Fuel 235 (2019) 85–91

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Carbon deposition on Ni-based catalyst with TiO_2 as additive during the syngas methanation process in a fluidized bed reactor

Fei Feng[a,b,c], Guohui Song[d], Jun Xiao[b], Laihong Shen[b], Sarma V. Pisupati[c,*]

[a] School of Intelligent Manufacturing, Nanjing Polytechnic Institute, 210048 Jiangsu, China
[b] State Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, 210096 Jiangsu, China
[c] John and Willie Leone Family Department of Energy and Mineral Engineering and The EMS Energy Institute, The Pennsylvania State University, University Park, PA 16802, USA
[d] School of Energy and Power, Nanjing Institute of Technology, 211167 Jiangsu, China

ARTICLE INFO

Keywords:
Carbon deposition
TiO_2 additive
Syngas
Methanation

ABSTRACT

Syngas methanation is a crucial step in industry to produce synthetic natural gas, but the Ni-based catalysts for this reaction often deactivate severely because of carbon formation. Tests were carried out in a pressurized fluidized bed methanation reactor in order to analyze the carbon deposition on the nickel-based methanation catalysts with TiO_2 as additive (Ni-Ti/Al_2O_3) and a conventional Ni-based catalyst (Ni/Al_2O_3). Test results showed that Ni-Ti/Al_2O_3 performed better compared to Ni/Al_2O_3. At higher operating temperature (823 K), CO conversion on Ni-Ti/Al_2O_3 was 13.6% higher than that on Ni/Al_2O_3, CH_4 yield was 39.7% higher and CH_4 selectivity was even 64.7% higher for Ni-Ti/Al_2O_3 compared to Ni/Al_2O_3. The raw and spent catalysts were characterized with XRD, EDS and N_2 adsorption-desorption measurements to describe the carbon deposits on them. The characterization results indicated that elemental carbon appeared on the surface of the catalysts after methanation reaction and with the increase in reaction temperature, the carbon deposition was getting more serious. The deposited carbon blocked the tiny porous channels of the catalysts and caused a drastic change in the surface topography, which led to the degradation of the catalysts' performance. The TiO_2 additive provided a physical barrier to hydrocarbon adsorption and decomposition on the catalyst surface and the oxygen vacancies on Ni-Ti/Al_2O_3 acted as the active sites to promote the removal carbon on the Ni particles. Thus, the TiO_2 additive can enhance the anti-coking properties and catalytic activity of Ni-Ti/Al_2O_3 compared to Ni/Al_2O_3. These findings aid in further improvement and optimization of highly carbon-resistant catalysts.

1. Introduction

Increasing demand for natural gas around the world spurs research for a new source of methane. Consequently, synthetic natural gas (SNG) from coal or biomass has attracted particular attention [1]. The conventional route for SNG production from biomass includes four steps: Syngas production via biomass gasification, Syngas cleaning and conditioning, Syngas catalytic conversion to crude SNG through methanation, and upgrading of the crude SNG. Among these, methanation is a key step in the production of SNG [2]. Researchers all over the world have made great efforts in the development of efficient methanation reactors and catalysts [3].

Methanation reactors are crucial for the Syngas methanation process. It is noted that CO methanation is a highly exothermic reaction (-206 kJ/mol), which makes it possible for hotspots to arise in the reactor thereby shortening the catalysts' life-time [4]. Therefore, it is crucial that the methanation reactor systems effectively remove the reaction heat [5]. Various methanation reactors have been developed to solve the limitation of heat transfer, which can be classified into three categories from the perspective of reactor structure, i.e. fixed bed reactor, fluidized bed reactor and slurry bed reactor. Researchers have conducted intensive study on these reactors [6–13] and found that fluidized bed reactor is promising for industrial scale-up due to its good catalyst mixing, high heat transfer rates inside the reactor [2] and its more flexible scalability. In this study, tests were carried out in a fluidized bed methanation reactor to study the carbon deposition phenomena in this kind of reactor.

Regarding the methanation catalysts, comprehensive studies have been carried out on methanation thermodynamics, catalytic mechanisms, catalyst activity and stability and carbon deposition since Sabatier

---

[*] Corresponding author.
E-mail address: sxp17@psu.edu (S.V. Pisupati).

https://doi.org/10.1016/j.fuel.2018.07.076
Received 25 February 2018; Received in revised form 18 April 2018; Accepted 18 July 2018

and Senderens [2] found the catalytic effects of some metals like nickel on the methanation reaction in 1902. Various catalysts developed for methanation reaction generally include transition metals such as Ni [14–17], Fe [18], Ru [19,20], Rh [21] and Co [22]. However, these kinds of catalysts have advantages and disadvantages. Among all these materials, Ni-based catalysts are widely used because of their relatively high activity and selectivity towards methanation and their low cost compared to noble-metal-based catalysts [23]. However, the stability of Ni-based catalysts is often compromised by deactivation, such as carbon deposition and sintering occurring under different operating conditions [24]. Consequently, various supports including Al_2O_3, SiO_2, TiO_2, CeO_2, and ZrO_2 that favor the dispersion of Ni particles and enhance their activity and stability, have been studied theoretically and experimentally [25–28]. Among these supports, the sintering of Ni particles supported on Al_2O_3 can be inhibited to some extent, and thus Al_2O_3 is considered superior to other supports [29]. Nevertheless, it is inevitable for carbon deposition to take place on the Ni-based catalysts supported on Al_2O_3 due to its high affinity for carbon [29–30]. Therefore, researchers have made great efforts and practice around the mechanism, influential factors, and catalytic performance of the carbon deposition [31–34]. Bai et al. [35] studied carbon deposition by emphasizing the effects of operating conditions and found that the operating temperature, reaction time and H_2/CO ratio are all significant influential factors for the morphology and amount of carbon deposits. Carbon deposition is favored by low pressure and low space velocity, according to the results from Bai et al. [35]. Since the methanation process of Syngas often takes place at atmospheric pressure or low pressure, taking the relatively small biomass utilization scale into account, carbon deposition invariably occurs. Therefore, it is necessary to understand the effects of operating parameters on the carbon formation over different catalysts for Syngas methanation. In recent years, further studies have been conducted to improve the resistance to carbon deposition of Ni-based catalysts supported on Al_2O_3. For instance, Liu et al. [26] prepared ZrO_2-decorated Ni/Al_2O_3 catalysts by a two-step process and the test results showed that this modified catalyst displayed a high stability and resistance to coke formation. This is because ZrO_2 can selectively deposit on the surface of NiO, which effectively enhances CO dissociation, produces oxygen intermediates and thus can facilitate the removal of carbon formed on the Ni particles. Yang et al. [36] developed Ni-based catalysts supported on different acid-treated clays. They reported that the dispersion and the states of nickel species on the support were strongly influenced by the pore structure of the acid-treated clays, and the mesopores composed by partly damaged clay layers. These can reduce the deposition of the inactive carbon and thus improve the stability of the catalyst.

Unfortunately, the mechanism of CO methanation on the Ni-based with carbon deposition is still unknown. Moreover, the influence of different operating conditions on the carbon deposition of different supported catalysts may differ from each other and metal support interaction may also have an effect on the amount and type of carbon formed [24]. Therefore, it is necessary to investigate the effects of operating conditions on the stability for different catalysts.

In our previous work [37], we carried out an investigation on methane production from Syngas in a pressurized fluidized bed reactor and summarized the optimal operating parameters for the highest CO conversion and CH_4 selectivity. In this work, we studied further the carbon deposition in this reactor and evaluated the effects of the carbon deposition on the catalytic performance of Ni-based catalysts with TiO_2 as additive. The purpose of this study to report the effects of carbon deposition on the surface topography, catalytic performances and the mechanism of the anti-coking performances of the additive TiO_2.

2. Methods

2.1. Catalyst preparation

The main catalyst used in the study is a Ni-based catalyst supported on Al_2O_3 with 3.0% of TiO_2 by weight added to it as additive (named Ni-Ti/Al_2O_3). This catalyst, provided by a Chinese catalyst manufacturer, was prepared using co-precipitation method and was used in our previous work and displayed a high catalytic performance [37]. Before testing, the raw catalyst was dried, ground and sieved to a desired particle size (60–100 mesh). The other Ni-based catalyst (named Ni/Al_2O_3) was prepared with a traditional impregnation method and tested in this study for comparison. The Ni loading in both catalysts was maintained at 17.8 wt% and the pellet size was 60–100 mesh. Both catalysts were tested in the fluidized bed reactor system for 6 h with the catalyst loading of 120 ml (86.89 g). The spent catalysts were all collected and analyzed after each test to study the extent of carbon deposition on the catalyst surfaces.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2500VL/PC diffractometer to identify the crystal structure of the catalysts. The scanned range was from 3° to 85°.

X-ray Energy Dispersive Spectroscopy (EDS) measurements were carried out on a Hitachi TM 3000 to quantify the element contents on the catalyst surfaces, especially the amount of carbon deposited on the spent catalysts.

N_2 adsorption-desorption measurements were conducted on an ASAP 2020M automated gas sorption analyzer, using high purity N_2 as adsorbing medium at 77 K. Then, the specific surface area, pore volume and pore size distribution of the catalysts were measured and determined by Brunauer-Emmett-Teller (BET) and Barret-Joyner-Hallender (BJH) method.

These measurements were carried out on both the raw Ni-Ti/Al_2O_3 catalyst and the spent ones for comparison.

2.3. Catalyst testing

The catalyst tests were performed in a fluidized bed reactor (i.d. 31 mm), whose construction was described in details in our previous work [37,38]. The major part of the experiment was performed at a reaction pressure of 0.3 MPa, which was controlled by a back-pressure valve on the gas outlet. The reaction temperature was monitored with two thermocouples and adjusted by an intelligent temperature controller. The Syngas of H_2 (99.99%) and CO (99.99%) was used as the feed gas with the H_2/CO molar ratio of 3 and the gas hourly space velocity (GHSV) of 10000 h^{-1}. N_2 (99.99%) was employed as the internal standard gas. The gas product was sampled after dedusting, cooling and drying and then analyzed with an Emerson NGA2000 Gas Analyzer. Every test lasted 6 h when the methanation reaction maintained stable. After each test, the spent catalysts were collected for further characterization.

CO conversion, CH_4 selectivity and CH_4 yield were used for catalytic performance evaluation, which were calculated as the following formula.

CO conversion:

$$X_{CO}(\%) = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} \times 100 \tag{1}$$

CH_4 selectivity:

$$S_{CH_4}(\%) = \frac{F_{CH_4,out}}{F_{CO,in} - F_{CO,out}} \times 100 \tag{2}$$

CH_4 yield: