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Water vapor adsorption and desorption of mesoporous materials derived from metakaolinite by hydrothermal treatment

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Abstract

Mesoporous materials were prepared by hydrothermal treatment of powder-compacts consisting of metakaolinite, quartz and slaked lime with different forming pressures. The hydrothermally solidified materials developed strength despite the formation of hydrogarnet. The hydrothermally solidified materials exhibited a broad pore size distribution of more than 3.4 nm, and the volume and specific surface area increased with decreasing the forming pressure. The hydrothermally solidified materials showed an excellent humidity-controlling ability due to adsorption and desorption of water vapor by utilizing their mesopores.

Keywords: B. Composites; D. Clays; E. Functional Applications; Hydrothermal treatment

1. Introduction

Some kinds of mesoporous materials have humidity control properties resulting from capillary condensation. The materials can adsorb water vapor at high humidity and release it at low humidity, and can thus maintain appropriate indoor humidity. In general, the relative humidity range in which a person feels comfortable is said to be 40–70%. The calculations based on the Kelvin equation of capillary condensation and Arai's correction equation yield pore diameters of 3.2 nm for 40% relative humidity and 7.4 nm for 70%. The introduction of pores with adequate diameters into the materials allows the humidity to be controlled. Research has been conducted on mesoporous materials with humidity-controlling properties, for example, silica gel, alumina gel, sepiolite and diatomaceous earth [1–5]. Humidity-controlling materials have already been reported to reduce energy consumption by 5–30% [6]. Because humidity-controlling materials can reduce the environmental load, their synthesis has attracted a great deal of attention.

The energy required to synthesis ceramics by hydrothermal treatment is even lower, about 2.7 GJ/m^3, which is only 1/6th that of the energy needed to synthesis ceramics by sintering [7]. Research has been conducted on the hydrothermal reactions and solidification behavior of typical calcium silicate hydrate materials, for example, tobermorite and C–S–H gel, in a CaO–SiO_2–H_2O system [8–10]. It was reported that the hydrogarnet as a main phase forms when the ratio of Al/(Al + Si) is more than 0.12 in a CaO–SiO_2–Al_2O_3–H_2O system, leading to a reduction of the strength of the materials [11,12]. In a CaO–SiO_2–Al_2O_3–H_2O system, there is little information on hydrothermally solidified materials made using clay minerals containing a large amount of Al as a starting material. We recently succeeded in preparing solidified materials with mesopores derived from kaolinite [$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$] or metakaolinite [$2SiO_2 \cdot Al_2O_3$] using a hydrothermal treatment [13,14]. It was reported that the formation of new deposits between the particles of each starting material leads to the formation of mesopores [14]. The prediction using the Kelvin equation and Arai's correction equation suggests that the mesopore volume of the material could play an important role in humidity control in airtight buildings. Our strategy for controlling of mesopore size and volume is to control the distance between the starting material particles of powder-compacts by uniaxially pressing them at different pressures for the purpose of enhancing their humidity-controlling properties. In the present work, we synthesized hydrothermally solidified

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materials using metakaolinite with different mesopore volumes to act as humidity-controlling materials in airtight buildings, and we also examined their humidity-controlling properties.

2. Experimental

Metakaolinite was obtained by heating motoyamakibushi clay composed predominantly of kaolinite at 600 °C for 2 h to dehydrate the lattice water in the kaolinite. The heat treatment was determined by a thermal analysis of motoyakakibushi clay. Chemical composition of motoyamakibushi clay was determined to be 48.8 mass% of SiO_2, 33.8 mass% of Al_2O_3, 1.2 mass% of Fe_2O_3, 0.1 mass% of CaO, 0.3 mass% of MgO, 0.8 mass% of K_2O, 0.9 mass% of TiO_2 and 13.1 mass% of Ig. Loss by X-ray fluorescence and X-ray analysis indicated that motoyamakibushi clay contains kaolinite, quartz and muscovite. The kaolinite content was estimated to be ~73 mass% by norm calculation. The X-ray diffraction (XRD) pattern of metakaolinite prepared in the present work showed no peaks corresponding to kaolinite. The specific surface area of metakaolinite was estimated to be 38 m^2/g by a nitrogen gas sorption analysis.

Metakaolinite, quartz (average particle size $d_{50} = 100\ \mu m$) and slaked lime (average particle size $d_{50} = 10\ \mu m$) were used as starting materials. The mass ratio of metakaolinite:quartz:slaked lime was 40:40:20 [Ca/Si = 0.27, Al/(Al + Si) = 0.21 mole ratio]. These materials were mixed, and the mixtures were added to 25 mass% of distilled water. This mixture was pressed uniaxially at 15, 30 and 45 MPa. The powder-compacts were hydrothermally treated under saturated steam pressure at 180 °C for 10 h.

The crystalline phases in the materials were identified by XRD analysis. The flexural strength of the materials (5 mm × 15 mm × 40 mm) was estimated by a three-point bending test at a loading rate of 0.5 mm/min. At least four samples were used for the flexural strength test. The specific surface area, pore volume and pore size distribution of the materials were measured by a nitrogen gas sorption analysis. The water vapor adsorption–desorption isotherms of the materials were measured at 25 °C by using a HydroWin (Quantachrome Instruments). To examine the water vapor adsorption–desorption abilities of the materials, the weight change of the materials was monitored. The materials (40 mm × 90 mm × 5 mm) were kept at 53% humidity and 25 °C in a 7-L airtight chamber. The materials, excluding their top surfaces, were covered with aluminum tape so they would adsorb and desorb water vapor only through the top surface. After the weight stabilized at a constant value, the humidity was changed to 75%. This humidity was kept for 24 h, and then, the humidity was changed to 53% again for 24 h. The 53% and 75% relative humidity levels were controlled with $Mg(NO_3)_2 \cdot 6H_2O$–H_2O mixtures and NaCl–H_2O mixtures, respectively. The experiment was carried out to evaluate the ability of these materials to function in practical application as humidity controllers. The materials (40 mm × 45 mm × 5 mm), which were covered with aluminum tape excluding the top surface, were kept at 53% humidity in a 6-L airtight chamber. That is, the chamber had 6.5×10^{-2} g of water vapor. The temperature was changed from 15 to 30 °C according to the following cycle, which resembles a sine curve. In brief, after 8 h, the temperature increased from 23 to 30 °C. The temperature decreased to 15 °C after 18 h, and subsequently, increased to 23 °C after 24 h. The cycle was repeated several times. The change in the relative humidity and temperature of the chamber with and without the materials was monitored.

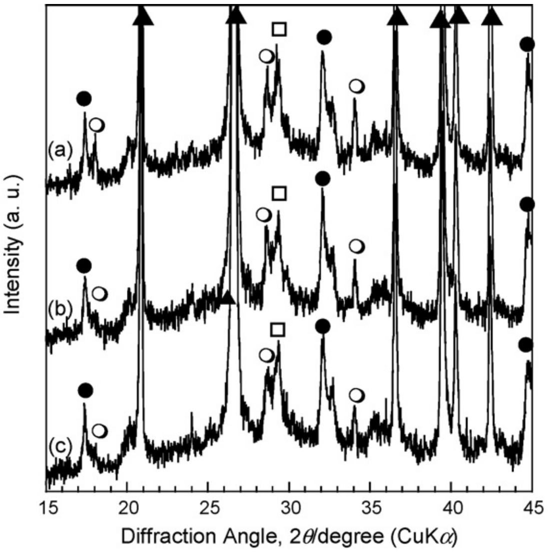

Fig. 1. XRD patterns of the hydrothermally solidified materials prepared at forming pressures of (a) 15 MPa, (b) 30 MPa and (c) 45 MPa of the powder-compacts. (●) hydrogarnet, (○) slaked lime, (□) calcite and (▲) quartz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the hydrothermally solidified materials prepared at different forming pressures. These XRD patterns show that only new peaks corresponding to hydrogarnet are seen after the hydrothermal treatment. That is, hydrogarnet is a major formed phase. In these XRD patterns of the hydrothermally solidified materials, almost no significant change due to the forming pressure is observed. The formation of hydrogarnet in the CaO–SiO_2–Al_2O_3–H_2O system was reported to cause the reduction of the strength [12]. However, the bending strengths of the hydrothermally solidified materials prepared at forming pressures of 15, 30 and 45 MPa were 7.2 ± 0.2, 8.4 ± 0.7 and 10.3 ± 0.4 MPa, respectively. That is, it is clear that the hydrothermally solidified materials develop strength despite the formation of hydrogarnet.

The porous properties of the hydrothermally solidified materials were measured using N_2 gas adsorption–desorption isotherms. Fig. 2 shows mesopore size distribution curves determined by the Barrett–Joyner–Halenda (BJH) method for N_2 gas desorption curves. It is evident that the hydrothermally solidified materials exhibit a broad pore size distribution of more than 3.4 nm, and the volume in each pore increases with decreasing the forming pressure. The Brunauer–Emmett–Teller (BET) surface areas of the hydrothermally solidified materials prepared at forming pressures

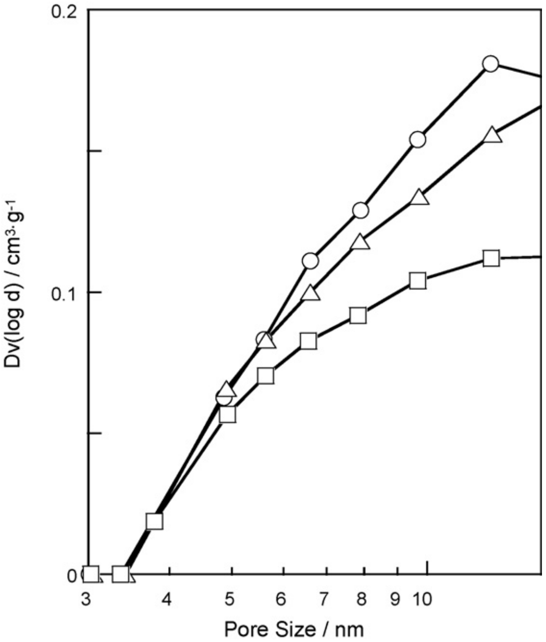

Fig. 2. Mesopore size distribution curves determined by the BJH equation using N_2 gas adsorption isotherms for the hydrothermally solidified materials prepared at forming pressures of (○)15 MPa, (△) 30 MPa and (□) 45 MPa.

of 15, 30 and 45 MPa were 20, 19 and 16 m^2/g, respectively. Note that the specific surface area and pore volume of the hydrothermally solidified materials increase with decrease in the forming pressure. The mesopore volume and the specific surface area of the hydrothermally solidified materials are readily controlled by the forming pressure of the powder-compacts.

Fig. 3 shows the water vapor adsorption–desorption isotherms of the hydrothermally solidified materials at 25 °C. These isotherms of hydrothermally solidified materials show type V behavior. The hydrothermally solidified materials prepared at a forming pressure of 15 MPa have the highest amount of adsorbed water vapor and hysteresis loop. The amount of adsorbed water vapor and hysteresis loop depends on the mesopore volume of the materials.

Fig. 4 shows the relationship between the weight change of the hydrothermally solidified materials and time at 25 °C in the range of 53–75% relative humidity. The weight change of the materials divided by the top surface area (3.6×10^{-3} m^2) of the materials was used as the moisture weight. After the humidity changes to 75%, the moisture weight increases gradually. On the other hand, the moisture weight decreases when the humidity changes from 75 to 53%. That is, water vapor in the chamber is suggested to be adsorbed and desorbed by mesopores of the hydrothermally solidified materials. It is noted that the amount of the weight change increases with a decrease in the forming pressure. It is proposed that the mesopore volume from 4.5 nm in pore diameter calculated by using the Kelvin equation and Arai's correction equation at 53% relative humidity to 9.0 nm at 75% increases, thus enhancing the water vapor adsorption–desorption ability of the materials. The increase in the mesopores in the materials is proposed to accelerate the diffusion of water vapor. Increase in specific surface area is thought to lead to enhance the adsorption and desorption of water vapor. The hydrothermally solidified materials prepared at a forming pressure of 15 MPa with various pore diameters from 3.2 to 7.4 nm are expected to be useful as humidity-controlling materials in airtight buildings.

The humidity-controlling ability of the hydrothermally solidified materials prepared at a forming pressure of 15 MPa was also investigated as shown in Fig. 5. In an empty chamber (without any materials), the humidity was in the range of 42–80%. On the other hand, the humidity was in the range of 46–63% in the chamber with the materials over the same

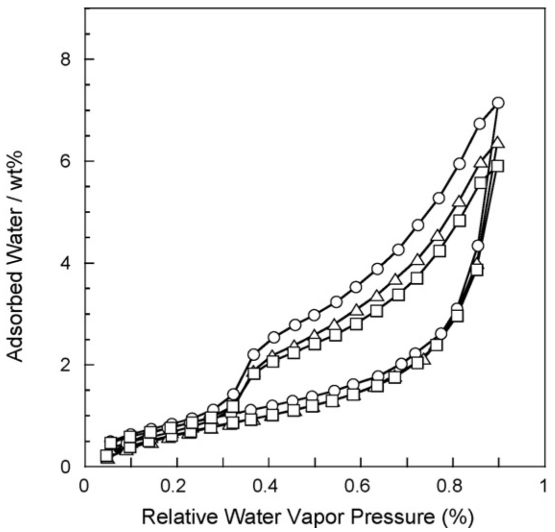

Fig. 3. Water vapor isotherms at 25 °C for the hydrothermally solidified materials prepared at forming pressures of (○)15 MPa, (△) 30 MPa and (□) 45 MPa.

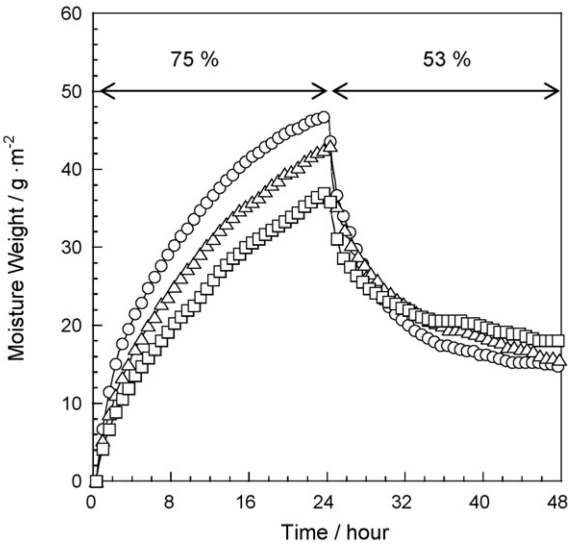

Fig. 4. The weight change of the hydrothermally solidified materials prepared at forming pressures of (○)15 MPa, (△) 30 MPa and (□) 45 MPa over the measurement time at 53–75% relative humidity at 25 °C.

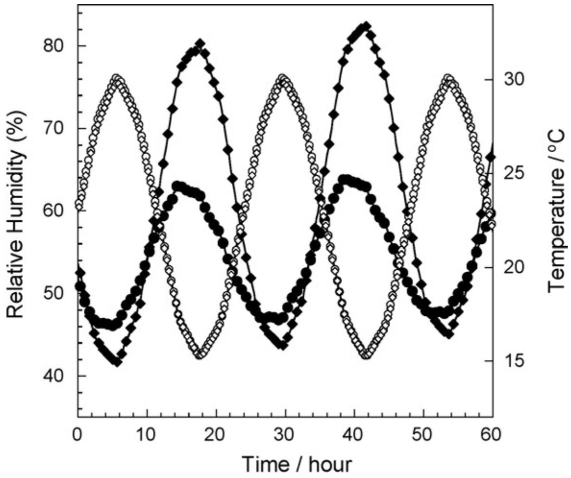

Fig. 5. The humidity (filled marks) and temperature (open marks) in the airtight chamber with (circular marks) and without (rhombic marks) the hydrothermally solidified materials prepared at a forming pressure of 15 MPa.

temperature change. It is supposed that the humidity change in the chamber with the hydrothermally solidified materials was suppressed by the water vapor adsorption–desorption of the materials.

4. Conclusions

Hydrothermally solidified materials with numerous mesopores were synthesized by using metakaolinite, slaked lime and quartz. The hydrothermally solidified materials showed bending strength over 7 MPa despite the formation of hydrogarnet. The specific surface area and pore volume of the hydrothermally solidified materials increased with the decrease in the forming pressure of the powder-compacts. The porous properties of the hydrothermally solidified materials were readily controlled by the forming pressure of the powder-compacts. The mesopore volume increased, thus enhancing the water vapor adsorption–desorption ability of the materials. This result agreed well with the prediction made using the Kelvin equation and Arai's correction equation. The hydrothermally solidified materials prepared at 15 MPa showed excellent humidity-controlling properties in the airtight chamber.

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