide.

It was found that the chemical reaction process of the hydrogenated diamond surface with benzoyl peroxide in acetonitrile introduces the CN group on the diamond surface, although other functional groups are also introduced onto the diamond surface.

4.3.2. Reaction with lauroyl peroxide in acetonitrile ($CH_3\text{-}C{\equiv}N$)

We have already reported that lauroyl peroxide can react with the hydrogenated diamond surface. Lauroyl peroxide was therefore used as a radical initiator for the CN group introduction reaction.

The IR spectra of the diamond powders after treatment with lauroyl peroxide are shown in Figure 4.7. A small peak assigned to the CN group appeared at 2255 cm^{-1}. The peak intensity for the CN group of the diamond treated with lauroyl peroxide was considerably less than that of the diamond treated with benzoyl peroxide. Moreover, the peak position of the CN group of the diamond powder treated with lauroyl peroxide was lower than that of the diamond powder treated with benzoyl peroxide. These results indicate that a smaller amount of the CN group is introduced by lauroyl peroxide than by benzoyl peroxide. *i.e.* benzoyl peroxide appears to be more effective in introducing the CN group onto the diamond surface. The difference in peak position is likely due to the difference in the interaction between the introduced CN group and other functional groups introduced onto the diamond surface.

4.3.3. Reaction with benzoyl peroxide in benzonitrile (C_6H_5-C≡N)

Benzonitrile, which includes a CN group in its structure, was used as a solvent for the reaction process. The IR spectra of the diamond powder treated in benzonitrile are shown in Figure 4.8. There is no peak assigned to the CN group in any of the IR spectra. No CN group, therefore, is introduced onto the diamond surface when benzonitrile is used as a solvent for the reaction process.

4.3.4. Reaction with lauroyl peroxide in benzonitrile (C_6H_5-C≡N)

The IR spectra of the diamond powder treated in benzonitrile are shown in Figure 4.9. There is no peak assigned to the CN group in any of the IR spectra. No C≡N group, therefore, was introduced onto the diamond surface when benzonitrile was adopted as a solvent for the reaction process.

We presume that the chemical reactions of Eq. (4) - Eq. (5) are the C≡N group introduction processes. There is no alkyl group in the structure of benzonitrile; that is, there is no hydrogen atom that can be abstracted with the radical species derived from benzoyl peroxide or derived from lauroyl peroxide. The experimental results, with no introduction of the CN group in the case of benzonitrile, support the presumption explained by the chemical reactions of Eq. (4) - Eq. (5).

4.4. Conclusion

Radical reactions using a benzoyl peroxide and lauroyl peroxide were performed to introduce the CN group onto the diamond surface. The CN group was introduced onto diamond surfaces treated with benzoyl peroxide or lauroyl peroxide when acetonitrile was used as the solvent for the reaction process. In contrast, no CN group was introduced onto diamond surfaces treated with benzoyl peroxide or lauroyl peroxide when benzonitrile was used as the solvent. There is an alkyl group in the structure of acetonitrile, and the hydrogen atoms in the alkyl group can be abstracted by the radical species generated from the diacyl peroxide. The radical species derived from acetonitrile should be able to react with the diamond surface activated by the radical species generated from benzoyl peroxide. There is no hydrogen atom that can be abstracted by radical species in the structure of benzoyl peroxide, thus explaining why no CN-group is introduced with benzonitrile

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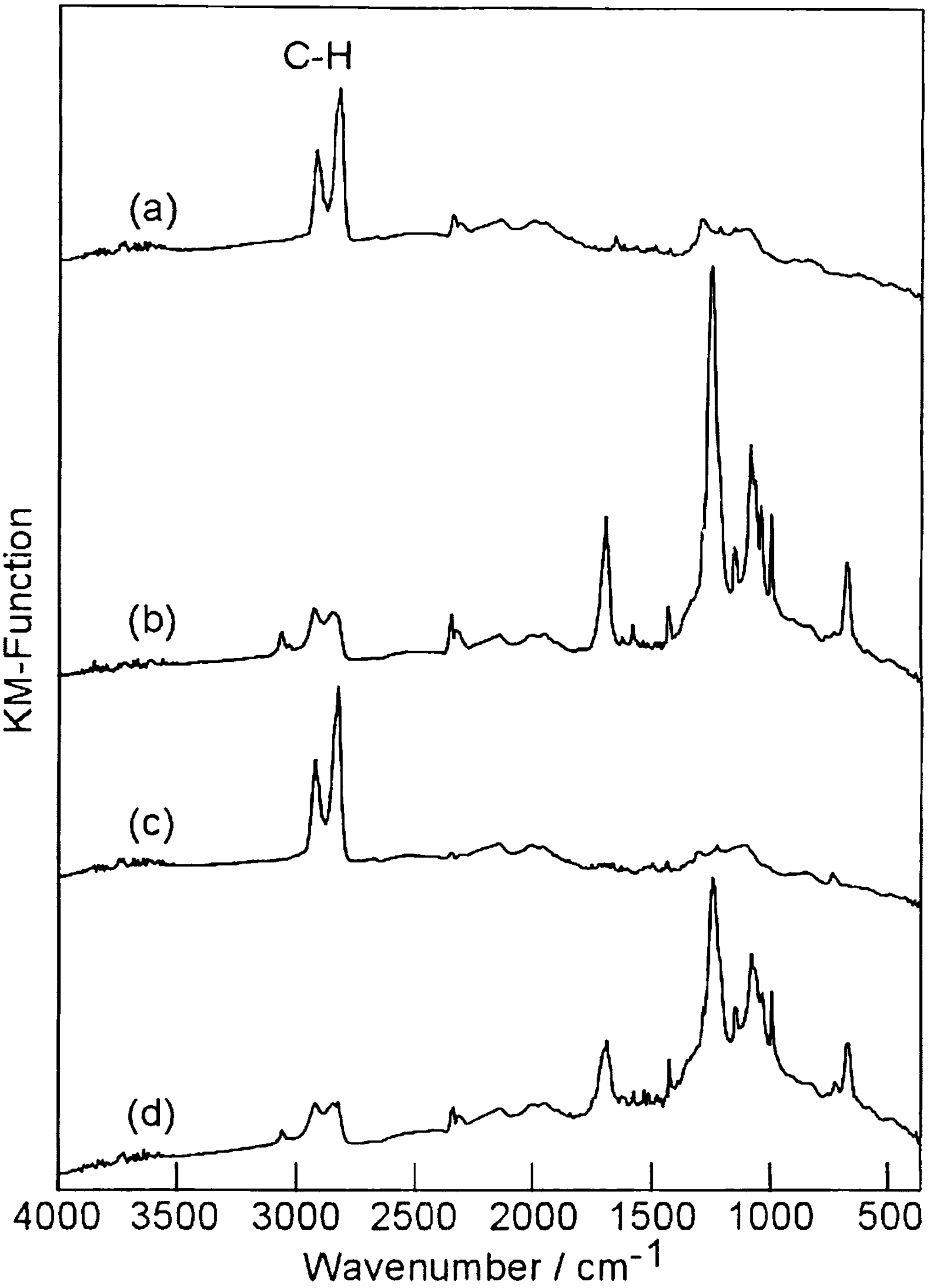

Figure 4.1 IR spectrum of the diamond powder. (a) hydrogenated diamond, (b) treated in toluene and washed with chloroform, (c) treated in acetonitrile without benzoyl peroxide, (d) treated in toluene and washed with acetonitrile.

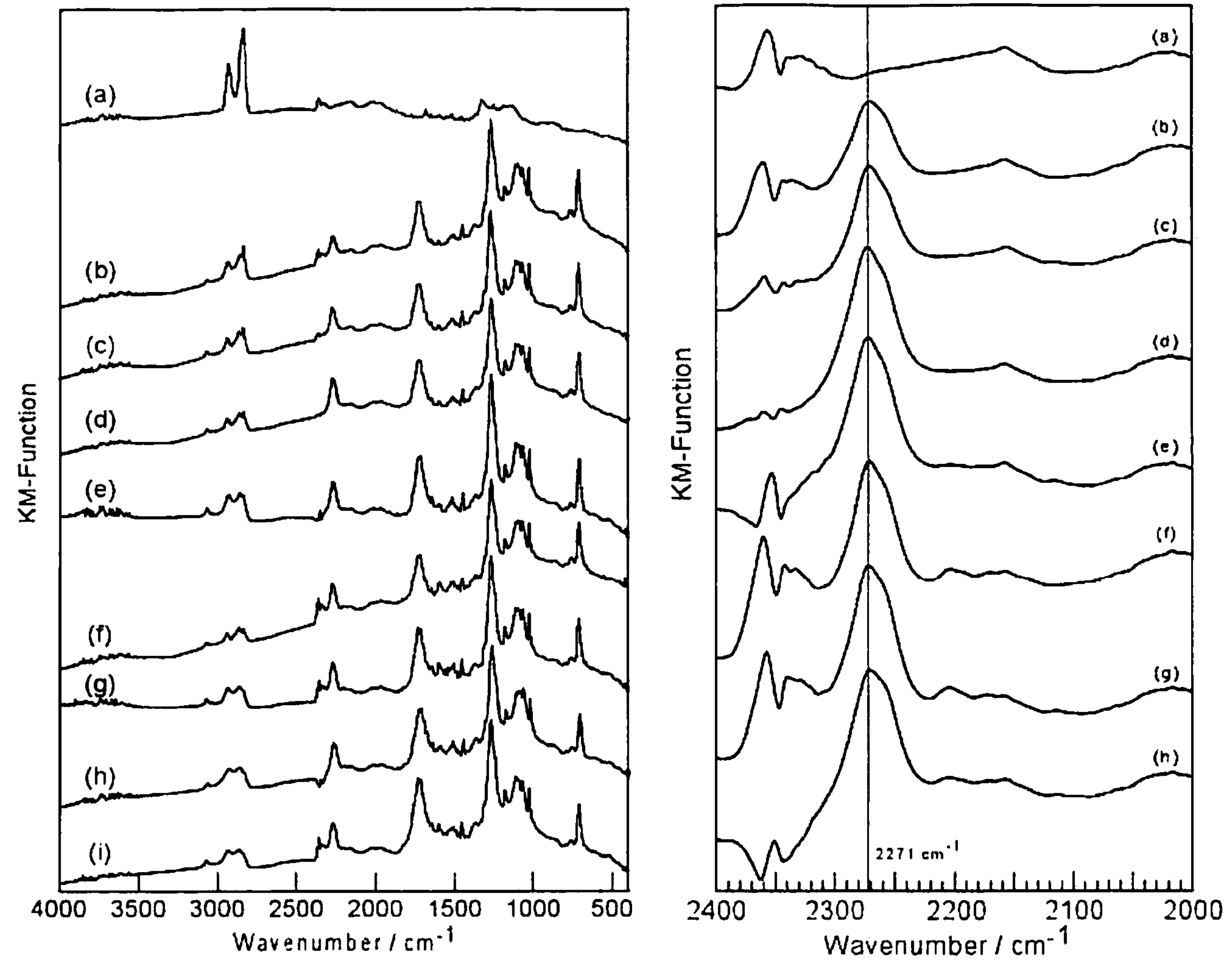

Figure 4.2 (A) IR spectra of the diamond powder treated with benzoyl peroxide in acetonitrile, (B) Expansion of (A).

(a), hydrogenated diamond; (b), 5 min.; (c), 15 min.; (d), 30 min.; (e), 60 min.; (f), 120 min.; (g), 240 min.; (h), 360 min.; (i), 480 min.

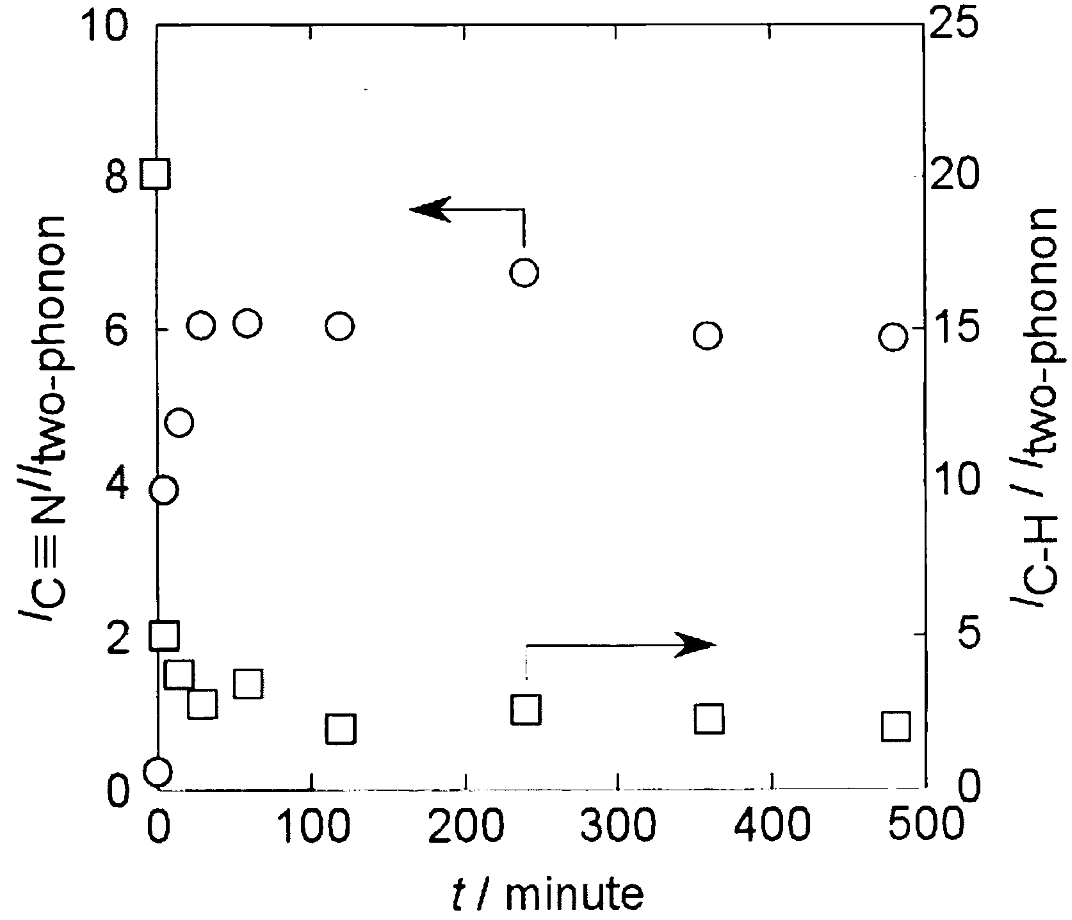

Figure 4.3 Reaction-time dependencies of the ($I_{C\equiv N}/I_{two\text{-}phonon}$) and ($I_{C\text{-}H}/I_{two\text{-}phonon}$) values of the diamond powder treated with benzoyl peroxide in acetonitrile.

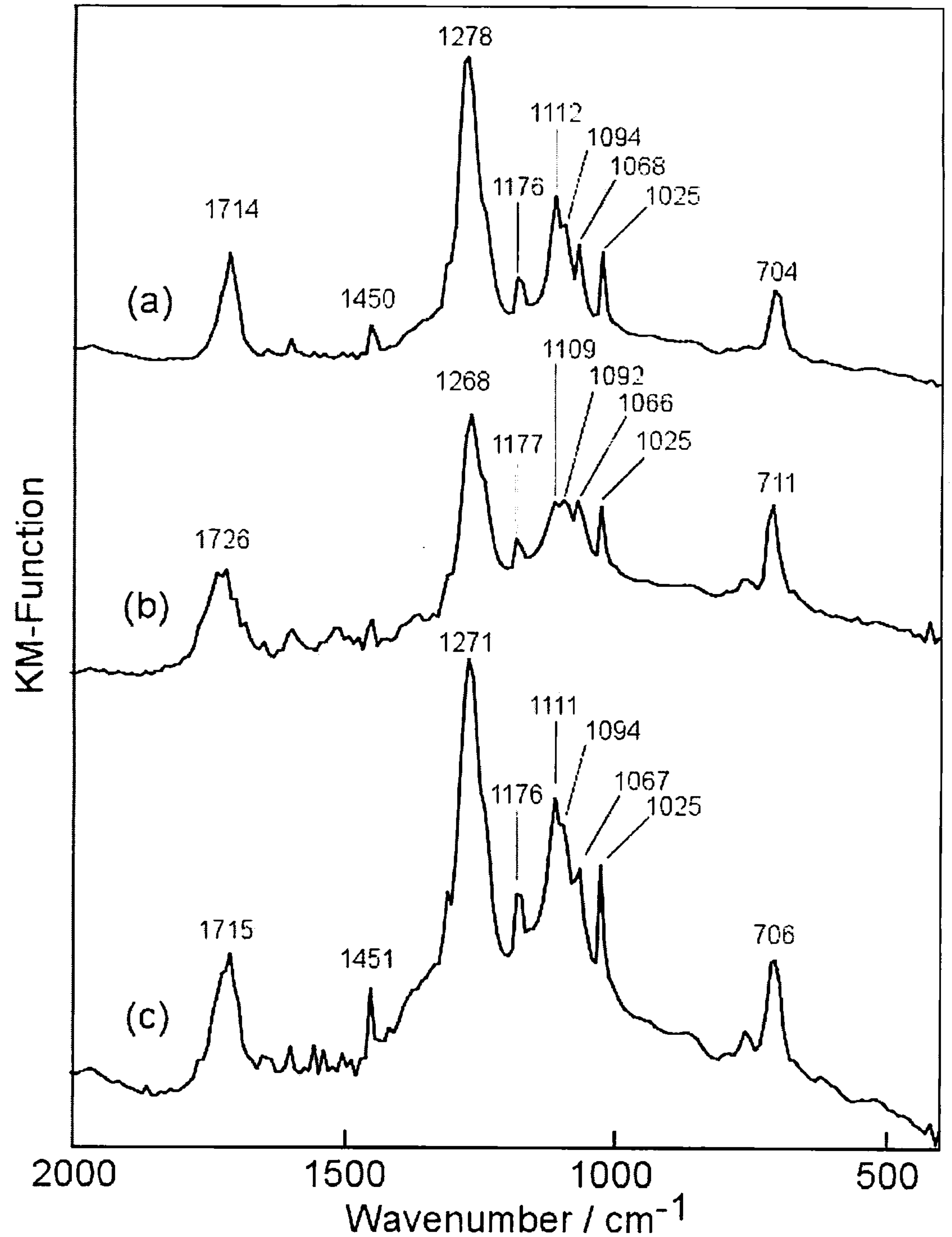

Figure 4.4 IR spectra of the diamond powder treated with benzoyl peroxide. (reaction time: 120 min.)

(a), treated in toluene and washed with chloroform;

(b), treated in acetonitrile and washed with chloroform;

(c), treated in toluene and washed with acetonitrile.

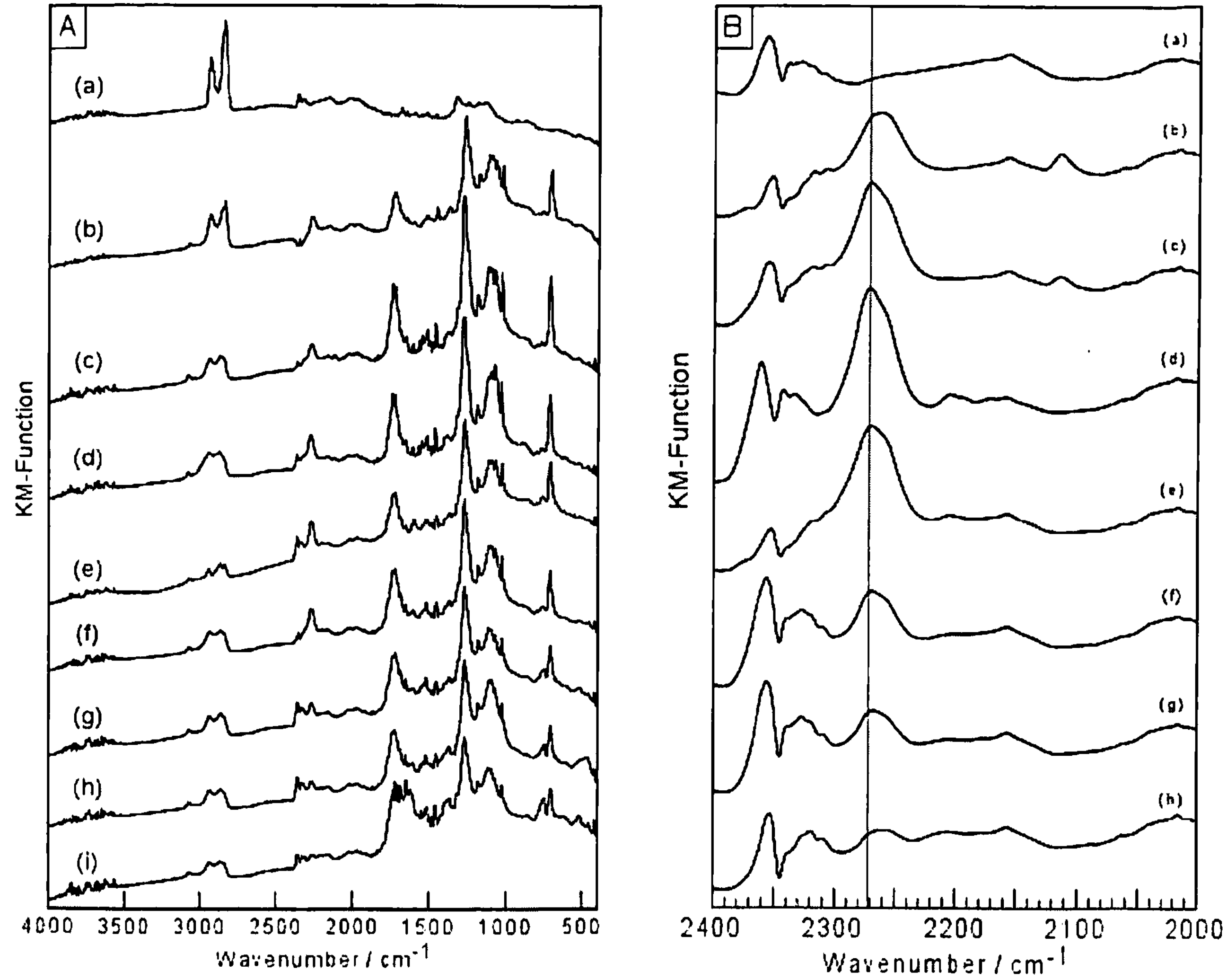

Figure 4.5 (A) IR spectra of the diamond powder treated with benzoyl peroxide in acetonitrile, (B) Expansion of (A). (a), hydrogenated diamond, (b), 0.001 g; (c), 0.005 g; (d), 0.01 g; (e), 0.05 g; (f), 0.1 g; (g), 0.3 g; (h), 0.5 g; (i), 1.0 g.

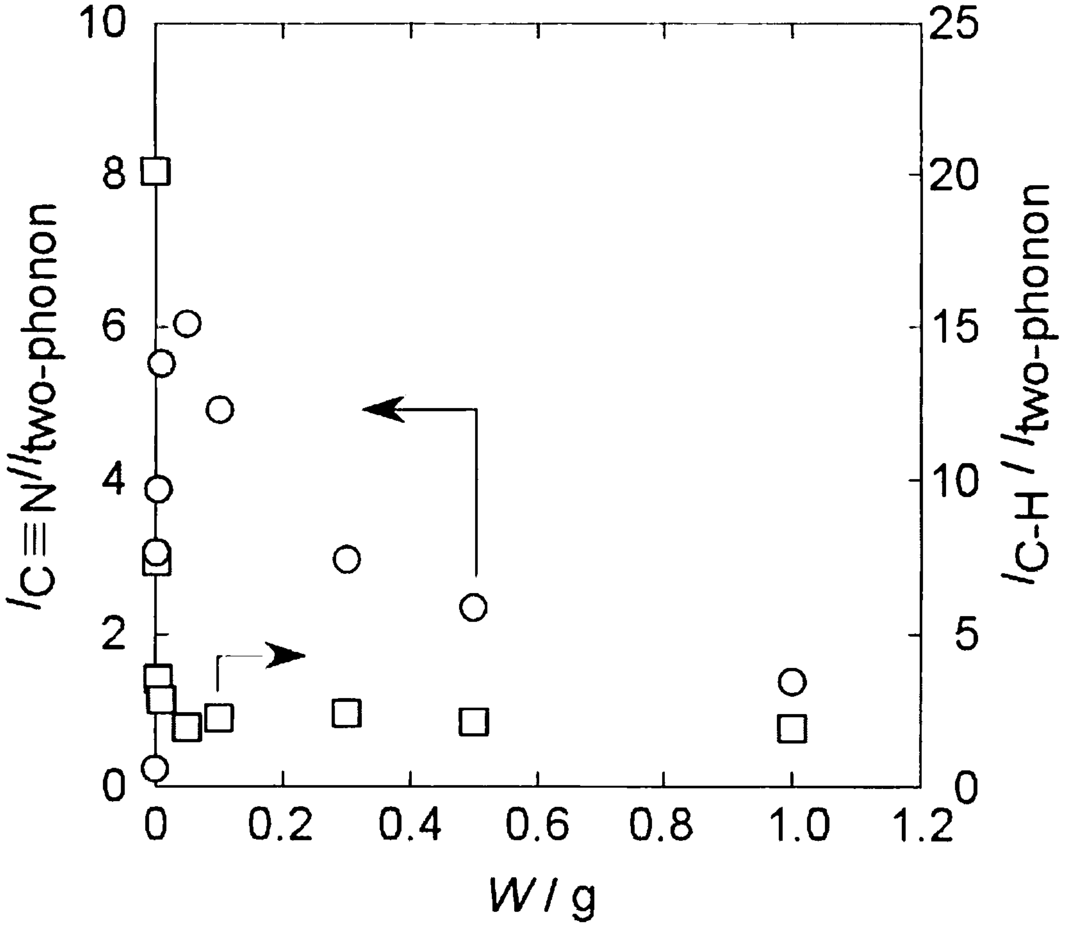

Figure 4.6 The degree of dependence on added benzoyl peroxide of the ($I_{C\equiv N}/I_{two\text{-}phonon}$) and ($I_{C\text{-}H}/I_{two\text{-}phonon}$) values of the diamond powder treated with benzoyl peroxide in acetonitrile.

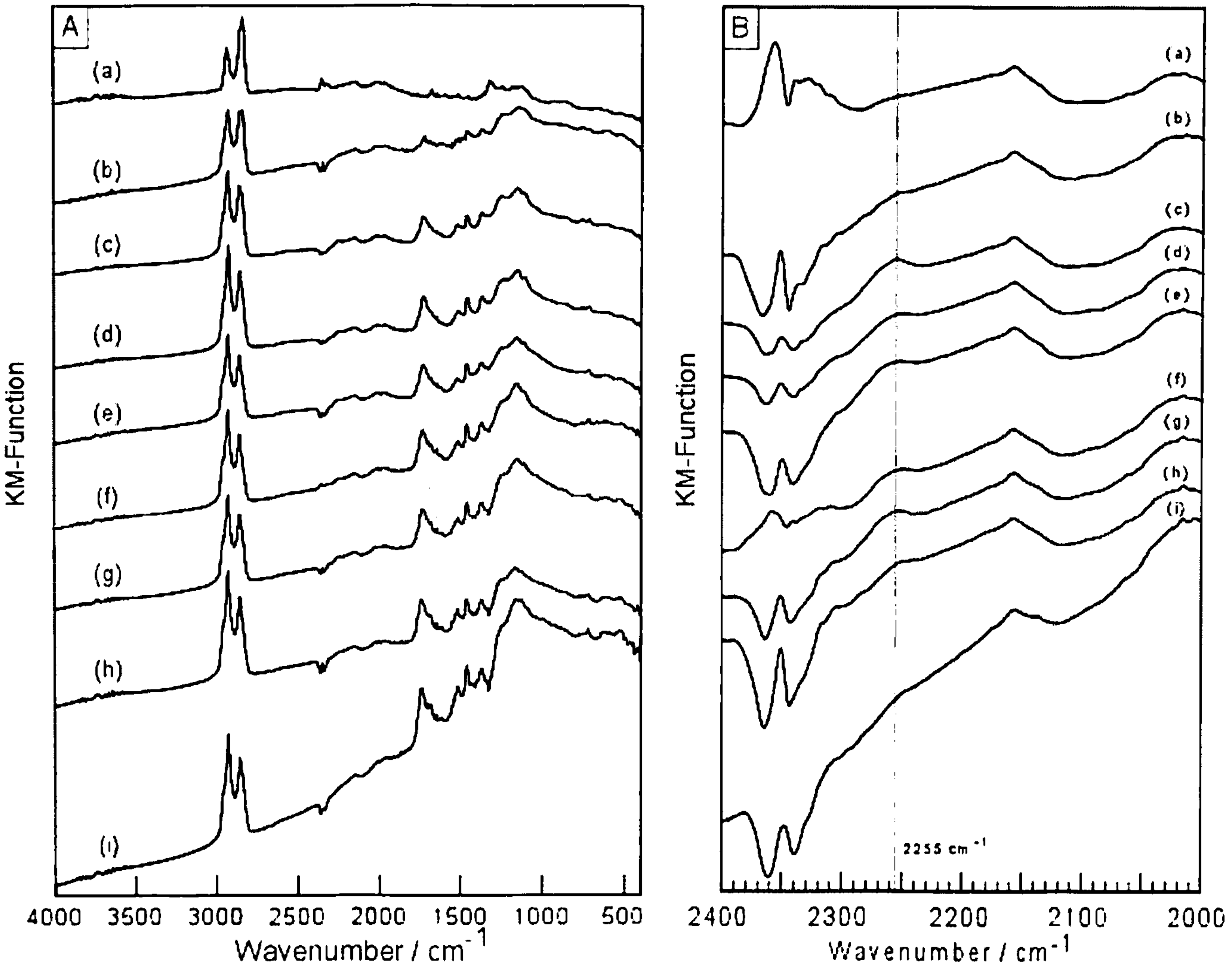

Figure 4.7 (A) IR spectra of the diamond powder treated with lauroyl peroxide in acetonitrile, (B) Expansion of (A). (a), hydrogenated diamond, (b), 0.001 g; (c), 0.005 g; (d), 0.01 g; (e), 0.05 g; (f), 0.1 g; (g), 0.3 g; (h), 0.5 g; (i), 1.0 g.

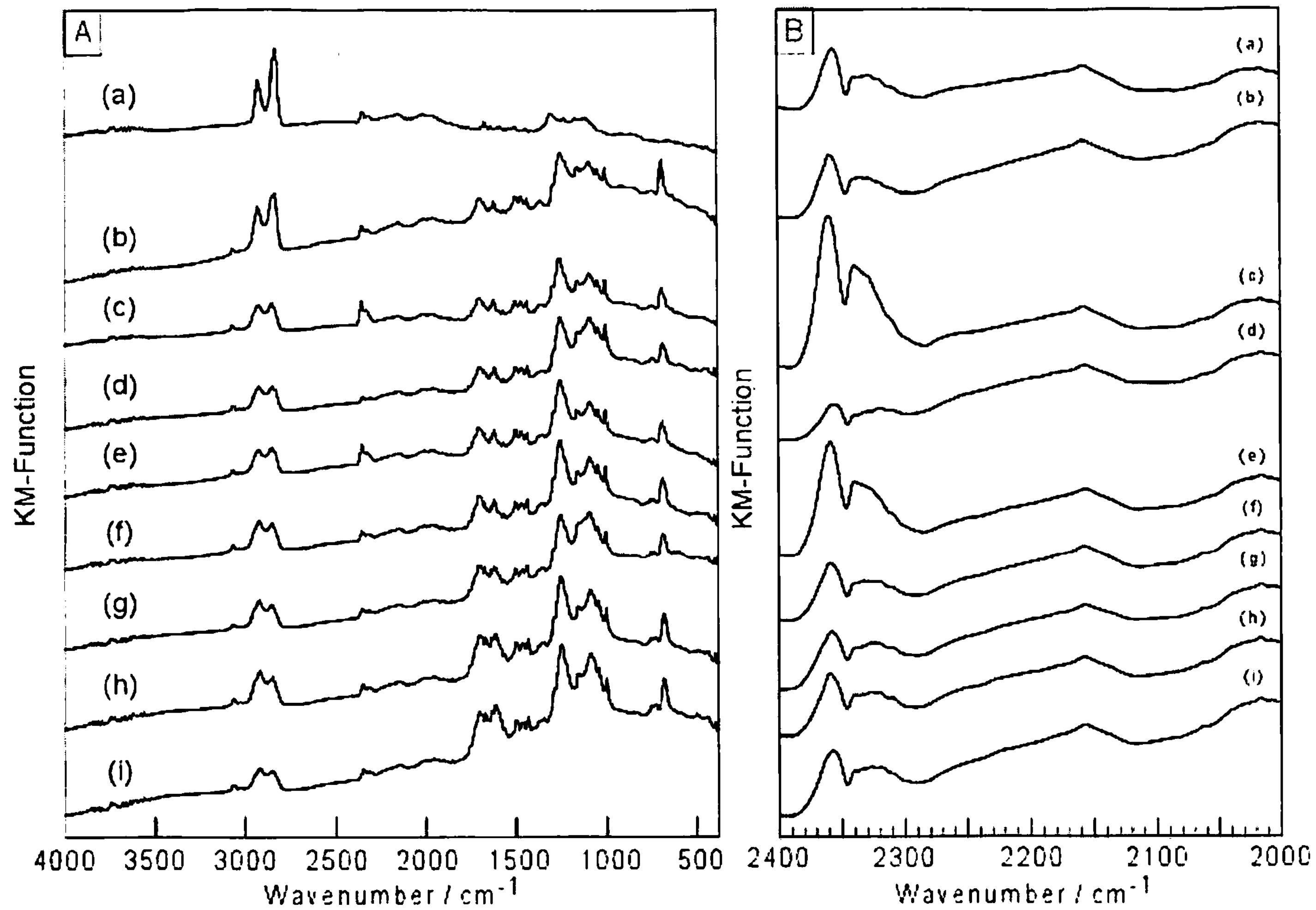

Figure 4.8 (A) IR spectra of the diamond powder treated with benzoyl peroxide in benzonitrile, (B) Expansion of (A). (a), hydrogenated diamond, (b), 0.001 g, (c), 0.005 g; (d), 0.01 g; (e), 0.05 g; (f), 0.1 g; (g), 0.3 g; (h), 0.5 g; (i), 1.0 g.

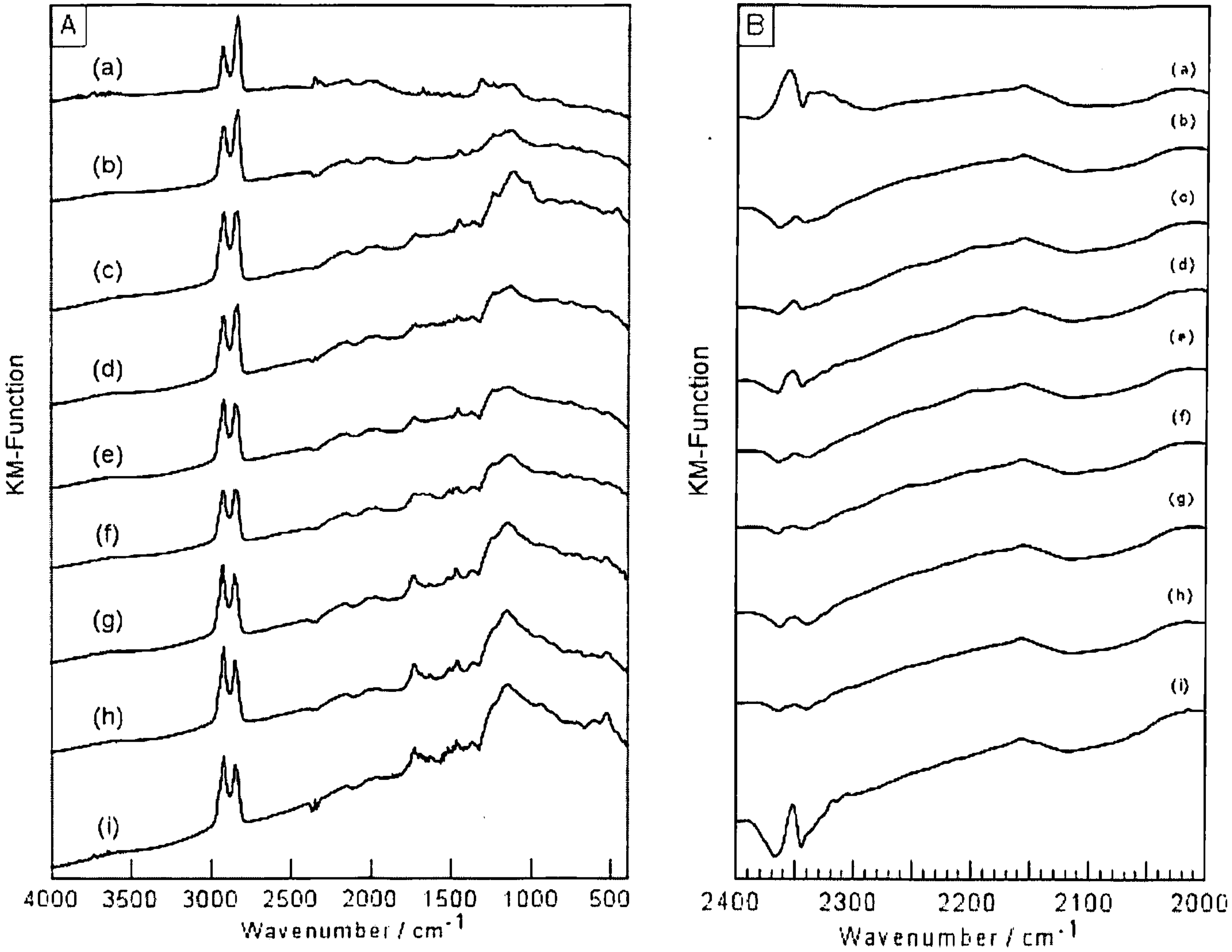

Figure 4.9 (A) IR spectra of the diamond powder treated with lauroyl peroxide in benzonitrile, (B) Expansion of (A). (a), hydrogenated diamond, (b), 0.001 g; (c), 0.005 g; (d), 0.01 g; (e), 0.05 g; (f), 0.1 g; (g), 0.3 g; (h), 0.5 g; (i), 1.0 g.

Chapter 5

Chemical modification of diamond surface with $CH_3(CH_2)_nCOOH$ using benzoyl peroxide

Chapter 5
Chemical modification of diamond surface with $CH_3(CH_2)_nCOOH$ using benzoyl peroxide

5.1. Introduction

Diamond is one of the most potentially useful industrial materials because of its properties, like hardness, large band gap, transparency over a wide wavelength region, high thermal conductivity. Therefore, much research has been performed regarding the application of diamond as an industrial material in various fields.[1] Recently, chemical modification of diamond surface have been received much attention. if diamond surface is controllably modified using organic functional groups, we can make a new organic–inorganic functional material. So far, several studies have focused on the chemical modification of diamond surface.[2–12]

In the present study, we report the specific chemical reaction between carboxylic acids [HCOOH, $CH_3(CH_2)_nCOOH$ ($0<n<16$)] and a diamond surface, and describe the modification of the diamond surface using aliphatic carboxylic acid in benzoyl peroxide containing solvent.

5.2. Experimental

Commercial diamond powder (tomei diamond, average diameter: 500 nm) was adopted as the diamond substrate for surface reactions. The diamond powder was washed with mixed acid (HF + HNO_3) at room temperature for 4 hours and rinsed with distilled water. After drying, the diamond powder was washed with mixed acid (H_2SO_4 + HNO_3) at 80℃ for 4 hours, and then rinsed with distilled water. After drying, the treated diamond powder was heated in a H_2 gas flow at 900℃ for 5 hours. This diamond powder heated in H_2 gas ("hydrogenated diamond") was utilized as the starting material for the chemical reaction.

The apparatus for the chemical reaction process has been described in chapter 2 Hydrogenated diamond powder (0.1 g), benzoyl peroxide (0.05 g), which is an effective radical initiator for the hydrogen abstraction reaction of the diamond surface, and carboxylic acid [HCOOH, $CH_3(CH_2)_nCOOH$ ($0<n<16$)] are suspended in toluene (5 ml). In the case of $CH_3(CH_2)_nCOOH$ ($0<n<4$), $CH_3(CH_2)_nCOOH$ ($0<n<4$) itself was used as the solvent for the chemical reaction process. Argon gas was bubbled into the suspensions while these were heated at 75 ℃ in order to activate the radical initiator. After this chemical reaction process, the diamond powder was washed a few times with chloroform or another solvent and then dried in a vacuum dryer. The dried powder was re-washed a few times with chloroform or another solvent for ensuring the complete removal of residue. Diffuse reflectance infrared Fourier-transform (FT-IR) spectroscopy (JASCO FT/IR-700) was used to characterize the surface condition of the diamond powder.

5.3. Results and discussion

5.3.1. Specific surface condition of diamond treated in acetic acid

We confirmed that the diamond particles used in this study had multi-faceted surfaces, and the specific surface area of the diamond powder was 9.94 $m^2 g^{-1}$ as has been reported in chapter 2.

So far, we have reported in chapter 2 and chapter 3 that hydrogenated diamond surface can react with the radical species generated from benzoyl peroxide, and that the C_6H_5COO group should be introduced on the diamond surface. In contrast, when acetic acid was used as the solvent for the hydrogen abstraction reaction employing benzoyl peroxide, the shape for the IR spectrum of the reacted diamond powder was obviously different from that of other samples, as shown in Figure 5.1(c).

5.3.2. Stability of a diamond surface modified using acetic acid

First of all, in order to investigate the stability of the diamond surface modified with acetic acid, several experiments were carried out. The experimental conditions and the IR spectra of the samples are shown in Table 5.1 and Figure 5.2, respectively. As shown in Figure 5.2, sample I–IX (the samples treated in acetic acid or treated in the toluene containing acetic acid) had the same peaks in the IR spectrum. That is, the diamond surface condition after the chemical reaction is independent of the kind of the solvent used in the washing process. Therefore, the IR peaks that appeared after the chemical reaction process must be assigned to the functional groups introduced during the chemical reaction process. Moreover, the diamond's surface condition after the chemical reaction process must be stable against organic solvent because the shape of the IR spectra is independent of the kind of solvent used in the washing process. It should be noticed that no peak assigned to the O–H bond, which exists in the chemical structure of acetic acid, appeared in the IR spectra of the reacted diamond powders. It should be considered, therefore, that the IR peaks generated after the reaction process must be assigned not to the acetic acid physically adhered on the diamond's surface but to the generated functional group on the diamond's surface.

Next, in order to examine the stability of the diamond's surface condition after the chemical reaction under severe conditions, sample I and sample XI were boiled in water for 3 h and then washed more than four times with water and dried in a dryer. The IR spectra after the boiling process are shown in Figure 5.1. As for sample I, the IR peaks generated after the reaction process remained although the intensities decreased after this boiling treatment. The intensities of the IR peak for sample XI also decreased after the boiling treatment. The presumed surface condition of the diamond treated in toluene with benzoyl peroxide is [(diamond)–$OOCC_6H_5$] in chapter 3.

The experimental results shown in Figure 5.1 indicate that the stability of the functional group introduced on the surface of sample I is almost as same as that of sample XI. It is known that acetic acid ionizes as follows,

$$CH_3COOH \rightarrow CH_3COO^- + H^+ \quad (1)$$

In general, ionic bonding is unstable in a polar solvent such as water. If CH_3COO^- ions adhere to a diamond surface during the chemical reaction process and this adhesion is responsible for the appearance of the IR peaks, the CH_3COO^- ions should desorb during the boiling process in water. Therefore, the adhesion of CH_3COO^- ions during the chemical reaction process in acetic acid should not be a reason for the appearance of the IR peaks after the chemical reaction process. We can consider, therefore, that the kind of the bonding between the functional group and the diamond surface of sample I is not ionic bonding. The presumed bonding of the functional group on sample XI is covalent bonding. Because the stability of the bonding between the functional group and the diamond surface of sample I is equivalent to that of sample XI, we can consider that the presumed bonding of the functional group on sample I should also be covalent bonding.

5.3.3. Surface condition of diamond reacted with acetic acid

We have previously discussed the IR peaks for the diamond powder treated in toluene in chapter 2. The C–H peaks at less than 3000 cm^{-1} are assigned to the aliphatic C–H bond, that is, the C–H bonds on the hydrogenated diamond surface. On the other hand, the C–H peaks at more than 3000 cm^{-1} are assigned to the aromatic C–H bond, that is, the C–H bonds of the phenyl group in the C_6H_5COO- group introduced onto the diamond surface. The peak at ca. 1715 cm^{-1} is assigned to the C=O bond in the C_6H_5COO- group introduced onto the diamond surface. Moreover, the peaks at 700–1500 cm^{-1} are assigned to the bonding in the aromatic group in the C_6H_5COO- group introduced onto the diamond surface. The shape of the IR spectrum of the diamond treated in acetic acid is rather different from that of the diamond treated in the other solvent, being simpler in the region from 700–1500 cm^{-1}. There is no peak assigned to the O–H group in the IR spectra of the diamond treated in acetic acid. Therefore, there should be no O–H group on the diamond surface after the chemical reaction process in acetic acid. As such, the presumed chemical reaction on the diamond surface is as follows:

$$C_6H_5\text{-}COO\text{-}OOC\text{-}C_6H_5 \rightarrow C_6H_5\text{-}COO\cdot + \cdot OOC\text{-}C_6H_5 \quad (2)$$

$$C_6H_5\text{-}COO\cdot + (\text{diamond})\text{-}H \rightarrow C_6H_5\text{-}COOH + (\text{diamond})\cdot \quad (3)$$

$$C_6H_5\text{-}COO\cdot + CH_3COOH \rightarrow C_6H_5\text{-}COOH + CH_3COO\cdot \quad (4)$$

$$(\text{diamond})\cdot + CH_3COO\cdot \rightarrow (\text{diamond})\text{-}OOC\text{-}CH_3 \quad (5)$$

The product of the chemical reaction process shown in Eqs. (2)–(5) has C–H bonds in its chemical structure. Therefore, the enhancement of the peak intensity assigned to the C–H bond may be expected in the IR spectrum for the diamond powder treated in acetic acid if the chemical reaction process of Eqs. (2)–(5) proceeded on the diamond surface. However, the IR peak intensity of the C–H bond of CH_3COOH in itself is obscure. The low intensity of the C–H bond for the diamond treated in acetic acid, therefore, is reasonable. In the case of the diamond treated in acetic acid, the peak assigned to the

C=O bond appeared at 1739 cm^{-1} [Figure 5.1(c)]. This was obviously higher than that of the diamond treated in toluene, 1718 cm^{-1} [Figure 5.1(a)]. Therefore, the chemical condition for the C=O bond of the diamond treated in acetic acid should be different from that of the diamond treated in toluene. In general, the peak position of the C=O bond in (aliphatic group)–COO–(aliphatic group), 1735–1755 cm^{-1}, is higher than that of the C=O bond in (aromatic group)–COO–(aliphatic group), 1710–1730 cm^{-1}. Therefore, the experimental results regarding the peak position of the C=O bond supports the chemical reaction process of Eqn. (2)–(5).

5.3.4. Chemical reaction rate of diamond surface modification using acetic acid

In order to examine the chemical reaction rate on the diamond surface treated in acetic acid, the time dependence of the reaction was investigated. The IR spectra of the diamond powder treated with benzoyl peroxide in acetic acid are shown in Figure 5.3. The peak intensities at ca. 3000 cm^{-1}, which are assigned to the C–H bond, decreased with increased reaction time.

We have reported in chapter 2 that the intensity of the peak assigned to two-phonon adsorption at 2160 cm^{-1}, $I_{\text{two-phonon}}$, is useful as an internal standard for the relative quantification of the diamond surface condition. The time dependence of the reaction on the ratio of the peak intensity at 2835 cm^{-1}, $I_{\text{C–H}}$, to the $I_{\text{two-phonon}}$ value is shown in Figure 5.4. In the case of the chemical reaction with acetic acid, the peaks at ca. 3000 cm^{-1} must consist of the peaks assigned to the original C–H bond on the diamond surface (hydrogenated diamond surface) and the C–H bond in the functional group derived from acetic acid if the presumed chemical reaction process of Eqs. (2)–(5) proceeded in acetic acid. Therefore, the amount of the hydrogen atoms abstracted from the diamond surface cannot be evaluated based on the C–H peaks intensities. However, the ($I_{\text{C–H}}/I_{\text{two-phonon}}$) value must be effective for estimating the diamond surface condition quantitatively. The ($I_{\text{C–H}}/I_{\text{two-phonon}}$) value decreased with increasing reaction times up to ca. 300 min, and then converged to ca. 7.0. We have reported in chapter 2 that the ($I_{\text{C–H}}/I_{\text{two-phonon}}$) value converged to *ca.* 3.0 when toluene was used as the solvent. The experimental result in which the converged ($I_{\text{C–H}}/I_{\text{two-phonon}}$) value of the diamond treated in acetic acid was larger than that of the diamond treated in toluene should be reasonable if the reaction schemes of Eqs. (2)–(5) proceeded on the diamond surface. The difference in the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) value, therefore, supports the reaction scheme of Eqs. (2)–(5).

In the case of the following chemical reaction,

$$A + B \rightarrow C \quad (6)$$

where A and B are reactants and C is a product, C is not affected by the reaction rate. The reaction rate, r_A, is given by

$$-r_A = kC_A^n C_B^m = k'C_A^n \quad (7)$$

$$k' = kC_B^m \quad (8)$$

where k and k' are the reaction rate constants, and C_A and C_B are the concentrations of the reactants.

In this study, we used the ($I_{C\text{-}H}/I_{two\text{-}phonon}$) values as the C_A value, and adopted the slope of the curved line shown in Figure 5.4 as the r_A value.

From Eq. (7),

$$\mathrm{Log}(-r_A) = n \log C_A + \log k' \quad (9)$$

The graph of log C_A *vs.* log ($-r_A$) is shown in Figure 5.5. From the line in Figure 5.5, the value of k' and n were determined as follows:

$$n = 5.69 \quad (10)$$

$$k' = 9.14 \times 10^{-9} \quad (11)$$

Therefore, the rate equation of this chemical reaction is as follows:

$$r_A = (9.14 \times 10^{-9}) C_A^{5.69} \quad (12)$$

The rate equations of the hydrogen abstraction reaction of a hydrogenated diamond surface with benzoyl peroxide in toluene were as follows:

$r_A = (5.75 \times 10^{-8}) C_A^{5.62}$

(The amount of added benzoyl peroxide is 0:001), (13)

$r_A = (1.25 \times 10^{-9}) C_A^{2.81}$

(The amount of added benzoyl peroxide is 0:05 g), (14)

The values of the apparent reaction order, n, and the apparent rate coefficient, k', of the chemical reaction in acetic acid is similar to that of the chemical reaction in toluene treated with (0.001 g) of benzoyl peroxide rather than with (0.05 g) of benzoyl peroxide. If the chemical reactions of Eqs. (2)–(5) proceeded in acetic acid, the amount of the $C_6H_5COO\cdot$ radicals that can attack the diamond surface in acetic acid should be smaller than that in toluene. Therefore, the similarities of the n value and the k' value of this study to that of the reaction using (0.001 g) of benzoyl peroxide may support the reaction scheme of Eqs. (2)–(5).

5.3.5. Reactivity of diamond surface in solvent

So far, we have used various organic compounds as the solvent for the chemical reaction process in chapter 2 and chapter 3. The diamond surface condition after the reaction process was summarized in Table 5.2 from the standpoint of the classification of the oxygen-containing functional group in the solvent's molecule. The diamond treated in the solvent containing the OH, C–O–C, C=O, or CHO group contained the C_6H_5COO group on the surface. On the other hand, the diamond treated in acetic acid, which contains the COOH group, had the CH_3COO group. From the experimental data shown in Table 5.2, we presumed that the COOH group peculiarly reacts with a diamond surface when benzoyl peroxide was used as radical initiator. Therefore, we attempted to react various aliphatic carboxylic acids (HCOOH, $CH_3(CH_2)_nCOOH$ $(0<n<16)$) with a diamond surface using benzoyl peroxide.

5.3.6. Chemical reaction of aliphatic carboxylic acid with a diamond surface

The IR spectra for the diamond powders reacted with aliphatic carboxylic acids

[HCOOH, $CH_3(CH_2)_nCOOH$ ($0<n<16$)] are shown in Figure 5.6. In the case of formic acid (HCOOH), the intensity of the peaks assigned to the C–H bond at 2800-3000 cm^{-1} slightly decreased and no peaks appeared at 500-2000 cm^{-1}. Based on the chemical reaction of acetic acid shown in Eqs. (2)–(5), we can expect the following chemical reaction for formic acid:

$C_6H_5\text{-}COO\text{-}OOC\text{-}C_6H_5 \rightarrow C_6H_5\text{-}COO\cdot + \cdot OOC\text{-}C_6H_5$ (15)

$C_6H_5\text{-}COO\cdot + \text{(diamond)-H} \rightarrow C_6H_5\text{-}COOH + \text{(diamond)}\cdot$ (16)

$C_6H_5\text{-}COO\cdot + HCOOH \rightarrow C_6H_5\text{-}COOH + HCOO\cdot$ (17)

$\text{(diamond)}\cdot + HCOO\cdot \rightarrow \text{(diamond)-OOC-H}$ (18)

If the chemical reactions of Eqs. (15)-(18) proceeded on the diamond surface, the peak assigned to the C=O bond should appear in the IR spectrum. However, no C=O bond peak was seen in the observed IR spectrum. Therefore, it should be considered that the chemical reactions of Eqs. (15)-(18) would not proceed when formic acid was used as the solvent for the reaction process. The amount of decrement of the intensity peaks at 2800-3000 cm^{-1} which are assigned to the C–H bond, of the diamond powder treated in formic acid is slight, and is smaller than that of the diamond treated in acetic acid. Therefore, most of the generated radical species derived from benzoyl peroxide should react with not the diamond surface but with formic acid, which was the solvent for the reaction process.

In the case of $CH_3(CH_2)_nCOOH$ ($0<n<16$), several peaks in the IR spectra are seen at the lower wave number region (500-2000 cm^{-1}). Moreover, the peak intensity at 2800-3000 cm^{-1} increased with an increased number of C–H bonds in the carboxylic acid. Based on the experimental results and the expansion of the chemical reaction scheme of Eqs. (2)–(5), the presumed schemes of the chemical reaction of $CH_3(CH_2)_nCOOH$ ($0<n<16$) with the diamond surface are as follows:

$C_6H_5\text{-}COO\text{-}OOC\text{-}C_6H_5 \rightarrow C_6H_5\text{-}COO\cdot + \cdot OOC\text{-}C_6H_5$ (19)

$C_6H_5\text{-}COO\cdot + (\text{diamond})\text{-}H \rightarrow C_6H_5\text{-}COOH + (\text{diamond})\cdot$ (20)

$C_6H_5\text{-}COO\cdot + CH_3(CH_2)_nCOOH \rightarrow C_6H_5\text{-}COOH + CH_3(CH_2)_nCOO\cdot$ (21)

$(\text{diamond})\cdot + CH_3(CH_2)_nCOO\cdot \rightarrow (\text{diamond})\text{-}OOC\text{-}(CH_2)_nCH_3$ (22)

The experimental results showing that the intensity peaks at 2800-3000 cm^{-1} increased with increasing the n values and that the peak assigned to the C=O bond appeared at *ca.* 1720 cm^{-1} are consistent with the chemical reaction scheme of Eqs. (19)–(22).

The C=O peak positions of all the diamond powders treated with $CH_3(CH_2)_nCOOH$ ($0<n<16$) were higher than that of the diamond powder treated with no carboxylic acid. Because in general the peak position of the C=O bond in (aliphaticgroup)–COO–(aliphatic group), 1735-1755 cm^{-1}, is higher than that of the C=O bond in (aromatic group)–COO–(aliphatic group), 1710-1730 cm^{-1}, the experimental results regarding the peak position of the C=O bond supports the chemical reaction process shown in Eqs. (19)–(22).

Several peaks are seen in the IR spectrum of the diamond not treated in carboxylic acid [Figure 5.6(b)]. The specific peaks at 3070 cm^{-1}, 1267 cm^{-1}, and 705 cm^{-1} should be assigned to the functional group derived from benzoyl peroxide. There were no peaks at 3070 cm^{-1}, 1267 cm^{-1}, and 705 cm^{-1} in the IR spectra for the diamond treated with $CH_3(CH_2)_nCOOH$ ($0<n<16$). Moreover, at a lower wavenumber region the shape for the IR spectrum of the diamond treated with $CH_3(CH_2)_nCOOH$ ($0<n<16$) was differed slightly from that of the diamond treated in toluene. Therefore, the predominant chemical reaction on the diamond surface should not be the chemical reaction scheme of Eqs. (2)–(5) but the chemical reaction scheme of Eqs. (19)–(22).

In order to quantitatively evaluate the C–H bond introduced on the diamond surface, the ratios of the area of the peaks related to the aliphatic C–H bond, $S_{\text{aliphatic C-H}}$, to the area of the peak assigned to the two-phonon absorption, $S_{\text{two-phonon}}$, are plotted in Figure 5.7. The ($S_{\text{aliphatic C-H}}/S_{\text{two-phonon}}$) value increased with increasing the numbers of carbon atoms in the alkyl group. The relationship is represented by the following equation.

$Y = 0.59\,X + 5.26$ (23)

where Y is the ($S_{\text{aliphatic C–H}}/S_{\text{two-phonon}}$) value and X is the number of the aliphatic C-H bond in the alkyl group in the $CH_3(CH_2)_nCOOH$. The y intercept in Eq. (23) is not null but 5.26. The existence of the y intercept should indicate that not all of the hydrogen atoms on the hydrogenated diamond surface are abstracted by the radical species derived from benzoyl peroxide even when no carboxylic acid has been added.

These experimental results are interesting because they demonstrate that the chemical condition of a diamond surface can be controlled. We can presume that the alkyl group introduced on the diamond surface by means of the method designed in this study possesses the same property as the alkyl group in organic compounds because the alkyl group is derived from organic compounds. Thus, our results suggest that carboxylic acid could be used to chemically modify the diamond surface, based on the techniques of organic chemistry.

5.4. Conclusion

Chemical modification of a diamond surface was performed in acetic acid using benzoyl peroxide. The diamond surface reacted in acetic acid was rather different from that reacted in other solvents. It was confirmed that the diamond surface modified with acetic acid is stable against organic solvents. The reaction rate of the chemical reaction in acetic acid was calculated based on experimental data. The condition of the diamond surface after the reaction process was discussed in terms of the classification of the oxygen-containing functional group in the solvent molecule. The reactivity of carboxylic acid [HCOOH, $CH_3(CH_2)_nCOOH$ ($0<n<16$)] was examined. Although formic acid was inactive against the diamond surface, $CH_3(CH_2)_nCOOH$ ($0<n<16$) reacted with the diamond surface according to the chemical reaction process used in this study. The chemical reaction process was observed to be very regular. Therefore, the chemical modification process used in this study constitutes an effective method for controlling the condition of a diamond's surface.

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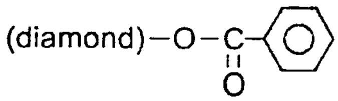
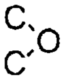
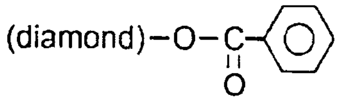
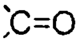
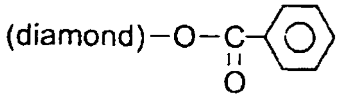
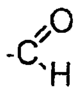
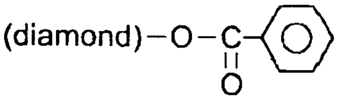
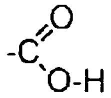
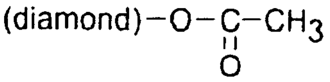
Table 5.1 Experimental conditions applied in this study.

Sample	Solvent for reaction process	Solvent for washing process
I	Acetic acid	Chloroform
II	Acetic acid	Toluene
III	Acetic acid	Water → chloroform
IV	Acetic acid	Methanol
V	Acetic acid	Chloroform → water
VI	Acetic acid	Benzene
VII	Acetic acid	Ethanol
VIII	Acetic acid	THF
IX	Toluene: acetic acid = 5 : 1 (ml)	Chloroform
X	Toluene	Acetic acid
XI	Toluene	Chloroform

Table 5.2 Diamond surface condition after the reaction process

Functional group	Solvent	Presumed functional group
-O-H	Ethanol	
	THF	
	Acetone	
	DMF benzaldehyde	
	Acetic acid	 $(\text{diamond})-O-\underset{\underset{O}{\|}}{C}-CH_3$

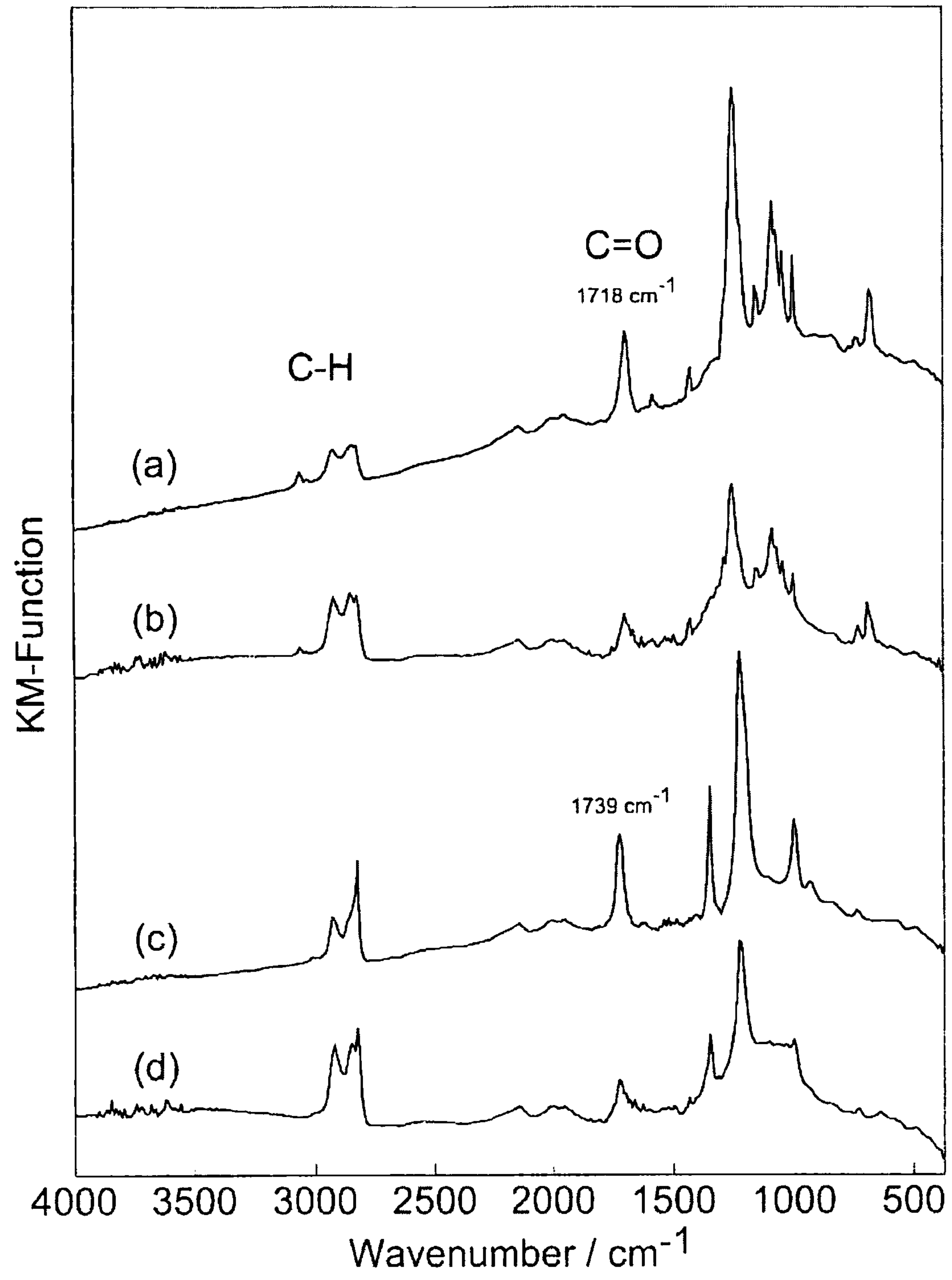


Figure 5.1 IR spectra for the diamond powders reacted with benzoyl peroxide. (a), treated in toluene (sample XI); (b), treated in toluene after the reflux in water; (c), treated in acetic acid (sample I); (d), treated in acetic acid after the reflux in water.

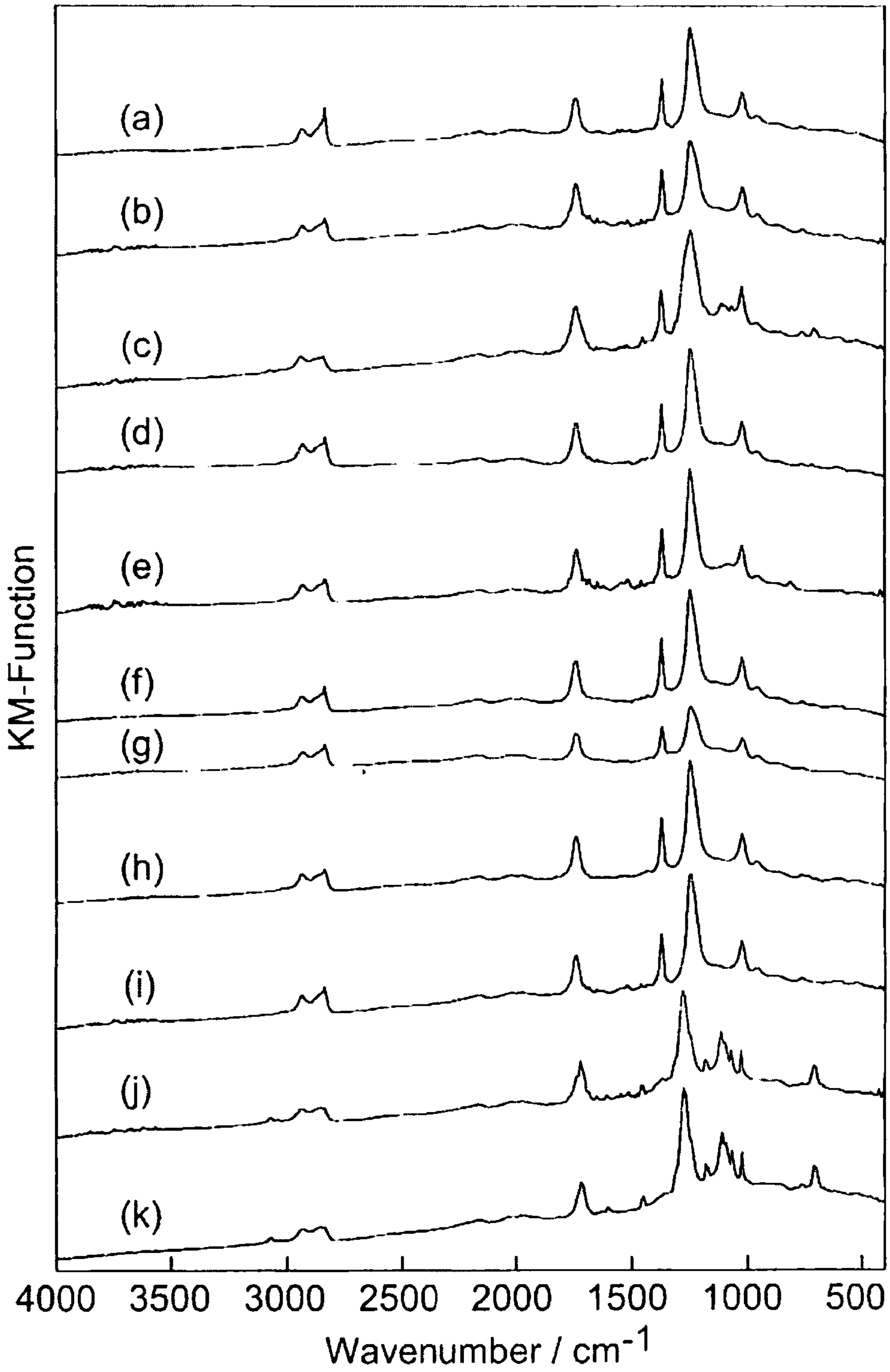


Figure 5.2 IR spectra for the diamond powders reacted with benzoyl peroxide. (a) sample I; (b) sample II; (c) sample III; (d) sample IV, (e) sample V; (f) sample VI; (g) sample VII; (h) sample VIII; (i) sample IX; (j) sample X; (k) sample XI.

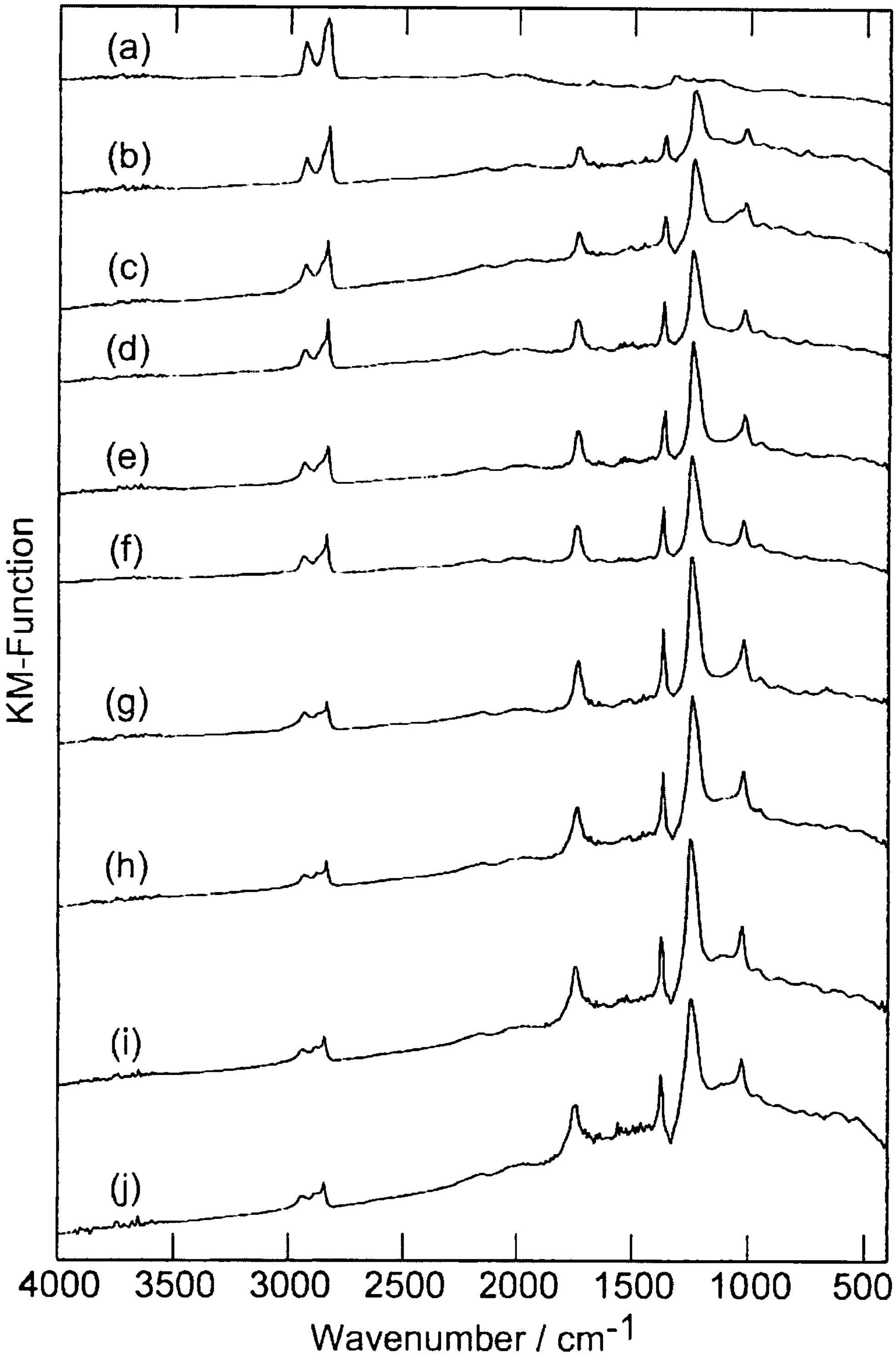


Figure 5.3 IR spectrum of the diamond powder treated with benzoyl peroxide in acetic acid. (a) Hydrogenated diamond, (b) 5 min, (c) 15 min, (d) 30 min, (e) 60 min, (f) 120 min, (g) 240 min, (h) 360 min, (i) 480 min, (j) 600 min.

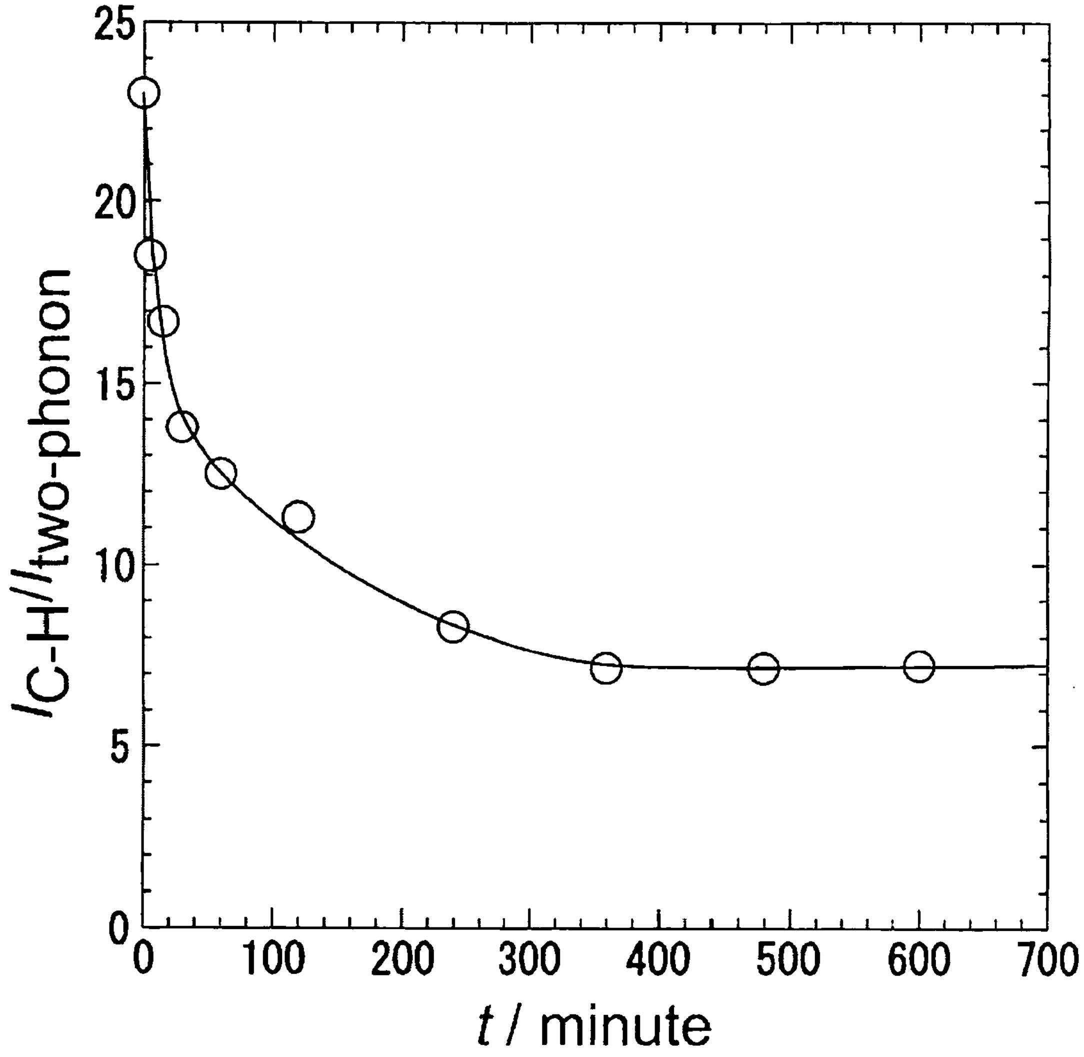


Figure 5.4 Treatment-time dependence of ($I_{C\text{–}H}/I_{two\text{-}phonon}$) value.

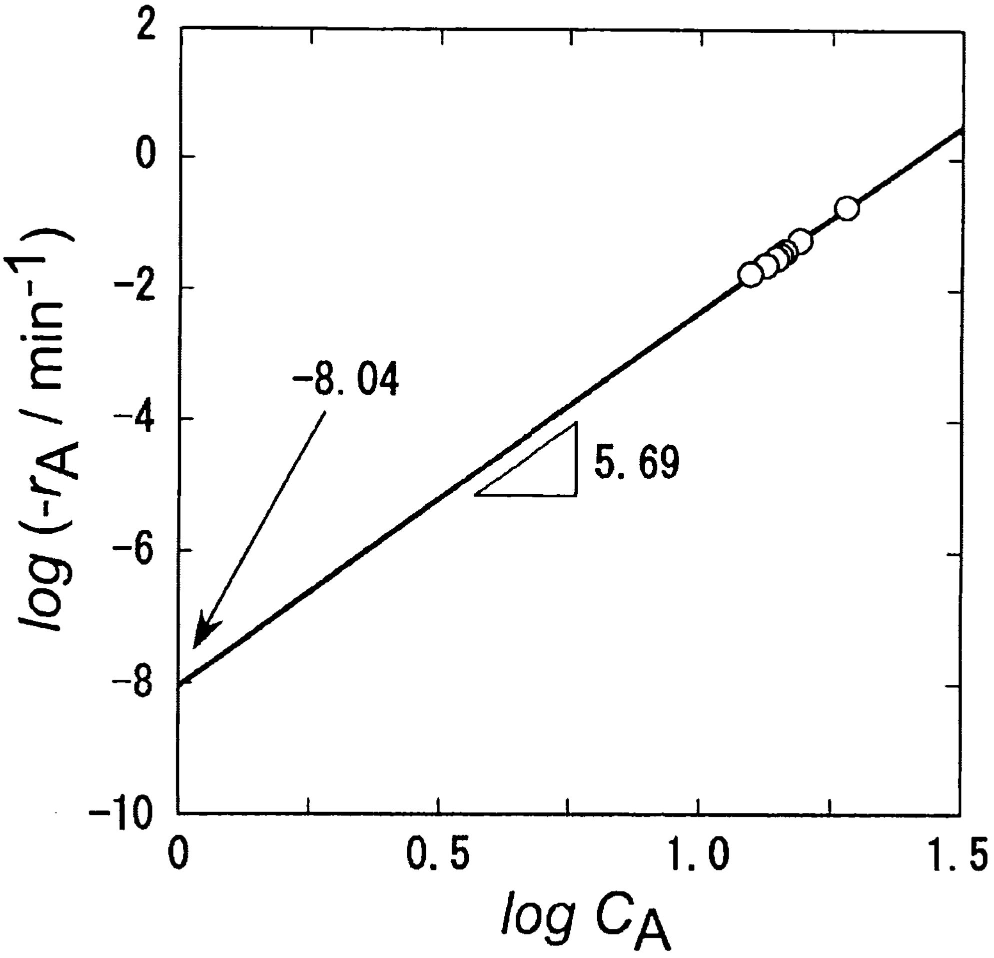


Figure 5.5 Plots of log C_A *vs.* log ($-r_A$).

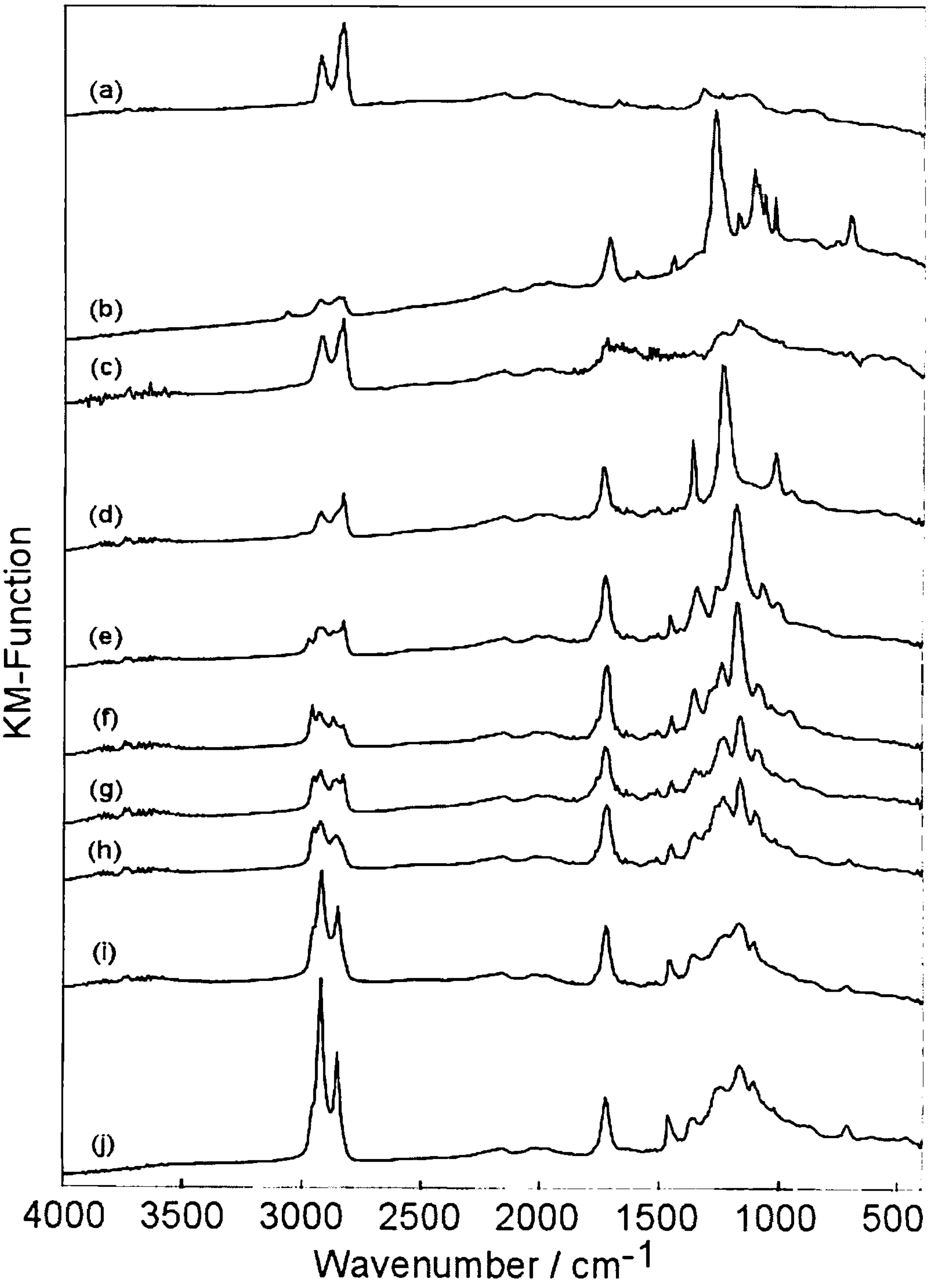


Figure 5.6 (A) IR spectra for the diamond powders. (a) Hydrogenated diamond, reacted with $CH_3(CH_2)_nCOOH$; (b) only benzoyl peroxide; (c) formic acid; (d) acetic acid (n = 0); (e) propanoic acid (n = 1); (f) butyric acid (n = 2); (g) valeric acid (n = 3); (h) hexanoic acid (n = 4); (i) lauric acid (n = 10); (j) stearic acid (n = 16).

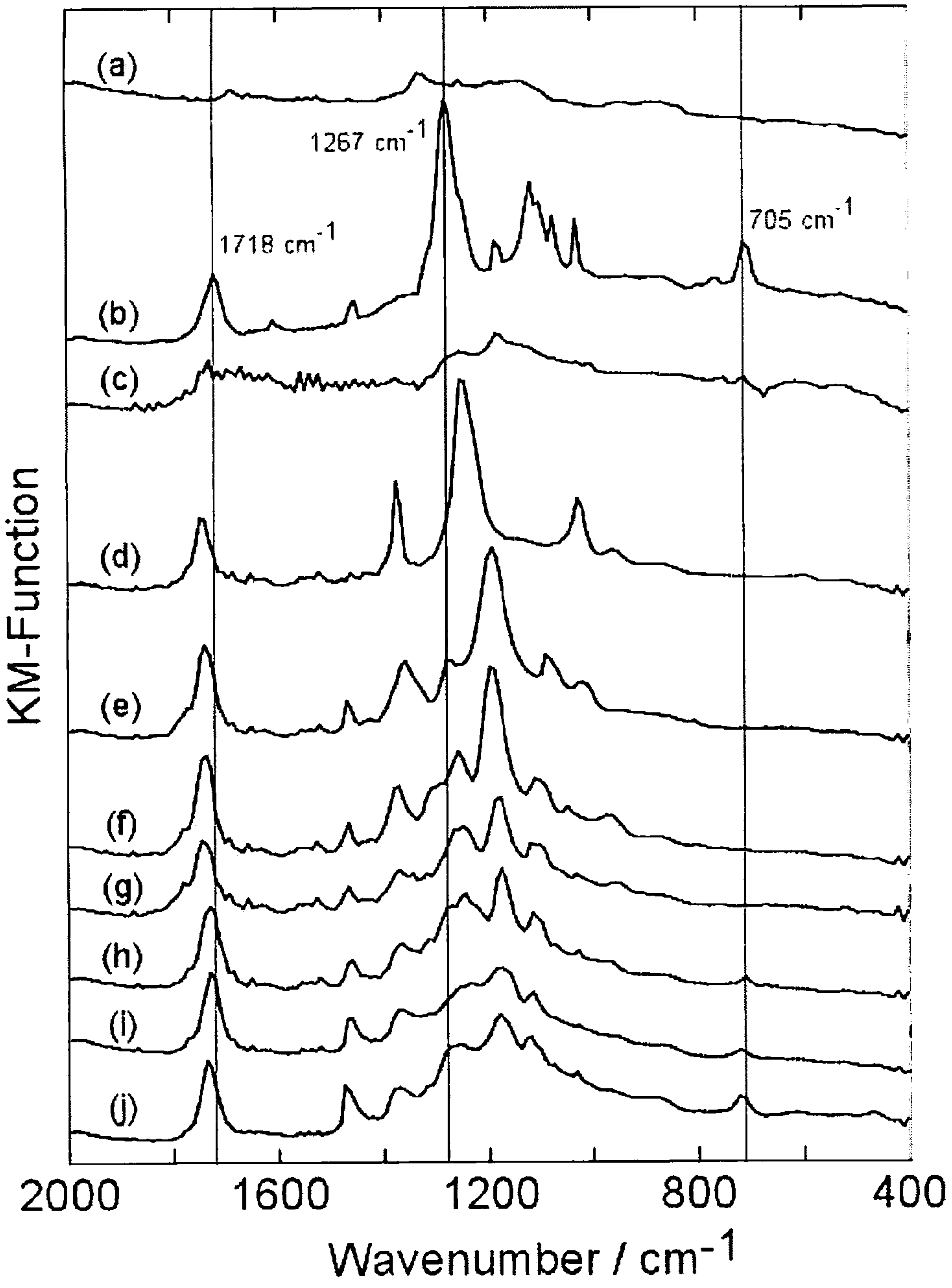


Figure 5.6 (B) IR spectra for the diamond powders. (a) Hydrogenated diamond, reacted with $CH_3(CH_2)_nCOOH$; (b) only benzoyl peroxide; (c) formic acid; (d) acetic acid (n = 0); (e) propanoic acid (n = 1); (f) butyric acid (n = 2); (g) valeric acid (n = 3); (h) hexanoic acid (n = 4); (i) lauric acid (n = 10); (j) stearic acid (n = 16).

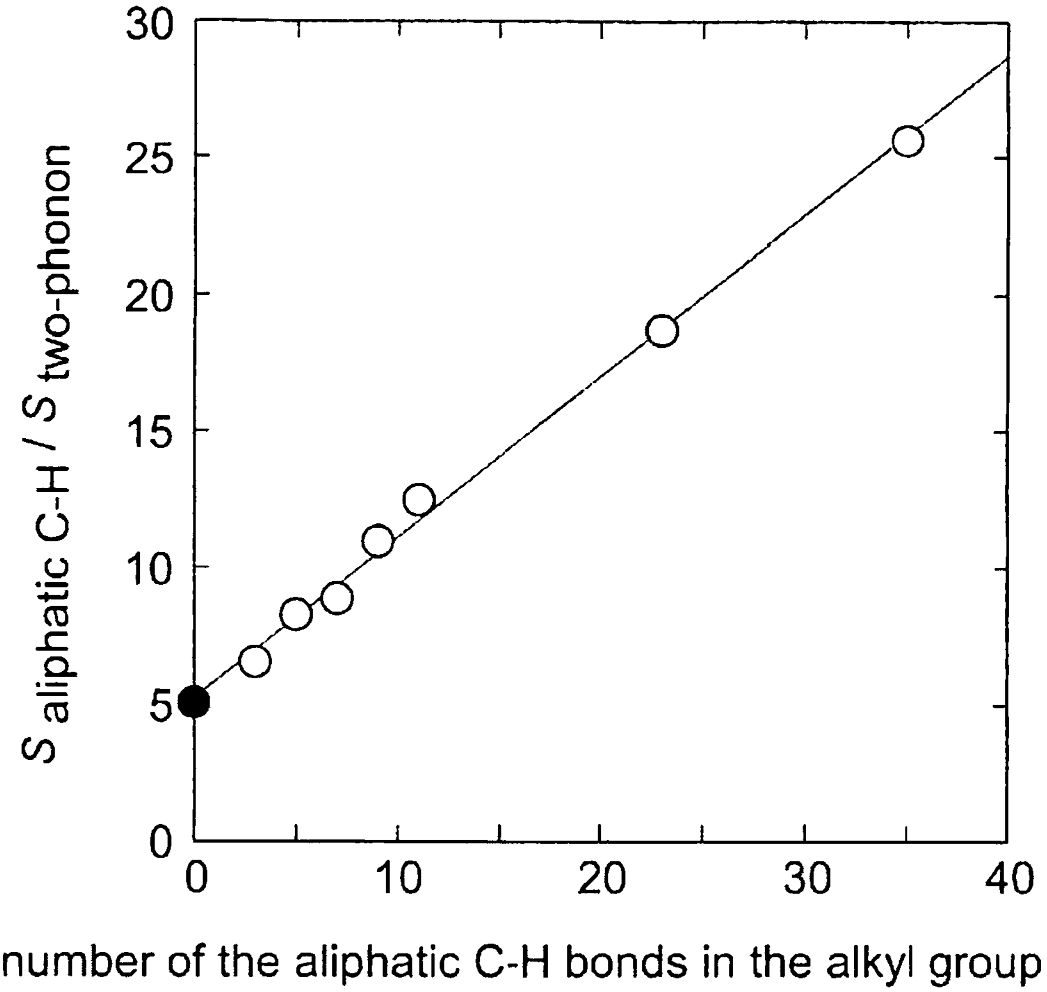


Figure 5.7 Dependence of the ($S_{\mathrm{aliphatic\ C\text{–}H}}/S_{\mathrm{two\text{-}phonon}}$) values on the number of the aliphatic C–H bond in the alkyl group. ● No addition of carboxylic acid.

Chapter 6

Preparation of HOOC-terminated diamond surface using benzoyl peroxide and dicarboxylic acid

Chapter 6

Preparation of HOOC-terminated diamond surface using benzoyl peroxide and dicarboxylic acid

6.1. Introduction

The reactivity and chemical modification of the diamond surface have been studied using various approaches [1-29]. These studies have largely focused on the interactions between diamond surfaces and functional groups, such as the thiol group[10], fluorinated compounds [11-14], and amino groups [10, 15-17]. The modification of the diamond surface with carboxylic groups or primary amine groups is particularly interesting because their reactivity is highly specific. Using a diamond surface terminated with carboxylic or primary amine groups, additional functional compounds can be immobilized on the diamond surface *via* the specific functional groups. An example of this is the immobilization of DNA on diamond surface [18, 19].

Several methods for the introduction of carboxylic or amine groups onto a diamond surface have been reported18-21. Strother *et al.*[20] and Yang *et al.*[19] reported a method for introducing organic compounds containing carboxylic or amine groups onto diamond surface. They employed ultraviolet irradiation of hydrogenated diamond surfaces covered with liquid films of the appropriate functionalized alkenes. This chemical modification method requires several steps. Ando *et al.* [21] reported a method for introducing amine groups onto Cl-terminated diamond surfaces.

When a hydrogenated diamond surface is heated in halogen gas, e.g, Cl_2 or F_2, halogenated diamond surfaces are generated [13-17, 22-24]. The reaction involves radical substitution, which is the characteristic reaction mechanism between alkane and halogen molecules. We have reported in chapter 2 and chapter 3 that organic compounds could be introduced onto the hydrogenated diamond surface *via* the analogous radical substitution reaction using benzoyl peroxide. Moreover, we confirmed that monocarboxylic acids bond to the diamond surface when the hydrogenated diamond surface is treated with monocarboxylic acids and benzoyl peroxide in chapter 5.

In this paper, we report a new method for introducing carboxylic groups onto diamond surfaces *via* a radical reaction using benzoyl peroxide and dicarboxylic acids. We attempted to generate a monolayer of organic molecules containing carboxylic groups on the diamond surface. This reaction is completed in a single step at a relatively low temperature.

6.2. Experimental

Commercial diamond powder (Tomei diamond MD500; average diameter: 500 nm) was used as the substrate. The diamond powder was treated with two kinds of acid mixtures: (HF + HNO_3, at room temperature) and (H_2SO_4 + HNO_3, at 353 K) to remove the impurities on the diamond surface. Following these acid treatments, the diamond powder was rinsed with distilled water, and then dried in a dryer. The dried diamond powder was heated in flowing H_2 or D_2 gas at 1173 K for 5 h. After this treatment, the diamond surfaces are terminated with hydrogen atoms or deuterium atoms [9]. The hydrogenated and deuterium-labeled diamond powders were used as starting materials.

The hydrogenated diamond powders (0.1 g) and the appropriate amount of benzoyl peroxide (0.1 g) were suspended in toluene (5 ml). Argon gas was bubbled through the suspension to release the oxygen molecules that inactivate the radical species derived from benzoyl peroxide. The suspension was maintained at 348 K for 120 min during this process. After the chemical reaction, the diamond powders were washed with chloroform, and then dried in a vacuum dryer. The diamond powders and diamond surfaces treated with benzoyl peroxide (BPO) will hereinafter be referred to as BPO powders and BPO surfaces, respectively.

The hydrogenated diamond powders (0.1 g), benzoyl peroxide (0.1 g) and dicarboxylic acid $HOOC\text{-}(CH_2)_n\text{-}COOH$ ($n = 2\text{-}8$) (0.5 g) were suspended in (5 ml of) toluene, ethanol, or water. Argon gas was bubbled through the suspension to remove the O_2 in the solvent, which was maintained at 348 K for 120 min during this process. After the chemical reaction, the diamond powders were thoroughly washed with water, ethanol, and chloroform, and then dried in a vacuum dryer.

To confirm that the hydrogenated diamond surfaces treated with benzoyl peroxide and dicarboxylic acids actually terminated with $HOOC\text{-}(CH_2)_n\text{-}COO\text{-}$ groups, the treated diamond powders were suspended in 1 M NaOH (*aq*) (10 ml) for 15 min at room temperature in a centrifuge tube (60 ml). The NaOH solution was subsequently removed by centrifugation, and the diamond powders were suspended in distilled water (50 ml; pH=10.8-11.3). The diamond powders were then centrifuged, and dried in a vacuum dryer.

The diamond surface was characterized by diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy (JASCO FT/IR-700). The DRIFT spectra were obtained over the range of 4000-400 cm^{-1}. For each spectrum, 256 scans were collected at a resolution of 4 cm^{-1}. The diffuse reflectance was converted into Kubelka-Munk function units.

6.3. Results and Discussion

6.3.1. Reaction of hydrogenated diamond surface with benzoyl peroxide.

Figure 6.1(a) shows the IR spectrum for the hydrogenated diamond powder. The two large peaks at 2837 cm^{-1} and 2936 cm^{-1} ascribed to the C-H bonds are similar in appearance to those previously reported [25-28]. Ando *et al.* reported that the large peak at *ca.* 2837 cm^{-1} and the smaller peak at *ca.* 2936 cm^{-1} are ascribable to the C-H symmetric and asymmetric stretching vibrations, respectively [9].

Benzoyl peroxide decomposed into organic radical species via:

$$C_6H_5\text{-}COO\text{-}OOC\text{-}C_6H_5 \rightarrow C_6H_5\text{-}COO\cdot + \cdot OOC\text{-}C_6H_5 \qquad (1)$$

Due to the low dissociation energy, the O-O bonds in benzoyl peroxide easily break, generating radical species. In the present study, experiments were performed at

348 K, which was the appropriate temperature for activation of the radical initiators.

Figure 6.1(b) shows the IR spectrum of the BPO powder. It was found that the C-H peak_intensity (2800-2950 cm^{-1}) decreased, and several peaks emerged after the reaction. We attribute the decrease in the C-H peak intensity to the abstraction of hydrogen atoms from the diamond surface by the radical species derived from benzoyl peroxide. The small peak at 3072 cm^{-1} is attributed to the stretching vibration mode of the C-H bonds of the aromatic compounds. The peaks in the 700-1450 cm^{-1} region are attributed to the ester group. The peak at 1718 cm^{-1} is attributable to the C=O group. We have previously reported that the positions of the additional peaks that appeared after the radical reaction were independent of the solvents used in the reaction [27, 28]. These results suggest that a free-radical substitution reaction occurred on the diamond surface treated with benzoyl peroxide, presumably *via* the following reaction schemes:

$$I \rightarrow R\cdot + \cdot R \qquad (2)$$

$$\text{(Diamond)-H} + R\cdot \rightarrow \text{(Diamond)}\cdot + \text{R-H} \qquad (3)$$

$$\text{(Diamond)}\cdot + R\cdot \rightarrow \text{(Diamond)-R} \qquad (4)$$

where "I" is the radical initiator, "(Diamond)-H" is hydrogenated diamond surface, and "R · " is the radical species derived from the radical initiator. In this reaction, first, the radical species derived from benzoyl peroxide abstracts the hydrogen atoms on the hydrogenated diamond surface (Eq. (3)). The resultant radical sites on the diamond surface bond to the radical species derived from benzoyl peroxide (Eq. (4)). After the treatment, the condition of the diamond surface is as follows[27]:

$$\text{(Diamond)-OOC-}C_6H_5 \; (5)$$

6.3.2. Reaction of hydrogenated diamond surface with a mixture of benzoyl peroxide and dicarboxylic acid.

Hydrogenated diamond powders ((Diamond)-H) or BPO powders ((Diamond)-OOC-C_6H_5) were suspended in toluene (5 ml) containing dicarboxylic acid (0.5 g) without benzoyl peroxide at 348 K for 120 min. After the reaction, the diamond surfaces were washed with ethanol, distilled water, and chloroform. Any reaction between the carboxylic acid and hydrogenated or BPO diamond surface would have altered the IR spectra for the diamond powders. However, the IR spectra of the diamond powders were virtually unaffected by the reaction. This confirmed that dicarboxylic acid does not react directly with hydrogenated or BPO diamond surface.

The IR spectra for hydrogenated diamond powders treated in toluene containing both benzoyl peroxide and dicarboxylic acid are shown in Figure 6.2. The fact that several characteristic peaks (707, 1111, and 1275 cm^{-1}) of the BPO surface were not observed suggested that the radical species derived from benzoyl peroxide (•OCO-C_6H_5) could not bond to the diamond surface. However, the presence of an aromatic C-H peak at 3072 cm^{-1}, though low in intensity, indicates that a small number of (-OCO-C_6H_5) radicals presumably bonded to the diamond surface (Figure 6.2B). It is believed that dicarboxylic acid prevented benzoyl peroxide-derived radical species from bonding to the diamond surface. The peaks that appeared at 1735 cm^{-1} were assigned to the C=O bond. Among the chemical compounds used in this experiment, the benzoyl peroxide-derived radical species, benzoyl peroxide, and dicarboxylic acid all contain C=O bonds. Since benzoyl peroxide and the radical species derived from it are not present on the diamond surfaces, the C=O peaks at 1735 cm^{-1} are most likely ascribable to chemical species derived from dicarboxylic acid. The intensities and shapes of the C-H peaks (2800-2960 cm^{-1}) depended on the type of dicarboxylic acid (Figure 2B). Thus, we can conclude that dicarboxylic acid-derived chemical species can chemically bond with the diamond surface.

In chapter 5, we succeeded in introducing monocarboxylic acid-derived chemical species on the diamond surface by treating the hydrogenated diamond surface with a mixture of benzoyl peroxide and monocarboxylic acid. In that particular reaction, we presumed that the hydrogen atom of the "–COOH" group in monocarboxylic acid was abstracted by the radical species derived from benzoyl peroxide, generating the "CH_3-$(CH_2)_n$-COO•" group, which bonded to the radical site generated on the diamond surface. It is believed that dicarboxylic molecules also produce "-COO•" groups. Thus, the reaction is believed to involve the following steps:

(Diamond)-H + C_6H_5COO• → (Diamond)• + C_6H_5COOH (6)

HOOC-$(CH_2)_n$-COOH + C_6H_5COO• → HOOC-$(CH_2)_n$-COO• + C_6H_5COOH (7)

(Diamond)• + HOOC-$(CH_2)_n$-COO• → (Diamond)-OOC-$(CH_2)_n$-COOH (8)

(Diamond) • + C_6H_5COO• → (Diamond)-OOC-C_6H_5 (9)

Thermal decomposition of benzoyl peroxide yields C_6H_5-COO• (Eq. (1)), which abstracts hydrogen atoms from the hydrogenated diamond surface, generating radical sites on the diamond surface (Eq. (6)). C_6H_5-COO• also abstracts hydrogen atoms from the –COOH groups in dicarboxylic acid molecules (Eq. (7)). The resultant radical species bond to the radical sites on the diamond surface (Eq. (8) and Eq. (9)).

The chemical state of the diamond surface is determined by the relative proportion of diamond surface modified with (-OOC-$(CH_2)_n$-COOH) versus (-OOC-C_6H_5). This ratio may depend on the reaction conditions. With toluene as the solvent, a peak ascribed to the aromatic C-H bond appeared at 3072 cm^{-1} (Figure 6.2B), which indicates that the chemical reaction in Eq. (9) proceeded to a slight extent. The fact that the intensities of the C-H peaks (2780-3010 cm^{-1}) increased with the dicarboxylic acid chain length indicates that the chemical reaction in Eq. (8) predominated. The C-H peaks (2780-3010 cm^{-1}) are ascribed to the C-H bonds of not only the hydrogenated diamond surface, but also the -$(CH_2)_n$- groups in the dicarboxylic acid molecules. In order to introduce an appreciable number of –COOH groups on the diamond surface, it is necessary that the reactions in Eqs. (6), (7), and (8) be accelerated, while the reaction in Eq. (9) be suppressed.

We attempted to introduce an appreciable number of –COOH groups on the diamond surface by changing the solvent because the reaction rate and selectivity are heavily influenced by the solvent type. Figure 6.3 shows the IR spectra for the hydrogenated diamond powder treated with both benzoyl peroxide and various dicarboxylic acids in ethanol or water. The C=O peak positions in the case of ethanol and water were identical to those in toluene. However, the peak at 3072 cm^{-1} assigned to the aromatic C-H bond did not appear (Figure 3). The C-H peak intensities increased in the order of molecular weight of the dicarboxlic acids. These results show that the radical reactions proceed in water or ethanol, and the organic species derived from the dicarboxylic acids are introduced onto the diamond surface. We are led to conclude that the introduction of the –$OOCC_6H_5$ groups onto the diamond surface is suppressed because the peaks assigned to the aromatic C-H groups are not observed in the IR spectra.

Solvent type affects the hydrogen abstraction reaction of the hydrogenated diamond surface shown in Eq. (6). The radical species derived from benzoyl peroxide abstract hydrogen atoms from not only the hydrogenated diamond surface but also the solvent molecules. The extent to which the hydrogen abstraction reaction proceeds depends on the solvent type. If the solvent used allows the hydrogen atoms in the molecules to be easily abstracted by the radical species, the reaction in Eq. (6) is suppressed. The relationship between the hydrogen abstraction reaction and the solvents (ethanol and toluene) was investigated based on the IR spectra of the reaction between hydrogenated diamond surface and benzoyl peroxide in chapter 2 and 3. In the reaction between hydrogenated diamond surface and benzoyl peroxide, the C-H peak intensities reflect the amount of C-H bonds on the hydrogenated diamond surface because the surface species ($-OOCC_6H_5$) have no aliphatic C-H bonds. Indeed, the radical species derived from a solvent like toluene may bond to the diamond surface to a slight extent, as in the case of acetonitrile-derived radical species [28]. However, in previous research on lauroyl peroxide, which generates the radical species ($C_{11}H_{23}$-COO•) as a radical initiator, the aromatic C-H peak was not observed [29]. Thus, the bonding of toluene-derived radical species to the diamond surface was neglected in this reaction [29]. To quantify the amount of hydrogen on the diamond surface, we normalized the area under the C-H peaks (2780-3010 cm^{-1}) in the IR spectra. The two-phonon peak at 2157 cm^{-1} was used as a reference [9, 25-28]. The area of the C-H peaks (2780-3010 cm^{-1}) was divided by the area of the two-phonon absorption peaks (2100-2230 cm^{-1}); the ratio was denoted by $S_{C\text{-}H}$. A low $S_{C\text{-}H}$ value means that a number of hydrogen atoms were abstracted from the diamond surface. Table 6.1 shows the $S_{C\text{-}H}$ values for samples treated in toluene, ethanol, or water. It is found that the $S_{C\text{-}H}$ value for the sample treated in water is the same as that treated in toluene, and lower than that treated in ethanol. Thus, the rate of the hydrogen abstraction reaction (Eq. (6)) is larger in water than in ethanol. No aromatic C-H peaks were observed with water as the solvent. This suggests that, in the presence of dicarboxylic acids, fewer $-OOC-C_6H_5$ groups were introduced on the diamond surface treated in water than on that treated in toluene. Given these observations, of the solvents used in the present study, water is the appropriate solvent for fixation of dicarboxylic acid-derived chemical species on the diamond surface.

6.3.3. Reaction of deuterium-labeled diamond surface with benzoyl peroxide and dicarboxylic acid.

Figure 6.4 shows the IR spectra for deuterium-labeled diamond powders treated in water containing benzoyl peroxide and a dicarboxylic acid. The peak at 2120 cm^{-1} is assigned to the C-D bond [9]. After the reaction, the C-D peak intensities decreased, and C=O peaks and C-H peaks appeared at 1735 cm^{-1} and

2800-2960 cm^{-1}, respectively. It is believed that the C-H peaks are assignable to the aliphatic C-H bond of dicarboxylic acids. Deuterium and hydrogen atoms on the diamond surface were abstracted by benzoyl peroxide-derived radical species, following which dicarboxylic acid-derived chemical species were introduced onto the diamond surface. This reveals that the reaction in Eq. (8) actually proceeded.

The deuterium atoms on the diamond surface were not completely abstracted. IR spectrum for BPO powder (Figure 6.1(b)) exhibits C-H peaks. The C-H peak intensity was the same before and after the BPO powder was treated with benzoyl peroxide. The hydrogen/deuterium abstraction reactions in Eq. (6) were suppressed as the amount of organic species introduced onto the diamond surface was increased, presumably as a result of steric hindrance.

6.3.4. The stability of the surface species.

Experiments were performed to evaluate the stability of the dicarboxylic acid-modified surface. The modified diamond powders were suspended in 1 M NaOH (*aq*) at room temperature. The diamond powders were then washed with distilled water until the wash water was neutral. Figure 6.5 shows the IR spectra for the modified diamond powder treated with NaOH (*aq*) for 1 h. The peak intensities of the C=O and C-H bonds decreased, and the peak intensity of the O-H bond in the region of 3200-3600 cm^{-1} increased. It is thought that the ester bonds between the diamond surface and carboxylic acids were hydrolyzed by NaOH (*aq*). However, in the case of dicarboxylic acids (n = 4-8), the C=O peaks were clearly observed. To quantify the degree of hydrolysis, we normalized the area under the C-H (2780-3010 cm^{-1}) and C=O (1735 cm^{-1}) peaks in the obtained IR spectra. The areas under the C-H and C=O peaks were divided by the area of the two-phonon peaks (2100-2230 cm^{-1}); these ratios are denoted by $S_{C\text{-}H}$ and $S_{C=O}$, respectively. Although $S_{C\text{-}H}$ and $S_{C=O}$ do not directly reflect the amount of surface species, they give an indication of the relative decrease in surface species. A decrease in $S_{C\text{-}H}$ and $S_{C=O}$ suggests that surface species have been hydrolyzed. Table 6.2 shows the $S_{C\text{-}H}$ and $S_{C=O}$ values before and after hydrolysis. $S_{C\text{-}H}$ and

$S_{C=O}$ both decreased as a result of the reaction. However, for reasons that remain unclear, the decrease in $S_{C\text{-}H}$ was significantly less than that in $S_{C=O}$. The stabilities of the surface species are expected to increase with the chain length of dicarboxylic acids. Longer molecules, such as sebacic acid (n = 8), would sterically hinder NaOH from attacking the ester bonds between the diamond surface and dicarboxylic acids, while shorter molecules, such as succinic acid (n = 2), would easily be attacked. IR spectra and $S_{C\text{-}H}$ data (Table 6.1) reveal that all the surface species are relatively stable except for succinic acid (n = 2).

6.3.5. Chemical state of hydrogenated diamond surface treated with benzoyl peroxide and dicarboxylic acids.

We expect the diamond surface to terminate mainly in $HOOC\text{-}(CH_2)_n\text{-}COO^-$ groups. However, the OH peaks of carboxylic groups were not observed in the IR spectra. Perhaps both the –COOH groups in dicarboxylic acids react with the diamond surface. The dicarboxylic acids would thus form a bridge bond between radical sites on the diamond surface. This reaction may be sterically unlikely, however, it may occur in the case of longer chain molecules to maximize flexibility. We investigated and discussed the evidence of free carboxylic acid groups, comparing existing data on monocarboxylic acids [29] with our results for dicarboxylic acids. The treatment conditions for monocarboxylic acids were the same as those for dicarboxylic acids expect for the following: benzoyl peroxide (0.05 g) and monocarboxylic acid [$CH_3(CH_2)_nCOOH$ ($0<n<16$)] were suspended in toluene (5 ml). In the case of $CH_3(CH_2)_nCOOH$ ($0<n<4$), $CH_3(CH_2)_nCOOH$ ($0<n<4$) itself was used as the solvent for the chemical reaction process[29].

Evidence for $HOOC\text{-}(CH_2)_n\text{-}COO\cdot$ groups on the diamond surface was sought through the neutralization reaction between free carboxylic groups and NaOH. Figure 6.6 shows the IR spectra for the diamond powder treated with dicarboxylic or monocarboxylic acids [butyric (n = 3) and hexanoic (n = 5) acid]. In the case of dicarboxylic acids (n = 4, 6, 8), peaks appeared at 1735 cm^{-1} and 1578 cm^{-1}. Figure 6.7 shows the IR spectra for dicarboxylic acid,

$NaOOC\text{-}(CH_2)_n\text{-}COONa$, ($n = 6$) and NaOH. The C=O (-COOH) peak appeared at 1697 cm^{-1}, and the C=O (-COONa) peak appeared at 1565 cm^{-1} (Figure 6.7(a), (b)). Thus, the peaks that appeared in the IR spectra for diamond powders at 1578 cm^{-1} are presumably assignable to the C=O bond of the –COONa groups. A trace amount of NaOH may be left over on the diamond surface after the neutralization reaction because it is difficult to determine the accurate neutralization points between free carboxylic groups on diamond surface and NaOH. However, because NaOH shows large peaks at 1457 cm^{-1} in the IR spectrum, the peaks at 1578 cm^{-1} are not ascribed to NaOH. Thus, the neutralization reaction between NaOH and the –COOH groups on the diamond surface is believed to have occurred. In the case of monocarboxylic acids (n = 3, 5), the C=O peak at 1565 cm^{-1} was observed neither before nor after the reaction because free carboxylic groups were absent on the diamond surface (Figure 6(e)). These results support the presence of (Diamond)-$OOC\text{-}(CH_2)_n\text{-}COONa$ type bonding on the diamond surface. Neutralization of the diamond surface treated with succinic acid (n = 2) was unsuccessful. The ester bonds between the diamond surface and succinic acid (n = 2) would easily be hydrolyzed by nucleophilic reagents. Because succinic acid (n = 2) molecules are shorter compared to other dicarboxylic acids, the ester bonds would easily be attacked by nucleophilic reagents.

Table 6.3 shows the $S_{C=O}$ values for monocarboxylic acid (n = 0-16). We note that these values (4.0-7.0) are lower compared to the $S_{C=O}$ values for dicarboxylic acids before treatment (16.0-20.0) tabulated in Table 6.2. It was previously reported that the molar amount of monocarboxylic acids introduced onto the diamond surface per unit area was approximately constant [29]. Thus, the number of sites that carboxylic acids bond to on the diamond surface would be approximately constant per unit area [29]. In view of all this, the lower $S_{C=O}$ values for monocarboxylic acids as compared to those for dicarboxylic acids presumably result from the introduction of dicarboxylic acids onto the diamond surface with one ester bond. Based on these results, we conclude that $HOOC\text{-}(CH_2)_n\text{-}COO\text{-}$ groups were introduced onto the diamond surface.

6.4. Conclusions

A hydrogenated diamond surface was treated in a solvent containing benzoyl peroxide and dicarboxylic acid. After the reaction, a C=O peak appeared, and the shape of the C-H peak depended on the dicarboxylic acid type. When deuterium-labeled diamond powder was treated in the same manner, aliphatic C-H peaks were observed. The C-H peak intensities increased with the molecular weight of the dicarboxylic acids. This increase is caused by dicarboxylic acid-derived species bonding to the diamond surface. The surface species were influenced by the solvents. To introduce $HOOC\text{-}(CH_2)_n\text{-}COO\text{-}$ groups onto the diamond surface at high density, $C_6H_5\text{-}COO\text{-}$ bonding to diamond surface had to be suppressed. Peaks assigned to aromatic C-H bonds were observed using toluene as the solvent for the reaction, while no such peaks were observed using ethanol or water as the solvent for the reaction. The hydrogen abstraction reaction proceeded faster in water than in ethanol. Thus, of the solvents examined, water was the most suitable for introducing $HOOC\text{-}(CH_2)_n\text{-}OCO\text{-}$ groups on the diamond surface. The surface species were relatively stable except for succinic acid ($n = 2$) in NaOH (*aq*). When the surface species were neutralized by NaOH (*aq*), clearly visible peaks assigned to the C=O bond of –COONa groups emerged at 1578 cm^{-1}, which indicated the presence of carboxylic groups on the treated diamond surface. In the case of succinic acid ($n = 2$), the surface species were easily hydrolyzed because of the short length of the molecules. In conclusion, $HOOC\text{-}(CH_2)_n\text{-}COO\text{-}$ groups were introduced onto the diamond surface *via* the reaction of the hydrogenated diamond surface with benzoyl peroxide and dicarboxylic acid through a single step.

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Table 6.1 $S_{C\text{-}H}$ values pertaining to the IR spectra for diamond powders treated in various solvents.

	Before treatment	Toluene	Ethanol	water
$S_{C\text{-}H}$	18	4.8	10.2	5.0

Table 6.2 $S_{C\text{-}H}$ and $S_{C=O}$ values pertaining to the IR spectra for dicarboxylic acid-modified diamond powder before and after treatment with NaOH (*aq*).

Dicarboxylic acid	$S_{C\text{-}H}$ (before)	$S_{C\text{-}H}$ (after)	$S_{C=O}$ (before)	$S_{C=O}$ (after)
Succinic acid ($n = 2$)	8.4	7.9	16.1	4.1
Adipic acid ($n = 4$)	9.9	7.8	19.3	5.8
Suberic acid ($n = 6$)	12.7	9.6	19.8	6.6
Sebacic acid ($n = 8$)	14.0	11.1	16.6	7.2

Table 6.3 $S_{C=O}$ values for the diamond powder treated with monocarboxylic acid.

Monocarbosylic acid	$S_{C=O}$
Acetic acid ($n = 1$)	4.0
Propanoic acid ($n = 2$)	6.1
Butyric acid ($n = 3$)	6.3
Hexanoic acid ($n = 5$)	6.3
Lauric acid ($n = 10$)	5.4
Stearic acid ($n = 16$)	5.7

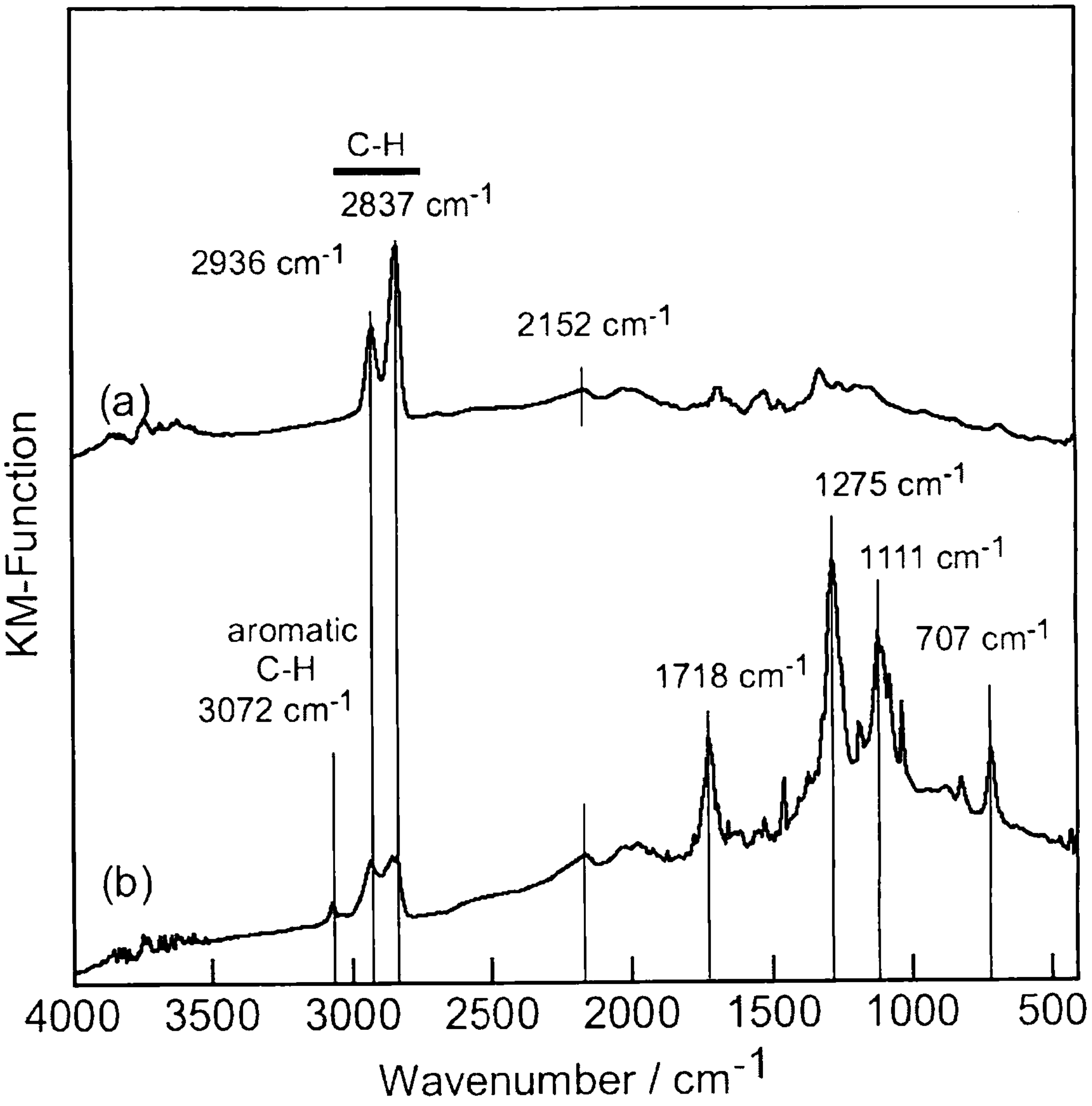

Figure 6.1 IR spectra for diamond powders: (a) hydrogenated diamond powder, (b) hydrogenated diamond powder treated with benzoyl peroxide.

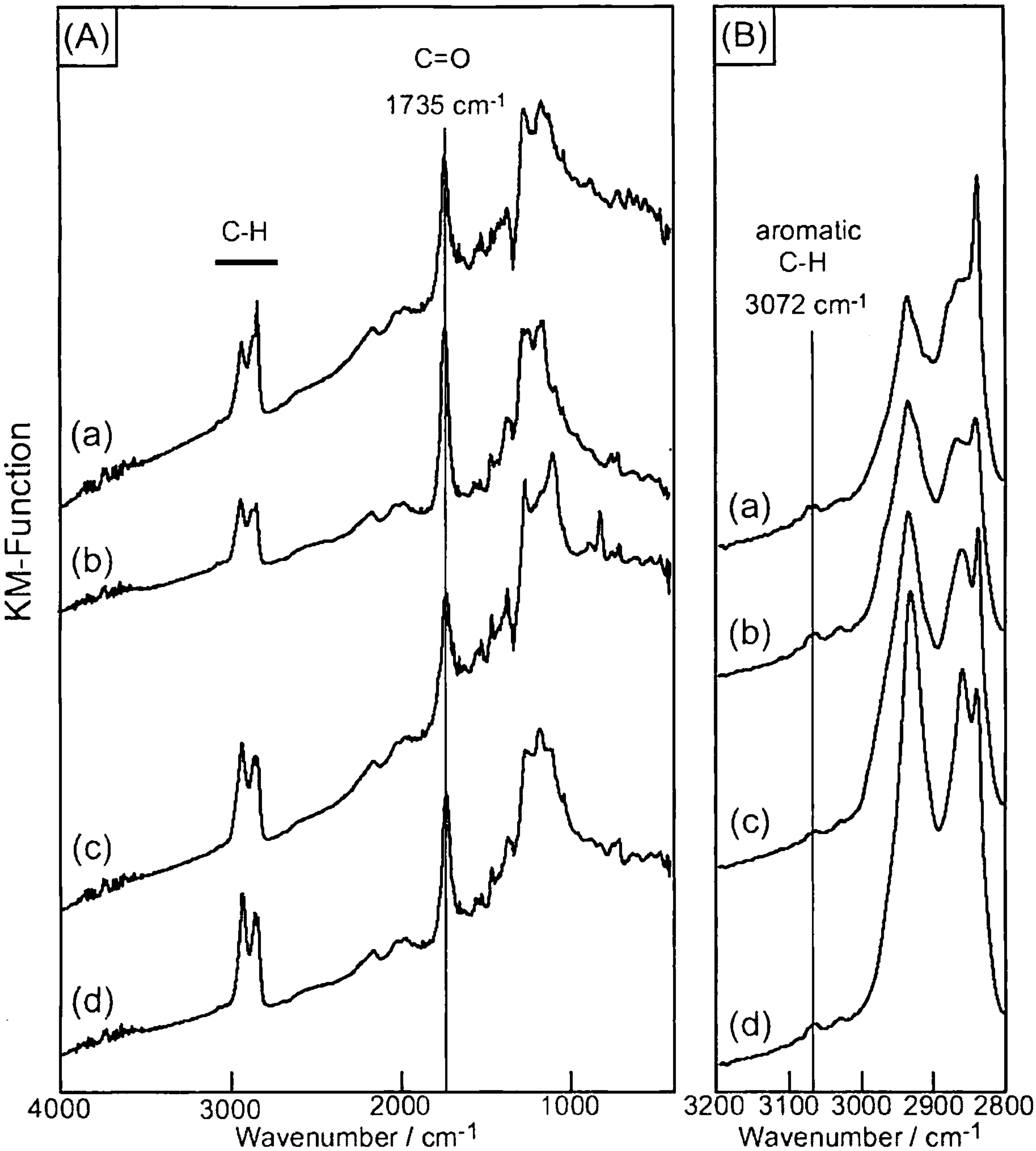

Figure 6.2 IR spectra for hydrogenated diamond powders treated with benzoyl peroxide and dicarboxylic acids in toluene: (A) wavenumber: 400-4000 cm^{-1}, (B) wavenumber: 3200-2800 cm^{-1}, (a) succinic acid (n = 2), (b) adipic acid (n = 4), (c) suberic acid (n = 6), (d) sebacic acid (n = 8).

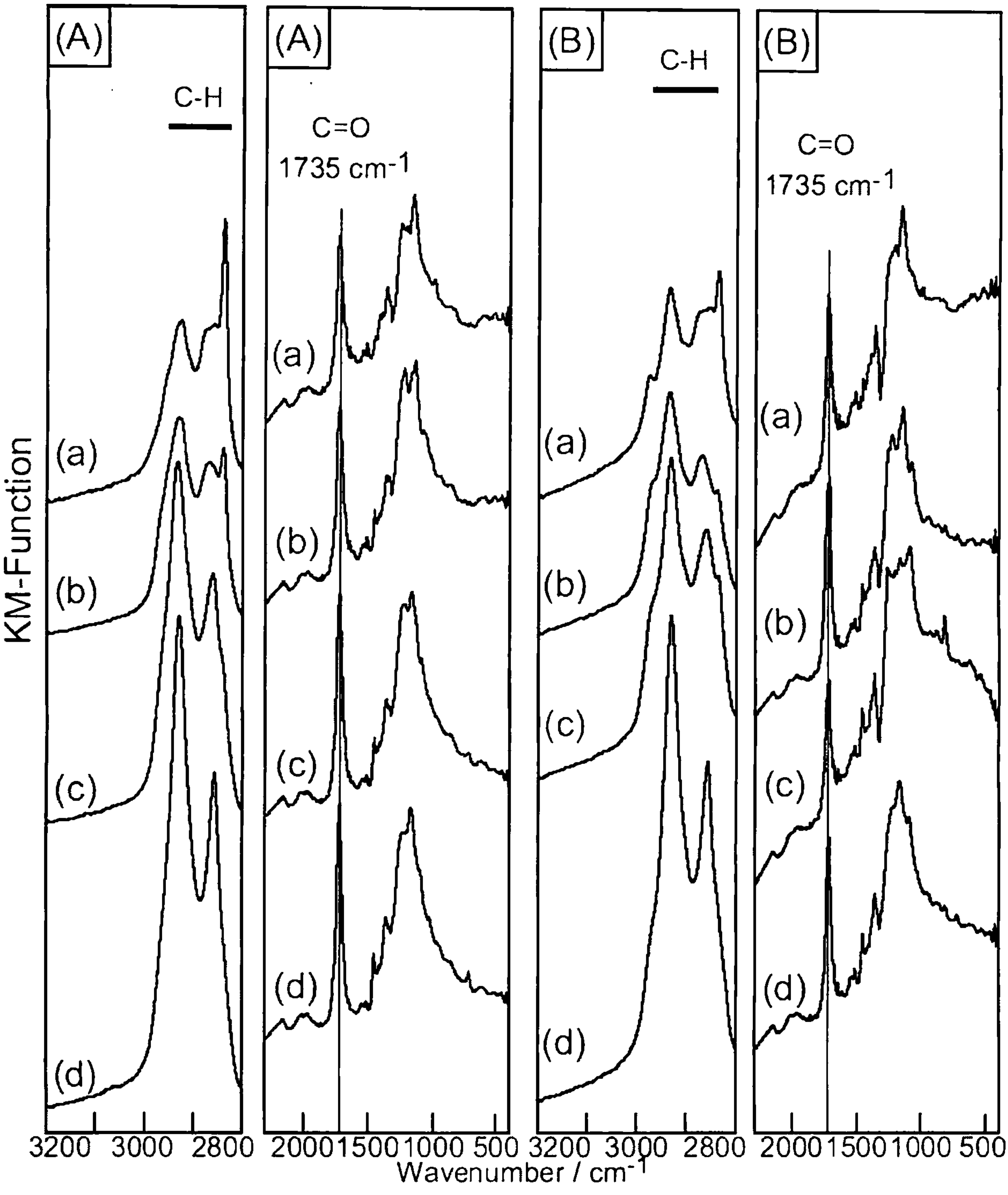

Figure 6.3 IR spectra for hydrogenated diamond powders treated with benzoyl peroxide and dicarboxylic acid: (A) in water, (B) in ethanol, (a) succinic acid ($n = 2$), (b) adipic acid ($n = 4$), (c) suberic acid ($n = 6$), (d) sebacic acid ($n = 8$).

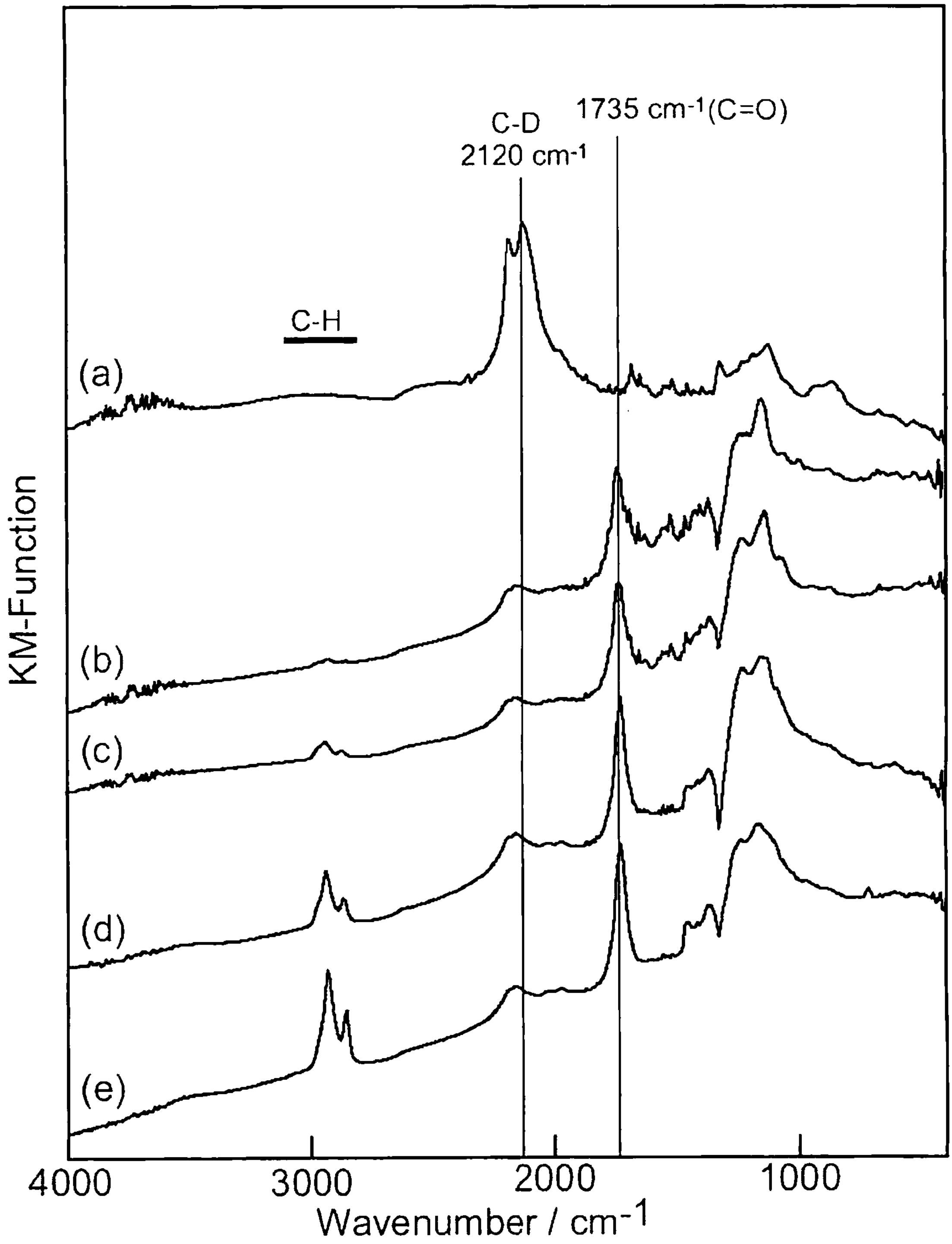

Figure 6.4 IR spectra for deuterium-labeled diamond powders treated with benzoyl peroxide and dicarboxylic acids in water: (A) wavenumber: 400-4000 cm^{-1}, (B) wavenumber: 3200-2800 cm^{-1}, (a) D_2 diamond, (b) succinic acid (n = 2), (c) adipic acid (n = 4), (d) suberic acid (n = 6), (e) sebacic acid (n = 8).

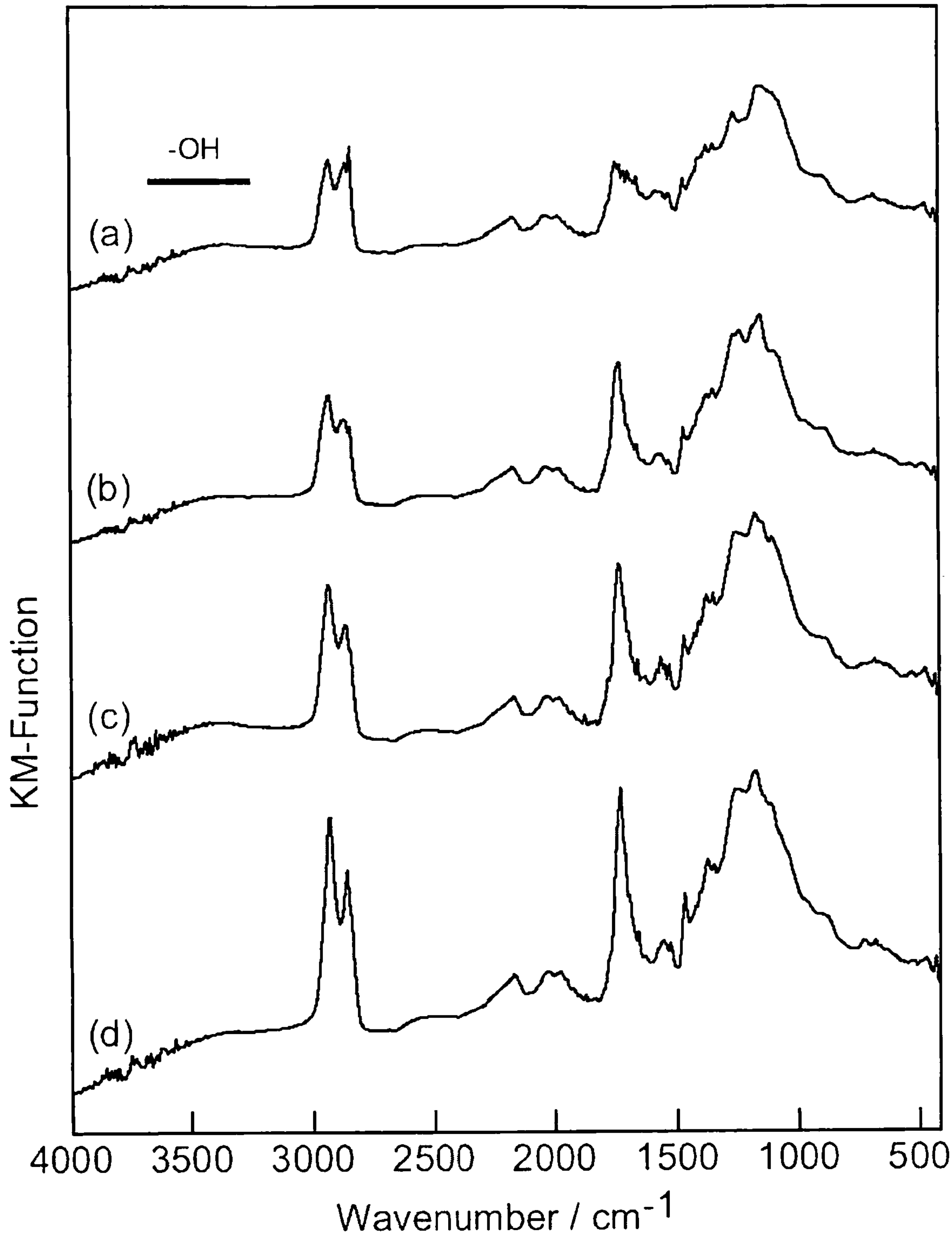

Figure 6.5 IR spectra for dicarboxylic acid-modified diamond powder after being treated in NaOH (*aq*) for 1 h: (a) succinic acid (n = 2), (b) adipic acid (n = 4), (c) suberic acid (n = 6), (d) sebacic acid (n = 8).

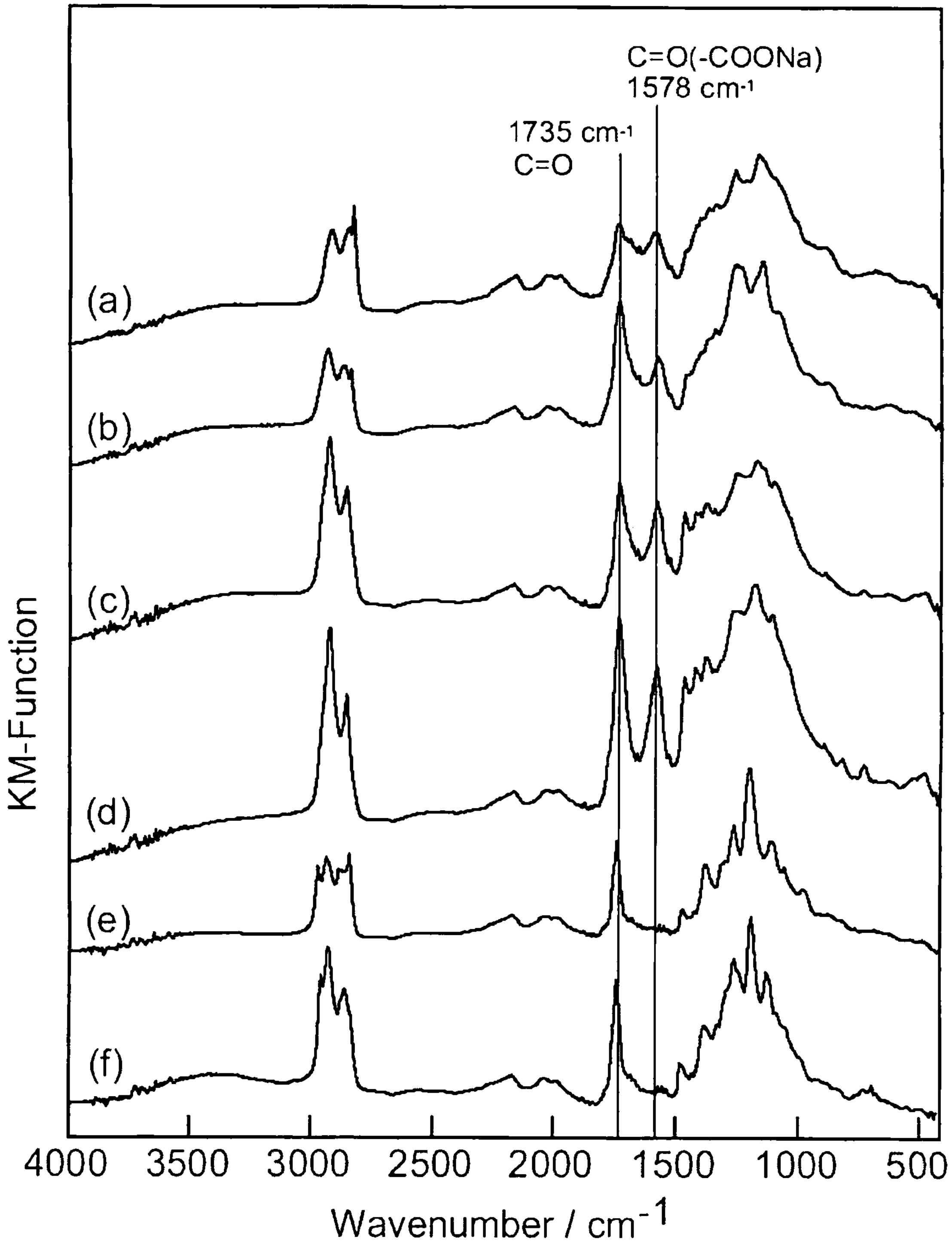

Figure 6.6 IR spectra for hydrogenated diamond powders treated with dicarboxylic acids and benzoyl peroxide, and subsequently neutralized by NaOH (*aq*). Dicarboxylic acids: (a) $n = 2$, (b) $n = 4$, (c) $n = 6$, (d) $n = 8$; monocarboxylic acids: (e) $n = 3$, (f) $n = 5$.

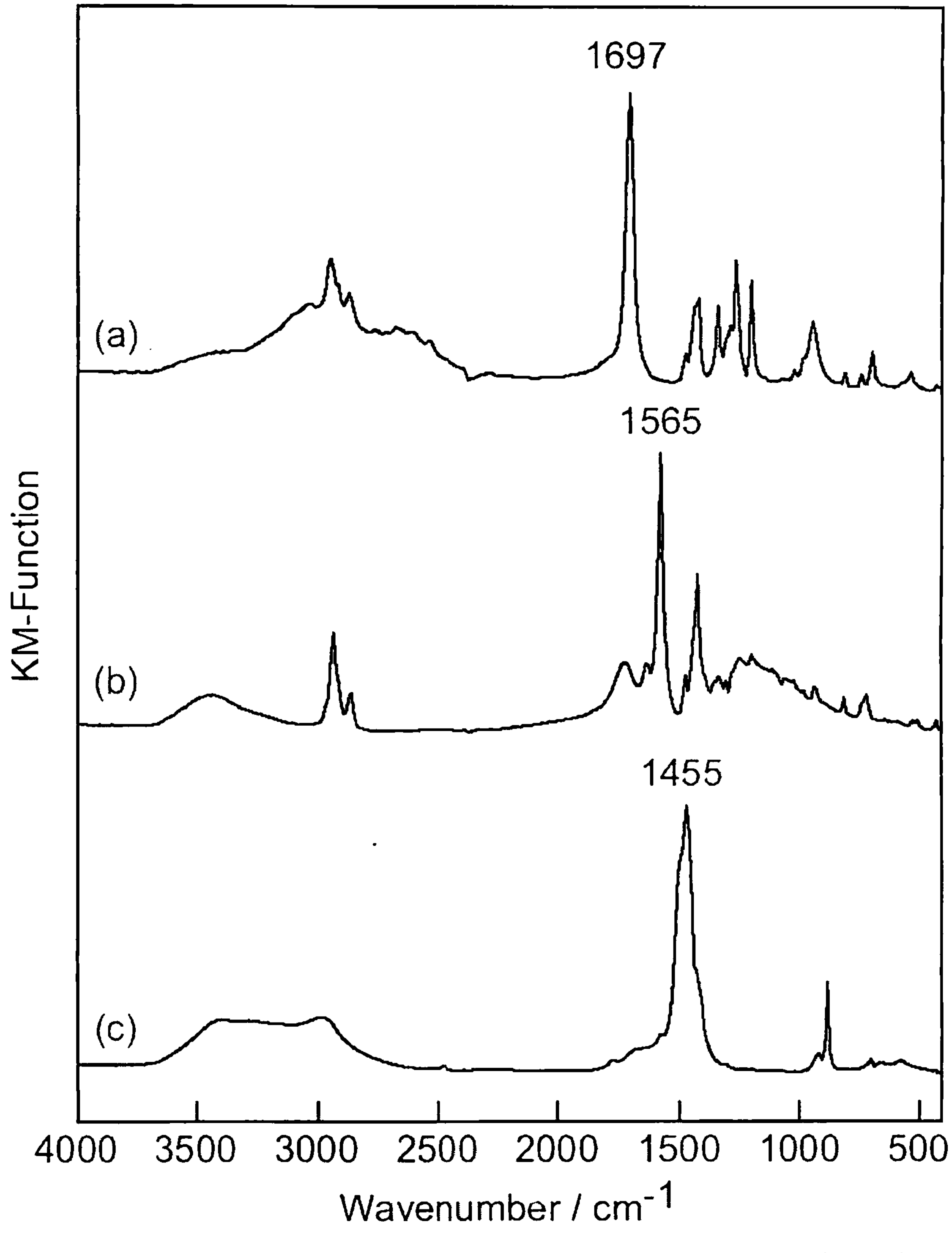

Figure 6.7 IR spectra for chemical species: (a) dicarboxylic acid (n = 6), (b) NaOOC-$(CH_2)_n$-COONa, (n = 6), (c) NaOH.

Chapter 7

Oxygenation of hydrogenated diamond surface in liquid phases

Chapter 7
Oxygenation of hydrogenated diamond surface in liquid phases

7.1. Introduction

Diamond exhibits superior physical and chemical properties such as hardness, large band gap, transparency over a wide wavelength region, high thermal conductivity, stability against chemical reagents, and so on. These properties result from its crystal structure. Diamond surface is stabilized by bonding to elements other than carbon, for example, oxygen and hydrogen atoms. The diamond surface covered with oxygen atoms and hydrogen atoms may be regarded as a giant organic compound. Therefore, as mentioned in chapter 2-6, it is possible that many organic reactions occur on the diamond surface. Indeed, it has been reported that diamond surface reacts with several chemical reagents, and functional groups are introduced onto the surface [1-7].

The terminal carbon atoms on the hydrogenated diamond surface are covered with hydrogen atoms. In other words, many C-H bonds exist on the diamond surface. The surface structure is similar to alkane. The typical chemical reactions of alkane are combustion reaction with oxygen and radical substitution reaction with halogens. In the same manner, it have been reported that the hydrogenated diamond surface reacts with fluorine and chlorine[8-9]. Diamond reacts with oxygen, but does not spontaneously continue progressing combustion reaction in the air. When hydrogenated diamond surface react with oxygen molecules, the diamond surface was terminated with oxygen atoms [10].

Reactivity of hydrogenated diamond surface with oxygen molecules has been reported in several publications [11-17]. With regard to the reaction between hydrogenated diamond surface and O_2 gas, during the initial stage of oxygenation, the hydrogen atoms on the diamond surface are substituted by oxygen atoms, and oxygen atoms bond to diamond surface with C-O-C (cyclic ether) and C=O (cyclic ketone). The C=O structures change to lactone and carboxylic anhydride structures with increasing oxygen coverage [10]. When reaction temperature further rises, the functional groups containing oxygen atoms are desorbed as CO_2 and CO.

Recently, oxygenated diamond surface has received attention as the substrate for immobilization of DNA [18]. Controlling the functional groups on the oxygenated diamond surface is necessary to effectively immobilized DNA onto the surface. In the same manner as the treatment with O_2 gas, hydrogenated diamond surface was oxygenated in liquid phase [10, 19]. Using wet process, it is possible to control the functional groups on the oxygenated diamond surface at lower temperature than using the O_2 gas. However, the detail study of the oxygenation of hydrogenated diamond surface in the liquid phase has not been reported. Therefore, in this work, we investigated the reactivity of the hydrogenated diamond surface in the liquid phases, and discussed the reaction mechanism. Inorganic acids and bases are used as the liquid phase.

7.2. Experimental

Commercial diamond powder (Tomei diamond MD500; average diameter: 500 nm) was used as the substrate. The diamond powder was treated with two kinds of acid mixtures: (HF + HNO_3, at room temperature) and (H_2SO_4 + HNO_3, at 80 ℃) to remove the impurities on the diamond surface. Following these acid treatments, the diamond powder was rinsed with distilled water, and then dried in a dryer. The dried diamond powder was heated in flowing H_2 gas at 950 ℃ for 5 h [20]. After this treatment, the diamond surfaces are terminated with hydrogen atoms. The hydrogenated diamond powders were used as starting materials.

Hydrogenated diamond powders (0.1 g) were suspended in inorganic acids (5 ml). HCl, HF, H_2SO_4, HNO_3, 1M NaOH (aq), 1 M KOH, H_2O_2, HCl:HNO_3 = 3:1, HCl:H_2O_2 = 1:1, and 1 M $KMnO_4$ (aq) were used as the inorganic acids. Relationship between stabilities of the C-H bonds on the hydrogenated diamond surface and reaction temperature was examined. After the reaction, the diamond powders were rinsed with distilled water, and then dried in a vacuum dryer.

The diamond surface was characterized by Diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy (JASCO FT/IR-700), X-ray photoelectron spectroscopy (XPS; VG scientific Σ-probe).

7.3. Results and discussion

7.3.1. Hydrogenated diamond powder

The IR spectrum of the hydrogenated diamond powder was shown in Figure 7.1. Two large peaks at 2837 cm^{-1} and 2930 cm^{-1} were observed. These peaks are assigned to the C-H bonds. The larger peak at 2837 cm^{-1} and the smaller peak at 2930 cm^{-1} are assigned to the C-H stretching vibration and the C-H asymmetric vibration, respectively [20]. The peak at 2157 cm^{-1} is ascribed to the diamond two-phonon absorption. XPS spectrum of the hydrogenated diamond powder was also shown in Figure 7.1. A large C 1s peak and a small O 1 s peak appeared at 285.0 eV and 532.1 eV, respectively. It is considered that the peak of O 1s is caused by physically adsorbed molecular water and the not-hydrogenated functional groups containing oxygen atoms on the diamond surface. Atomic rate of (O/C) estimated on the basis of the peak intensities of C1s and O1s was 3.0 %.

7.3.2. Reactivity of hydrogenated diamond with various acids or bases (Room temperature)

Figure 7.2 shows the IR spectra for the hydrogenated diamond powders treated with HCl, HF, H_2SO_4, HNO_3, 1M NaOH (aq) or 1 M KOH (aq) for 3 h at room temperature. The intensities of C-H peak of the obtained IR spectra were the same as that of hydrogenated diamond powder. It was found that hydrogenated diamond surface was chemically stable against these solvents at room temperature.

As the reason for the stability of the hydrogenated diamond surface against these solvents, we propose as follows. Hydrogenated diamond surface was covered with the C-H bonds. When the concept of organic chemistry is extended to the hydrogenated diamond surface, the surface is regarded as a giant alkane. Alkane is classified into the weakest acids. HCl, HF, H_2SO_4, HNO_3, 1M NaOH and so on are stronger acids compared with the alkane. The acidity constant (pK_a) of the species used in this study are smaller than that of alkane. For example, at room temperature the pK_a of H_2SO_4 and H_2O are -9 and 15.7, respectively, whereas the pK_a of ethane (CH_3CH_3) is 50 [21]. Weaker acid has larger value of the pK_a. Although the pK_a of hydrogenated diamond surface have never been measured, if the pK_a of hydrogenated diamond surface is the largely same as ethane, the dissociation of the protons from hydrogenated diamond surface such as follows hardly occur.

$$(\text{Diamond})\text{C-H} \rightarrow (\text{Dimond})\text{C}^- + \text{H}^+ \quad (1)$$

The "(Diamond)C-H" shows the hydrogenated diamond surface. That is to say, the reason for the stability of the hydrogenated diamond surface is because the C-H bond on the diamond surface do not dissociate into ions in the liquid phases. Indeed, IR spectra for the deuterium-labeled diamond powders suspended in H_2SO_4 or 1 M NaOH for 3 h had no the peak assigned to the C-H bond. If the dissociation of the C-D bonds on the diamond surface occurs such as Eq. (1), the exchange between the deuterium atoms and hydrogen atoms must occur on the diamond surface. According to the result, at least, it is found that the dissociation of the protons from hydrogenated diamond surface do not occur in the liquid phases used in this study.

7.3.3. Reactivity of hydrogenated diamond with various acids or bases (the effect of the reaction temperature)

The IR spectra for hydrogenated diamond powder treated with various acids or bases (HCl, HF. 1 M NaOH (aq) and 1 M KOH (aq)) for 3 h at 100 ℃ are shown in Figure 7.3. After the reaction, the intensities of the C-H peak of the obtained IR spectra were unaffected by the reaction. However, the shape of the low wave region in the IR spectra for hydrogenated diamond powder treated with HCl or HF slightly changed. XPS spectra of the diamond powder treated with HCl or HF is shown in Figure 7.4. The peaks of C 1s and O 1s were observed, but that of species except for carbon and oxygen were not observed. The atomic percentages of O/C were 3.0 (HCl) and 2.9 (HF). The values were the same as that of the hydrogenated diamond surface. According to the results, it was possible that the hydrogenated diamond surfaces slightly reacted with HCl or HF because the shape of the low wave region in the IR spectra for hydrogenated diamond powder treated with HCl or HF slightly changed. However, we conclude that hydrogenated diamond surface was fundamentally stable against HCl, HF, 1 M NaOH (aq) and 1 M KOH (aq)) for 3 h at 100 ℃ because the decrease in the intensities of the C-H peak of the obtained IR spectra were observed.

Figure 7.5 shows the IR spectra for hydrogenated diamond powders treated with H_2SO_4 for 3 h at different temperature. The peak intensities assigned to the C-H bond hardly changed at 60-130 ℃. The decrease in the C-H peak intensity was observed at 150 ℃. It was found that hydrogenated diamond surface begin to react with H_2SO_4 from 150 ℃. When hydrogenated diamond surface was refluxed, the peak assigned to the C-H bond completely disappeared, and new peaks appeared at 1500 cm^{-1}, 1719 cm^{-1}, 1773 cm^{-1} and 3100-3600 cm^{-1}. The peak at 1773 cm^{-1} and 3100-3600 cm^{-1} was assigned to the C=O bond and the O-H bond, respectively. The assignment of the peaks at 1500 cm^{-1} and 1719 cm^{-1} were not clarified. The peaks of C 1s and O 1s were observed in the XPS spectrum of the refluxed diamond powder (Figure 7.4(c)). The value of O/C was 8.4 %. The results of XPS agreed with the appearance of the C=O peak and O-H peak in the IR spectra. The detailed mechanism for the oxygenation of the diamond surface is expected to be complicated because many chemical species are activated at higher temperature.

Figure 7.6 shows the IR spectra for the hydrogenated diamond powder treated with HNO_3 for 3h at 65-110 ℃. The peak intensities assigned to the C-H bond largely decreased above 90 ℃. The C-H peaks intensity was the smallest at 114 ℃, and new peaks appeared at 1000-1300 cm^{-1}, 1646 cm^{-1}, 1738 cm^{-1} and 3100-3600 cm^{-1}. The peak at 1000-1300 cm^{-1} was assigned to the C-O-C bond, and the peak at 1738 cm^{-1}

was assigned to the species containing C=O groups. The peak at 3100-3600 cm^{-1} was ascribed to the O-H bond. The peak at 1646 cm^{-1} was not defined. XPS spectrum for the diamond powder treated at 115 ℃ is shown in Figure 7.4(d). The C 1s and O 1s peaks appeared. The value of O/C was 6.5 %.

With regard to the reaction mechanism, HNO_3 is decomposed by heat treatment as follows [22]:

$$4\ HNO_3 \rightarrow 4\ NO_2 + O_2 + 2\ H_2O \quad (2)$$

It is known that alkane is subjected to combustion to CO_2 by O_2. The combustion is the reaction related to the oxygen radicals. It is possible that the oxygenation of hydrogenated diamond surface is radical reaction. After the decomposition of HNO_3, O_2 and NO_2 are generated. It is considered that these species containing oxygen atoms become free radicals in the solvent, and then the radicals react with hydrogenated diamond surface.

7.3.4. The reactivity of hydrogenated diamond surface with $HCl:HNO_3$ = 3:1, $HCl:H_2O_2$ = 1:1 and H_2O_2.

Figure 7.7 shows the IR spectra for hydrogenated diamond powders reacted with $HCl:HNO_3$ = 3:1 for 3 h. With increasing the reaction temperature, the peak intensities of the C-H peak decreased, and new peaks appeared at 1137 cm^{-1} and 1719 cm^{-1}. It was found that the hydrogen abstraction reaction was observed above 60 ℃. The peak at 1137 cm^{-1} and 719 cm^{-1} is assigned to the C-O-C bond and the functional groups containing the C=O bond, respectively. In the XPS spectrum for the diamond powder treated at 105 ℃, the peak ascribed to Cl 2p, C 1s and O 1s appeared (Figure 7.4(e)). The atomic percentage of O/C and Cl/C were 4.7 % and 0.8 %, respectively. The following reaction occur in the solvent of $HCl:HNO_3$ = 3:1 [22]:

$$3\ HCl + HNO_3 \rightarrow Cl_2 + NOCl + 2\ H_2O \quad (3)$$

Cl_2 gas are generated in $HCl:HNO_3$ = 3:1. It had been reported that hydrogenated diamond surface is chlorinated by Cl radicals. With regard to results that Cl atoms were present on the diamond surface, it is considered that Cl_2 gas generated in the solvent were decomposed into free Cl radicals, and the Cl radicals reacted with hydrogenated diamond surface. However, in the reaction between hydrogenated diamond surface and in $HCl:HNO_3$, the reaction mechanism may be much complicated because the decomposition reaction of HNO_3 must simultaneously occur.

The reaction between HCl and H_2O_2 also generates Cl_2 gas. Hydrogenated diamond powder was suspended in HCl:H_2O_2 = 1:1 (10 ml) at 60 ℃ for 3h. After the reaction, the peak intensity of C-H peak decreased (Figure 7.7(e)). The peak assigned to Cl 2p, C 1s and O 1s were observed in the XPS spectrum (Figure 4(f)). The atomic percentage of O/C and Cl/C were 3.9 % and 0.6 %, respectively. In the same manner as the reaction with HCl:HNO_3 = 3:1, it is considered that hydrogenated diamond surface was chlorinated by Cl radicals in the in HCl:H_2O_2 = 1:1.

The reaction temperature dependence between hydrogenated diamond surface and H_2O_2 are shown in Figure 7.8. The shape of the IR spectrum of the diamond powder treated at room temperature was the same as that of hydrogenated diamond powder. However, the decrease of the C-H peak intensity was observed at 90 ℃, and the peak assigned to the O-H bond appeared at 3200-3400 cm^{-1}. It was found that the O-H peak intensity of IR spectrum of diamond powder treated with H_2O_2 was larger than that of diamond powder treated various solvents such as above description. H_2O_2 is decomposed by heat treatment as follows [22]:

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ (4)

The generated oxygen molecule may become free radicals in the solvent. It is considered that the generated oxygen free radicals react with hydrogenated diamond surface, and then the diamond surface was oxygenated. As another reaction mechanism, it is reported that H_2O_2 is decomposed into OH radicals by UV irradiation as follows [23]:

$H_2O_2 \rightarrow HO\cdot + \cdot OH$ (5)

In the same manner, H_2O_2 may be partly decomposed into OH radicals by heat treatment. The OH radicals abstracted the hydrogen atoms on the diamond surface, and the other OH radicals bonded to the diamond surface. Therefore, the C-H peak intensity decreased, and the O-H peak intensity increased.

7.3.5. The mechanism of the oxygenation of the hydrogenated diamond surface in the liquid phase.

To quantitatively estimate the hydrogen abstraction reaction on diamond surface by H_2SO_4, HNO_3 or HCl:HNO_3=3:1, we normalized the area under the C-H peaks (2780-3010 cm^{-1}). The peak at 2157 cm^{-1} was ascribed to the diamond two-phonon absorption, and was used as a reference [19]. The area of the C-H peaks (2780-3010 cm^{-1}) was divided by the area of the two-phonon absorption peaks (2100-2230 cm^{-1}). The ratio was denoted by $S_{C\text{-}H}$. In order to normalize $S_{C\text{-}H}$, the $S_{C\text{-}H}$ value for the diamond powders treated with each solvent was divided by the $S_{C\text{-}H}$ value for hydrogenated diamond powder. The ($S_{C\text{-}H}$ / $S_{C\text{-}H(\mathrm{hydrogenated})}$) value for each solvent is shown as a function of treatment temperature in Figure 7.9. The decrease of the ($S_{C\text{-}H}$ / $S_{C\text{-}H(\mathrm{hydrogenated})}$) value means abstraction of hydrogen atoms on the diamond surface. The ($S_{C\text{-}H}$ / $S_{C\text{-}H(\mathrm{hydrogenated})}$) value of hydrogenate diamond surface is 1.0. it was found that these value largely decreased from 60 ℃ ($HCl:HNO_3=3:1$), 90 ℃ (HNO_3) and 150 ℃ (H_2SO_4). This results shows that the hydrogen abstraction reaction is accelerated above a certain temperature.

It is found that H_2SO_4, HNO_3 and H_2O_2 that oxygenated the hydrogenated diamond surface are strong oxidizing agents. It is expected that hydrogenated diamond surface is oxygenated by other strong oxidizing agents. The IR spectra for the hydrogenated diamond powder treated with 1 M $KMnO_4$ (aq) is shown in Figure 7.10. The MnO_4^- is also a strong oxidizing agent. The C-H peak intensities largely decreased above 45 ℃, and the C=O peaks appeared at 1750-1770 cm^{-1}. It is possible that MnO^- is also decomposed and generated O_2 by heat treatment as the HNO_3 and H_2O_2. The generated O_2 may be related to the oxygenation of the diamond surface. The detailed reaction mechanism was unclear. However, it was found that hydrogenated diamond surface is oxygenated by strong oxidizing agents.

In general, the oxidizing agents accept electrons from other species, and then the species are oxidized. If the reaction between oxidizing agent and hydrogenated diamond surface directly occur, the reaction as follows occur on the diamond surface because it is considered as above mentioned that the C-H bond on the diamond surface do not dissociate into ions in the liquid phases.

$$\text{(Diamond)C-H} \rightarrow \text{(Diamond)C}\bullet + H^+ + e^- \quad (6)$$

If the reaction as Eq. (6) occur on the diamond surface, it is possible the reaction between oxidizing agent and hydrogenated diamond surface directly occur. It was unclear if the reaction as Eq. (6) occur on the diamond surface. However, it is obvious that $KMnO_4$ is effectively oxygenated hydrogenated diamond surface.

7.4. Conclusions

We briefly summarize the main conclusions of our present work for the reactivity of the hydrogenated diamond surface in various liquid phases as follows: In the cases of the treatment with HCl, HF, 1M NaOH (aq) or 1 M KOH (aq) below 100 ℃, the hydrogenated diamond surfaces were stable, whereas in the cases of the treatment with H_2SO_4 above 150 ℃, HNO_3 above 90 ℃, H_2O_2 above 90 ℃ or 1 M $KMnO_4$ (aq) above 45 ℃, the hydrogen atoms on the hydrogenated diamond surface were abstracted, and then the diamond surface were oxygenated. In the cases of $HCl:HNO_3=3:1$ or $HCl:H_2O_2=1:1$ above 60 ℃, the hydrogen abstraction reaction were observed, the diamond surfaces were oxygenated and chlorinated. It is expected that the oxygenation of hydrogenated diamond surface in the liquid phase proceed via not the ion reaction, but the radical reaction as the fundamental reaction mechanism.

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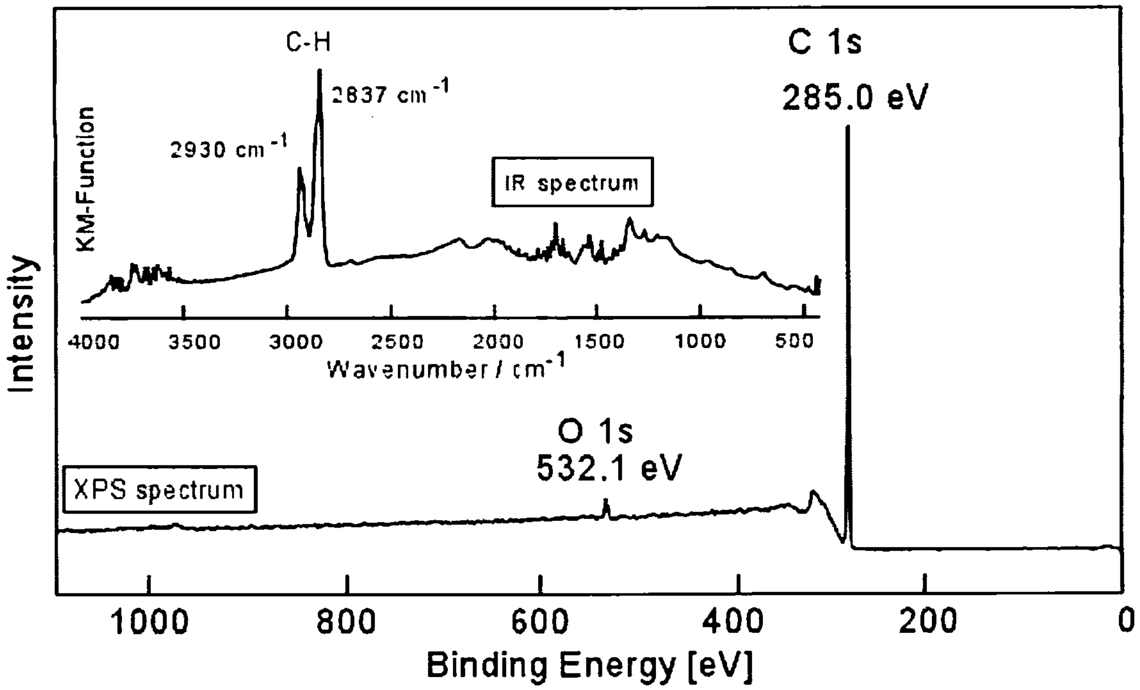

Figure 7.1 XPS and IR spectrum for hydrogenated diamond powder.

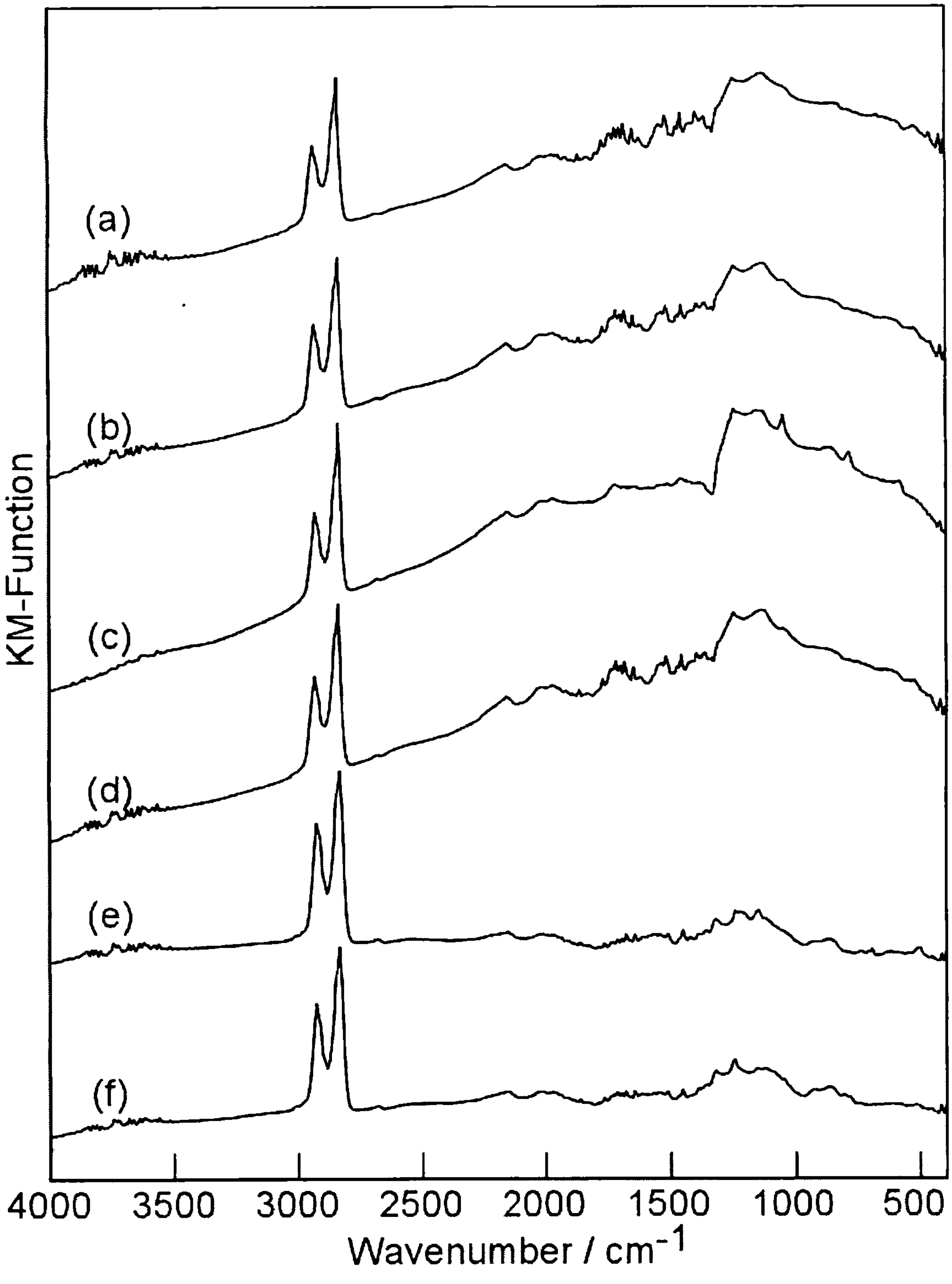

Figure 7.2 IR spectra for hydrogenated diamond powders treated with various solvents for 3 h at the room temperature. (a) HCl, (b) HF, (c) H_2SO_4, (d) HNO_3, (e) NaOH, (f) KOH.

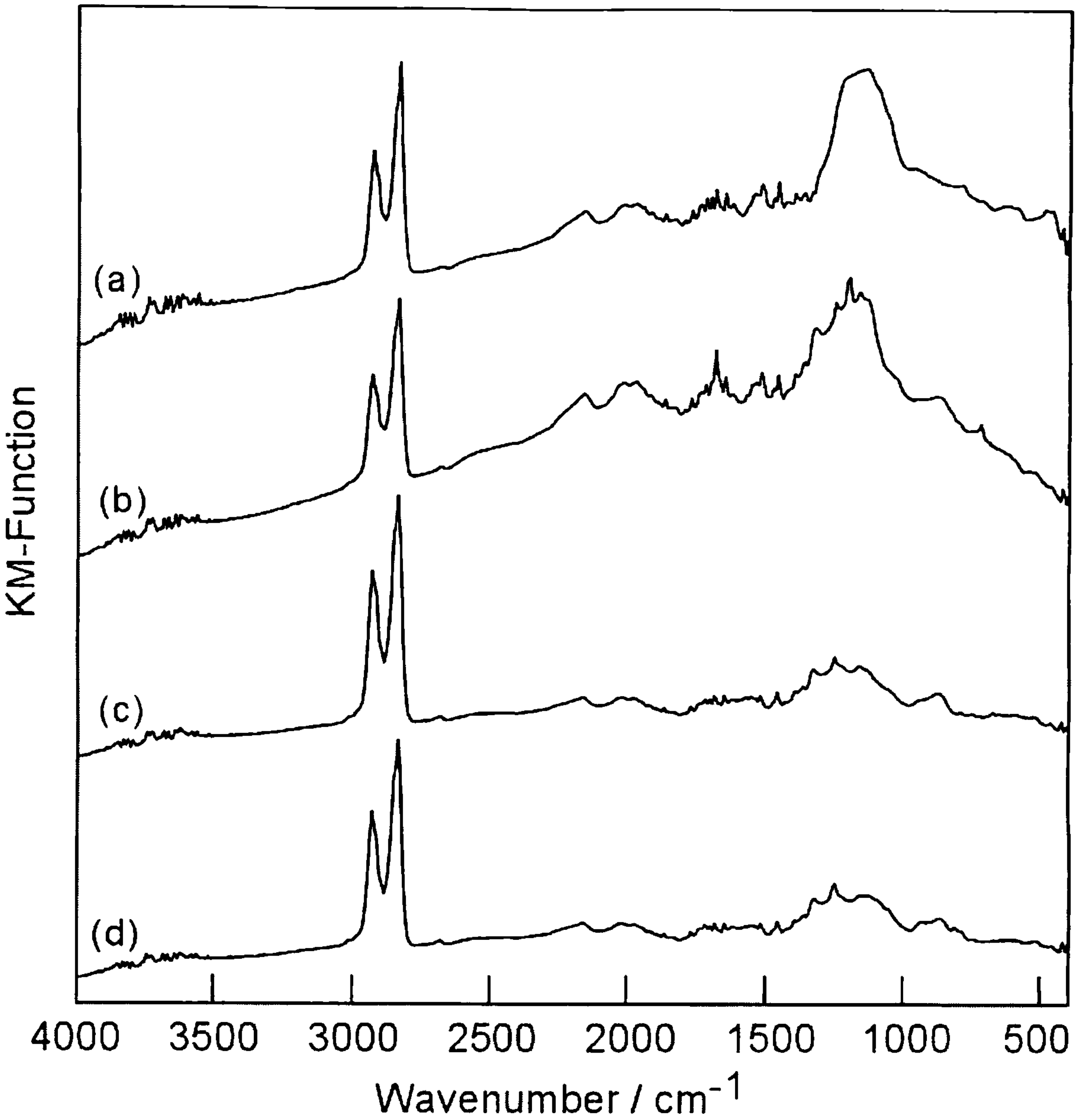

Figure 7.3 IR spectra of hydrogenated diamond powders treated with various solvents for 3 h at 100 ℃. (a) HCl, (b) HF, (c) NaOH, (d) KOH.

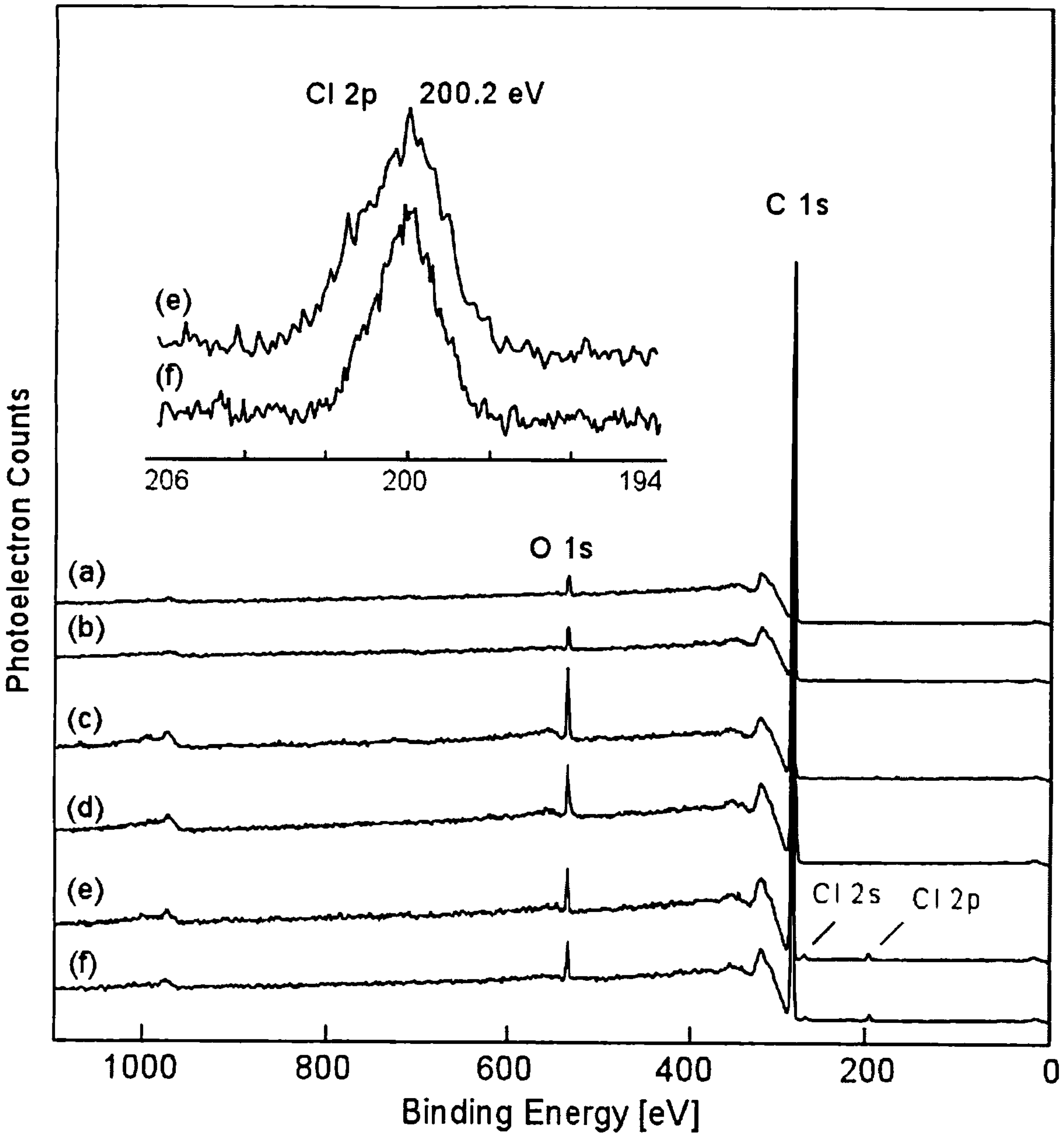

Figure 7.4 XPS spectra for diamond powders treated with (a) HCl, (b) HF, (c) H_2SO_4, (d) HNO_3, (e) HCl:HNO_3 = 3:1, (f) HCl + H_2O_2.

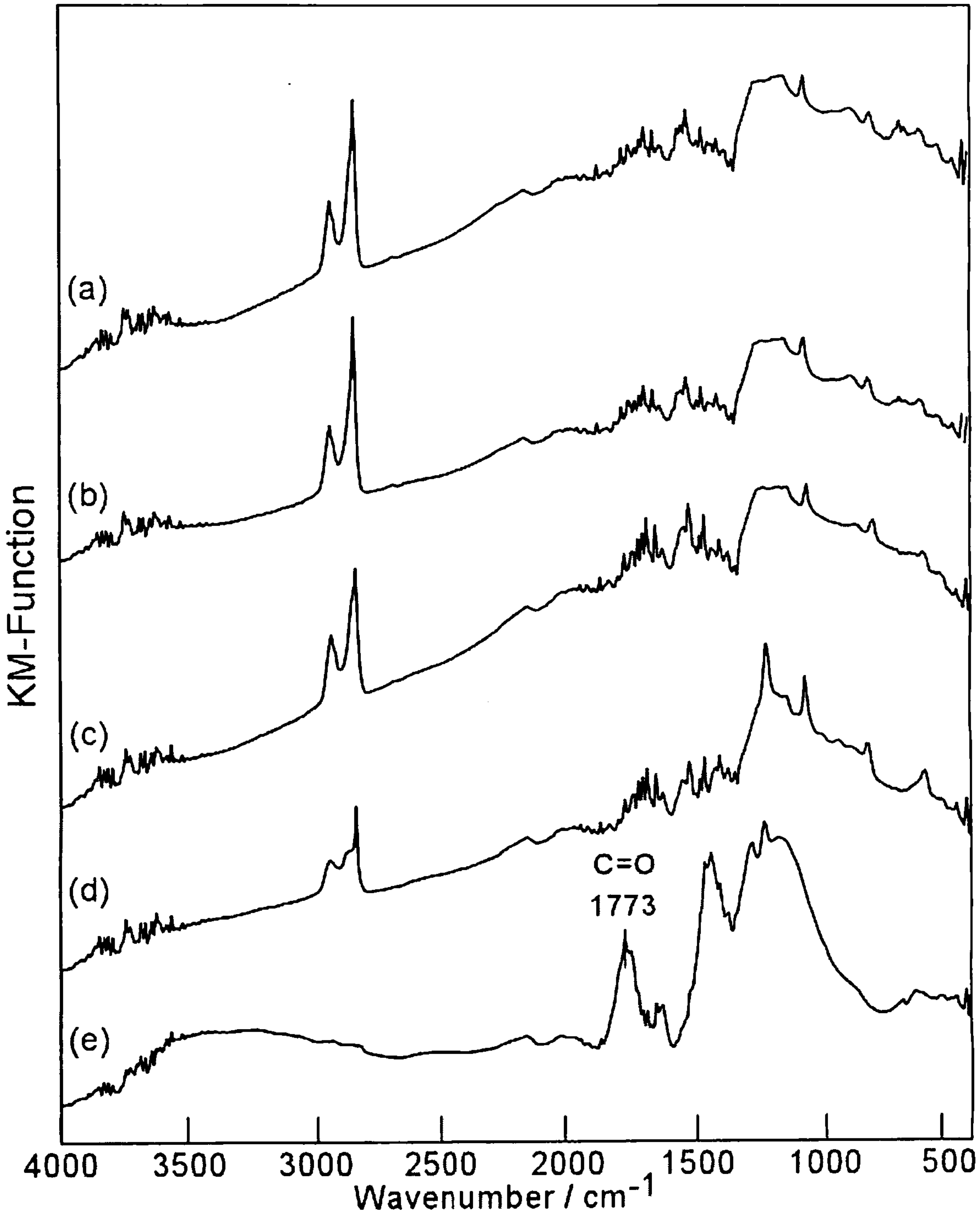

Figure 7.5 IR spectra for hydrogenated diamond powders treated with H_2SO_4 for 3 h, (a) 60 ℃, (b) 95 ℃, (c) 130 ℃, (d) 150 ℃, (e) reflux.

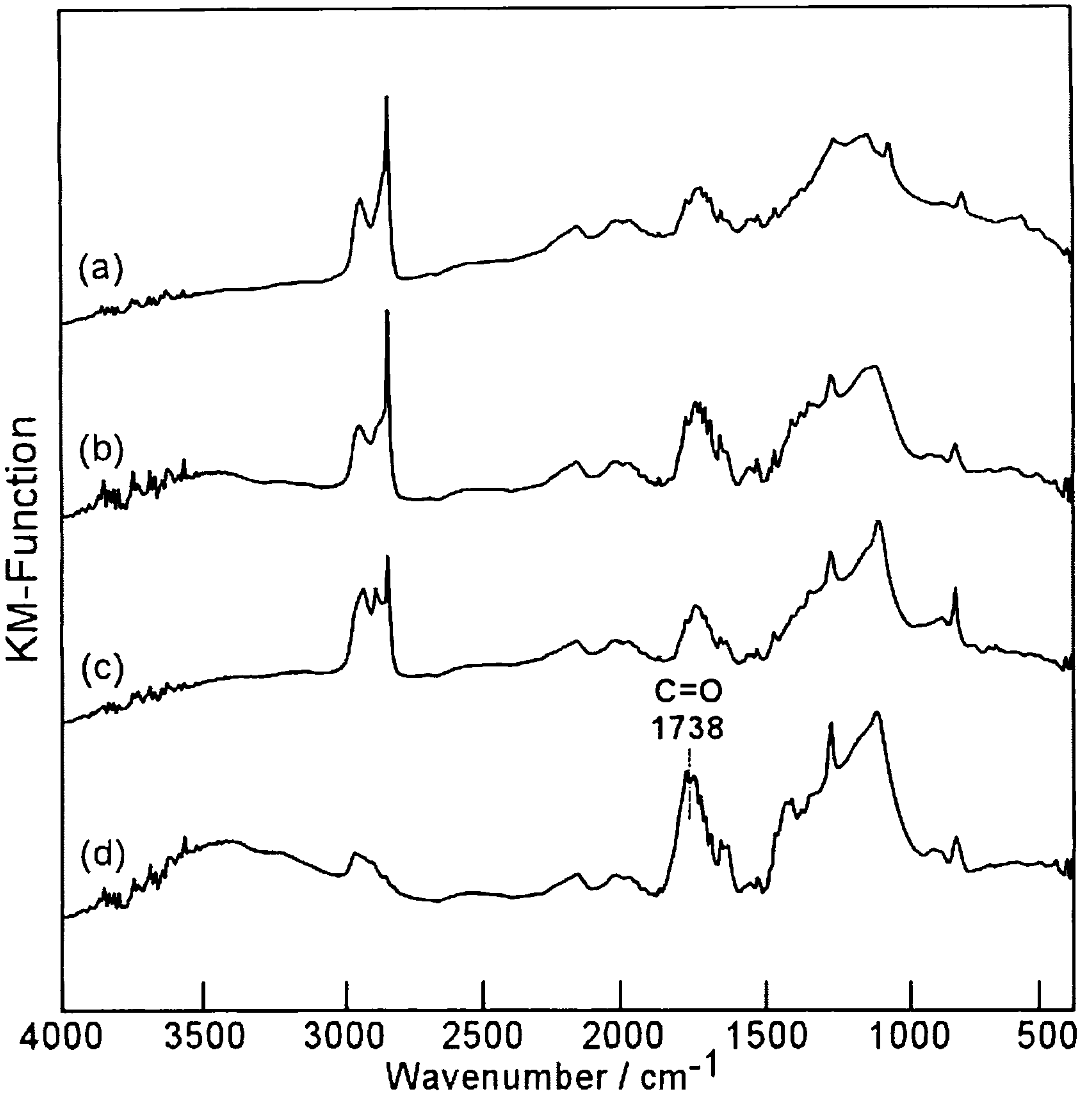

Figure 7.6 IR spectra for hydrogenated diamond powders treated with HNO_3 for 3h, (a) 65 ℃, (b) 90 ℃, (c) 105 ℃, (d) 115 ℃.

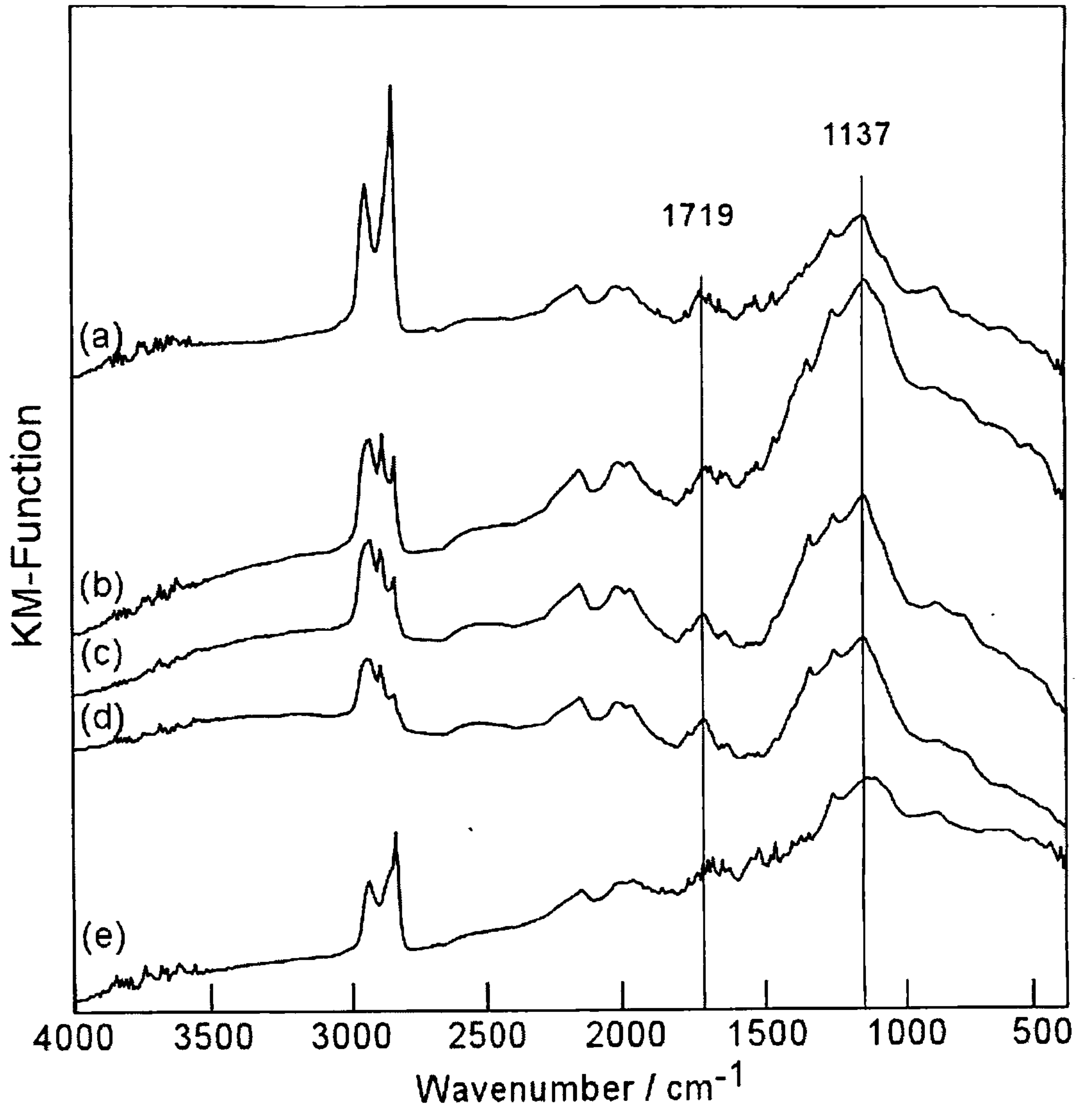

Figure 7.7 IR spectra for hydrogenated diamond powders treated with HCl:HNO3 = 3:1 for 3h,(a) at room temperature, (b) 60 ℃, (c) 80 ℃, (d) 105 ℃, (e) treated with HCl + H_2O_2.

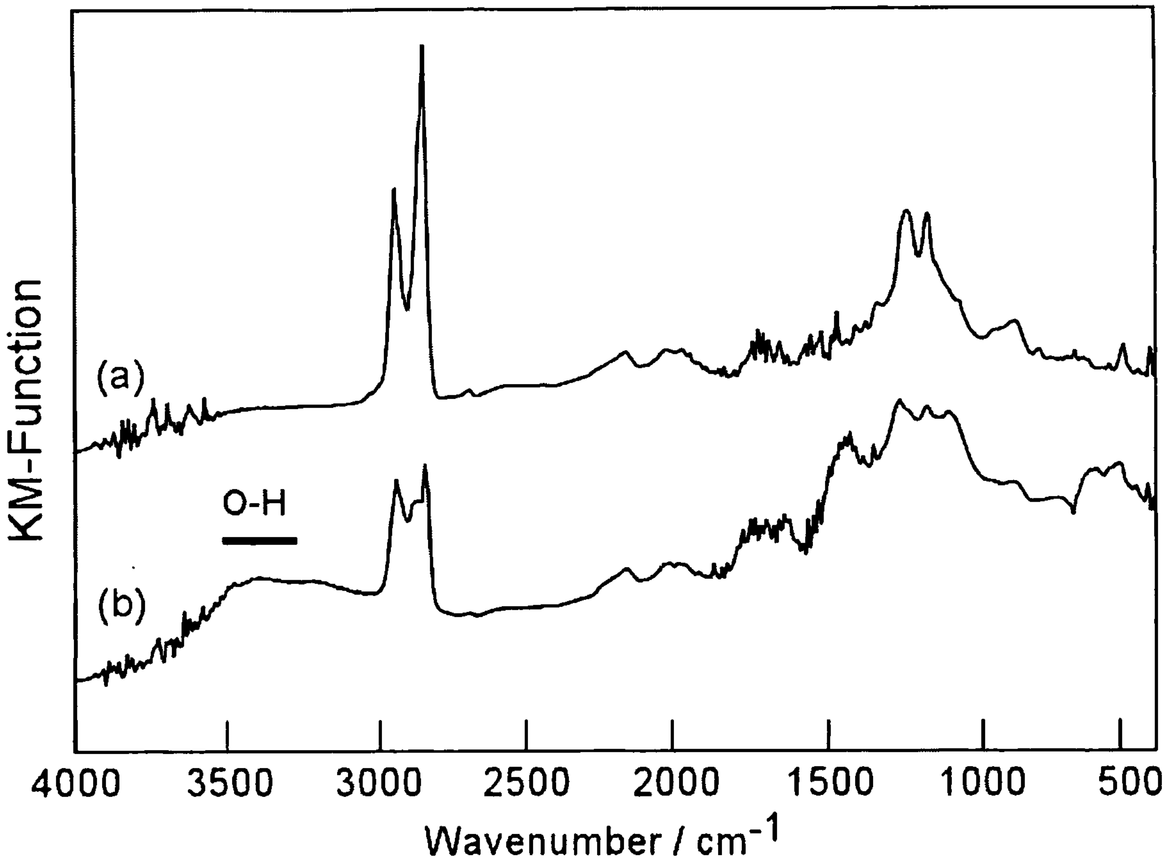

Figure 7.8 IR spectra for hydrogenated diamond powders treated with H_2O_2 for 3h, (a) room temperature, (b) 90 ℃.

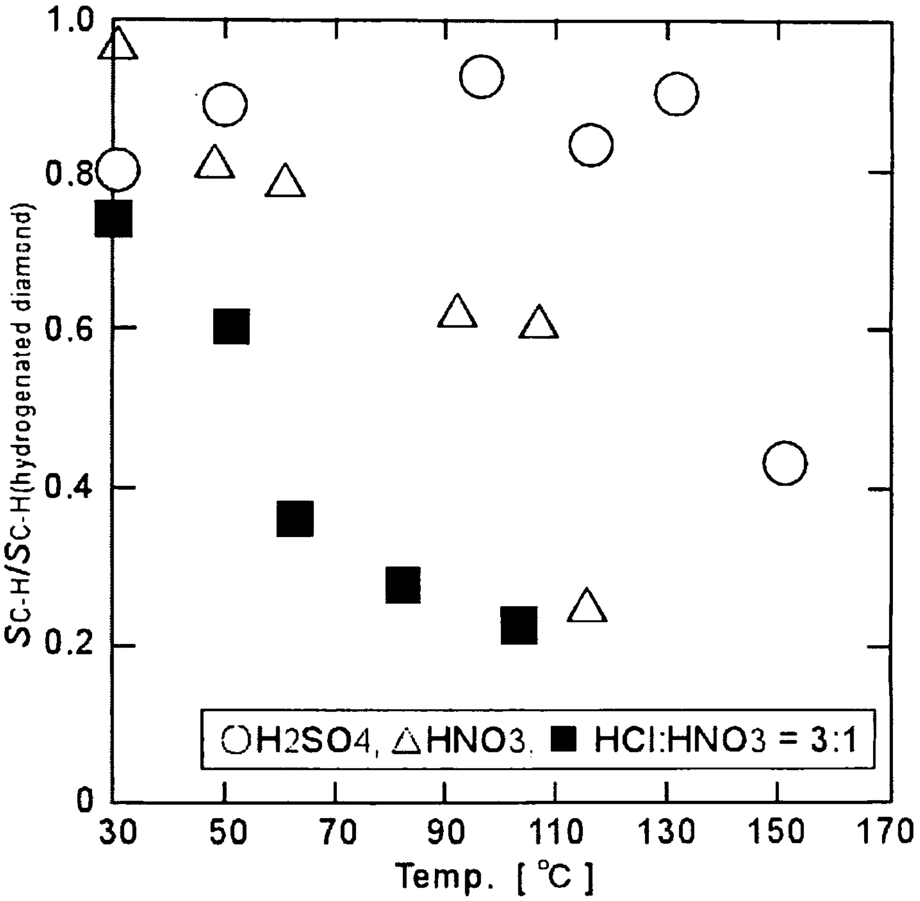

Figure 7.9 Temperature dependence of the values of the $S_{C\text{-}H}/S_{C\text{-}H(\text{hydrogenated diamond})}$.

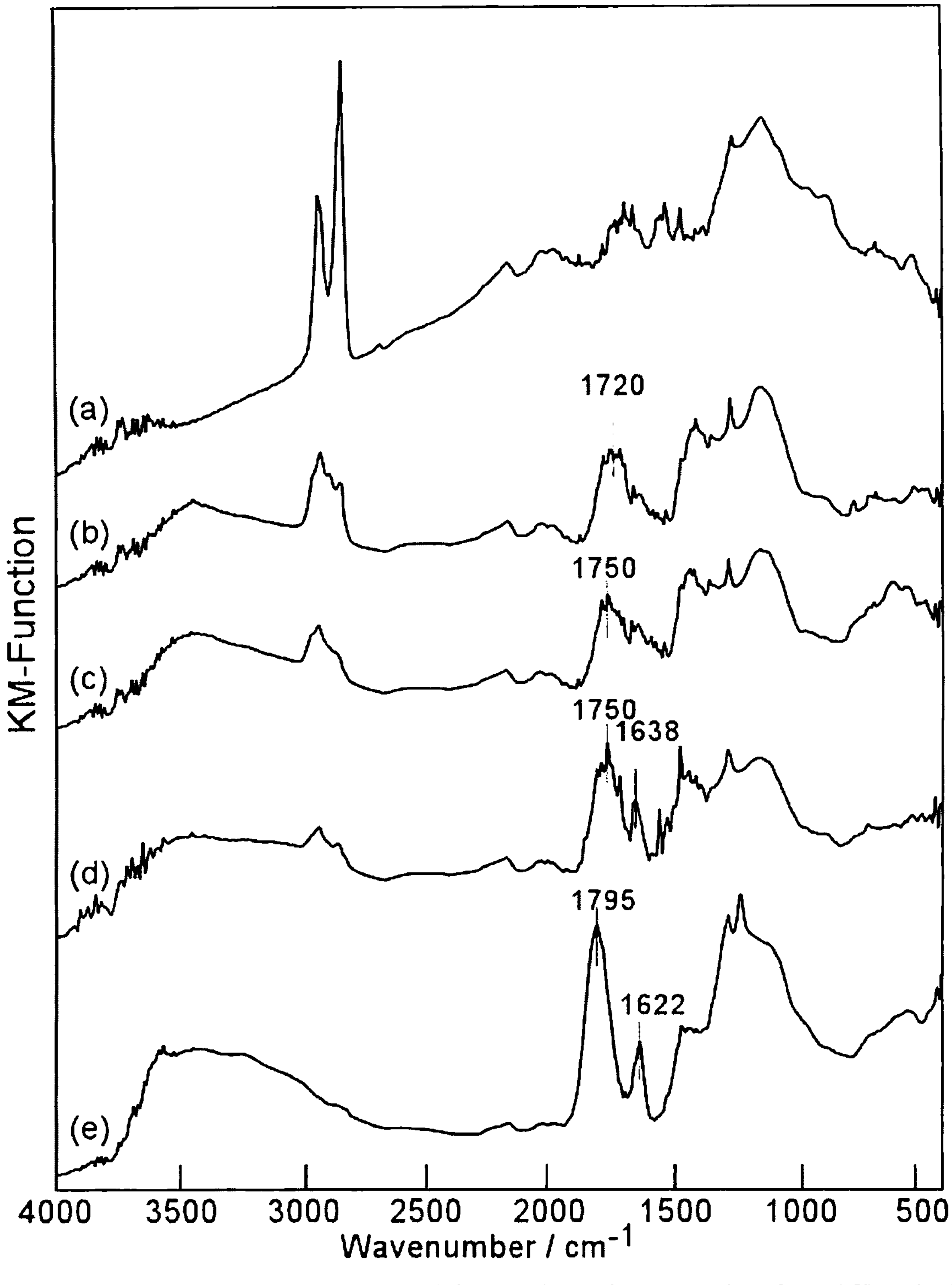

Figure 7.10 IR spectra for hydrogenated diamond powder treated with 1 M $KMnO_4$ for 3h, (a) at room temperature, (b) 45 ℃, (c) 60 ℃, (d) 80 ℃, (e) 95 ℃.

Chapter 8

Chemical reaction of carbonyl groups of diamond surface with $LiAlH_4$

Chapter 8
Chemical reaction of carbonyl groups of diamond surface with $LiAlH_4$

8.1. Introduction

Modification of the diamond surface has recently been studied in connection with applications such as electrode [1], sensors [2] and fixing material for biomolecules [3]. Extensive data on diamond surface reactivity is necessary to achieve a desired modification of the diamond surface. Diamond surface reactivity has been reported in several publications [1-19].

Diamond surface is stabilized by bonding to elements other than carbon. The hydrogen terminated diamond surface is a p-type conductor and hydrophobic, while the oxygen terminated diamond surface is an insulator and hydrophilic. Thus, the chemical bonding state of the diamond surface strongly affects its chemical and physical properties. Organic molecules, such as amino acids and proteins, that are introduced to the diamond surface as terminal chemical species, impart new functionalities to the diamond surface. The theory and practice of organic chemistry seems to be helpful of the modification of the diamond surface because diamond is composed of carbon atoms.

In present study, we report on the reactivity of oxygen terminated diamond surface (oxygenated diamond surface). The reactivity of the oxygenated diamond surface has barely been covered in the literature from the viewpoint of organic chemistry. For the surface modification of diamond, a database of the fundamental reactivity of surface chemical species is essential. On the oxygenated diamond surface (ODS), a mixture of carbonyl, hydroxyl, and ether groups is present13). One purpose of our study is to gather the data required to control the ODS through organic chemistry. We investigated diamond surface chemistry with respect to functional groups including oxygen atoms. We attempted to reduce ODS using lithium aluminium hydride ($LiAlH_4$), a powerful reduction reagent. We discuss the reactivity of the C=O bonds on the diamond surface.

8.2. Experimental

Commercial diamond powder (Tomei diamond MD500; average diameter 500 nm, specific surface area 9.94 $m^2 g^{-1}$) and polycrystalline free-standing diamond film were used as diamond substrate. Diamond film was prepared by the combustion flame method, in which oxygen and acetylene are used [14-15]. The diamond powder was treated with two kinds of acid mixtures: (HF + HNO_3, at room temperature) and (H_2SO_4 + HNO_3, at 353 K). These acid treatments were performed to remove any impurities on the diamond surface. The diamond powder was then rinsed with distilled water, dried in a vacuum dryer, and heated in flowing H_2 at 1173 K for 5 h in order to hydrogenate the diamond surface [16]. The hydrogenated diamond powder was refluxed in H_2SO_4/HNO_3 (9:1 by volume) for 4 h. This powder was used as the oxygenated diamond substrate. The diamond film was also heated in flowing H_2 at 1173 K for 5 h, and refluxed in H_2SO_4/HNO_3 (9:1 by volume) for 4 h.

The oxygenated diamond powder (0.5 g) and $LiAlH_4$ (0.001-0.3 g) were suspended in diethyl ether or tetrahydrofuran (5 ml). Upon the addition of 1 mol dm^{-3} HCl in the suspension, $LiAlH_4$ decomposed and lost its reduction ability (note: HCl must be added gradually in order not to ignite the $LiAlH_4$). After the reaction process, the diamond powders were thoroughly washed with HCl and water to remove the impurity generated by decomposition of $LiAlH_4$, and then dried in a vacuum dryer.

The diamond surface was characterized by Diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy (JASCO FT/IR-700), X-ray photoelectron spectroscopy (XPS; VG scientific Σ-probe). DRIFT spectra were obtained in the 4000-400 cm^{-1} range, and 256 scans were accumulated for each spectrum at a resolution of 4 cm^{-1}. The diffuse reflectance was converted into Kubelka-Munk function units. High-resolution X-ray photoelectron spectra were recorded at a base pressure of *ca.* 10^{-4} Pa using monochromatised AlKα (1486.6 eV) X-ray radiation with an electron energy resolution of 0.1 eV (narrow scans) or 1 eV (survey scans). Carbon species in the diamond were evaluated by laser-Raman spectroscopy at 514.5 nm (Raman, Japan Spectroscopic NRS-2000).

8.3. Results and Discussion

8.3.1. Preparation of oxygenated diamond surface

Figure 8.1(a) shows the IR spectrum of hydrogenated diamond powder. There are two large peaks between 2800-2900 cm^{-1}, which are assigned to the stretching vibrations of sp^3 hybridized C-H bonds [13, 16]. After the hydrogenated diamond powder was refluxed in the acid (H_2SO_4:HNO_3= 9:1) for 4 h, the intensity of the peaks assigned to the C-H bond decreased significantly, and new peaks emerged at 1322 cm^{-1}, 1506 cm^{-1}, 1623 cm^{-1}, 1818 cm^{-1} and 3181 cm^{-1} (Figure 8.1(b)). The peak at 1818 cm^{-1} is due to species containing C=O groups, and has been assigned to C=O vibrations of carboxylic anhydride (-COOCO-), carboxylic acid (-COOH), lactone (-COO) or cyclic ketone (-CO-) structures [13]. It was reported that carboxylic anhydride structures correspond to relatively high frequencies (above 1800 cm^{-1}) [13]. Thus, the peak at 1818 cm^{-1} is ascribed to the C=O bonds of carboxylic anhydride structures. The peak at 1322 cm^{-1} is assigned to the C-O-C stretching vibrations of either cyclic ether or cyclic ester [13, 16]. The peaks at 1623 cm^{-1} and 3181 cm^{-1} could be assigned to physically absorbed water16). The assignment of the peak at 1506 cm^{-1} is unclear. It may be ascribed to the C-O-C bonds of the carboxylic anhydride structures.

The Raman spectrum of the diamond film treated with acid is shown in Figure 8.2. The diamond peak at 1333 cm^{-1} was clearly observed. XPS analysis of the diamond film surface showed the complete absence of any elements other than C, O, and N.

8.3.2. Oxygenated diamond surface (ODS) treated with $LiAlH_4$

$LiAlH_4$ reduces aldehyde and ketone to primary alcohol and secondary alcohol, respectively, via the following reactions:

$4R_2C{=}O + LiAlH_4 \rightarrow (R_2CHO)_4AlLi$ (1)

$(R_2CHO)_4AlLi + 4H_2O \rightarrow 4R_2CHOH + LiOH + Al(OH)_3$ (2)

($LiAlH_4$) also reduces the carboxyl group to alcohol:

$4R\text{-}COOH + 3LiAlH_4 \rightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4AlLi$ (3)
$(RCH_2O)_4AlLi + 4H_2O \rightarrow 4R\text{-}CH_2OH + LiOH + Al(OH)_3$ (4)

It is possible that the carbonyl groups on the diamond surface react with $LiAlH_4$.

The IR spectrum of the oxygenated diamond powder treated with $LiAlH_4$ (0.1 g) and refluxed in the presence of diethyl ether for 1 h is shown in Figure 8.1(c). After the reaction with $LiAlH_4$, the peak at 1818 cm^{-1} assigned to the C=O bonds largely shifted to 1785 cm^{-1} with decreasing the peak intensity. Meanwhile, the intensity of the peak at 3497 cm^{-1} assigned to the O-H bond increased. However, the peak at 1322 cm^{-1} ascribed to the C-O-C bond shifted up slightly to 1332 cm^{-1} without any decrease in the peak intensity. The peak intensity at 1506 cm^{-1} decreased with no peak shift, and a new peak emerged at 1646 cm^{-1}.

To make sure that $LiAlH_4$ modified the ODS, the diamond surface was also treated with $LiAlH_4$ whose reductive capacity had been deactivated as follows: $LiAlH_4$ was dissolved in diethyl ether; HCl was added; the solution was stirred for 1 h to ensure complete deactivation of the $LiAlH_4$. The solution became transparent upon deactivation. During this process, $LiAlH_4$ decomposed into hydrogen gas, aluminum hydride and lithium hydride in the presence of H_2O. These hydrides dissolved in HCl (aq.). Once the $LiAlH_4$ had been completely deactivated, the oxygenated diamond powder was suspended in the deactivated solution. This suspension was refluxed for 1 h. The shape of the IR spectrum of oxygenated diamond powder treated with deactivated $LiAlH_4$ (Figure 8.1(d)) almost exactly matches that of untreated oxygenated diamond powder.

XPS spectra of the oxygenated diamond films before and after treatment with $LiAlH_4$ are shown in Figures. 8.3(a) and 8.3(b), respectively. No peaks showed up in the survey spectra except for carbon and oxygen peaks. It was found that the impurities generated by deactivated $LiAlH_4$ were absent. In the narrow spectra of O1s and high-energy side of C1s, when ODS was treated with $LiAlH_4$, the O1s peak shifted to 531.7 eV from 531.2 eV, and the peak intensity at 287.3 eV assigned to the C=O bond decreased. The O1s peak assigned to the O-H bond appears at a higher energy than that assigned to the C=O bond. Thus, the shift in the O1s peak reveals that some of the C=O bonds are replaced by O-H bonds.

The likely conclusion is that the C=O bonds on the ODS were reduced to O-H bonds by $LiAlH_4$.

8.3.3. The effect of the amount of $LiAlH_4$ and reaction time

To fully characterize the chemical reactivity of the ODS towards $LiAlH_4$, further experiments were performed. Figure 8.4 displays the effect of the amount of $LiAlH_4$ on the IR spectra of oxygenated diamond powders treated in diethyl ether. Reaction was performed with a suspension that was refluxed for 1 h at 305 K. The C=O peak at 1818 cm^{-1} shifted to 1780 cm^{-1} with increasing the amount of the $LiAlH_4$, and the peak intensity at 1506 cm^{-1} decreased. The intensity of the peaks at 1646 cm^{-1} and at around 3500 cm^{-1} (ascribed to the O-H bond) increased. Thus, the reactivity of the ODS towards $LiAlH_4$ depends on the amount of $LiAlH_4$.

The number of moles of $LiAlH_4$ is *ca.* 7×10^{-3} mol for 0.3 g. The number of C=O bonds on the diamond powder (0.05 g, 9.94 $m^2\ g^{-1}$ specific surface area) is estimated to be *ca.* 7×10^{-6} mol, presuming every carbon atom on the diamond surface forms a double bond with an oxygen atom; the actual number, however, is less than 7×10^{-6} mol because of the presence of ether and hydroxyl groups on ODS. In general, when organic compounds containing C=O bond are treated with $LiAlH_4$, C=O bonds are immediately reduced to O-H bonds, resulting in a high yield of alcohol. Although $LiAlH_4$ was three orders of magnitude more abundant than C=O bonds on ODS, the all of the C=O bonds on the diamond surface do not react with $LiAlH_4$. This suggests that some of the C=O bonds on ODS have a lower reactivity than those found in organic compounds.

Figure 8.5 shows the time course of IR spectra of diamond powder treated with $LiAlH_4$. Even though the reaction time was short (5 min), the peak at 1818 cm^{-1} shifted to a lower wavenumber and its intensity decreased. As the reaction time increased, the peak at 1818 cm^{-1} assigned to the C=O bond shifted to a lower wavenumber, finally reaching 1765 cm^{-1}, where it remained for 3 weeks. The peak at 1322 cm^{-1} assigned to the ether bond shifted to a slightly higher wavenumber (1337 cm^{-1}). The large shift in the C=O bond peak toward lower wavenumbers indicates that functional groups containing the C=O bond which absorbs at high frequencies (1765-1818 cm^{-1}) reacted with $LiAlH_4$. The slight shift in the peak assigned to the C-O-C bond is probably due to the interaction among the functional groups on the diamond surface.

To determine which C=O-containing functional groups react with $LiAlH_4$, the oxygenated diamond powder was suspended, either directly or following a 1-hour $LiAlH_4$ treatment, in 1 mol dm^{-3} NaOH solution at 333 K for 3 h. Figure 8.6 shows the IR spectra of the diamond powder treated with NaOH solution. If -COOH and -OCOCO- groups are present on the treated diamond surface, they will form -COONa groups, yielding the C=O peaks assigned to –COO^- groups. Figures 8.6(a) and 8.6(b) show the IR spectra of oxygenated diamond powders treated with $LiAlH_4$ and treated with NaOH following the $LiAlH_4$ treatment, respectively. The shape of the IR spectrum of the diamond powder treated with NaOH largely resembled that of the untreated powder (Figure. 8.6(a) and 8.6(b)). It was found that -COOH and -OCOCO- groups were not present on the $LiAlH_4$ treated diamond surface. Figure 8.6(c) shows the IR spectrum of oxygenated diamond powder treated with NaOH, and Figure 8.6(d) shows that of oxygenated diamond powder. In the case of oxygenated diamond powder, the peak at 1818 cm^{-1} shifted to 1795 cm^{-1}, and the peak intensity at 1646 cm^{-1} increased (Figures 8.6(c) and 8.6(d)). This peak shift was caused by the hydrolysis of the -OCOCO- groups. The peak at 1646 cm^{-1} may be ascribed to the COO^- groups [13]. These results indicate that the –COOH and

-OCOCO- groups on ODS were probably reduced by $LiAlH_4$.

The difference in reactivity of carbonyl towards $LiAlH_4$ on ODS may be partly due to the degree of polarity of the carbonyl carbon. The hydride ion (H^-) of $LiAlH_4$ attacks the carbon of the carbonyl group at its positive pole, reducing the C=O bond to the O-H bond. The carbonyl carbon, with its large positive pole, is much more subject to nucleophilic addition. Because they are bonded to two oxygen atoms, the carbonyl carbons of the -OCOCO- and -COOH groups have larger positive poles than those of cyclic ketone. Thus, -COOH and -OCOCO- groups would be more likely to react than the ketone (C=O) groups.

It is known that C=O-containing functional groups on graphite or polymer surfaces are simply reduced to hydroxyl groups by $LiAlH_4$ [22, 23]. In this research, it was found that C=O-containing functional groups of diamond surface were unlikely to be reduced to hydroxyl groups by $LiAlH_4$ compared to that of other carbon materials. Diamond consists of carbon atoms bonded together via sp^3 hybrid orbitals, while the carbon atoms in graphite are bonded together via sp^2 hybrid orbitals. It is considered that the difference of the structures between diamond (sp^3 hybrid orbital) and graphite (sp^2 hybrid orbital) would affects the chemical reactivity of C=O-containing functional groups on surface.

8.4. Conclusion

We confirmed the chemical reaction between the oxygenated diamond surface (ODS) and an organic chemical reagent. The C=O groups on ODS were reduced to O-H groups by $LiAlH_4$. However, the reactivity of the C=O bonds on the diamond surface was not homogeneous. The -COOH and –OCOCO- groups on ODS are readily reduced by $LiAlH_4$, whereas C-O-C groups were stable to $LiAlH_4$.

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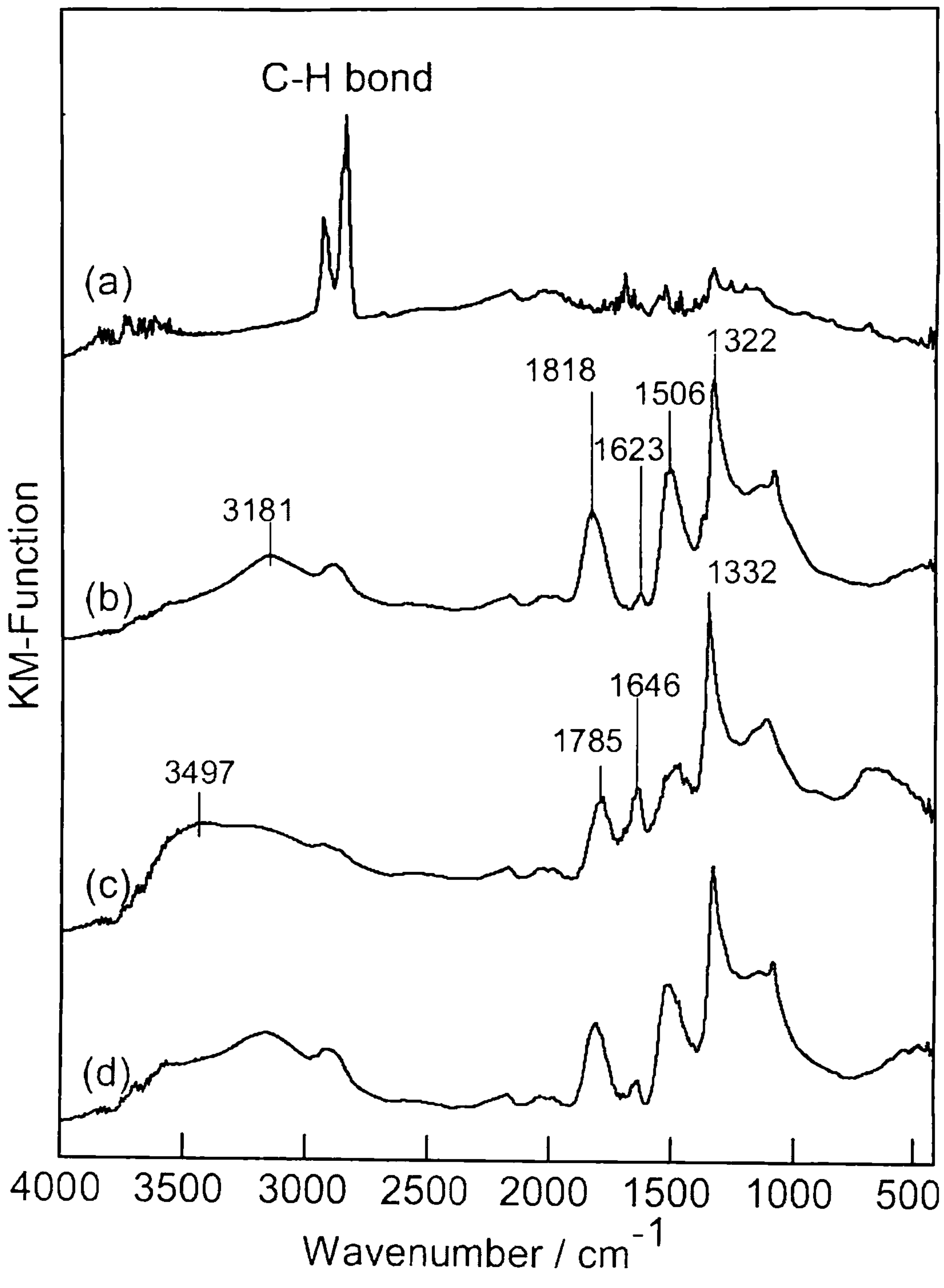

Figure 8.1 IR spectra of diamond powders: (a) hydrogenated diamond, (b) oxygenated diamond, (c) oxygenated diamond treated with $LiAlH_4$, (d) oxygenated diamond treated with deactivated $LiAlH_4$.

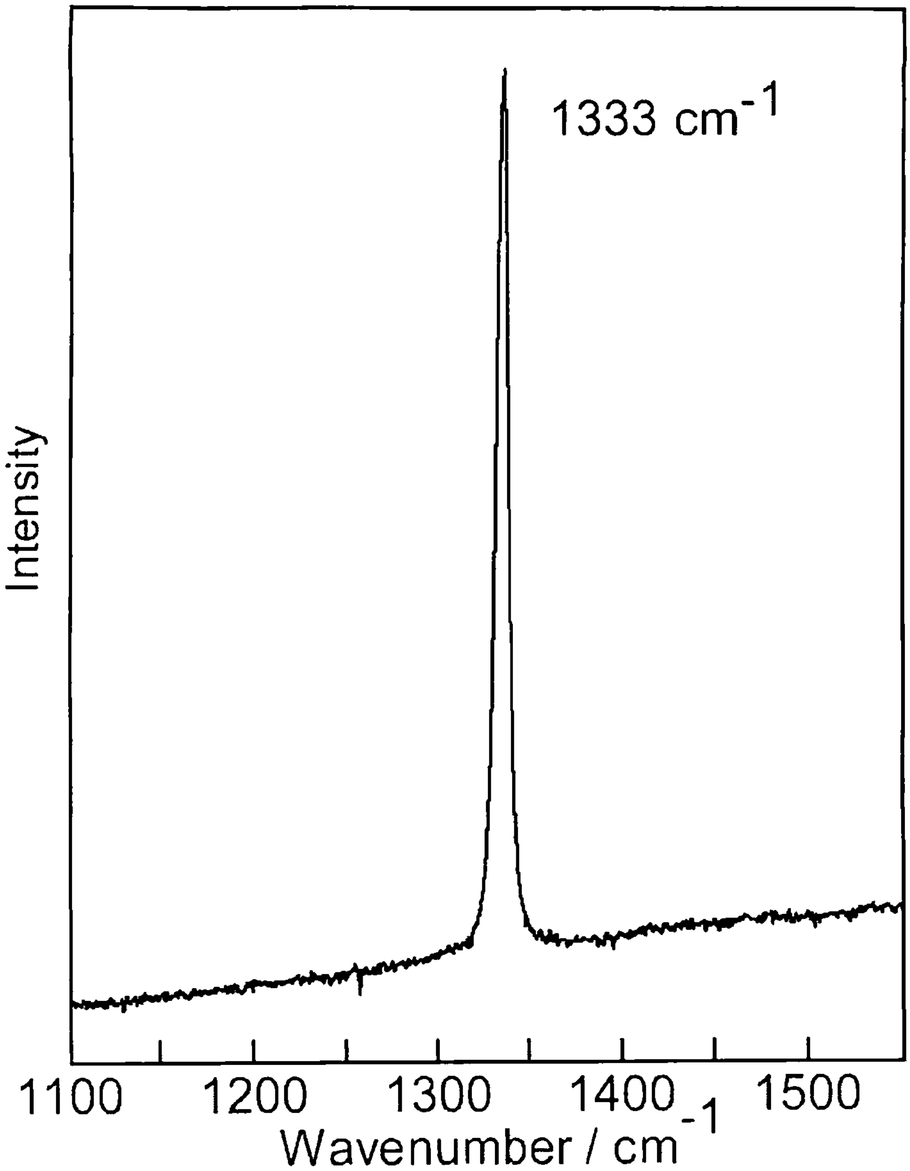

Figure 8.2 Raman spectrum of diamond film.

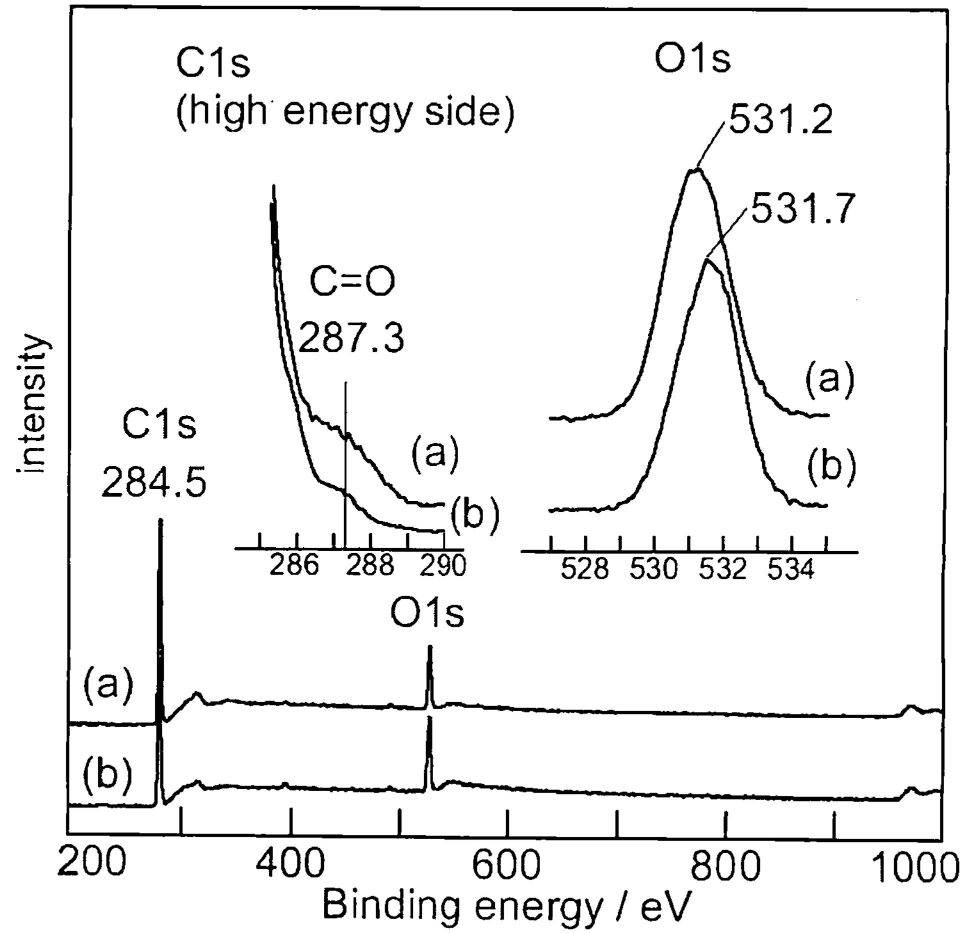

Figure 8.3 XPS spectra of oxygenated diamond films (a) before and (b) after $LiAlH_4$ treatment.

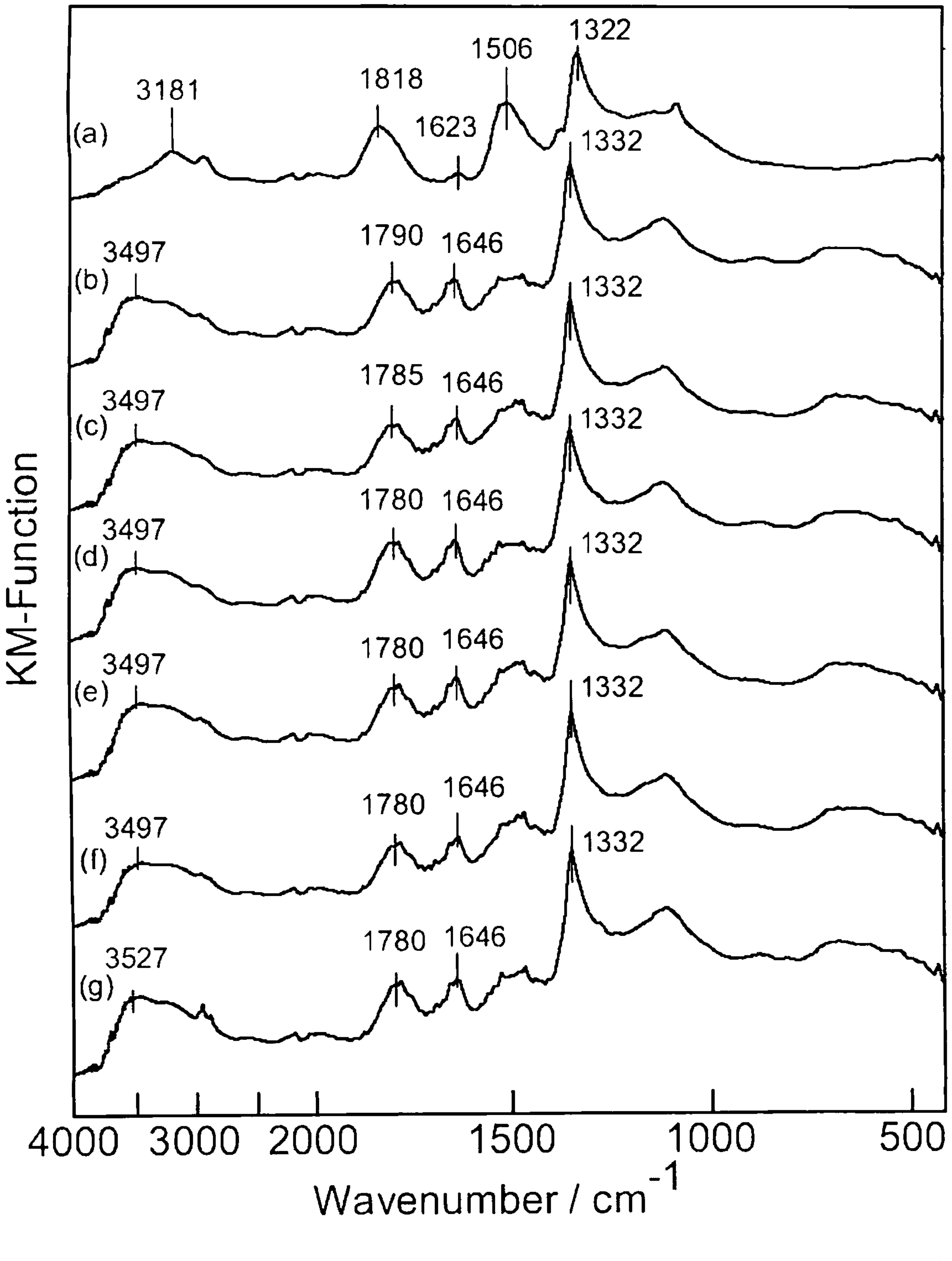

Figure 8.4 IR spectra of the diamond powders reacted with $LiAlH_4$ in $C_2H_5OC_2H_5$. (a) The amount of $LiAlH_4$ = 0 g, (b) 0.005 g, (c) 0.01 g, (d) 0.03 g, (e) 0.05 g, (f) 0.1 g, (g) 0.3 g.

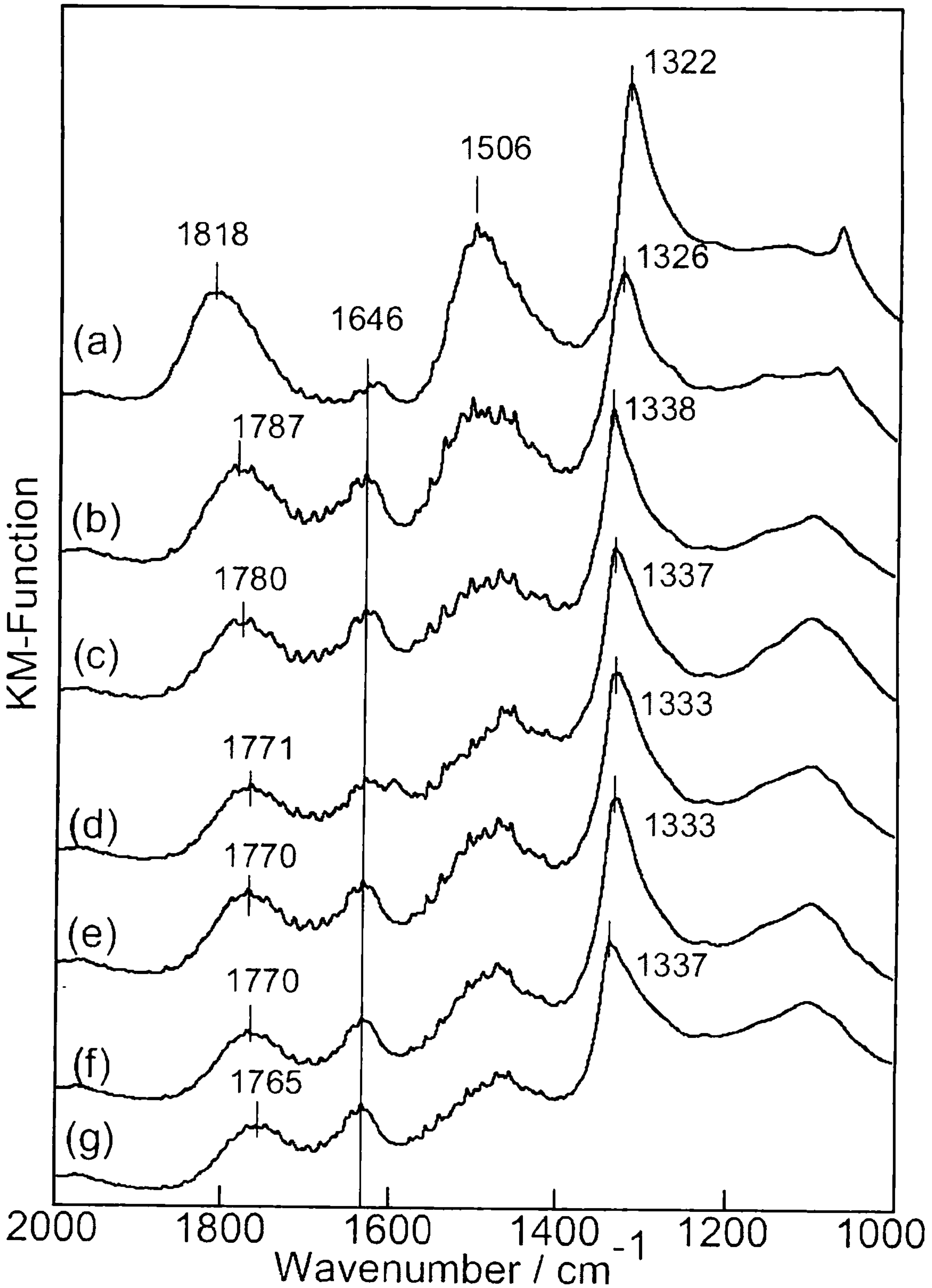

Figure 8.5 IR spectra of diamond powders treated with $LiAlH_4$ (0.1 g): (a) reaction time = 0 min, (b) 5 min, (c) 2 h, (d) 1 day, (e) 3 days, (f) 7 days, (g) 3 weeks.

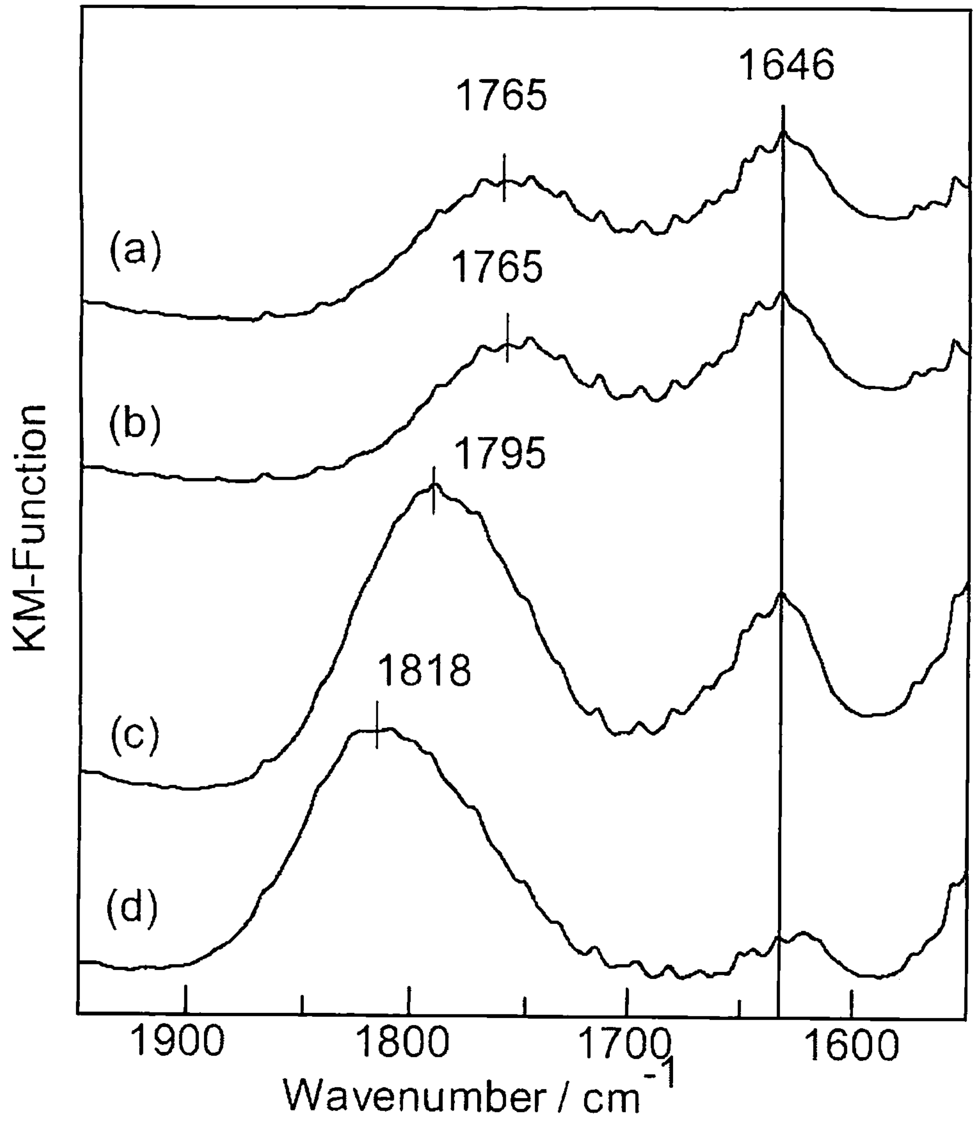

Figure 8.6 IR spectra of oxygenated diamond powders (a) treated with $LiAlH_4$, (b) treated with NaOH following the $LiAlH_4$ treatment, (c) treated with NaOH, (d) prior to any treatment.

Chapter 9

Surface modification of the oxygenated diamond surface with silane coupling reagents

Chapter 9

Surface modification of the oxygenated diamond surface with silane coupling reagents

9.1. Introduction

Diamond is one of the most promising materials for industrial applications because of its excellent properties such as high hardness, large band gap, and transparency over a wide wavelength region. So far, a number of researchers have studied synthesized diamond for industrial applications. Most of the studies have focused on the properties of diamond as a bulk material. Nowadays, several researchers are interested in the properties of the diamond surface [1-21]. However, the reactivity, as well as the properties, of the diamond surface remains unclear to date.

Diamond as a bulk material is inert to chemical reagents. This is one of the reasons why diamond is a promising industrial material. However, this inertness prevents diamond from forming composites with other materials. If a technique for diamond surface reforming were to be established, diamond composite materials would be easy to develop. Diamond as a bulk material has various specific properties. On the other hand, organic functional groups also possess various functions such as ion exchange, molecular recognition, and so on. If functional groups were controllably introduced on the diamond surface, we could develop new types of organic-inorganic hybrid materials.

Silane coupling reagents are utilized for the surface reforming of fillers. In general, there are two kinds of functional groups comprising the silane coupling reagents. One of the functional groups reacts with the surface of inorganic materials such as SiO_2. The other functional group reacts with the functional group of organic compounds. If silane coupling reagent reacts with the diamond surface, organic functional groups will be introduced on the diamond surface.

In this study, we carried out the silane coupling reaction of oxidized diamond surfaces using silane coupling reagents for diamond surface reforming.

9.2. Experimental

Commercial diamond powder (average diameter: 500 nm) was used as the diamond substrate in this study. In order to remove impurities from the diamond surface, we washed the diamond powder with mineral acids. First, the diamond powder was washed with mixed acid (HF + HNO_3) at room temperature for 4 hours, and then rinsed with distilled water a few times. After drying, the diamond powder was washed with mixed acid (H_2SO_4 + HNO_3) at 80℃ for 4 hours, and then rinsed with distilled water a few times. The oxidized diamond powder was dried in a desiccator. The diamond powder obtained after these processes is called "washed diamond" in this study.

Hydrogenated surface diamond powder was prepared in order to control the oxygenation conditions of the diamond surface. A portion of the "washed diamond" powder was heated in H_2 gas flow at 900℃ for 5 hours. The diamond powder obtained after these processes is called "hydrogenated surface diamond" in this study.

The hydrogenated surface diamond powder was treated with mineral acid (H_2SO_4, HNO_3 + H_2SO_4, or aqua regia) for the oxygenation of the diamond surface. The hydrogenated diamond powder was suspended in these mineral acids, and then these suspensions were refluxed for 4 hours. After this oxygenation process, the diamond powders were washed with distilled water, and dried in a desiccator. The diamond powders obtained after these processes are called "oxidized surface diamond", and were used as the diamond substrate for the silane coupling reagents in this study.

The silane coupling reagents used in this study are I: *n*-octyltrimethoxysilane, II: 3-aminopropyltrimethoxysilane, and III: 3-mercaptopropyltrimethoxysilane. The chemical structures of these reagents are as follows.

I: $CH_3(CH_2)_6CH_2\text{-}Si(\text{-}OCH_3)_3$
II: $H_2NCH_2CH_2CH_2\text{-}Si(\text{-}OCH_3)_3$
III: $HSCH_2CH_2CH_2\text{-}Si(\text{-}OCH_3)_3$

Oxidized surface diamond powder (0.1 g) and a silane coupling reagent (1 ml) were added to a solvent (methanol, toluene or acetone), and the mixture was stirred. The mixture was heated at 60℃ for 16 hours. After this reaction process, the diamond powder was separated from the solvent, and then dried in a desiccator at 110℃ for 16 hours. We carried out the (washing -> drying -> measurement) process repeatedly to evaluate the stability of the diamond surface.

Surface conditions of diamond powder were characterized by diffuse reflectance infrared Fourier-transform (FT-IR) spectroscopy (JASCO FT/IR-700).

9.3. Results and discussion

9.3.1. Oxidation of hydrogenated diamond surface with mineral acids

In general, the chemical formula of the silane coupling reagent is as follows:

$$X\text{-}Si(\text{-}OR)_3 \qquad (1)$$

(X: alkyl group, amino group, mercapto group and so on, OR: methoxy group, ethoxy group)

It is known that the OR group (methoxy group, ethoxy group) in the silane coupling reagent reacts with the OH group on inorganic materials such as metal oxide and glass.

It has been reported in chapter 7 that there is a peak assigned to the OH group in the IR spectrum of the diamond powder treated with mineral acid. We attempted to introduce the OH group on the diamond surface using strong mineral acids. The IR spectra of hydrogenated surface diamond and oxidized surface diamond powders are shown in Figure 9.1. There are two peaks assigned to the C-H bond in the IR spectrum of hydrogenated diamond powder. It was reported that the peak at *ca.* 2840 cm^{-1} is assigned to the symmetric vibration of the C-H bond and the peak at *ca.* 2930 cm^{-1} is the assigned to asymmetric vibration of the C-H bond. The shape of the IR spectrum of the hydrogenated surface diamond powder agrees with that of the IR spectrum of the hydrogenated diamond powder reported in chapter 2.

The IR spectrum of the diamond powder refluxed in H_2SO_4 had a rather different shape from that of the hydrogenated surface diamond powder. The sharp peaks assigned to the C-H bond disappeared after the treatment with H_2SO_4. The broad peak appearing at *ca.* 3200 cm^{-1} is assigned to the O-H bond. The small peak at *ca.* 1630 cm^{-1} and the large peak at *ca.* 1760 cm^{-1} are assigned to the C=O bond in the carboxyl group and the C=O bond in the anhydrous carboxyl group, respectively. The assignment of the large complex peaks at 800-1500 cm^{-1} is difficult, but we can presume that these peaks are assigned to the chemical bonds between carbon and oxygen atoms such as the C-O-C bond and so on. The peaks assigned to the oxygen-containing functional groups, such as the O-H bond, the C=O bond and the C-O-C bond, appeared in the IR spectrum after the H_2SO_4 treatment. It is unclear from the experimental data in this study whether these peaks are derived from the chemical bond on the diamond surface or from adsorbates such as H_2O and CO_2. However, the chemical reaction of the diamond surface must have taken place during treatment with H_2SO_4 because the peaks assigned to the C-H bond disappeared after the treatment.

After the treatment with H_2SO_4 + HNO_3 mixed acid, the peaks assigned to the C-H bond disappeared from the IR spectrum. In their place, a peak assigned to the O-H bond appeared at *ca.* 3200 cm^{-1}. However, the shape of this peak differed from that of the diamond treated with H_2SO_4. In this IR spectrum, we can observe peaks assigned to the C=O bond of the carboxyl group or the anhydrous carboxyl group. However, the peak assigned to the anhydrous carboxyl group of this diamond powder was found at *ca.* 1820 cm^{-1}, and was shifted to the higher field compared to that of the diamond powder treated with H_2SO_4. The shape of the peaks at 800-1500 cm^{-1} for this diamond powder was also different from that of the diamond powder treated with H_2SO_4. These differences are believed to indicate the difference in the diamond surface conditions.

The IR spectrum of the diamond powder treated with aqua regia is rather different from that of the diamond powders treated with H_2SO_4 or H_2SO_4+HNO_3. The intensity of the peak assigned to the C-H bond decreased after the treatment with aqua regia. However, the peaks remained to some extent. The broad peak assigned to the O-H bond did not appear after this treatment. The peak assigned to the C=O bond appeared although its intensity is low. The shape of the IR spectrum at 800-1500 cm^{-1} of this sample was rather different from that of the diamond powders treated with H_2SO_4 or H_2SO_4+HNO_3. The conspicuous peak at 1440-1500 cm^{-1} in the spectrum of the diamond powder treated with H_2SO_4 or H_2SO_4+HNO_3 was absent in the spectrum of the diamond powder treated with aqua regia.

From these experimental results, it was confirmed that the diamond surface conditions depended on the mineral acids utilized. It is known that the O-H group combines with the functional group in the silane coupling reagents. Because the purpose of this study is to realized diamond surface reforming with silane coupling reagents, we used the diamond powder treated with H_2SO_4 or H_2SO_4+HNO_3 as the diamond substrate for the silane coupling reagent.

9.3.2. IR spectra of diamond powders

First, the diamond powder treated with H_2SO_4 was used as the diamond substrate. The IR spectra after the treatment with the silane coupling reagent are shown in Figure 9.2.

The peaks assigned to the C-H bond appeared in all the IR spectra for the diamond powder after the treatment with *n*-octyltrimethoxysilane even after three washings. Alkyl groups, which are contained in *n*-octyltrimethoxysilane, must exist on the treated diamond powder.

After the treatment with 3-aminopropyltrimethoxysilane, new peaks appeared in the IR spectra even after three washings. These peaks are assigned to the C-H bond and the N-H bond, which are contained in 3-aminopropyltrimethoxysilane. When methanol was used as the solvent (for the reaction process and for the washing process), the peak assigned to the N-H bond at *ca.* 3300 cm^{-1} was negligible.

When 3-mercaptopropyltrimethoxysilane was used as the silane coupling reagent, the peak assigned to the S-H bond appeared at *ca.* 2560 cm^{-1} in all of the IR spectra. The silane coupling reagent, therefore, must exist on the diamond treated with 3-mercaptopropyltrimethoxysilane even after three washings. The intensity of the peak assigned to the S-H bond depended on the kind of solvent used. The peak assigned to the S-H bond of the diamond treated in acetone was smaller than those of the others. When toluene was used as the solvent, a large peak appeared at *ca.* 1100 cm^{-1}, which was assigned to the Si-O bond.

Next, the diamond powder treated with H_2SO_4 + HNO_3 was used as the diamond substrate. The IR spectra obtained after the treatment processes are shown in Figure 9.3. The characteristics of these IR spectra are similar to those of the spectra of the diamond treated with H_2SO_4. We can surmise, therefore, that the diamond surface conditions after treatment with the silane coupling reagent are essentially independent of the difference between the diamond surface treated with H_2SO_4 and that treated with H_2SO_4 + HNO_3.

We attempted to estimate the stability of the diamond surface quantitatively. The small peak at *ca.* 2160 cm^{-1} in the IR spectra is assigned to the two-phonon absorption. The two-phonon adsorption is attributed not to diamond surface, but to diamond as a bulk. The peak intensity of the two-phonon absorption, $I_{\text{two-phonon}}$, was used as an internal standard, as in previous reports[12, 18, 19]. All the silane coupling reagents used in this study have the C-H bond in their structures. In contrast, there is no peak assigned to the C-H bond in the IR spectra of the diamond substrates. The peak intensity of the C-H bond, $I_{\text{C-H}}$, therefore, is suitable for the estimation of the relative proportion of the silane coupling reagent on the diamond surface. Figure 9.4 shows $I_{\text{C-H}}/I_{\text{two-phonon}}$ values of the IR spectra for diamond powders treated with silane coupling reagents. The $I_{\text{C-H}}/I_{\text{two-phonon}}$ values remained high after the three times washing process. The silane coupling reagents on the diamond surface are therefore stable against the organic solvents used in this study. The $I_{\text{C-H}}/I_{\text{two-phonon}}$ value clearly increased with increasing washing time in Figure 9.4 B(a) and Figure 9.4 B(b). The reason for this increase is unclear. However, it is clear that three times washing process with organic solvent cannot remove the silane coupling reagent on the diamond surface.

From these experimental results, it is obvious that:

1. The diamond surface conditions after treatment with the silane coupling reagent are essentially independent of the difference between the diamond surface treated with H_2SO_4 and that treated with H_2SO_4 + HNO_3.
2. Silane coupling reagents exist on the diamond surface even after three times washing process with organic solvent.

3. The surface conditions after treatment with the silane coupling reagent depend on the kind of the solvent (for the reaction process and for the washing process) to some extent.

Based on the reaction mechanism of the silane coupling reagent with the SiO_2 surface, the reaction of the silane coupling reagent with oxidized surface diamond surface was presumed to be as follows:

$$\begin{aligned}&\mathrm{X\text{-}Si(\text{-}OCH_3)_3 + (diamond)(\text{-}OH)_3}\\ &\rightarrow \mathrm{(diamond)(\text{-}OH)_2(\text{-}O\text{-}Si(\text{-}OCH_3)_2(\text{-}X)) + CH_3OH} \qquad (2)\end{aligned}$$

$$\begin{aligned}&\mathrm{(diamond)(\text{-}OH)_2(\text{-}O\text{-}Si(\text{-}OCH_3)_2(\text{-}X))}\\ &\rightarrow \mathrm{(diamond)(\text{-}OH)((\text{-}O\text{-})_2Si(\text{-}OCH_3)(\text{-}X)) + CH_3OH} \qquad (3)\end{aligned}$$

$$\begin{aligned}&\mathrm{(diamond)(\text{-}OH)((\text{-}O\text{-})_2Si(\text{-}OCH_3)(\text{-}X))}\\ &\rightarrow \mathrm{(diamond)((\text{-}O\text{-})_3Si\text{-}X) + CH_3OH} \qquad (4)\end{aligned}$$

If the chemical reactions shown in eqs. (2)-(4) proceed, the silane coupling reagents will be introduced on the diamond surface. However, another chemical reaction must be considered. Each of the silane coupling reagents used in this study have three methoxy groups in their structures. The following chemical reactions, therefore, are also presumed.

$$\mathrm{X\text{-}Si(\text{-}OR)_3} + n\,\mathrm{H_2O} \rightarrow \mathrm{X\text{-}Si(\text{-}OR)_{3\text{-}n}(\text{-}OH)_n} + n\,\mathrm{ROH} \qquad (5)$$

$$\begin{aligned}&m\ \mathrm{X\text{-}Si(\text{-}OR)_{3\text{-}n}(\text{-}OH)_n}\\ &\rightarrow \mathrm{(\text{-}O\text{-}Si(\text{-}X)(\text{-}OR)\text{-}O\text{-}Si(\text{-}X)(\text{-}OR)\text{-}O\text{-}Si(\text{-}X)(\text{-}OR)\text{-}O\text{-})_m}\\ &\quad + ((m\text{-}1)+a)\mathrm{H_2O}\ \text{(network structure)} \qquad (6)\end{aligned}$$

The network structure derived from the silane coupling reagent may exist on the diamond surface treated with the silane coupling reagent. We were unable to determine the condition of the silane coupling reagents on the diamond surface. However, in any event, the silane coupling reagents must be strongly retained on the diamond surface.

9.3.3. Conditions of diamond powders treated with silane coupling reagents

In order to confirm the effectiveness of the silane coupling reagent in diamond surface reforming, the diamond powder conditions were investigated. The properties of diamond powders after the washing process are summarized in Tables 9.1 and 9.2. When the diamond powder treated with H_2SO_4 was used as the diamond substrate, the diamond powders treated with *n*-octyltrimethoxysilane or 3-mercaptopropyltrimethoxysilane in ethanol exhibited adhesiveness, and the diamond powder treated with 3-aminopropyltrimethoxysilane exhibited hardness.

The properties of the diamond powders treated with H_2SO_4 + HNO_3 were similar to those of the diamond powders treated with H_2SO_4. The properties of the diamond powders treated with silane coupling reagents, therefore, depend not on the kind of solvent, but on the kind of reacted solvent. The diamond powder treated with *n*-octyltrimethoxysilane was soft, while the diamond powders treated with 3-aminopropyltrimethoxysilane or 3-mercaptopropyltrimethoxysilane were hard.

From the observations of the diamond powder, we note that:

1. The diamond powder conditions after treatment with the silane coupling reagent are essentially independent of the oxidized surface condition.
2. The diamond powder conditions depend on the kind of silane coupling reagent.
3. The kind of solvent weakly affects the diamond powder conditions.

9.3.4. Electrophoresis of diamond powders

Electrophoresis was performed to examine the surface reforming of diamond powder treated with silane coupling reagents. Diamond powders were suspended in water using an ultrasonic wave generation apparatus. Two Cu electrodes were dipped in the water, and then voltage was applied between the electrodes. The experimental results are shown in Table 9.3. The diamond powder treated with H_2SO_4 + HNO_3 was deposited on the anode. This result means that the zeta potential of the diamond surface treated with H_2SO_4 + HNO_3 is a negative value. If the diamond surface is covered with oxygen-containing functional groups such as the O-H group and the COOH group, then the zeta potential of the diamond surface should be a negative value. The experimental result, therefore, supports the existence of oxygen-containing functional groups on the diamond surface. The diamond powder treated with *n*-octyltrimethoxysilane did not disperse in water. There is an *n*-octyl group, which is a typical hydrophobic group, in *n*-octyltrimethoxysilane. This experimental result, therefore, supprts that the surface of the diamond powder treated with *n*-octyltrimethoxysilane is covered with *n*-octyl groups.

The diamond powder treated with 3-aminopropyltrimethoxysilane was deposited on the cathode. There is an amino group in 3-aminopropyltrimethoxysilane. The amino group reacts with water, and then ionizes as follows:

$$\text{-NH}_2 + \text{H}_2\text{O} \rightarrow \text{-NH}_3^+ + \text{OH}^-. \quad (7)$$

If the diamond surface is covered with 3-aminopropyltrimethoxysilane, then the diamond surface should have a positive zeta potential. The experimental result, therefore, indicates that the surface of the diamond powder treated with 3-aminopropyltrimethoxysilane is covered with amino groups.

The diamond powder treated with 3-mercaptopropyltrimethoxysilane deposited on the anode. There is a mercapto group in 3-mercaptopropyltrimethoxysilane. The mercapto group reacts with water, and then ionizes as follows:

$$\text{-SH} + \text{H}_2\text{O} \rightarrow \text{-S}^- + \text{H}_3\text{O}^+. \quad (8)$$

If the diamond surface is covered with 3-mercaptopropyltrimethoxysilane, then the diamond surface should have a negative zeta potential. The experimental result, therefore, indicates that the surface of the diamond powder treated with 3-mercaptopropyltrimethoxysilane is covered with amino groups.

9.3.5. Dispersion condition of diamond powders in solvent

A (water : *n*-hexane) solvent was used to confirm the change in the chemical properties of the diamond surface. The diamond powders treated with the silane coupling reagents were suspended in the (water : *n*-hexane) solvent. Diamond powder treated with H_2SO_4 + HNO_3 was also suspended in the (water : *n*-hexane) solvent. A photograph of these solvents is shown in Figure 9.5. The diamond powder treated with H_2SO_4 + HNO_3 dispersed well in water. It is known that the oxidized diamond surface is hydrophilic. The dispersion of the diamond powder treated with H_2SO_4 + HNO_3 in water is expected. On the other hand, all the diamond powders treated with the silane coupling reagents stayed at the interface between water and *n*-hexane.

In order to examine the dispersion conditions of the diamond powders in solvent in detail, the diamond powders were suspended in water or *n*-hexane using the ultrasonic wave generation apparatus. The experimental results are shown in Figure 9.6. The containers were set on their sides to observe solvent conditions.

The diamond powder treated with H_2SO_4 + HNO_3 smoothly dispersed in water without the ultrasonic wave treatment. The diamond powder treated with *n*-octyltrimethoxysilane did not disperse in water even after the ultrasonic wave treatment. The diamond powder treated with 3-aminopropyltrimethoxysilane smoothly dispersed in water without the ultrasonic wave treatment. The diamond powder treated with 3-mercaptopropyltrimethoxysilane dispersed in water with the ultrasonic wave treatment.

The diamond powder treated with H_2SO_4 + HNO_3 dispersed in *n*-hexane with the ultrasonic wave treatment. However, the diamond powder precipitated after a while. Moreover, a portion of the diamond powder adhered to the side of the container.

The diamond powder treated with *n*-octyltrimethoxysilane dispersed in *n*-hexane after the ultrasonic wave treatment. The diamond powder did not adhere to the side of the container.

The diamond powder treated with 3-aminopropyltrimethoxysilane dispersed in *n*-hexane with the ultrasonic wave treatment. However, the diamond powder precipitated after a few minutes. Moreover, a portion of the diamond powder adhered to the side of the container.

The diamond powder treated with 3-mercaptopropyltrimethoxysilane dispersed in *n*-hexane with the ultrasonic wave treatment. However, the diamond powder precipitated after a while. Moreover, a portion of the diamond powder adhered to the side of the container.

The diamond surface treated with H_2SO_4 + HNO_3 is thought to be covered with oxygen atoms. We can consider that these oxygen atoms are part of the oxygen-containing functional groups such as the O-H group and the COOH group on the diamond surface, and that the functional groups ionize in water as follows:

$$\text{-OH} + H_2O \rightarrow \text{-O}^- + H_3O^+ \qquad (9)$$

$$\text{-COOH} + H_2O \rightarrow \text{-COO}^- + H_3O^+. \qquad (10)$$

These ionization processes may account for the smooth dispersion of the diamond powder treated with H_2SO_4 + HNO_3 in water. It is known that polar groups such as the OH group and the COOH group do not dissolve in *n*-hexane, which is one of the most typical nonpolar solvents. This is believed to be the reason for the precipitation of the diamond powder treated with H_2SO_4 + HNO_3 in *n*-hexane.

The diamond surface treated with *n*-octyltrimethoxysilane is thought to be covered with *n*-octyl groups. It is known that the *n*-octyl group, which is a nonpolar group, dissolves not in polar solvent such as water but in nonpolar solvent such as *n*-hexane. This is considered to be the reason for the difference in the dispersion conditions.

The diamond powder treated with 3-aminopropyltrimethoxysilane is thought to be covered with the 3-aminopropyl group ($-CH_2CH_2CH_2NH_2$). The NH_2 group in the 3-aminopropyl group may be responsible for the dispersion conditions of the diamond powder water and in *n*-hexane. In (water: *n*-hexane) solvent, the diamond powder treated with 3-aminopropyltrimethoxysilane stayed at the interface between water and *n*-hexane. The propyl group ($-CH_2CH_2CH_2-$) in the 3-aminopropyl group is hydrophobic and the amino group in the 3-aminopropyl group is hydrophilic. These properties of the functional groups introduced on the diamond surface may be the reason that the diamond powder stayed at the interface.

The diamond powder treated with 3-mercaptopropyltrimethoxysilane is thought to be covered with the 3-mercaptopropyl group (-$CH_2CH_2CH_2SH$). The SH group in the 3-mercaptopropyl group may be responsible for the dispersion conditions of the diamond powder in water and *n*-hexane. In (water: *n*-hexane) solvent, the diamond powder treated with 3- mercaptopropyltrimethoxysilane stayed at the interface between water and *n*-hexane. The propyl group (-$CH_2CH_2CH_2$-) in the 3-mercaptopropyl group is hydrophobic and the mercapto group in the 3-mercaptopropyl group is hydrophilic. These properties of the functional groups introduced on the diamond surface may be the reason that the stay on the diamond powder stayed at the interface.

9.4. Conclusion

Silane coupling reagents were used for diamond surface reforming. The IR spectrum of the diamond powder after treatment with the silane coupling reagent depended on the kind of silane coupling reagent used. The diamond surfaces treated with silane coupling reagents were stable in the presence of organic solvents. It was confirmed that silane coupling reagent is effective in changing the chemical properties of the diamond surface.

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Table 9.1 Characteristics of diamond powders treated with silane coupling reagents (diamond substrate: diamond powder treated with H_2SO_4)

	methanol	toluene	acetone
n-octyltrimethoxysilane	Viscous coagulation	Soft and slightly viscous coagulation	Soft and slightly viscous coagulation
3-aminopropyltrimethoxysilane	Hard coagulation	Hard coagulation	Hard coagulation
3-mercaptopropyltrimethoxysilane	Viscous coagulation	Hard coagulation	Hard coagulation

Table 9.2 Characteristics of diamond powders treated with silane coupling reagents (diamond substrate: diamond powder treated with H_2SO_4 + HNO_3)

	methanol	toluene	acetone
n-octyltrimethoxysilane	Soft and slightly coagulation	Soft and slightly viscous coagulation	Soft and slightly viscous coagulation
3-aminopropyltrimethoxysilane	Hard coagulation	Hard coagulation	Hardest coagulation
3-mercaptopropyltrimethoxysilane	Hard coagulation	Hard coagulation	Hard coagulation

Table 9.3 Electrophoresis of the diamond powder.

	Electrode deposited diamond powder
Diamond treated with H_2SO_4 + HNO_3	anode
Diamond treated with *n*-octyltrimethoxysilane	No dispersion in water
Diamond treated with 3-aminopropyltrimethoxysilane	cathode
Diamond treated with 3-mercaptopropyltrimethoxysilane	anode

Solvent: water

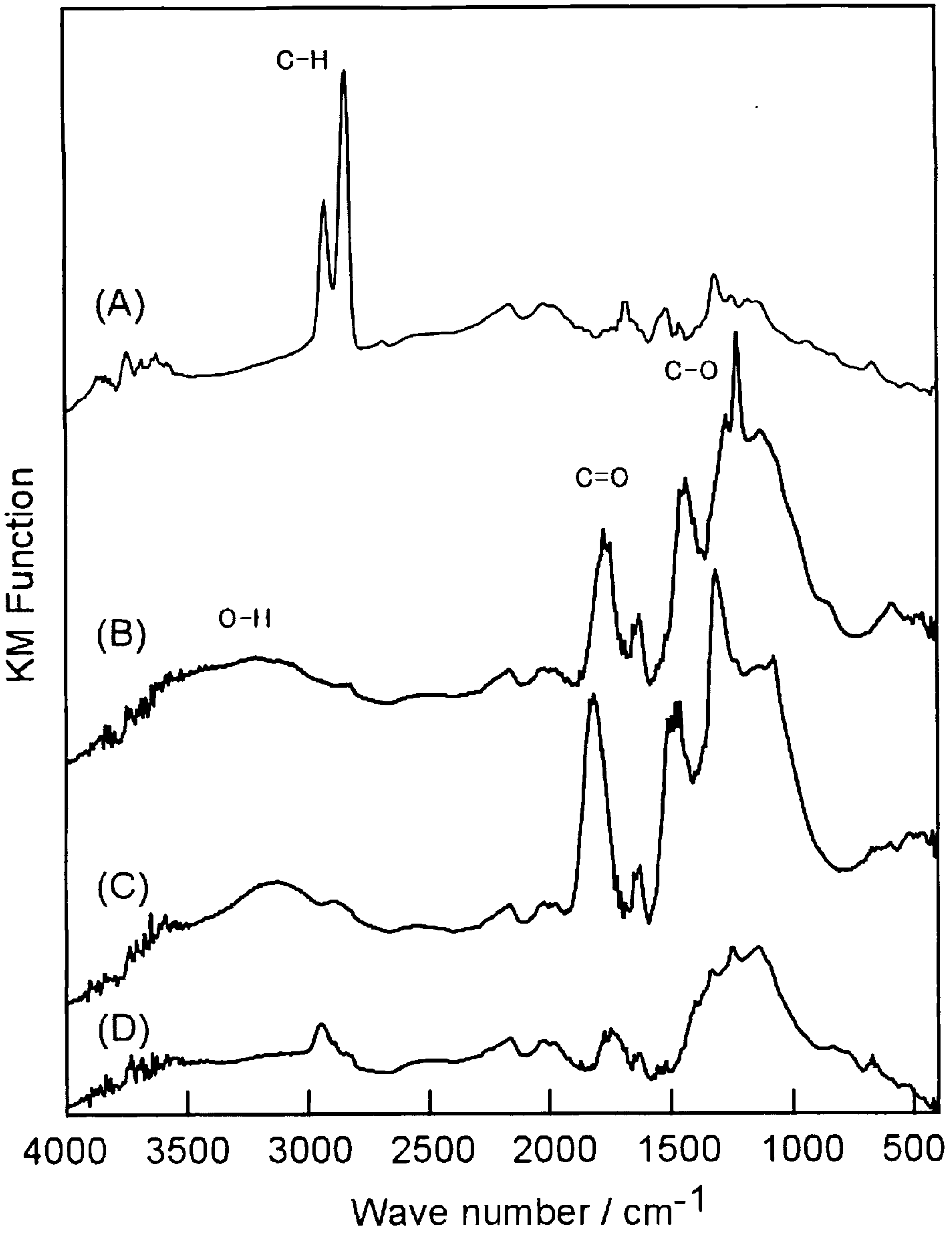

Figure 9.1 IR spectra of hydrogenated diamond powder and oxidized diamond powder. (A) hydrogenated diamond powder, (B) treated with H_2SO_4, (C) treated with H_2SO_4 + HNO_3, (D) treated with aqua regia.

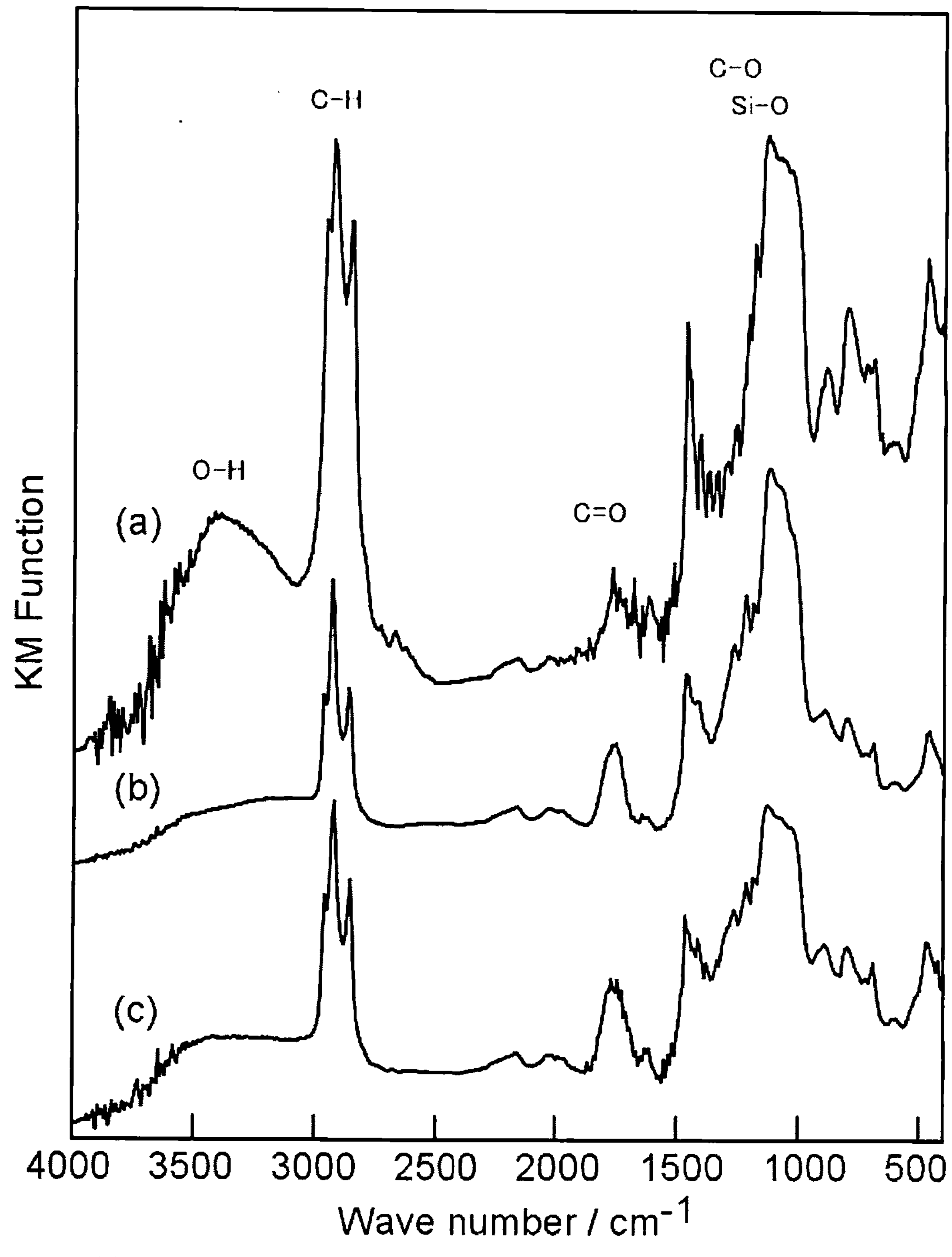

Figure 9.2(a) IR spectra of the diamond powder treated with n-octyltrimethoxysilane after three times washing process.

Diamond substrate: diamond treated with H_2SO_4 (sample(B) in Figure 9.1):

solvent:(a) methanol, (b) toluene, (c) acetone.

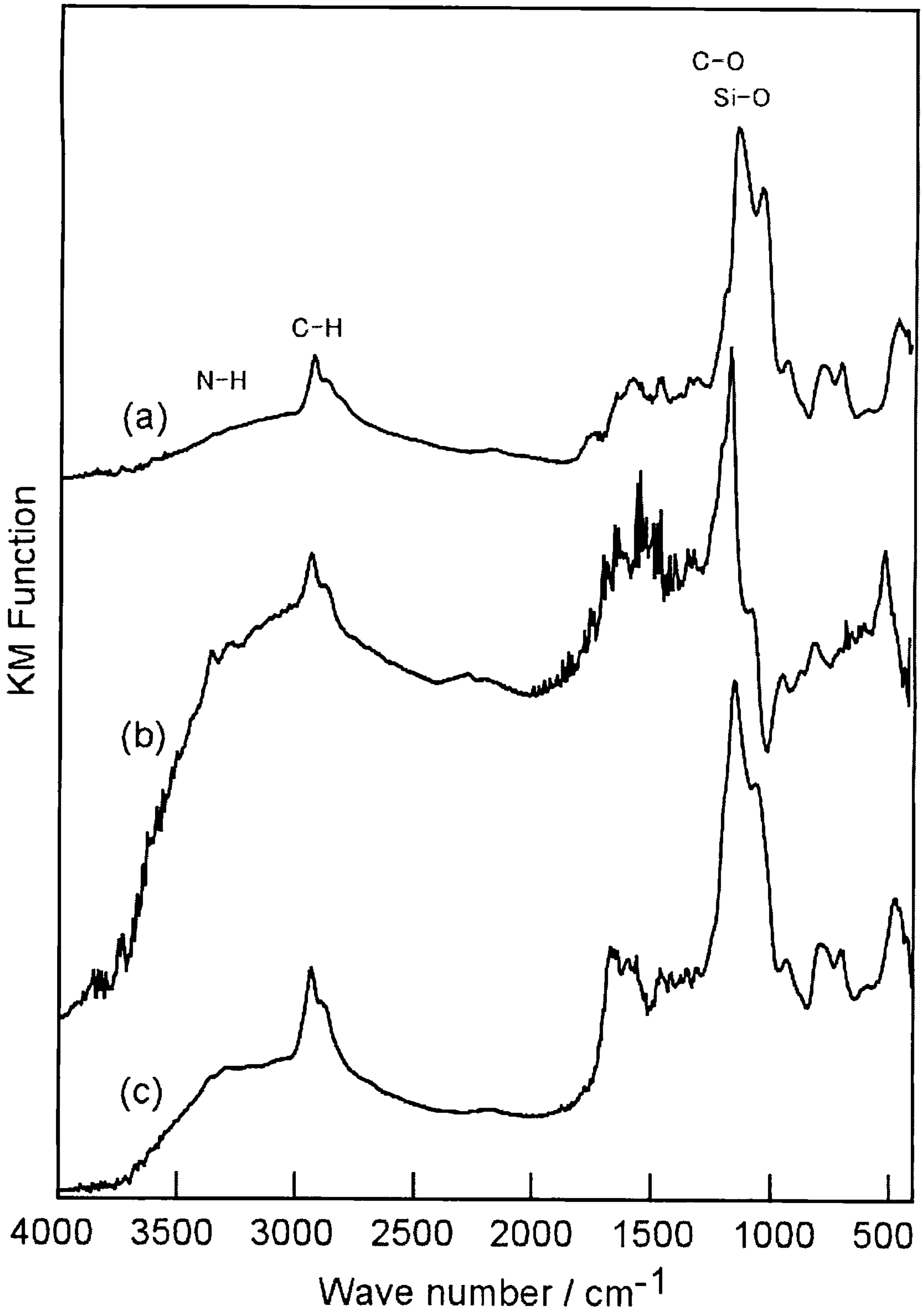

Figure 9.2(b) IR spectra of the diamond powder treated with 3-aminopropyltrimethoxysilane after three times washing process.
Diamond substrate: diamond treated with H_2SO_4 (sample(B) in Figure 9.1):
solvent:(a) methanol, (b) toluene, (c) acetone.

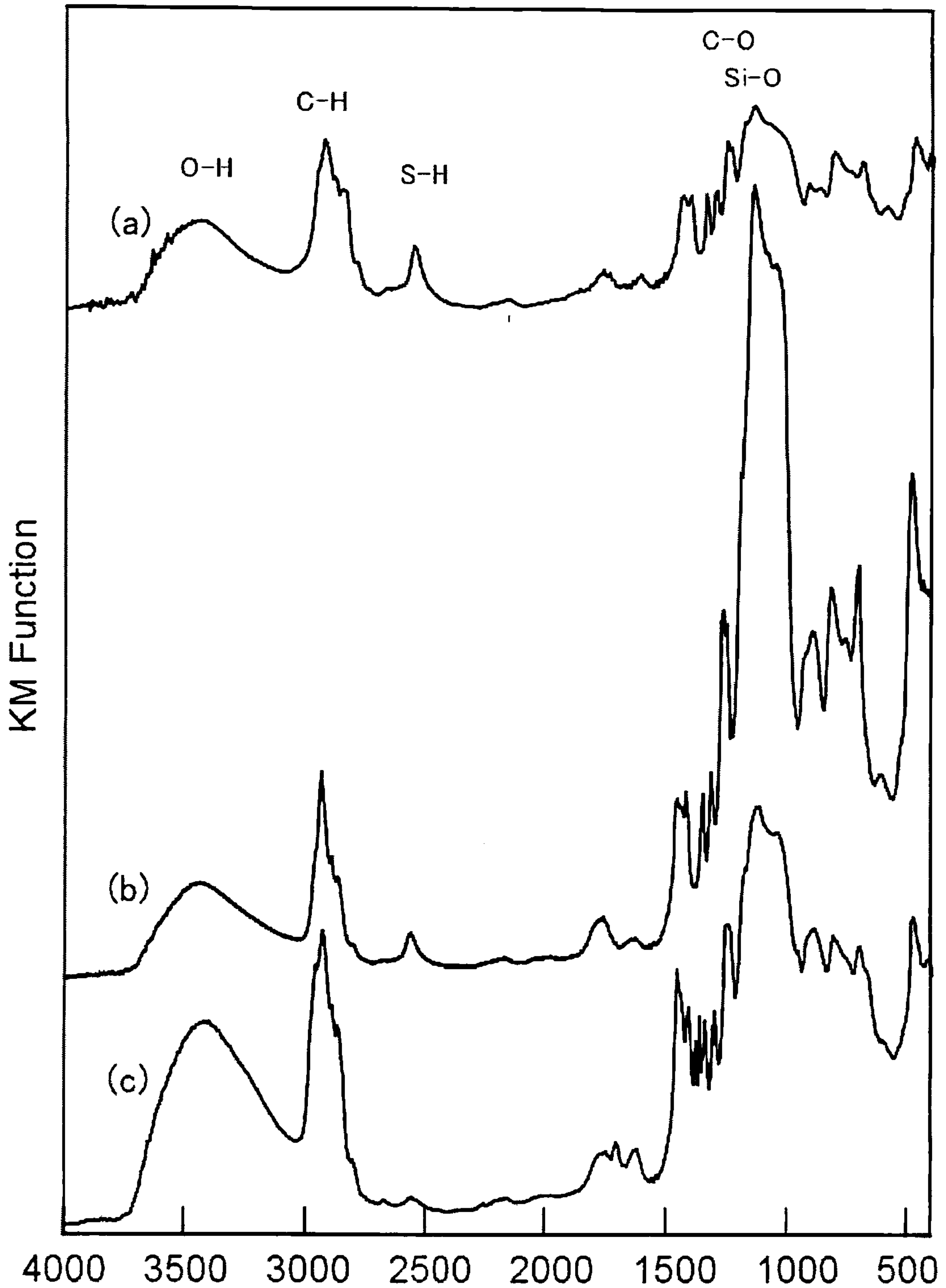

Figure 9.2(c) IR spectra of the diamond powder treated with 3-mercaptopropyltrimethoxysilane after three times washing process.
Diamond substrate: diamond treated with H_2SO_4 (sample(B) in Figure 9.1):
solvent:(a) methanol, (b) toluene, (c) acetone.

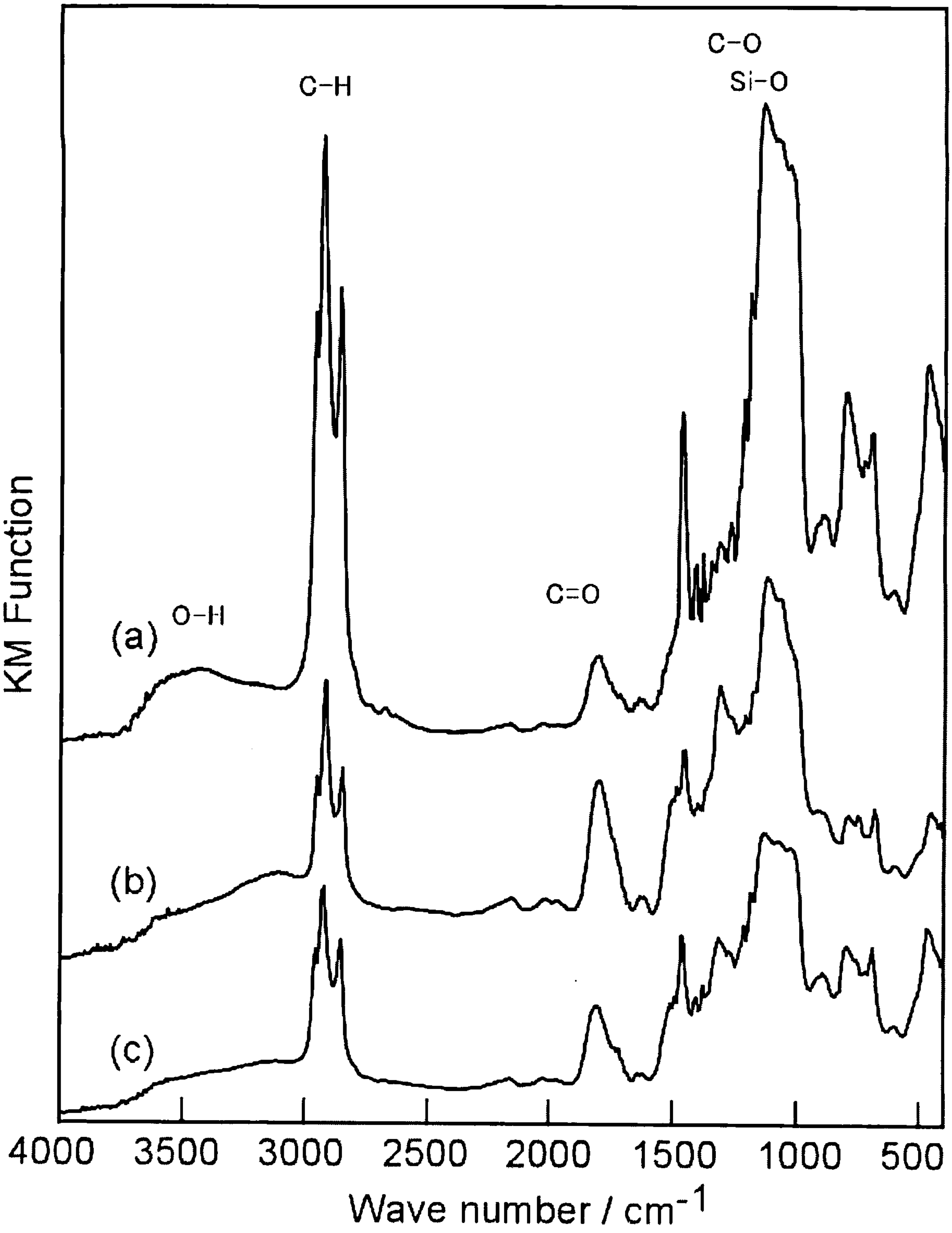

Figure 9.3(a) IR spectra of the diamond powder treated with n-octyltrimethoxysilane after three times washing process.

Diamond substrate: diamond treated with H_2SO_4 + HNO_3 (sample(C) in Figure 9.1): solvent:(a) methanol, (b) toluene, (c) acetone.

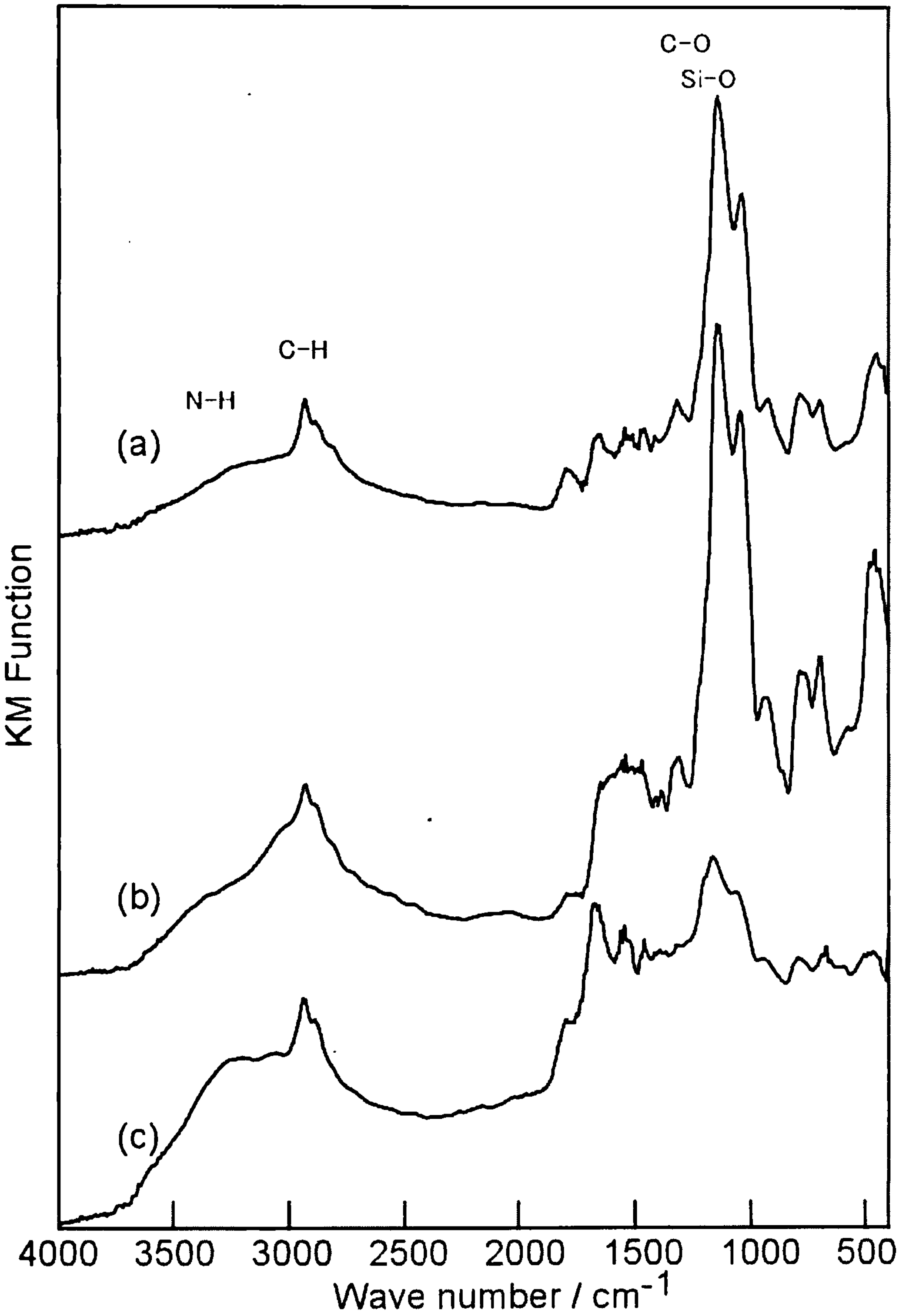

Figure 9.3(b) IR spectra of the diamond powder treated with 3-aminopropyltrimethoxysilane after three times washing process.

Diamond substrate: diamond treated with H_2SO_4 + HNO_3 (sample(C) in Figure 9.1): solvent:(a) methanol, (b) toluene, (c) acetone.

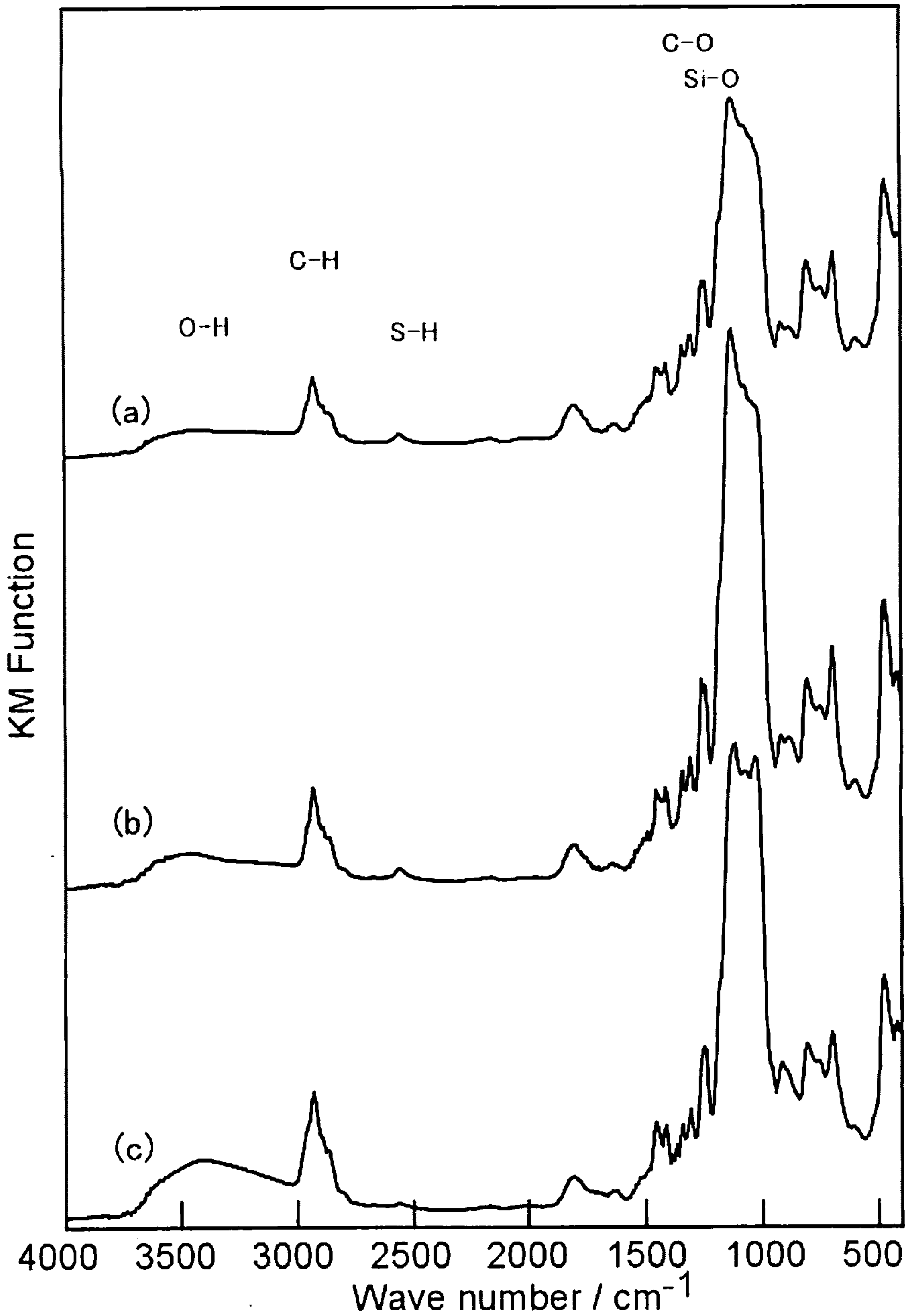

Figure 9.3(c) IR spectra of the diamond powder treated with 3-mercaptopropyltrimethoxysilane after three times washing process.

Diamond substrate: diamond treated with H_2SO_4 + HNO_3 (sample(C) in Figure 9.1): solvent:(a) methanol, (b) toluene, (c) acetone.

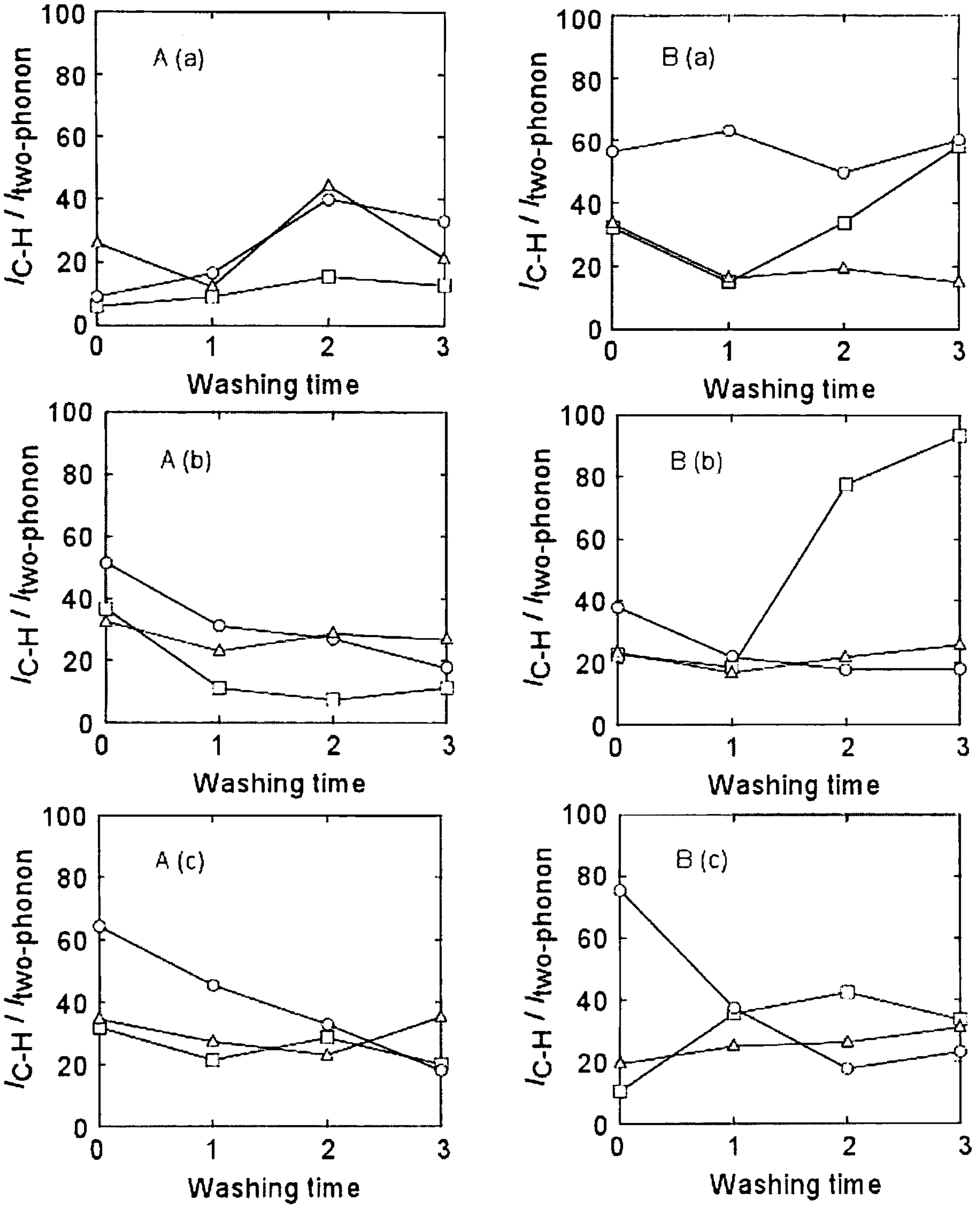

Figure 9.4 $I_{C\text{-}H} / I_{\text{two-phonon}}$ values of the IR spectra of diamond powders treated with silane coupling reagents.

A: diamond powder treated with H_2SO_4, B: diamond powder treated with H_2SO_4 + HNO_3, (a) methanol, (b) toluene, (c) acetone, ○ : n-octyltrimethoxysilane, □ : 3-aminopropyltrimethoxysilane, △: 3-mercaptopropyltrimethoxysilane.

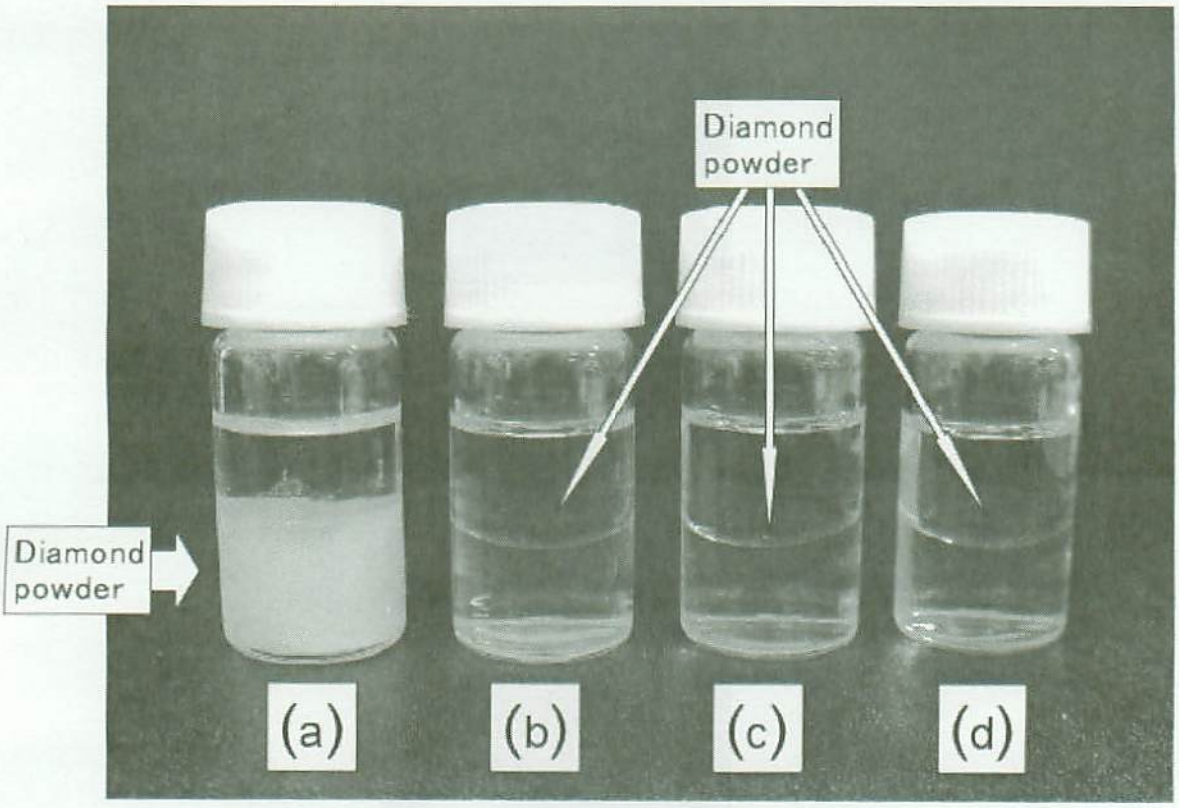

Figure 9.5 Dispersion of diamond powder.
(upper layer): n-hexane, (bottom layer): water, (a) diamond powder treated with H_2SO_4 +HNO_3, (b) diamond powder treated with n-octyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO4 +HNO_3), (c) diamond powder treated with 3-aminopropyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO_4 +HNO_3), (d) diamond powder treated with 3-mercaptopropyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO_4 +HNO_3)

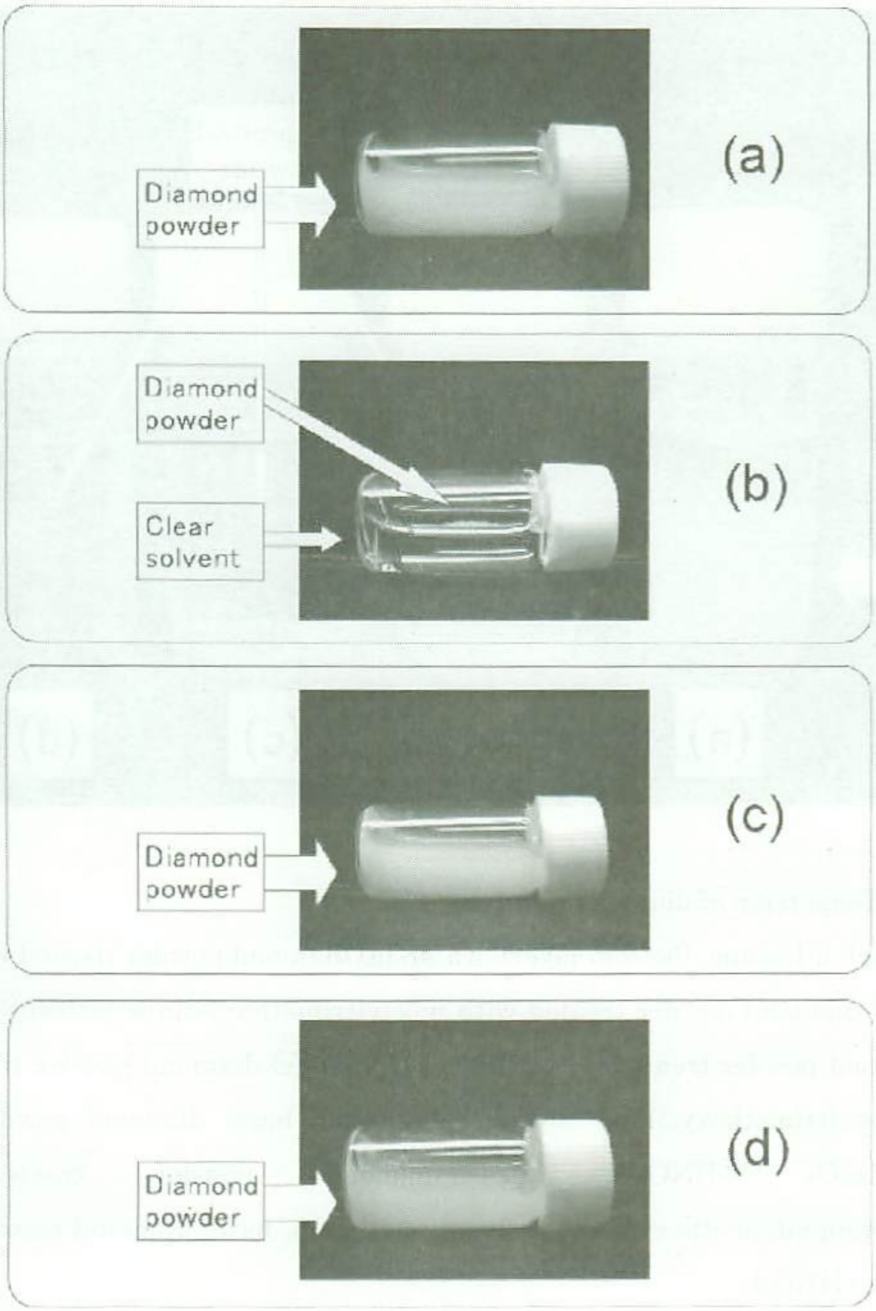

Figure 9.6(A) Dispersion of diamond powder after ultrasonic treatment.(solvent: water)

(a) diamond powder treated with H_2SO_4 +HNO_3, (b) diamond powder treated with n-octyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO4 +HNO_3), (c) diamond powder treated with 3-aminopropyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO_4 +HNO_3), (d) diamond powder treated with 3-mercaptopropyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO_4 +HNO_3)

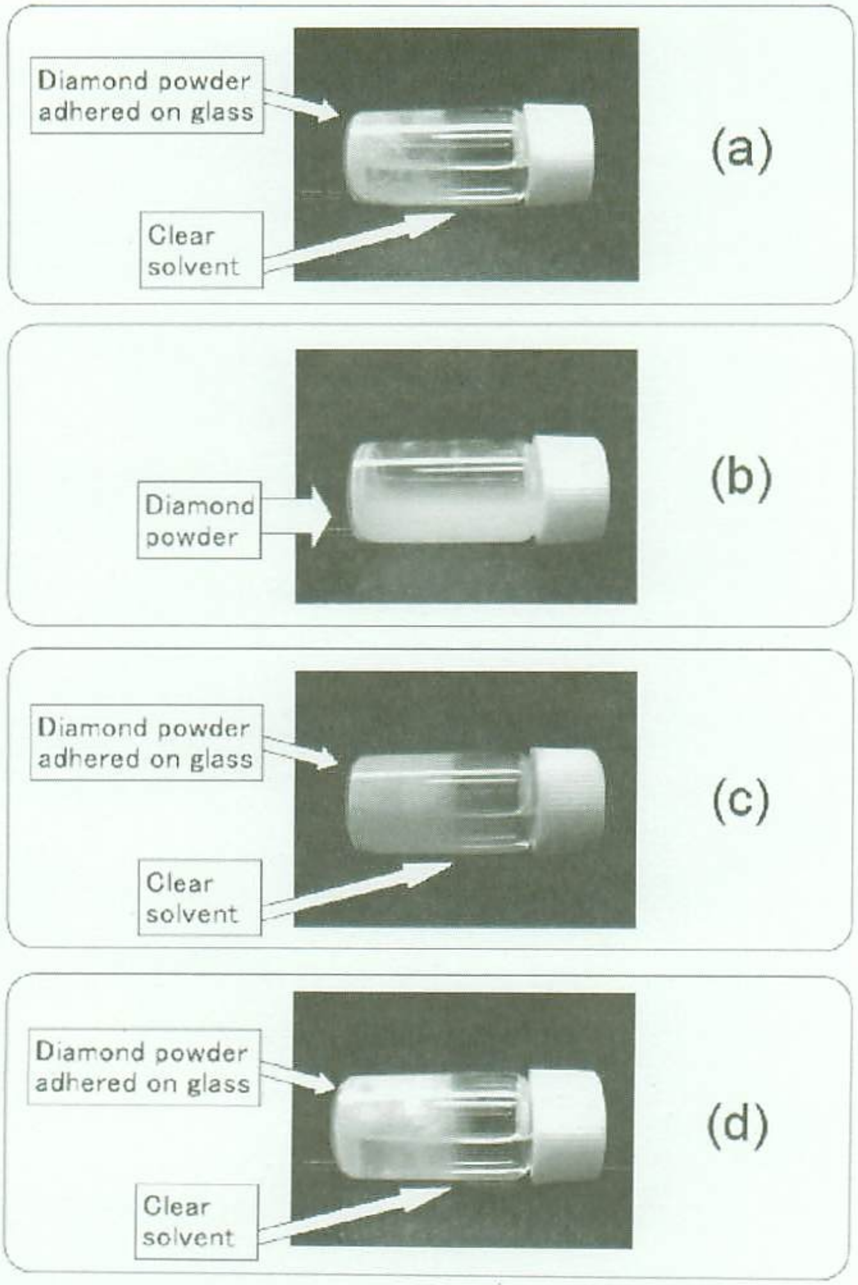

Figure 9.6(B) Dispersion of diamond powder after ultrasonic treatment. (solvent: n-hexane)

(a) diamond powder treated with H_2SO_4 +HNO_3, (b) diamond powder treated with n-octyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO4 +HNO_3), (c) diamond powder treated with 3-aminopropyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO_4 +HNO_3), (d) diamond powder treated with 3-mercaptopropyltrimethoxysilane (solvent: methanol, base: diamond powder treated with H_2SO_4 +HNO_3)

Chapter 10

General Conclusion

Chapter 10
General Conclusion

In this study, we investigated the chemical reactivity of diamond surface with organic species, and discovered the specific reactivity of hydrogenated diamond surface with CN-containing compound and carboxylic acid under the presence of diacyl peroxide, and revealed the chemical reaction of oxygenated diamond surface with $LiAlH_4$ and silane coupling reagents. It was revealed that diamond surface reacts with specific organic reagents under mild conditions. We were able to show new chemical modification method of diamond surface using organic reaction in liquid phase.

The summary of each chapter is described as follows;

Chapter 1 Introduction

In this chapter, the general background of chemical modification of diamond surface, aim of the present study, general properties of diamond, diamond growth overview and application of diamond were described.

Chapter 2 Hydrogen abstraction reaction on hydrogenated diamond surface using benzoyl peroxide

The chemical reaction of hydrogenated diamond surface using benzoyl peroxide was performed. After reaction, the area under the C-H peaks in IR spectrum for hydrogenated diamond powder decreased with increasing treatment time and amount of benzoyl peroxide, and several peaks assigned to the (C_6H_5-COO) group emerged in the IR spectra. These results suggest that a free-radical substitution reaction occurred on the diamond surface treated with benzoyl peroxide via the following reaction schemes:

$$C_6H_5\text{-COO-OOC-}C_6H_5 \rightarrow 2\ C_6H_5\text{-COO}\cdot \qquad (1)$$

$$\text{(diamond)-H} + C_6H_5\text{-COO}\cdot \rightarrow \text{(diamond)}\cdot + C_6H_5\text{-COOH} \qquad (2)$$

$$\text{(diamond)}\cdot + C_6H_5\text{-COO}\cdot \rightarrow \text{(diamond)-OOC-}C_6H_5 \qquad (3)$$

where "(diamond)-H" is hydrogenated diamond surface. Due to the low dissociation energy, O-O bonds in benzoyl peroxide break easily, resulting in the generation of radical species (Eq (1)). Next, the hydrogen atoms on the hydrogenated diamond surface are abstracted by the radical species (C_6H_5-COO・). Subsequently, another organic radical, namely (C_6H_5COO・), bonds to the radical sites on the diamond surface through a termination reaction.

In this chapter, it was reveled that a free-radical substitution reaction occurred on the diamond surface treated with benzoyl peroxide.

Chapter 3 Reactivity of the hydrogenated diamond surface with various radical initiators

The reactivity of hydrogenated diamond surface with various radical initiators was described. Benzophenone, azo compounds, dialkyl peroxides and diacyl peroxides were used as the radial initiator. The reaction mechanism between hydrogenated diamond surface and racial initiators was discussed. When benzophenone was used for the reaction process, most of the hydrogen atoms on diamond surface were not abstracted. The radical species derived from azo compounds and from dialkyl peroxides also cannot abstract most of the hydrogen atoms on diamond surface. On the other hand, the radical species derived from diacyl peroxides such as benzoyl peroxide and lauroyl peroxide can abstract the hydrogen atoms on diamond surface. This study revealed that the reactivity for the hydrogen abstraction reaction with organic radical reagents depends on the kind of the radical species. The radical species derived from diacyl peroxide such as benzoyl and lauroyl peroxide was found to react with hydrogenated diamond surface (introducing (C_6H_5-COO) and ($C_{11}H_{23}$-COO) groups on the surface, respectively), while those derived from dicumyl and di-*t*-butyl peroxide did not react sufficiently.

Chapter 4 Chemical modification of diamond surface using diacyl peroxide and CN group containing compounds for the introduction of the CN group

Radical reactions using a benzoyl peroxide and lauroyl peroxide were performed to introduce the CN group onto the diamond surface. The CN group was introduced onto diamond surfaces treated with benzoyl peroxide or lauroyl peroxide when acetonitrile was used as the solvent for the reaction process. In contrast, no CN group was introduced onto diamond surfaces treated with benzoyl peroxide or lauroyl peroxide when benzonitrile was used as the solvent. There is an alkyl group in the structure of acetonitrile, and the hydrogen atoms in the alkyl group can be abstracted by the radical species generated from the diacyl peroxide. The radical species derived from acetonitrile should be able to react with the diamond surface activated by the radical species generated from benzoyl peroxide. There is no hydrogen atom that can be abstracted by radical species in the structure of benzoyl peroxide, thus explaining why no CN-group is introduced with benzonitrile.

Chapter 5 Chemical modification of diamond surface with $CH_3(CH_2)_nCOOH$ using benzoyl peroxide

The chemical modification of diamond surface using benzoyl peroxide and $CH_3(CH_2)_nCOOH$ was performed. The diamond surface reacted in acetic acid was rather different from that reacted in other solvents. It was confirmed that the diamond surface modified with acetic acid is stable against organic solvents. The reaction rate of the chemical reaction in acetic acid was calculated based on experimental data. The condition of the diamond surface after the reaction process was discussed in terms of the classification of the oxygen-containing functional group in the solvent molecule. The reactivity of carboxylic acid [HCOOH, $CH_3(CH_2)_nCOOH$ ($0<n<16$)] was examined. Although formic acid was inactive against the diamond surface, $CH_3(CH_2)_nCOOH$ ($0<n<16$) reacted with the diamond surface according to the chemical reaction process.

In the case of $CH_3(CH_2)_nCOOH$ ($0<n<16$), several peaks in the IR spectra were seen at the lower wave number region (500-2000 cm^{-1}). Moreover, the peak intensity at 2800-3000 cm^{-1} increased with an increased number of C–H bonds in the carboxylic acid. Based on the experimental results and the expansion of the chemical reaction between hydrogenated diamond surface and benzoyl peroxide, the presumed schemes of the chemical reaction of $CH_3(CH_2)_nCOOH$ ($0<n<16$) with the diamond surface are as follows:

$$C_6H_5\text{-}COO\text{-}OOC\text{-}C_6H_5 \rightarrow C_6H_5\text{-}COO\cdot + \cdot OOC\text{-}C_6H_5 \quad (4)$$

$$C_6H_5\text{-}COO\cdot + (\text{diamond})\text{-}H \rightarrow C_6H_5\text{-}COOH + (\text{diamond})\cdot \quad (5)$$

$C_6H_5\text{-}COO\cdot + CH_3(CH_2)_nCOOH \rightarrow C_6H_5\text{-}COOH + CH_3(CH_2)_nCOO\cdot$ (6)

$(\text{diamond})\cdot + CH_3(CH_2)_nCOO\cdot \rightarrow (\text{diamond})\text{-}OOC\text{-}(CH_2)_nCH_3$ (7)

The chemical reaction process was observed to be very regular. Therefore, the chemical modification process used in this study constitutes an effective method for controlling the condition of a diamond's surface.

Chapter 6 Preparation of HOOC-terminated diamond surface using benzoyl peroxide and dicarboxylic acid

Chemical modification of hydrogenated diamond surface using benzoyl peroxide and dicarboxylic acid was performed. A hydrogenated diamond surface was treated in a solvent containing benzoyl peroxide and dicarboxylic acid. After the reaction, a C=O peak appeared, and the shape of the C-H peak depended on the dicarboxylic acid type. When deuterium-labeled diamond powder was treated in the same manner, aliphatic C-H peaks were observed. The C-H peak intensities increased with the molecular weight of the dicarboxylic acids. This increase is caused by dicarboxylic acid-derived species bonding to the diamond surface.

To introduce $HOOC\text{-}(CH_2)_n\text{-}COO\text{-}$ groups onto the diamond surface at high density, $C_6H_5\text{-}COO\text{-}$ bonding to diamond surface had to be suppressed. Peaks assigned to aromatic C-H bonds were observed using toluene as the solvent for the reaction, while no such peaks were observed using ethanol or water as the solvent for the reaction. The hydrogen abstraction reaction proceeded faster in water than in ethanol. Thus, of the solvents examined, water was the most suitable for introducing $HOOC\text{-}(CH_2)_n\text{-}OCO\text{-}$ groups on the diamond surface. The surface species were relatively stable except for succinic acid ($n = 2$) in NaOH (*aq*). When the surface species were neutralized by NaOH (*aq*), clearly visible peaks assigned to the C=O bond of –COONa groups emerged at 1578 cm^{-1}, which indicated the presence of carboxylic groups on the treated diamond surface. In the case of succinic acid ($n = 2$), the surface species were easily hydrolyzed because of the short length of the molecules. In conclusion, $HOOC\text{-}(CH_2)_n\text{-}COO\text{-}$ groups were introduced onto the diamond surface *via* the reaction of the hydrogenated diamond surface with benzoyl peroxide and dicarboxylic acid through a single step.

Chapter 7 Oxygenation of hydrogenated diamond surface in liquid phases

The reactivity of hydrogenated diamond surface with inorganic acid and basis was demonstrated. In the cases of the treatment with HCl, HF, 1M NaOH (aq) or 1 M KOH (aq) below 100 ℃, the hydrogenated diamond surfaces were stable, whereas in the cases of the treatment with H_2SO_4 above 150 ℃, HNO_3 above 90 ℃, H_2O_2 above 90 ℃ or 1 M $KMnO_4$ (aq) above 45 ℃, the hydrogen atoms on the hydrogenated diamond surface were abstracted, and then the diamond surface were oxygenated. In the cases of $HCl:HNO_3=3:1$ or $HCl:H_2O_2=1:1$ above 60 ℃, the hydrogen abstraction reaction were observed, the diamond surfaces were oxygenated and chlorinated. It was expected that the oxygenation of hydrogenated diamond surface in the liquid phase proceed via not the ion reaction, but the radical reaction as the fundamental reaction mechanism.

Chapter 8 Chemical reaction of carbonyl groups of diamond surface with $LiAlH_4$

The reactivity of oxygenated diamond surface with $LiAlH_4$ was demonstrated. The chemical reaction between carbonyl groups on oxygenated diamond surface and $LiAlH_4$ was discussed. We confirmed the chemical reaction between the oxygenated diamond surface (ODS) and an organic chemical reagent. The C=O groups on ODS were reduced to O-H groups by $LiAlH_4$. However, the reactivity of the C=O bonds on the diamond surface was not homogeneous. The -COOH and –OCOCO- groups on ODS were readily reduced by $LiAlH_4$, whereas C-O-C groups were stable to $LiAlH_4$.

Chapter 9 Surface modification of the oxygenated diamond surface with silane coupling reagents

Chemical modification of oxygenated diamond surface reforming using various silane coupling reagents were demonstrated. The IR spectrum of the diamond powder after treatment with the silane coupling reagent depended on the kind of silane coupling reagent used. The diamond surfaces treated with silane coupling reagents were stable in the presence of organic solvents. It was confirmed that silane coupling reagent is effective in changing the chemical properties of the diamond surface.

Future view

We can presume that the functional group introduced on diamond surface acts as a normal organic functional group. Therefore, if the diamond surfaces modified with monocarboxylic acid or dicarboxylic acids are used as the base material for diamond chemical modification, we will adopt the theory and technology of ordinary organic chemistry for the chemical modification of diamond surface, and will create new type intelligent hybrid materials.