論 文 の 内 容 の 要 旨

論文題目 Development of phase change material-inserted adsorbent for the recovery of the heat of adsorption
（相変化物質内包吸着材の開発による吸着熱の制御）

氏　　名　　　　　　崔　　　智慧

Chapter 1. General introduction

In the chapter 1, general backgrounds and the objective of this dissertation are described. Adsorption is an adhesion of gas or liquid molecules on the surface of solid material. Since adsorption is exothermic phenomena, the temperature of the adsorption system is remarkably increased/decreased, during the adsorption/desorption. Hence, the equilibrium of adsorption is subsequently changed, and the apparent rate of adsorption is decreased. Therefore, the removal of the heat of adsorption is essential to avoid the degradation of adsorption performance. In order to remove the heat of adsorption in the adsorption process, there is a method that using the latent heat of PCM. So far, in the most of previous researches that dealt with the heat removal using PCM in adsorption process, PCM is confined in own containers such as polymer capsule and metallic void. In these cases, the released heat is transferred in 2 steps, i.e. from the adsorption site to the gas flow, then from gas flow to the PCM container. Therefore, there was a limitation in the rate of heat transfer. Also, a non-uniform distribution of the PCM containers in the adsorbent-bed and a low stability of the PCM containers increase the difficulty to handle the PCM containers in adsorption process.

In this research, to rapidly remove and storage the heat of adsorption using latent heat, PCM-inserted adsorbent is newly designed and proposed. By inserting PCM directly into the adsorbent itself, the generation of the heat of adsorption and removal of the heat of adsorption

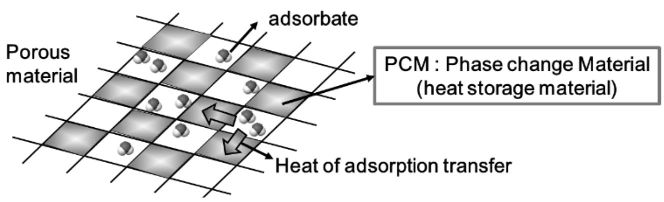

Figure 1. Schematic image of PCM-inserted adsorbent.

can be completed inside one unit as shown in Figure 1. In this time, PCM barely leaked from the pores of adsorbent, due to the strong surface tension of confined PCM. In the concept of PCM-inserted adsorbent, the heat transfer distance is very short, which is few nanometers. Also, the heat transferred in 1 step, directly from adsorption site to PCM. Hence, a rapid and effective removal of the heat of adsorption can be expected.

Chapter 2. Melting properties of PCM confined in the mesoporous structure

In the chapter 2, the melting point and the enthalpy of fusion of confined PCM were studied. A pore diameter, a functional group of PCM, the amount of surface functional group of host material are studied as key parameters for effecting melting properties. Three different pore size of mesoporous silica SBA-15 (5.6 nm, 7.6 nm, and 12.5 nm) was prepared. Then, 6 different species of PCMs, which including paraffin, fatty alcohol, and fatty acid, were confined into each SBA-15, and the melting point and the enthalpy of fusion are measured by DSC. Also, mesoporous carbon (MC), and oxidized MC (OMC) was prepared. MC and OMC have the same physical conditions, but have different amounts of surface functional groups. As for the PCM, paraffin and fatty alcohol were confined in MC and OMC respectively, and the melting properties were measured by DSC.

When the pore diameter is in the range of 5.6 nm to 12.5 nm, the relative enthalpy of fusion of the confined to the bulk, was linearly increased with the increase of the pore diameter. This indicates that the enthalpy of fusion in the mesopores approaches the value of bulk, with increase of the pore diameters. When pore diameter was approximately larger than 10 nm, the relative enthalpy of fusion was nearly 50% or more was obtained. Also, a higher relative enthalpy of fsuion was obtained in the order of alkane, acid, and alcohol. This indicates that when the functional group of the PCM molecule interacts weakly with the silanol group (Si-OH) exist on SBA-15, higher enthalpy of fusion inside the mesopores can be obtained. Furthermore, when PCM molecules interact strongly, the enthalpy of fusion was significantly decreased by the amount of surface functional groups. When the PCM interacts strongly, the increase of the amount of surface functional groups by about 5 times, resulting in a significant reduction of the enthalpy of fusion, by about 1/3.

Consequently, to achieve high enthalpy of fusion to increase the latent-heat storage capacity of PCM, confining PCM with weakly interact PCM, such as paraffin, in the mesopores with large pore diameter, is required.

Chapter 3. Conceptual studies of PCM-inserted adsorbent

To realize the PCM-inserted adsorbent, it is necessary to establish specific concept of PCM-inserted adsorbent that the PCM-existing site and the adsorbate-existing site are separated inside one material. In the chapter 3, three different concepts of PCM-inserted adsorbent is proposed in this chapter, i.e. PCM-inserted SBA-15, PCM-inserted CNT and PCM-inserted MSSZ-13 and successfully prepared. Also, the effectiveness of each proposed concept on adsorption performance is evaluated through the simulation of dehumidifying fixed-bed adsorption process.

Basically, mathematical model and the assumptions are established by referenced from the previous research to increase the validity. The fluid temperature changes at the outlet, and the adsorbed amounts of water vapor in the whole bed of PCM-inserted SBA-15, PCM-inserted CNT, and PCM-inserted MSSZ-13, with changes of time, are calculated.

All of the proposed concepts of PCM-inserted adsorbent showed isothermal behavior during initial several minutes and temperature increase was suppressed, owing to the successful heat recovery through PCM. However, there was a difference in the improvement of adsorption performance between each concept. With inserting PCM, PCM-inserted SBA-15 showed most improved adsorption performance. On the other hand, the adsorption performance of PCM-inserted CNT was very slightly increased, and the adsorption performance of PCM-inserted MSSZ-13 was decreased, not increased. These results indicates that, the effect of heat recovery through PCM on adsorption performance, can be differed by changes of some other parameters, such as the shape of adsorption isotherm branch, and the degree of decreasing q^* with inserting PCM.

Consequently, among three concepts, PCM-inserted SBA-15 can be considered as most adequate concept for the PCM-inserted adsorbent. From the summarized results, just having the heat-storage site in adsorbent was not enough to achieve high adsorption performance. It is clarified that adequate condition is required to achieve the enhancement of adsorption performance through the heat-recovery. Hence, optimization of PCM-inserted SBA-15, through the parametric study, is necessary to effectively use the PCM-inserted SBA-15 as adsorbent.

Chapter 4. Optimization of PCM-inserted SBA-15 through parametric study

Understanding of key parameters for fabrication and operating condition of PCM-inserted SBA-15 is necessary to optimize the performance of PCM-inserted SBA-15. In the chapter 4, the enthalpy of fusion of the inserted PCM, the ratio of inserted amount of PCM, and the temperature of fluid at the inlet, were investigated as key parameters. For the parametric studies, the simulation of fixed-bed dehumidifying adsorption process was performed. In the simulation of individual key parameters, three different values of each parameters are selected. Higher enthalpy of fusion of the inserted PCM, larger amount of inserted PCM, and higher fluid temperature at the inlet resulted in more improved adsorption performance. The increase of the enthalpy of fusion, and the amount of inserted PCM increased the heat storage capacity of PCM. The increase of fluid temperature at the inlet affected to the apparent rate of adsorption, resulted in drastic improvement of the performance of adsorption process. Based on these individual parametric studies, PCM-inserted SBA-15 with the most adequate parameter values was modeled. Then, the simulations by using SBA-15 without PCM, experimentally prepared PCM-inserted SBA-15, and modeled PCM-inserted SBA-15 were run. The modeled adsorbent achieved significantly improved performance in the fixed-bed dehumidifying adsorption process, which was 4 times improved performance, at the initial few minutes.

Accordingly, PCM-inserted SBA-15 could applied on dehumidifying adsorption process with enhanced performance. Also, PCM-inserted SBA-15 have a potential to be used in highly exothermic and rapid adsorption process, where the inserted PCM is expected to work more effectively for the recovery of the heat of adsorption.

Chapter 5. Experimental evaluation of PCM-inserted adsorbent

In the chapter 5, evaluation of PCM-inserted adsorbent through the experiment of dehumidifying fixed-bed adsorption process was performed. The gas flow including water vapor was supplied by bubbling the liquid water. As for the PCM-inserted adsorbents, prepared PCM-inserted SBA-15 in chapter 3, were used. The fluid temperatures measured at the inlet and at the outlet, respectively. Also, the amount of water-vapor adsorbed in whole fixed-bed was calculated. Subsequently, the relative amount of adsorbed water vapor to equilibrium amount, q/q^*, was calculated.

As a result, the increase of fluid temperature was suppressed in anytime, whether at the inlet or at the outlet, by using PMC-inserted SBA-15. The suppression of the fluid temperature of PCM-inserted SBA-15 obviously suggests that inserted PCM was successfully worked as heat storage material. Even though PCM succeed to recover the heat of adsorption, the amount of adsorbed water vapor did not increase. However, the value of q/q^* of PCM-inserted SBA-15 was higher than that of SBA-15, during initial 8 minutes. This suggest that PCM-inserted SBA-15 was successfully recovered the heat of adsorption, and resulted in the increase of apparent rate of adsorption, during initial 8 minutes. These results suggests that the concept of PCM-inserted SBA-15 is effective for the recovery of the heat of adsorption.

Chapter 6. General conclusions

In the chapter 6, general conclusions and future perspectives are described. In this dissertation, as a new concept for the recovery of heat of adsorption using PCM, PCM-inserted adsorbent is proposed, prepared, and evaluated. PCM-inserted adsorbent is a concept that inserting PCM directly into the pores of adsorbent itself. A rapid latent-heat storage and recovery through PCM is an advantage of PCM-inserted adsorbent. Through the conceptual studies and parametric studies of PCM-inserted adsorbent, PCM-inserted SBA-15 was considered as an effective concept for the PCM-inserted adsorbent. PCM-inserted SBA-15 successfully recovered the heat of adsorption and showed improved performance. And, by optimizing the PCM-inserted SBA-15 with adequate conditions, significant improvement of performance, which is nearly 4 times larger during initial stage, was achieved. The PCM-inserted SBA-15 was also evaluated by experiment of adsorption process, proved as effective concept for the recovery of adsorption. For the future, PCM-inserted adsorbent with further improved performance, will contribute to the highly exothermic and rapid adsorption process, such as separation of bio-gas, storage of hydrogen, and PSA.