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Gravimetric Characterization of Porous Ceramic Thin Films with Quartz Crystal Microbalance

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Direct measurement of N_2 adsorption onto porous Al_2O_3 films was examined with a quartz crystal microbalance at 77 K. Nitrogen adsorption led to the change in resonant frequency (ΔF) of the Al_2O_3 coated quartz crystal. A cumulative plot of ΔF at the relative pressure corresponds to the N_2 adsorption isotherm, from which pore size distribution and surface area of the Al_2O_3 thin films (ca. 0.1 mg) were successfully obtained.

Porous ceramic films have much interest because of the importance for industrial applications such as separation or filtration. Many chemical processes have been developed to prepare porous ceramic films in the last decade, e.g., the sol-gel process is believed to be one of the most excellent method to attain "nanometer porosity" for micro-filtration and for gas separation.[1-3] In order to realize these new applications, ceramic films must have well-designed microstructures within limited thickness enough to bring about the excellent permeability or selectivity. The design of a porous solid requires the information of the surface area, pore volume and pore size distribution, which are conventionally obtained by means of gas adsorption in a volumetric vacuum system. As concerns thin films, however, the direct measurement of these characters is quite difficult because of extremely small quantities. A sensitive and simple method for gas adsorption measurement is strongly desired to characterize the porous ceramic thin films.

Recently, a new gravimetric microanalysis with quartz crystal microbalance (QCM) has been developed to detect an extremely small change of weight. Many application of QCM has been proposed so far such as gas detector, gas sensor, liquid phase microbalance, and electrochemical systems.[4-7] In this method, the change of mass of the coating films is detected by measuring the resonant frequency of an oscillating quartz crystal. The QCM is sensitive to the change of weight less than 10^{-8} g, being useful for accurate detection of a trace amount of gas adsorption.

In this communication, we have developed a new gravimetric adsorption measurement for characterization of porous films by the use of QCM. The pore size distribution and surface area are successfully obtained from N_2 adsorption isotherms which are calibrated by the change of the frequency of QCM.

Commercially available AT-cut piezoelectric quartz crystals (6 MHz) were used for the gravimetric measurement of N_2 adsorption at liquid nitrogen temperature (77 K). Silver electrodes (0.5 cm^2) were deposited by evaporation onto both surfaces of the quartz crystal. Alumina was selected as the porous coating materials. They were coated on the quartz by dipping of the sol, which was prepared by hydrolysis of the metal alkoxide. Figure 1 shows the fracture surface of the coated quartz crystal thus obtained. The film deposited on an Ag electrode is about 2 μm in thickness. Besides this film, γ-alumina powders were coated on the quartz crystal as suspension of turpentine oil and were also submitted to N_2 adsorption measurements. The weight of the porous film is estimated by measuring the change of the frequency caused by the coating.

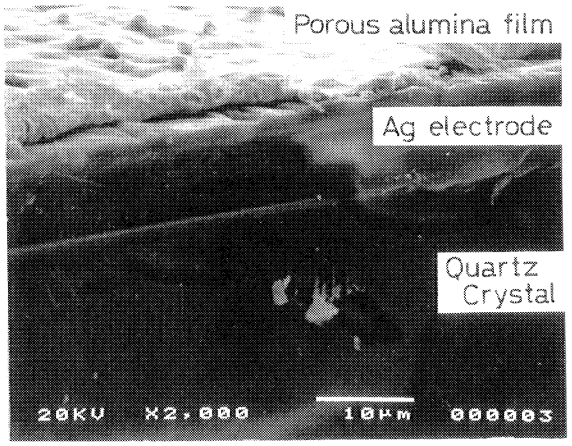

Fig. 1. SEM image of fracture surface of Al_2O_3 coated quartz crystal.

Nitrogen adsorption was examined by the QCM equipped to a volumetric vacuum system (Fig. 2), which consists of the coated quartz crystal and a Colpitts-type oscillating circuit made of TTL-IC (SN74-LS00). The oscillating circuit is powered by constant voltage supply at DC 5 V. The output frequency from the oscillator was measured with a frequency counter (Iwatsu SC7101) with a resolution of 1 Hz. After evacuating the coated quartz crystal at 527-673 K in vacuo, the amount of N_2 adsorption was measured as the corresponding change of the frequency. For comparison, a nitrogen adsorption isotherm of the bulk sample, which was obtained by drying the sol at room temperature, was measured by the conventional manometric method.

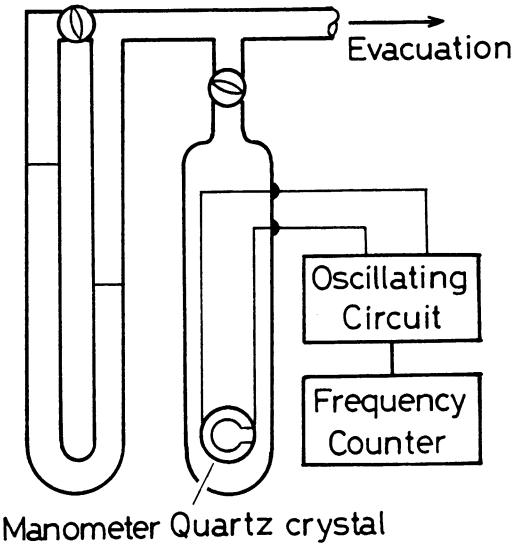

Fig. 2. Experimental arrangement for gravimetric adsorption measurement.

The quantitative relation between the frequency of the AT-cut quartz crystals and the change in weight of coated film has been proposed by Sauerbrey[8] as follows:

$$\Delta F = (-2.3 \times 10^{-6}) \times F^2 \times \Delta W/S \qquad (1)$$

where ΔF is the change in frequency (Hz), F is the resonant frequency of the crystal (Hz), ΔW is the change in weight (g) and S is the area of coating films (cm^2). The coefficient, 2.3×10^{-6}, results from the density and the acoustic wave velocity of the quartz crystal. We confirmed the relation both by galvanostatic

electrodeposition of Cu on the Ag electrode in a liquid phase and by manometric measurement of N_2 adsorption in a vapor phase. The equation (1) means that the limit of detection of this gravimetric method is 4 X 10^{-10} mol (ca. 10^{-5} cm^3 at STP) of N_2. The sensitivity of QCM is much higher than any conventional volumetric or gravimetric method used so far.

Prior to N_2 adsorption measurement, pressure dependence of resonant frequency of a non-coated quartz crystal was measured in a vacuum system. When the temperature was maintained constantly at 77 K, the resonant frequency was independent of pressure with an error of 10 Hz at 1-10^5 Pa of He. Therefore, when N_2 adsorption onto the coating leads to the change of the resonant frequency,the adsorption amount is directly obtained from the net ΔF value at any relative pressure. Figure 3 shows a cumulative plots of ΔF at the relative pressure for the porous Al_2O_3 film. The amounts of N_2 adsorption obtained from cumulative ΔF value agreed with those from manometric measurement for the bulk gel of Al_2O_3. Table 1 shows BET surface areas of the film and γ-Al_2O_3 powders calculated from the amount of N_2 adsorption. Regardless of the difference in sample weight (0.8-2.0 g for manometric measurement and ca. 0.1 mg for the QCM), the results from these two methods agreed very well.

Pore size distribution of a Al_2O_3 film was calculated by the method of Inkley. The curves of

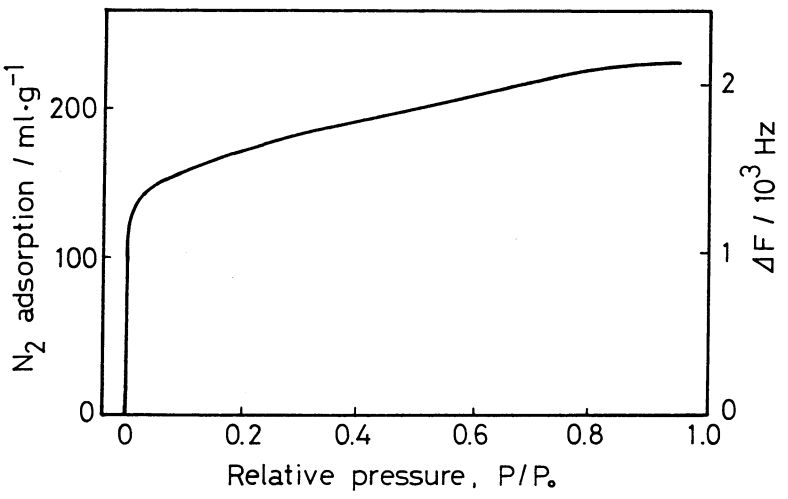

Fig. 3. Nitrogen adsorption isotherms for the Al_2O_3 coating measured with QCM.

Table 1. BET surface areas of porous Al_2O_3 coatings

Coating, temp [a]	Surface area / m^2g^{-1} QCM	Manometry
Sol-gel derived film, 673 K	303	354
powder, 873 K	178	179
powder, 1373 K	63	71

a) Heat treatment temperature.

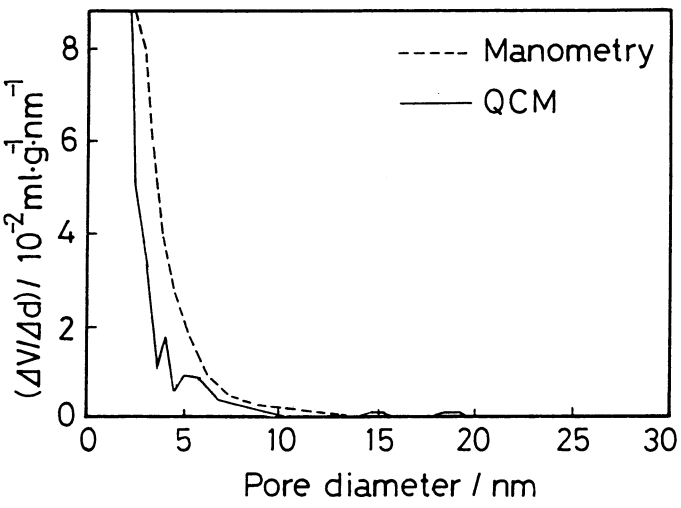

Fig. 4. Pore size distribution of the Al_2O_3 measured with QCM and manometry.

adsorption isotherm of N_2 obtained from the plot of cumulative ΔF against the relative pressure ($0 < P/P_o < 1.0$) are differentiated numerically to obtain the pore size distribution. Figure 4 shows the result in comparison with the manometric data for the bulk Al_2O_3 gel. These pore size distributions are very similar on their shapes and cumulative pore volume. In both cases, most of pores are smaller than 5 nm in diameter. This result was confirmed by TEM observation, which showed that the diameter of alkoxide-derived partile is about 5 nm.

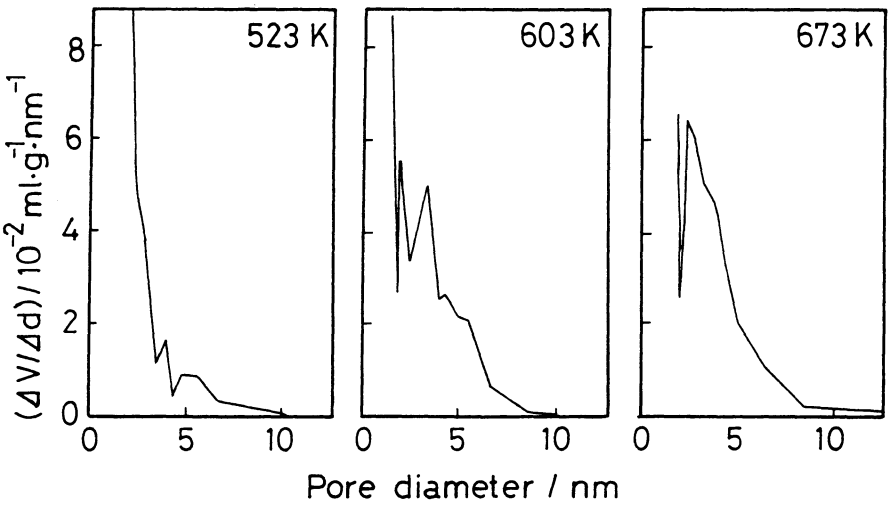

Fig. 5. Effect of heat treatment on the pore size distribution of the Al_2O_3 coating measured with QCM.

Figure 5 shows the effect of heat treatment on the pore size distribution of Al_2O_3 coating. Although the population of pores smaller than 2 nm decreased with elevating the heating temperature, the pore distribution shifts to the larger pore size. The gravimetric measurement with QCM is effective in detecting such a small change of microstructures of the porous thin films.

Consequently, direct characterization of the porous ceramic thin film was first developed by the use of QCM. This method is very useful for measurement of surface area and pore size distribution of a slight amount of porous solids. Since the quartz crystal oscillates stably in a wide temperature range (77-673 K), the QCM can make a variety of application to detect chemical or physical adsorption onto porous films.

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