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Studies on Salt Hydrates for Latent Heat Storage. VII. The Relation between Activation Process of Crystal Nucleation Catalysts for Sodium Acetate Trihydrate and Their Deactivation Temperatures

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Influences of preheating temperature were studied on crystallization of $CH_3CO_2Na \cdot 3H_2O$ from its melts containing a small amount of $Na_4P_2O_7$ or Na_2HPO_4 as a crystal nucleation catalyst. The relation between the activation process of these nucleation catalysts and their deactivation temperatures was investigated in detail. Aging of nucleation catalyst which was preceded by forced crystallization of $CH_3CO_2Na \cdot 3H_2O$ from its melt containing the catalyst, largely affects the catalyst's deactivation temperature. Whenever $Na_4P_2O_7$ or Na_2HPO_4 was used as a nucleation catalyst, the deactivation temperature was raised by lengthening aging time at a constant aging temperature. When the catalysts were aged for 4 d at 20 °C, the aging effect on them was almost saturated. At lower temperatures, longer aging times were required for saturation of the effect. The results obtained are discussed with a modified adsorption model, which takes into account commensurate-incommensurate phase transition of solid adsorbate.

Sodium acetate trihydrate ($CH_3CO_2Na \cdot 3H_2O$) has attracted attention as a useful heat storage material because of its large latent heat of fusion (264 J/g).[1,2] Pure $CH_3CO_2Na \cdot 3H_2O$ melt supercools to a considerably lower temperature than its melting point (58.4 °C).[3,4] Its practical application has been impaired by this supercooling phenomenon.[5] Wada and Yamamoto[6] first found that addition of $Na_4P_2O_7 \cdot 10H_2O$ is very effective for preventing this supercooling. Afterward, Kimura[7] reported that addition of a mixture of Na_2HPO_4 and anhydrous CH_3CO_2Na also is effective for prevention of the supercooling.

Recently, Wada *et al.*[8,9] studied the influence of preheating on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from aqueous solutions containing a nucleation catalyst ($Na_4P_2O_7$[10] or Na_2HPO_4[11]). They found that these nucleation catalysts were deactivated at an elevated temperature above the melting point of $CH_3CO_2Na \cdot 3H_2O$ and that temperatures at which the catalysts began to get deactivated were raised with increasing CH_3CO_2Na concentration in the solution. They explained these results on the basis of the crystalline adsorption model proposed by Richards.[12] This model is illustrated in Fig. 1. Adsorbed crystalline layers (crystalline adsorbate) are retained on the nucleation catalyst (adsorbent) surface under such condition as preclude the existence of bulk crystals.

In our previous studies[8,9] the deactivation temperature of nucleation catalysts sometimes varied widely, and the reason for this variation has not yet been understood. In order to elucidate the cause of the variation, we investigated in detail the relation between the activation process of a nucleation catalyst and its deactivation temperature. This paper reports that aging of a nucleation catalyst preceded by forced crystallization of $CH_3CO_2Na \cdot 3H_2O$ from a melt containing the catalyst, largely affects its deactivation temperature. The results obtained are discussed with a modified adsorption model, which takes into account commensurate-incommensurate phase transition of solid adsorbate.

Experimental

$CH_3CO_2Na \cdot 3H_2O$, $Na_4P_2O_7$, and Na_2HPO_4 were guaranteed grade reagents from Wako Pure Chemical Industries Ltd. Eight grams of $CH_3CO_2Na \cdot 3H_2O$ and 0.16 g of nucleation catalyst were placed in a container, about 3 mm in thickness, made of four-layered laminate film: Polyethylene terephthalate (12 µm)/nylon (15 µm)/aluminium film (9 µm)/polyethylene (70 µm). The sample temperature was measured by a chromel–alumel thermocouple attached to the outer wall of the container. The container was placed between plate heaters.

Experimental runs were performed according to the temperature program shown in Fig. 2. Eight containers, each containing 8 g of $CH_3CO_2Na \cdot 3H_2O$ and 0.16 g of nucleation catallyst, were heated at 95 °C for 1 h (D→E) in order to deactivate the nucleation catalyst completely. Then, they were cooled to room temperature (E→F), and the supercooled melts were seeded (F); this is forced crystallization of $CH_3CO_2Na \cdot 3H_2O$. Immediately, the temperature was raised to the freezing point (F→G→H). Then they were cooled to the aging temperature in a thermostat (H→I) and kept there for the aging time (I→J). After that, the containers were heated to a predetermined temperature (J→M), kept there for 1 h (M→N), and then cooled to 40 °C at a rate of 30 °C/h (N→R). In this cooling process, crystallization of $CH_3CO_2Na \cdot 3H_2O$ was detected by a sudden rise in the temperature of the sample (O→P→Q). This process was repeated with the preheating temperature raised stepwise. In some of the eight containers preheated at a certain temperature, $CH_3CO_2Na \cdot 3H_2O$ failed to crystallize on cooling to 40 °C. The nucleation catalyst in such containers must have been deactivated or degraded to lose nucleation ability. The percentage of the containers with

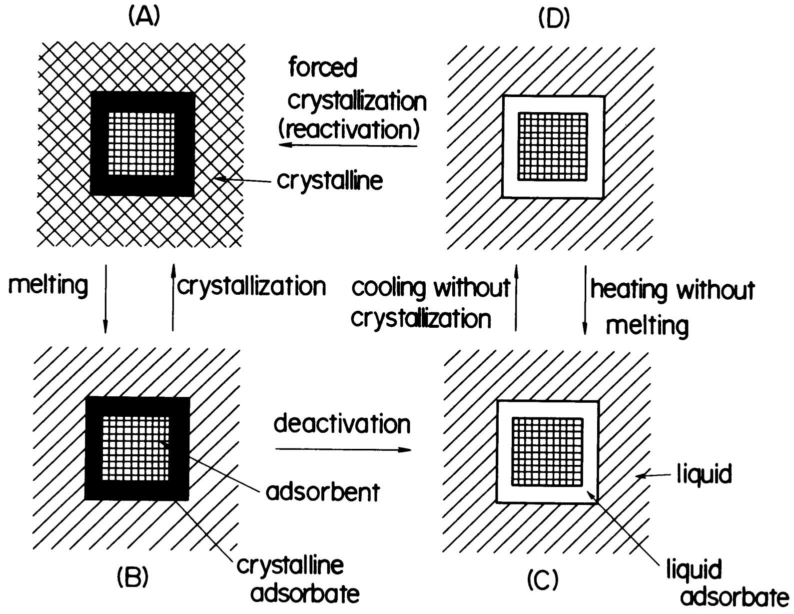

Fig. 1. The crystalline adsorption model for heterogeneous nucleation. (A): Crystalline state, (B): melting state with crystalline adsorbate, (C): melting state with liquid adsorbate, (D): supercooled state.

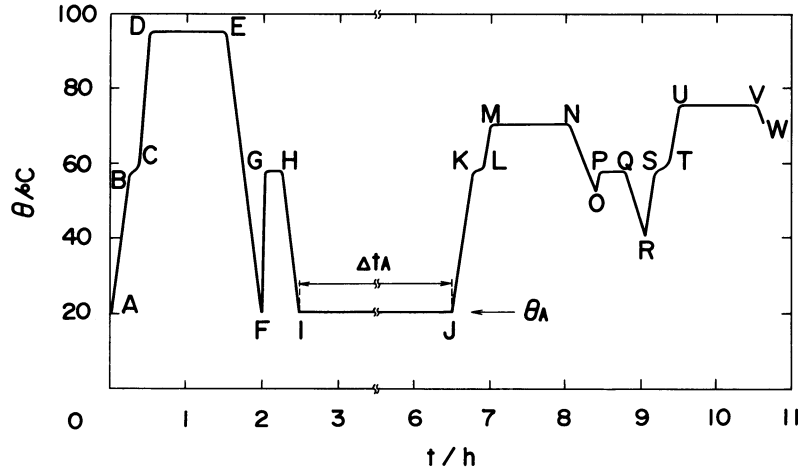

Fig. 2. The temperaure program of a typical sample. The nucleation catalyst is activated during the first crystallization of $CH_3CO_2Na \cdot 3H_2O$.

such deactivated nucleation catalysts was plotted against the difference ($\Delta\theta$) between the preheating temperature (θ) and the melting point of $CH_3CO_2Na \cdot 3H_2O$ (58.4 °C), the results being shown in Figs. 3—6.

Results

$Na_4P_2O_7$ as a Nucleation Catalyst. It is clear from Fig. 3 that the nucleation catalyst which was aged for 0.5 h at 20 °C began to get deactivated at 69 °C, higher by about 10 °C than the melting point of $CH_3CO_2Na \cdot 3H_2O$, and that all of the catalysts were deactivated at about 80 °C. The nucleation catalysts which were aged for 4, 20, and 96 h began to get deactivated at 74, 84, and 86 °C, and all of them were deactivated at 86, 92, and 93 °C, respectively. It is understood from Fig. 3 that the deactivation temperature of nucleation catalyst is raised with lengthening aging time at a constant aging temperature. The deactivation behavior of the nucleation catalyst aged for 500 h at 20 °C, which is not shown in Fig. 3, is almost the same as that of the nucleation catalyst aged for 96 h at 20 °C. It is evident that the aging effect at 20 °C is almost saturated within 96 h.

It can be seen from Fig. 4 that the nucleation catalyst aged for 96 h at −20 °C began to get deactivated at 76 °C and that all of them were deactivated at about 83 °C. The deactivation temperature of the nucleation catalyst aged for 96 h at −20 °C is about 10 °C lower than that of the nucleation catalyst aged for 96 h at 20 °C. With the 8 samples which

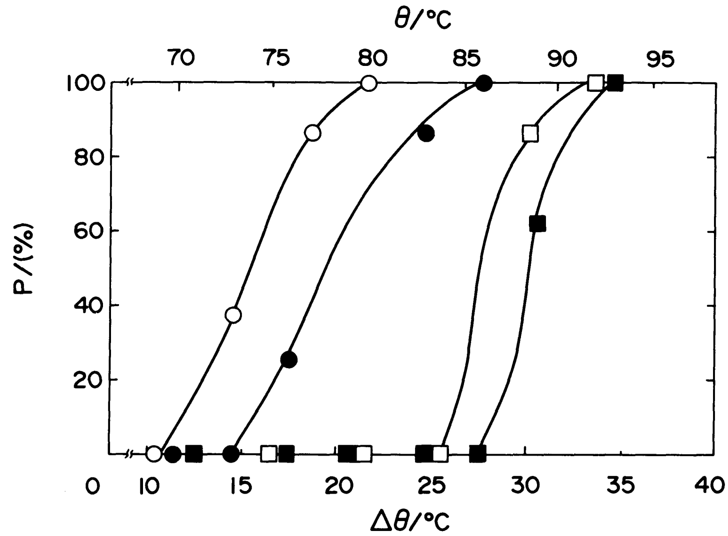

Fig. 3. The influence of preheating temperature on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the melts containing a small amount of $Na_4P_2O_7$ as a nucleation contalyst, which were aged at 20 °C. ○: Δt_A(aging time)=0.5 h, ●: Δt_A=4.0 h, □: Δt_A=20 h, ■: Δt_A=96 h.

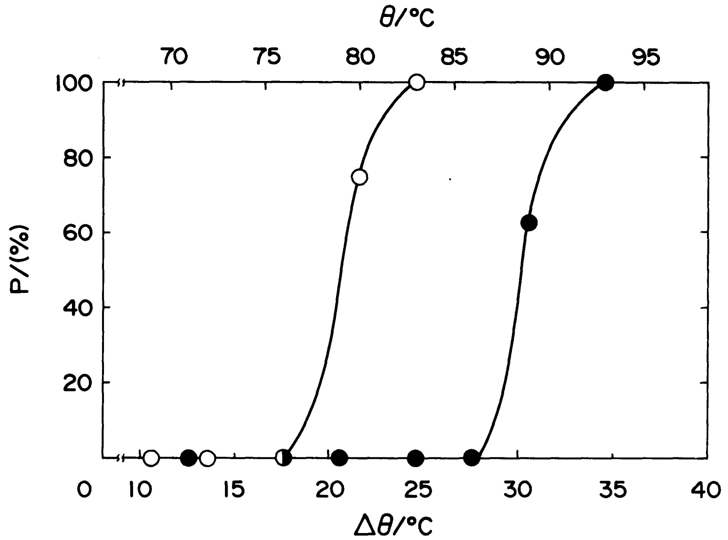

Fig. 4. The influence of preheating temperature on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the melts containing a smal amount of $Na_4P_2O_7$, which were aged for 96 h. ○: θ_A(aging temperature)=−20 °C, ●: θ_A=20 °C.

were aged for 96 h in liquid N_2, the cooling to 40 °C preceded by the preheating at 65 °C for 1 h caused no $CH_3CO_2Na \cdot 3H_2O$ to crystallize. It is evident that at lower temperatures, longer aging times are required for the full aging effect on nucleation catalyst.

Na_2HPO_4 as a Nucleation Catalyst. It is clear from Fig. 5 that the nucleation catalyst aged for 0.5 h at 20 °C began to get deactivated at 81 °C and that all of them were deactivated at about 88 °C. The nucleation catalyst aged for 20 h or 96 h began to get deactivated at 84 or 86 °C and all of them were deactivated at 89 or 91 °C, respectively. It is understood from Fig. 5 that the deactivation temperature of nucleation catalyst is a little raised with lengthening aging time. The deactivation behavior of the nucleation catalyst aged for 500 h at 20 °C, which is not shown in Fig. 5, is almost the same as that of the nucleation catalyst aged for 96 h at 20 °C. These phenomena are similar to those observed with $Na_4P_2O_7$ as a nucleation catalyst. The time required for saturation of the aging effect is much shorter than in the case of $Na_4P_2O_7$.

It can be seen from Fig. 6 that the nucleation catalyst aged for 96 h at −20 °C began to get deactivated at 84 °C and that all of them were deactivated at 89 °C. This deactivation temperature of the nucleation catalyst is a little lower than that of the nucleation catalyst aged for 96 h at 20 °C. These phenomena are also similar to those observed with $Na_4P_2O_7$. However, the

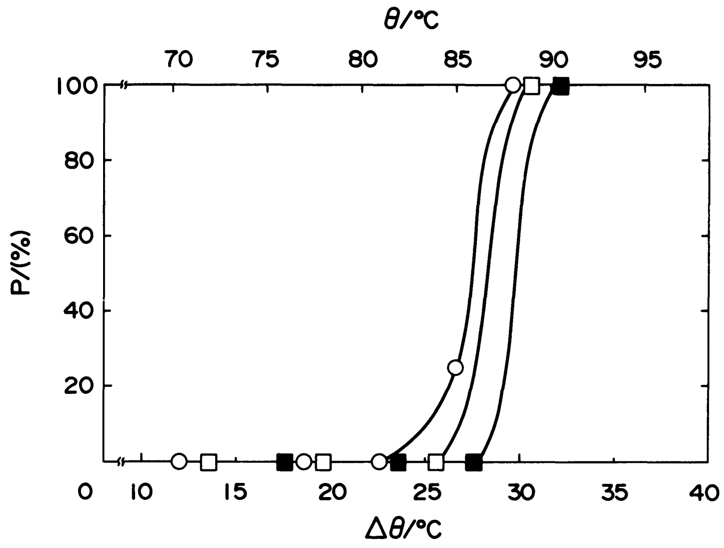

Fig. 5. The influence of preheating temperature on the crystallizaiton of $CH_3CO_2Na\cdot3H_2O$ from the melts containing a small amount of Na_2HPO_4, which were aged at 20 °C.
○: $\Delta t_A=0.5$ h, □: $\Delta t_A=20$ h, ■: $\Delta t_A=96$ h.

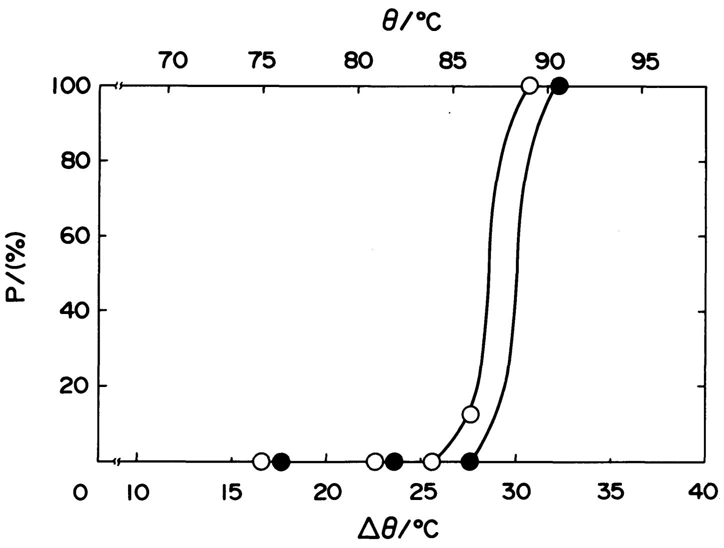

Fig. 6. The influence of preheating temperature on the crystallizaiton of $CH_3CO_2Na\cdot3H_2O$ from the melts containing a small amount of Na_2HPO_4, which were aged for 96 h.
○: $\theta_A=-20$ °C, ●: $\theta_A=20$ °C.

aging-temperature dependence of the deactivation temperature is not so pronounced as in the case of $Na_4P_2O_7$.

Discussion

Previously, we investigated the preheating effect on crystallization of $CH_3CO_2Na\cdot3H_2O$ from a solution containing a small amount of nucleation catalyst ($Na_4P_2O_7$ or Na_2HPO_4).[8,9] In that investigation we did not fully take into account the aging effect on nucleation catalysis. However, in every experiment previously reported, we kept the coagulum containing a nucleation catalyst for more than one week at room temperature, in order to obtain some steady, reproducible deactivation temperature. Therefore, the reported deactivation temperatures are considered to corresponde to fully aged nucleation catalysts.

Two general explanations have been applied to the thermal history of heterogeneous nucleation. One is that crystalline germs are retained in fissures or cavities in the nucleation catalyst surface as a result of a (postulated) concave crystalline meniscus under such condition as preclude the existence of bulk crystals.[13] The other is that adsorbed crystalline layers are retained on the nucleation catalyst surface, as illustrated in Fig. 1 (B). The first explanation has received most attention because, when certain assumptions are given concerning the size of fissures and the contact angle of the crystal thereon, estimation of the activated nucleation temperature (*i.e.*, the temperature at which crystallization is initiated) can be made.[14] However, we are not satisfied with this explanation because high, sharp deactivation temperatures of fully activated nucleation catalysts would require a very small associated fissure and a sharp limit to its geometry. The relation between the degree of supercooling and the preheating temperature for the nucleation catalysts, $Na_4P_2O_7$ and Na_2HPO_4, which will be reported in the near future, is not in agreement with the relation which is expected from the cavity model. In any cases of $Na_4P_2O_7$ and Na_2HPO_4 as nucleation catalysts, the degree of supercooling is not directly proportional to the difference between preheating temperature and bulk melting point, but is kept almost constant, about 6 °C, until catalysts begin to get deactivated. Furthermore, the theory is considered to be unable to explain the aging effect on nucleation catalyst as observed in the present experiment.

The second explanation, that is, the crystalline adsorption model, has received little consideration because thermodynamic properties of adsorbed layer have hitherto been speculative. Evans *et al.*[15–17] have studied the ability of a solid substrate to nucleate ice in supercooled water under high pressure, and explained results on the basis of an assumption that on certain substrates the heterogeneous nucleation of ice is preceded by a change of state (order-disorder transition) of the water monolayer adsorbed on the substrate.

Recently, the monolayer adsorbed on substrate has been studied extensively. From this study, possible phase diagrams of the adsorbed monolayer on substrate, such as that shown in Fig. 7,[18] are postulated.[19,20] The competition of adsorbate-adsorbate interaction with adsorbate-substrate lateral periodic potential can produce a structure which is either commensurate or incommensurate with the substrate, depending on the fitness between substrate and natural adsorbate lattice spacing; the fitness depends on both temperature and chemical potential (two-dimensional pressure). In Fig. 7, the low-dimensional (where the ratio of the periodicity of substrate to that of adsorbed monolayer is very simple) commensurate solid adsorbate is transformed directly into the fluid (liquid) adsorbate with rise in temperature (order-disorder transition), and the high-dimentional commensurate solid adsorbate is transformed into the fluid adsorbate through the incommensurate solid adsorbate with rise in temperature. Jaubert *et al.* evidenced the existence of a uniaxial commensurate-incommensurate transition in a solid monolayer of xenon adsorbed on the (110) face of copper by low-energy electron diffraction and Auger electron spectroscopy. The crystalline adsorption model, shown in Fig. 1, may be modified by considering the commensurate-incommensurate transition into solid adsorbate, as shown in Fig. 8. The results obtained in the present experiment will be dicussed on the basis of this modified crystalline adsorption model.

In a pervious paper, we considered that the crystalline adsorbate is formed on the nucleation catalyst as soon as $CH_3CO_2Na\cdot 3H_2O$ is forced to crystallize from a supercooled melt. However, $CH_3CO_2Na\cdot 3H_2O$ solid adsorbate which is formed as soon as $CH_3CO_2Na\cdot 3H_2O$ is forced to crystallize from a supercooled melt containing a nucleation catalyst (adsorbent), is considered to be incommensurate with the adsorbent. The negative heat of adsorption of metastable incommensurate solid adsorbate on the nucleation catalyst is not so large as that of liquid (fluid) adsorbate. Therefore, the incommensurate solid adsorbate melts near the bulk melting point of $CH_3CO_2Na\cdot 3H_2O$ and thus the deactivation temperature of the nucleation catalyst in this state is not so high.

The incommensurate solid adsorbate is transformed into the commensurate solid adsorbate (crystalline adsorbate) with elapse of time, because incommensurate solid adsorbate is considered to be a metastable phase. The negative heat of adsorption

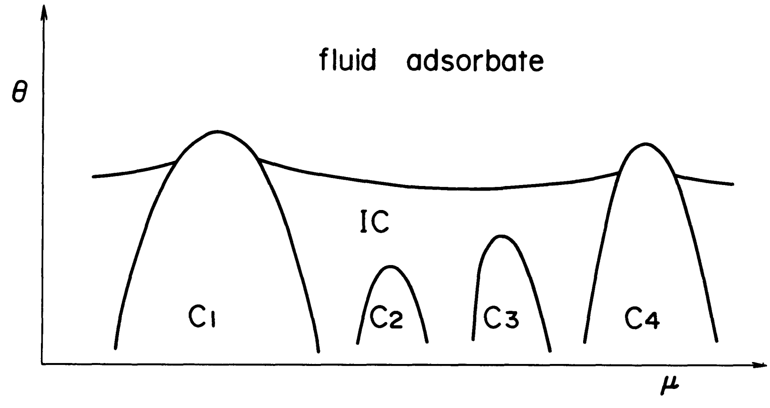

Fig. 7. The shematic phase diagram of the monolayer on the substrate as a function of temperature (ordinate) and chemical potential (abscissa).
C_n: commensurate solid adsorbate (crystalline adsorbate), IC: incommensurate solid adsorbate.

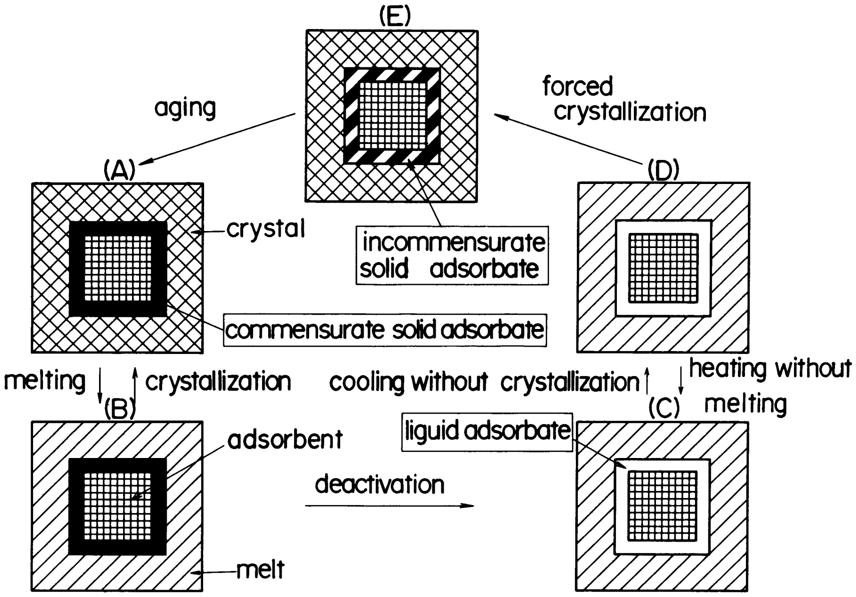

Fig. 8. The modified adsorption model for heterogeneous nucleation. (A): crystalline state with commensurate solid adsorbate, (B): melting state with commensurate solid adsorbate, (C): melting state with fluid adsorbate, (D): supercooled state, (E): crystalline state with incommensurate solid adsorbate.

of commensurate solid adsorbate on the adsorbent is considered to be much larger than that of liquid adsorbent. Therefore, the commensurate solid adsorbate does not melt near the bulk melting point of $CH_3CO_2Na\cdot3H_2O$ and thus the deactivation temperature of the fully aged nucleation catalyst is much higher.

The transformation of incommensurate into commensurate solid adsorbate is considered to proceed with atomic (ionic) diffusion, because the rate of transformation is dependent on aging temperature. In the modified adsorption model illustrated in Fig. 8 as well as the crystalline adsorption model shown in Fig. 1, the commensurate solid adsorbate is transformed directly into the liquid adsorbate at elevated temperatures.

According to the modified crystalline adsorption model, a satisfactory, though qualitative, explanation has been given to the obserbations on the heterogeneous nucleation of $CH_3CO_2Na\cdot3H_2O$, including the aging effect on nucleation catalyst. The modified crystalline adsorption model is expected to apply to heterogeneous nucleation of other salt hydrates such as $CaCl_2\cdot6H_2O$. Some quantitative explanation of these crystal nucleation catalytic actions remains to be given.

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