

## Study of RF Power Dependence of CF<sub>4</sub> Plasma Treatment for H-Y Zeolite

K. NISHIHARA\*, K. FURUKAWA\*, H. IJIRI\*\*, S. YAMAZAKI\*\*\*

\* Advanced Science and Technology Center for Cooperative Research, Kyushu University, 6-1 Kasugakouen, Kasuga City, Fukuoka 816-8580, JAPAN; TEL/FAX: 81-92-583-7873, e-mail: nishihara@astec.kyushu-u.ac.jp

\*\* Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakouen, Kasuga City, Fukuoka 816-8580, JAPAN; TEL/FAX: 81-92-583-7873, e-mail: ijiri@ence.kyushu-u.ac.jp

\*\*\* Department of Materials Science, Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka 437-8555, JAPAN; TEL/FAX: 81-538-45-0167, e-mail: yamazaki@ms.sist.ac.jp

H-Y zeolite modified by a radio-frequency CF<sub>4</sub> plasma was characterized using X-ray diffraction, nitrogen adsorption, energy dispersive X-ray and infrared absorption techniques. X-ray diffraction measurements showed that the crystallinity of zeolite slightly decreased by the plasma treatment with the RF power of 75 W and that the zeolites plasma-treated at P<sub>RF</sub>=0-50W maintain the crystallinity. The adsorption measurements indicated that hydrophobic bulky groups were introduced to the micropore surface of zeolites by the plasma treatment. The infrared absorption measurements clarified that replacements of -OH groups by -CF<sub>3</sub> or -F groups on the micropore surface was responsible for the hydrophobic surface and the degree of replacements increased with a radio-frequency power.

Key words: zeolite, plasma treatment, surface reaction, radio-frequency, power dependence

### 1. INTRODUCTION

Zeolites are widely used as adsorption materials for industrial use. In order to enhance their usefulness in various applications, novel modifying methods have been proposed [1-3]. The hydroxyl groups of zeolites are reactive centers of adsorption reactions. Therefore, if these sites can be changed, it is expected that the physical and chemical properties of zeolites can be significantly modified. Recently, we reported that the surface treatment using CF<sub>4</sub> as a plasma source could easily prepare hydrophobic surfaces of zeolite [4]. These hydrophobic properties are due to -CF<sub>n</sub> (n=1-3) or -F groups, which arise on the material surfaces. This method has a potential of making novel surfaces having new functionalities of zeolite, which would not be possible otherwise. However, this plasma reaction on the zeolite has been not clear.

In this study, we examine radio-frequency (RF) power dependence of the plasma treatment on H-Y zeolite to investigate the plasma reaction on the zeolite. The examination was performed using X-ray diffraction (XRD), nitrogen adsorption, and infrared (IR) absorption techniques.

### 2. EXPERIMENTS

The discharge apparatus shown in Fig. 1, with two parallel-plate electrodes, was used for an RF plasma treatment. The grounded electrode, which served both as the ground and sample holder, was 115 mm in diameter, and the powered electrode was 120 mm in diameter. The two electrodes were set 70 mm apart. RF power was supplied to the powered electrode from a 13.56 MHz power supply through an impedance matching box, and glow discharge plasma was generated between the electrodes. 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.

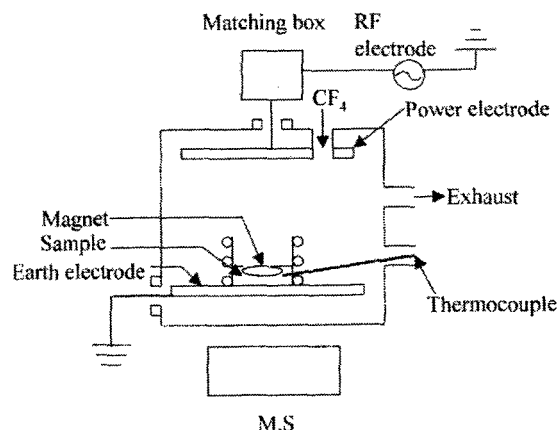


Fig. 1 Plasma treatment apparatus

The zeolite used for this study was H-Y zeolite, obtained from Shokubai Kasei Corporation. CF<sub>4</sub> gas (99.99%) was introduced through a mass flow controller after the treatment chamber was evacuated to a base pressure of  $2.5 \times 10^{-2}$  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<sub>RF</sub>) ranging from 0 to 75 W, for 30 min at each power. The temperature during the treatment was kept constant at 450 °C. After the plasma treatment, the physically adsorptive CF<sub>4</sub> derivatives that remained on the zeolite surface were desorbed by evacuation at 450 °C for 1 hour.

XRD patterns were obtained at room temperature on a Rigaku miniflex diffractometer using CuK $\alpha$  radiation.

The surface areas of zeolite were determined by applying the method of nitrogen adsorption, using a Micromeritics Shimadzu ASAP2000 apparatus. IR spectra were obtained from KBr disks (1 wt%) using a Jasco FT-IR550 spectrometer.

### 3. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of the zeolites treated at  $P_{RF}=0-75W$ . It can be seen that the zeolite plasma-treated at  $P_{RF}=75W$  has slightly decreased intensities for the reflections compared to the zeolites plasma-treated at  $P_{RF}=0-50W$ , indicating that the crystallinity of zeolite slightly decreased by the plasma treatment with the RF power of 75 W and that the zeolites plasma-treated at  $P_{RF}=0-50W$  maintain the crystallinity.  $^{29}Si$  MAS NMR spectra [4] show that dealumination is responsible for the decrease in the crystallinity of the zeolite caused by the plasma treatment. It is thought from this result that the dealumination is increased remarkably in the zeolite plasma-treated at  $P_{RF}=75W$ .

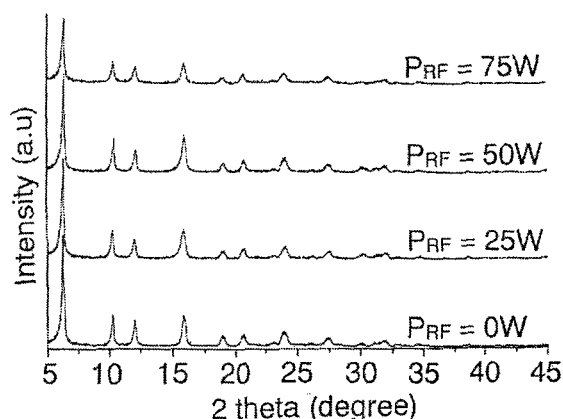


Fig. 2 X-ray diffraction patterns of zeolites treated at  $P_{RF}=0-75W$

Figure 3 shows BET (Brunauer-Emmett-Teller) total and external surface areas of the zeolites treated at  $P_{RF}=0-75W$ . It exhibits that both areas decrease with the increase of an RF power and the reduced area of BET total surface by plasma treatment under condition of  $P_{RF}=75W$  is about twice the external surface area of the parent zeolite. When it is assumed that the plasma treatment is exerted only on the external surface of the zeolites, it is difficult to explain the above results. Thus, it is believed that the micropore and external surfaces of the zeolite are plasma treated homogeneously. Also, it can be seen from Fig. 3 that the degree of reduction of BET total surface area by the plasma treatment is relatively large in comparison with that prepared using usual modified methods [5]. Although the decrease of crystallinity and micropore volume of zeolite may be thought as the explanation of the decrease of BET total surface area, the former is unlikely because zeolite structure is maintained under the plasma conditions in the range of  $P_{RF}=0-50W$ . Thus, we conclude that the decrease of zeolite micropore volume was responsible for the large decrease of BET total surfaces area and that the

bulky substituent groups were introduced onto the micropore surface. As the EDX experiments showed that the zeolite  $CF_4$  plasma-treated at  $P_{RF}=75W$  has carbon and fluorine atoms [4], it is thought that the bulky substituent groups are made up of carbon and fluorine atoms.

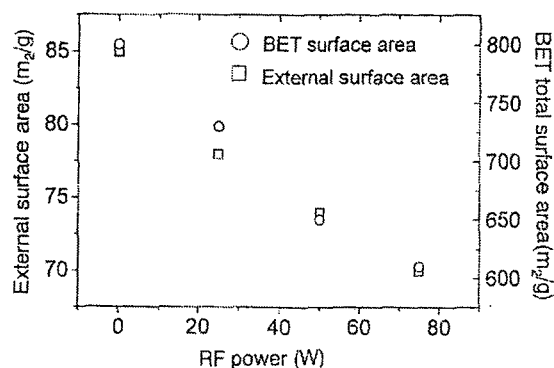


Fig. 3 BET total and external surface areas of zeolites treated at  $P_{RF}=0-75W$

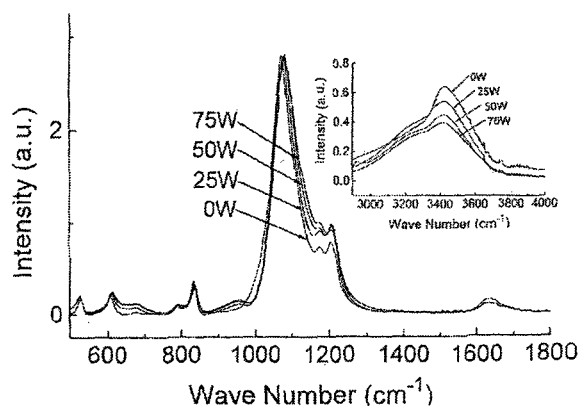


Fig. 4 Infrared transmission spectra (KBr discs) for zeolites treated at  $P_{RF}=0-75W$

IR spectra the zeolites treated at  $P_{RF}=0-75W$  are displayed in Fig.4. These spectra are normalized for comparison and plotted in the wave-number range of  $500-1800\text{ cm}^{-1}$ . Also, as can be seen from Fig. 4, the additional band is observed at  $1600-1630\text{ cm}^{-1}$ . It is believed that band arises mainly from the carboxyl groups (C=O stretching) due to  $CO_2$ , not from olefinic structure (C=C stretching), because the intensity of this band is not correlated with an RF power.

The intense bands are shifted from  $1070\text{ cm}^{-1}$  to  $1080\text{ cm}^{-1}$  with an increasing RF power and the band shape around  $1160\text{ cm}^{-1}$  humps increasingly with the increase of an RF power as shown in Fig. 4. Those facts indicate that C-F bonds on the zeolite surfaces increase with an RF power. Also, it can be seen that the peaks around

960, and 800  $\text{cm}^{-1}$  distinctly appear, indicating the existence of  $\text{SiF}_n$  bonds. Moreover, the peak intensities around 680  $\text{cm}^{-1}$ , being responsible for Si-C bond, increase with an RF power. This fact indicates that the Si-C bond to the zeolite surface links the  $\text{CF}_4$  derivatives. The inset of Fig. 4 shows IR spectra plotted in the range of 2900-4000  $\text{cm}^{-1}$ , illustrating that the band around 3400  $\text{cm}^{-1}$  due to Si-OH stretching mode is gradually crushed with the increase of the RF power. These observations indicate that replacements of -OH groups by  $-\text{CF}_n$  or -F groups on the zeolite surface occurred by the plasma treatment, in which the degree of replacements increased with an RF power. The rate of occurrence of the replacements of -OH groups by  $-\text{CF}_n$  or -F groups can be estimated from the inset of Fig. 4. The estimated rates of occurrence of the replacements are about 15%, 30%, and 39% with the RF power of 25W, 50W, and 75W, respectively.

The computer simulation of  $\text{CF}_4$  plasma under the plasma condition, which is similar with those of the present experiment, indicated that the steady state concentrations of  $\text{CF}_3$  and F radicals are about  $10_4$  times those of the generated ions, and the density of other radical species is also relatively small [6]. According to the above plasma consideration, it is expected that the plasma reactions on the zeolite surface under the present discharge conditions are governed by the neutral radical species. It suggests that the  $-\text{CF}_n$  groups generated on the zeolite by the plasma treatment are almost  $-\text{CF}_3$  groups. Noting that  $n_e$  is proportional to an RF power and  $T_e$  is almost constant under the present plasma conditions, we see that the degree of dissociation would vary in proportional to the RF power. Thus, the density of neutral radicals can be considered to proportional to the RF power in the range of less than 75 W. The increase of replacements of -OH groups by  $-\text{CF}_3$  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 zeolites modified by an RF  $\text{CF}_4$  plasma, using XRD, nitrogen adsorption, and IR adsorption measurements. XRD measurements showed the crystallinity of zeolite slightly decreased by the plasma treatment with the RF power of 75 W and that the zeolites plasma-treated at  $P_{\text{RF}}=0-50\text{W}$  maintain the crystallinity. The nitrogen adsorption measurements indicated the micropore and external surfaces of the H-Y zeolites are homogeneously plasma-treated and the bulky substituent groups, comprised of carbon and fluorine atoms, are formed on treated zeolite surface. IR measurements showed that replacements of -OH groups by  $-\text{CF}_n$  groups on the zeolite surface occurred by the plasma treatment, in which the degree of replacements increased with an RF power. Based on the consideration of the plasma processes, we can see that  $-\text{CF}_n$  groups generated on the zeolite surfaces are almost  $-\text{CF}_3$  groups and the increase of replacements is due to the increase of the neutral radical density in plasmas with the increase of an RF power.

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