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ABSTRACT

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 CO_2 and used relatively large particles as the catalysts. Since the emulsion phase of the fluidized bed with these particles does not expand, we expected that the bed was not affected by the gas-volume decrease. However, we found that the fluidization quality decreased and the defluidization occurred. We studied the effects of the reduction rate of the gas volume and the maximum gas contraction ratio on the fluidization behavior.

1. INTRODUCTION

It is reported [1] that the fluidization quality was drastically decreased when the hydrogenation of CO_2 was carried out in a fluidized catalyst bed (FCB). Recently, the phenomena occurring in the bed were directly observed [2] and it was found that the upper part of the emulsion phase was defluidized and this packed particles was lifted up through the column like a moving piston.

Bavarian and Fan [3, 4] reported a similar 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 in both cases.

In the case of a FCB, the gas volume decreases when the reaction involving a decrease in the volume is carried out at constant temperature and under constant pressure. If the gas in the emulsion phase cannot be compensated by the gas supply from bubbles, 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 will be lifted up like a moving piston.

In the case of a FCB with small particles, the emulsion phase expands [5, 6, 7] when the bed is fluidized. This would make the bed sensitive to the decrease in the gas volume in the emulsion phase. If this assumption is true, we can postulate that the fluidization quality is hardly affected by the gas-volume reduction when the particles, which induce a small emulsion phase expansion, are used. The emulsion phase expansion decreases with increasing particle size and density [6]. In the present study, therefore, the particles used were larger and heavier than that generally used in the FCB. We carried out the hydrogenation of CO_2 in a

FCB using these catalyst particles. We investigated the effects of the gas-volume reduction rate and the maximum contraction ratio on the fluidization behavior during the reaction.

2. EXPERIMENTAL

In the present study, we carried out the hydrogenation of CO_2. We did not use any inert components in the feed. We changed the value of η by changing the molar ratio of H_2 to CO_2 in the feed gases, α. The parameter η is defined as the volume ratio of the product gas to the reactant gas when the reaction completely proceeds 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. As given in Eq.(1), η is the function of only the parameter α and the expression of η is affected by α. When $\alpha > 4$, the limiting reactant is H_2, while it is CO_2 in the case of $\alpha < 4$.

$$\eta = (\alpha - 1)/(\alpha + 1) \quad (\alpha \geq 4), \qquad \eta = (\alpha/2 + 1)/(\alpha + 1) \quad (\alpha < 4) \tag{1}$$

In the case of $\alpha = 4$, α is a stoichiometric value and η is 0.6. This is the lowest value for this reaction system.

The column made of glass with a 50-mm inner diameter was used as the reactor in order to observe the inside of the column. A transparent electrical resistant material was coated on the outer surface of the glass tube and it worked as an electrical heater.

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. The catalyst particles were "A group" particles [8], whereas they were not classified as the "AA group" [9]. The average particle diameter was 120 μm, and the bed density was 1.09 kg m^{-3}. The minimum fluidization velocity was 9.6 mm s^{-1}. The settled bed height was around 400 mm. The superficial gas velocity was 40-60 mm s^{-1}. The reaction rate was controlled by changing the reaction temperature.

The gas composition at the outlet of the reactor was determined using 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 [10] during the reaction.

3. RESULTS AND DISCUSSION

3.1. Effect of temperature on fluidization quality

The fluidization quality was affected by the reaction conditions. Although we used the catalyst particles of which expansion was very small, the defluidization was observed. Fig.1 shows the conversion of CO_2 when the temperature was raised from 453 to 523 K. The conversion was higher for higher value of α, while the conversion increased with increasing temperature for all α. In the case of $\alpha=4.2$, the fluidization quality began to decrease around 473 K. In addition, when the temperature reached 493 K, the motion of the emulsion phase began to be slow-moving and channeling was sometimes observed. The intermittent generation of a defluidized part was observed at above 503 K. Above this temperature, the bed was defluidized and this part was lifted up through the column by the fluidizing gas. This packed particles collapsed from its bottom at 503 K while it rose in the column. On the other
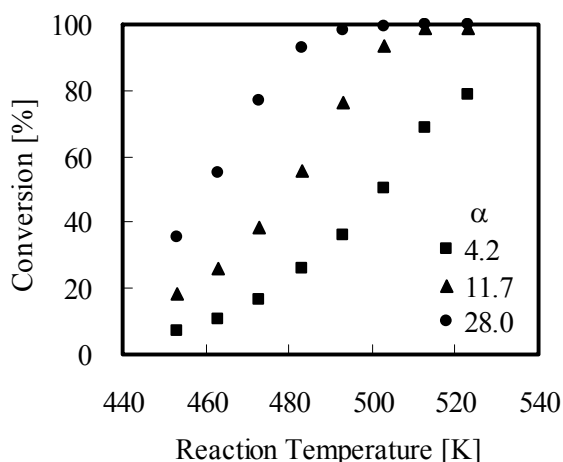
Fig. 1. Relationship between reaction temperature and conversion of CO_2.
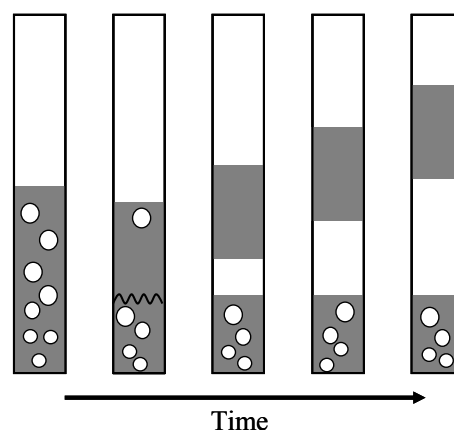

Fig. 2. Schematic time-series pictures of the formation and movement of a defluidized part.

hand, it did not break when the temperature was 523 K. It was difficult to predict when the defluidization occurred, while it invariably occurred within several minutes at this temperature level. Fig.2 is a time-series schematic picture of the defluidization based on the recorded video pictures. The defluidized part of the bed formed a packed bed and it was lifted up through the column. The rising velocity of this part was almost equal to the superficial gas velocity of the feed. The length of this part was 150 - 200 mm. Since the bed height was 400 mm, the defluidization first occurred at the height of around 200 mm.

When α=8.8 at 523 K, similar phenomena were observed. On the other hand, when the value of α was 37, the good fluidization state was maintained even at 523 K. There was no direct relationship between the conversion and fluidization quality. This is because that the effect of the gas-volume reduction was low at high α values.

3.2. Contraction rate of the bed

The apparent reaction rate constant for the first order reaction, k, was calculated from the conversion of CO_2. Since the gas-volume reduction rate increased with k, a poor fluidization was induced by 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 $r_c=\varepsilon_A(dx_A/dt)$, 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 by η - 1. When the parameter, ε_A, is negative, the gas volume decreases as the reaction proceeds.

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 relationship is finally obtained.

$$-r_c = -k\varepsilon_A \tag{2}$$

Fig.3 shows the emulsion phased expansion measured by the bed collapse method [10] under the reaction conditions. In this case, the value of α was 3.9. The expansion ratio when the bed was fluidized by only H_2 shows that the emulsion phase slightly expanded, and that the ratio was not influenced by the temperature. On the other hand, when H_2 and CO_2 were supplied as fluidizing gases, the expansion ratio decreased with the reaction temperature when
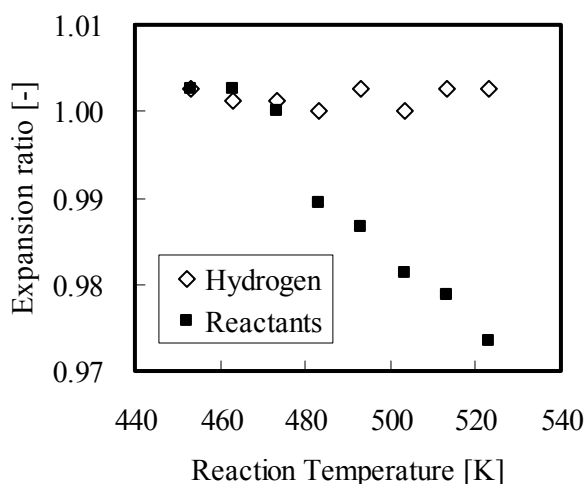
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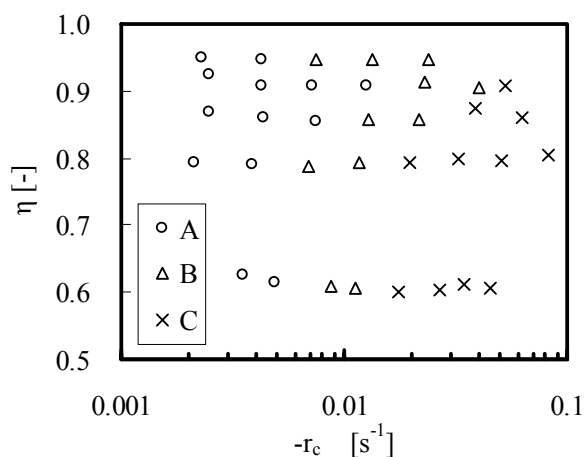Fig. 3. Effect of reaction temperature on the emulsion-phase expansion.

Fig. 4. Evaluation of fluidization qualities by $-r_C$ and η.

the temperature was greater than 473 K and it became smaller than that of a settled bed. This result means that the gas-volume reduction in the emulsion phase due to the reaction was not compensated by the gas supply from the bubble phase.

3.3. Evaluation of the fluidization quality

Based on direct observations, we classified the fluidization quality into three regions: A (good fluidization), B (poor fluidization) and C (defluidization). In region A, a good fluidization state occurred, which is usually observed in cold model experiments. In region B, we sometimes observed channeling. In region C, defluidization was observed and channeling intermittently occurred and a defluidized particles were lifted up through the column. In order to stably operate the FCB, the conditions should be chosen to avoid regions B and C.

Fig.4 shows the fluidization quality when $-r_c$ and η are used as indices. When $-r_c$ was low, the good fluidization was maintained regardless of the value of η. The fluidization quality gradually decreased with increasing $-r_c$. When $-r_c > 0.02$ s^{-1}, the fluidization quality sharply decreased and the possibility of defluidization increased. Under these conditions, the effect of η was clearly observed. When η was near unity, defluidization was not observed even when $-r_c$ was high. 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 FCB.

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