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Total methanation of syngas to synthetic natural gas over Ni catalyst in a micro-channel reactor

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ABSTRACT

Methanation reaction from syngas to synthetic natural gas (SNG) has been successfully implemented over Ni catalyst in a micro-channel reactor with high conversion and selectivity in milliseconds contact time. A new method called improved thermal spray to manufacture the metal-ceramics complex substrate as catalyst support was presented. The substrate demonstrated dual functions, i.e., the superior heat conduction as metal and stable catalyst coating on it as ceramics (e.g., Al_2O_3). The experiments verified that the fall-off proportion of the catalyst can be neglected after the plates experienced methanation reaction and strong vibration in ultrasonic cleaner. Meanwhile, the catalyst coatings on the walls of micro-channel reactor showed high activity and stability, having the excellent catalytic performance for methanation reaction in micro-channel reactors and the reliability in long-term use as well. At the temperature of 550 °C and the pressure of 30 atm, CO conversion and CH_4 selectivity can remain above 98% and 92%, respectively, at a high GHSV of 71,000 h^{-1}, where the corresponding residence time is only about 50 ms. Extensive characterizations of these Ni catalyst plates were also made to get a better understanding of the catalytic performance. The results of XRD, SEM, TEM and TPR characterizations demonstrated that Ni catalysts prepared in this work did not show any sign of deactivation after being used in the micro-channel system. It is expected that the methanation reactor technique based on the metal-ceramics complex substrate as the catalyst support in (micro-)channel reactors would open opportunities for the reliable engineering applications of either distributed or mass production of SNG from syngas.

1. Introduction

For the limited reserves and increased price of oil, coal utilization becomes more and more significant nowadays. Among the different routes of coal conversion, coal to SNG (synthetic or substitute natural gas) [1] has attracted much attention in recent years in parallel to the processes of coal to liquid fuels and coal to light olefins [2–4]. It is well-known that SNG is a versatile energy carrier, which can be readily produced from coal or biomass, and is inter-changeable with Natural Gas (>95% methane, high HHV (i.e., higher heating value)) [5]. The advantages of SNG are the high conversion efficiency from either coal or biomass, the already existing gas distribution infrastructure such as pipelines and the well-established and efficient end use technologies. As an example in China, natural gas resources are very much short of supply but coal is rather abundant. In the remote, western areas of China, Xinjiang Province possesses 40% of the coal reserves in China, but the long distance transportation of solid coals are not allowed from the viewpoint of economics. Alternatively, the natural gas pipelines from the west to the east are already available, and extra pipelines are being constructed for the energy supply (i.e., natural gas) to the developed areas in the east of China. Therefore, coal to SNG project becomes particularly important and feasible in China.

Kopyscinski et al. [1] made a thorough review on the technologies for the production of SNG from coal and dry biomass from 1950 to 2009. So far, there is only one commercialized industrial technology to implement the coal to SNG process in the world, that is, the Great Plains Synfuels Plant (GPSP) in Beulah, North Dakota (USA), producing approximately 15 TWh/year of SNG from lignite coal. For the mature development of gasification, water–gas–shift (WGS) and gas cleaning techniques, we only focus our attention on the methanation process in this work.

Methanation ($CO + 3H_2 = CH_4 + H_2O$) is an important process in the chemical industry, including removal of trace amounts of CO from H_2-rich feed gas, purification of the reformate gas for fuel cell, and processes in relation to Fischer–Tropsch synthesis [6–9]. From the thermodynamic point of view, it can be concluded that the methanation is favored at low temperature and high pressure. Operating at high pressure produces a large amount of heat per volume compared to a low-pressure process. In the context, ***total methanation*** is referred to the methanation reaction with pure

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syngas (i.e., CO and H_2) as the feedstock, where the mole ratio of H_2 to CO is about 3.0. As a comparison, the ***partial methanation*** indicates the conversion of little amount of CO in the feedstock, which is generally used to increase the heat-value of city gas. A distinct difference in these two processes is the amount of heat released from the reaction. In the former case (i.e., the total methanation), the reactor design and the catalyst activity meet more challenges due to the much higher exothermicity than the partial methanation, especially under the high pressure conditions (e.g., 3–5 MPa). Except for the total methanation reaction in the SNG production process, the WGS reaction ($CO + H_2O = CO_2 + H_2$) must be suppressed as a side reaction, which reduces the selectivity of methane. In the industrial SNG production, the mole ratio of H_2/CO in the feed gas is 3.0–3.1, slightly higher than the stoichiometry.

Since the 1970s a number of methanation processes have been developed, comprising both fixed bed and fluidized bed methanation [1]. As mentioned above, the heat removal of ***total-methanation*** reaction for the production of SNG is a major concern for reactor design, which can be solved by a series of fixed bed methanation reactors with intermediate gas cooling or recycle of product gas considering the thermodynamics, reactions mechanism and kinetics of total methanation [1,10,11]. As a comparison, fluidized bed is inherently suitable for the highly exothermic reaction systems due to the excellent heat transfer and removal capabilities. Meanwhile, fluidized bed technique particularly fits the mass production of chemicals in industry. However, a challenging problem is inevitably encountered for the methanation process that high conversion and selectivity of the reactor performance is difficult to be implemented in a fluidized bed, in which gas and solids backmixing plays a negative role in the overall reactor performance. Up to now, fluidized bed methanation reactor is still under-development in a lab or a pilot-plant scale [12–14].

Different from the conventional reactor techniques, we aim to develop (micro-)channel reactors (or in other words, structured reactors) to facilitate the highly exothermic methanation reaction under high pressure operation. It has been acknowledged that micro-channel reactors have unique features of process intensification, for example, the excellent temperature control and improved mass transfer especially in the applications of highly exothermic and endothermic reactions [15,16]. A metallic structured support, with its inherent high thermal conductivity, can be used as the substrate of catalysts and integrated for micro-channel reactor applications. Researchers from Velocys and Pacific Northwest National Laboratory (PNNL) reported the development of a millisecond micro-reactor concept for steam reforming of methane (SRM) process (i.e., the reverse reaction of total methanation) with highly efficient integration of an exothermic combustion channel and an endothermic reforming channel with high thermal efficiency through the channel (metal) wall [17–20]. This concept can be alternatively applied for a highly exothermic reaction, such as the methanation reaction, F–T synthesis [21,22] and so on. It can be expected that it would be much easier to remove the heat from the exothermic reaction through the metal wall by either liquid media or steam in micro-channel reactor than to supply the heat to a high-temperature endothermic reaction in a short time. In addition to the advantage of heat management, (micro-)channel reactors would also offer the following features to favor the methanation reaction:

- The small sized reactor space with highly conductive metal wall can guarantee the uniform temperature profile in the catalyst coating layers in the reactor, which provides excellent conditions to maintain the catalyst stability and reach the desired thermodynamic equilibrium under a constant operating condition.
- Plug flow pattern in the channels helps to obtain the ideal reactor performance (i.e., high conversion and selectivity) for methanation reaction.
- Catalysts are coated on the channel walls so that there is little pressure drop across the empty channel.
- Reactor scale-up is easy by the so-called “number-up” methodology. Subsequently, the reactor technique can be suited for distributed and/or mass production of SNG from different syngas resources (e.g., from coal or biomass gasification, or from coke oven gas).

The key issues to implement the methanation process in above-mentioned micro-reactor technique lie in the two aspects at the lab-scale research. The first is the stable catalyst coating on metal surface considering the potential risk of the catalyst layer falling off due to the difference of thermal expansion coefficients between the metallic substrate and the catalyst layer. The second is the catalyst activity and stability. Our earlier work [23,24] has demonstrated that using the metal-ceramic complex substrate can successfully overwhelm the bottleneck of catalyst layer stability. Ni catalyst was adopted to catalyze the SRM reaction in milliseconds. In particular, a 500-h on stream experiment was successfully carried out under the temperature of 900 °C, showing wonderful catalyst stability with high activity. In this work, we will inherit the above experience to further investigate the methanation reaction in the micro-channel reactor. Since the methanation reaction is one of the representative exothermic reactions, this work should be able to suit for many other applications that need well-controlled temperature conditions.

2. Experimental

2.1. Catalyst plate preparation

As mentioned above, we have developed a type of metal-ceramics complex substrate as the support plate to load catalyst in order to implement stable and active catalyst coatings for methanation reaction in micro-channels [24]. The specific approach is briefly described as below.

2.1.1. Manufacture of metal-ceramics complex substrate

First of all, a layer of nano-particles, γ-Al_2O_3, is thermally sprayed on a metallic substrate, usually FeCrAlloy, to manufacture the metal-ceramics complex substrate. But different from the traditional thermal spraying, the metallic substrate is preheated to an appropriate temperature (e.g., 1200 °C) before deposition. Then the binding force between the two different substances can be greatly enhanced because the ceramic particles would embed into the bulk phase of metal very firmly.

2.1.2. Deposition of AlOOH sol

According to the method indicated in the Ref. [25], the AlOOH sol was prepared in the following procedure: a commercial aluminum hydroxide powder was dispersed in water (e.g., 15–20 wt%) with continuous agitation, then a 5 mol/L HNO_3 aqueous solution was used to adjust its pH value from 7 to 2. The solution was stirred for 5 h at 85 °C and a stable sol was obtained as a result. Afterwards, the metal-ceramics complex substrate is immersed into this boehmite sol for 3 min, and then withdrawn at a constant speed of 3 cm/min to ensure the uniform coating, dried at room temperature for 30 min, then calcined at 600 °C for 6 h. As a result, a layer of γ-Al_2O_3 with a higher specific surface area is obtained. The above procedures can be repeated until the thickness of the coating layer is up to the desired value [26]. In this work, the thickness of boehmite sol after immersing is about 200 μm, and the thickness