Effect of Gas Adsorption on Defluidization after Switching Fluidizing Gases

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In the development of a fluidized catalyst-bed reactor, engineers have unexpectedly encountered poor fluidizing quality when the reaction is carried out in a fluidized bed, whereas good fluidization is observed when the catalyst particles are fluidized in a cold model. This phenomenon could be caused by some of the following mechanisms: (1) the adhesion caused by the melting of the active component at the reaction temperature (Siegell, 1984; Compo et al., 1987; Tardos and Pfeffer, 1995; Mikami et al., 1996); (2) the agglomeration of the emulsion phase caused by the reduction in the volume of reactant gases due to the reaction (Kai and Furusaki, 1987); and (3) the agglomeration of the emulsion phase caused by the difference in the gas density in the bubble and the emulsion phases (Kai and Takahashi, 1997).

The decrease in fluidity by the third mechanism is clearly observed by switching the fluidizing gas from a low-density gas to a high-density gas (Rietema and Hoebink, 1977; Kai and Takahashi, 1997). According to these observations, the emulsion phase agglomerated when the molecular weight of the gas in the bubble phase was greater than that in the emulsion phase. In an earlier article (Kai and Takahashi, 1997), we considered that this phenomenon was caused by the nonequimolar diffusion of the two gases. In the present article, we quantitatively analyze the phenomenon in a fluidized bed using an index.

Because this phenomenon was observed for both porous catalyst particles and glass beads, Rietema and Hoebink considered that this disturbance was unrelated to the gas adsorption on the particles. We also ignored the effect of gas adsorption in the earlier article. Xie and Geldart (1995) have reported the defluidization phenomena when CO_2 and Freon-12 were used. Their observation indicates the negative effects of gas adsorption on the fluidization quality. We also observed unusual phenomena that were conjectured to be caused by gas adsorption for the particles having very large surface area. Therefore, in the present study we studied the adsorption effect on the fluidization quality after the gas switching. Using the index, and taking the diffusion and the adsorption into consideration, we evaluated the intensity of the pressure-drop decrease after the gas switching.

Experimental Studies

The apparatus and experimental procedure have been described in detail elsewhere (Kai and Takahashi, 1997). Eight gases from gas cylinders were used as fluidizing gases. The surface area of particles was measured by the N_2 adsorption method in which the BET equation was used for calculation. The amount of gas adsorption was measured by the pressure change in a constant volume vessel using a conventional apparatus (AccuSorb 2100E, Micromeritics) at 298 K.

The fluidized bed consisted of a transparent acrylic resin pipe 55 mm ID and 2 m in height. In this study, the velocity of the fluidized gas was 0.04 $m \cdot s^{-1}$. Pressures in the bottom of the bed and in the freeboard region were measured using pressure transducers. After the analog signals from the transducers were converted to digital signals, they were processed using a computer. The fluidizing gases were changed by controlling two solenoid valves. The valve connected to the line of the second gas was opened the moment the first solenoid valve was closed.

Results and Discussion

As described in the earlier article (Kai and Takahashi, 1997), when a fluidizing gas is switched from a low-density gas to a high-density gas, the emulsion phase shrinks, bubbles disappear, channeling occurs, and a decrease in the pressure drop over the bed is observed for some time. This pressure drop decrease was used to present the intensity of the transient defluidization.

The pressure change in a packed bed caused by the nonequimolar diffusion was well correlated by the following parameter, ΔM, in the earlier article:

$$\Delta M = \frac{\mu_a}{d_p^2}\left(\frac{1}{M_b^{1/2}} - \frac{1}{M_a^{1/2}}\right), \qquad (1)$$

where μ is the viscosity of the gas in the bed, and M is the molecular weight. In fluidized beds, however, a correlation between the pressure drop decrease, ΔP_F, and the parameter, ΔM, was very poor. This is because the expansion of the emulsion phase was not considered in the comparison.

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As is well known, the emulsion phase in the bubbling fluidization expands and the voidage is greater than that of the bed at the minimum fluidizing velocity. The emulsion phase voidage was presented by the following equation (Kai et al., 1987):

$$\epsilon - \epsilon_{mf} = \frac{1.26 \mu \rho^{0.12}}{d_p^{1.5}(\rho_p - \rho)} \tag{2}$$

where ϵ is the voidage of the emulsion phase. Because the net gas flow was from the emulsion phase to the bubble phase during the transient period, the intensity of the transient defluidization would be great for the system in which the emulsion-phase expansion was large. In addition, the ratio of the voidage before and after the gas switching was also considered to affect the transient phenomena. When the ratio defined by Eq. 3 is greater than unity, the emulsion phase tends to expand after the gas switching. However, the gas effluence from the emulsion phase caused by the difference in the gas exchange rates would prevent the expansion of the emulsion phase:

$$R = \frac{(\epsilon - \epsilon_{mf})_b}{(\epsilon - \epsilon_{mf})_a} = \frac{\mu_b}{\mu_a}\left(\frac{\rho_b}{\rho_a}\right)^{0.12}. \tag{3}$$

It is difficult to represent the exact mechanism and to obtain a mathematical expression. We obtained an index as a simple form using the parameters in Eqs. 1–3 and the experimental data of Si – 1 particles measured by varying the gas combination:

$$I_M = \Delta M R(\epsilon - \epsilon_{mf}). \tag{4}$$

Because Si – 1 particles are balloon-like and have only a small surface (7.3 $m^2 \cdot g^{-1}$), the effect of the gas adsorption is negligible.

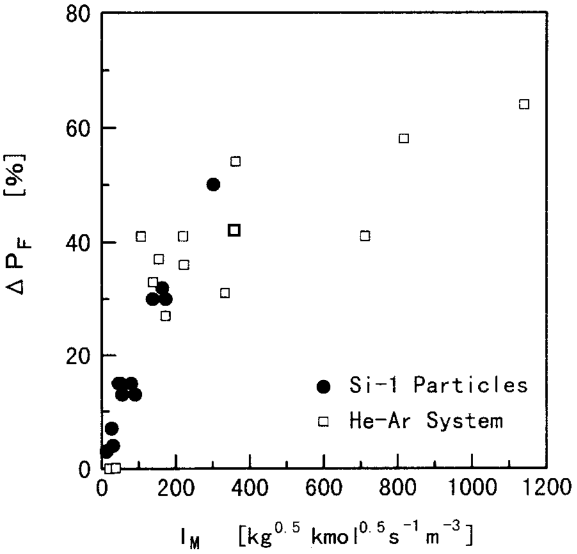

Figure 1. Correlation of the relative decrease in pressure drop in a fluidized bed with the index considering the emulsion phase expansion.

First Gas	Second Gas	Phenomena	
H_2	He N_2 Ar	Channeling	
H_2	C_2H_4 C_3H_6 CO_2	Bed was raised	

Figure 2. Observed phenomena in a fluidized bed of active carbon after gas switching from H_2 to another gas.

Figure 1 shows the relationship between ΔP_F and I_M for Si – 1 particles. The results for all the particles when the fluidizing gas was switched from He to Ar are also shown in this figure. In the He-Ar system, the adsorption effect was considered to be small. As seen in this figure, the effect of gas switching on the decrease in the fluidization quality can be well presented by considering the emulsion phase expansion. It is confirmed that the transient phenomena were dominated by the mechanism of the difference in gas exchange rate.

According to the mechanism described in the earlier article (Kai and Takahashi, 1997), the influence of the gas switching should not be observed when the particle diameter was above 200 μm, because the parameter, ΔM, becomes very small when the particle size is large. In this case, the nonequimolar diffusion does not occur, because the gases in the bubble phase and the emulsion phase exchange by bulk flow. In addition, when the particle diameter is large, the emulsion-phase expansion is small, and the term, $\epsilon - \epsilon_{mf}$ becomes negligible.

Although the particle diameter of the active carbon was 293 μm, we observed a decrease in the pressure drop. Figure 2 shows the phenomena observed in the fluidized bed after switching the fluidizing gas from H_2 to another gas. In all the cases, the agglomeration of the emulsion phase and a decrease in fluidization quality were observed. When the second gas was He, N_2 and Ar, channeling occurred after the gas switching. When the gas was switched to CO_2, C_2H_4, and C_3H_6, the agglomeration of the emulsion phase was so strong that channels were not formed and the bed was raised up. The amount of adsorption of these gases was greater than that of N_2 or Ar, as given in Table 1. These phenomena cannot be explained by the mechanism based on the nonequimo-

Table 1. Amount of Gas Adsorption on Active Carbon at 298 K

Gas	Adsorption [$mol \cdot kg^{-1}$]
N_2	0.94
Ar	0.08
C_2H_4	5.7
C_3H_6	5.9
CO_2	4.7

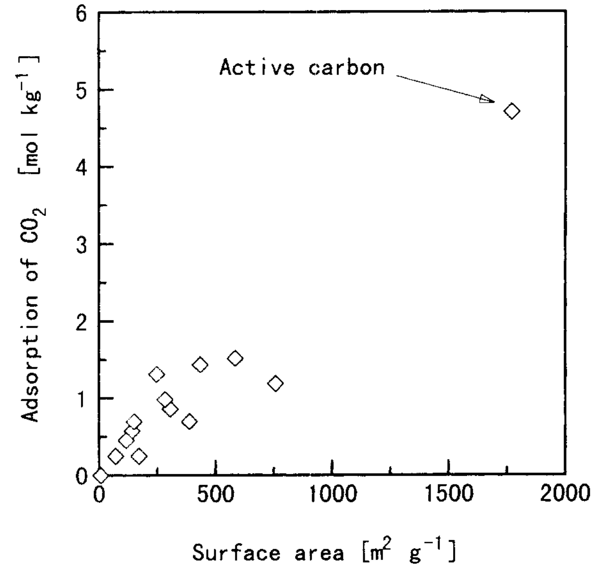

Figure 3. Comparison of the amount of CO_2 adsorption at 298 K with the surface area of particles.

lar gas diffusion. These results indicate that the decrease in the fluidization quality was induced by the gas adsorption in the case of the active carbon.

We studied the relationship between the surface area of the particles used and the amount of gas adsorption on them. The result for CO_2 at 298 K is shown in Figure 3. The amount of CO_2 adsorption increased with the surface area of the particles. The surface area of the active carbon was very large, 1,770 $m^2 \cdot g^{-1}$. The amount of CO_2 adsorption on the inorganic particles with large surface area was about 30% of that on the active carbon. Therefore, the adsorption effect could not be ignored in the case of these inorganic particles, such as FCC and porous alumina.

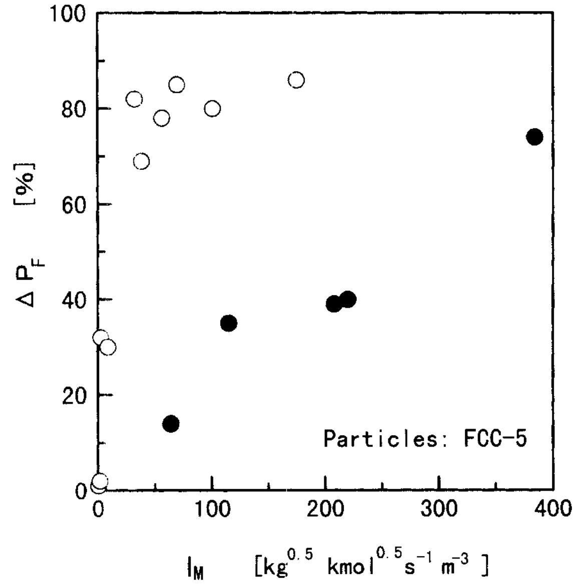

Figure 4. Relationship between the index, I_M, and the relative decrease in pressure drop in a fluidized bed for FCC-5 particles: (●) second gas in nonadsorptive; (○) second gas is adsorptive.

Figure 4 shows the comparison of the pressure drop decrease with the index given by Eq. 4 for FCC-5 particles that have a large surface area (757 $m^2 \cdot g^{-1}$). In this case, considering only the effect of nonequimolar gas diffusion, it is certainly found that the transient phenomena were not correlated by the index. When the second gas was CO_2 and hydrocarbons, although the index, I_M, was small, the value of ΔP_F became very large, as shown in Figure 4. When we took the adsorption effect in the index into consideration, the following equation was obtained based on the experimental data of FCC-5 particles. The effect was presented approximately by the amount of adsorption of gases and gas diffusivity:

$$I = I_M + I_D \tag{5}$$

$$I_D = kQ_V D_{AB} \tag{6}$$

where k is a constant that has the unit of $kg^{0.5}\ s^{-1} \cdot m^{-2}$, and Q_V is the amount of gas adsorption per particle volume based on the diameter. Figure 5 shows the relationship between the new index, I, and the pressure drop decrease in a fluidized bed for all the systems. Although the index was obtained by rough approximation, a good correlation was found when the value of k was 2.5×10^7.

In the case of active carbon, because the particle diameter was large, the effect of the diffusion in molecular weights was negligible, but the effect of gas adsorption dominated. The transient phenomena can be predicted to be significant when the index is above 500 under the conditions of the present study.

From the preceding, it is found that the decrease in the fluidization quality after the gas switching was caused by the nonequimolar diffusion due to the difference in molecular weights and the gas adsorption on particle surfaces. In the

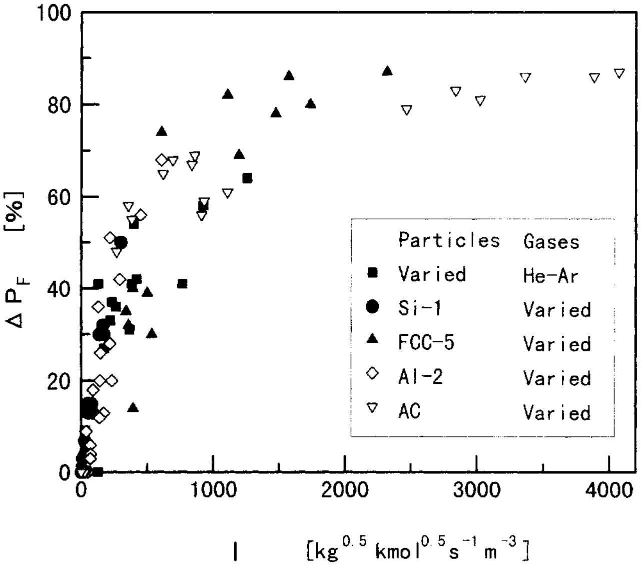

Figure 5. Correlation of the relative decrease in pressure drop in a fluidized bed with the index considering the adsorption effect for all the systems.

steady-state operation of a fluid catalytic reactor, the effect of gas adsorption can be ignored and the nonequimolar diffusion is the main cause of defluidization. When molecules with small weight are produced by the reaction such as disproportionation, a decrease in fluidization quality will be observed in the operation of the catalytic reaction even though good fluidity was observed in a cold model experiment.

Conclusions

In the present study we investigated the shrinkage of the emulsion phase when a fluidizing gas was switched from a low-density gas to a high-density gas. When the particle diameter was small and the difference in the molecular weight was large, the difference in the gas exchange rate dominated the transient defluidization. In addition, when the second fluidizing gas was a high adsorptive gas, a decrease in the gas flow rate in the emulsion phase promoted the transient defluidization. Under the experimental conditions of this study, we quantitatively evaluated the intensity of the transient defluidization in a fluidized bed by an index containing these two effects.

Notation

D_{AB} = gas diffusivity, $m^2 \cdot s^{-1}$
d_p = particle diameter, m
I_D = index considering adsorption effect, $kg^{0.5} \cdot kmol^{0.5}\ s^{-1} \cdot m^{-3}$
I_M = index considering nonequimolar diffusion, $kg^{0.5} \cdot kmol^{0.5} \cdot s^{-1} \cdot m^{-3}$
ϵ_{mf} = bed voidage at minimum fluidization
ρ = gas density, $kg \cdot m^{-3}$
ρ_p = particle density, $kg \cdot m^{-3}$

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