Transactions of the Materials Research Society of Japan 26 [4] 1205-1206 (2001)

Characterization of Silica Gel Modified by a Radio-frequency of CF_4 Plasma (II)

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Silica gel modified by a radio-frequency CF_4 plasma was characterized using thermogravimetry-differential thermal (TG) analysis, energy dispersive X-ray (EDX), and infrared (IR) absorption techniques. The TG analysis revealed that the hydrophobic character of silica gel was enhanced by the plasma treatment. The EDX and infrared absorption measurements clarified that replacements of –OH groups by $-CF_3$ or –F groups on the surface was responsible for the hydrophobic surface and the degree of the replacements increased with a radio-frequency power.

Key words: silica gel, plasma treatment, surface reaction

1. INTRODUCTION

Silica gel is widely used as adsorption materials for industrial use. In order to enhance its usefulness several modifications have been carried out by replacing hydroxyl groups of silica gel with organofunctional groups [1-5]. Recently, we reported that the silica gel surface could easily be modified using CF_4 plasma treatment to prepare lipophobic and hydrophobic surfaces [6]. These lipophobic and hydrophobic properties are due to $-CF_n$ (n=1–3) or -F groups, which are formed on the treated material surfaces. This modified method has a potential of making novel surfaces of silica gel as well, which would not be possible otherwise.

In this study, we examine radio-frequency (RF) power dependence of the plasma treatment on silica gel. The examination was performed using thermogravientry-differential thermal (TG) analysis, energy dispersive X-ray (EDX), and infrared (IR) absorption techniques.

2. EXPERIMENTS

The discharge apparatus were described elsewhere [6]. The temperature of sample was monitored using a thermocouple attached to the sample holder. A magnetic stirrer attached to the chamber and magnet in the sample holder play a role in mixing the powdered sample effectively.

The sample used for this study was A-type silica gel, obtained from Wako Junyaku Corporation. CF_4 gas (99.99%) was introduced through a mass flow controller after the treatment chamber was evacuated to a base pressure of 0.1 Pa. The gas flow was controlled at 10 sccm and the pressure in the chamber was adjusted to 10 Pa. The plasma treatment was carried out by changing RF power (P_{RF}) ranging from 0 to 70 W, for 90 min at each power. The temperature during the treatment was kept constant at 200 °C.

TG profiles were obtained on a Rigaku thermogravientry-differential thermal apparatus. EDX measurements were carried out using a Philips EDAX DX-4 spectrometer. IR spectra were obtained from KBr disks (1 wt%) using a Jasco FT-IR550 spectrometer.

3. RESULTS AND DISCUSSION

Figure 1 shows TG profiles of the silica gel plasma-treated at P_{RF}=0-70W, indicating that the dehydrated temperature of the sample is decreased with the RF power. This decrease is due to the weak Van der Waals interaction between the silica gel surfaces and the adsorbed water molecules. These results suggest that the RF CF4 plasma enhanced the hydrophobic character.

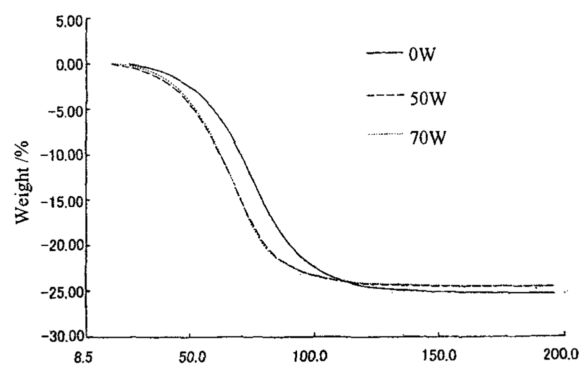

Fig. 1. TG spectra of the plasma –treated silica gel

Figure 2 shows EDX spectra of the silica gel plasma-treated at P_{RF}=0-70W, indicating that the fluorine containing of silica gel is increased with the RF power. Since physically adsorbed CF_4 derivatives on the silica gel surfaces was desorbed by evacuation at 200 °C, it is thought that new groups bonded to the silica gel surfaces were generated by the plasma treatment. The peaks around 0.3 keV are associated with carbon atoms of oil diffused from vacuum system, thus it is unable to identify the generation of carbon atoms on the silica gel surfaces by the plasma treatment. Above results indicate that the hydrophobic character of silica gel is due to the fluorine containing of silica gel.

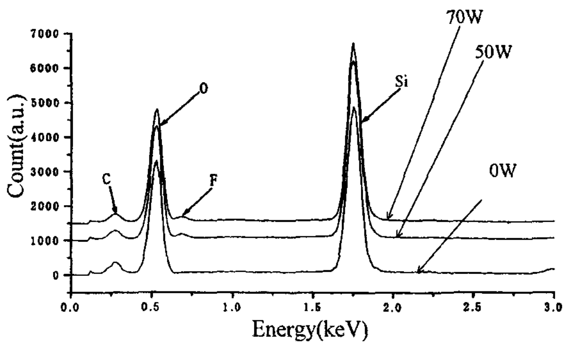

Fig. 2. EDX spectra of the plasma –treated silica gel

IR spectra of the silica gel plasma-treated at P_{RF}=0-70W are displayed in Fig. 3. These spectra were normalized for comparison and plotted in the wave-number range of 3000–4000 cm^{-1}. Fig. 3 shows that the band around 3400 cm^{-1} due to Si-OH stretching mode was crushed by the plasma treatment, indicating that O-H bonds were reduced on the silica gel in proportional with the RF power. EDX and IR results indicate that the replacements of –OH groups by -CF_n or –F groups on the silica gel surface occurred by the plasma treatment, in which the degree of the replacements increased with an RF power.

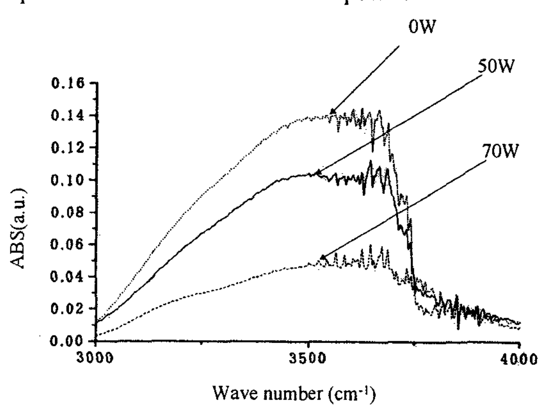

Fig. 3. IR spectra of the plasma –treated silica gel

The computer simulation of CF_4 plasma under the plasma condition, which is similar with those of the present experiment, indicated that the steady state concentrations of CF_3 and F radicals in the CF_4 plasma are about 10^4 times those of the generated ions, and the density of other radical species is also relatively small [7]. According to the above plasma consideration, it is expected that the plasma reactions on the silica gel surface under the present discharge conditions are governed by the neutral radical species. It suggests that the –CF_n or –F groups generated on the silica gel by the plasma treatment are almost –CF_3 groups. Noting that average electron density n_e is proportional to an RF power and average electron temperature T_e is almost constant under the present plasma conditions, we see that the degree of dissociation of CF_4 gas would vary in proportional to the RF power. Thus, the density of neutral radicals can be considered to be proportional to the RF power in the range of less than 75 W. The increase of replacements of –OH groups by –CF_3 or –F groups can be accounted for by the increase of neutral radical density in plasmas with the increase of the RF power.

4. CONCLUSION

We characterized the silica gel modified by an RF CF_4 plasma, using TG, EDX, and IR adsorption measurements. The TG analysis revealed that the hydrophobic character of silica gel was enhanced by the plasma treatment. The EDX and infrared absorption measurements clarified that replacements of –OH groups by –CF_3 or –F groups on the surface was responsible for the hydrophobic character of silica gel. The degree of replacements increased with a radio-frequency power. Based on the consideration of the plasma processes, we can see that -CF_n groups generated on the silica gel surfaces are almost –CF_3 groups and the increase of the replacements is due to the increase of neutral radical density in plasmas with the increase of an RF power.

This study was supported by Industrial Technology Research Grant Program in '00 from the New Energy and Industrial technology development Organization (NEDO) of Japan.

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(Received December 7, 2000; Accepted January 31, 2001)