Transactions of the Materials Research Society of Japan 27 [3] 483-486 (2002)

Surface Treatment of Powdery Silica Gel Using a Dielectric Barrier Discharge

T. Sakoda, S. Maeda, K. Nishihara* and K. Furukawa*
Department of Electrical System and Computer Engineering, Sojo University,
4-22-1 Ikeda, Kumamoto 860-0082, JAPAN, Fax: 81-96-326-3000, e-mail: sakoda@pe.sojo-u.ac.jp
*Advanced Science and Technology Center for Cooperative Research, Kyushu University,
6-1 Kasugakouen, Fukuoka 816-8580, JAPAN, Fax: 81-92-583-7873, e-mail: furukawa@astec.kyushu-u.ac.jp

In order to enhance the usefulness of silica gel, a novel surface treatment of powdery silica gel was performed using a dielectric barrier discharge in which CF_4 was used as the carrier gas. After the treatment, the existence of the treated fluorine, the endothermic change and the surface area were evaluated. The results showed that the dielectric barrier discharged plasma could effectively modify the surface of silica gel and achieve replacement of -OH groups by -CF_n or -F groups. Also, it was found that the endothermic reaction on silica gel obtained by a brief surface treatment extremely shifted to the low temperature side compared with those obtained by the conventional plasma treatment technique.
Key words: silica gel, surface treatment, dielectric barrier discharge

1. INTRODUCTION

Silica gel made up of micro-pore is widely used as adsorption materials for industry. However, when the silica gel is reproduced after use, a large electric power for the heating processes is demanded. Silica gel utilized for moisture absorption, for example, needs the heating process carried out at elevated temperature around 150℃. In order to lower the reproduction cost, it is necessary to change the surface characteristics of silica gel.

Until now, we have performed a surface treatment of powdery silica gel to prepare lipophobic and hydrophobic surfaces by a radio-frequency (RF) CF_4 plasma operated at low pressure [1-3]. The plasma treatment was carried out at the RF power of 70 W for 90 min. Such plasma modification is possible to change surface characteristics of materials by fact that chemically reactive species produced in the plasma react at the material surfaces, easily. The results showed that the low energy surface due to replacement of -OH groups by -CF_n (n=1–3) or -F groups was formed on silica gel. However, this technique had the weak point of taking time for the treatment. Therefore, we proposed a novel treatment technique using a dielectric barrier discharge that might achieve a brief treatment. A main characteristic of the dielectric barrier discharge is the presence of a dielectric layer between the discharge gap and at least one of the electrodes [4-5]. The presence of the dielectric materials leads to the formation of a large number of short-lived micro-discharge in the discharge gap. Although the dielectric barrier discharge operates at atmospheric pressure, the non-equilibrium plasma such as the RF discharges operated at low pressure is produced. Therefore, a large number of reactive species is produced compared with the RF discharge, and it can allow us to perform a brief treatment.

In this study, we performed the surface treatments of powdery silica gels for 5, 10 and 15 min by the dielectric barrier discharge. The surface characterization such as fluorine content, the endothermic reactions and the surface area were investigated by an energy dispersive X-ray(EDX), a differential scanning calorimeter (DSC) and a nitrogen adsorption technique, respectively. Based on these results, we showed that a surface treatment technique using a dielectric barrier discharge is a powerful technique for preparing the low energy surface of silica gel.

2. EXPERIMENTS

Figure 1 shows a schematic diagram of surface treatment system. A parallel electrode type was used for generating the dielectric barrier discharge plasma in CF_4 atmosphere. Each electrode with a diameter of 70mm was made of stainless steel and was cooled by passing the cooling water of about 13℃ through the inside of it. As the dielectric material, we used a vessel made of quartz. Its inner diameter and height were 80 and 10mm, respectively. The vessel was placed on an earth electrode.

Silica gel used for this study was A type obtained from Kishida Kagaku Corporation, and the particle diameters were from 0.07 to 0.14 mm. The silica gels of 1g in weight were placed on the vessel bottom and formed a sort of layer with a thickness of about 1 mm. The gap length between the upper electrode and the surface of silica gel layer was arranged at 0.2 mm. The dielectric barrier discharge was operated by applying the pseudo sinusoidal wave of which maximum value was 7kV and frequency was 8 kHz (see Figure 2, latter). CF_4 gas (99.99%) controlled by a mass flow controller entered into the chamber from the upper side of the chamber, in which the flow rate was kept at 1.2l/min. All experiments reported here were made under atmospheric pressure. Gas passed through the discharge region was exhausted from a small hole with a diameter of 10mm in the center of the upper electrode. The discharge voltage was measured by a high voltage probe and the discharge current by a Rogowski coil. The discharge power was obtained by integration of the product of discharge voltage and current for a period of pseudo sinusoidal wave.

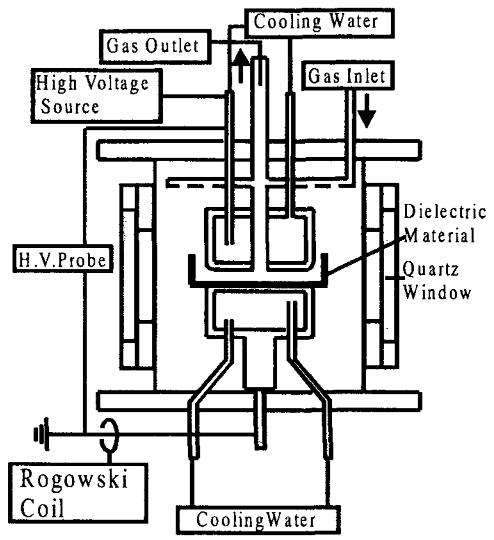

Fig. 1 Schematic arrangement of experimental apparatus

The surface characterization of silica gel was performed using the EDX, the DSC and the nitrogen adsorption technique. The EDX measurement using a Philips EDAX DX-4 spectrometer can easily investigate the existence of the treated fluorine on silica gel. The DSC is possible to reveal the endothermic change character of the treated surface. For the case of DSC measurement, water vapor was first adsorbed on the treated silica gel surface. Silica gels of 15 mg in weight were sampled for each DSC measurement carried out at the heating rate of 1℃/min. In the nitrogen adsorption technique, nitrogen was adsorbed in advance. After that, the surface area was measured using a Quantachrome AUTO SORB-1-MP.

3. RESULTS AND DISCUSSIONS

Typical waveforms of discharge voltage and discharge current are shown in Fig. 2. It can be seen from this figure that the discharge current consists of the displacement current due to capacitance and current pulses brought by the short lived micro-discharges. It is well known that each micro-discharge consists of a thin cylindrical channel with a radius of about 100 μm [4]. An accumulation of charge starts in the area where the micro-discharge reaches the dielectric. This leads the reduction of the electric field in the discharge gap, and therefore the discharge is choked. Because the micro-discharge formation is terminated within a short time, as shown in Fig. 2, the thermal equilibrium can not be achieved. By this fact, it is considered that the micro-discharge channel behaves like a transient glow discharge [4]. The electron temperature in the channel was around 5 eV which is a similar value obtained in the RF plasmas operated at low pressure. The discharge power obtained by integration of the discharge voltage and discharge current for a period of pseudo sinusoidal wave was about 15 W.

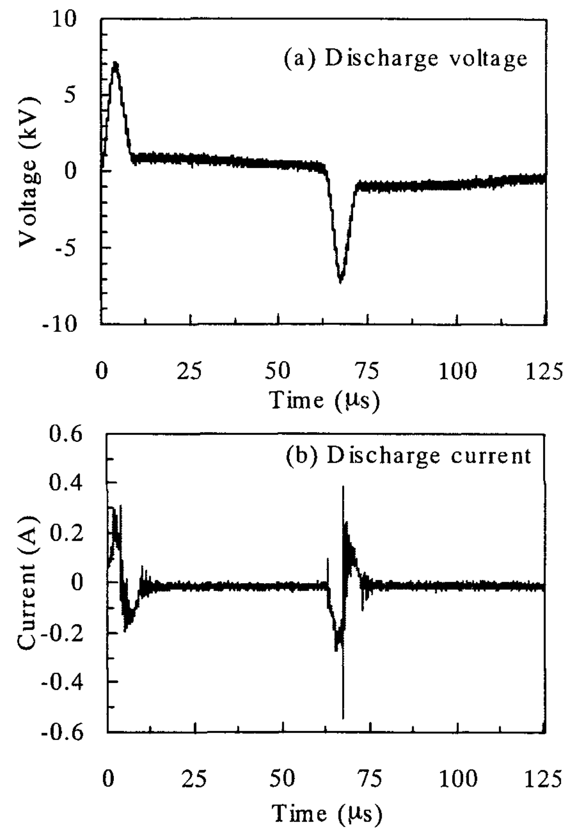

Fig. 2 Waveforms of discharge voltage and current

Figure 3 shows the EDX spectra of the parent and the silica gels treated for 5, 10 and 15 min using the dielectric barrier discharge. From this figure, it is found that the plasma-treated silica gels contain fluorine clearly. Silica gels treated for 5, 10 and 15 min contain 1.5, 2.1 and 3.5 at% of fluorine, respectively. Because the physically adsorptive CF_4 derivatives on the silica gel surface was desorbed by evacuation at 200℃ for 1 hour, it was considered that new groups bonded to the silica gel surface were obviously produced by the plasma treatment. Considering the previous results [1-3] obtained using the RF plasma of which plasma parameters such as electron temperature are similar to those of dielectric barrier discharges, it is expected that the dielectric barrier discharge plasma can achieve replacement of -OH groups by $-CF_n$ or -F groups. In Fig. 3, the peaks around 0.3 kV associated with carbon atoms are confirmed. Although their peaks may be of CF_n bonds, the EDX measurement reported here was impossible to identify it because a sticking agent on a sample stage for fixation of silica gel contained carbon atom. Studies on such identification are now in progress.

Figure 4 shows the measurement results of BET (Brunauer-Emmett-Teller) total surface areas of silica gels treated for 5, 10 and 15 min, obtained by nitrogen absorption technique. As can be seen from this figure, the surface area of silica gel slightly decreases with the increase of plasma treatment time. This tendency well agrees with those obtained by the RF discharge plasma. Taking into account of the result of EDX measurement, it is considered that the decrease of BET total surface area is brought by fact that the substitute groups such as $-CF_n$ and -F are introduced onto the micro-pore surface.

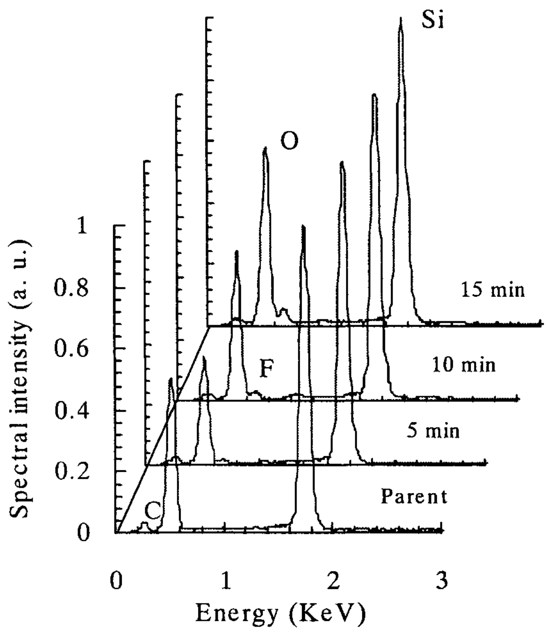

Fig. 3 EDX spectra of the parent and plasma-treated silica gels.

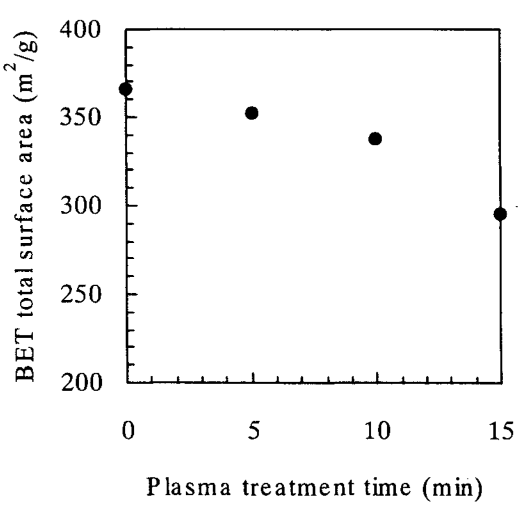

Fig. 4 BET total surface areas of the parent and plasma-treated silica gels.

Figure 5 shows DSC spectra of the parent and plasma-treated silica gels. The ordinate means an endothermic heat change of the adsorbed water vapor. Also, in order to indicate the amount of scatter in measured values obtained by 4 times measurements, the typical difference between minimum and maximum values is shown by the vertical and horizontal error bars. When the surface treatment was performed, silica gel placed on a vessel was not stirred whereby silica gel formed a sort of layer. However, as shown in the error bars, every silica gel sampled for DSC measurement indicates that the hydrophobic character is enhanced by the plasma treatment. This suggests that the micro-discharge might be generated even between silica gels. Anyway, it will be able to make the vertical and horizontal error bars minimal by an introduction of a stirrer system.

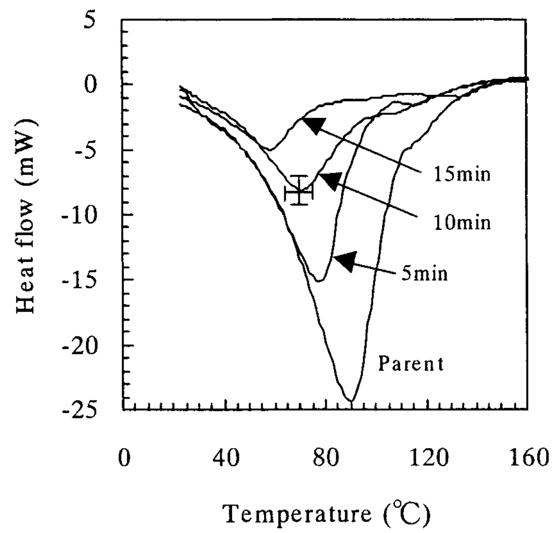

Fig. 5 DSC spectra of the parent and plasma-treated silica gels.

In Fig. 5, it is found that the endothermic reaction of plasma-treated silica gel shifts to the low temperature side compared with that of the parent one. The minimum heat flow on each reaction curve gives us an index of the dehydrated temperature. The dehydrated temperature of the silica gel becomes low with the increase of the treatment time. The dehydrated temperatures for the cases of 5, 10 and 15 min are 77.6, 71.2 and 58.3℃ respectively while the value of the parent one is 93℃. The dehydrated temperature obtained by RF plasma treatment for 90 min [3] is the closest to that by the dielectric barrier discharge treatment for 5min. Therefore, compared with the RF plasma treatment, the dielectric barrier discharge could promote to lower the dehydrated temperature extremely. The rates of replacement of -OH groups by $-CF_n$ or -F groups introduced onto the silica gel surface, as shown in Fig. 3, increases with the increase of the treatment time. When such low energy surface is formed, the chemical adsorption between the silica gel surface and water molecules is not dominant but Van der Waals interaction between the adsorbed water molecules will be. Therefore, as shown in Fig. 5, the quantum of the adsorbed water vapor decreases with the increase of plasma treatment time. Also, one of the most interesting characteristics of the treated silica gel is how long the formed low energy surface is maintained. Studies on the details of the problem are now in progress.

However, we have already confirmed that the second spectrum obtained from the same sample used in the first DSC measurement corresponded to that from the first measurement within a range indicated by the horizontal and vertical error bars shown in Fig. 5. That is, it was corroborated that the treated silica gel could stand the reproduction use at least 2 times. Thus, it was found that the dielectric barrier discharge operated with a low discharge power could produce a low energy surface in a short time.

4. CONCLUSION

The surface treatment of powdery silica gel using a dielectric barrier discharge was performed, which had the potential to make novel surfaces having new functions. The treated silica gels were characterized using EDX, DSC and a nitrogen adsorption technique. The results showed that the dielectric barrier discharge could form the low energy surface by the introduction of $-CF_n$ or -F groups on the surface of silica gel. It was also found that the endothermic reaction on silica gel obtained by a brief surface treatment extremely shifted to the low temperature side more than those obtained by the conventional RF plasma treatments. Thus, our proposed treatment technique is useful to change the character of silica gel surface in a short time. In addition, the treatment system using the dielectric barrier discharge need not a vacuum system whereby it makes the treatment system compact.

Finally, the authors wish to thank to Professor H. Nakajima of Kyushu University for his valuable contribution. They would also like to thank to Miss. N. Uchiyama of Kyushu University for her assistance with the experiment.

REFERENCES

[1] K. Furukawa, H. Ijiri, H. Terahara, H. Nagata, S. Yamazaki, H. Yamauchi and K. Muraoka, J. Matter. Sci. Lett., **19**, 1545-47 (2000)

[2] K. Nishihara, K. Furukawa, H. Ijiri, S. Yamazaki, Trans. of the MRS-J, **26**, 1201-03 (2001)

[3] H. Ijiri, K. Furukawa, S. Yamazaki, K. Nisihara, Trans. of the MRS-J, **26**, 1205-06 (2001)

[4] B. Eliasson, M. Hirth and U. Kogelschatz, J. Phys. D: Appl. Phys., **20**, 1421-37 (1987)

[5] S. Yagi and M. Tabata, J.Phys.D:Appl.Phys., **12**, 1509 -20 (1979)

(Received April 30, 2002; Accepted May 31, 2002)