Characterization of Molecular-Sieving Carbon for CO_2-Adsorbers in Controlled Atmosphere Storage System

Ichiro TANAHASHI,* Hiroto NAKAMA,† Atsushi NISHINO,†† and Jun TAKEDA†
Central Research Laboratories, Matsushita Electric Industrial Co., Ltd.,
Yagumo-Nakamachi, Moriguchi, Osaka 570
† Engineering Center, Matsushita Refrigeration Co., Takaida-Hondori, Higashi-Osakashi, Osaka 577
††Living System Research Center, Matsushita Electric Industrial Co., Ltd.,
Yagumo-Nakamachi, Moriguchi, Osaka 570
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Molecular sieving carbon (MSC) has been characterized for CO_2-adsorbers in a controlled atmosphere storage (CA storage) system by a gas-adsorption method. Experimental data were analyzed by means of the Dubinin–Astakhov equation, the *t*-method, and the micropore analysis method. The BET surface area of MSC was 592 m^2 g^{-1}. In the pore size distribution curve of MSC, the most common pore diameter was 0.68 nm. The temperature and the space velocity dependence of adsorbers with MSC have been investigated. The CO_2 adsorption capacity of adsorbers was determined by the gas-flow method. The capacity of the adsorbers at 60 °C decreased to 55%, compared with that at 20 °C; it decreased with increasing space velocity.

It has been known that the decay of fruits and vegetables can be reduced under atmospheres of highly concentrated CO_2 (2—15%) and low concentrations of O_2 (2—10%) during storage at low temperatures of 0—10 °C.[1,2]

The controlled atmosphere storage (CA-storage) system has been used practically for reducing the decay of fruits and vegetables. Several types of CA-storage have been proposed.[3] They mainly comprise of three parts; a storeroom, a CO_2-generator, and a CO_2-adsorber. In a previous paper we reported that the reliability of CO_2-adsorbers with molecular sieving carbon (MSC) is better than that of an adsorber with an X-type zeolite.[4] The difference in reliability of the two types of adsorbers was probably attributed to a difference in the micropore structure between MSC and X-type zeolite. The temperature and space velocity (flow rate/volume of the adsorbent) dependence of CO_2-adsorbers with MSC are also influenced by the micropore structure. However, the characterization of MSC by the gas-adsorption method using different analysis approaches has not yet been carried out.

Adsorption methods are frequently used and several adsorbates have been proposed to analyze the micropores of activated carbons.[5-7] Micropores are defined as pores that do not exceed 2 nm, according to the IUPAC classification of pore size. Recent experimental measurements have revealed that micropores influence the adsorption properties of adsorbents.[8,9]

In this report, experimental data concerning adsorption isotherms are analyzed using three different approaches. The first one is the Dubinin–Astakhov (DA) equation (1),[10] which is a general expression of the Dubinin–Radushkevich (DR) equation,[11]

$$W=W_0\{\exp-(A/E)^n\}. \quad (1)$$

Here, W is the volume of the gas adsorbed at a relative pressure, P/P_0, considered to be a characteristic similar to a bulk liquid at the experimental temperature, W_0 the micropore volume, n an additional parameter, and E the characteristic free energy of adsorption for the given system. At the relative pressure, P/P_0, the adsorption potential, or the differential free energy of adsorption, A, is given by

$$A=RT\ln(P_0/P). \quad (2)$$

The second approach is the so-called "*t*-method",[12-14] which is an empirical procedure used for the analysis of adsorption isotherms. This method is based on a comparison between the isotherm on a specimen (porous carbon) and the standard isotherm on a nonporous reference carbon. The amount of adsorbed gas on a porous carbon is plotted against the statistical film thickness, t, for a nonporous reference carbon.

The third approach is the so-called "MP-method" (micropore analysis method).[15] The MP-method is based on the de Boer V–t plot obtained from an adsorption isotherm on nonporous carbons.[15] In the de Boer plot, V is the volume of adsorbed gas. The pore-size distribution and the specific surface area of porous carbon are obtained from this method. Details of the analytical procedure were reported in Ref. 15.

In the present study, MSC was characterized by the gas adsorption method and analyzed by the above-mentioned three methods. The temperature and space velocity dependences of the CO_2-adsorber with MSC were also investigated.

Experimental

1. Materials. The molecular sieving carbon (MSC) used is a product of Takeda Chemical Industries Co., Ltd., (X_2M), the size being about 3 mm in diameter and 3 to 8 mm in length. The nonporous carbon black of Spheron 6 was supplied by Cabot Carbon Co., Ltd. The isotherm of the carbon black was used as the standard adsorption isotherm in the "*t*-method".

2. Apparatus and Procedure. Adsorption experiments for

characterizing MSC were carried out in a conventional volumetric apparatus of BEL Japan, Inc. (BELSORP28) equipped with a high-precision Baratron capacitance manometer. Before the experiments, the samples were out-gassed at 423 K for 2 h. N_2 and CO_2 adsorption isotherms were measured at 77 and 195 K, respectively.

The CO_2 adsorption capacity of the adsorber was measured by the flow method using the same apparatus reported in a previous paper.[4] The apparatus comprises three parts: an adsorber, gas-mixing equipment, and gas-analyzing equipment. The adsorber was 55 mm in diameter and 700 mm in height. To carry out the adsorption experiment, gas of 3.4—14.0% CO_2 was introduced from the bottom of the adsorber at a space velocity of 140—700 h^{-1}. The adsorption temperature was controlled by heating the adsorber with a tape-heater. During adsorption, small portions of the leaked gas were withdrawn from the adsorber, and the concentration of CO_2 was measured by a combustion gas analyzer (Shimadzu, CGT-10-1A).

Results and Discussion

1. Properties of MSC. Figure 1 shows the adsorption (a) and desorption (b), N_2 isotherms of MSC at 77 K and CO_2 adsorption (c) at 195 K. The hysterisis of the N_2 isotherm is small. Brunauer et al. proposed to classify the adsorption isotherms into five different groups.[16] According to their classification, the isotherms of N_2 and O_2 belong to type I. From the N_2 isotherm, the BET surface area (S_{BET}) was calculated to be 592 $m^2 g^{-1}$ by using the well-known BET equation. The S_{BET} of MSC is not so large as that of conventional activated carbons.[7]

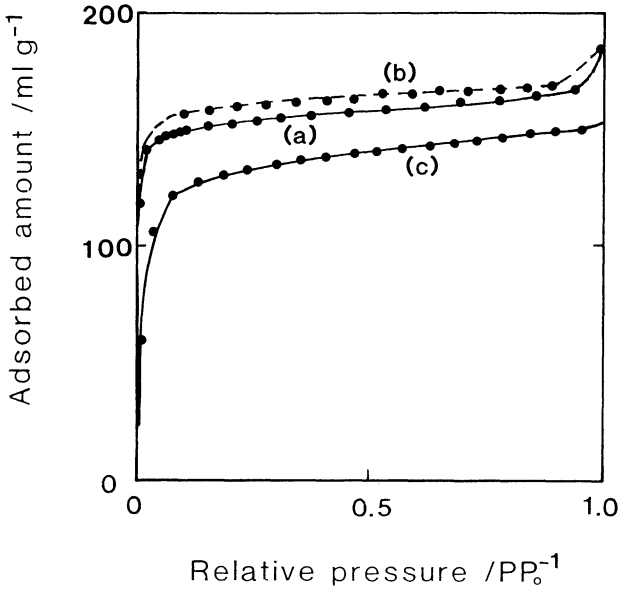

Fig. 1. Adsorption-desorption isotherm of MSC for N_2 at 77 K and for CO_2 at 195 K. (a): adsorption of N_2, (b): desorption of N_2, and (c): adsorption of CO_2.

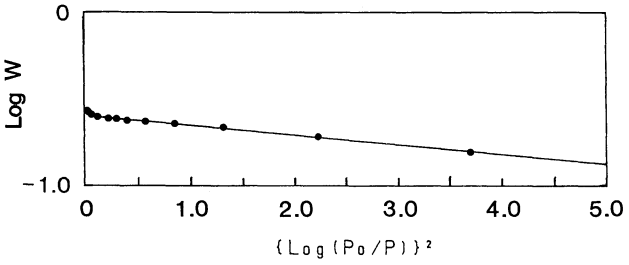

Fig. 2. DA-plots of MSC.

The CO_2 adsorption data were fitted to the DA equation (1). In Fig. 2, $\log W$ is plotted against $\log^2 (P_0 / P)$. The DA plot of MSC lies on a straight line in the case of n=2. According to Eq. 1, the intercept of the linear DA plot should equal to $\log W_0$; from the slope, the value E is obtained. It is known that decreases in the characteristic free energy of the DA equation, E, are correlated with increases in the micropore sizes.[9] The value of n was determined by the relative size between adsorbate and adsorbent. In fact, the value of n on MSC was 3 due to the adsorption of benzene.[17] In this experiment, the value seemed to be 2. This is because the volume of CO_2 was smaller than that of benzene. The E and W_0 values of MSC were 10.43 kJ mol^{-1} and 0.254 ml g^{-1}, respectively. The E value of MSC was larger than that of carbon black and activated carbon.[10] The larger E value suggested that the size of the micropore is smaller than that of carbon black and activated carbon.

Figure 3 shows a t-plot of MSC obtained from the N_2 adsorption isotherm shown in Fig. 1. Carrott et al.[8] has proposed that back extrapolation of the linear portion of the plot to the ordinate yields the total micropore volume, V; the slope of the linear section provides the external area, S_{EXT}, of the adsorbent; and extrapolation to the origin of the initial part of the plot provides the total surface area, S_t. From the figure, S_t and S_{EXT} were calculated to be 711 and 16.4 $m^2 g^{-1}$, respectively. The

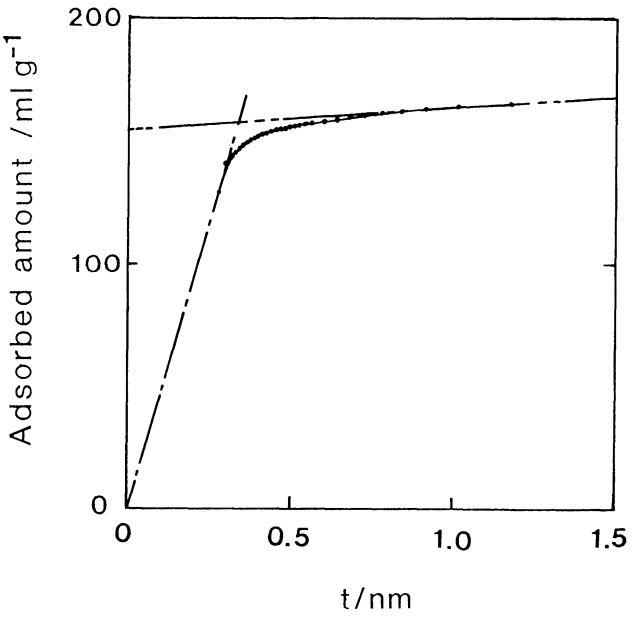

Fig. 3. t-plots of MSC.

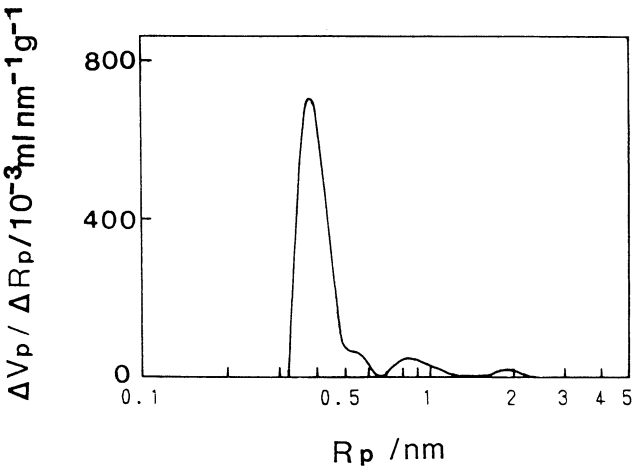

Fig. 4. Pore size distribution of MSC.

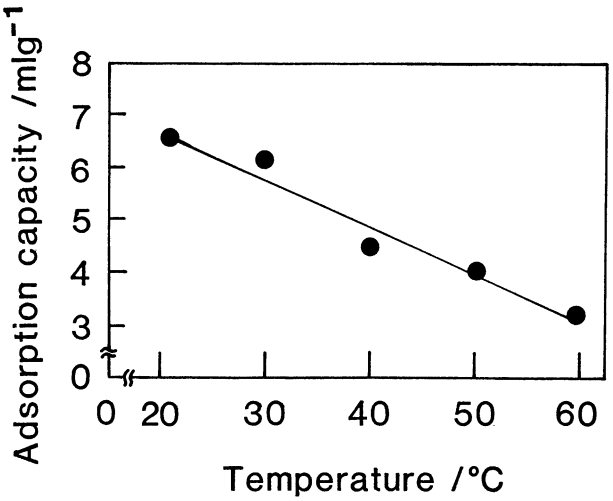

Fig. 5. Temperature dependence of CO_2-adsorber with MSC.

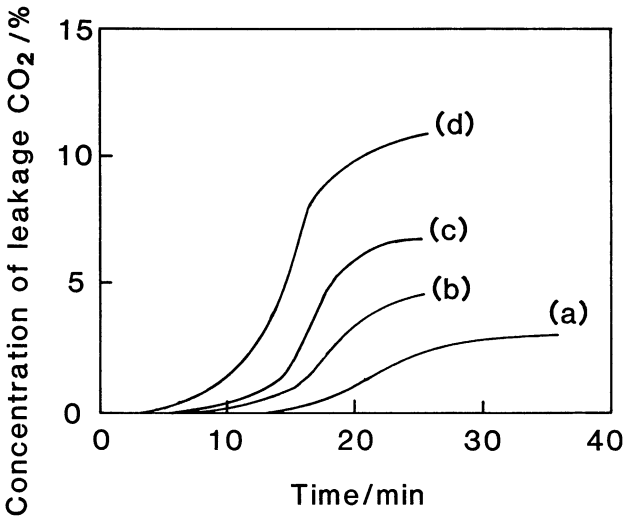

Fig. 6. Leaked CO_2 concentration vs. adsorption time for various concentration of introduced CO_2. (a): 3.4; (b): 5.7, (c): 8.0, and (d): 12.4%.

S_{BET} was smaller than S_t. The difference seems to be due to the fact that the t-method is based on a standard adsorption isotherm of nonporous carbon.

The pore-size distribution of MSC obtained from N_2 adsorption isotherms by using the MP-method is shown in Fig. 4. In the figure, R_p shows the micropore radius, and V_p the pore volume. The maximum of $\Delta V_p/\Delta R_p$ (differential value of V_p/R_p) is located at R_p=0.34 nm. Assuming that the walls of the pores are parallel plates, the most common pore diameter is 0.68 nm. The MSC is, thus, concluded to contain only micropores.

2. Characteristics of Adsorber. In a CA storage system, the adsorption of CO_2 was usually carried out in a temperature range of 5 to 60 °C. The concentration and the space velocity of adsorbed CO_2 varied with the concentration of CO_2 in the storeroom. It is therefore important to study both the temperature and the space velocity dependence of adsorbers with MSC.

The CO_2 adsorption capacity was estimated as follows: The concentration of leaked CO_2 was plotted against the time of adsorption and the amount of adsorbed CO_2 was accumulated until the time when CO_2 began to leak (break point).

Figure 5 shows the temperature dependence of the CO_2 adsorption capacity of adsorbers with MSC. The gas used in this experiment was a mixture of 9% CO_2 and 91% N_2. The adsorption capacity of adsorbers at 20 °C is 6.5 ml g^{-1}. In this experiment, the adsorption pressure of CO_2 was not clear; therefore, the estimated amount of adsorbed CO_2 by the flow method could not be compared with that by the conventional volumetric method. The CO_2 adsorption capacity decreases with increasing the temperature of adsorption. This result indicates that the physical adsorption of CO_2 onto MSC occurred. The adsorption capacity of CO_2 at 60 °C decreased to 55% in comparison with that at 20 °C. Almost all of the adsorbed CO_2 was desorbed from MSC by blowing air into the adsorber over a temperature range of 20 to 60 °C. It is known that the pore shape of MSC was a parallel plate slit;[17] the desorption of gases from MSC was therefore easy. In accordance with this fact, the hysterisis of the adsorption isotherm for MSC was small, as is shown in Fig. 1.

The CO_2 breakthrough curves for CO_2 adsorbers with MSC at various concentrations of introduced CO_2 are shown in Fig. 6. The concentrations of introduced CO_2 were 3.4% (curve a), 5.7% (curve b), 8.0% (curve c), and 12.4% (curve d). In this experiment, the space velocity was 270 h^{-1} and the adsorption was carried out at 17 °C. In the figure, the break points are inversely proportional to the concentration of introduced CO_2. In the CO_2 adsorption isotherm of MSC shown in Fig. 1, the adsorbed amount of CO_2 increases rapidly within the low relative pressure region. It is reported[17] that gas adsorption on MSC within the low relative pressure

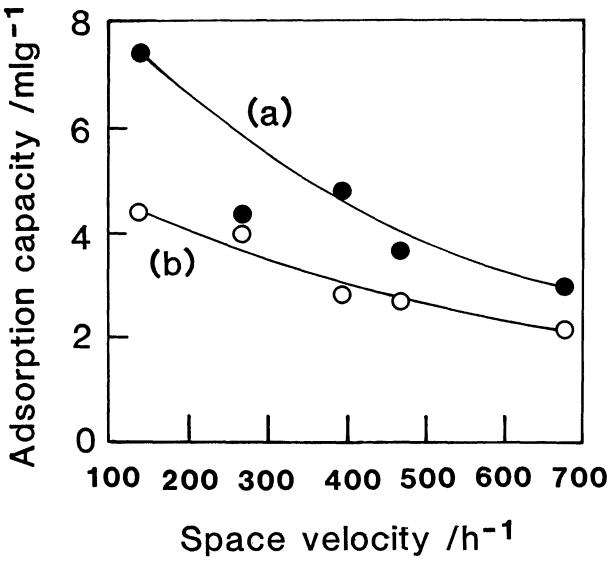

Fig. 7. Space velocity dependence of CO_2-adsorber with MSC for different concentration of introduced CO_2. (a): 12.4 and (b): 3.4%.

region can be attributed to adsorption by micropores. Therefore, MSC was a suitable adsorbent for CO_2 adsorbers in a CA storage system.

Figure 7 shows the space-velocity dependence of CO_2 adsorbers with MSC for different concentrations of introduced CO_2. The experiment was carried out at 17 °C. The concentration of introduced CO_2 was 12.4% (curve a) and 3.4% (curve b). In the case of (b), the CO_2 adsorption capacity gradually decreases with increasing space velocity. In the cass of (a), the capacity decreses largely with increasing space velocity. Thus, the CO_2 adsorption capacity in this experiment seems to be smaller than that of the volumetric method (saturated adsorption amount of CO_2). In order to operate the adsorber effectively, it was important to study the dependence on both the temperature and space velocity of the adsorbers.

Only MSC with micropores showed a large CO_2 adsorption capacity over a wide range of temperature, concentration, and space velocity. It is, thus, a suitable adsorbent for CO_2-adsorbers in a CA storage system.

Conclusion

1) The BET surface area of MSC was 592 $m^2 g^{-1}$. In the pore size distribution curve of MSC, the most common pore diameter was 0.68 nm. From the *t*-plot of MSC obtained from the N_2 adsorption isotherm, the specific surface area (S_t) and external surface area (S_{EXT}) of the MSC were calculated to be 711 and 16.4 $m^2 g^{-1}$, respectively. The S_{BET} was smaller than S_t.

2) The adsorption capacity of CO_2-adsorber with MSC was determined by the gas-flow method. The capacity of the adsorbers at 60 °C decreased to 55% in comparison with that at 20 °C; it decreased with increasing the space velocity.

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