A-2.2 Recovery and Emission Control of Fluorocarbons and Alternative Fluorocarbons by Adsorption(Final Report)

Contact Person Koichi Mizuno
General Research Counselor
National Institute for Resources and Environment,
Agency of Industrial Science and Technology,
Ministry of International Trade and Industry
16-3 Onogawa, Tsukuba, Ibaraki 305, Japan
Phone+81-298-58-8190 Fax+81-298-58-8191

Total Budget for FY1993-FY1995 50,591,000 Yen (FY1995;17,633,000 Yen)

Abstract Adsorption process as well as adsorbents for recovery of dilute fluorocarbons have been studied.

Using microwave, we have studied the adsorption of fluorocarbon on zeolite from gas mixture containing water which interferes with adsorption. It was found that the adsorption of fluorocarbon improved outstandingly when adsorption was conducted under microwave irradiation.

As for adsorbents, the following conclusions were obtained. Ion exchange of NaY zeolite by lead ion raised the fluorocarbon adsorption ability in the low concentration range. Activated carbon of high adsorbability can be prepared by controlled gasification of char with carbon dioxide or steam.

Key Words Adsorption, Adsorbents, Fluorocarbon, Microwave

1. Introduction

There is an increasing need to stop releasing fluorocarbon into the atmosphere, owing to its ozone depletion potential. Adsorption method is considered to be one of the most efficient fluorocarbon recovery processes. The existing adsorption process is, however, insufficient to apply effluents containing low concentrations of fluorocarbons.

The purpose of this study is to establish an adsorption process as well as adsorbents for recovery of dilute fluorocarbons.

2. Research Method

2.1. Adsorption System

The experiment was conducted in combination with adsorbing apparatus capable of flowing through multi-component gas with a microwave irradiation system.

Adsorption of CFC (Chlorofluorocarbon) and H_2O (moisture=water) was carried out under the following conditions : 1)The adsorbent used was about 0.6g of NaY, KY etc zeolites the hygroscopicity of which is very strong. 2)Adsorption gases were 1000ppm of CFC and 8000ppm of H_2O in helium, and the flow rate was 400ml/min. 3)Adsorption temperature was controlled at 25 ° C with cooling medium (CFC-112). 4)Concentration of H_2O and CFC at the outlet was analyzed instantly with a mass spectrometer. 5)The microwave irradiation apparatus used had the specification of 2.45GHz, 1.2kW.

By the way, it was revealed that no adsorption of CFC-113 occurred, when H_2O adsorption completed under these conditions without microwave irradiation,

2.2. Adsorbents for Fluorocarbon

The Research was performed on the surface modification of porous material such as ion exchange, carbon deposition from pyrolysis of hydrocarbon and gasification with carbon dioxide or steam.

Na in NaY zeolite was exchanged by Cu or Pb. To control the pore size of activated carbon, butane or neopentane was cracked on to the pore mouths at 1023-1273K. Carbonized raw materials were partially gasified with carbon dioxide or steam. The carbon is subjected to controlled gasification at 1073-1273K.

Adsorption measurements of fluorocarbons were carried out in the CAHN 2000 microbalance at 298K.

3. Result and Discussion

3.1. Adsorption System

Fig. 1 shows concentration curves at the outlet of the adsorption tube with a certain microwave irradiation power. Abscissa is the passage of time with operation. Ordinate is the concentrations of CFC-113 (1,1,2-trichloro, 1,2,2-trifluoroethane) and H2O.

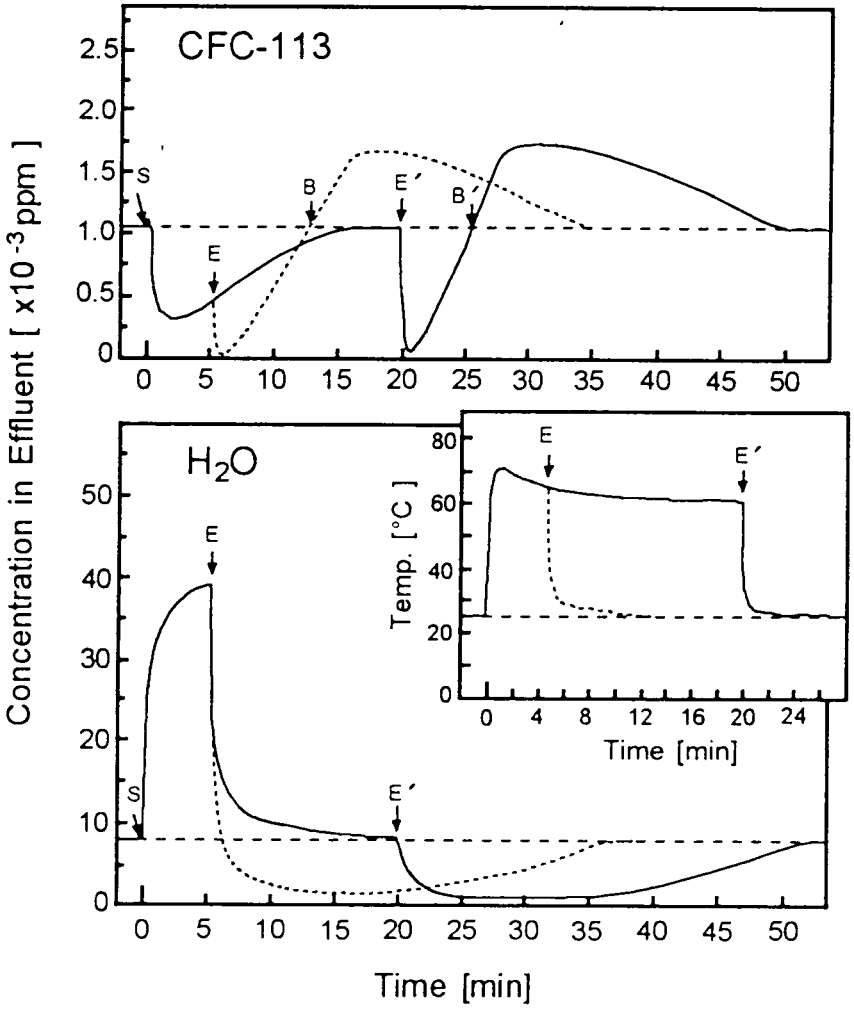

Figure 1. Adsorption and desorption curves.

The curves above the dashed line represent the desorption and the ones below represent the adsorption. The solid line at upper figure is the concentration curve of CFC-113; the one below is that of H_2O. First, the adsorbent was saturated by H_2O and CFC-113 without microwave irradiation. And then microwave was irradiated, this is Point S. At that time, adsorption temperature had risen from 25 ° C to 32 ° C. From the point when microwave was irradiated (Point S), H_2O concentration at the outlet became intense, indicating that H_2O desorption had begun. Conversely, CFC-113 concentration decreased, showing that CFC-113 was adsorbed. From the point (E, E') when microwave irradiation was stopped, H_2O concentration decreased, making it clear that H_2O adsorption in fact occurs. By contrast, the concentration of CFC-113 further decreased, which shows that CFC-113 adsorption resumes. This adsorption continues to Point B, B'. The desorption of CFC-13 from Point B, B' was caused by displacement adsorption of H_2O.

The other important results are as follows : 1)Adsorption amount of CFC is not influenced by adsorption temperature. 2)Adsorption amount of CFC increases with increasing microwave power. 3)The increasing of H_2O concentration increases the concentration of desorbed CFC.

3.2. Adsorbents for Fluorocarbons

The performance of adsorption apparatus is influenced by adsorbents. Therefore selection of adsorbents is very important. The purpose of this work for adsorbents is to get data of basic adsorption properties of commercial adsorbents and to clarify the preparation conditions of adsorbents with high adsorption ability.

Figures 2 and 3 illustrates the relationship between the adsorption amount of fluorocarbon and the specific surface area of activated carbon. The results demonstrate that the adsorption of fluorocarbon in the low concentration range has no correlation to surface area.

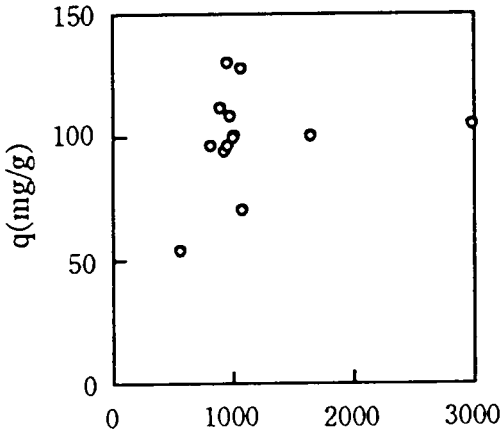

Fig.2 Relation between q and surface area(HCFC-123., 208ppm)

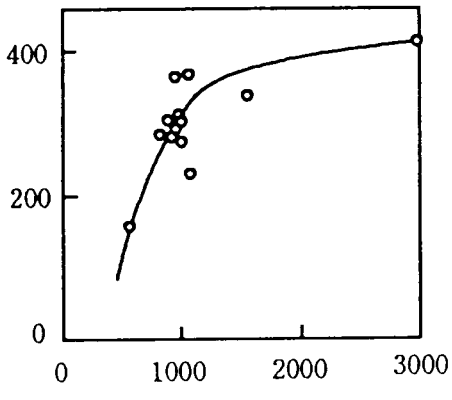

Fig.3 Relation between q and surface area(HCFC-123., 1040ppm)

Effect of ion exchange of NaY zeolite on adsorption of fluorocarbon is shown in Figure 4.

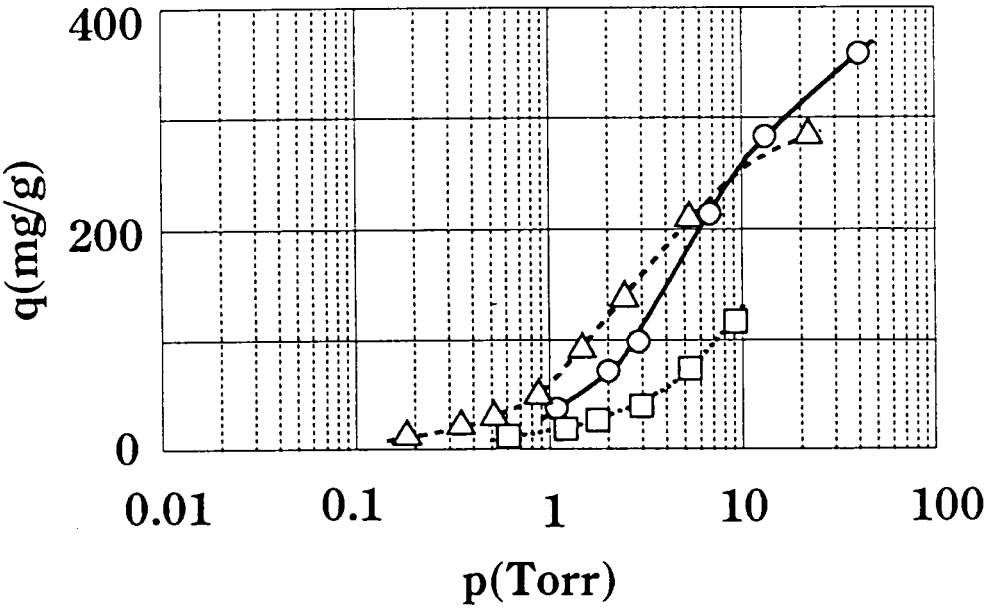

Fig.4 Adsorption isotherms of CFC－12 at 298K(○ :NaY, △ : PbY, □ :CuY)

Ion exchange of NaY zeolite by lead ion raised the fluorocarbon adsorption ability in the low concentration range,while exchange by copper ion decreased adsorption ability.

As activation enlarges the pore size , adsorbate interaction with wall of the pore decreases with increasing weight loss. Therefore,even though surface area of the activated carbon increases, uptake of fluorocarbon at low concentrations may decrease as the pore enlarges.

Activated carbon of high adsorbability can be prepared by controlled gasification of coconut shell char. The relationship between the adsorption ability for fluorocarbon and the burn-off of carbon are shown in Figure 5.

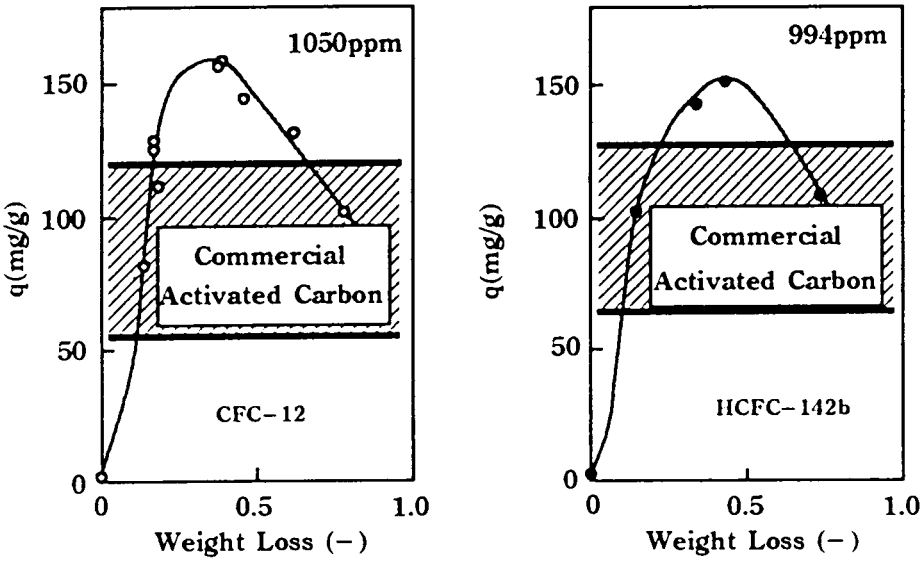

Fig.5 Relationship between adsorption amount and weight loss of carbon

For example, activated carbon of high adsorbability for CFC-12 , compared to commercial activated carbons, can be prepared by gasification of char with carbon dioxide in the weight loss range of 0.17 - 0.65.

4. Conclusion

The study revealed that if there was water as coexistent material, the adsorption amount of CFCs declined remarkably on adsorbent the hygroscopicity of which was very strong. However, when adsorption was processed under of microwave irradiation, we found that CFCs adsorption improved outstandingly. According to this result, we made sure of a basic concept for a new system which works by flowing moisture and CFCs at the same time, by turning microwave irradiation ON and OFF. Consequently, it is possible to conduct adsorption and desorption using a single adsorbing tower.

Ion exchange of NaY zeolite by lead ion raised the fluorocarbon adsorption ability in the low concentration range. Activated carbon of high adsorbability can be prepared by controlled gasification of char with carbon dioxide or steam.

List of Publications

1) S.Kobayashi et al., "Adsorption Recovery and Decomposition Reaction of Fluorocarbon by Zeolite", Kyuchak Gijutu Handbook, p.788(1993)
2) H. Kitagawa, "Recovery of Fluorocarbon by Adsorption", Kagaku Souchi, 35, No.6, 38(1993)
3) S. Kobayashi, "Application of Micro Wave and High Frequency Wave to Control of Adsorption and Desorption" , Kagaku Souchi, 35, No.11, 28(1993)
4) S. Kobayashi,、 "Recovery of Low Concentration Gases by Adsorption", Tosoh Kogaku, 29, No.6, 245(1994)
5) S.Kobayashi e al., "Recovery of Chlorofluorocarbons by Adsorption - Study of Adsorption Isotherm", Shigen to Kankyo, 3,No.4, 249(1994)
6) S. Kobayashi et al., "Study of Adsorption Isotherm for Chlorofluorocarbons on Zeolites", Nippon Kagaku Kaishi, 1994, No.9, 828
7) H. Kitagawa et al., "Adsorption Properties of Fluorocarbon on Various Porous Materials", Shigen Kankyo Taisaku, 31, No.2, 45(1995)
8) H. Kitagawa et al., "Preparation of Activated Carbon for Adsorption of Fluorocarbon 1", Shigen Kankyo Taisaku, 31, No.8, 29(1995)
9) H. Kitagawa , "Preparation of Activated Carbon for Adsorption of Fluorocarbon 2", Shigen Kankyo Taisaku, 31, No.11, 45(1995)
10) H.Kitagawa, "Production and Properties of Fibrous Adsorbents", Kagaku Souchi, 37, No.8, 107(1995)