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Prevention of defluidization by gas dilution for reactions involving gas–volume reduction

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ABSTRACT

In industrial fluidized bed processes, the system often involved a change in volumetric flow. Defluidization occurs when reactions involving a decrease in gas volume are carried out in a fluidized catalyst bed. This is due to decrease in gas velocity below the minimum fluidization velocity in the emulsion phase. One method to improve fluidization quality is to supply an inert gas with reactant gases: similar effect can be obtained by supplying an excessive amount of one of the reactants. In the present study, the effect of a diluted reactant gas on fluidization quality is quantitatively analyzed by performing CO_2 hydrogenation in a fluidized catalyst bed. Stable operation can be established by operating the fluidized bed to avoid the conditions contained in the defluidization zone using two parameters that influence fluidization quality.

1. Introduction

A significant decrease in fluidization quality was observed when reactions involving decrease in gas volume were conducted in a fluidized catalyst bed [1]. The gas velocity decreased in the emulsion phase, and the amount of gas consumed in the emulsion phase was not completely compensated by the gas supplied from the bubble phase. In this case, the gas drag force becomes too small to balance the gravitational and buoyancy forces acting on the particles in the emulsion phase [2]. Formation of a locally defluidized part prevents the smooth rise of bubbles and disturbs the gas exchange between the bubble and emulsion phases. Consequently, the defluidized part expands and forms a large packed bed. Abba et al. [3] also pointed out the possibility of defluidization caused by gas volume reduction in a fluidized bed reactor.

Defluidization was also observed after the fluidizing gas is switched from low to high density. These phenomena were discovered by Rietema and Hoebink [4]. Kai and Takahashi [5] reported the mechanism of defluidization, and they also stated that the main cause for defluidization was the decrease in gas velocity in the emulsion phase. However, the defluidization observed in this case was transitional, and the fluidization quality recovered after several minutes [4–7].

Defluidization due to gas–volume decrease has not been properly recognized during the past half century. After the successful execution of the fluidized catalyst cracking (FCC) process, the development of Fischer–Tropsch (FT) synthesis using fluidized catalyst beds was initiated in 1950. The production of liquid hydrocarbons for gasoline from natural gas via CO and H_2 was planned. Several papers described the outline of this project [8–10]. This necessitated the construction of two reactors (18 m height, 4 m diameter, and a nominal capacity of 180,000 t year^{-1}) in Brownsville, Texas. These reactors were much larger than the fixed-bed FT plant previously operated in Germany.

Unfortunately, the immense oil fields of Saudi Arabia were discovered before construction of the plant was completed. This revelation removed the driving force needed to conquer many of the plant's operational problems. Further, a sharp increase in methane price finally caused the plant to shut down in 1956. Knowlton et al. [11] pointed out that the choice of Geldart's Group B particles made the scale-up difficult.

Squires [12] described details of the Brownsville project's history and the few acknowledged reasons for its failure. One of the operational problems was poor fluidization including bubble bypassing and defluidization of sticky solids. The mole number of this reaction decreases to below half of the initial mole number when the conversion is high. Therefore, we suppose that serious deterioration in fluidization quality was induced by the gas volume reduction as the reactions proceeded. When the opposite phenomenon (increase in a volumetric flow) was occurred, good

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fluidization quality was observed [13]. It would be the important factor for the successful development of the FCC process.

We performed CO_2 hydrogenation, accompanied with a decrease in gas volume in a fluidized bed. Recently, the phenomena occurring in the fluidized beds were directly observed [14]. The emulsion phase was defluidized and the bed was divided at around its middle into two parts: the upper part, forming a packed bed, was lifted up through the column by the reactant gas, while the lower part was continuously fluidized. The settled bed height was 0.4 m, and the bed was broken at a height of around 0.2 m.

We initially considered the possibility of inadequate gas distribution and agglomeration due to metal sintering of catalyst components. However, the bed was properly fluidized by hydrogen or nitrogen at elevated temperatures. Since poor fluidization was reported for other reactions involving gas–volume reduction, defluidization was not intrinsic to CO_2 hydrogenation. Reichhold et al. [7] reported that the fluidization quality decreased with increasing temperature when iron reduction of converter dust was performed. In this case, the fluidizing gas flow was reduced by concurrent carbonization and the Boudouard reaction. Go et al. [15] reported that defluidization was observed in the oxidation stage of two-step oxychlorination reactions.

Methanation from CO and H_2 is a highly exothermic reaction and is accompanied by a large decrease in mole number. Many processes were previously developed to produce synthetic natural gas utilizing this reaction. Three processes using fluidized beds have been described in the review article [16], and a part of the results of the Bi-Gas project was analyzed using a fluidized bed model [17]. However, information on the fluidization quality in the reactors has not been found in literature, while we encountered poor fluidization for hydrogenation of CO and CO_2 to methane in our study.

Since defluidization due to a decrease in volumetric flow is concerned with the principle of fluidization, a fluidized bed is considered to be unsuitable by nature for the reactions involving gas–volume reduction. However, since some important industrial reactions involve decrease in gas volume, it is important to obtain the conditions and operation methods to improve the fluidization quality for such reactions.

We evaluated the fluidization quality by two parameters [18]: gas–volume ratio and gas–volume reduction rate. The former is the parameter showing the relative gas volume when the conversion is 100%, and the latter is the relative gas–volume decrease per unit time.

The detail in these parameters was reported in the previous papers [19]. For CO_2 methanation, the gas–volume ratio, η, is defined by the following equation:

$$\eta = 1 - 2y_{A0} \tag{1}$$

where y_{A0} presents the initial mole fraction of CO_2 in the feed. When the reactant gas was supplied in a stoichiometric ratio, $y_{A0} = 0.2$, and hence $\eta = 0.6$. The gas–volume reduction rate, $-r_V$, is can be written:

$$-r_V = 2y_{A0}\frac{dx_A}{dt} \tag{2}$$

When the conversion increase is 10% during 1 s, $-r_V$ is obtained to be $0.04\,s^{-1}$.

The values of the parameters are predominantly affected by temperature and gas composition. The gas–volume reduction rate together with the reaction rate increases with temperature. The gas–volume ratio is mainly affected by the gas composition. The reaction rate decreases with increasing bed height. In order to avoid defluidization by decreasing the peak value of the reaction rate and homogenizing the axial distribution of the reaction rate, the effects of two-stage feeding of the fluidizing gas on the improvement of the fluidization quality was investigated. Defluidization could be successfully avoided by feeding a portion of CO_2 gas, one of the reactants, from the secondary gas inlet [2,19]. Since an excess amount of H_2 was contained below the level of the secondary gas inlet, the gas–volume ratio increased; therefore, the influence of the gas–volume reduction weakened. The remaining CO_2 was supplied from the secondary gas inlet. Since the fluidizing gas contained products, the gas–volume reduction rate was smaller, and defluidization was also avoided above the secondary gas inlet.

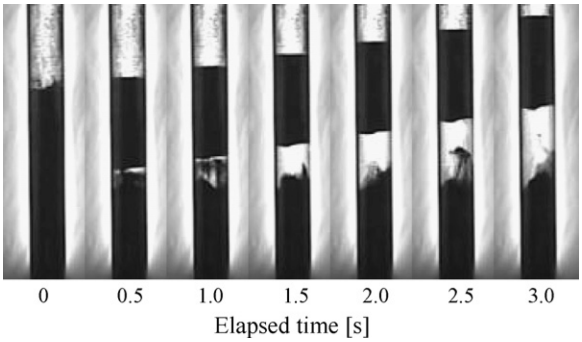

Fig. 1. Time series schematic pictures of the formation of a defluidized part.

It is possible to avoid defluidization by dilution of reactant gases with inert gases. In this case, the gas–volume ratio is increased. When the reactant gas comprises certain components, the same effect can be obtained by enrichment of one of the reactants. In the present study, we performed CO_2 hydrogenation, and the gas–volume ratio at the reactor inlet was increased by utilizing an excess amount of H_2. The effects of the dilution of the reactants on the improvement of the fluidization quality are quantitatively studied using the two parameters described above.

2. Experimental

The methanation of carbon dioxide was performed as the model reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{3}$$

The feed gas was composed of H_2 and CO_2 and did not contain any inert components. When the reaction is carried out using reactants of stoichiometric composition, the gas–volume ratio at the reactor inlet, η, is 0.6.

The support material of the catalyst was porous γ-alumina. The metal loading was 20 wt% for Ni and 10 wt% for La_2O_3. The average diameter of the catalyst particles was 56 μm, and bed density was $600\,kg\,m^{-3}$.

A glass column of 50-mm inner diameter and 1.2 m length was used as the reactor. Since a transparent electrical resistance material coated the outer surface of the glass tube, enabling the tube to function as an electrical heater, the phenomena inside the column could be observed during the reaction. The fluidizing gas was distributed through a glass-bead bed with a bead diameter of 0.7 mm.

The superficial gas velocity at the reactor inlet was $0.05\,m\,s^{-1}$. The height of the settled bed was changed from 0.1 to 0.4 m, and the reaction temperature was changed from 443 to 543 K. The excess hydrogen was used as dilution gas. The molar ratio of H_2 to CO_2 was changed from 4 to 20. Reactants and products were analyzed by on-line gas chromatography. A more detailed description of the equipment used in the experiment has been published elsewhere [18].