Coupling relationship of fluidization behavior, reaction and particle structure of Ni/MgO catalyst toward fluidized CO methanation

Jun Li[a],[*], Hui Wang[a], Qingshan Zhu[a],[b],[*], Hongzhong Li[a]

[a] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Relationship of fluidization, reaction and catalyst structure for methanation is studied.
- Defluidization results in great changes in structure of the Ni/MgO catalyst.
- Defluidization of poor fluidized catalyst is caused by rapid decrease in gas volume derived by reaction.
- The better fluidization quality lead to the higher reaction activity.

ABSTRACT

The coupling relationship of fluidization behavior, reaction activity and particle structure of Ni/MgO catalyst toward fluidized CO methanation is systematically investigated. The poor fluidization quality or defluidization, to a large extent, is caused by the rapid decrease in gas volume induced by methanation reaction. This reaction derived defluidization or poor fluidization results in great changes in structure and chemical compositions of the Ni/MgO catalyst, and which in turn lead to a decrease of reaction activity. The better fluidization quality catalyst is beneficial for maintaining the catalyst structure and exhibits the higher resistance to the negative effect by rapid decrease of the gas volume. The fluidization quality of the stable fluidized catalyst can be improved by addition of N_2. However, the catalyst particles with poor fluidization quality are easy to be defluidized due to the rapidly decrease in gas volume even with addition of inert components.

1. Introduction

Recently, the increased in demand for natural gas has lead one to pursue high efficient routes to produce synthetic natural gas (SNG). Production of SNG via methanation of the syngas ($CO + 3H_2 \rightarrow CH_4 + H_2O$) obtained by coal or biomass gasification is an energy efficient process [1,2]. Two typical characteristics of the methanation reaction are the strong exothermicity and large decrease in mole number [3–5]. The heat removal of methanation reaction has been a major concern of the industrial methanation process for avoiding higher temperature sites, which usually induces sintering of metal particles and carbon deposition, consequently causes a rapid deactivation of catalysts [6]. In the case of fixed bed reactors, several reactors connected in series with intermediate cooling gas components or product gas recycling are required to avoid the formation of hot spots [7]. However, this mode of operation consumes high amounts of energy and is low in efficiency.

Compared to the fixed bed, the fluidization of catalyst particles in fluidized bed leads to superior transfer and hydrodynamic characteristics which are suitable for reactions with significant thermal effect and involving catalyst regeneration. Since 1950s, several fluidized-bed methanation reactors have been investigated at a large scale including the multiple-feed fluidized-bed reactor process [8,9], the coal derived Bi-Gas project [10–12], the Comflux process [13], and the biomass-derived SNG process developed by the Paul Scherrer Institute (PSI) [14–19]. The biomass-derived SNG process is currently undergoing a development on the market that could be connected to coal/biomass gasifier [14,20]. However, the other three fluidized methanation processes were discontinued due to economical considerations [10–13] and poor fluidization problems including axial gas and solids back-mixing, bubble bypassing and defluidization of the sticky fine catalyst particles [9].

In order to improve the fluidization quality of catalyst particles, process intensification based on addition of fluidizable particle, such as Al_2O_3 [21], addition of magnetic field [22] and creation of fluidizable hierarchical Ni/MgO particles to match with fluidized-bed reactors [23] has been proposed. The results demonstrated that the strengthenation in fluidization quality of catalyst particles is effective to enhance the catalytic activity and stability of the catalysts. However, for a long time, researchers have paid little attention to the negative influence of large decrease in gas volume on fluidization quality of catalyst particles during the CO methanation reaction, although these negative effects have been reported for the CO_2 methanation by T. Kai et al [24–26]. The results showed that significant defluidization phenomenon is caused by decrease in the gas velocity in the emulsion phase during the hydrogenation of CO_2 in fluidized bed. The fluidization quality can be improved by decreasing the gas-volume reduction rate by means of decreasing the reaction rate, controlling the gas-volume ratio and diluting reactant gas, but it is not desirable for industrial reactors because it produces low conversion [24,25]. However, up to now, the effect of fluidization quality on the structure of the catalyst as well as the relationship between the fluidization and structure of the catalyst are not clear. Therefore, insight analysis of the relationship among fluidization behavior, reaction activity and particle structure of the catalyst is extremely important for understanding the defluidization phenomenon during CO methanation in fluidized bed reactor.

In this contribution, the coupling relationship of fluidization behavior, reaction activity and catalyst structure over Ni/MgO catalysts toward fluidized CO methanation was systematically investigated, which is especially focus on the influence of the large decrease in gas volume on the fluidized quality, as well as the particle structure of the Ni/MgO catalysts.

2. Experimental

2.1. Catalyst preparation

The Ni/MgO catalyst was prepared by an incipient-wetness impregnation method. A commercial MgO powder with particle sizes less than 10 μm, apparent density of 300 kg/m^3 was selected as the catalyst support. Firstly, Ni(NO$_3$)$_2$·6H$_2$O was dissolved in distilled water, followed by the addition of MgO powder. The impregnated catalyst precursor was rested at 60 °C overnight for the metal dispersion and the catalyst granulation. Then the granulated catalyst was crushed, sieved to get the catalyst particle. The catalyst particle was afterwards calcined at 400 °C for 6 h in air. In order to investigate the relationship between fluidization behavior and reaction activity, three kinds of the Ni/MgO catalysts were designed by changing the contents of Ni loaded and the size of the particles. The contents of Ni on support was determined by X-ray fluorescence spectroscopy. The properties of the Ni/MgO catalysts are shown in Table 1.

2.2. Catalytic reaction

All the experiments were performed in a transparent visual fluidized bed apparatus consisting of a transparent visual furnace, a digital mass flow controller and a pressure sensor. All the control devices were integrated into a personal computer, and the test data were recorded by the computer. The schematic diagram of fluidized-bed apparatus is shown in Fig. 1. Methanation performance of the Ni/MgO catalyst was carried out in a quartz fluidized bed reactor with an inner diameter of 14 mm and a height of 600 mm at atmospheric pressure.

In all cases, the amounts of catalyst were fixed to be 2.0 g with settled bed height to diameter ratio (H/D) of 1.5. The feed gas system consisted of CO: H$_2$ with a molar ratio of 1:3. In some experiments, N$_2$ was added as an inert component for decreasing the gas-volume reduction rate. The minimum fluidization velocity (u_{mf}) of the catalyst sample was tested with the feed gas at room temperature based on

Table 1
Properties of the Ni/MgO catalysts.

Catalysts	10Ni-80	10Ni-50	5Ni-50
Ni content, wt%	10	10	5
[a]Average diameter (d_p), μm	80	50	50
[b]Agglomerates particles size (d_a), μm	163	211	218
Ni particle size, nm	8.4	8.5	8.1
BET area, m^2/g	64.3	67.1	68.6
Bulk density (ρ_b), kg/m^3	790	750	730
Particle density (ρ_p), kg/m^3	1050	980	920
[c]Measured minimum fluidization velocity ($u_{mf,m}$), m/s	0.020	0.030	0.030
[d]Theoretical minimum fluidization velocity ($u_{mf,t}$), m/s	0.0055	0.0022	0.0020

  [a] The classical d10, d50 and d90 diameters of the 10Ni-80 are 3.9, 80.1 and 152.2 μm; of the 10Ni-50 are 12.4, 49.8 and 79.4 μm; of the 10Ni-50 are 13.2, 50.4 and 100.7 μm respectively.
  [b] Calculated based on Eq. (5).
  [c] Experimental results from Fig. 2.
  [d] Calculated based on Eq. (4).

pressure drop versus superficial gas velocity diagram. The bed pressure drop was measured by differential pressure transducer equipped with high/low pressure port, which was put into the bottom of fluidized bed apparatus. A thermocouple was put into the central section of catalyst bed to measure the reaction temperature with average error less than 5%.

Prior to the catalytic reaction, the Ni catalyst was reduced in pure H$_2$ with flow rate of 300 mL/min at 600 °C for 4 h. Then, the catalytic reaction was carried out over a temperature range of 375–500 °C. The superficial gas velocity at the reactor inlet was 0.065 m/s and 0.10 m/s under standard conditions with all gases supplied up-flow through a porous quartz sintered distributor on the bottom of the reactor to make the catalyst particles fluidization. The outlet gas stream was cooled by using an ice trap. To determine the composition of outlet gas products, the gas products (H$_2$, N$_2$, CH$_4$, CO$_2$ and CO) were collected after half an hour of steady-state operation for each temperature and analyzed by using GC (SP3420, BEIFEN, China) equipped with 13X and GDC-104 columns.

The calculation formulas for CO conversion, CH$_4$ selectivity and yield were described as follows:

$$\text{CO conversion: } X_{CO}(\%) = \frac{V_{CO,in} - V_{CO,out}}{V_{CO,in}} \times 100 \tag{1}$$

$$\text{CH}_4 \text{ selectivity: } S_{CH_4}(\%) = \frac{V_{CH_4,out}}{V_{CO,in} - V_{CO,out}} \times 100 \tag{2}$$

$$\text{CH}_4 \text{ yield: } Y_{CH_4}(\%) = \frac{V_{CH4,out}}{V_{CO,in}} \times 100 \tag{3}$$

where X is the conversion of CO, S is the selectivity of CH$_4$, Y is the yield of CH$_4$, $V_{i,in}$ (mL/min) and $V_{i,out}$ (mL/min) are the inlet and outlet volumetric flow rate of species i (i = CO, CO$_2$, H$_2$, and CH$_4$) under standard conditions, respectively.

The CH$_4$ production rate (mol·h^{-1}·kg^{-1}cat) was calculated based on the CH$_4$ yield, gas feed volume and the amount of the catalyst used. Different CH$_4$ production rate could be obtained via controlling the addition of N$_2$ and the reaction temperature. The gas concentration distribution along the axial direction was recorded by moving the gas sampling probe that inserted in the fluidized bed to collect the gases at different axial height of the bed.

2.3. Catalyst characterization

The phase structure of the spent and fresh catalysts was analyzed by using X-ray diffractometer (XRD, X'Pert MPD Pro, Panalytical, Netherlands) with Cu Kα radiation (λ = 1.5408 Å) at 40 KV and 40 mA.