Effect of Volume Decrease on Fluidization Quality of Fluidized Catalyst Beds

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DOI 10.1002/aic.10925

The fluidization quality significantly decreased when the reaction involving a decrease in the gas volume was carried out in a fluidized catalyst bed. In the present study, we carried out the hydrogenation of carbon dioxide in a transparent column to observe the bed behavior. When the reaction rate was increased, the fluidity of the emulsion phase decreased and channeling occurred. When the fluidity of the emulsion phase decreased even further, the upper part of the bed was defluidized and this part was lifted up through the column. This phenomenon caused the entrainment of a large amount of catalyst particles from the reactor. We studied the effects of the reduction rate of the gas volume and the maximum gas contraction ratio on the fluidization behavior. The criterion for a stable operation, which could be successfully given by the gas-volume reduction rate, is useful for determining the operating conditions needed to establish good fluidization when the reactions involving a decrease in the gas volume are carried out in a fluidized catalyst bed. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3210–3215, 2006

Introduction

Because the change in the gas volume accompanied by reactions influence the conversion and selectivity, these effects were previously considered in the fluidized-bed reactor models.[1-4] In the reactor models, the effects of the gas-volume change were taken into account, such as the changes in bubble volume and bubble frequency. However, these phenomena influence the hydrodynamic behavior of a fluidized bed. It has been reported that the fluidization quality was drastically decreased when the reactions, which involved a decrease in the gas volume, were carried out in a fluidized catalyst bed[5] in the hydrogenation of carbon dioxide. The pressure fluctuation significantly increased and, occasionally, a large amount of catalyst particles was entrained from the beds without being trapped by the cyclones. By analyzing the signal pattern of the pressure fluctuations measured at the bed bottom, the presence of channeling and slugging was estimated. Recently, the phenomena occurring in the bed were directly observed[6] when the hydrogenation of carbon dioxide was carried out in a fluidized catalyst bed. It was observed that the upper part of the emulsion phase was defluidized and this part was lifted up through the column as a moving piston. This part then collapsed in the column and caused large pressure fluctuations. They were sometimes lifted up without collapse and a large amount of the catalyst particles was entrained from the bed.

Defluidization is caused by the agglomeration and sintering of fluidized particles for metal, metal oxide, and polymer particles when these fluidized beds are operated above the sintering point of the particles.[7-12] In addition, it has been reported that contraction of the emulsion phase and channeling are caused by the difference between the gas properties in the bubble and emulsion phases.[13-15] Although a metal nickel catalyst was used in the present experiments, no agglomeration or sintering of particles was observed when the bed was fluidized by hydrogen at the reaction temperature.

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Bavarian and Fan[16,17] reported the unusual phenomenon occurring in a three-phase fluidized bed. In their case, the hydraulic transport of a packed bed occurred at the start-up of a gas–liquid–solid fluidized bed. Although the cause was different from the case reported in the present study, similar phenomena were observed. The packed bed behaved like a moving piston in both cases.

The gas volume will decrease when the reaction involving a decrease in the number of moles is carried out at constant temperature and under constant pressure. Although a good fluidization depends on the expansion of the emulsion phase,[18,19] the reduction in gas volume will cause a decrease in the emulsion-phase voidage. If the gas in the emulsion phase cannot be compensated by the gas supply from the bubble phase, the emulsion phase is condensed and bubbles cannot rise through the emulsion phase. Finally, defluidization in the bed occurs. This part of the packed bed was lifted up like a moving piston in previous studies. Kai et al.[6] studied these effects and concluded that the cause of these phenomena was the reduction of the emulsion-phase voidage caused by the reaction involving a decrease in the gas volume.

Because the gas-volume reduction rate increases with the reaction rate, these phenomena are considered to be significant when the reaction rate is high for the reaction involving a decrease in gas volume. On the other hand, even if the reaction rate is high, the influence of the gas-volume reduction will be insignificant when the maximum contraction ratio of the reactant gas is small. The maximum contraction ratio (η) is defined as the volume ratio of the product gas when the conversion is 100% to the reactant gas at a constant temperature and under a constant pressure. The extent of the gas-volume reduction is affected by the stoichiometric relation of the reaction and the content of the inert components in the feed.

In the present study, we investigated the effects of these two parameters on the fluidization behavior when the reaction involving a decrease in the gas volume was carried out in a fluidized catalyst bed. We also discuss the criteria to maintain good fluidization.

Experimental

In the present study, we carried out methane synthesis by hydrogenation of carbon dioxide, as shown by the following equation:

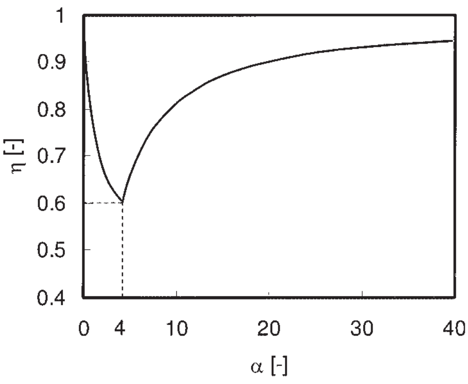


Figure 1. Relationship between α and η.

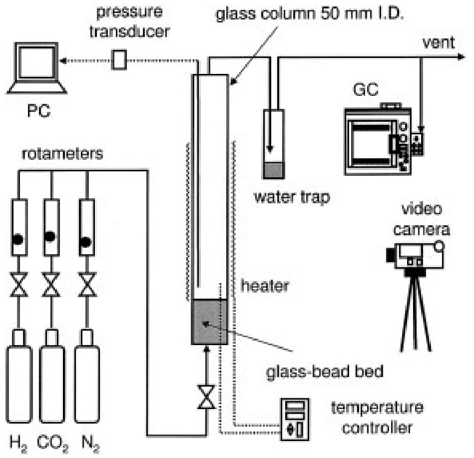


Figure 2. Experimental setup.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{1}$$

The feed gases did not contain any inert components. We changed the maximum contraction ratio (η) by changing the molar ratio of hydrogen to carbon dioxide in the feed gases (α). As shown in Eq. 2, η is a function of only the parameter α and the expression of η is affected by the value of α. When α is >4, the limiting reactant is hydrogen and

$$\eta = \frac{\alpha - 1}{\alpha + 1} \tag{2}$$

whereas it is carbon dioxide in the case of $\alpha < 4$ and

$$\eta = \frac{(\alpha/2) + 1}{\alpha + 1} \tag{3}$$

Figure 1 shows the relation between α and η when inert gases are not used in the methanation of carbon dioxide. In the case of $\alpha = 4$, the molar ratio of hydrogen to carbon dioxide is a stoichiometric value and the value of η is 0.6. This is the lowest value of the gas-volume contraction ratio for this reaction system.

The experimental setup in the present study is schematically represented in Figure 2. A glass column (inner diameter = 50 mm) was used as the reactor to observe the inside of the column. A transparent electrical resistant material, coated onto the outer surface of the glass tube, worked as an electrical heater. Even when the column was heated, the transparency was sufficient to observe any particle movement.

The catalyst was prepared by impregnating porous alumina particles with a solution of nickel and lanthanum nitrates. The metal loading was 20 wt % for nickel and 10 wt % for lanthanum oxide. After being impregnated with a solution of the nitrates, the porous alumina was dried at 383 K and calcined in flowing air at 623 K. Finally, we activated the catalyst by regeneration in flowing hydrogen at 573 K.

The average particle diameter was 55 μm and the bed density was 600 kg m^{-3}. The minimum fluidizing velocity, measured by air under ambient conditions, was 1.9 mm s^{-1}. Not only were the catalyst particles “A group” particles,[20] but

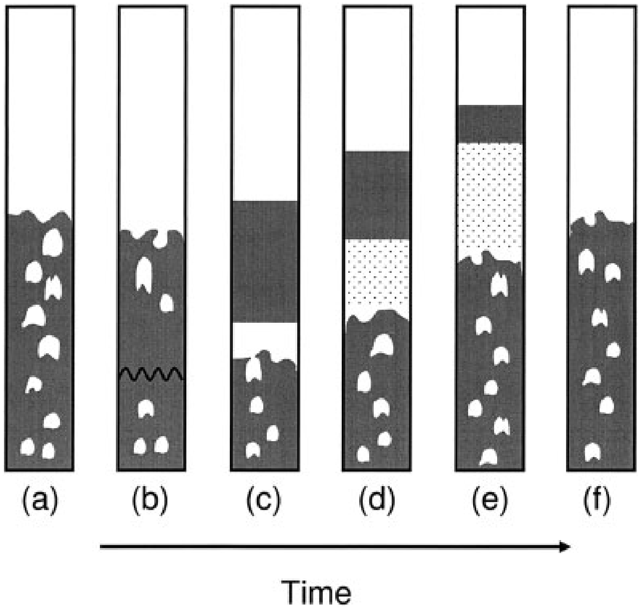


Figure 3. Particle agglomerate lifted up through the column.

they were also classified as the “AA group.”[21] The settled bed height was around 350 mm. The superficial gas velocity was 50 mm s^{-1}. The reaction rate was controlled by changing the reaction temperature.

The gas composition at the outlet of the reactor was determined by gas chromatography. The selectivity of methane was almost 100%. We directly observed the fluidization behavior and photographed it using a video camera with recording onto a videotape. We also measured the expansion of the emulsion by the bed collapse method[22] during the reaction. The pressure fluctuation in the bed was measured by a pressure transducer that was connected to a pressure tap at the tip of a vertical rod. The outer diameter of the rod was 3 mm. After being digitized by an A/D converter, the signals from the transducer were analyzed by a computer.

Results and Discussion

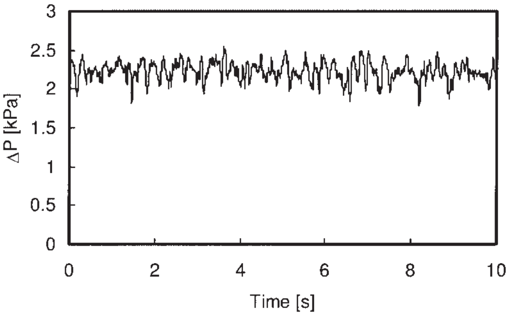
Effect of temperature on fluidization quality

The fluidization quality was affected by the reaction conditions. When the value of α was small ($4 < \alpha < 10$), the motion of the emulsion phase began to be slow moving and channeling was sometimes observed as the temperature was increased. When the temperature was further increased, the bed was defluidized and the defluidized bed (~150 mm long) was lifted up through the column by the fluidizing gas. The diameter of this part was equal to the inner diameter of the column.

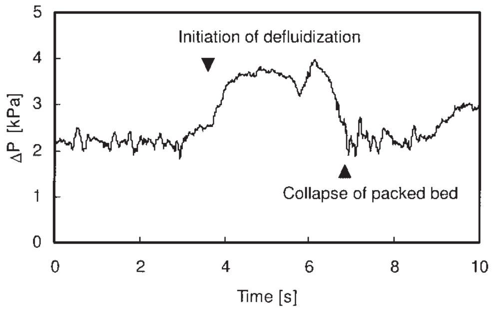
Figure 3 shows time-series schematic pictures based on the recorded video pictures. This figure shows the defluidized part that was lifted up through the column when α was 7.8 and the temperature was 523 K. The defluidized part of the bed formed a packed bed, which was lifted up through the column. The ascending velocity of the moving bed was almost the same as the superficial gas velocity. The length of the moving bed was 150–200 mm. Given that the bed height was about 400 mm, this fact indicates that the defluidization first occurred at the height of about 200 mm. The moving part gradually collapsed from its bottom. Although the fluidization quality was basically poor under this condition, this phenomenon occurred only intermittently. It was impossible to predict when the defluidization occurred, but it invariably occurred within several minutes at this temperature level.

Figure 4 shows the pressure-drop fluctuations observed when α was 7.8. Figure 4a shows the signals measured at 493 K. At this temperature, the fluidization quality was good. The pressure drop fluctuated regularly between 2 and 2.5 kPa. Figure 4b shows the fluctuation pattern when defluidization was initiated at 523 K. When the bed was fluidized normally at this temperature, the average pressure drop was about 2.2 kPa and the amplitude of the pressure fluctuations was <0.3 kPa; the large peak was observed from 3.5 to 7 s. When the fluidization initiated as shown in Figure 3b, a sharp increase was observed in Figure 4. The pressure drop was increased because the gas could not flow through the bed as bubbles, as shown in Figure 3c. After the moving bed broke (Figure 3f), the average pressure drop returned to normal level. In the previous study,[5] this peak was considered to be a result of the generation of a slug. Actually, however, the increase in the pressure drop was caused by defluidization of the upper part of the bed as shown in Figure 3. Based on these signal patterns, the defluidization is detected by measuring the pressure drop in the bed.

Figure 5 shows the conversion of carbon dioxide when the reaction temperature was raised from 423 to 533 K. The conversion was higher for the higher value of α at the same temperature, while the conversion increased with increasing temperature for all α values. In the case of $\alpha = 7.8$, the fluidization quality began to decrease around 483 K. In addition, when the temperature reached 493 K, channeling was



(a) T = 493 K, α = 7.8



(b) T = 523 K, α = 7.8

Figure 4. Pressure fluctuation pattern measured at bottom.

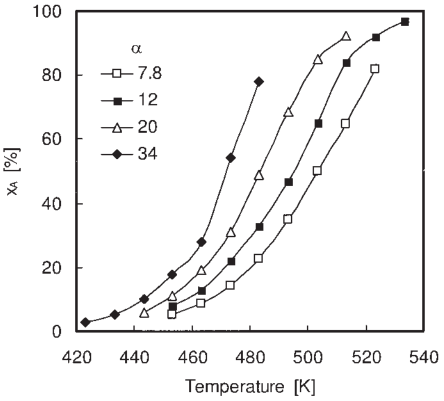


Figure 5. Relation between temperature and conversion for different gas compositions.

observed. The defluidization then occurred, and the defluidized part was lifted up through the column above 503 K. This cake collapsed from its bottom at 503 K while it rose in the column. On the other hand, it did not break when the temperature was >513 K. In this case, therefore, we needed to stop the gas supply. When $\alpha = 12$ at 513 K, similar phenomena were observed. When the value of α was 20, a good fluidization state was maintained even at 513 K. There was no direct relationship between the conversion and fluidization quality, explained by the fact that the effect of the gas-volume reduction was low at high α values.

Contraction rate of the bed

The reaction rate increases with the reaction temperature. The apparent reaction rate constant for the first-order reaction (k) was calculated from the conversion of carbon dioxide. Because the gas-volume reduction rate increased with the reaction rate, a poor fluidization was induced by the high reaction rate. We investigated the effect of the rate of the gas-volume change on the fluidization quality. The rate of the gas-volume change can be defined as

$$r_c = \varepsilon_A \frac{dx_A}{dt} \tag{4}$$

where ε_A is the increase in the number of moles when the reactants completely react per the initial number of moles. This parameter is given as

$$\varepsilon_A = y_{A0}\delta_A \tag{5}$$

where y_{A0} is the initial mole fraction of CO_2, expressed as $1/(1 + \alpha)$. The parameter δ_A is the balance between the sums of the stoichiometric coefficients of products and reactants. The value of δ_A is -2 for the methanation (Eq. 1). When the parameter ε_A is negative, the gas volume decreases as the reaction proceeds.

Given that the reaction rate of the hydrogenation of carbon dioxide depends more on CO_2 pressure than on H_2 pressure, we assumed that the reaction rate was first order of H_2 pressure. By considering the small region in the emulsion phase where the distribution of the gas concentration can be regarded as flat, the equation for a batch reactor can be adapted and the following equation is obtained:

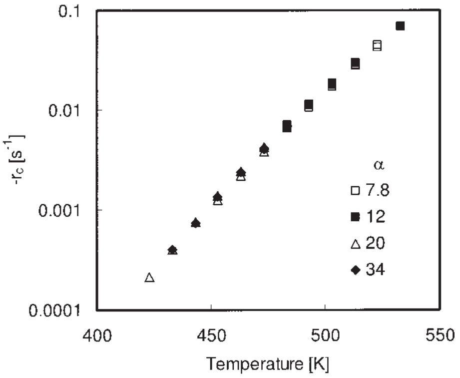


Figure 6. Effect of temperature on the gas-volume contraction rate.

$$\frac{dx_A}{dt} = k\,\frac{\alpha - 4x_A}{1 + \varepsilon_A x_A} \tag{6}$$

Because the value of r_c was affected by the carbon dioxide conversion, we used the value at $x_A = 0$ as an index indicating the fluidization quality. Therefore, this is the value at the reactor inlet. By substituting Eqs. 5 and 6 into Eq. 4, one obtains

$$-r_c = \frac{2k\alpha}{1 + \alpha} \tag{7}$$

Figure 6 shows the relationship between the reaction temperature and gas-volume contraction rate ($-r_c$). Because $-r_c$ is almost proportional to the rate constant as shown by Eq. 7, it exponentially increases with the reaction temperature. Because the reaction rate increased with the partial pressure of H_2, the conversion increased with α at a given temperature, as shown in Figure 5. On the other hand, because the value of α was >7.8, $-r_c$ was almost independent of α. The gas-volume contraction rate was almost dependent on only the reaction temperature under this reaction condition.

Figure 7 shows the emulsion-phase expansion under the reaction conditions measured by the bed-collapse method.[22] In this case, the value of α was 7.8. The voidage when the bed was

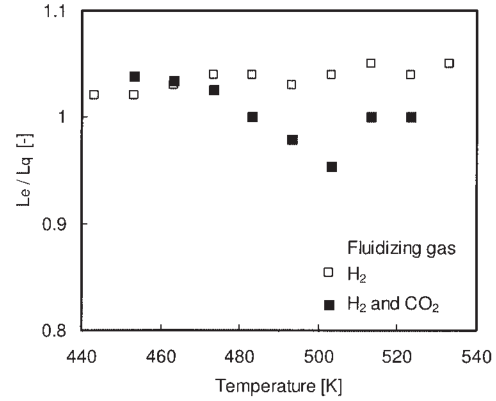


Figure 7. Effect of temperature on the emulsion-phase expansion.

fluidized by only hydrogen shows that the emulsion phase expanded, and that the expansion ratio slightly increased with increasing temperature. On the other hand, when hydrogen and carbon dioxide were supplied as the fluidizing gases, the emulsion-phase voidage decreased with the reaction temperature when the temperature was >473 K and it became smaller than that of a settled bed. This result means that the gas-volume reduction in the emulsion phase arising from the reaction was not compensated by the gas supply from the bubble phase.

As shown in this figure, the emulsion-phase expansion increased again with the temperature > 500 K. When the reaction rate was high, the main part of the reaction proceeded in the bottom of the bed. In this case, the main component of the fluidizing gas in the upper part was the products. Therefore, the volume decrease in the fluidizing gas was small and the fluidity did not severely decrease. In the bottom region where the reaction rate was high, the defluidized part formed would be broken by the high turbulence in the distributor zone.

We changed α from 7.8 to 34 at the reaction temperature of 513 K. Figure 8 shows the effect of the maximum gas reduction ratio η on the emulsion-phase expansion. The parameter η was calculated from α using Eq. 2. When $\alpha = 7.8$, the gas volume will be reduced to 77% of the feed gas volume at 100% conversion under a constant pressure; in this case, $\eta = 0.77$. As shown in this figure, the expansion ratio was >1.05 and the fluidization quality was good when η was >0.94. When η was smaller than this value, the emulsion phase expansion decreased with decreasing η. Channeling was observed when η was <0.85. When η was <0.8, defluidization occurred and the particles were lifted up through the column.

Evaluation of the fluidization quality

Based on direct observations, we classified the fluidization quality into region A (good), region B (fair), region C (poor), and region D (defluidization). In region A, a good fluidization state occurred, which is usually observed in cold model experiments. The fluidization quality was slightly worse for region B than that for region A. In region C, we sometimes observed channeling. In region D, defluidization was observed, channeling intermittently occurred, and a part of the bed was lifted up through the column. To stably operate the fluidized catalyst bed, the conditions should be chosen to avoid regions C and D.

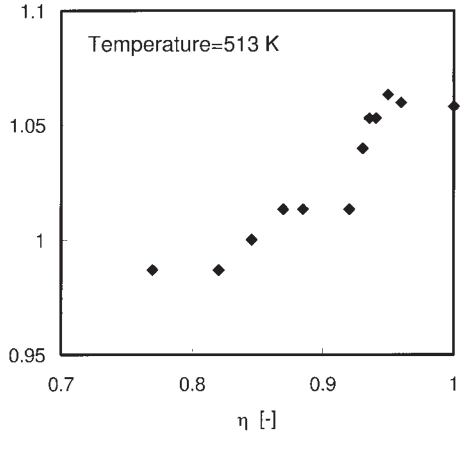


Figure 8. Effect of relative volume reduction ratio on the height of fluidized bed.

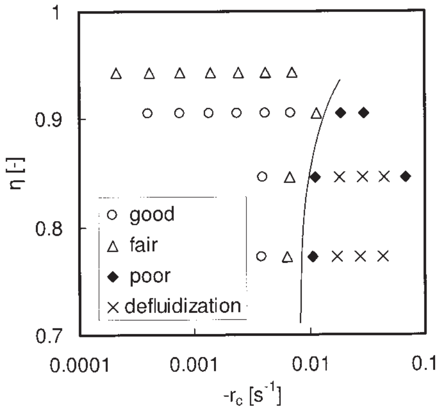


Figure 9. Effect of reaction rate on the fluidization quality.

Figure 9 shows the fluidization quality when the gas-volume reduction rate $-r_c$ and the maximum contraction ratio η are used as indices. When the gas-volume reduction rate was low, a good fluidization was maintained regardless of the maximum contraction ratio. The fluidization quality gradually decreased with increasing gas-volume reduction rate. When $-r_c$ was $>0.02\ s^{-1}$, the fluidization quality sharply decreased and the possibility of defluidization increased. Under these conditions, the effect of the maximum contraction ratio was clearly observed. When the maximum contraction ratio was >0.9, defluidization was not observed even when $-r_c$ was high. The index did not show a good condition when η was 0.94 even for a small $-r_c$ value. This is because the hydrogen-rich gas does not provide a good condition for the fluidization. Given that the density and viscosity of hydrogen are low, the expansion ratio of the emulsion phase is small even without the reaction.[23] However, the fluidization quality was not so seriously decreased and the bed could be stably fluidized.

The stable operation of the fluidized catalyst bed is possible when the parameters are in the left-side region of the line shown in Figure 9. However, it is inconvenient to calculate the value of $-r_c$. Therefore, the parameters were converted to the other ones. The critical value of $-r_c$ corresponding to a value of ε_A $(=\eta - 1)$ is obtained using the solid line in Figure 9. The value of k can be determined from the critical value of $-r_c$ using Eq. 7. Figure 10 shows the map for the stable operation based on the two parameters. The value of ε_A can be obtained from the stoichiometric relation and the composition of the inert gases, and the first reaction rate constant can be calculated from the results in a fixed-bed reactor.

When the reaction conditions correspond to the area above the line in this figure, a very poor fluidization will occur during the reaction. Based on this figure, when the reaction involves a decrease in the gas volume, the composition of the feed gas should be controlled to adjust $-\varepsilon_A$ to <0.1 to avoid defluidization arising from the gas-volume reduction. When inert gases cannot be used or the feed composition of the reactant gases cannot be changed, the reaction rate constant should be reduced to $<0.004\ s^{-1}$, although this value is dependent on the reaction rate expression. The reaction rate should be controlled to keep the volume contraction rate $< 0.01\ s^{-1}$.

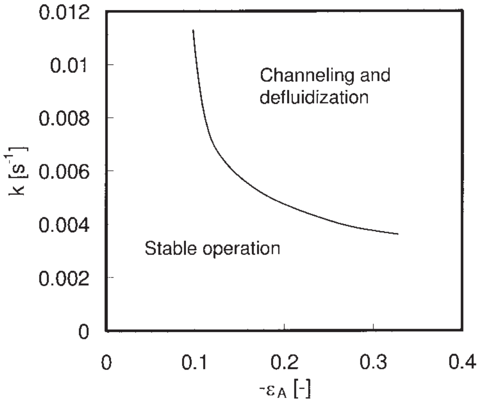


Figure 10. Stable operation map based on two basic parameters.

Conclusion

Defluidization was observed under some conditions when the hydrogenation of carbon dioxide was carried out in a fluidized catalyst bed. The cause of this condition is that the gas volume in the emulsion phase decreased and the emulsion phase contracted. We studied the effects of the reduction rate of the gas volume and the maximum gas contraction ratio on the fluidization behavior. The criterion for the stable operation could be given by the gas-volume reduction rate. When the reactions involve a decrease in the gas volume, it is better to choose the conditions where $-\varepsilon_A$ is <0.1 or the volume contraction rate is <0.01 s^{-1}. Under these conditions, we can avoid defluidization arising from a gas-volume reduction. This criterion is useful for determining the operating conditions to establish a good fluidization when the reaction involving a decrease in the gas volume was carried out in a fluidized catalyst bed.

Notation

k = apparent reaction rate constant for first-order reaction, s^{-1}
L_e = equivalent height of emulsion phase, m
L_q = height of settled bed, m
$-r_c$ = gas-volume contraction rate, s^{-1}
t = time, s
x_A = conversion of carbon dioxide
y_{A0} = initial mole fraction of carbon dioxide

Greek letters

α = molar ratio of hydrogen to carbon dioxide in feed gas
$\delta_A = \varepsilon_A / y_{A0}$
$\varepsilon_A = \eta - 1$
η = ratio of gas volume at $x_A = 1$ to that at $x_A = 0$

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Manuscript received Oct. 28, 2005, and revision received May 19, 2006.