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Measurement of adsorption characteristics of alumina and activated carbon using a quartz crystal resonator with *i*-butane

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Abstract−A new device for measuring the pore characteristics of adsorbents is developed for fast measurement and convenient sample handling. The proposed device utilizes a quartz crystal resonator capable of detecting the change of mass loading in nanogram scale. The measured material is coated on the electrode surface of the resonator, and the change of resonant frequency of the resonator at different pressures of adsorbate gas is converted into the adsorbed amount used in the computation of the adsorption surface area and pore size. For the performance evaluation of the device, alumina and activated carbon are tested with the adsorbate, *i*-butane. The experimental results show that the proposed device gives comparable measurements with some deviation to the reference values of the adsorption characteristics. It is proved that the device is relatively simple and requires short measurement time and the mild condition of sample handling.

Key words: Quartz Crystal Resonator, Adsorbent, Adsorption Characteristic, *i*-Butane Adsorption

INTRODUCTION

One of the common characteristics of an adsorbent is the specific surface area representing its adsorption capacity. Among various techniques measuring the characteristic capacity a gravitational method measures the mass of adsorbed amount at different pressures of adsorbate, and the surface area is computed from an isotherm utilizing the measurements. As the sensors for detecting a tiny change of pressure have been developed lately, a more convenient technique of volumetric method is widely employed instead of the gravitational method by measuring pressure variation and converting into the adsorbed volume of the adsorbate. These current techniques are applied at the cryogenic condition near the boiling point of the adsorbate, such as nitrogen and argon. At the low temperature the adsorbed amount is large enough to be measured as a change of mass or pressure, but it takes time to reach equilibrium due to the low temperature. When a small amount of mass variation can be measured, the adsorbed amount is not necessarily large to be detected and the measurement can be conducted near the room temperature.

As other than the nitrogen adsorption, combined NMR cryoporometry, relaxometry and diffusometry were used to monitor the molecular transport of the adsorbate and to characterize the adsorbent structure [1]. In case of thin films, the pore characteristic was determined with the optical ellipsometry porosity [2]. Though the measurement was conducted at an ambient temperature, the results were comparable to those of classical adsorption measurements. The pore size distribution of mesoporous material was measured from the adsorption and desorption curves of *n*-nonane [3] at a mildly high temperature, and pore characteristics were examined with *n*-hexane [4].

A quartz crystal resonator has a thin quartz crystal plate with two metal electrodes on both sides that establish an alternating electric field across the plate, causing vibrational motion of the plate at its resonant frequency. This frequency is sensitive to mass loading on the electrodes [5]. For example, a 9 MHz resonator detects mass variation with a sensitivity of 1.4 ng/Hz [6]. Quartz crystal microbalances utilize the characteristic of frequency variation with changed mass loading. A measurement technique of the sensitivity for practical materials in air and water has been introduced for the application of the quartz crystal resonator [7].

Instead of the direct measurements of surface loading [8], a modification of the electrode surface of the quartz crystal resonator has been used for the entrapment of target materials inducing a load change. In the determination of organic substances either in gas or liquid phase, organic film has commonly been coated on the surface of one of its electrodes [9,10]. Though polymer film-coated resonators [11-13] have been improved in terms of the stability of the coated material and selectivity of the detected material, they have different characteristics from solid adsorbent coated resonators. Carbon-coated quartz crystal resonators have high stability for a wide range of applications. Kim et al. [14] investigated the stability of a carbon-coated resonator to find that it is very stable and easy to regenerate by simple thermal treatment. In another study [15], activated carbon was coated on the electrode surface by using a binder of phenol resin, and its detection performance was examined with various organic substances in air. The activated carbon is a good adsorbent for organic substances having relatively small molecules due to its micropores. In the measurement of large molecules a mesoporous material was coated on the resonator, and the concentration of dye in water solution was determined in Kim et al. [16]. While the specific adsorbents

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Table 1. Computed surface area and pore size and their reference values of activated alumina and activated carbon

Adsorbate	Surface area (m^2/g)		Pore diameter (nm)	
	Measured	Reference	Measured	Reference
Alumina-1	282	270	5.5	5.7
-2	379		5.7	
-3	373		6.7	
Activated carbon-1	850	1,042	1.5	2.0
-2	771		3.1	
-3	1,025		2.5	

have been used to detect target substances, an adsorbent can be characterized by using the adsorbate readily obtainable and handled.

In this study, a new measurement device of the adsorption capacity of adsorbents is proposed, and its performance is examined with alumina and activated carbon. A quartz crystal resonator coated with the adsorbents is employed to determine the amount of gas adsorbed. For the measurement readiness, *i*-butane is used as adsorbate instead of nitrogen commonly used in the measurement. The adsorption experiment is conducted at its boiling point close to the room temperature, which makes the sample handling easy. The variation of resonant frequency of the resonator is used to calculate the amount of gas adsorbed at different pressures, and the BET isotherm is employed to estimate the surface area and average pore size of the adsorbents.

BET ISOTHERM

To calculate pore characteristics from the adsorption measurements in this study the Brunauer, Emmett and Teller (BET) isotherm is employed. From the measured variation of the resonant frequency at a given pressure, the adsorbed volume of adsorbate is calculated at the standard condition for a unit mass of adsorbent. The volume of adsorbate necessary to cover unit mass of the adsorbent with a monomolecular layer is found from the following BET isotherm from the measurements of the adsorbed volume, V_a, at different pressures.

$$\frac{p}{V_a(p_0-p)}=\frac{1}{V_mC}+\frac{C-1}{V_mCp_0}p \tag{1}$$

where p_0 is the saturation pressure, C is a parameter related to the heat of adsorption and V_m is the monomolecular layer volume. The slope and intercept of the relationship between the measured volume of adsorption and pressure give the monomolecular layer volume. Then, the surface area, a_s, is computed from the following equation.

$$a_S=L\sigma\frac{V_m}{22414} \tag{2}$$

where L is the Avogadro number and σ is

$$\sigma=2\sqrt{3}\left(\frac{M}{4\sqrt{2}L\rho}\right)^{2/3} \tag{3}$$

In Eq. (3), M is the molecular weight of adsorbate and ρ is its density. Also, from the adsorbed volume at the saturation pressure the total pore volume, V_p, is found from adsorbate molecular weight and density using

$$V_P=\frac{VM_g}{22414\rho_g} \tag{4}$$

Finally, the average pore size is calculated from the surface area and pore volume by assuming that the pores are cylindrical.

EXPERIMENTAL

1. Materials

Activated alumina (Sumitomo Chemical, Japan, KHD) and activated carbon (Borim Chemical, Korea) were used as sample materials in the examination of measurement performance of the proposed device. The adsorption characteristics of the samples are listed in Table 1 as reference. The characteristic of the alumina was provided by the manufacturer, and that of the activated carbon was measured

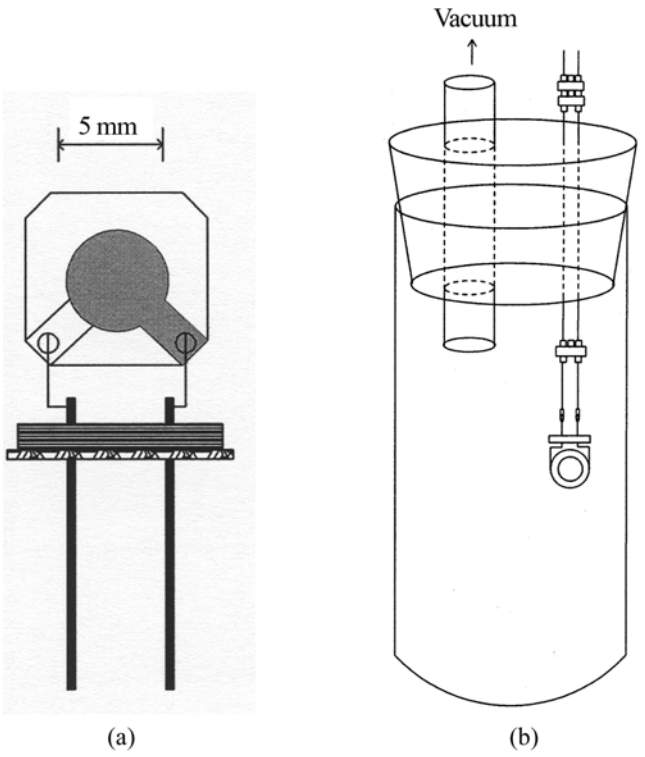


Fig. 1. Schematic diagrams of a quartz crystal resonator (a) and measuring cell module (b).

with an adsorption apparatus (Micromeritics Instrument, U.S.A., TriStar 3000). The adsorbate was *i*-butane (Yeungil Butane, Korea).

2. Equipments

An AT-cut quartz crystal resonator having base frequency of 8 MHz (Sunny Electronics Co., Korea) was utilized in this experiment, and its schematic is shown in Fig. 1(a). The electrodes of the resonator were silver finished. The fine particles of sample were coated on the one side of the resonator using phenol resin (Novolac, Dong Kwang Chem., Korea) as a binder. A 0.3 g of the phenol resin and a 0.3 g of coupling agent (Hansol Fine Chemical, Korea, LICA 38) was dissolved in a 7.6 mL of methanol, and the solution was stirred for an hour. After a 1 μL of the binder solution was spread on the surface of electrode, the sample particles were mildly sprayed with a brush. The treated resonator was heated at a temperature of 130 °C for half an hour followed by a cooling of 10 minutes at the room temperature. For the determination of the particle amount, a separate quartz crystal resonator was prepared only with the binder coated. The sample amount is obtained from the differences between the frequencies of the binder only resonator and particle-coated resonator. Because the adsorbed amount of adsorbate per unit gram of adsorbent is used in the isotherm calculation and the amounts of adsorbate and adsorbent are determined from the frequency variation, the resonant sensitivity of the resonator is not significant in the computation.

A cell module holding the resonator was built with a glass cylinder - 30 mm in diameter and 95 mm in length - of which the schematic is illustrated in Fig. 1(b). A rubber stopper sealed the cylinder. A glass tube was placed in the stopper for air evacuation and *i*-butane supply. Two thin wires were installed through the stopper to connect the resonator and an oscillation circuit. The resonant frequency was measured with a home-made frequency counter, which was connected to a PC for data collection. The module pressure was monitored with a dial gauge for experimental manipulation and a pressure transducer for continuous data collection in the PC.

3. Procedures

The resonator was installed in the specially designed module as depicted in Fig. 1(b), and the resonator was directly attached to the oscillation circuit for the minimum noise to the measurement signal. The digital signals of the resonant frequency and the module pressure were provided to the PC for data processing. The module was placed in a water bath described in Fig. 2, and the bath contained 3 L of water and 1 L of methanol. While the methanol solution was continuously stirred, an immersion cooler provided the bath cooling at a temperature of −11.7 °C, the boiling point of *i*-butane. After the temperature had become stable, the air in the sample bottle was completely evacuated and waited for about 15 min until the resonant frequency settled. For the supply of a small amount of *i*-butane, a balloon was placed between gas cylinder and the sample module. In the beginning the gas was supplied to the balloon, and the valve connected to the cylinder was closed. The gas supply during the experiment was provided from the balloon. The gas supply of small amount from the balloon is much easier than that from the high pressure cylinder. When the frequency was stable, the gas was supplied until the module pressure was raised by about 100 mmHg. The frequency measurement was waited for about one minute to be steady. Then the pressure adjustment and frequency measurement were repeated until the pressure reached at the saturation pressure.

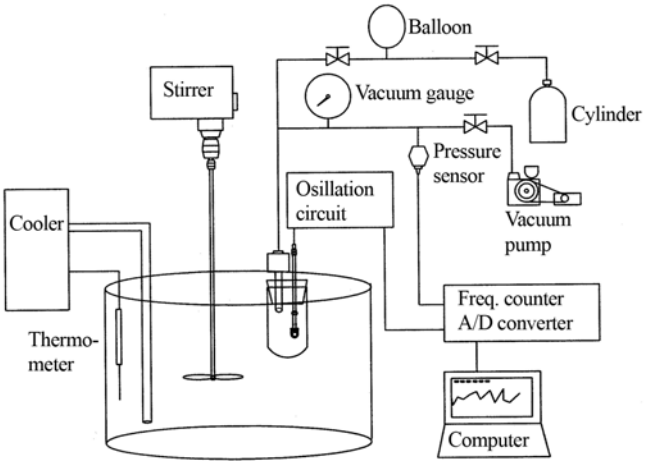


Fig. 2. Experimental setup.

RESULTS AND DISCUSSION

After the air in the measuring cell had been evacuated, the adsorbate, *i*-butane, was supplied for a step-wise increase of cell pressure, while the cell temperature was maintained at a temperature of −11.7 °C. When the resonant frequency had settled at a pressure, the next step of the pressure was applied. The bottom plot of Fig. 3 indicates the pressure variation, and the top shows the variation of resonant frequency. During the measurement of resonant frequency, resonant resistance was also determined for reference as given in the middle of the figure. The adsorption experiment was conducted until the adsorbent was saturated. After the saturation desorption experiment was continued by evacuating the adsorbate gas as shown in the right half of the plots in Fig. 3. Though the pressure returned to the initial pressure, the initial resonant frequency was not obtained, indicating a hysteresis between the adsorption and desorption. Because the quartz crystal resonator of this study is sensitive to pres-

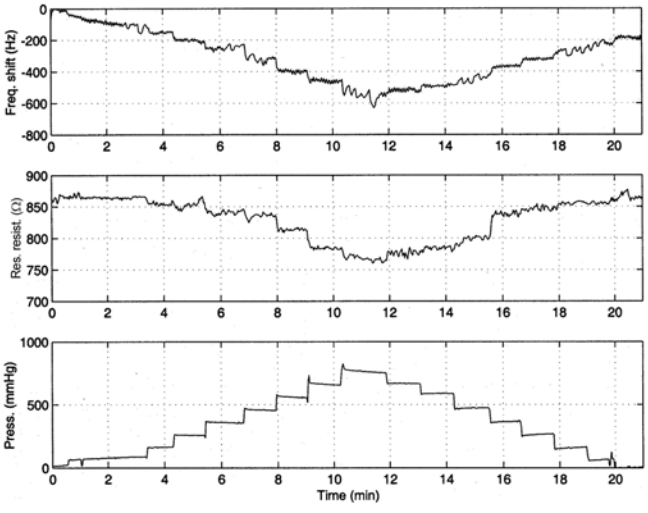


Fig. 3. The variations of resonant frequency and resonant resistance of alumina coated resonator while the pressure is increased and then decreased in step.

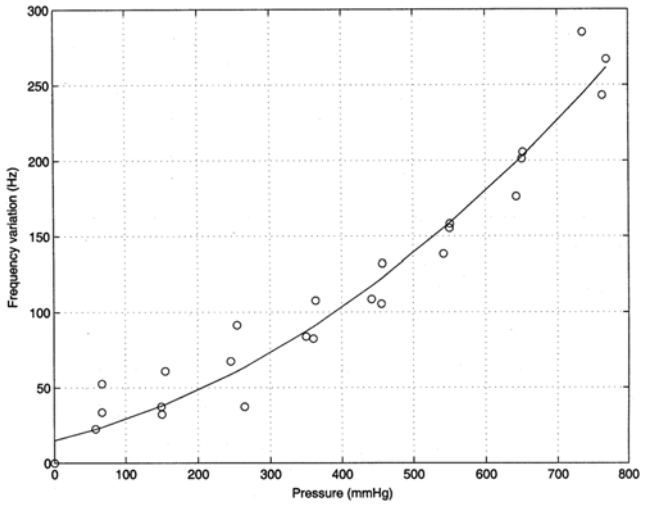


Fig. 4. The variation of resonant frequency with three blank resonators.

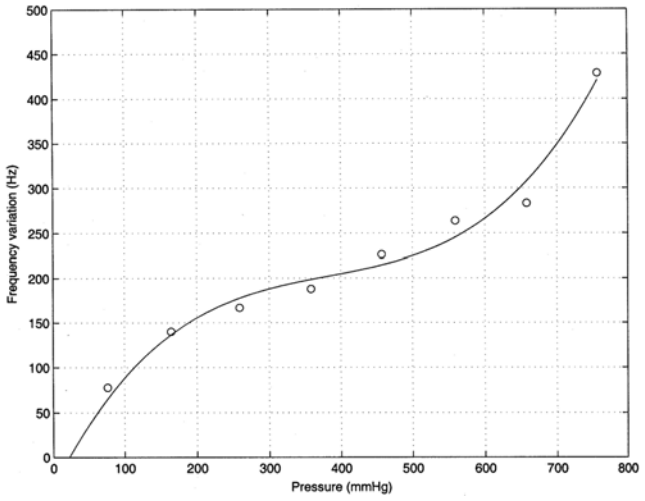
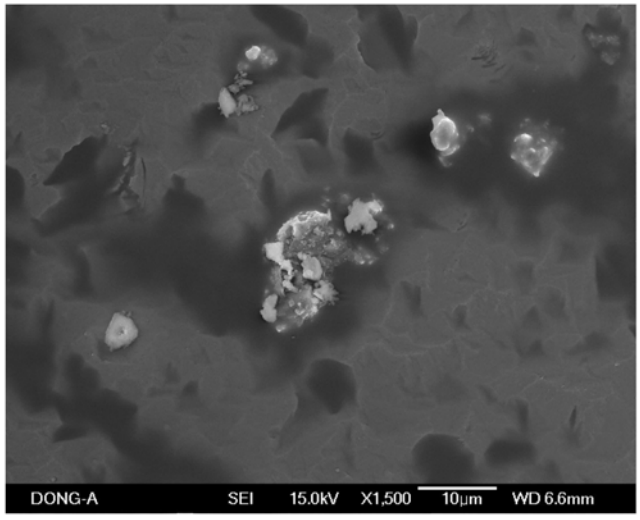


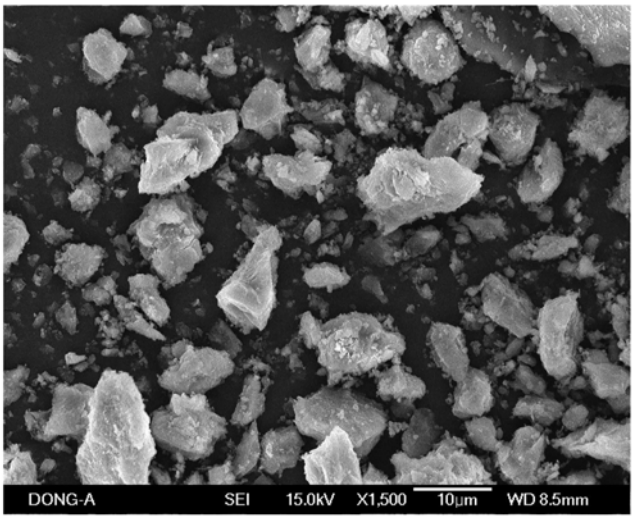
Fig. 5. The variation of resonant frequency of alumina-1 with pressure change. The variation of blank resonator is deduced.

sure change, a blank test was conducted with the resonator only coated with the binder. The test result includes the effects of the pressure change and the binder coated on the electrode surface of the resonator. The variations of resonant frequency with three different resonators are illustrated in Fig. 4. Though there was some deviation among the measurements, a steady increase of the variation was observed, and the computed values from the fitted curve at a given pressure were deduced from the adsorption measurement of samples.

The first measurement of alumina adsorption is demonstrated in Fig. 5. The variation of resonant frequency indicates the amount of adsorbed *i*-butane. The adsorption in the alumina particles coated on the electrode surface of the resonator increases mass loading on the electrode, resulting in the reduction of resonant frequency of the resonator. Therefore, the frequency variation is converted to the adsorbed amount of the adsorbate. The isotherm of Fig. 5 is the type IV adsorption of a mesoporous adsorbent as defined in the IUPAC classification. Considering the pore size of alumina, a mesoporous adsorbent, it is reasonable that the isotherm is similar to that of the mesoporous adsorbent. The adsorption surface area of the alumina was computed by using the BET isotherm, and the average pore size was also obtained using the assumption of cylindrical pore shape. The calculated surface area and pore size are listed for three different measurements and compared with the reference values in Table 1. The values of alumina were provided by the manufacturer, and those of the activated carbon were measured with the adsorption apparatus. While the calculated surface area of the alumina is about 28% larger than the reference, the pore size is close to that. In the adsorption measurement that much difference is often yielded. A microscopic observation was conducted with a scanning electron microscope (Hitachi, Japan, S-3400N). Figs. 6(a) and 6(b) show the surface of alumina coated resonator and the alumina particles, respectively. Though the amount of coated particles is small, the shape of the particles is similar to the uncoated particles. It indicates that the effect of binder used in the preparation of the resonator is minimal.



(a)



(b)

Fig. 6. SEM photographs of alumina coated resonator (a) and uncoated particles (b).

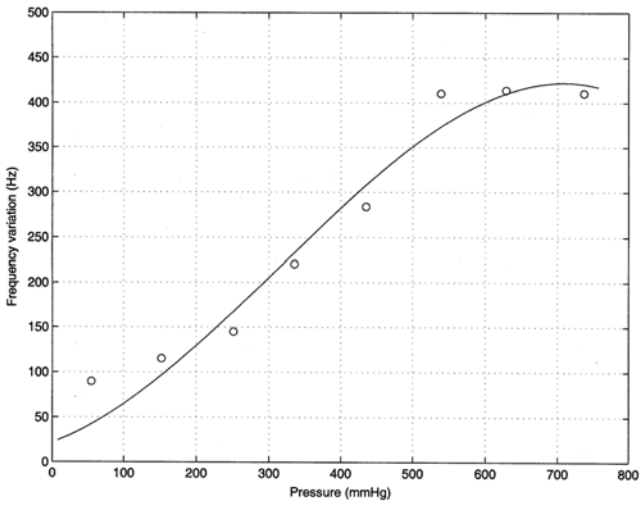
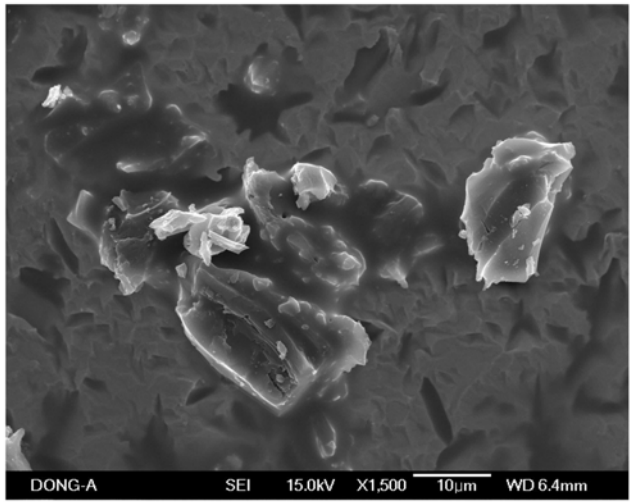
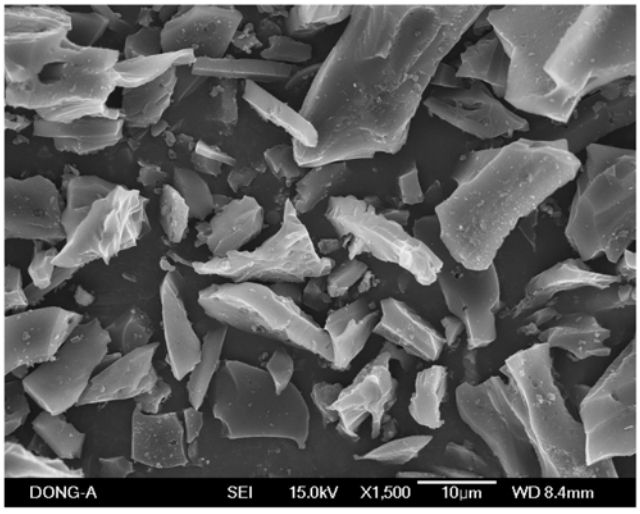


Fig. 7. The variation of resonant frequency of activated carbon-1 with pressure change. The variation of blank resonator is deduced.



(a)



(b)

Fig. 8. SEM photographs of activated carbon coated resonator (a) and uncoated particles (b).

The pore characteristic of activated carbon was measured in the same manner. Fig. 7 demonstrates the variation of resonant frequency at different pressures of *i*-butane. The isotherm is the type IV adsorption of a mesoporous adsorbent in the IUPAC classification. Because the pore size of the activated carbon is smaller than that of alumina, the uptake in the isotherm occurs at lower pressure than that of alumina. The calculated surface area and pore size are also listed in Table 1. The results of three measurements indicate that the surface are is about 15% less than the reference value and the average pore size is close to the reference with some variation. To reduce the deviation between the measurements and the reference values, it is suggested to minimize the size of measuring cell for the accurate control of measurement temperature. A comparison of the coated and uncoated particles with microscopic observation is shown in Figs. 8(a) and 8(b). Though some particles are buried in the binder, a large portion of particles are exposed.

The measurement of pore characteristics is a time consuming process, and requires a special instrument with cryogenic experimental wares. In this experiment a relatively simple device which can replace the current technique of the measurement was introduced, and its performance was exhibited with the measurements of pore characteristics of activated alumina and activated carbon. Because the molecular size of the adsorbate, *i*-butane, is much larger than nitrogen or argon, commonly used adsorbates in the measurements of pore characteristics, the measurement of microporous adsorbent is not available. However, the results of adsorption characteristic measurement are comparable to those of the current method of nitrogen adsorption. Because the measurement temperature is mild compared with nitrogen adsorption, the required time to reach adsorption equilibrium is very small and the whole measurements consume much less time than the conventional adsorption techniques.

The BET isotherm used here for the computation of surface area and pore size has been employed most of nitrogen adsorption at 77.4 K. The application of the BET isotherm in this study is based on the assumptions of: (1) *i*-butane is non-polar, its interaction with the adsorbents is limited; (2) intermolecular interaction between adsorbate molecules is weak; (3) the heat of adsorption of the second monolayer is assumed to be the condensation enthalpy because the adsorption heat of the first monolayer is small and the intermolecular interaction is weak. These assumptions have been used in the adsorption of hexane [4].

CONCLUSION

A new device measuring the pore characteristics of porous material is proposed, and its performance is examined with activated alumina and activated carbon. The device utilizes a quartz crystal resonator coated with the measured adsorbents and *i*-butane as an adsorbate having a mild boiling point. The variation of resonant frequency of the resonator is converted into the adsorbed amount. The measuring device is relatively simple compared with the existing adsorption apparatus, and requires no cryogenic experimental wares. Also, the measurement is much faster than the current techniques. The experimental results indicate that the device gives some variation, but the measurements are comparable to the values from the current technique of nitrogen adsorption.

ACKNOWLEDGMENTS

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NOMENCLATURE

a_S : BET surface area [m^2/g]
C : parameter related to adsorption heat [-]
L : Avogadro number [-]
M_g : molecular weight of adsorbate [-]
p : pressure [Pa]
p_0 : saturation pressure [Pa]
V : adsorbed volume at adsorption pressure [cm^3]
V_a : adsorbed volume [cm^3]
V_m : monomolecular layer volume [cm^3]
V_p : pore volume [cm^3/g]

Greek Letters

ρ_g : adsorbate density [g/cm^3]
σ : monomolecular layer surface area [m^2]

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