PERFORMANCE COMPARISON OF SYNGAS METHANATION ON FLUIDIZED AND FIXED BED REACTORS

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Abstract: The performance was compared on Syngas Completely Methanation at atmospheric pressure on fluidized and fixed bed reactors. From space-time yield of CH_4, coke content and hot spots of bed temperature, fluidized bed technology was demonstrated to be more applicable to Syngas Completely Methanation. Characterization results showed that different carbon deposition forms were presented on the two operation modes.

Keywords: Fluidized bed; Fixed bed; Syngas Completely Methanation

1 Introduction

Conversion of coal or biomass to Substituted Natural Gas（SNG）via gasification and subsequent methanation process drew a lot of interest recently([1]). Driven by a world oil crisis, syngas from coal or biomass to SNG had been extensively studied since 1970s in America and Europe. Therefore a number of processes had been developed for the production of SNG. In general, based on the reactors used for methanation, the process could be classified into two types, namely multi-stage adiabatic and isothermal reactor considering heat removal since the methanation is a very exothermic process .

Adiabatic methanation normally is a fixed bed reactor packed with pelleted catalyst. In this system, a large part of product gas is recycled to the inlet to dilute the feed gas for avoidance of the superheat occurred in the methanation. In addition, there are many heat exchangers between reactors for remove the heat derived from reaction. Existing commercial scale adiabatic methanation includes Plaster Mold (RPM) process([2]), four-stage circulating fixed-bed Topsoe TREMP^{TM} process([3]), and five-stage circulating fixed-bed HICOM process. On contrast, for isothermal methanation, a fluidized-bed reactor was employed with a built-in heat transfer device to remove an appreciable amount of reaction heat. In 1977, Streeter team([4]) testified the feasibility of the isothermal fluidized bed for methanation process. Lately, Bituminous Coal Research (BCR) developed a fluidized bed methanation reactor with a Dowtherm jacket to remove reaction heat, and stable operation was achieved in a 200 Nm^3/h pilot plant. Considering the high output capacitiy of SNG from coal, isothermal fluidized bed for methanation may be more desirable.

On the other hand, methanation was a volume-reduced reaction, high pressure was helpful for the methanation reactions leading to high CH_4 selectivity. Thus, coal to SNG process always worked under high pressure resulting in larger-scale investment. Due to the dispersed biomass resources and the lower utilization rate of

biomass energy equipment, atmospheric methanation process with lower investment may be more suitable for biomass to SNG. However, the report on isothermal fluidized-bed for methanation at atmospheric pressure is very few.

In this work, we report the performance of Syngas Methanation with fluidized bed reactor at atmospheric pressure and compared with a fixed bed reactor. From space-time yield of CH_4, coke content and hot spots of bed temperature, the technology traits were contrasted on fluidized and fixed bed reactor. And the spent catalysts were characterized by XRD, TG and TEM.

2 Experimental

Methanation catalyst N182 was purchased in JGC catalyst Kasei Co., Ltd., the basis component was $NiMg/Al_2O_3$. The feed gas, such as H_2, CO, N_2 and air was commercially available industrial gas.

The investigation of methanation process was performed using a $\Phi18\times360$ mm single-tube quartz reactor, equipped with a tube-type gold-plated furnace. A 4 g of catalyst with a given particle size range of 250-400 μm was loaded into the tube. Before testing, the reactor was purged with N_2 firstly, and then H_2 was introduced into the reactor to reduce the catalyst at 400 ℃ for 4 h. When the reactor temperature was cooled down to 300 ℃, syngas with a certain composition of reactant gases (H_2:CO:N_2 =3:1:1) was introduced for methanation reaction. The gases from outlet after catalytic conversion were condensed for collecting the liquid products. The product gas was analyzed quantitatively uisng a Agilent Micro3000, and the products in the liquid solution were identified with GC-MS (HP5970).

The catalysts were characterized with Powder X-ray diffraction (XRD) on a Rigaku D/MAX-γB powder diffractometer with Cu K*a* radiation. Thermalgravity analysis（TG）was measures on a SDT Q600 V8.3 analyzer. The catalyst morphology was observed on Philips EM400T transmission electron microscope with operation voltage 100 kV.

3 Results and discussion

3.1 Catalytic performance comparison on fluidized and fixed bed reactor

Figure 1 showed the product gas composition of syngas methanation at different space velocities. The side reactions, such as the carbon chain growth reaction associated with ethane and propane, and Friedel-Crafts reaction associated with methanol, ethanol and other liquid fuels, were not observed. CO_2 acted as the major by-product of CH_4. Results showed that a severe carbon deposition occured based on the calculation of system element balance(5). Therefore, it is believed that the disproportionation reaction $2CO = C+CO_2(2)$ may take place during Methanation at atmospheric pressure except for the major reaction process of methanation reaction $CO+3H_2=2CH_4+H_2O(1)$. In addition, reduction reaction $CO+H_2 = C+H_2O(3)$ and methane decomposition reaction $CH_4 = C+2H_2(4)$ would be likely to take place.
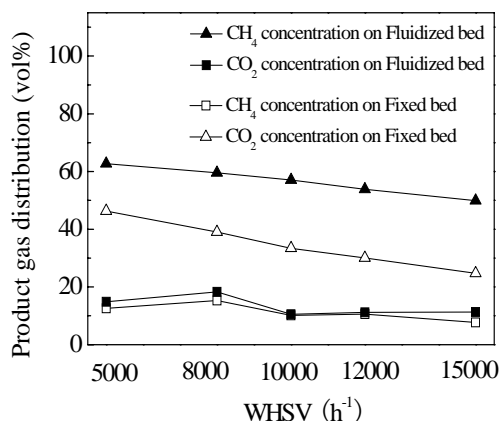
Figure 1 The influence of different space velocity on the distribution of product gas
Reaction condition：reaction temperature 300 ℃, reaction time 30 min, atmospheric pressure

When the space velocity varied within 5000-15000 h^{-1}, the percentage composition in the volume of CO_2 changed little, while that of CH_4 was gradually decreased on the two operation modes. Results showed that in the system of Syngas Completely Methanation, disproportionation reaction (2) was a rapid process and could complete in a very short period, while methanation reaction (1) was a relatively slow process. Due to shortening contact time between reactant gas and catalyst bed, methanation performance would be inhibited with the increasing of space velocity, which resulted in CO_2 composition unchanged and that of CH_4 composition decreased gradually. Otherwise, the compared results of the methanation performance on fluidized and fixed bed reactors showed that, the highest 62.9 vol% CH_4 in the distribution of product gas was obtained on fluidized bed reactor, while only 46.5 vol% CH_4 was observed on fixed bed reactor. And the decrease of the percentage composition in the volume of CH_4 was more obvious on fixed bed reactor. This possible reason was that catalyst particles remain was improved due to better back-mixing phenomenon on fluidized bed reactor, which prolong the contact time between reactant gas and catalyst particles.

3.2 Fluidized and fixed bed technology traits analysis

The results above proposed that fluidized bed reactor appeared to be more favor of the CH_4 selectivity on Syngas Completely Methanation at atmospheric pressure. However, in catalytic reaction, fixed bed reactor had the unparalleled advantage due to controllable residence time, easy operation, as well as shortening development cycle. In order to investigate the influence of reactor type to methanation performance, fluidized and fixed bed technology traits were contracted on Syngas Completely Methanation from space-time yield of CH_4, coke content and hot spots of bed temperature. Table 1 listed the quantitative results on fluidized and fixed bed reactors. In the process of data acquisition and data calculation, the as-known flow rate N_2 was adopted as internal standard gas to quantitate the volume flow rate of CH_4 and CO_2 in product gas, which were denoted as $V(CH_4)$和 $V(CO_2)$, respectively. Space-time yield of CH_4 on the two modes were obtained by theoretical calculation. Then, according to the carbon balance in the system, the coke content in the catalyst was estimated, which was listed in Table 1 also. Figure 2 compared the hot spots of bed temperature on fluidized and fixed bed reactors in different space velocity.

Table 1 The quantitative results on Syngas Completely Methanation

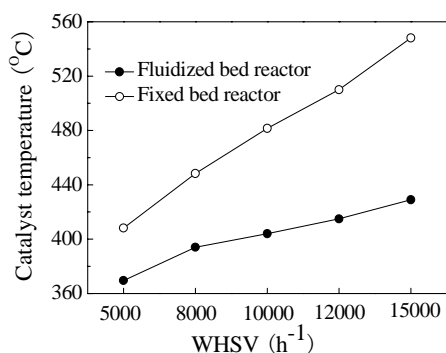|		Space velocity / h^{-1}				
		5000	8000	10000	12000	15000
CH_4 Yield	Fluilized bed	0.87	1.32	1.58	1.79	2.08
$(l \cdot g^{-1} h^{-1})$	Fixed bed	0.64	0.87	0.93	1.00	1.03
Coke content	Fluilized bed	8.72	8.60	12.60	13.60	15.10
（%）	Fixed bed	15.97	17.76	21.93	23.07	26.26

Figure 2 The variety of hot-spots of bed temperature on fluilized and fixed bed reactor

Firstly, fluidized and fixed bed process was compared from space-time yield of CH_4. There were two directional requirements for achieving high space-time yield of CH_4 on Syngas Completely Methanation: the promotion of methanation reaction (1), and the prevention of further reaction or conversion of CH_4 once it was formed, i.e. methanation decomposition reaction (2). As a strong exothermic reaction, methanation reaction (1) was inhibited with the increasing of reaction temperature, while methanation decomposition reaction (2) was in reverse. Therefore, fluidized bed process with better heat transfer efficiency was more conducive to obtain higher space-time yield of CH_4, which was consistent with our quantitative results.

Secondly, fluidized and fixed bed process was compared from coke content. Three types of carbon deposition reactions would be likely to exist on the basis of above study in the system of Syngas Completely Methanation at atmospheric pressure. Disproportionation reaction (2) and reduction reaction (3) were based on CO and H_2 as the reactant gas, and methanation decomposition reaction (4) was based on CH_4 as the raw material. Therefore, whether the relative concentration of CO and H_2 or that of CH_4 was on the dominant area, carbon deposition reaction would be likely to happen to increase the coke content over the catalyst. The gas flow routes were similar on the two operation modes: CO and H_2 entered the reactor from the bottom of catalyst bed, CH_4 concentration was increased with the upward flow of gas, and CH_4 would be the dominant components when the gas left the top of catalyst bed. For convenience, the catalyst bed was divided into two regions: one was the CO, H_2-rich region at the bottom, the other was CH_4-rich region on the upper bed. The position of catalyst particles and the gas atmosphere were anchored on fixed bed reactor, which was likely to cause more severe carbon deposition reaction whether at the bottom or on the upper bed. While on fluidized bed process, the catalyst particles held circulating continually and were located the alternative

atmosphere. When the catalyst particles entered into CO and H_2-rich region from CH_4-rich region, the carbon consumption role of H_2 would cause some coke disappeared and coke content decreased. Thus, fluidized bed process with less coke content was more suitable on Syngas Completely Methanation.

At last, hot spots of bed temperature were investigated on the two operation modes. As Figure 2 shown, the hot spots of bed temperature on fixed bed reactor rose from 407 ℃ quickly to 548 ℃ in the space velocity within5000-15000 h^{-1}, while that on fluidized bed reactor changed within 368-428 ℃. Gas-solid heat transfer model on the steady state proposed that, the total amount of heat transfer included the heat transfer amount through flow gas and that through solid particles. Due to little particles collision frequency, the role in heat transfer through solid particles was usually ignored in the sparse gas-solid flow system in the early study. However, in the dense gas-solid system involved in the heterogeneous catalysis field, particles collision would be the main mechanism of flow and heat transfer process. Particles collision played a more important contribution on the heat exchange. On fluidized bed process, the turbulence within the catalyst bed improved the contact conditions of particles to particles, and temperature gradients were minimized and hot spots were less likely to occur due to particles collision, which were in consistence with the study of Wen andChang(6), Delvosalle(7), McKenna(8). Thus, fluidized bed process must be more applicable to Syngas Completely Methanation from hot spots of bed temperature.

3.3 Catalysts characterization

Syngas Completely Methanation was a strong exothermic reaction. On fixed bed reactor, temperature gradient occurred and the channels between catalyst particles were possibly plugged; On fluidized bed reactor, the gas concentration and bed temperature was uniform. Due to the above differences between fluidized and fixed bed reactor, the environment of carbon growth was different on the two modes. The carbon deposition behaviors were compared on fluidized and fixed bed reactor by physical and chemical characterizations.
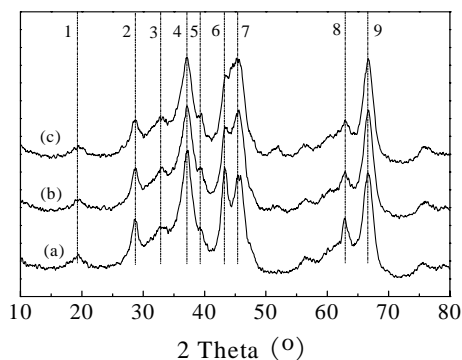

Figure 3 XRD patterns of fresh and spent catalysts
(a) Fresh catalyst; (b) Spent catalyst on fluidized bed reactor; (c) Spent catalyst on fixed bed reactor

Figure 3 showed the XRD patterns of fresh catalyst N182 and the spent catalyst on fluidized and fixed bed reactor. The typical diffraction peaks of NiMg/Al_2O_3 methanation catalyst were ascribed to: (i) Spectrum lines 1(2θ＝19.28^O)、3(2θ＝

32.78^O)、$4(2\theta=37.04^O$)、$7(2\theta=45.47^O$)、$9(2\theta=66.57^O$) were corresponding to the typical diffraction peaks of γ-Al_2O_3 or $NiAl_2O_4$. According to the standard XRD spectra and the relative diffraction intensity values supported in JCPDS cards, several spectrum lines of γ-Al_2O_3 and $NiAl_2O_4$ XRD spectrum overlapped, and further analysis was very difficult; (ii) Spectrum line $2(2\theta=28.75^O$) was corresponding to the typical diffraction peaks of Mg-Al hydrotalcite crystal phase; (iii) Spectrum line $5(2\theta=39.25^O$) was the proprietary line of γ-Al_2O_3; (iV) Spectrum lines $6(2\theta=43.28^O$) 、$8(2\theta=62.92^O$) was corresponding to the typical diffraction peaks of NiO. Results showed that N182 was a kind of methanation catalyst with γ-Al_2O_3 crystal phase as the carrier. Due to the strong interact between NiO、MgO and γ-Al_2O_3, Mg-Al hydrotalcite crystal structure could be observed on N182, and $NiAl_2O_4$ spinel structure may be also contained in N182 structure. As shown in Figure 3, the phenomenon of diffraction intensity decreasing and diffraction peaks broadening in the NiO typical diffraction peaks (lines 6 and 8) could be observed. The physical model about the carbon deposition on the metal surface bring forward by Alstrup([9]) was proposed that, metal carbide was formed between carbon and the active component firstly, then carbon produced in carbide decomposition may remain in the metal structure and spread to some crystal face; Or other type of carbon may be formed on the surface of metal particles, and the metal active component would be coated([10]). Due to the metal structure defects or carbon deposition species coated, NiO typical diffraction peaks exhibited diffraction intensity decreasing and diffraction peaks broadening. Compared the XRD patterns of the spent catalysts on fluidized and fixed bed reactor, the spent catalyst on fluidized bed reactor showed slightly stronger in diffraction peak intensity than that on fixed bed reactor, which may be due to the difference on the carbon deposition amount and coke species([11]) on the two operating modes.
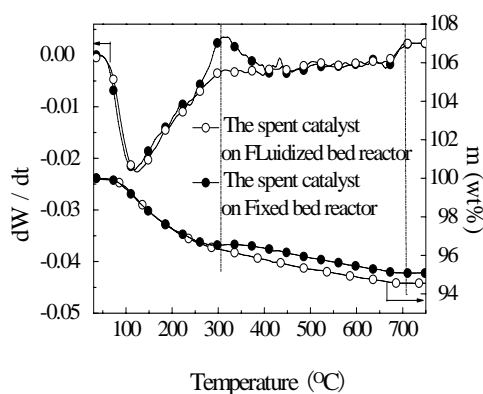

Figure 4　TG-DTG curves of the spent catalysts

TG curves of the spent catalysts on fluidized and fixed bed reactor were shown in Figure 4, and the overlapping successive reaction process was separated through DTG curves. The similar phenomenon was observed in the reaction of coke combustion on the two spent catalysts: two obvious mass loss temperature range were observed within 30 to 750 ℃, and more than 70% of the amount of carbon deposition could be burned prior to 302 ℃. Results suggested that methanation system may lead to two kinds of carbon deposits. As reported in methanation decomposition reaction on Ni-based catalysts ([12-14]), that three different types of

carbon deposits would generate on the catalyst surface, which were named as carbon filament, carbon polymer and carbon graphite, and the combustion peak of carbon polymer tended to overlap with that of carbon graphite, which was in consistence with our results above. The same type coke species was slightly discriminated in the combustion peak area and peak temperature on the two operation modes, which may be caused by the difference in the carbon deposition amount, coke species structure and aggregation method over the catalyst(15).
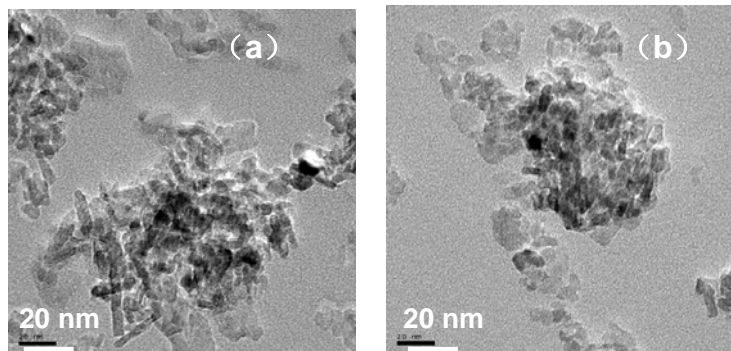

Figure 5 The TEM images of the spent catalysts

(a) Spent catalyst on fluidized bed; (b) Spent catalyst on fixed bed

Figure 5 showed the TEM images of the spent catalysts on fluidized and fixed bed reactor. The different morphology was observed on the two operation mode. A fibrous structure of tubular shape was shown over the spent catalyst on fluidized bed reactor, while a dense accumulation distribution appeared over the spent catalyst on fixed bed reactor. This may be caused by the different gas atmosphere that carbon deposition grew in: As referred above, the catalyst bed was divided into CO, H_2-rich and CH_4-rich regions. Due to the anchored location of catalyst particles and fixed atmosphere of gas flow on fixed bed reactor, a severe CO reduction reaction must happen at the bottom and a severe CH_4 decomposition reaction on the upper catalyst bed would take place. The coke formation rate was much higher than carbon diffusion and growth rate, which resulted in the fast generation of coke in a short time, and the dense accumulation carbon particles was formed; While on fluidized bed reactor, catalyst bed was recycled in CO, H_2-rich and CH_4-rich regions, the carbon deposition reaction rates of CO reduction and CH_4 decomposition were reduced, resulted in the coke generating gradually as carbon fiber. Results were consistent with the above XRD and TG analysis.

4．Conclusion

The performance of Syngas Completely Methanation at atmospheric pressure was compared on fluidized and fixed bed reactor over N182 catalyst. N182 catalyst showed excellent selectivity on the two operation modes. The composition of product gas was simple, CO_2 acted as the major competitive by-product of CH_4;

From space-time yield of CH_4, coke content and hot spots of bed temperature, the fluidized and fixed bed technology traits were contrasted on Syngas Completely Methanation. Due to alternative gas flow and catalyst particles collision, coke content

was reduced and hot spots were less likely to occur on fluidized bed reactor. Fluidized bed process was more suitable for Syngas Completely Methanation.

The spent catalysts were characterized by XRD, TG and TEM. Results showed that a fibrous structure of tubular shape was shown over the spent catalyst on fluidized bed reactor, while a dense accumulation distribution appeared over the spent catalyst on fixed bed reactor.

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